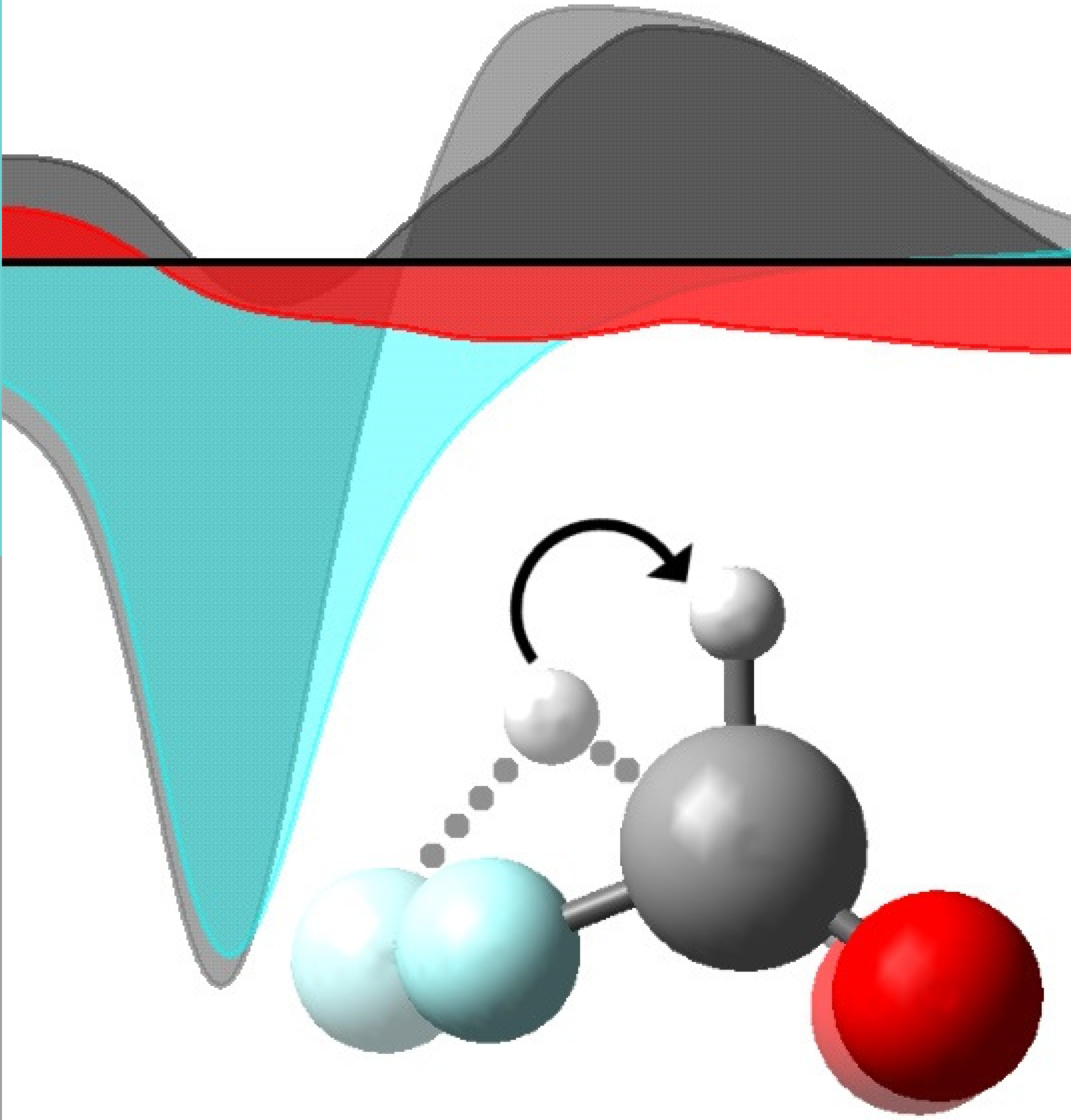

# Effect of molecular deformations on the chemical DFT indices

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Translation of this paper into English has been made by the group of friends and coworkers of the author in May 2023, as a gift to Dr Piotr Ordon on the 20th anniversary of his doctorate, and to commemorate the lasting value of the paper, that has founded ground for many other papers in the area of Conceptual Density Functional Theory in Wrocław and elsewhere.

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# Introduction

The role and importance of chemical reactivity indices derived from the density functional theory (DFT) have been analyzed in this work. In Chapter 1, the theoretical results have been presented, which were used to define the electronegativity, hardness, and Fukui function indices. The DFT theory has been discussed starting from the work of Hohenberg and Kohn, which made electron density a fundamental variable for the theory. This idea enabled creation of the theoretical apparatus that describes energy changes caused by changes in electron density. Such a direct approach (bypassing the wave function) is extremely attractive from a chemical point of view. It enabled the theoretical definition of quantities known from chemical practice such as electronegativity, hardness, and the Fukui function. In the final part of Chapter 1 the role of forces in the description of electronic systems has been discussed - the Hellmann-Feynman theorem and the electrostatic theorem have also been presented.

The main content of this work is the detailed analysis of couplings between the electron density and geometric variables describing the position of atoms in the molecule (Chapter 2). For this purpose, two types of selection of independent variables were used - canonical ensemble and grand canonical ensemble. Energy derivatives appearing in both cases have been defined and analyzed. Nuclear stiffness has been defined, and the basic importance of this quantity was demonstrated, apart from nuclear reactivity, for the coupling between the number of electrons, chemical potential and geometric variables describing the position of atoms. The influence of these couplings on molecule oscillations, including anharmonic ones, has been described. Chapter 3 presents computational illustrations of the concepts derived from Chapter 2. A few molecules, both diatomic and polyatomic, were tested. Particularly noteworthy is an attempt to describe the first stages of the decomposition of the RDX explosive compound.

# 1

# Susceptibility of the electronic system in the Conceptual Density Functional Theory

A chemical reaction can be defined as a spontaneous change in the electron density of a system under the influence of an external disturbance. Such a disturbance may be a change in the external potential (e.g., due to the approach of another molecule) or a change in the geometry of the molecule due to external stress. In this work, special emphasis will be placed on examining whether there are quantities that may be used to describe a chemical reaction in a similar way as susceptibility predicts a phase transition. Since a chemical reaction is a collective phenomenon, electronic correlation plays a huge role in its description. DFT has the advantage of being able to take the electron correlation directly into account. However, the fluctuating nature of vulnerability draws my attention to statistical mechanics. For these reasons this chapter has been focused on the discussion of DFT and the statistical way of describing susceptibilities. The basics of the theory and its applications is presented. The approximations needed to obtain numerical results has also been discussed.

## 1.1 Density Functional Theory (DFT) as an apparatus for describing changes in electron density.

The density functional theory describes an electronic system using the electron density function as the fundamental variable. This approach makes it easier to imagine a multi-body interacting system and leads to the validation of the chemical concepts of electronegativity and hardness. The theorem on the existence of an energy functional defined in the domain of all possible electron densities of a system of $N$ electrons was presented by Hohenberg and Kohn [1]. In the same work, the authors also proved that the value of this functional is the smallest for the density, which is the true density of the system in the ground state, and that its value at this point is equal to the true energy of the ground state. Proving these theorems gave rise to a variety of works in which the authors extended the applicability of the H-K theorems and indicated possible applications of the theory to numerical calculations. Currently, DFT is the basic tool for describing electronic systems - isolated molecules, crystals, and superconductors [2, 3, 4, 5, 6].

Consider a system of $N$ electrons located in an external field coming from system of positively charged atomic nuclei. The Hamiltonian of such a system has the form.

$$H = T + U + V \tag{1.1.1}$$

where T is the kinetic energy of the system, U is the electron-electron interaction, and V is the interaction of electrons with the external potential. To describe such a system, it is necessary to solve the equation for the eigenvalues of this Hamiltonian.

$$H\left|\Psi\right\rangle = E\left|\Psi\right\rangle \tag{1.1.2}$$

The eigenstate state $|\Psi\rangle$ carries complete information. We are usually just interested the ground state of the system, that is $|\Psi^{o}\rangle$, which corresponds to the lowest energy – $E_o$. Since the Hamiltonian is an operator bounded from below, it was possible to formulate the Ritz variational principle, which states that there is a functional $E[\Psi] = \langle\Psi|H|\Psi^{*}\rangle$, the minimum of which is determined by the ground state of the tested system and its energy. The theorem is fulfilled:

$$E^{o} = E[\left|\Psi^{o}\right\rangle] \leq E[\left|\Psi\right\rangle] \tag{1.1.3}$$

True energy of the ground state is lower than that of any other state. The theory of the density functional is based on theorem [1], which says that another energy functional can also be defined - one whose argument will be the electron density - which also satisfies the variational principle analogous to equation (eq. 1.1.3).

We define the electron density as the probability density of finding an electron in a small volume element around point r. According to the Born interpretation of quantum mechanics [4], this probability density is given by the square of the wave function, and may be integrated over space variables:

$$\rho(\mathbf{r}) = N\int \ldots \int \left|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)\right|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{1.1.4}$$

Here vector $\mathbf{r}_i$ describes the electron. Due to the indistinguishability of particles, it is not important which variable $\mathbf{r}_i$ we leave out when calculating the integral. Since the function is a probability density, the calculation over the selected fragment of the molecule $\rho(\mathbf{r})$ is the total probability of finding all electrons in this region $\int_{\Omega} \rho(\mathbf{r}) d\mathbf{r}$ :

$$N(\Omega) = \int_{\Omega} \rho(\mathbf{r}) d\mathbf{r} = N\int_{\Omega} d\mathbf{r}_1 \int \ldots \int \left|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\right|^2 d\mathbf{r}_2 \ldots d\mathbf{r}_N \tag{1.1.5}$$

When the subsystem is the whole system, then the integral in formula (eq. 1.1.5) is:

$$\int \rho(\mathbf{r})d\mathbf{r} = N \tag{1.1.6}$$

The topological properties of electron density and the method of dividing it into atoms were presented by Bader [7]. The surface between the atoms meets the condition (1.1.7) at each point $\mathbf{r}$ on that surface [8, 9]:

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \tag{1.1.7}$$

It has been shown that for atoms defined in this way, the principle of least action and the atomic virial theorem are satisfied. Critical indexes describing the topological properties of chemical bonds have been defined.

The basis of the density functional theory (DFT) was the theorem of Hohenberg and Kohn [1]. For a non-degenerate ground state, there is a functional relationship between the external potential $\mathrm{v}(\mathbf{r})$ and the electron density $\rho(\mathbf{r})$. A given electron density $\rho(\mathbf{r})$ corresponds to exactly one potential value $\mathrm{v}(\mathbf{r})$. This unity is up to an additive constant, since potentials that differ by a constant are physically equivalent.

There are important consequences from Hohenberg and Kohn's theorem. Since $\rho(\mathbf{r})$ determines both the number of particles and the external potential in an unambiguous way, it determines completely the Hamiltonian of the system and thus its ground state $|\Psi\rangle$. In this way, the electron density determines all the properties of the system. It determines its total energy as well as kinetic and potential energy - individual types of energy are electron density functionals. Thus, the total energy functional $E_{\mathrm{v}}[\rho]$ and the universal functional $F_{HK}[\rho]$ covering only the internal interactions of electrons in the system have been defined [1].

$$F_{HK}[\rho] = T[\rho] + U[\rho]. \tag{1.1.8}$$

The energy of a system is defined by:

$$E_{\mathrm{v}}[\rho] = T[\rho] + U[\rho] + \int \rho(\mathbf{r})\mathrm{v}(\mathbf{r})d\mathbf{r} \tag{1.1.9}$$

The subscript “v” means that the energy functional is defined for a fixed external potential. A functional is an assignment where the density function corresponds to a numerical value, e.g. $\int \rho(\mathbf{r})d\mathbf{r}$. The domain of the density function are the density values at individual points, and the domain of the functional are the various density functions. This difference is important for understanding the variational method based on the Hohenberg and Kohn theorem [1]. The functional

$E_{\mathrm{v}}[\rho]$ takes a minimum for the density, which is the true density of the ground state $\rho^{\mathrm{o}}$. The value of the functional for this minimum is equal to the true value of the ground state energy $E_{\mathrm{v}}[\rho]$:

$$E_{\mathrm{v}}[\rho^{\mathrm{o}}] = E^{\mathrm{o}} \tag{1.1.10}$$

This functional determines the ground state of an electronic system, and thus makes it possible to describe an electronic system using electron density as the fundamental variable. The way of determining the energy functional given by Hohenberg and Kohn assumed that any electron density is the integral square of the modulus of some wave function being a solution to the Schrödinger equation with some external potential $\mathrm{v}(\mathbf{r})$. Thus, the domain of the Hohenberg and Kohn functional is restricted to v-representable functions. An issue to be clarified to enable the practical applicability of Hohenberg's and Kohn's theorems is also the problem of *N*-representability. In other words, can every density be assigned an *N*-electron wave function. A negative answer to this question could seriously limit the applicability of the Hohenberg and Kohn theorem because the energy functional is defined only for those densities that come from *N*-electron wavefunctions. The problem of representability consists in answering the question about the completeness of the domain of the functional $E_{\mathrm{v}}[\rho]$. In the variational method, however, we need a priori certainty that the test density we choose belongs to the domain of our functional (it comes from some external potential). The problem of v-representability was solved by Levy. Hohenberg and Kohn [1] reported that they are unable to prove that for any function $\rho(\mathbf{r})$ (satisfying the conditions: $\rho(\mathbf{r}) \geq 0$ and $\int \rho(\mathbf{r})d\mathbf{r} = N$), there is a potential $\mathrm{v}(\mathbf{r})$ from which the function $\rho(\mathbf{r})$. Lieb gave an example of a test density, which could not be assigned unequivocally to an external potential [11]. Similarly, Levy gave an example of a density that is not v-representable [12]. Levy also showed that for the purposes of variational methods, the Hohenberg and Kohn functional must be redefined [13]. He proposed a very simple way to change the definition $F_{HK}[\rho]$ so that the domain of this functional were only v-representable functions. This approach is called the constrained search. It results from the following premises. First, it can be shown that the ground state density is v-representable. Second, because the Ritz principle is satisfied, the evaluation of type expressions $\langle \Psi[\rho] | H | \Psi[\rho] \rangle$ can be split into two steps. First look for which wave function gives a minimum for a given density; then, among all the test densities, choose the one that leads to the minimum value of the functional:

$$F_{Levy}[\rho] = \min_{\Psi \to \rho} \langle \Psi[\rho] | \hat{T} + \hat{U} | \Psi[\rho] \rangle \tag{1.1.11}$$

This is the definition of a constrained search functional. The problem is to calculate the expected value of the operator $T+U$ for each state leading to $\rho$. The value of the functional is the smallest of these numbers. Let the state for which this minimum is reached be $\left|\Psi^{\rho}_{\min}\right\rangle$. Hence:

$$F_{Levy}[\rho] = \left\langle \Psi^{\rho}_{\min} \middle| T + U \middle| \Psi^{\rho}_{\min} \right\rangle . \tag{1.1.12}$$

Levy has demonstrated that his functional satisfies the Hohenberg and Kohn theorems:

$$F_{Levy}[\rho] + \int \rho(\mathbf{r})\mathrm{v}(\mathbf{r})d\mathbf{r} \geq E^{\mathrm{o}} \tag{1.1.13}$$

$$F_{Levy}[\rho] + \int \rho^{\mathrm{o}}(\mathbf{r})\mathrm{v}(\mathbf{r})d\mathbf{r} = E^{\mathrm{o}} \tag{1.1.14}$$

The problem of $N$-representability was solved by Harriman [14], who proved that for any electron density $\rho(\mathbf{r})$ describing an $N$-electron system, an $N$-electron wave function can be generated.

The most important extension of Hohenberg and Kohn's theory is its application to finite temperatures. This was done by Mermin in 1965 [15]. He showed that the grand canonical potential is a functional of the electron density:

$$\Omega_{\mathrm{v}}[\rho] = \int \mathrm{v}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho]$$

(1.1.15)

It satisfies the appropriate variational principle:

$$\Omega_{\mathrm{v}}[\rho^{\mathrm{o}}] \leq \Omega_{\mathrm{v}}[\rho] . \tag{1.1.16}$$

where $\rho^{\mathrm{o}}$ is the average thermodynamic electron density for the ground state. Of course, the form of the functional $F[\rho]$ is different than in the zero-temperature case. Specifying explicitly which types of energy constitute the functional $F[\rho]$ at finite temperatures is an achievement of Mermin [15]. First, the finite-temperature system is in a mixed state. As a result of thermal motions, there is a finite probability of transition to an excited state. Therefore, to take this fact into account in the description of the system, we assume that its properties are affected by all possible states. However, we know that in practice, individual states are not equally filled. The higher the energy, the lower the probability of occupancy. In other words, the role of each state is different. Therefore, a weight is needed that will differentiate the influence of individual states on the observables. This role is fulfilled by the density matrix. Observable quantities are calculated as a trace of the density matrix multiplied by the operator describing a given quantity. The electron density is expressed by [16]:

$$\rho(\mathbf{r}) = Tr\{\hat{\rho}\hat{n}(\mathbf{r})\} \tag{1.1.17}$$

The electron density $\rho(\mathbf{r})$ is a local function. It may be calculated as an expectation value of the density operator $\hat{n}(\mathbf{r})$ for a given quantum state $|\Psi\rangle$. In the second quantization representation, the density operator has the form [16]:

$$\hat{n}(\mathbf{r}) = \hat{\psi}^{+}(\mathbf{r})\hat{\psi}(\mathbf{r})\,. \qquad (1.1.18)$$

Hence: $\rho(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ (1.1.19)

Operators $\hat{\psi}^{+}(\mathbf{r})$ and $\hat{\psi}(\mathbf{r})$ are fermion field operators. They are defined by the following anticommutation relations:

$$[\hat{\psi}^{+}(\mathbf{r}), \hat{\psi}^{+}(\mathbf{r}')]_{+} = 0 \qquad (1.1.20)$$

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')]_{+} = 0 \qquad (1.1.21)$$

$$[\hat{\psi}(\mathbf{r}), \hat{\psi}^{+}(\mathbf{r}')]_{+} = \langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$$

Their relationship with the operators of creation and annihilation is as follows:

$$\hat{\psi}^{+}(\mathbf{r}) = \sum_{\alpha} \psi_{\alpha}^{*}(\mathbf{r})\hat{a}_{\alpha}^{+} \qquad (1.1.22)$$

and $$\hat{\psi}(\mathbf{r}) = \sum_{\alpha} \psi_{\alpha}(\mathbf{r})\hat{a}_{\alpha} \qquad (1.1.23)$$

Definitions and properties of creation and annihilation operators ($\hat{a}_{\alpha}^{+}$ and $\hat{a}_{\alpha}$) are described in textbooks of quantum and statistical mechanics [16, 17]. $\hat{a}_{\alpha}^{+}$ creates an electron in an orbital and $\hat{a}_{\alpha}$ removes it from there. The density matrix has the following form:

$$\hat{\rho} = \frac{\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]}{Tr\left(\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]\right)}\,. \qquad (1.1.24)$$

The canonical grand potential written as the density matrix functional is [18]:

$$\boldsymbol{\Omega[\hat{\rho}] = Tr\left\{\hat{\rho}\left(H - \mu N + \frac{ln\hat{\rho}}{\beta}\right)\right\}} \qquad (1.1.25)$$

For the test $\hat{\rho}$, we get different values of the thermodynamic potential. However, the variational principle is satisfied: $\Omega[\hat{\rho}]$ assumes a minimum for the density matrix given by the formula. For the true density matrix describing the ground state of the system, denoted by:

$$\Omega[\hat{\rho}] \geq \Omega[\hat{\rho}^{\mathrm{o}}] \qquad (1.1.26)$$

This principle (eq. 1.1.26) plays a key role in constructing the electron density functional. It is analogous to the Ritz principle in the zero-temperature theory. Mermin [15] and Feynman [16] gave an elementary proof of theorem (eq. 1.1.26). Then it was noticed that the density matrix is the electronic density functional:

$$\hat{\rho} = \hat{\rho}[\rho(\mathbf{r})]. \tag{1.1.27}$$

The grand canonical potential (eq. 1.1.25) is a functional of the electron density:

$$\Omega[\hat{\rho}] = \Omega_{\mathrm{v}}[\rho(\mathbf{r})] \tag{1.1.28}$$

The universal functional relationship is:

$$F[\rho(\mathbf{r})] = Tr\left\{\hat{\rho}\left(T + U + \tfrac{\ln\hat{\rho}}{\beta}\right)\right\}. \tag{1.1.29}$$

The variational principle has been proven:

$$\Omega_{\mathrm{v}}[\rho] \le \Omega_{\mathrm{v}}[\rho^{\mathrm{o}}]. \tag{1.1.30}$$

In the same way, Parr and Yang have demonstrated that the electron density determines the ground state in the canonical ensemble [2]. This concept will be used to define electronegativity in the canonical ensemble.

In an analogous way the Hohenberg's and Kohn's theorem has been proved to hold for relativistic systems [19] and for the time-dependent Hamiltonian [20]. Although the form of equations was different, the idea of determining the external potential as a functional of electron density was common to all these works. Excited states were accounted for by the construction of the super-Hamiltonian by Theophilou [21] and Katriel [22]. Valone and Capitani formulated the MacDonald theorem on excited states in density functional theory [23]. Another extension of Hohenberg's and Kohn's theory was the concept of Capitani, Nalewajski and Parr, which included multi-component systems in the functional description [24]. It was a formal way of describing systems, to which the Born Oppenheimer approximation does not apply - the network of atomic nuclei, initially treated as the source of the external field, is now the inherent component interacting with electrons.

Kohn and Sham have shown how to obtain a one-electron approximation within the framework of DFT theory [25]. From the kinetic energy functional $T[\rho]$, they extracted the kinetic energy of a hypothetical system of non-interacting electrons $T_s[\rho]$:

$$T[\rho] = T_s[\rho] + K[\rho] + E_{xc}[\rho]. \tag{1.1.31}$$

where $$T_s[\rho] = -\frac{1}{2}\sum_{k}^{N}\langle\phi_k|\nabla^2|\phi_k\rangle \tag{1.1.32}$$

and $$E[\rho] = T_s[\rho] + U[\rho] + E_{xc}[\rho] + J[\rho] \tag{1.1.33}$$

Electron density has been separated:

$$\rho(\mathbf{r}) = \sum_k \left|\phi_k(\mathbf{r})\right|^2 . \tag{1.1.34}$$

The densities of the Kohn Sham orbitals add up to the total density. However, it is impossible to construct a real wave function as a Slater determinant composed of orbitals $\phi_k(\mathbf{r})$. Energy minimization leads to the Kohn Sham equations which are equivalent to the Hartree–Fock approximation in DFT theory.

$$\left\{-\frac{1}{2}\nabla^2 + \mathrm{v}_{\mathrm{eff}}\right\}\phi_k = \varepsilon_i \phi_k \tag{1.1.35}$$

where: $\mathrm{v}_{\mathrm{eff}}(\mathbf{r}) = \mathrm{v}(\mathbf{r}) + \int \frac{\rho(\mathbf{r})}{\left|\mathbf{r}-\mathbf{r}'\right|} d\mathbf{r} + \mathrm{v}_{\mathrm{xc}}(\mathbf{r})$ **(**1.1.36)

$\mathrm{v}_{\mathrm{xc}}(\mathbf{r})$ stands for the derivative of the correlation energy functional over the electron density function [3]:

$$\mathrm{v}_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} \tag{1.1.37}$$

This computational scheme allowed for the practical determination of ground state properties in DFT theory. Finding the exact form of the correlation and exchange energy functional ($E_{xc}[\rho]$) is a prerequisite for the success of this theory. Approximations used have been collected by Dreizler and Gross [3] and Parr and Yang [2]. The most important consequence of the Hohenberg–Kohn–Sham DFT theory is the Euler–Lagrange equation [1, 26], defining the value of the functional derivative of the functional $E_{\mathrm{v}}[\rho]$.

The variational Hohenberg–Kohn principle holds for the constant number of electrons:

$$\delta E_{\mathrm{v}}[\rho] = 0 \tag{1.1.38}$$

$$\int \rho(\mathbf{r}) d\mathbf{r} = N[\rho] = const \tag{1.1.39}$$

Hence: $\delta N[\rho] = 0$. **(**1.1.40)

In consequence, any linear combination of these two variances must also vanish:

$$\delta\left\{E_{\mathrm{v}}[\rho] - \mu N[\rho]\right\} = 0 . \tag{1.1.41}$$

The constant value $\mu$ is called the chemical potential and is equal in every point of a system [26]:

$$\frac{\delta E_{\mathrm{v}}[\rho]}{\delta\rho(\mathbf{r})} = \mu(\mathbf{r}) = \mu(\mathbf{r}') = ... = \mu \tag{1.1.42}$$

The last equation represents a test for the determined electron density in the ground state [27]. Parr and coworkers have identified $\mu$ as the electronegativity of a system [26] given by the derivative of energy over the electron number:

$$\left(\frac{\partial E(N,\mathrm{v}(\mathbf{r}))}{\partial N}\right)_{\mathrm{v}(\mathbf{r})}=\mu=-\chi \qquad (1.1.43)$$

## 1.2 Applications of the DFT theory to the description of chemical systems

Iczkowski and Margrave proposed the definition of the electronegativity for a system as the negative of the energy derivative over the number of electrons [28]. The DFT theory thus provided evidence for their intuitive concept. On the other hand, the definition of electronegativity by Mulliken stated that:

$$\chi=\frac{I+A}{2}\,. \qquad (1.2.1)$$

However, applying the finite difference approximation to the definition of eq. 1.1.43 proves that the Mulliken definition provides an approximation of electronegativity. The relationship of electronegativity defined as the negative chemical potential of the electron system with chemical definitions of electronegativity has been discussed by Komorowski [29, 30], as well as by Orsky and Whitehead [31]. Eq. 1.1.42 provides a proof to the Sanderson's principle of electronegativity equalization, stating that the electronegativity of a system in equilibrium is identical to the electronegativity of any fragment of the system under study [32]. Perdew, Parr, Levy and Balduz provided a method for differentiating energy as a function of a discrete variable [33]. They extended the DFT theory to the fractional electron case by using a mixed state, which is a ground state made up of pure states with an integer number of electrons. This construction leads to the differentiable energy function and the Mulliken expression for electronegativity was confirmed.

Another concept has also been present in the chemical vocabulary for many years: the chemical hardness [34]. The HSAB rule formulated by Pearson (Hard and Soft Acids and Bases) stating that hard acids react readily with hard bases, and soft acids with soft bases, was an experimental regularity that required theoretical justification. The definition of hardness derived from DFT meets these expectations [35].

The hardness index together with the Fukui index gives an account of the change in chemical potential when going from one equilibrium state to another. This change is caused by two factors: a change in the number of electrons $dN$ and a perturbation of the external potential $d\mathrm{v}(\mathbf{r})$:

$$d\mu = \left(\frac{\partial\mu}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} dN + \int\left(\frac{\delta\mu}{\delta \mathrm{v}(\mathbf{r})}\right)_N d\mathrm{v}(\mathbf{r})d\mathbf{r} \qquad (1.2.2)$$

The chemical hardness has been defined at the DFT level as a derivative of the chemical potential over the electron number:

$$\eta = \left(\frac{\partial\mu}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial^2 E(N,\mathrm{v}(\mathbf{r}))}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})} \cong I - A \qquad (1.2.3)$$

$\mathrm{v}(\mathbf{r})$ is an external potential, $\mu$ is the chemical potential of a system. The Fukui function $f(\mathbf{r})$ determines the change in the chemical potential over the variation of the external potential [36].

$$f(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\delta\mu}{\delta \mathrm{v}(\mathbf{r})}\right)_N \qquad (1.2.4)$$

A very important property of hardness is its role in the charge transfer processes. When a system exchanges electrons, the change in chemical potential is given by:

$$d\mu = \eta dN + \int f(\mathbf{r})d\mathrm{v}(\mathbf{r})d\mathbf{r} \qquad (1.2.5)$$

A large difference in chemical potentials ($d\mu$) gives a strong stimulus to change the electron density $\rho(\mathbf{r})$, therefore also $N$ and $\mathrm{v}(\mathbf{r})$. The first term (eq. 1.2.5) reflects the change in the number of electrons - thus it defines the change in binding energy caused by the charge transfer (CT) process. The second term (non-disappearing at $\eta\to 0$) contains the remaining interactions. For interacting uncharged objects, this second term is the covalent energy. Although both terms are equally important, the CT part has received special attention. The charge transfer energy associated with ionic bond energy was the source of Pauling's original definition of electronegativity. A working formula describing the energy gain in the CT process comes from Parr and Pearson [35] (many other have also been proposed):

$$\Delta E_{AB} = -\frac{(\Delta\mu)^2}{4(\eta_A + \eta_B)} \qquad (1.2.6)$$

This energy disappears if $\Delta\mu = 0$, such as the interaction of two identical atoms that form a covalent bond, which justifies $\Delta E_{AB}$ as the energy of an ionic bond between initially uncharged atoms.

An interesting proof of the HSAB rule proposed by Parr *et al*. it is also based on CT energy analysis [39]. The authors exploit the grand canonical potential close to an equilibrium state

$\Omega_i = E_i - (N_i - N_i^0)\mu$. They then proved that for any subsystem, the magnitude $\Delta\Omega_i$ is maximally negative:

$$\Delta\Omega_i = -\left(\Delta\mu\right)^2 \frac{\eta_i}{4(\eta_i + \eta_{rest})^2} \qquad (1.2.7)$$

The role of hardness in bond formation has been studied by many authors. Nalewajski found that the interaction of very hard molecules leads to ionic bonds [40], and the interaction of two very soft molecules leads to covalent bonds. Berkowitz found that the flow of electrons increases with the softness of the particles involved in the process [41]. Another important rule proposed by Pearson [42] and substantiated by Parr and Chattaraj [43] is the principle of maximum hardness: the electronic state reached by a molecule in equilibrium maximizes the global hardness if the external potential is constant. Pearson and Palke justified a similar rule which states that hardness is at its maximum with respect to any non-full symmetric deformation of the molecule [44]. The maximum hardness rule was supplemented by Zhou and Parr who introduced the concept of activation hardness - the increase in hardness when going from substrates to products along the reaction path [45]. The lower the activation hardness, the greater the electron transfer; also the higher the hardness, the more stable the molecule. In this chapter, we will examine the effect of changes in the relative positions of atoms in a molecule on hardness and electronegativity, and thus on the intermolecular process of electron exchange.

However, the principle of maximum hardness seems not to present the universal rule. Sebastian reasoned, considering the fluctuations in the grand canonical ensemble, that the hardness cannot take a maximum value as described by Parr and Chattaraj [46]. The results of this work also prove that the hardness is not at its maximum with respect to geometrical variables [1]. This is in good agreement with the results of Pearson and Palke (whenever the Jahn-Teller effect does not occur) [4] and [5], that lowering the hardness leads to an easier flow of electrons, and thus to an increase in reactivity.

The inverse of hardness is softness [47]:

$$S = \frac{1}{\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} \qquad (1.2.8)$$

The global softness reports the change in the number of electrons for a unit change in chemical potential. Politzer demonstrated the relationship between softness and polarizability [48]. The relationship between global softness and covalent radius was analyzed by Komorowski [49]. By analogy with global hardness, local hardness was initially also defined [50]:

$$\eta(\mathbf{r}) = \left(\frac{\delta\mu}{\delta\rho(\mathbf{r})}\right)_{\mathrm{v}(\mathbf{r})} \tag{1.2.9}$$

This quantity is meant to determine how the chemical potential of a molecule changes with a change in the electron density at a fixed external potential at a point. However, Harbola, Chattaraj and Parr pointed out that due to the interdependence $\rho(\mathbf{r})$ and $\mathrm{v}(\mathbf{r})$ resulting from the theorems of Hohenberg and Kohn, the derivatives $\left(\frac{\delta\mu}{\delta\rho(\mathbf{r})}\right)_{\mathrm{v}(\mathbf{r})}$ and $\left(\frac{\delta\mu}{\delta \mathrm{v}(\mathbf{r})}\right)_{\rho(\mathbf{r})}$ are not independent of each other [51]. The ambiguity of derivatives has been demonstrated:

$$\left(\frac{\delta\mu}{\delta\rho(\mathbf{r})}\right)_{\mathrm{v}(\mathbf{r})} = \eta + \int \lambda(\mathbf{r}')\frac{\delta \mathrm{v}(\mathbf{r}')}{\delta\rho(\mathbf{r})}d\mathbf{r}' \tag{1.2.10}$$

and $$\left(\frac{\delta\mu}{\delta \mathrm{v}(\mathbf{r})}\right)_{\rho(\mathbf{r})} = f(\mathbf{r}) - \lambda(\mathbf{r}) \tag{1.2.11}$$

$\lambda(\mathbf{r})$ may be any function. The authors suggested the choice of function $\lambda(\mathbf{r}) = 0$. Then the local hardness becomes equal to the global hardness, and the Fukui function is the derivative of the chemical potential with respect to the external potential:

$$\eta(\mathbf{r}) = \left(\frac{\delta\mu}{\delta\rho(\mathbf{r})}\right)_{\mathrm{v}(\mathbf{r})} = \eta \tag{1.2.12}$$

and $$\left(\frac{\delta\mu}{\delta \mathrm{v}(\mathbf{r})}\right)_{\rho(\mathbf{r})} = f(\mathbf{r})\,. \tag{1.2.13}$$

Local softness is free from the difficulty described above:

$$s(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial\mu}\right)_{\mathrm{v}(\mathbf{r})} \tag{1.2.14}$$

It reports the electron density changes $\rho(\mathbf{r})$ with a variation of the chemical potential $\mu$. Local hardness and softness are inverse of each other:

$$\int s(\mathbf{r})\eta(\mathbf{r})d\mathbf{r} = 1 \tag{1.2.15}$$

Another type of the response function represents the non-local functions, e. g. the hardness kernel [52]:

$$\eta(\mathbf{r},\mathbf{r}') = -\frac{\delta u(\mathbf{r})}{\delta\rho(\mathbf{r}')} = -\frac{\delta u(\mathbf{r}')}{\delta\rho(\mathbf{r})} \tag{1.2.16}$$

where $u(\mathbf{r}) = \mathrm{v}(\mathbf{r}) - \mu = \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}$ (1.2.17)

hence [53]: $\eta(\mathbf{r},\mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}$ (1.2.18)

The reciprocal to the hardness kernel is the softness kernel:

$$s(\mathbf{r},\mathbf{r}') = -\frac{\delta\rho(\mathbf{r}')}{\delta u(\mathbf{r})} = -\frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')} \tag{1.2.19}$$

Both kernels are related:

$$\int s(\mathbf{r},\mathbf{r}')\eta(\mathbf{r}',\mathbf{r}'')d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}'') \tag{1.2.20}$$

The local softness results by integration of the softness kernel:

$$\int s(\mathbf{r},\mathbf{r}')d\mathbf{r}' = s(\mathbf{r}) \tag{1.2.21}$$

and $\int \eta(\mathbf{r},\mathbf{r}') f(\mathbf{r}')d\mathbf{r}' = \eta_f(\mathbf{r}) = \eta$ (1.2.22)

Another frequently used alternative for a local hardness is:

$$\frac{1}{N}\int \eta(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' = \eta_\rho(\mathbf{r}). \tag{1.2.23}$$

The overriding relation that local hardness must satisfy is the inverse relation to local softness (eq. 1.2.15). This condition is always met when the function is integrated with the hardness kernel [54]:

$$\eta(\mathbf{r}) = \int \eta(\mathbf{r},\mathbf{r}')g(\mathbf{r}')d\mathbf{r}' \tag{1.2.24}$$

In eq. 1.2.22 or eq. 1.2.23 the sum is integrated to unity, e. g.:

$$\int g(\mathbf{r})d\mathbf{r} = \frac{1}{N}\int \rho(\mathbf{r})d\mathbf{r} = \int f(\mathbf{r})d\mathbf{r} = 1. \tag{1.2.25}$$

Fuentealba proposed an approximation for the local hardness [55]:

$$\eta(\mathbf{r}) = \frac{1}{N}\frac{\rho(\mathbf{r})}{s(\mathbf{r})}. \tag{1.2.26}$$

Also, the relations of the above kernels to the linear response function (eq. 1.2.27) have been established (eq. 1.2.28):

$$\omega(\mathbf{r},\mathbf{r}') = \left(\frac{\delta\rho(\mathbf{r}')}{\delta \mathrm{v}(\mathbf{r})}\right)_N = \left(\frac{\delta\rho(\mathbf{r})}{\delta \mathrm{v}(\mathbf{r}')}\right)_N = \frac{\delta^2 E}{\delta \mathrm{v}(\mathbf{r})\delta \mathrm{v}(\mathbf{r}')} \qquad (1.2.27)$$

$$\omega(\mathbf{r},\mathbf{r}') = \frac{s(\mathbf{r})s(\mathbf{r}')}{S} - s(\mathbf{r},\mathbf{r}')\,. \qquad (1.2.28)$$

The relationship between reactivity indices and polarizability was also studied by Vela and Gazquez [56]. They showed that the polarizability is proportional both to the global softness and (indirectly) to the Fukui function $f(\mathbf{r})$, well in accord to the intuition. Both the high values of softness S and the Fukui function $f(\mathbf{r})$ reflect the ease with which the electronic structure of the molecule is deformed. Fuentealba and Reyes presented numerical correlations between polarizability and softness [57]. Fuentealba and Parr have defined the derivatives of hardness [58]:

$$\gamma \equiv \left(\frac{\partial\eta}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial^3 E}{\partial N^3}\right)_{\mathrm{v}(\mathbf{r})} \qquad (1.2.29)$$

and
$$h(\mathbf{r}) \equiv \left(\frac{\delta\eta}{\delta \mathrm{v}(\mathbf{r})}\right)_N = \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\delta}{\delta \mathrm{v}(\mathbf{r})}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})}\right)_N . \qquad (1.2.30)$$

A calculation scheme was proposed for $\gamma$ and it was found that for many compounds it is a small value. Expanding on the concept of derivative reactivity indexes, Cohen, Ganduglia-Pirovano and Kudrnovsky defined the nuclear reactivity [59]:

$$\mathbf{\Phi}_i \equiv \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} \qquad (1.2.31)$$

where $\mathbf{F}_i$ represents a force acting on a nucleus of *i*-th atom. Similarly, the nuclear softness followed:

$$\boldsymbol{\sigma}_i \equiv \left(\frac{\partial \mathbf{F}_i}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} . \qquad (1.2.32)$$

Relations of the above quantities to the electric field have been described:

$$\mathbf{\Phi}_i = \int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} \qquad (1.2.33)$$

$$\boldsymbol{\sigma}_i = \int s(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} \qquad (1.2.34)$$

Then, expressions for the above quantities have been proposed in terms of the density of the boundary orbitals. Berkowitz, Ghosh, and Parr first reported Maxwell's relation combining the nuclear reactivity with changes in chemical potential with respect to a geometric coordinate [60]:

$$\mathbf{\Phi}_i = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_{N} \tag{1.2.35}$$

Baekelandt, Cedillo, and Parr proposed the term nuclear Fukui function for the nuclear reactivity [61]. Luty analyzed the dependence of energy (and global hardness) on the normal coordinate and presented a scheme for renormalizing hardness using a coupling constant [62]. This concept makes it possible to give a quantitative condition for the instability of the electronic system called local metallization. It consists in the fact that an external disturbance may cause the global hardness to reach a value of zero (release of electrons). This condition will be discussed in more detail in Chapter 3 when describing the explosive properties of the RDX compound.

A description of chemical reactivity was introduced to DFT by Nalewajski. Legendre transforms of the density functional were formulated and appropriate variation rules were formulated [63, 64]. This allowed for the selection of independent variables adequate to the description of a given system. In analogy to phenomenological thermodynamics, Maxwell's relations were formulated, which result from the equality of the second mixed derivatives and connect the local and global quantities describing the system. The concept of selecting independent variables by means of assemblies made it possible to carry out the analysis described in Chapter 2.

## 1.3 The Hellmann-Feynman theorem

The Schrödinger equation allows fo determination of the electronic state of the system and its energy at a given external potential: $E|\Psi\rangle = \hat{H}|\Psi\rangle$. Variation principle states that the ground state of a system is the lowest energy state: $E^0 \leq E[\Psi]$. These two laws of nature make energy the fundamental quantity needed to describe any system under study. In addition, the knowledge of the electronic state ensures the availability of complete information about the system. However, obtaining this information is often computationally complicated and expensive. Therefore, other quantities are of the interest, that provide essential knowledge about the system and do not require solving the Schrödinger equation. One of the most important quantities of this kind is force. The starting point is the definition of force as an energy gradient:

$$F = -\frac{\partial \langle \hat{H} \rangle}{\partial \lambda} \tag{1.3.1}$$

$\lambda$ is the chosen parameter and $\left\langle\hat{H}\right\rangle=\langle\Psi|\hat{H}|\Psi\rangle$ represents the average energy of a system described by the wave function $|\Psi\rangle$. The common choice for $\lambda$ is the vector $\mathbf{Q}_i$ describing the location of a nucleus, then eq. 1.3.1 provides a definition of force acting on that nucleus.

$$\mathbf{F}_i=-\frac{\partial\left\langle\hat{H}\right\rangle}{\partial\mathbf{Q}_i}\tag{1.3.2}$$

However, another definition of force is possible. Instead of calculating the derivative from the average energy, the average from the derivative of the operator $H$ over the selected parameter $\lambda$ may be calculated:

$$F'=-\left\langle\frac{\partial\hat{H}}{\partial\lambda}\right\rangle=-\langle\Psi|\frac{\partial\hat{H}}{\partial\lambda}|\Psi\rangle\tag{1.3.3}$$

Naturally, eq. 1.3.2 provides a way to calculate force without having to solve the Schrödinger equation. It is enough to know the dependence of the Hamiltonian on the parameter $\lambda$ and to calculate the quantum mechanical average in the state of interest $\frac{\partial\hat{H}}{\partial\lambda}$. Feynman has also demonstrated the equivalence of definitions (eq. 1.3.1 and 1.3.2) and to determine this force (from definition eq. 1.3.2) for the case of an infinitesimal change of the position of the *i*-th atom in the electric field coming from all electrons and nuclei [65]. The demonstration of the equivalence of definitions eq. 1.3.1 and eq. 1.3.2 is as follows:

$$\begin{aligned}
F&=-\frac{\partial}{\partial\lambda}\left\langle\hat{H}\right\rangle=-\int\frac{\partial}{\partial\lambda}\left(\Psi^*\hat{H}\Psi\right)d\mathbf{r}=\\
&=-\left\{\int\left(\frac{\partial}{\partial\lambda}\Psi^*\right)\hat{H}\Psi d\mathbf{r}+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}+\int\Psi^*\hat{H}\left(\frac{\partial}{\partial\lambda}\Psi\right)d\mathbf{r}\right\}=\\
&=-\left\{\int\left(\frac{\partial}{\partial\lambda}\Psi^*\right)\left(\hat{H}\Psi\right)d\mathbf{r}+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}+\int\left(\frac{\partial}{\partial\lambda}\Psi\right)\left(\hat{H}\Psi\right)^*d\mathbf{r}\right\}=\\
&=-\left\{E\int\left(\frac{\partial}{\partial\lambda}\Psi^*\right)\Psi d\mathbf{r}+E\int\left(\frac{\partial}{\partial\lambda}\Psi\right)\Psi^*d\mathbf{r}+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}\right\}=\\
&=-\left\{E\left(\int\frac{\partial}{\partial\lambda}\left(\Psi^*\Psi\right)d\mathbf{r}\right)+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}\right\}=-\left\{E\frac{\partial}{\partial\lambda}\int\left(\Psi^*\Psi\right)d\mathbf{r}+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}\right\}=\\
&=-\left\{0+\int\Psi^*\frac{\partial\hat{H}}{\partial\lambda}\Psi d\mathbf{r}\right\}=-\left\langle\frac{\partial\hat{H}}{\partial\lambda}\right\rangle=F'
\end{aligned}$$

$d\mathbf{r}$ has been used to replace all arguments of the wave function. Hence:

$$F = -\frac{\partial}{\partial\lambda}\langle\hat{H}\rangle = -\left\langle\frac{\partial\hat{H}}{\partial\lambda}\right\rangle = F' \qquad (1.3.4)$$

The Hermitian character of the Hamiltonian has been assumed and the wave function has been normalized. In a quantum system where $\hat{H} = \hat{T} + \hat{V}$ with the kinetic energy operator $\hat{T}$ independent on $\lambda$, the force may be calculated as the derivative of the potential since $\frac{\partial\hat{H}}{\partial\lambda} = \frac{\partial\hat{V}}{\partial\lambda}$. Finally:

$$F = -\left\langle\frac{\partial\hat{H}}{\partial\lambda}\right\rangle = -\left\langle\frac{\partial\hat{V}}{\partial\lambda}\right\rangle = -\int\frac{\partial\hat{V}}{\partial\lambda}\Psi\Psi^{*}d\mathbf{r}\,. \qquad (1.3.5)$$

The force can be determined for any interactions and parameters. For the simplest case of electrostatic interactions in a chemical molecule whose electronic state is $\psi$, (the Hamiltonian $\hat{H} = \hat{T} + \hat{V}$ describes the electron gas in the external field of stationary nuclei) Feynman presented the following solution [65]. Let $\mathbf{Q}_i = (X_i, Y_i, Z_i)$ be a vector defining the position of the *i*-th nucleus in the molecule, and $\mathbf{r}_\alpha = (x_\alpha, y_\alpha, z_\alpha)$ denotes the position of the $\alpha$-th electron, then the natural choice of the parameter $\lambda$ is $\mathbf{Q}_i$. In other words:

$$\mathbf{F}_i = -\left\langle\frac{\partial\hat{V}}{\partial\mathbf{Q}_i}\right\rangle = (F_i^X, F_i^Y, F_i^Z) = -\left(\left\langle\frac{\partial\hat{V}}{\partial X_i}\right\rangle, \left\langle\frac{\partial\hat{V}}{\partial Y_i}\right\rangle, \left\langle\frac{\partial\hat{V}}{\partial Z_i}\right\rangle\right). \qquad (1.3.6)$$

The interaction operator is:

$$\hat{V} = \sum_{i,j}\hat{V}_{ij} + \sum_{\alpha,i}\hat{V}_{\alpha i} + \sum_{\alpha,\beta}\hat{V}_{\alpha\beta} \qquad (1.3.7)$$

where $\hat{V}_{ij} = \frac{1}{4\pi\varepsilon_0}\frac{Z_i Z_j}{Q_{ij}}$ (1.3.8)

$\hat{V}_{ij}$ represents the repulsion between the nuclei $Z_i$ and $Z_j$ ($i \neq j$), with ($i \neq j$) and $\mathbf{Q}_{ij} = \mathbf{Q}_i - \mathbf{Q}_j$ and $Q_{ij} = |\mathbf{Q}_{ij}|$. The interaction energy between electron $\alpha$ nucleus *i* is given by:

$$\hat{V}_{\alpha i} = \frac{1}{4\pi\varepsilon_0}\frac{Z_i e}{Q_{\alpha i}} \qquad (1.3.9)$$

Here *e* stands for the elementary charge and:

$$(Q_{\alpha i})^2 = (\mathbf{Q}_i - \mathbf{r}_\alpha)^2 = (X_i - x_\alpha)^2 + (Y_i - y_\alpha)^2 + (Z_i - z_\alpha)^2\,, \qquad (1.3.10)$$

Every pair of electrons in the sum $\sum_{\alpha,i}\hat{V}_{\alpha i}$ is represented by the repulsion potential for $\alpha$ i $\beta$ at a distance $r_{\alpha\beta}$ ($\alpha \neq \beta$):

$$\hat{V}_{\alpha\beta} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{\alpha\beta}} \tag{1.3.11}$$

$$(r_{\alpha\beta})^2 = (\mathbf{r}_\alpha - \mathbf{r}_\beta)^2 = (x_\alpha - x_\beta)^2 + (y_\alpha - y_\beta)^2 + (z_\alpha - z_\beta)^2 \tag{1.3.12}$$

The natural identities are:

$$\hat{V}_{ij} = \hat{V}_{ji} \tag{1.3.13}$$

$$\hat{V}_{\alpha\beta} = \hat{V}_{\beta\alpha} \tag{1.3.14}$$

In eq. 1.3.6 each pair is considered exactly once in the summations.

$$\frac{\partial\hat{V}}{\partial\mathbf{Q}_i} = \sum_{j,k}\frac{\partial\hat{V}_{jk}}{\partial\mathbf{Q}_i} + \sum_{\alpha,j}\frac{\partial\hat{V}_{\alpha j}}{\partial\mathbf{Q}_i} + \sum_{\alpha,\beta}\frac{\partial\hat{V}_{\alpha\beta}}{\partial\mathbf{Q}_i} \tag{1.3.15}$$

Also: $$\frac{\partial\hat{V}_{\alpha j}}{\partial\mathbf{Q}_i} = -\delta_{ij}\frac{\partial\hat{V}_{\alpha j}}{\partial\mathbf{r}_\alpha} \tag{1.3.16}$$

and $$\frac{\partial\hat{V}_{\alpha\beta}}{\partial\mathbf{Q}_i} = 0 \tag{1.3.17}$$

hence: $$\sum_{\alpha,j}\frac{\partial\hat{V}_{\alpha j}}{\partial\mathbf{Q}_i} = -\sum_{\alpha,j}\delta_{ij}\frac{\partial\hat{V}_{\alpha j}}{\partial\mathbf{r}_\alpha} = -\sum_{\alpha}\frac{\partial\hat{V}_{\alpha i}}{\partial\mathbf{r}_\alpha}\,. \tag{1.3.18}$$

Also: $$\sum_{j,k}\frac{\partial\hat{V}_{jk}}{\partial\mathbf{Q}_i} = \sum_{j,k}\delta_{ik}\frac{\partial\hat{V}_{jk}}{\partial\mathbf{Q}_i} = \sum_{j}\frac{\partial\hat{V}_{ij}}{\partial\mathbf{Q}_i}\,. \tag{1.3.19}$$

Therefore: $$\mathbf{F}_i = -\left\langle\frac{\partial\hat{V}}{\partial\mathbf{Q}_i}\right\rangle = +\int\left\{\sum_{\alpha}\frac{\partial\hat{V}_{\alpha i}}{\partial\mathbf{r}_\alpha}\psi^*\psi\right\}d\mathbf{r} - \int\left\{\sum_{j}\frac{\partial\hat{V}_{ij}}{\partial\mathbf{Q}_i}\psi^*\psi\right\}d\mathbf{r} =$$

$$= +\int\left\{\sum_{\alpha}\frac{\partial\hat{V}_{\alpha i}}{\partial\mathbf{r}_\alpha}\int_{\alpha}\int\psi^*\psi d\mathbf{r}\right\}d\mathbf{r} - \sum_{j}\frac{\partial\hat{V}_{ij}}{\partial\mathbf{Q}_i} \tag{1.3.20}$$

The derivative $\frac{\partial\hat{V}_{\alpha i}}{\partial\mathbf{r}_\alpha}$ depends only on a single electron parameter. $\int_{\alpha}\int\psi^*\psi d\mathbf{r}$ stands for the integration of $\psi^*\psi$ over $3N$ arguments except those for electron $\alpha$. No electron parameters are present in the derivative $\frac{\partial\hat{V}_{ij}}{\partial\mathbf{Q}_i}$.

The derivative of the nucleus-electron interaction over the electron coordinate $\frac{\partial\hat{V}_{\alpha i}}{\partial\mathbf{r}_\alpha}$ is recognized as the electric field generated by the *i*-th nucleus at the point where the electron $\alpha$ is located:

$\frac{\partial \hat{V}_{\alpha i}}{\partial \mathbf{r}_{\alpha}} = \boldsymbol{\varepsilon}_i(\mathbf{r}_{\alpha})$. However, this derivative does not depend on which electron is at $\mathbf{r}$; index $\alpha$ may be neglected.

$$\mathbf{F}_i = +\int \left\{ \sum_{\alpha} \boldsymbol{\varepsilon}_i(\mathbf{r}) \int_{\alpha} \int \psi^* \psi d\mathbf{r} \right\} d\mathbf{r} - \sum_j \frac{\partial \hat{V}_{ij}}{\partial \mathbf{Q}_i} \tag{1.3.21}$$

Finally, the density of the electron cloud at $\mathbf{r}$ is (eq. 1.1.4):

$$\sum_{\alpha} \int_{\alpha} \int \psi^* \psi d\mathbf{r} = N \int_{\alpha} \int \psi^* \psi d\mathbf{r} = \rho(\mathbf{r})$$

This leads to the result:

$$\mathbf{F}_i = \int \boldsymbol{\varepsilon}_i(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - \sum_j \frac{\partial \hat{V}_{ij}}{\partial \mathbf{Q}_i} \tag{1.3.22}$$

The strength of the electrostatic interaction in a molecule is given by two terms. First is the force coming from the electron cloud, and the second is the interaction with the other nuclei. The 3*N*-dimensional space has been reduced to three dimensions.

The Hellmann–Feynman theorem (eq. 1.3.4) is satisfied for the exact wave function and for some of the approximate methods [66]. The author showed that for some approximate methods (e. g. limited CI) the discrepancy with theorem (eq. 1.3.4) can be very large. Also, electronic properties of molecules, such as static tensors of polarizability (calculated using the dipole expansion) do not meet the appropriate symmetry conditions, and the determined quantities may be considered non-physical. It was found that to determine the electronic properties of a molecule qualitatively correctly for methods that do not satisfy theorem (eq. 1.3.4), the force should be determined as the energy gradient (eq. 1.3.1) and not as the average of the Hamiltonian derivative (eq. 1.3.3) [66]. With the above in mind, I conclude that the forces for the purposes of this work have only been calculated as a negative energy gradient.

# 2

# Coupling between the electron density and the position of atoms in the molecule

In this chapter, the coupling between the coordinate of the number of electrons and the Cartesian and normal coordinates of the positions of atomic nuclei will be discussed. The analysis is based on the nuclear coordinate representation introduced in section 2.1 and the application of the canonical and grand canonical ensemble descriptions (sections 2.2 and 2.3). Next, the taxonomy of derivatives appearing in both groups and their mutual relations are presented (2.4 and 2.5). Derivatives and their mutual relations are used in energy expansions (2.6), renormalization of the oscillating system properties (2.7) and in the analysis of thermal fluctuations of the system (2.8).

## 2.1 Representation [$N$, $\mathbf{Q}_i$]

Calculations of the total differential energy in the DFT theory, has commonly been limited to the electron energy; the electrostatic potential of nuclei is an external potential for the electron density. The electron energy is a functional of the number of electrons and the external potential. The analysis of couplings of electronic properties of a molecular system with oscillations requires the formulation of an expression for the total differential of the total energy:

$$E_c = E + E_n + E_{e-n}\,. \tag{2.1.1}$$

$E$ represents the electronic energy together with the interaction with the external potential coming from the nuclei, $E_n$ is the nuclear energy, and $E_{e-n}$ represents the coupling between electronic and nuclear variables. Such an approach means going beyond the Born–Oppenheimer approximation; if the last term in equation 2.1.1 were to be discarded, the analysis described below would be flawed. Changes in the total energy of the system will be represented by changes in the coordinates describing the position of the atomic nuclei $\mathbf{Q}_i$ instead of the potential $\mathrm{v}(\mathbf{r})$; $\mathbf{Q}_i$ is the vector defining the position of the *i*-th nucleus. The increment $d\mathbf{Q}_i$ defines the infinitesimal change of this position. The change in energy that occurs is equal to the virtual work needed to perform this deformation. The external potential interacting with which the electrons is given by:

$$\mathrm{v}(\mathbf{r}) = \sum_i \frac{Z_i}{|\mathbf{Q}_i - \mathbf{r}|} \, . \qquad (2.1.2)$$

The gradient of this potential is equal to the electric field (generated by all atomic nuclei) at point **r**:

$$\nabla \mathrm{v}(\mathbf{r}) = -\boldsymbol{\varepsilon}(\mathbf{r}) \, . \qquad (2.1.3)$$

Another derivative will be shown as much informative:

$$\nabla_i \mathrm{v}(\mathbf{r}) \equiv \left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_\mathrm{i}} \right)_X = -\boldsymbol{\varepsilon}_i(\mathbf{r}) \qquad (2.1.4)$$

Equation 2.2.4 describes the electric field of the *i*-th nucleus at the point **r**. X stands for a set of variables including the position of the other nuclei except for the one for differentiation, and an additional parameter appropriate for a given set. For the canonical ensemble it is the number of electrons $N$, and for the grand canonical ensemble it is the chemical potential $\mu$. Compared to the traditional description of reactivity in ensembles [64, 53], the change is in replacing derivatives over $\mathrm{v}(\mathbf{r})$ with derivatives over $\mathbf{Q}_i$. The relationship between traditional derivative and those over $\mathbf{Q}_i$ is given by the electric field. Differentiation with a constant $N$ in the canonical ensemble and with constant $\mu$ in grand canonical ensemble give the same result, since in the canonical ensemble $[N, \mathbf{Q}_i]$

$$d\mathrm{v}(\mathbf{r}) = \sum_i \left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i} \right)_N d\mathbf{Q}_i + \left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial N} \right)_{\mathbf{Q}} dN \qquad (2.1.5)$$

$\mathrm{v}(\mathbf{r})$ i $N$ are independent in this ensemble, hence:

$$\left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial N} \right)_{\mathbf{Q}} = 0 \qquad (2.1.6)$$

and $$d\mathrm{v}(\mathbf{r}) = \sum_i \left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i} \right)_N d\mathbf{Q}_i \, . \qquad (2.1.7)$$

In the grand canonical ensemble:

$$\left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mu} \right)_{\mathbf{Q}} = 0 \, . \qquad (2.1.8)$$

In an isolated system $\mathrm{v}(\mathbf{r})$ cannot be altered with all $\mathbf{Q}_i$ =const.

$$d\mathrm{v}(\mathbf{r}) = \sum_i \left( \frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i} \right)_\mu d\mathbf{Q}_i \, . \qquad (2.1.9)$$

Since all $\mathbf{Q}_i$ are mutually independent, the important identity results:

$$\left(\frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_\mu = -\boldsymbol{\varepsilon}_i(\mathbf{r}) \qquad (2.1.10)$$

The differentia for the electronic energy in the canonical ensemble in $[N, \mathrm{v}(\mathbf{r})]$ representation is:

$$dE = \mu dN + \int \rho(\mathbf{r}) \delta\, \mathrm{v}(\mathbf{r}) d\mathbf{r} \qquad (2.1.11)$$

The consequence is:

$$\left(\frac{\delta E(N, \mathrm{v}(\mathbf{r}))}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N = \rho(\mathbf{r})\,. \qquad (2.1.12)$$

since $E(N, \mathrm{v}(\mathbf{r}))$ does not include the internuclear interactions. Otherwise $\left(\frac{\delta E_c}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N$ would be:

$$\left(\frac{\delta E_c}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N = \rho(\mathbf{r}) + \rho_+(\mathbf{r})\,, \qquad (2.1.13)$$

Here $E_c$ – is the total energy and $\rho_+(\mathbf{r})$ stands for the density of the +charge in a molecule. The limitation to electron energy seems unnatural in the $[N, \mathbf{Q}_i]$ coordinates. The force is derived from the total energy at the position of the *i*-th atom, and includes the repulsion of the nuclei. The agreement of energy in both representations is crucial for determination the relationships between the quantities present in both images:

$$\begin{aligned} -\left(\frac{\partial E_c(N, \mathbf{Q})}{\partial \mathbf{Q}_i}\right)_N &= -\int \left(\frac{\delta E_c(N, \mathrm{v}(\mathbf{r}))}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N \left(\frac{\partial\, \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N = \\ &= \int \rho(\mathbf{r}) \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r} + \int \rho_+(\mathbf{r}) \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r} = \int \rho(\mathbf{r}) \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r} + \mathbf{F}_i^{n-n} = \mathbf{F}_i \end{aligned} \qquad (2.1.14)$$

This is in accord with Hellmann – Feynman theorem [65]. The problem does not appear when calculating derivatives with respect to the number of electrons. The internuclear interactions do not depend on N, therefore:

$$\left(\frac{\partial E_c(N, \mathrm{v}(\mathbf{r}))}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial E(N, \mathrm{v}(\mathbf{r}))}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial E_c(N, \mathbf{Q}_i)}{\partial N}\right)_{\mathbf{Q}} = \mu = -\chi\,. \qquad (2.1.15)$$

The global hardness in the $[N, \mathbf{Q}_i]$ representation is [2]:

$$\left(\frac{\partial E_c^2(N, \mathrm{v}(\mathbf{r}))}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial E^2(N, \mathrm{v}(\mathbf{r}))}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial E_c^2(N, \mathbf{Q}_i)}{\partial N^2}\right)_{\mathbf{Q}} \equiv \eta\,. \qquad (2.1.16)$$

## 2.2 Canonical ensemble

The analysis exploring the statistical ensembles has been introduced in the work of Nalewajski [63, 64] and by Liu and Parr [67]. In the canonical ensemble, the energy is a function of the global variable *N* and the local variable v(r). In this present work the energy changes have been related to $N$ and $\mathbf{Q}_i$ rather than to the external potential v(r). These variables allow for a convenient analysis of the coupling effect between the change in the position of atomic nuclei and the change in the number of electrons in a chemical reaction. For this purpose, the DFT equations will be transformed accordingly. By the classical analysis:

$$dE = \mu dN + \int \rho(\mathbf{r})\delta \,\mathrm{v}(\mathbf{r})d\mathbf{r}\,. \qquad (2.2.1)$$

In the $N$ and $\mathbf{Q}_i$ representation:

$$dE_c = \mu dN - \sum_i \mathbf{F}_i \cdot d\mathbf{Q}_i\,. \qquad (2.2.2)$$

The chemical potential $\mu$ is also related to the same variables [$N$, v(r)], hence, classically:

$$d\mu = \eta dN + \int f(\mathbf{r})\delta \,\mathrm{v}(\mathbf{r})d\mathbf{r}\,. \qquad (2.2.3)$$

This is transformed to:

$$d\mu = \eta dN - \sum_i \mathbf{\Phi}_i \cdot d\mathbf{Q}_i \qquad (2.2.4)$$

where [1]: $$\mathbf{\Phi}_i = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_N . \qquad (2.2.5)$$

DFT Maxwell relations in representation $[N, \mathrm{v}(\mathbf{r})]$ are:

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\delta \mu}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N = f(\mathbf{r}) \qquad (2.2.6)$$

and $$\left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\delta \eta}{\delta\, \mathrm{v}(\mathbf{r})}\right)_N \qquad (2.2.7)$$

In the [$N$, $\mathbf{Q}_i$ ] representation they become [1]:

$$\left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_{N} \equiv \mathbf{\Phi}_i \qquad (2.2.8)$$

and $$-\left(\frac{\partial\eta}{\partial\mathbf{Q}_i}\right)_{\boldsymbol{N}}=\left(\frac{\partial^2\mathbf{F}_i}{\partial N^2}\right)_{\mathbf{Q}}=\left(\frac{\partial\mathbf{\Phi}_i}{\partial N}\right)_{\mathbf{Q}}\equiv-\mathbf{G}_i\,. \tag{2.2.9}$$

The differential of hardness provides an additional relation:

$$d\eta=\gamma dN+\int h(\mathbf{r})\delta\,\mathrm{v}(\mathbf{r})d\mathbf{r} \tag{2.2.10}$$

In eq. 2.2.10 $\gamma$ and $h(\mathbf{r})$ are indices introduces by Fuentealba and Parr [58] (eq. 1.2.29):

$$\gamma\equiv\left(\frac{\partial\eta}{\partial N}\right)_{\mathrm{v}(\mathbf{r})}=\left(\frac{\partial^3E}{\partial N^3}\right)_{\mathrm{v}(\mathbf{r})} \tag{2.2.11}$$

and $$h(\mathbf{r})\equiv\left(\frac{\delta\eta}{\delta\,\mathrm{v}(\mathbf{r})}\right)_N=\left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})}=\left(\frac{\delta}{\delta\,\mathrm{v}(\mathbf{r})}\left(\frac{\partial^2E}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})}\right)_N\,. \tag{2.2.12}$$

Integration of $h(\mathbf{r})$ must be zero:

$$\int h(\mathbf{r})d\mathbf{r}=\left(\frac{\partial}{\partial N}\int f(\mathbf{r})d\mathbf{r}\right)_{\mathrm{v}(\mathbf{r})}=\left(\frac{\partial}{\partial N}1\right)_{\mathrm{v}(\mathbf{r})}=0$$

The Maxwell relations for eq. 2.2.10 is:

$$\left(\frac{\delta\gamma}{\delta\,\mathrm{v}(\mathbf{r})}\right)_N=\left(\frac{\partial h(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} \tag{2.2.13}$$

In the $[N,\mathbf{Q}_i]$ representation the infinitesimal change in hardness is expressed by [62]:

$$d\eta=\gamma dN+\sum_i\mathbf{G}_i\cdot d\mathbf{Q}_i \tag{2.2.14}$$

Here $\gamma$ calculated at constant $\mathrm{v}(\mathbf{r})$ and constant $\mathbf{Q}$ is identical to eq. 2.2.11:

$$\gamma=\left(\frac{\partial\eta}{\partial N}\right)_{\mathbf{Q}}=\left(\frac{\partial^3E}{\partial N^3}\right)_{\mathbf{Q}} \tag{2.2.15}$$

Since: $$\left(\frac{\partial\eta}{\partial N}\right)_{\mathrm{v}(\mathbf{r})}=\left(\frac{\partial\eta}{\partial N}\right)_{\mathbf{Q}}\,. \tag{2.2.16}$$

The Maxwell relations for eq. 2.2.14 is:

$$\left(\frac{\partial\gamma}{\partial\mathbf{Q}_i}\right)_{\boldsymbol{N}}=\left(\frac{\partial\mathbf{G}_i}{\partial N}\right)_{\mathbf{Q}} \tag{2.2.17}$$

The differential of the electron density may also be expressed in two alternative representations:

$[N, \mathrm{v}(\mathbf{r})]$ or $[N, \mathbf{Q}_i]$. The classical equation is:

$$d\rho(\mathbf{r}) = f(\mathbf{r})dN + \int \omega(\mathbf{r},\mathbf{r}')\delta\,\mathrm{v}(\mathbf{r}')d\mathbf{r}' \qquad (2.2.18)$$

Here $\omega(\mathbf{r},\mathbf{r}')$ in the Linear Response Function:

$$\omega(\mathbf{r},\mathbf{r}') = \left(\frac{\delta\rho(\mathbf{r})}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_N . \qquad (2.2.19)$$

$\omega(\mathbf{r},\mathbf{r}')$ is integrated to zero:

$$\int \omega(\mathbf{r},\mathbf{r}')d\mathbf{r} = \int\left(\frac{\delta\rho(\mathbf{r})}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_N d\mathbf{r} = \left(\frac{\delta}{\delta\,\mathrm{v}(\mathbf{r}')}\int \rho(\mathbf{r})d\mathbf{r}\right)_N = 0 \qquad (2.2.20)$$

The Maxwell relation is:

$$\left(\frac{\partial\omega(\mathbf{r},\mathbf{r}')}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\delta f(\mathbf{r})}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_N . \qquad (2.2.21)$$

In the representation $[N, \mathbf{Q}_i]$ eq. 2.2.18 becomes:

$$d\rho(\mathbf{r}) = f(\mathbf{r})dN + \sum_i \boldsymbol{\varpi}_i(\mathbf{r})\cdot d\mathbf{Q}_i \qquad (2.2.22)$$

where: $\boldsymbol{\varpi}_i(\mathbf{r}) = \left(\frac{\partial\rho(\mathbf{r})}{\partial\mathbf{Q}_i}\right)_N$ (2.2.23)

This represents a new, electron–nuclear response function like $\omega(\mathbf{r},\mathbf{r}')$; it is integrated to zero and the relation analogous to eq. 2.2.21 is:

$$\left(\frac{\partial\boldsymbol{\varpi}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial f(\mathbf{r})}{\partial\mathbf{Q}_i}\right)_N . \qquad (2.2.24)$$

The relations between the derivatives in both representation in the canonical ensemble are obtained taking into account that the nucleus-nucleus interaction does not depend on $N$ and therefore the equation in the representation $[N, \mathbf{Q}_i]$ may be expanded to the ones in representation $[N, \mathrm{v}(\mathbf{r})]$(eq. 1.2.33 – 1.2.35):

$$\boldsymbol{\Phi}_i = \left(\frac{\partial\mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = -\left(\frac{\partial\mu}{\partial\mathbf{Q}_i}\right)_N = -\int\left(\frac{\delta\mu}{\delta\,\mathrm{v}(\mathbf{r})}\right)_N\left(\frac{\partial\,\mathrm{v}(\mathbf{r})}{\partial\mathbf{Q}_i}\right)_N d\mathbf{r} = \int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} . \qquad (2.2.25)$$

and:
$$\begin{aligned}\mathbf{G}_i &= -\left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2}\right)_{\mathbf{Q}} = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = \int \left(\frac{\delta \eta}{\delta \mathrm{v}(\mathbf{r})}\right)_N \left(\frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r} = \\ &= -\int \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r} = -\int h(\mathbf{r}) \boldsymbol{\varepsilon}_i(\mathbf{r}) d\mathbf{r}\end{aligned} \tag{2.2.26}$$

Also:
$$\boldsymbol{\varpi}_i(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N = \int \left(\frac{\delta \rho(\mathbf{r})}{\delta \mathrm{v}(\mathbf{r}')}\right)_N \left(\frac{\delta \mathrm{v}(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r}' = \int \omega(\mathbf{r},\mathbf{r}') \boldsymbol{\varepsilon}_i(\mathbf{r}') d\mathbf{r}', \tag{2.2.27}$$

and
$$\begin{aligned}\left(\frac{\partial \boldsymbol{\varpi}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} &= \left(\frac{\partial f(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_N = \int \left(\frac{\delta f(\mathbf{r})}{\delta \mathrm{v}(\mathbf{r}')}\right)_N \left(\frac{\delta \mathrm{v}(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_N d\mathbf{r}' = \\ &= \int \left(\frac{\partial \omega(\mathbf{r},\mathbf{r}')}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} \boldsymbol{\varepsilon}_i(\mathbf{r}') d\mathbf{r}'\end{aligned}. \tag{2.2.28}$$

The electric field vector $\boldsymbol{\varepsilon}_i(\mathbf{r})$ calculated for ich point $\mathbf{r}$ is the crucial quantity that links together equation in two alternative representations.

### 2.3 Grand canonical ensemble

The independent variables in the grand canonical ensemble are $\mu$ and v(**r**). The thermodynamical potential minimized for this ensemble is defined:

$$\Omega = E - \mu N . \tag{2.3.1}$$

The differential of $\Omega$ is:

$$d\Omega = dE - \mu dN - N d\mu . \tag{2.3.2}$$

Using eq. 2.2.1 leads to:

$$d\Omega = -N d\mu + \int \rho(\mathbf{r}) \delta \mathrm{v}(\mathbf{r}) d\mathbf{r} \tag{2.3.3}$$

Hence:
$$\left(\frac{\partial \Omega}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} = -N \tag{2.3.4}$$

and
$$\left(\frac{\partial \Omega}{\partial \mathrm{v}(\mathbf{r})}\right)_{\mu} = \rho(\mathbf{r}) . \tag{2.3.5}$$

The local softness results from the Maxwell relation (2.3.3):

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} = -\left(\frac{\delta N}{\delta \mathrm{v}(\mathbf{r})}\right)_{\mu} = s(\mathbf{r}) . \tag{2.3.6}$$

The differentia for $N$ and $\rho(\mathbf{r})$ are readily expressed by $\mu$ and v(**r**):

$$dN = Sd\mu - \int s(\mathbf{r})\delta\,\mathrm{v}(\mathbf{r})d\mathbf{r} \tag{2.3.7}$$

$$d\rho(\mathbf{r}) = s(\mathbf{r})d\mu - \int s(\mathbf{r},\mathbf{r}')\delta\,\mathrm{v}(\mathbf{r})d\mathbf{r} \tag{2.3.8}$$

since $$\left(\frac{\partial N}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} = S \tag{2.3.9}$$

Using eq. 1.2.19 and eq. 1.2.17:

$$s(\mathbf{r},\mathbf{r}') = -\left(\frac{\delta\rho(\mathbf{r})}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_{\mu} . \tag{2.3.10}$$

Since the second mixed derivatives in $N(\mu, \mathrm{v}(\mathbf{r}))$ (eq. 2.3.7) and $\rho(\mu, \mathrm{v}(\mathbf{r});\mathbf{r})$ (eq. 2.3.8) are equal, the following equations result:

$$\left(\frac{\partial s(\mathbf{r})}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} = -\left(\frac{\delta S}{\delta\,\mathrm{v}(\mathbf{r})}\right)_{\mu} \tag{2.3.11}$$

$$\left(\frac{\partial s(\mathbf{r},\mathbf{r}')}{\partial \mu}\right)_{\mathrm{v}(\mathbf{r})} = -\left(\frac{\delta s(\mathbf{r})}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_{\mu} . \tag{2.3.12}$$

The above formalism must be transformed to representation $\mu$ and $\mathbf{Q}_i$ .

$$d\Omega_c = dE_c - \mu dN - Nd\mu \tag{2.3.13}$$

Taking $dE_c$ from eq. 2.2.2 the differential for the thermodynamic potential is:

$$d\Omega_c = -Nd\mu - \sum_i \mathbf{F}_i \cdot d\mathbf{Q}_i \tag{2.3.14}$$

Hence: $$\left(\frac{\partial \Omega_c}{\partial \mu}\right)_{\mathbf{Q}} = -N \tag{2.3.15}$$

and $$\left(\frac{\partial \Omega_c}{\partial \mathbf{Q}_i}\right)_{\mu} = -\mathbf{F}_i \tag{2.3.16}$$

The Maxwell relation for eq. 2.3.14:

$$\left(\frac{\partial \mathbf{F}_i}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} = \boldsymbol{\sigma}_i \tag{2.3.17}$$

Also: $\left(\frac{\partial \mathbf{F}_i}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} \left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = \mathbf{\Phi}_i S$ (2.3.18)

hence: $\boldsymbol{\sigma}_i = \mathbf{\Phi}_i S$ (2.3.19)

where $\left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = S$ (2.3.20)

The global softness $S$ is identical in two representations as proved above (p. 2.1), and the nuclear softness $\boldsymbol{\sigma}_i$ may be alternatively calculated on two ways [58]. The global softness $S$, and the nuclear softness $\boldsymbol{\sigma}_i$ may be used for calculation of the electron exchange *dN*:

$$dN = Sd\mu + \sum_i \boldsymbol{\sigma}_i \cdot d\mathbf{Q}_i \ . \qquad (2.3.21)$$

Hence Maxwell relation combines the global and the nuclear softness’.

$$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_{\mu} . \qquad (2.3.22)$$

Also: $d\rho(\mathbf{r}) = s(\mathbf{r})d\mu + \sum_i \boldsymbol{\sigma}_{\boldsymbol{i}}(\mathbf{r}) d\mathbf{Q}_{\boldsymbol{i}}$ (2.3.23)

where $\boldsymbol{\sigma}_{\boldsymbol{i}}(\mathbf{r})$ is the local counterpart for the nuclear softness:

$$\boldsymbol{\sigma}_{\boldsymbol{i}}(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_{\boldsymbol{i}}}\right)_{\mu} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mu} \left(\frac{\partial N}{\partial \mathbf{Q}_{\boldsymbol{i}}}\right)_{\mu} = \tilde{f}(\mathbf{r})\boldsymbol{\sigma}_{\boldsymbol{i}} \qquad (2.3.24)$$

and $s(\mathbf{r})$ is the local softness:

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right)_{\mathbf{Q}} \qquad (2.3.25)$$

The analogue of the Fukui function is defined at constant $\mu$:

$$\tilde{f}(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mu} \qquad (2.3.26)$$

Therefore: $\left(\frac{\partial s(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} \left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} S$ (2.3.27)

The local nuclear softness $\boldsymbol{\sigma}_i(\mathbf{r})$ is integrated in the similar way as the softness kernel:

$$\int s(\mathbf{r},\mathbf{r}')d\mathbf{r}' = s(\mathbf{r}) , \qquad (2.3.28)$$

$$\int \boldsymbol{\sigma}_i(\mathbf{r})d\mathbf{r} = \int \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} d\mathbf{r} = \left(\frac{\partial}{\partial \mathbf{Q}_i}\int \rho(\mathbf{r})d\mathbf{r}\right)_{\mu} = \left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} = \boldsymbol{\sigma}_i\,. \tag{2.3.29}$$

The most interesting relations for two alternative representations in the grand canonical ensemble are:

$$\left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{Q_i}}\right)_{\boldsymbol{\mu}} = \int \left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{v(r)}}\right)_{\boldsymbol{\mu}} \left(\frac{\partial \boldsymbol{v(r)}}{\partial \boldsymbol{Q_i}}\right)_{\boldsymbol{\mu}} \boldsymbol{dr} = -\int \left(\frac{\partial \boldsymbol{S}}{\partial \boldsymbol{v(r)}}\right)_{\boldsymbol{\mu}} \boldsymbol{\varepsilon_i(r)dr} = \int \left(\frac{\partial \boldsymbol{s(r)}}{\partial \boldsymbol{\mu}}\right)_{\boldsymbol{v}} \boldsymbol{\varepsilon_i(r)dr} \tag{2.3.30}$$

$$\left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} = \boldsymbol{\sigma}_i = \int \left(\frac{\partial N}{\partial \mathrm{v}(\mathbf{r})}\right)_{\mu} \left(\frac{\partial \mathrm{v}(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} d\mathbf{r} = \int s(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = S\int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = S\boldsymbol{\Phi}_\iota \tag{2.3.31}$$

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} = \boldsymbol{\sigma}_i(\mathbf{r}) = \int \left(\frac{\partial \rho(\mathbf{r})}{\partial \mathrm{v}(\mathbf{r}')}\right)_{\mu} \left(\frac{\partial \mathrm{v}(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_{\mu} d\mathbf{r}' = \int s(\mathbf{r},\mathbf{r}')\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} \tag{2.3.32}$$

$$\begin{aligned}\left(\frac{\partial f(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} &= \int \left(\frac{\partial f(\mathbf{r})}{\partial \mathrm{v}(\mathbf{r}')}\right)_{\mu} \left(\frac{\partial \mathrm{v}(\mathbf{r}')}{\partial \mathbf{Q}_i}\right)_{\mu} d\mathbf{r}' = \\ &= -\int \left(\frac{\partial f(\mathbf{r})}{\partial \mathrm{v}(\mathbf{r}')}\right)_{\mu} \boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = -\int \left(\frac{\partial s(\mathbf{r},\mathbf{r}')}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} \boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}\end{aligned} \tag{2.3.33}$$

## 2.4 Relationships between derivatives in the ensembles

By comparing the differential $d\rho(\mathbf{r})$ in the canonical ensemble and the grand canonical ensemble (eq. 2.2. 22 and 2.3.23) and by exploring the result for the chemical potential (eq. 2.2.3) the result for the Fukui function in the representation $[N, \mathbf{Q}_i]$ is obtained:

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \eta s(\mathbf{r}) = f(\mathbf{r}) \tag{2.4.1}$$

This is identical to the original definition in $[N, \mathrm{v}(\mathbf{r})]$:

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \eta s(\mathbf{r})\,. \tag{2.4.2}$$

The most important result is the relation between the nuclear response function and the nuclear softness kernel:

$$\left(\frac{\partial \rho(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{N} \equiv \boldsymbol{\varpi}_i(\mathbf{r}) = -s(\mathbf{r})\boldsymbol{\Phi}_i + \boldsymbol{\sigma}_i(\mathbf{r}) = S\boldsymbol{\Phi}_i(\tilde{f}(\mathbf{r}) - f(\mathbf{r})) \tag{2.4.3}$$

where: $\tilde{f}(\mathbf{r}) \equiv \left(\frac{\partial \rho(\mathbf{r})}{\partial N}\right)_{\mu}$ . (2.4.4)

$\tilde{f}(\mathbf{r})$, identical in both representations $[N, \mathrm{v}(\mathbf{r})]$ i $[N, \mathbf{Q}_i]$ is the analogue of the Fukui function at constant $\mu$. The analogous result in representation $[N, \mathrm{v}(\mathbf{r})]$ is (eq. 1.2.27):

$$\omega(\mathbf{r},\mathbf{r}') = \frac{s(\mathbf{r})s(\mathbf{r}')}{S} - s(\mathbf{r},\mathbf{r}') \,. \tag{2.4.5}$$

Using the appropriate definition, the combination of the energy derivatives is:

$$\left(\frac{\partial \Omega_c}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial E_c}{\partial \mathbf{Q}_i}\right)_{\mu} - \mu\left(\frac{\partial N}{\partial \mathbf{Q}_i}\right)_{\mu} \tag{2.4.6}$$

or $$\left(\frac{\partial E_c}{\partial \mathbf{Q}_i}\right)_{\mu} = -\mathbf{F}_i + \mu\boldsymbol{\sigma}_i = -(\mathbf{F}_i - \mu S\boldsymbol{\Phi}_i) \tag{2.4.7}$$

Hence: $$\left(\frac{\partial E_c}{\partial \mathbf{Q}_i}\right)_{N} = \left(\frac{\partial E_c}{\partial \mathbf{Q}_i}\right)_{\mu} - \mu\boldsymbol{\sigma}_i = \left(\frac{\partial E_c}{\partial \mathbf{Q}_i}\right)_{\mu} - \mu S\boldsymbol{\Phi}_i \tag{2.4.8}$$

The following identity will be necessary for further analysis:

$$\left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial \eta}{\partial N}\right)_{\mathbf{Q}}\left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = \gamma S \,. \tag{2.4.9}$$

The hardness derivative $\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu}$ will be calculated by comparing the differentials of hardness in two ensembles:

$$d\eta = \gamma dN + \sum_i \mathbf{G}_i \cdot d\mathbf{Q}_i \tag{2.4.10}$$

$$d\eta = \left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} d\mu + \sum_i \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} \cdot d\mathbf{Q}_i \,. \tag{2.4.11}$$

Since $d\mu = \eta dN - \sum_i \boldsymbol{\Phi}_i \cdot d\mathbf{Q}_i$ (eq. 2.2.4):

$$d\eta = \left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} (\eta dN - \sum_i \boldsymbol{\Phi}_i \cdot d\mathbf{Q}_i) + \sum_i \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} \cdot d\mathbf{Q}_i \tag{2.4.12}$$

$$d\eta = \eta\left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} dN + \sum_i \left(\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} - \left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} \boldsymbol{\Phi}_i\right) \cdot d\mathbf{Q}_i \tag{2.4.13}$$

Using eq. 2.4.9:

$$d\eta = \frac{1}{S}\left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} dN + \sum_i \left( \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} - \gamma S \mathbf{\Phi}_i \right) \cdot d\mathbf{Q}_i \tag{2.4.14}$$

The coefficient at $dN$ and $d\mathbf{Q}_i$ in equations 2.4.10 and 2.4.14 must be equal, hence: $\frac{1}{S}\left(\frac{\partial \eta}{\partial \mu}\right)_{\mathbf{Q}} = \gamma$.

This is in accord with eq. 2.4.9, and the new relationship is:

$$\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} = \mathbf{G}_i + \gamma S \mathbf{\Phi}_i \tag{2.4.15}$$

The new global softness derivatives $\left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_N$ and $\left(\frac{\partial S}{\partial \mu}\right)_{\mathbf{Q}_i}$ are:

$$\left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial}{\partial \mathbf{Q}_i}\frac{1}{\eta}\right)_N = -\frac{1}{\eta^2}\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = -S^2 \mathbf{G}_i \, . \tag{2.4.16}$$

and: $$\left(\frac{\partial S}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial}{\partial N}\frac{1}{\eta}\right)_{\mathbf{Q}} = -\frac{1}{\eta^2}\left(\frac{\partial \eta}{\partial N}\right)_{\mathbf{Q}} = -S^2 \gamma \tag{2.4.17}$$

$$\left(\frac{\partial S}{\partial \mu}\right)_{\mathbf{Q}} = \left(\frac{\partial S}{\partial N}\right)_{\mathbf{Q}} \left(\frac{\partial N}{\partial \mu}\right)_{\mathbf{Q}} = -\gamma S^3 \tag{2.4.18}$$

Analogous operation with eq. 2.4.16 using eq. 2.4.15 leads directly to $\left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_{\mu}$ :

$$\left(\frac{\partial S}{\partial \mathbf{Q}_\mathrm{i}}\right)_{\mu} = \left(\frac{\partial S}{\partial \mathbf{Q}_\mathrm{i}}\right)_N - \gamma S^3 \mathbf{\Phi}_i = -S^2[\mathbf{G}_i + \gamma S \mathbf{\Phi}_i] = \left(\frac{\partial \boldsymbol{\sigma}_\mathrm{i}}{\partial \mu}\right)_{\mathbf{Q}} \tag{2.4.19}$$

The relation between $\boldsymbol{\sigma}_i$ and $N$ in grand canonical ensemble; it is found by using eq. 2.3.22 and eq. 2.4.19.

$$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial \boldsymbol{\sigma}_i}{\partial \mu}\right)_{\mathbf{Q}} \left(\frac{\partial \mu}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial S}{\partial \mathbf{Q}_i}\right)_{\mu} \left(\frac{\partial \mu}{\partial N}\right)_{\mathbf{Q}} = -S[\mathbf{G}_i + \gamma S \mathbf{\Phi}_i] \tag{2.4.20}$$

The new relation:

$$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial N}\right)_{\mathbf{Q}} = -S\left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_{\mu} \tag{2.4.21}$$

This opens the perspective for discovering the explicit relationship between $s(\mathbf{r})$ and $\boldsymbol{\sigma}_i(\mathbf{r})$ on $N$ (from eq. 2.3.25):

$$\left(\frac{\partial s(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial f(\mathbf{r})}{\partial \mu}\right)_{\mathbf{Q}} = Sh(\mathbf{r}) - \gamma S^2 f(\mathbf{r}) \tag{2.4.22}$$

From eq. 2.3.27:

$$\left(\frac{\partial \boldsymbol{\sigma}_i(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = \frac{1}{S}\left(\frac{\partial s(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial f(\mathbf{r})}{\partial \mathbf{Q}_i}\right)_{\mu} = \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mu} S\boldsymbol{\Phi}_i - \tilde{f}(\mathbf{r})S\left(\mathbf{G}_i + \gamma S\boldsymbol{\Phi}_i\right) \tag{2.4.23}$$

The following relation will be useful in further analysis:

$$\left(\frac{\partial \boldsymbol{\Phi}_i}{\partial \mathbf{Q}_j}\right)_{\mu} = -\lambda_{ij} - S\mathbf{G}_i \cdot \boldsymbol{\Phi}_j, \tag{2.4.24}$$

It will be proved in section 2.5 (eq. 2.5.20**).**

## 2.5 Systematic presentation of the derivatives

The analysis presented above allows for the systematic presentation of the entire field of the derivatives in the representation $[N, \mathbf{Q}_i]$. The derivatives of the total energy of the system by the number of electrons and the position of the atomic nuclei including the third order have been shown in Table 2.1. The second and third energy derivatives over the nuclear displacement - the force constants $k_{ij}$ and the anharmonic tensors $\mathbf{a}_{ijk}$ are:

$$k_{ij} = \left(\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial E_c}{\partial \mathbf{Q}_j}\right)_N\right)_N = -\left(\frac{\partial F_i}{\partial \mathbf{Q}_j}\right)_N, \tag{2.5.1}$$

$$\mathbf{a}_{ijk} = \left(\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial}{\partial \mathbf{Q}_j} \cdot \left(\frac{\partial E_c}{\partial \mathbf{Q}_k}\right)_N\right)_N\right)_N = \left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_N, \tag{2.5.2}$$

The mixed derivative is also interesting:

$$\lambda_{ij} = \left(\frac{\partial}{\partial N}\left(\frac{\partial}{\partial \mathbf{Q}_i} \cdot \left(\frac{\partial E_c}{\partial \mathbf{Q}_j}\right)_N\right)_N\right)_{\mathbf{Q}} = \left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}}. \tag{2.5.3}$$

The collection of the analogous derivative in representation $[N, \mathrm{v}(\mathbf{r})]$ has been presented in Table 2.2. The derivatives in the grand canonical ensemble have been presented in Table 2.3.

## Table 2.1

The energy derivatives over the number of electrons $N$
and over the displacement of the nuclei $\mathbf{Q}_i$ up to the third order.

| Canonical ensemble | | $\frac{\partial}{\partial N}$ | $\frac{\partial^2}{\partial N^2}$ | $\frac{\partial^3}{\partial N^3}$ |
|---|---|---|---|---|
| | $E_c$ | $\mu$ | $\eta$ | $\gamma$ |
| $\frac{\partial}{\partial \mathbf{Q}_i}$ | $-\mathbf{F}_i$ | $-\mathbf{\Phi}_i$ | $\mathbf{G}_i$ | |
| $\frac{\partial}{\partial \mathbf{Q}_i} \cdot \frac{\partial}{\partial \mathbf{Q}_j}$ | $k_{ij}$ | $\lambda_{ij}$ | | |
| $\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial}{\partial \mathbf{Q}_j} \cdot \frac{\partial}{\partial \mathbf{Q}_k}\right)$ | $\mathbf{a}_{ijk}$ | | | |

## Table 2.2

The energy derivatives over the number of electrons $N$
and over the external potential.

| Canonical ensemble | | $\left(\frac{\partial}{\partial N}\right)_{\mathrm{v}(\mathbf{r})}$ | $\left(\frac{\partial^2}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})}$ | $\left(\frac{\partial^3}{\partial N^3}\right)_{\mathrm{v}(\mathbf{r})}$ |
|---|---|---|---|---|
| | $E_c$ | $\mu$ | $\eta$ | $\gamma$ |
| $\left(\frac{\delta}{\delta \mathrm{v}(\mathbf{r})}\right)_N$ | $\rho(\mathbf{r})$ | $f(\mathbf{r})$ | $h(\mathbf{r})$ | |
| $\left(\frac{\delta^2}{\delta \mathrm{v}(\mathbf{r}) \delta \mathrm{v}(\mathbf{r}')}\right)_N$ | $\omega(\mathbf{r},\mathbf{r}')$ | | | |

**Table 2.3**

The derivatives of the thermodynamical potential $\Omega_c$ over the chemical potential and over the displacement of the nuclei $\mathbf{Q}_i$ up to the third order.

| Grand canonical ensemble | | $\frac{\partial}{\partial\mu}$ | $\frac{\partial^2}{\partial\mu^2}$ | $\frac{\partial^3}{\partial\mu^3}$ |
|---|---|---|---|---|
| | $\Omega_c$ | $-N$ | $-S$ | $\gamma S^3$ |
| $\frac{\partial}{\partial\mathbf{Q}_i}$ | $-\mathbf{F}_i$ | $-\boldsymbol{\sigma}_i$ | $S^2[\mathbf{G}_i+\gamma S\boldsymbol{\Phi}_i]$ | |
| $\frac{\partial}{\partial\mathbf{Q}_i}\cdot\frac{\partial}{\partial\mathbf{Q}_j}$ | $\tilde{k}_{ij}$ | $\tilde{\lambda}_{ij}$ | | |
| $\frac{\partial}{\partial\mathbf{Q}_i}\left(\frac{\partial}{\partial\mathbf{Q}_j}\cdot\frac{\partial}{\partial\mathbf{Q}_k}\right)$ | $\tilde{\mathbf{a}}_{ijk}$ | | | |

The derivative $\left(\frac{\partial\boldsymbol{\sigma}_i}{\partial\mu}\right)_{\mathbf{Q}}$ and $\left(\frac{\partial S}{\partial\mu}\right)_{\mathbf{Q}}$, involve other derivatives as it has been presented. Derivatives $\tilde{k}_{ij}$, $\tilde{\lambda}_{ij}$ and $\tilde{\mathbf{a}}_{ijk}$ are the analogues of the force constants $k_{ij}$, the mixed derivative $\lambda_{ij}$ and the anharmonic tensor $\mathbf{a}_{ijk}$. The mutual relations between the derivatives have been presented below. First, the derivative of force $\mathbf{F}_i$.

$$\left(\frac{\partial\mathbf{F}_i}{\partial\mathbf{Q}_j}\right)_N=-k_{ij}\ \text{and}\ \left(\frac{\partial\mathbf{F}_i}{\partial\mathbf{Q}_j}\right)_\mu=-\tilde{k}_{ij}\tag{2.5.4}$$

The differential of force in the canonical ensemble is:

$$d\mathbf{F}_i=\left(\frac{\partial\mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}}dN+\sum_j\left(\frac{\partial\mathbf{F}_i}{\partial\mathbf{Q}_j}\right)_N d\mathbf{Q}_j=\boldsymbol{\Phi}_i dN-\sum_j k_{ij}d\mathbf{Q}_j\,,\tag{2.5.5}$$

In the grand canonical ensemble:

$$d\mathbf{F}_i=\left(\frac{\partial\mathbf{F}_i}{\partial\mu}\right)_{\mathbf{Q}}d\mu+\sum_j\left(\frac{\partial\mathbf{F}_i}{\partial\mathbf{Q}_j}\right)_\mu d\mathbf{Q}_j=\boldsymbol{\sigma}_i d\mu-\sum_j\tilde{k}_{ij}d\mathbf{Q}_j\,.\tag{2.5.6}$$

Hence: $\boldsymbol{\Phi}_i dN-\sum_j k_{ij}d\mathbf{Q}_j=\boldsymbol{\sigma}_i d\mu-\sum_j\tilde{k}_{ij}d\mathbf{Q}_j$ (2.5.7)

Using $d\mu$ from eq. 2.2.4 leads to:

$$\mathbf{\Phi}_i dN - \sum_j k_{ij} d\mathbf{Q}_j = \boldsymbol{\sigma}_i \eta dN - \boldsymbol{\sigma}_i \sum_j \mathbf{\Phi}_j \cdot d\mathbf{Q}_j - \sum_j \tilde{k}_{ij} d\mathbf{Q}_j \tag{2.5.8}$$

Since the variables $\mathbf{Q}_i$ and $N$ are independent, eq. 2.3.19 has been confirmed: $\mathbf{\Phi}_i = \eta\boldsymbol{\sigma}_i$, and:

$$k_{ij} - \tilde{k}_{ij} = \boldsymbol{\sigma}_i \cdot \mathbf{\Phi}_j = S\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j \tag{2.5.9}$$

Both $k_{ij}$ and $\tilde{k}_{ij}$ are symmetric. By taking the derivative over $N$ (eq. 2.5.9) the following relation results:

$$\left(\frac{\partial k_{ij}}{\partial N}\right)_{\mathbf{Q}} - \left(\frac{\partial \tilde{k}_{ij}}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial(\boldsymbol{\sigma}_i \cdot \mathbf{\Phi}_j)}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial(S\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j)}{\partial N}\right)_{\mathbf{Q}} \tag{2.5.10}$$

But also $\left(\frac{\partial \tilde{k}_{ij}}{\partial N}\right)_{\mathbf{Q}} = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mu}\right)_{\mathbf{Q}} \left(\frac{\partial \mu}{\partial N}\right)_{\mathbf{Q}} = \tilde{\lambda}_{ij}\eta$ (2.5.11)

Hence $\tilde{\lambda}_{ij}$ is redundant and symmetric:

$$\lambda_{ij} - \eta\tilde{\lambda}_{ij} = \left(\frac{\partial(S\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j)}{\partial N}\right)_{\mathbf{Q}} = -\gamma S^2 \mathbf{\Phi}_i \cdot \mathbf{\Phi}_j - S\mathbf{\Phi}_i \cdot \mathbf{G}_j - S\mathbf{\Phi}_j \cdot \mathbf{G}_i\,. \tag{2.5.12}$$

Finally:

$$\tilde{\lambda}_{ij} = \gamma S^3 \mathbf{\Phi}_i \cdot \mathbf{\Phi}_j + S^2(\mathbf{\Phi}_i \cdot \mathbf{G}_j + \mathbf{\Phi}_j \cdot \mathbf{G}_i) + S\lambda_{ij} \tag{2.5.13}$$

This result allows for calculation of the anharmonic tensor (Table 3):

$$\tilde{\mathbf{a}}_{ijk} = \left(\frac{\partial \tilde{k}_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \left(\frac{\partial}{\partial \mathbf{Q}_k}\left(k_{ij} - S\mathbf{\Phi}_i \cdot \mathbf{\Phi}_j\right)\right)_{\mu} \tag{2.5.14}$$

The derivative $\left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu}$ may be calculated by the method tested before. To achieve the goal, the differential of the force constant is expressed in both ensembles.

$$dk_{ij} = \lambda_{ij} dN + \sum_k \mathbf{a}_{ijk} \cdot d\mathbf{Q}_k \tag{2.5.15}$$

$$dk_{ij} = \left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} d\mu + \sum_k \left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} \cdot d\mathbf{Q}_k \tag{2.5.16}$$

$d\mu$ has been known (eq. 2.2.4); the results are obtained by the comparison of the coefficients in eq. 2.5.15 and eq. 2.5.16:

$$\left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \mathbf{a}_{ijk} + \mathbf{\Phi}_k \left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} \tag{2.5.17}$$

and $$\lambda_{ij} = \left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} \eta . \tag{2.5.18}$$

Hence: $$\left(\frac{\partial k_{ij}}{\partial \mu}\right)_{\mathbf{Q}} = \lambda_{ij} S \tag{2.5.19}$$

Therefore: $$\left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \mathbf{a}_{ijk} + S\lambda_{ij}\mathbf{\Phi}_k \tag{2.5.20}$$

The necessary derivative $\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu}$ will be obtained from the definition of $\tilde{\lambda}_{ij}$ :

$$\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{N} = -\lambda_{ik} \neq \left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} \tag{2.5.21}$$

But: $$\left(\frac{\partial \boldsymbol{\sigma}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = -\tilde{\lambda}_{ik} = \left(\frac{\partial S\mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = \left(\frac{\partial S}{\partial \mathbf{Q}_k}\right)_{\mu} \cdot \mathbf{\Phi}_i + S\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} \tag{2.5.22}$$

hence: $$S\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = -\tilde{\lambda}_{ik} + S^2\mathbf{\Phi}_i \cdot [\mathbf{G}_k + \gamma S\mathbf{\Phi}_k] \tag{2.5.23}$$

Upon introducing into eq. **2.5.13** the result is:

$$\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} = -\lambda_{ik} + S\mathbf{\Phi}_k \cdot \mathbf{G}_i \tag{2.5.24}$$

Eq. 2.5.14 may then be transformed to:

$$\tilde{\mathbf{a}}_{ijk} \equiv \left(\frac{\partial \tilde{k}_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} = \left(\frac{\partial k_{ij}}{\partial \mathbf{Q}_k}\right)_{\mu} - \left(\frac{\partial S}{\partial \mathbf{Q}_k}\right)_{\mu} \mathbf{\Phi}_i \cdot \mathbf{\Phi}_j - S\left(\frac{\partial \mathbf{\Phi}_i}{\partial \mathbf{Q}_k}\right)_{\mu} \mathbf{\Phi}_j - S\left(\frac{\partial \mathbf{\Phi}_j}{\partial \mathbf{Q}_k}\right)_{\mu} \mathbf{\Phi}_i \tag{2.5.25}$$

By using eq. 2.5.24 the result is:

$$\begin{aligned} \tilde{\mathbf{a}}_{ijk} &= \mathbf{a}_{ijk} + S(\lambda_{ij}\mathbf{\Phi}_k + \lambda_{ik}\mathbf{\Phi}_j + \lambda_{jk}\mathbf{\Phi}_i) + \\ &+ S^2(\mathbf{\Phi}_j \cdot \mathbf{\Phi}_k\mathbf{G}_i + \mathbf{\Phi}_i \cdot \mathbf{\Phi}_k\mathbf{G}_j + \mathbf{\Phi}_i \cdot \mathbf{\Phi}_j\mathbf{G}_k) + \gamma S\mathbf{\Phi}_i\mathbf{\Phi}_i \cdot \mathbf{\Phi}_k \end{aligned} \tag{2.5.26}$$

The final results (eq. 2.5.9, 2.5.13 and 2.5.26) expose the physical meaning of the derivatives $\tilde{k}_{ij}$, $\tilde{\lambda}_{ij}$ and $\tilde{\mathbf{a}}_{ijk}$, since the only experimental quantities are the force constants $k_{ij}$ (the derivatives of energy $E_c$), not $\tilde{k}_{ij}$, the derivatives of the thermodynamical potential $\Omega_c$. The derivatives in Table 2.4 are analogous to the derivatives of the thermodynamical potential in the grand canonical ensemble in the representation $[N, \mathrm{v}(\mathbf{r})]$ as presented in Table 2.2

**Table 2.4**

The derivatives of the thermodynamic potential
over the chemical potential $\mu$ and over the external potential.

| Grand canonical ensemble | | $\left(\frac{\partial}{\partial\mu}\right)_{\mathrm{v}(\mathbf{r})}$ | $\left(\frac{\partial^2}{\partial\mu^2}\right)_{\mathrm{v}(\mathbf{r})}$ |
|---|---|---|---|
| | $\Omega$ | $-N$ | $-S$ |
| $\left(\frac{\delta}{\delta\,\mathrm{v}(\mathbf{r})}\right)_{\mu}$ | $\rho(\mathbf{r})$ | $s(\mathbf{r})$ | |
| $\left(\frac{\delta^2}{\delta\,\mathrm{v}(\mathbf{r})\delta\,\mathrm{v}(\mathbf{r}')}\right)_{\mu}$ | $-s(\mathbf{r},\mathbf{r}')$ | | |

By expanding the electron density, the role of new density derivatives $\boldsymbol{\varpi}_i(\mathbf{r})$ and $\boldsymbol{\sigma}_i(\mathbf{r})$ has been exposed in the canonical and grand canonical ensembles, respectively (Table 2.5 and Table 2.6).

**Table2.5**

Derivatives of the electron density in the canonical ensemble in $[N,\mathbf{Q}_i]$ representation

| Electron density derivatives | | $\left(\frac{\partial}{\partial N}\right)_{\mathbf{Q}_i}$ |
|---|---|---|
| | $\rho(\mathbf{r})$ | $f(\mathbf{r})$ |
| $\left(\frac{\partial}{\partial \mathbf{Q}_i}\right)_{N}$ | $\boldsymbol{\varpi}_i(\mathbf{r})$ | |

**Table 2.6**

Derivatives of the electron density in the grand canonical ensemble in $[\mu,\mathbf{Q}_i]$ representation

| Electron density derivatives | | $\left(\frac{\partial}{\partial \mu}\right)_{\mathbf{Q}_i}$ |
|---|---|---|
| | $\rho(\mathbf{r})$ | $s(\mathbf{r})$ |
| $\left(\frac{\partial}{\partial \mathbf{Q}_i}\right)_{\mu}$ | $\boldsymbol{\sigma}_i(\mathbf{r})$ | |

## 2.6 The energy expansion

As it has been demonstrated by Liu and Parr, any functional may be expanded into a series up to second order [67]:

$$Q[g,l] = Const + \left\{ g\left(\frac{\partial Q}{\partial g}\right)_l + \int l(\mathbf{r})\left(\frac{\delta Q}{\delta l(\mathbf{r})}\right)_g d\mathbf{r} \right\} - \frac{1}{2}\left\{ g^2\left(\frac{\partial^2 Q}{\partial g^2}\right)_l + 2g\int l(\mathbf{r})\left(\frac{\partial}{\partial g}\left(\frac{\delta Q}{\delta l(\mathbf{r})}\right)_g\right)_l d\mathbf{r} + \int\int l(\mathbf{r})l(\mathbf{r}')\left(\frac{\delta^2 Q}{\delta l(\mathbf{r})\delta l(\mathbf{r}')}\right)_g d\mathbf{r}d\mathbf{r}' \right\} \qquad \text{(2.6.1)}$$

Here $Q[g,l(\mathbf{r})]$ is a functional of the global variable $g$ and the local variable $l(\mathbf{r})$. *Const.*=0 has been assumed. Application of this result to the energy in representation $[N,\mathrm{v}(\mathbf{r})]$ leads to:

$$E[N,\mathrm{v}(\mathbf{r})] = \left\{ N\left(\frac{\partial E}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} + \int \mathrm{v}(\mathbf{r})\left(\frac{\delta E}{\delta\,\mathrm{v}(\mathbf{r})}\right)_N d\mathbf{r} \right\} - \frac{1}{2}\left\{ N^2\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})} + 2N\int \mathrm{v}(\mathbf{r})\left(\frac{\partial}{\partial N}\left(\frac{\delta E}{\delta\,\mathrm{v}(\mathbf{r})}\right)_N\right)_{\mathrm{v}(\mathbf{r})} d\mathbf{r} + \int\int \mathrm{v}(\mathbf{r})\,\mathrm{v}(\mathbf{r}')\left(\frac{\delta}{\delta\,\mathrm{v}(\mathbf{r})}\left(\frac{\delta E}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_N\right)_N d\mathbf{r}d\mathbf{r}' \right\}$$

Using the results presented in the preceding section allows for transformation to:

$$E[N,\mathrm{v}(\mathbf{r})] = N\mu - \frac{1}{2}N^2\eta + \int \mathrm{v}(\mathbf{r})(\rho(\mathbf{r}) - Nf(\mathbf{r}))d\mathbf{r} - \frac{1}{2}\int\int \mathrm{v}(\mathbf{r})\,\mathrm{v}(\mathbf{r}')\omega(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}' \qquad \text{(2.6.2)}$$

The energy expansion in the representation [ $N$ , $\mathbf{Q}_i$ ] becomes:

$$E[N,\mathbf{Q}_i] = \left\{ N\left(\frac{\partial E}{\partial N}\right)_Q + \sum_i \mathbf{Q}_i\left(\frac{\partial E}{\partial \mathbf{Q}_i}\right)_N \right\} - \frac{1}{2}\left\{ N^2\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathbf{Q}} + 2N\sum_i \mathbf{Q}_i\left(\frac{\partial}{\partial N}\left(\frac{\partial E}{\partial \mathbf{Q}_i}\right)_N\right)_Q + \sum_{i,j}\mathbf{Q}_i\cdot\mathbf{Q}_j\left(\frac{\partial}{\partial \mathbf{Q}_i}\cdot\left(\frac{\partial E}{\partial \mathbf{Q}_j}\right)_N\right)_N \right\}$$

By recognizing the derivatives this is simplified to:

$$E[N,\mathbf{Q}_i] = \mu N - \sum_i \mathbf{F}_i\cdot\mathbf{Q}_i - \frac{1}{2}\eta N^2 + N\sum_i \mathbf{\Phi}_i\cdot\mathbf{Q}_i - \frac{1}{2}\sum_{i,j}k_{ij}\mathbf{Q}_i\cdot\mathbf{Q}_j\,. \qquad \text{(2.6.3)}$$

The forces $\mathbf{F}_i$ are non-zero since this is not a Taylor expansion at the point of equilibrium. The derivatives $\mathbf{F}_i$, $\mu$ , $\eta$ and $k_{ij}$ are functions, not the coefficients as in Taylor expansion [67]. In the grand canonical ensemble, the analogous result is:

$$\Omega[\mu,\mathrm{v}(\mathbf{r})]=\left\{\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{\mathrm{v}(\mathbf{r})}+\int\mathrm{v}(\mathbf{r})\left(\frac{\delta\Omega}{\delta\,\mathrm{v}(\mathbf{r})}\right)_{\mu}d\mathbf{r}\right\}-$$
$$\frac{1}{2}\left\{\mu^2\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{\mathrm{v}(\mathbf{r})}+2\mu\int\mathrm{v}(\mathbf{r})\left(\frac{\partial}{\partial\mu}\left(\frac{\delta\Omega}{\delta\,\mathrm{v}(\mathbf{r})}\right)_{\mu}\right)_{\mathrm{v}(\mathbf{r})}d\mathbf{r}+\iint\mathrm{v}(\mathbf{r})\,\mathrm{v}(\mathbf{r}')\left(\frac{\delta}{\delta\,\mathrm{v}(\mathbf{r})}\left(\frac{\delta\Omega}{\delta\,\mathrm{v}(\mathbf{r}')}\right)_{\mu}\right)_{\mu}d\mathbf{r}d\mathbf{r}'\right\}$$

Hence:

$$\Omega[\mu,\mathrm{v}(\mathbf{r})]=-N\mu+\frac{1}{2}\mu^2S+\int\mathrm{v}(\mathbf{r})(\rho(\mathbf{r})-\mu s(\mathbf{r}))d\mathbf{r}+\frac{1}{2}\iint\mathrm{v}(\mathbf{r})\,\mathrm{v}(\mathbf{r}')s(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'\,.\qquad(2.6.4)$$

By using the identity $\Omega=E-\mu N$, eq. 2.6.4 is transformed to the explicit relation between energy and the susceptibilities $S$, $s(\mathbf{r})$, $s(\mathbf{r},\mathbf{r}')$:

$$E[N,\mathrm{v}(\mathbf{r})]=\frac{1}{2}\mu^2S+\int\mathrm{v}(\mathbf{r})(\rho(\mathbf{r})-\mu s(\mathbf{r}))d\mathbf{r}+\frac{1}{2}\iint\mathrm{v}(\mathbf{r})\,\mathrm{v}(\mathbf{r}')s(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'\,.\qquad(2.6.5)$$

In the representation [ $N$ , $\mathbf{Q}_i$ ]:

$$\Omega[\mu,\mathbf{Q}_i]=\left\{\mu\left(\frac{\partial\Omega}{\partial\mu}\right)_{Q}+\sum_i\mathbf{Q}_i\left(\frac{\partial\Omega}{\partial\mathbf{Q}_i}\right)_{\mu}\right\}-$$
$$\frac{1}{2}\left\{\mu^2\left(\frac{\partial^2\Omega}{\partial\mu^2}\right)_{\mathbf{Q}}+2\mu\sum_i\mathbf{Q}_i\left(\frac{\partial}{\partial\mu}\left(\frac{\partial\Omega}{\partial\mathbf{Q}_i}\right)_N\right)_Q+\sum_{i,j}\mathbf{Q}_i\cdot\mathbf{Q}_j\left(\frac{\partial}{\partial\mathbf{Q}_i}\cdot\left(\frac{\partial\Omega}{\partial\mathbf{Q}_j}\right)_{\mu}\right)_{\mu}\right\}$$

Using the appropriate symbols for the derivatives:

$$\Omega[\mu,\mathbf{Q}_i]=-\mu N-\sum_i\mathbf{Q}_i\cdot\mathbf{F}_i+\frac{1}{2}\mu^2S+\mu\sum_i\mathbf{Q}_i\cdot\boldsymbol{\sigma}_i-\frac{1}{2}\sum_{i,j}\mathbf{Q}_i\cdot\mathbf{Q}_j\tilde{k}_{ij}\,.\qquad(2.6.6)$$

Hence:

$$E[N,\mathbf{Q}_i]=-\sum_i\mathbf{F}_i\cdot\mathbf{Q}_i+\frac{1}{2}\mu^2S+\mu\sum_i\boldsymbol{\sigma}_i\cdot\mathbf{Q}_i-\frac{1}{2}\sum_{i,j}\tilde{k}_{ij}\mathbf{Q}_i\cdot\mathbf{Q}_j\,.\qquad(2.6.7)$$

Two equations for the energy in the representations $[N,\mathbf{Q}_i]$ and $[\mu,\mathbf{Q}_i]$ determine the proportions how the individual derivatives (multiplied by the appropriate variables) reproduce the total energy. The expression for energy in the canonical ensemble (eq. 2.6.2) has served for Liu and Parr as a contribution to the justification of the principle of maximum hardness: the higher the hardness, the lower the energy [67]. Equation (2.6.5) is a premise that can justify the principle of maximum hardness. An increase in softness results in an increase in energy and a decrease in hardness $\eta=1/S$. However, the principle of maximum hardness is not a law of nature; it is only a rule supported by many premises [63]. To simplify the picture and to get an analytic expression for couplings between variables, the normal coordinates must be introduced:

$$Q_\alpha = \sum_i \mathbf{Q}_i \cdot \mathbf{l}_i^\alpha \,. \qquad (2.6.8)$$

Since $\sum_i \mathbf{l}_i^\alpha \mathbf{l}_i^\beta = \delta_{\alpha\beta}$, the reverse transformation is [16, 68]:

$$\mathbf{Q}_i = \sum_\alpha Q_\alpha \mathbf{l}_i^\alpha \qquad (2.6.9)$$

The expansion becomes:

$$E[N,\mathbf{Q}_i] = \mu N - \sum_i \mathbf{F}_i \cdot \sum_\alpha Q_\alpha \mathbf{l}_i^\alpha - \frac{1}{2}\eta N^2 + N\sum_i \mathbf{\Phi}_\iota \sum_\alpha Q_\alpha \mathbf{l}_i^\alpha - \frac{1}{2}\sum_{i,j} k_{ij} \sum_\alpha Q_\alpha \mathbf{l}_i^\alpha \cdot \sum_\beta Q_\beta \mathbf{l}_j^\beta$$

This leads to the relation:

$$E[N,Q_\alpha] = \mu N - \sum_\alpha F_\alpha Q_\alpha - \frac{1}{2}\eta N^2 + N\sum_\alpha Q_\alpha \varphi_\alpha - \frac{1}{2}\sum_\alpha k_\alpha Q_\alpha^2 \qquad (2.6.10)$$

where $\sum_i \mathbf{l}_i^\alpha \cdot \mathbf{\Phi}_i = \varphi_\alpha \,,$ (2.6.11)

and $\sum_i \mathbf{l}_i^\alpha \cdot \mathbf{F}_i = F_\alpha \,.$ (2.6.12)

The force constant matrix is diagonalized by the normal coordinates:

$$\sum_{i,j} (\mathbf{l}_i^\alpha \cdot \mathbf{l}_j^\beta) k_{ij} = k_\alpha \delta_{\alpha\beta} \,. \qquad (2.6.13)$$

For the thermodynamical potential in the grand canonical ensemble the result is:

$$\Omega[\mu,Q_\alpha] = -\mu N - \sum_\alpha F_\alpha Q_\alpha + \frac{1}{2}\mu^2 S + \mu S \sum_\alpha \varphi_\alpha Q_\alpha - \frac{1}{2}\sum_\alpha k_\alpha Q_\alpha^2 + \frac{1}{2} S \sum_{\alpha,\beta} \varphi_\alpha \varphi_\beta Q_\alpha Q_\beta \qquad (2.6.14)$$

or $$\Omega[\mu,Q_\alpha] = -\frac{1}{2}\mu^2 S + \sum_\alpha Q_\alpha (\mu S \varphi_\alpha - F_\alpha) - \frac{1}{2}\sum_\alpha k_\alpha Q_\alpha^2 + \frac{1}{2} S \sum_{\alpha,\beta} \varphi_\alpha \varphi_\beta Q_\alpha Q_\beta \,, \qquad (2.6.15)$$

The final expression is qualitatively different from the previous one (2.6.10), because the function (at constant *N*) shows the mixing term of normal vibrations between all non-zero modes $\varphi_\alpha$. This coupling already appears as a term of the second order. To fully discover the couplings between coordinates $N$ and $\mathbf{Q}_i$, the expansion of Liu and Parr [67] to the third order should be repeated. The quantities of the type $\left(\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathbf{Q}}\right)_N$ should not be omitted as they represent changes in chemical reactivity due to a strain. I consider these indices to be crucial for the description of many chemical reactions. Unfortunately, by repeating the mathematical construction that led to the expansion to the second order, it will not be possible to obtain the expansion of the third order in a form identical to the original (the constant in eq. 2.6.1 does not exist). Therefore, the traditional Taylor series expansion will be presented. The result is as follows:

$$\begin{aligned}
&E[N+\Delta N,\mathbf{Q}_{\boldsymbol{i}}+\Delta\mathbf{Q}_i]=E^0+\Delta N\left(\frac{\partial E}{\partial N}\right)_{\mathbf{Q}}\\
&+\frac{1}{2}\left\{(\Delta N)^2\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathbf{Q}}+2\Delta N\sum_i\Delta\mathbf{Q}_i\left(\frac{\partial}{\partial N}\left(\frac{\partial E}{\partial \mathbf{Q}_i}\right)_N\right)_{\mathbf{Q}}+\sum_{i,j}(\Delta\mathbf{Q}_i)\cdot(\Delta\mathbf{Q}_j)\left(\frac{\partial}{\partial \mathbf{Q}_i}\cdot\left(\frac{\partial E}{\partial \mathbf{Q}_j}\right)_N\right)_N\right\}+\\
&\frac{1}{6}\sum_{i,j,k}\big((\Delta\mathbf{Q}_{\boldsymbol{i}})(\Delta\mathbf{Q}_{\boldsymbol{j}})\cdot(\Delta\mathbf{Q}_{\boldsymbol{k}})\big)\cdot\left(\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial}{\partial \mathbf{Q}_j}\cdot\left(\frac{\partial E}{\partial \mathbf{Q}_k}\right)_N\right)_N\right)_N+\frac{1}{6}(\Delta N)^3\left(\frac{\partial^3 E}{\partial N^3}\right)_{\mathbf{Q}}+\\
&\frac{1}{2}(\Delta N)^2\sum_i\Delta\mathbf{Q}_i\left(\frac{\partial}{\partial \mathbf{Q}_i}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathbf{Q}}\right)_N+\frac{1}{2}\Delta N\sum_{i,j}(\Delta\mathbf{Q}_i)\cdot(\Delta\mathbf{Q}_j)\left(\frac{\partial}{\partial N}\left(\frac{\partial}{\partial \mathbf{Q}_i}\cdot\left(\frac{\partial E}{\partial \mathbf{Q}_j}\right)_N\right)_N\right)_{\mathbf{Q}}
\end{aligned}$$

Hence

$$\begin{aligned}
&E[N+\Delta N,\mathbf{Q}_{\boldsymbol{i}}+\Delta\mathbf{Q}_{\boldsymbol{i}}]=E^{\mathrm{o}}[N,\mathbf{Q}_{\boldsymbol{i}}]+\Delta N\mu+\frac{1}{2}(\Delta N)^2\eta-\Delta N\sum_i\Delta\mathbf{Q}_{\boldsymbol{i}}\cdot\boldsymbol{\Phi}_i+\\
&\frac{1}{2}\sum_{i,j}(\Delta\mathbf{Q}_{\boldsymbol{i}})\cdot(\Delta\mathbf{Q}_{\boldsymbol{j}})k_{ij}+\frac{1}{6}\sum_{i,j,k}\big(\Delta\mathbf{Q}_i\cdot\Delta\mathbf{Q}_j\big)\big(\Delta\mathbf{Q}_k\cdot\mathbf{a}_{ijk}\big)+\frac{1}{6}(\Delta N)^3\gamma+\\
&\frac{1}{2}(\Delta N)^2\sum_i\Delta\mathbf{Q}_{\boldsymbol{i}}\cdot\mathbf{G}_{\boldsymbol{i}}+\frac{1}{2}\Delta N\sum_{i,j}(\Delta\mathbf{Q}_{\boldsymbol{i}})\cdot(\Delta\mathbf{Q}_{\boldsymbol{j}})\lambda_{ij}
\end{aligned}\tag{2.6.16}$$

To simplify the picture and get an analytic expression for possible couplings, the normal coordinates must be introduced. Since the term responsible for the harmonic interaction is diagonal in normal coordinates, and the anharmonic term is not diagonalized, we obtain:

$$\begin{aligned}
&E[N+\Delta N,Q_\alpha+\Delta Q_\alpha]=E^0+\Delta N\mu+\frac{1}{2}(\Delta N)^2\eta-\Delta N\sum_\alpha\varphi_\alpha\Delta Q_\alpha+\\
&\frac{1}{2}\sum_\alpha k_\alpha\Delta Q_\alpha^2+\frac{1}{6}\sum_{\alpha,\beta,\gamma}\Delta Q_\alpha^2\Delta Q_\gamma a_{\alpha\gamma}+\frac{1}{6}(\Delta N)^3\gamma+\\
&\frac{1}{2}(\Delta N)^2\sum_\alpha G_\alpha\Delta Q_\alpha+\frac{1}{2}\Delta N\sum_\alpha\lambda_\alpha\Delta Q_\alpha^2
\end{aligned}\tag{2.6.17}$$

The nuclear stiffness index has been projected onto a normal mode $\alpha$ [4, 5]:

$$\sum_i\mathbf{l}_i^\alpha\cdot\mathbf{G}_{\boldsymbol{i}}=G_\alpha\tag{2.6.18}$$

By taking a derivative over *N* from eq. 2.6.13 the result for $\lambda_\alpha$ is exposed:

$$\sum_{i,j}(\mathbf{l}_i^{\alpha}\cdot\mathbf{l}_j^{\beta})\lambda_{ij}=\lambda_{\alpha}\delta_{\alpha\beta} \qquad (2.6.19)$$

Similarly, the derivative of eq. 2.6.13 over $\mathbf{Q}_k$ leads to the anharmonic vector in the normal coordinates:

$$\mathbf{a}_{\alpha\beta}=\sum_i\frac{\partial k_{\alpha}}{\partial\mathbf{Q}_i}\cdot\mathbf{l}_i^{\beta} \qquad (2.6.20)$$

By expanding the thermodynamical potential into the Taylor series (cf. 2.6.17) the following result is obtained:

$$\begin{aligned}\Omega[\mu,\mathbf{Q}_i]&=\Omega^0-N\Delta\mu-\frac{1}{2}S(\Delta\mu)^2-\sum_i\boldsymbol{\sigma}_i\cdot\Delta\mathbf{Q}_i\Delta\mu-\frac{1}{2}\sum_{i,j}\tilde{k}_{ij}\Delta\mathbf{Q}_i\cdot\Delta\mathbf{Q}_j+\\&\frac{1}{6}\sum_{i,j,k}\tilde{\mathbf{a}}_{ijk}\cdot\Delta\mathbf{Q}_i\Delta\mathbf{Q}_j\cdot\Delta\mathbf{Q}_k+\frac{1}{6}\left(\frac{\partial^3\Omega}{\partial\mu^3}\right)_{\mathbf{Q}}(\Delta\mu)^3+\frac{1}{2}\sum_i\left(\frac{\partial^3\Omega}{\partial\mu^2\partial\mathbf{Q}_i}\right)\Delta\mathbf{Q}_i(\Delta\mu)^2+\\&\frac{1}{2}\sum_{i,j}\tilde{\lambda}_{ij}\Delta\mathbf{Q}_i\Delta\mathbf{Q}_j\Delta\mu\end{aligned} \qquad (2.6.21)$$

By considering equations 2.3.31 and 2.4.19, and the definition of the thermodynamical potential $\Omega$ (eq. 2.3.1), the following result appears:

$$\begin{aligned}E[\mu,\mathbf{Q}_i]&=\Omega^0-\frac{1}{2}S(\Delta\mu)^2-S\sum_i\boldsymbol{\Phi}_i\cdot\Delta\mathbf{Q}_i\Delta\mu-\frac{1}{2}\sum_{i,j}\tilde{k}_{ij}\Delta\mathbf{Q}_i\cdot\Delta\mathbf{Q}_j+\\&\frac{1}{6}\sum_{i,j,k}\tilde{\mathbf{a}}_{ijk}\cdot\Delta\mathbf{Q}_i\Delta\mathbf{Q}_j\cdot\Delta\mathbf{Q}_k+\frac{1}{6}\gamma S^3(\Delta\mu)^3+\frac{1}{2}\sum_i(\mathbf{G}_i+\gamma S\boldsymbol{\Phi}_i)\cdot\Delta\mathbf{Q}_i(\Delta\mu)^2+\\&\frac{1}{2}\sum_{i,j}\tilde{\lambda}_{ij}\Delta\mathbf{Q}_i\Delta\mathbf{Q}_j\Delta\mu\end{aligned} \qquad (2.6.22)$$

Introducing the normal coordinates requires a replacement of coefficients $\tilde{k}_{ij}$, $\tilde{\lambda}_{ij}$ and $\tilde{\mathbf{a}}_{ijk}$ by $k_{ij}$, $\lambda_{ij}$ and $\mathbf{a}_{ijk}$. To achieve this, relations 2.5.9, 2.5.13 and eq. 2.5.24 have been used:

$$\sum_{i,j}\tilde{k}_{ij}\Delta\mathbf{Q}_i\cdot\Delta\mathbf{Q}_j=\sum_{\alpha}k_{\alpha}(\Delta Q_{\alpha})^2-S\sum_{\alpha,\beta}\varphi_{\alpha}\varphi_{\beta}\Delta Q_{\alpha}\Delta Q_{\beta}\,, \qquad (2.6.23)$$

$$\sum_{i,j}\tilde{\lambda}_{ij}\Delta\mathbf{Q}_i\cdot\Delta\mathbf{Q}_j=S\sum_{\alpha}\lambda_{\alpha}(\Delta Q_{\alpha})^2+2S^2\sum_{\alpha,\beta}\varphi_{\alpha}G_{\beta}\Delta Q_{\alpha}\Delta Q_{\beta}+\gamma S^3\sum_{\alpha,\beta}\varphi_{\alpha}\varphi_{\beta}\Delta Q_{\alpha}\Delta Q_{\beta} \qquad (2.6.\ 24)$$

$$\begin{aligned}\sum_{i,j,k}\tilde{\mathbf{a}}_{ijk}\cdot\Delta\mathbf{Q}_i\Delta\mathbf{Q}_j\cdot\Delta\mathbf{Q}_k&=\sum_{\alpha,\beta}a_{\alpha\beta}(\Delta Q_{\alpha})^2\Delta Q_{\beta}+3S\sum_{\alpha,\beta}\lambda_{\alpha}\varphi_{\beta}(\Delta Q_{\alpha})^2\Delta Q_{\beta}+\\&+3S^2\sum_{\alpha,\beta,\gamma}G_{\alpha}\varphi_{\beta}\varphi_{\gamma}\Delta Q_{\alpha}\Delta Q_{\beta}\Delta Q_{\gamma}+\gamma S^3\sum_{\alpha,\beta,\gamma}\varphi_{\alpha}\varphi_{\beta}\varphi_{\gamma}\Delta Q_{\alpha}\Delta Q_{\beta}\Delta Q_{\gamma}\end{aligned} \qquad (2.6.25)$$

In the final expression for the energy, the coupling terms for two and three modes have been exposed:

$$
\begin{aligned}
E[\mu,\mathbf{Q}_i] &= \Omega^0 - \frac{1}{2}S(\Delta\mu)^2 - S\Delta\mu\sum_{\alpha}(\varphi_\alpha - \frac{1}{2}S\Delta\mu(G_\alpha + \gamma S\varphi_\alpha))\Delta Q_\alpha + \\
&\frac{1}{2}\sum_{\alpha}(k_\alpha + S\lambda_\alpha\Delta\mu)(\Delta Q_\alpha)^2 - \frac{1}{2}S\sum_{\alpha,\beta}(\varphi_\alpha\varphi_\beta - 2S\varphi_\alpha G_\beta\Delta\mu - \gamma S^2\varphi_\alpha\varphi_\beta\Delta\mu)\Delta Q_\alpha\Delta Q_\beta + \qquad (2.6.26) \\
&\frac{1}{6}\sum_{\alpha,\beta}(a_{\alpha\beta} + 3S\lambda_\alpha\varphi_\beta)(\Delta Q_\alpha)^2\Delta Q_\beta + \frac{1}{6}S^2\sum_{\alpha,\beta,\gamma}\varphi_\beta\varphi_\gamma(3G_\alpha + \gamma S\varphi_\alpha)\Delta Q_\alpha\Delta Q_\beta\Delta Q_\gamma
\end{aligned}
$$

The energy change resulting by a change both in $N$ and in geometry $\Delta Q_\alpha$ may be calculated, provided that the ground state indices have been determined.

## 2.7 Renormalization of the hardness, softness, and the chemical potential

The coupling between the variables $\Delta N$ and $\Delta Q_\alpha$ will be determined next. The energy expansion will be used for this purpose (eq. 2.6.3) [2, 62]:

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

An approximate change at a given point $[\Delta N, \Delta Q_\alpha]$ is calculated by takin a derivative over $Q_\alpha$. This provides a generalized force for the mode $\alpha$:

$$
\left(\frac{\partial E}{\partial Q_\alpha}\right)_N = -F_\alpha + N\varphi_\alpha - k_\alpha Q_\alpha . \qquad (2.7.1)
$$

And, by definition: $\left(\frac{\partial E}{\partial Q_\alpha}\right)_N = -F_\alpha$.

Hence: $N\varphi_\alpha = k_\alpha Q_\alpha$. (2.7.2)

This approximate relation will be explored first to determination of changes in the hardness and the thermodynamical potential resulting from coupling with oscillations:

$$
Q_\alpha = \frac{N\varphi_\alpha}{k_\alpha} \qquad (2.7.3)
$$

The energy is:

$$
\begin{aligned}
E[N,Q_\alpha] &= \mu N - N\sum_{\alpha}\frac{\varphi_\alpha F_\alpha}{k_\alpha} - \frac{1}{2}\eta N^2 + \frac{1}{2}N^2\sum_{\alpha}\frac{\varphi_\alpha^2}{k_\alpha} = \\
&= N\left(\mu - \sum_{\alpha}\frac{\varphi_\alpha F_\alpha}{k_\alpha}\right) - N^2\frac{1}{2}\left(\eta - \sum_{\alpha}\frac{\varphi_\alpha^2}{k_\alpha}\right)
\end{aligned}
\qquad (2.7.4)
$$

The terms in parentheses are renormalized chemical potential and hardness, respectively. The above relationship shows that because of coupling with molecular oscillations $(N,Q)$, the hardness decreases regardless of the point (on the potential energy surface) where the system is located. The chemical potential is renormalized (both upwards and downwards) only outside the local extreme when $F_\alpha \neq 0$.

The renormalization of softness will be found next. The expansion for the thermodynamical potential is recalled in the coordinate system chosen as to warrant the diagonal coefficient at the square of a coordinate (eq. 2.6.14).

$$\Omega[\mu,\tilde{Q}_\alpha] = -\mu N - \sum_\alpha \tilde{Q}_\alpha \tilde{F}_\alpha + \frac{1}{2}\mu^2 S + \mu \sum_\alpha \tilde{Q}_\alpha \cdot \tilde{\sigma}_\alpha - \frac{1}{2}\sum_\alpha \tilde{Q}_\alpha^2 \tilde{k}_\alpha \qquad (2.7.5)$$

Where: $\tilde{F}_\alpha = \sum_i \tilde{\mathbf{I}}_i^\alpha \cdot \mathbf{F}_{\boldsymbol{i}}$, (2.7.6)

and $\tilde{Q}_\alpha = \sum_i \tilde{\mathbf{I}}_i^\alpha \cdot \mathbf{Q}_{\boldsymbol{i}}$

Also $\tilde{\sigma}_\alpha = \sum_i \tilde{\mathbf{I}}_i^\alpha \cdot \boldsymbol{\sigma}_i = S \sum_i \tilde{\mathbf{I}}_i^\alpha \cdot \boldsymbol{\Phi}_i = S\tilde{\varphi}_\alpha$ (2.7.7)

and $\sum_{i,j} (\tilde{\mathbf{I}}_i^\alpha \cdot \tilde{\mathbf{I}}_j^\beta)\tilde{k}_{ij} = \tilde{k}_\alpha \delta_{\alpha\beta}$. (2.7.8)

New matrix $\tilde{\mathbf{I}}_i^\alpha$ has been chosen to diagonalize $\tilde{k}_{ij}$. The force is:

$$\left(\frac{\partial \Omega}{\partial \tilde{Q}_\alpha}\right)_\mu = -\tilde{F}_\alpha + \mu\tilde{\sigma}_\alpha - \tilde{Q}_\alpha \tilde{k}_\alpha . \qquad (2.7.9)$$

Since: $\left(\frac{\partial \Omega}{\partial \tilde{Q}_\alpha}\right)_\mu = -\tilde{F}_\alpha$ (2.7.10)

The result is:

$$\tilde{k}_\alpha \tilde{Q}_\alpha = \mu\tilde{\sigma}_\alpha . \qquad (2.7.11)$$

This will be used for renormalization of the softness and the electron number. The following substitution to $\Omega[\mu,\tilde{Q}_\alpha]$ has been used:

$$\tilde{Q}_\alpha = \frac{\mu\tilde{\sigma}_\alpha}{\tilde{k}_\alpha} \qquad (2.7.12)$$

The result is:

$$\Omega[\mu,\tilde{Q}_\alpha] = -\mu\left(N + \sum_\alpha \frac{\tilde{\sigma}_\alpha}{\tilde{k}_\alpha}\tilde{F}_\alpha\right) - \mu^2\left(\frac{1}{2}\left(S - \sum_\alpha \frac{\tilde{\sigma}_\alpha^2}{\tilde{k}_\alpha}\right)\right). \qquad (2.7.13)$$

By substitution $\tilde{\sigma}_\alpha = \tilde{\varphi}_\alpha S$ :

$$\Omega[\mu,\tilde{Q}_\alpha] = -\mu\left(N + \sum_\alpha \frac{\tilde{\sigma}_\alpha}{\tilde{k}_\alpha}\tilde{F}_\alpha\right) - \frac{1}{2}\mu^2 S\left(1 + S\sum_\alpha \frac{\tilde{\varphi}_\alpha^2}{\tilde{k}_\alpha}\right) \qquad (2.7.14)$$

The term proportional to $\mu$ determines the change in the number of electrons under the influence of a force appearing because the system is not in equilibrium. The term proportional to $\mu^2$ gives the renormalization of softness. The latter does not meet the inverse condition (eq. 1.2.15) to the renormalized hardness (eq. 2.7.4) but it is higher than for the system without oscillations. The quantities $\tilde{\varphi}_\alpha$ and $\tilde{F}_\alpha$ must be found numerically using eq. 2.7.6 and eq. 2.7.7.

### 2.8 The role of indices $\phi_\alpha$ and $G_\alpha$ in shaping fluctuations of electronegativity and hardness.

The method for determination of the fluctuations in chemical reactivity indices and their relationships with nuclear reactivity indices will be presented in this section. The key role is played by the deformation of the molecule due to the filling successive oscillatory (anharmonic) levels. It induces a change in the geometry of the molecule, and thus a change in its electron density and, consequently, also in its reactivity. In the case of harmonic vibrations, there are fluctuations in reactivity around the initial value. We reserve the term chemical potential for a variable in the grand canonical ensemble, where its constant value is forced by a reservoir external to the tested system. The value of the energy derivative over the number of electrons in the canonical ensemble depends on the microstate in which the system is located. Therefore, we reserve the name of electronegativity (with a minus sign) for this derivative. The main goal is to determine the changes in electronegativity and hardness resulting from occupying higher energy levels and comparing them with the change resulting from the change in molecular geometry and nuclear reactivity indices.

The electronegativity analysis is done in the canonical ensemble. The number of electrons is fixed, as is the external potential $\mathrm{v}(\mathbf{r})$. The constant of the external potential is realized by the fixed coordinates of the atomic nuclei $\mathbf{Q}_i$. The energy fluctuates due to the reservoir at temperature $T$, which causes the molecule to occupy higher energy levels: $E_\nu$ ($\nu$=0, 1, 2…).

There are two possible ways to the definition of electronegativity. First, the average electronegativity can be defined as the thermodynamic average of the electronegativity of the microstate:

$$\langle \chi_\nu \rangle = \frac{\sum_\nu \chi_\nu e^{-\beta E_\nu}}{Z} \tag{2.8.1}$$

where $\chi_\nu = -\left(\frac{\partial E_\nu}{\partial N}\right)_Q$ (2.8.2)

represents electronegativity of a microstate

$$Z = \sum_\nu e^{-\beta E_\nu} \tag{2.8.3}$$

*Z* is the sum of states for the canonical ensemble, and $\beta = 1/k_B T$ (2.8.4)

An alternative method for calculating of the electronegativity for the average energy represents the average energy in the canonical ensemble:

$$\langle \chi \rangle = -\left(\frac{\partial \langle E \rangle}{\partial N}\right)_Q \tag{2.8.5}$$

where $\langle E \rangle = \frac{\sum_\nu E_\nu e^{-\beta E_\nu}}{Z}$ (2.8.6)

To reach the conclusions from each of these two definitions, one should refer to the DFT theory at finite temperatures in the canonical ensemble [2]. The key quantity is the average electron density of the mixed state. The thermodynamic potential, the minimum of which is determined by the ground state, is:

$$A[\rho] = E[\rho] - TS[\rho]. \tag{2.8.7}$$

Where $S[\rho]$ is a entropy functional of a system. In the canonical ensemble ($N = const$) the variational principle holds for the thermodynamical potential: $A_v[\langle \rho_{eq} \rangle] \le A_v[\langle \rho' \rangle]$. Equality holds for $\langle \rho_{eq} \rangle = \langle \rho' \rangle$ [2]. Then the thermodynamical potential is:

$$A_v[\langle \rho_{eq} \rangle] = \langle A \rangle = \langle E \rangle - TS \tag{2.8.8}$$

Since $\int \langle \rho(\mathbf{r}) \rangle d\mathbf{r} = N = const$ the Lagrange factor appears ($\mu$):

$$\mu = \frac{\delta A_v[\langle \rho \rangle]}{\delta \langle \rho(\mathbf{r}) \rangle}. \tag{2.8.9}$$

Using the standard procedure (Parr, Donnelly, Levy and Palke [2, 26]) the following result is proved:

$$\mu = \frac{\delta A_v[\langle\rho\rangle]}{\delta\langle\rho(\mathbf{r})\rangle} = \left(\frac{\partial\langle A\rangle}{\partial N}\right)_Q \qquad \textbf{(}2.8.10)$$

Hence: $\mu = \left(\frac{\partial}{\partial N}\left(\langle E(N,Q_\alpha)\rangle - TS(N,Q_\alpha)\right)\right)_Q$ (2.8.11)

where $S(N,Q_\alpha)$ is the entropy of a system.

But [69]: $S = k_B\beta\langle E\rangle + k_B \ln Z$ **(**2.8.12)

and $\left(\frac{\partial \ln Z}{\partial N}\right)_Q = \beta\langle\chi_v\rangle$ **(**2.8.13)

hence: $\frac{\partial(ST)}{\partial N} = -\langle\chi\rangle + \langle\chi_v\rangle$ **(**2.8.14)

Finally: $\mu = \left(\frac{\partial A}{\partial N}\right)_Q = -\langle\chi_v\rangle$ **(**2.8.15)

$\langle\chi_v\rangle$ represents electronegativity in the canonical ensemble. Similar difficulties have been encountered in the analysis of hardness at finite temperature. Here, there are three possible choices. First – the temperature average $\langle\eta_v\rangle$ for the microstates:

$$\langle\eta_v\rangle = \frac{\sum_v \eta_v e^{-\beta E_v}}{Z} \qquad \textbf{(}2.8.16)$$

where: $\eta_v = \left(\frac{\partial^2 E_v}{\partial N^2}\right)_Q = -\left(\frac{\partial\chi_v}{\partial N}\right)_Q$ . **(**2.8.17)

The second possible choice is the second derivative of the average energy:

$$\langle\eta\rangle = \left(\frac{\partial^2\langle E\rangle}{\partial N^2}\right)_Q = -\left(\frac{\partial\langle\chi\rangle}{\partial N}\right)_Q \ . \qquad \textbf{(}2.8.18)$$

The third choice may be the negative of the derivative from the average electronegativity $\langle\chi_v\rangle$:

$$\langle\eta_v'\rangle = -\left(\frac{\partial\langle\chi_v\rangle}{\partial N}\right)_Q \ . \qquad \textbf{(}2.8.19)$$

The following relations are readily obtained by the direct derivatives:

$$\left(\frac{\partial \ln Z}{\partial N}\right)_Q = \beta\langle\chi_v\rangle \qquad \textbf{(}2.8.20)$$

$$\left(\frac{\partial^2 \ln Z}{\partial N^2}\right)_Q = -\beta\langle\eta_v'\rangle \tag{2.8.21}$$

The above equations correspond to the derivatives over $\beta$ :

$$\frac{\partial \ln Z}{\partial\beta} = -\langle E\rangle . \tag{2.8.22}$$

and $$\frac{\partial^2 \ln Z}{\partial\beta^2} = -\frac{\partial\langle E\rangle}{\partial\beta} = \left\langle(\delta E)^2\right\rangle . \tag{2.8.23}$$

The relation between two definitions of the electronegativity may be demonstrated:

$$\langle\chi\rangle = \frac{\partial}{\partial N}\frac{\partial \ln Z}{\partial\beta} = \frac{\partial}{\partial\beta}\frac{\partial \ln Z}{\partial N} = \frac{\partial}{\partial\beta}\left(\beta\langle\chi_v\rangle\right) = \langle\chi_v\rangle + \beta\frac{\partial\langle\chi_v\rangle}{\partial\beta} \tag{2.8.24}$$

Hence $\langle\chi\rangle = \langle\chi_v\rangle + \beta\langle E\rangle\langle\chi_v\rangle - \beta\langle E_v\chi_v\rangle$ . (2.8.25)

The similar relation for hardness may be demonstrated by calculating the second derivatives over N.

$$\langle\eta\rangle = \langle\eta_v'\rangle + \beta\frac{\partial\langle\eta_v'\rangle}{\partial\beta} . \tag{2.8.26}$$

Hence $\langle\eta\rangle = \langle\eta_v'\rangle + \beta\langle E\rangle\langle\eta_v'\rangle - \beta\langle E_v\eta_v'\rangle$ . (2.8.27)

The following result is obtained from eq. 2.8.21:

$$\left(\frac{\partial^2 \ln Z}{\partial N^2}\right)_Q = -\beta^2\langle\chi_v\rangle^2 - \beta\langle\eta_v\rangle + \beta^2\langle\chi_v^2\rangle \tag{2.8.28}$$

Using eq. 2.8.2 and eq. 2.8.20 the interesting relation is born:

$$\langle\eta_v\rangle - \langle\eta_v'\rangle = \beta\left\langle(\delta\chi_v)^2\right\rangle \tag{2.8.29}$$

Eq. 2.8.26 leads to the relation between fluctuations of electronegativity with fluctuations of hardness:

$$\beta\left\langle(\delta\chi_v)^2\right\rangle = \langle\eta_v\rangle - \langle\eta\rangle + \beta\frac{\partial\langle\eta_v'\rangle}{\partial\beta} \tag{2.8.30}$$

From the above relationships it can be seen, that if in the canonical ensemble the dependence of the energy of the energy levels on the number of electrons ( $E_v(N)$ ) is considered, then the derivative of the average is not equal to the average of the derivative. Both quantities differ by fluctuations. This applies to both the first derivative and the second one. This does not apply to external force. Then, the derivative of the average energy is equal to the thermodynamic mean of the derivative of the microstate energy for a given parameter, and the fluctuation term disappears [69]:

$$\left\langle \frac{\partial E}{\partial Q} \right\rangle = \frac{\partial \langle E \rangle}{\partial Q} . \qquad (2.8.31)$$

Within the linear response approximation, the change in electronegativity and hardness is proportional to the change in the position of the atoms. The proportionality factor is $\mathbf{\Phi}_i$ for electronegativity and $\mathbf{G}_i$ in for hardness:

$$\Delta\chi = \sum_i \mathbf{\Phi}_i \cdot \delta\mathbf{Q}_i \qquad (2.8.32)$$

$$\Delta\eta = \sum_i \mathbf{G}_i \cdot \delta\mathbf{Q}_i \qquad (2.8.33)$$

Here $\delta\mathbf{Q}_i$ is the variation of the position of *i*-th atom. Since in the first approximation (when only the harmonic nature of vibrations is considered) $\langle \delta\mathbf{Q}_i \rangle = 0$, we calculate the fluctuations $\left\langle (\delta\chi)^2 \right\rangle$ and $\left\langle (\delta\eta)^2 \right\rangle$, which are proportional to the fluctuation of average position $\left\langle (\delta\mathbf{Q}_i)^2 \right\rangle$, and not to the change in average position $\langle \delta\mathbf{Q}_i \rangle$. In the normal coordinates, the expression for electronegativity fluctuations is:

$$\begin{aligned} \left\langle (\delta\chi)^2 \right\rangle &\cong \left\langle \left( -\sum_\alpha \varphi_\alpha (\delta Q_\alpha) \right)^2 \right\rangle = \left\langle \sum_\alpha (\varphi_\alpha \delta Q_\alpha)^2 + \sum_{\alpha\beta} (1-\delta_{\alpha\beta}) \varphi_\alpha \varphi_\beta \delta Q_\alpha \delta Q_\beta \right\rangle = \\ &= \sum_\alpha \varphi_\alpha^2 \left\langle (\delta Q_\alpha)^2 \right\rangle + \sum_{\alpha\beta} (1-\delta_{\alpha\beta}) \varphi_\alpha \varphi_\beta \left\langle \delta Q_\alpha \delta Q_\beta \right\rangle = \sum_\alpha \varphi_\alpha^2 \left\langle (\delta Q_\alpha)^2 \right\rangle \end{aligned} \qquad (2.8.34)$$

This has been based on the relation $\left\langle \delta Q_\alpha \delta Q_\beta \right\rangle = 0$ [70]. The analogue for hardness reads:

$$\left\langle (\delta\eta)^2 \right\rangle \cong \sum_\alpha G_\alpha^2 \left\langle (\delta Q_\alpha)^2 \right\rangle . \qquad (2.8.35)$$

For a diatomic molecule:

$$\left\langle (\delta\chi)^2 \right\rangle \cong \varphi^2 \left\langle (\delta Q)^2 \right\rangle \qquad (2.8.36)$$

and $$\left\langle (\delta\eta)^2 \right\rangle \cong G^2 \left\langle (\delta Q)^2 \right\rangle . \qquad (2.8.37)$$

By taking the average over the ensemble the expression for $\left\langle (\delta Q)^2 \right\rangle$ is obtained [70]. The average is by definition:

$$\left\langle (\delta Q)^2 \right\rangle = \frac{1}{Z} \sum_{\nu} (\delta Q_{\nu})^2 e^{-\beta E_{\nu}} \tag{2.8.38}$$

For the quantum harmonic oscillator:

$$(\delta Q_{\nu})^2 = \left( \frac{\hbar^2}{Mk} \right)^{1/2} \left( \nu + \tfrac{1}{2} \right) \tag{2.8.39}$$

Here $M$ is the reduces mass and $k$ the force constant. By a standard procedure [70, 71]:

$$\left\langle (\delta Q)^2 \right\rangle = \frac{\hbar}{2M\omega} \operatorname{ctgh} \frac{\hbar\omega}{2k_B T} = \frac{\hbar\omega}{2k} \operatorname{ctgh} \frac{u}{2} \tag{2.8.40}$$

where $u = \dfrac{\hbar\omega}{2k_B T}$ . (2.8.41)

Finally, the fluctuation for electronegativity and hardness are given by:

$$\left\langle (\delta \chi_{\nu})^2 \right\rangle = (\hbar\omega) \frac{\varphi^2}{2k} \operatorname{ctgh} \frac{u}{2} \tag{2.8.42}$$

$$\left\langle (\delta \eta_{\nu})^2 \right\rangle = (\hbar\omega) \frac{G^2}{2k} \operatorname{ctgh} \frac{u}{2} \tag{2.8.43}$$

For the sake of completeness, the result form the grand canonical ensemble should also be looked upon. The average number of electrons in a molecule in the grand canonical ensemble is [2, 43]:

$$\left\langle N \right\rangle = \frac{\sum_{\nu} N_{\nu} e^{-\beta (E_{\nu} - \mu N_{\nu})}}{\Xi}$$

where $\Xi = \sum_{\nu} e^{-\beta (E_{\nu} - \mu N_{\nu})}$ is the grand statical sum. By taking the derivative leads to:

$$\frac{1}{\beta} \frac{\partial \left\langle N \right\rangle}{\partial \mu} = \left\langle N^2 \right\rangle - \left\langle N \right\rangle^2 = \left\langle (\delta N)^2 \right\rangle$$

The derivative is readily identified: $\dfrac{\partial \left\langle N \right\rangle}{\partial \mu} \equiv S$ The global softness is determined by the fluctuations in the number of electrons.

# 3

## Application of the nuclear atomic indexes

This chapter is aimed at illustration of the previously introduced concepts and results. A pair of atomic indices is responsible for the coupling between atomic displacements and electronic properties: the nuclear reactivity $\mathbf{\Phi}_i$ and the nuclear stiffness $\mathbf{G}_i$. This chapter presents the calculation scheme for approximate values of $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ [A1, A3, A4, A5]. Numerical results for a series of diatomic molecules are presented. These indices well reproduce the actual changes in electronegativity and hardness. Also, the influence of the symmetry of the molecule on the symmetry of the indices $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ has been discussed [A4, A5]. The method of calculating indices for normal vibrations is presented – definitions for $\varphi_\alpha$ and $G_\alpha$ differ from those presented in Chapter 2 by their normalization. The symmetry properties have also been discussed - conditions are given when a given vibration has non-zero $\varphi_\alpha$ and $G_\alpha$; the results for simple polyatomic molecules are demonstrated [A5]. The effect of harmonic and anharmonic oscillations on hardness and electronegativity has been analyzed in two ways. Firstly, by means of indices $\varphi_\alpha$ and $G_\alpha$ [A5], and secondly, by means of the temperature statistical averages of electronegativity and hardness, which for the canonical set were given in Chapter 2 [A3]. The role of fluctuations, which seem to have a key impact on modifications of the reactivity of molecules has been exposed [A2], [A5]. Since the canonical ensemble has been consequently used in this chapter, the term electronegativity (minus) is used instead of chemical potential:

$$\chi = -\mu \tag{3.1}$$

Also, in this chapter the standard definition of hardness has been used (as opposed to the formal definition presented in Chapter 2):

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})} \tag{3.2}$$

Other definitions and the relations between the defined quantities have not been altered.

### 3.1 Calculations of the nuclear reactivity $\boldsymbol{\phi}_i$ and nuclear stiffness $\mathbf{G}_i$

The following quantities have been defined and analyzed in Chapter 2 [A1]:

$$\boldsymbol{\Phi}_i = -\left(\frac{\partial \mu}{\partial \mathbf{Q}_i}\right)_N = \left(\frac{\partial \mathbf{F}_i}{\partial N}\right)_{\mathbf{Q}} = \int f(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} \tag{3.1.1}$$

$$\mathbf{G}_i = \left(\frac{\partial \eta}{\partial \mathbf{Q}_i}\right)_N = -\left(\frac{\partial^2 \mathbf{F}_i}{\partial N^2}\right)_{\mathbf{Q}} = -\left(\frac{\partial \boldsymbol{\Phi}_i}{\partial N}\right)_{\mathbf{Q}} = -\int h(\mathbf{r})\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} \tag{3.1.2}$$

A working approach to the hardness function is needed: $h(\mathbf{r}) = \left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{\mathrm{v}(\mathbf{r})} = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2}\right)_{\mathrm{v}(\mathbf{r})}$. The finite difference approximation provides a reasonable starting point to calculation of the derivatives $\rho(N)$ [A1]. By expanding $\rho(N)$ in a series over $N$ we get:

$$\rho(N+\Delta N,\mathbf{r}) = \rho(N,\mathbf{r}) + \left[\frac{\partial \rho(N,\mathbf{r})}{\partial N}\right]_{\mathrm{v}(\mathbf{r})} \Delta N + \frac{1}{2}\left[\frac{\partial^2 \rho(N,\mathbf{r})}{\partial N^2}\right]_{\mathrm{v}(\mathbf{r})} (\Delta N)^2 + \ldots \tag{3.1.3}$$

For the limiting values $\Delta N = 1$ and $\Delta N = -1$:

$$\rho(N+1,\mathbf{r}) = \rho(N,\mathbf{r}) + \left[\frac{\partial \rho(N,\mathbf{r})}{\partial N}\right]_{\mathrm{v}(\mathbf{r})} + \frac{1}{2}\left[\frac{\partial^2 \rho(N,\mathbf{r})}{\partial N^2}\right]_{\mathrm{v}(\mathbf{r})} \tag{3.1.4}$$

$$\rho(N-1,\mathbf{r}) = \rho(N,\mathbf{r}) - \left[\frac{\partial \rho(N,\mathbf{r})}{\partial N}\right]_{\mathrm{v}(\mathbf{r})} + \frac{1}{2}\left[\frac{\partial^2 \rho(N,\mathbf{r})}{\partial N^2}\right]_{\mathrm{v}(\mathbf{r})} \tag{3.1.5}$$

The simplified notation will be helpful: $\rho(N,\mathbf{r}) = \rho(\mathbf{r})^{\mathrm{o}}$, $\rho(N+1,\mathbf{r}) = \rho(\mathbf{r})^{+}$ and $\rho(N-1,\mathbf{r}) = \rho(\mathbf{r})^{-}$
With this notation the derivatives are:

$$\left[\frac{\partial \rho(N,\mathbf{r})}{\partial N}\right]_{v(\mathbf{r})} = f(N,\mathbf{r}) \cong \frac{1}{2}(\rho(\mathbf{r})^{+} - \rho(\mathbf{r})^{-}) \tag{3.1.6}$$

$$\left[\frac{\partial^2 \rho(N,\mathbf{r})}{\partial N^2}\right]_{\mathrm{v}(\mathbf{r})} = \left[\frac{\partial f(N,\mathbf{r})}{\partial N}\right]_{\mathrm{v}(\mathbf{r})} \cong \rho(\mathbf{r})^{+} + \rho(\mathbf{r})^{-} - 2\rho(\mathbf{r})^{\mathrm{o}} \tag{3.1.7}$$

The result for nuclear stiffness vector $\mathbf{G}_i$ is [A1]:

$$\begin{aligned}\mathbf{G}_i &\cong -\frac{1}{2}\int[\rho(\mathbf{r})^{+} + \rho(\mathbf{r})^{-} - 2\rho(\mathbf{r})^{\mathrm{o}}]\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = \\ &= -\frac{1}{2}(\mathbf{F}_i^{+} + \mathbf{F}_i^{-}) - \mathbf{F}_i^{\mathrm{o}} = -\frac{1}{2}(\mathbf{F}_i^{+} + \mathbf{F}_i^{-})\end{aligned} \tag{3.1.9}$$

The result for the nuclear reactivity vector $\mathbf{\Phi}_i$ is [A1]:

$$\mathbf{\Phi}_i \cong \frac{1}{2}\int[\rho(\mathbf{r})^+ - \rho(\mathbf{r})^-]\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r} = \frac{1}{2}(\mathbf{F}_i^+ - \mathbf{F}_i^-) \qquad (3.1.10)$$

$\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ represent the force vectors acting on the *i*-th nucleus in an ionized molecule. Since the geometry of the system has been fixed ($\mathrm{v}(\mathbf{r}) = const$) also $\mathbf{F}_i^{n-n}$ force is constant. For a system in equilibrium this force is $\mathbf{F}_i^{n\text{-}n} = -\int \rho(\mathbf{r})^{\mathrm{o}}\boldsymbol{\varepsilon}_i(\mathbf{r})d\mathbf{r}$; this has justified eq. 3.1.9 and eq. 3.1.10. The total force $\mathbf{F}_i$ acting on *i*-th nucleus in a neutral molecule is zero in the state of its equilibrium. However, the vertical ionization prevents a system from adopting to the new electronic state. The non-zero $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ forces are consequences of the hypothetic non-relaxed structure of the frozen molecule. The forces have been calculated as the negative energy gradient.

**Table 3.1**

Reactivity indices for selected diatomic molecules

| Molecule | η= ½ (*I*-*A*) [eV] | $\mathbf{\Phi}_i$ [eV/Å] | $\mathbf{G}_i$ [eV/Å] | $\mathbf{F}_i^+$ [eV/Å] | $\mathbf{F}_i^-$ [eV/Å] | $\mathbf{\Phi}^2/2k$ [eV] |
|---|---|---|---|---|---|---|
| **LiH** | 3.729 | 0.530 | 0.928 | 1.457 | 0.397 | 0.0167 |
| **HF** | 9.465 | 0.139 | 3.684 | 1.886 | 3.494 | 0.0001 |
| **$F_2$** | 7.578 | -9.169 | 8.120 | -1.049 | 17.289 | 0.6157 |
| **$Cl_2$** | 5.332 | -4.883 | 2.939 | -1.944 | 7.822 | 0.2778 |
| **$Li_2$** | 0.046 | 0.042 | 0.444 | 0.486 | 0.402 | 0.0003 |
| **FCl** | 6.154 | -6.562 | 2.340 | -4.223 | 8.902 | 0.4092 |
| **CO** | 7.899 | -4.054 | -4.393 | -8.415 | -0.338 | 0.0366 |
| **LiF** | 5.592 | -1.272 | 1.920 | 0.646 | 3.189 | 0.0153 |
| **BCl** | 5.063 | -3.010 | -0.663 | -3.672 | 2.364 | 0.1250 |
| **BH** | 4.682 | -0.570 | -0.178 | -0.747 | 0.392 | 0.0068 |
| **CS** | 5.767 | -3.968 | -0.740 | -4.707 | 3.228 | 0.0861 |
| **NF** | 4.421 | -6.524 | -0.149 | -6.673 | 6.375 | 0.2305 |
| **SO** | 3.552 | -2.619 | -0.594 | -3.214 | 2.024 | 0.0453 |
| **HCl** | 7.277 | -0.280 | 1.445 | 1.164 | 1.726 | 0.0011 |
| **LiCl** | 4.675 | 0.590 | 1.248 | 1.837 | 0.658 | 0.0148 |
| **BF** | 5.928 | -2.830 | -0.372 | -3.203 | 2.458 | 0.0422 |
| **SiO** | 6.089 | -1.058 | 0.958 | -0.099 | 2.016 | 0.0057 |

### 3.1.1 Diatomic molecules

The results for a series of diatomic molecules were obtained by the MP2 method in the functional base 6-311+G (3*df*, 3*dp*) using the GAUSSIAN 94 calculation package [72]. It is interesting to compare how the nuclear reactivity indexes $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ reproduce changes in chemical potential and hardness. For this purpose, the modification of hardness and electronegativity for diatomic molecules from Table 3.1 stretched by $\Delta\mathbf{Q} = 0.1\text{Å}$ have been calculated. The ionization energies for deformed molecules allowed for calculation the new hardness and electronegativity. The change in these values in relation to the initial values was compared with the change in electronegativity and hardness calculated with the use of nuclear reactivity indices. Fig. 3.1 and 3.2 demonstrate that the nuclear reactivity indices reproduce changes in hardness and electronegativity quite well.

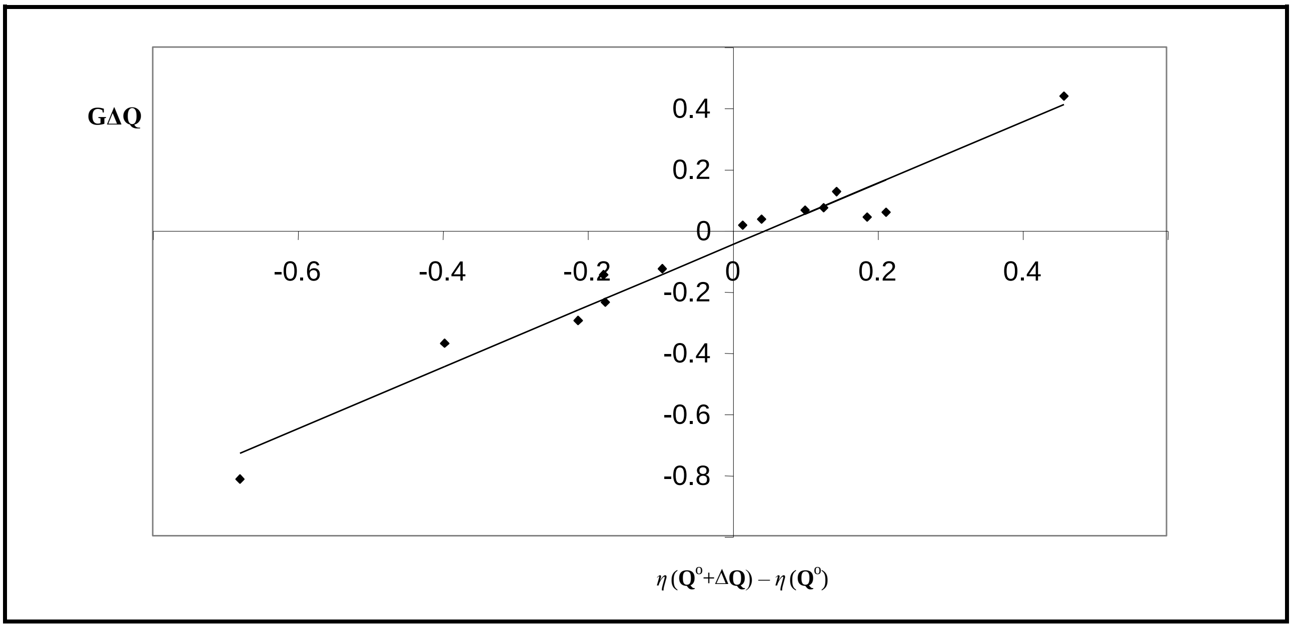

**Fig. 3.1** Correlation between the modified hardness calculated by two methods: from the classical definition $\frac{I-A}{2}$ and from the nuclear stiffness $\mathbf{G}$ for a set of diatomic molecules in Table 3.1.

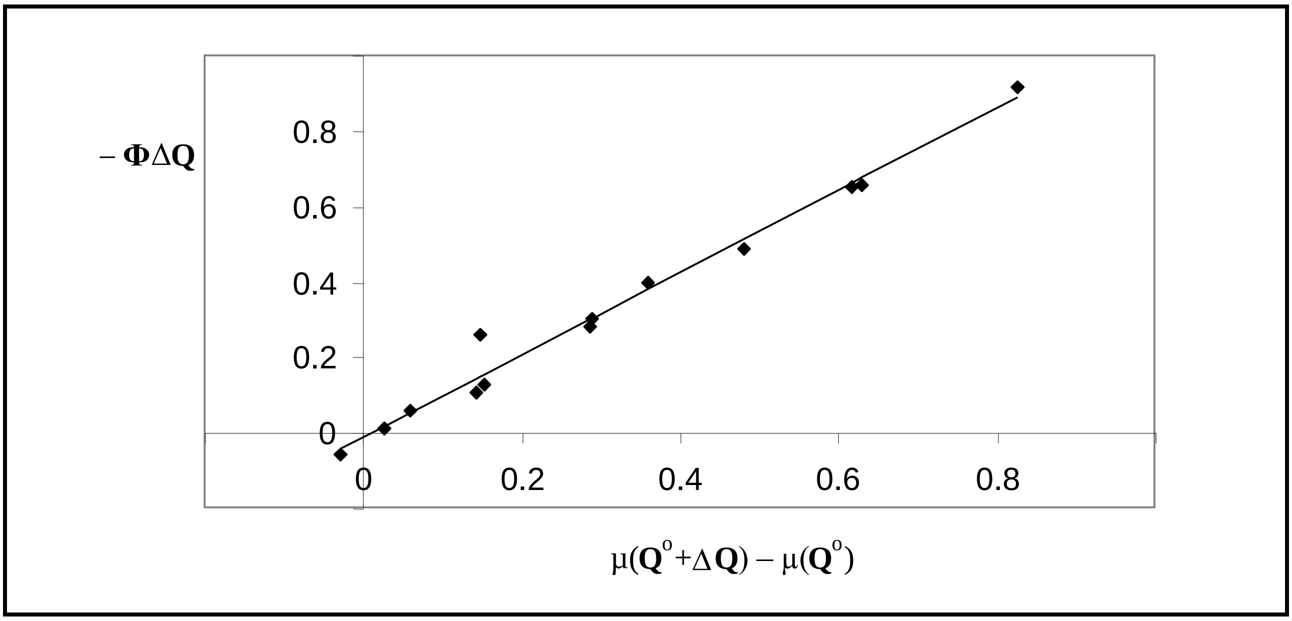

**Fig. 3.2** Correlation between the electronegativity calculated by two methods: from the classical definition $\frac{I+A}{2}$ and from the nuclear reactivity $\mathbf{\Phi}_i$ for a set of diatomic molecules in Table 3.1.

### 3.1.2 Polyatomic molecules

The results for a series of polyatomic molecules were obtained by the B3-LYP method in the functional base 6-31G**. The geometry was optimized for a neutral molecule using the quasi-Newton-Raphson procedure [73, 74]. Frequencies of individual normal vibrations, their force constants, and the normalized amplitudes of oscillations of atoms from their equilibrium positions were obtained. The anion and cation energies and forces were determined for the geometry of the neutral molecule. They were determined as the negative energy gradient of the ionized particle [A5] In chapter 2 the following quantities have been defined:

$$\sum_i \mathbf{l}_i^{\alpha}\cdot\mathbf{F}_{\boldsymbol{i}} = F_{\alpha}^{o} \qquad (3.1.11)$$

$$\sum_i \mathbf{l}_i^{\alpha}\cdot\mathbf{\Phi}_i = \varphi_{\alpha}^{o} \qquad (3.1.12)$$

$$\sum_i \mathbf{l}_i^{\alpha}\cdot\mathbf{G}_{\boldsymbol{i}} = G_{\alpha}^{o} \qquad (3.1.13)$$

But [68]:
$$\mathbf{l}_i^{\alpha} = \frac{\mathbf{Q}_i^{\alpha}}{\left[\sum_i (\mathbf{Q}_i^{\alpha})^2\right]^{1/2}} \qquad (3.1.14)$$

By definition [A5]:
$$\varphi_{\alpha} = \sum_i \mathbf{Q}_i^{\alpha}\cdot\mathbf{\Phi}_i \qquad (3.1.15)$$

and $$G_\alpha = \sum_i \mathbf{Q}_i^\alpha \cdot \mathbf{G}_i \ . \qquad \textbf{(}3.1.16)$$

Hence $$\varphi_\alpha = \varphi_\alpha^{\mathrm{o}} \left[ \sum_i (\mathbf{Q}_i^\alpha)^2 \right]^{1/2} \qquad \textbf{(}3.1.17)$$

and $$G_\alpha = G_\alpha^{\mathrm{o}} \left[ \sum_i (\mathbf{Q}_i^\alpha)^2 \right]^{1/2} \qquad \textbf{(}3.1.18)$$

$\varphi_\alpha$ and $G_\alpha$ are indexes describing actual displacements of atoms from the equilibrium, not their relative positions [A5]:

$$\varphi_\alpha^{\mathrm{o}} = \tfrac{1}{2} \sum_i (\mathbf{F}_i^+ - \mathbf{F}_i^-)\, \mathbf{l}_i^\alpha \qquad \textbf{(}3.1.19)$$

$$G_\alpha^{\mathrm{o}} = -\tfrac{1}{2} \sum_i (\mathbf{F}_i^+ + \mathbf{F}_i^-)\, \mathbf{l}_i^\alpha \qquad \textbf{(}3.1.20)$$

The symmetry properties of the vector reactivity indices must be noted [A4], [A5]. For a non-degenerate ionized state $(+/-)$ $\mathbf{F}_i^{+/-}$ keep a symmetry of a molecule. However, the normal coordinates $\mathbf{l}_i^\alpha$ are not necessary fully symmetric for every $\alpha$ . Since $\varphi_\alpha^{\mathrm{o}}$ and $G_\alpha^{\mathrm{o}}$ are scalars invariant with respect to symmetry transformations, we obtain non-zero values for vibrations with symmetry equal to the symmetry of the molecule, i.e., for fully symmetric vibrations. This follows from the general theorem:

$$\Gamma_\gamma \times \Gamma_\alpha \supset \Gamma_\gamma \qquad \textbf{(}3.1.21)$$

Here $\Gamma_\gamma$ is the irreducible representation of the symmetry group of forces $\mathbf{F}_i^{+/-}$. $\Gamma_\alpha$ is an irreducible representation according to which the vibration is transformed $\alpha$ . If the irreducible representation $\Gamma_\gamma$ is contained in the simple product $\Gamma_\gamma$ and $\Gamma_\alpha$ then $\varphi_\alpha^{\mathrm{o}}$ and $G_\alpha^{\mathrm{o}}$ may have a non-zero value [75, 76]. If $\boldsymbol{\Phi}_i$ and $\mathbf{G}_i$ have molecular symmetry, then only fully symmetric vibrations contribute. However, if degeneracy of the ionized states occurs then the forces $\mathbf{F}_i^{+/-}$ no longer have molecular symmetry due to the Jahn-Teller effect. The general theorem states that a symmetric state cannot be degenerate. Thus, if degeneration occurs because of vertical ionization, there will be forces tending to break the symmetry. They obviously no longer have the symmetry of the point group of the molecule under study. In this case, non-zero values of $\varphi_\alpha^{\mathrm{o}}$ and $G_\alpha^{\mathrm{o}}$ are also obtained for non-fully symmetric normal vibrations according to eq. 3.1.21. The indexes $\varphi_\alpha$ and $G_\alpha$ allow to compare normal vibrations with each other in terms of changes in hardness and electronegativity:

$$\Delta\chi = \sum_i \mathbf{\Phi}_i \cdot \Delta\mathbf{Q}_i = \sum_i \mathbf{\Phi}_i \cdot \sum_\alpha \mathbf{Q}_i^\alpha = \sum_\alpha \sum_i \mathbf{\Phi}_i \cdot \mathbf{l}_i^\alpha \left[ \sum_j (\mathbf{Q}_j^\alpha)^2 \right]^{1/2} = \sum_\alpha \varphi_\alpha^{\mathrm{o}} \left[ \sum_j (\mathbf{Q}_j^\alpha)^2 \right]^{1/2} = \sum_\alpha \varphi_\alpha \qquad (3.1.22)$$

$$\Delta\eta = \sum_i \mathbf{G}_{\boldsymbol{i}} \cdot \Delta\mathbf{Q}_i = \sum_i \mathbf{G}_{\boldsymbol{i}} \cdot \sum_\alpha \mathbf{Q}_i^\alpha = \sum_\alpha \sum_i \mathbf{G}_{\boldsymbol{i}} \cdot \mathbf{l}_i^\alpha \left[ \sum_j (\mathbf{Q}_j^\alpha)^2 \right]^{1/2} = \sum_\alpha G_\alpha^{\mathrm{o}} \left[ \sum_j (\mathbf{Q}_j^\alpha)^2 \right]^{1/2} = \sum_\alpha G_\alpha \qquad (3.1.23)$$

The results have been summarized in Table 3.2. The results are given only for those vibrations that make a clear contribution to changes in electronegativity or hardness. From Table 3.2, one can identify the vibrational modes that play a key role. For some molecules, the Jahn-Teller effect is visible - non-zero values $\Delta\eta$ and $\Delta\chi$ for non-full symmetric vibrations. (e. g. with *E* symmetry for the symmetry of a $C_{3v}$ molecule). This is the case for $CH_3F$, $CH_3Cl$, $BH_3$ and for benzene - $C_6H_6$. Participation of non-full-symmetric vibrations opens the way to symmetry breaking during a chemical reaction. This effect will also be discussed for the decomposition of the explosive compound RDX [A4]. Deformation of a molecule consistent with a mode that is accompanied by a large value $\left|\varphi_\alpha^{\mathrm{o}}\right|$ or $\left|G_\alpha^{\mathrm{o}}\right|$ causes the largest modifications in the reactivity of the molecule. For a given deformation $\{\Delta\mathbf{Q}_i\}$, the sign of $\Delta\eta$ and $\Delta\chi$ is of great importance because it shows whether a given deformation increases or decreases the reactivity of the molecule. However, in the case of harmonic oscillations, the magnitudes $\Delta\eta$ and $\Delta\chi$ oscillate from $-\Delta\eta$ to $+\Delta\eta$ and from $-\Delta\chi$ to $+\Delta\chi$. The mean change is zero and $\Delta\chi$, $\Delta\eta$ are just the amplitudes of these changes. Therefore, if it is necessary to specify these amplitudes for harmonic vibrations, the following modules will be given: $|\Delta\chi|$ and $|\Delta\eta|$ hence $|\varphi_\alpha|$ and $|G_\alpha|$.

**Table 3.2**

Nuclear reactivity indices for selected normal vibrations in simple molecules.
Only significant values are included if $\left|G_\alpha^\mathrm{o}\right|$ or $|\phi_\alpha^o| > 0.1\ eV/\text{Å}$

| Molecule | Vibrational mode | | $\left\|\varphi_\alpha^\mathrm{o}\right\|$ [eV/Å] | $\left\|G_\alpha^\mathrm{o}\right\|$ [eV/Å] |
|---|---|---|---|---|
| | Symmetry | Frequency [cm$^{-1}$] | | |
| **$H_2O$** | $A_1$ | 1665 | 0.513 | 0.117 |
| | $A_1$ | 3800 | 0.779 | 3.918 |
| **$H_3O^+$** | $A_1$ | 783 | 1.404 | 1.131 |
| | $A_1$ | 3584 | 0.918 | 5.840 |
| **$H_2S$** | $A_1$ | 1226 | 0.990 | 0.906 |
| | $A_1$ | 2692 | 1.904 | 2.572 |
| **$H_2CO$** | $A_1$ | 1554 | 0.874 | 0.380 |
| | $A_1$ | 1846 | 3.300 | 3.106 |
| **$BCl_3$** | $A_1'$ | 869 | 4.155 | 4.252 |
| **$BF_3$** | $A_1'$ | 472 | 2.155 | 1.312 |
| **$BH_3$** | E' | 1198 | 1.348 | 1.348 |
| | $A_1'$ | 2553 | 0.835 | 2.258 |
| | E' | 2682 | 1.436 | 1.343 |
| **$BH_4^+$** | E | 1239 | 4.311 | 2.272 |
| | E | 1239 | 1.511 | 0.274 |
| | $A_1$ | 2291 | 1.678 | 5.121 |
| **HOCl** | A’ | 723 | 7.260 | 3.764 |
| | A’ | 1272 | 0.202 | 0.272 |
| | A’ | 3764 | 0.527 | 0.777 |
| **HOF** | A’ | 998 | 13.400 | 7.93 |
| | A’ | 1396 | 0.495 | 0.782 |
| | A’ | 3736 | 0.870 | 1.296 |
| **HCN** | $S_g$ | 2214 | 0.953 | 6.964 |
| | $S_g$ | 3475 | 0.918 | 0.913 |
| **HCNO** | $S_g$ | 1308 | 3.367 | 3.619 |
| | $S_g$ | 2362 | 1.183 | 2.261 |
| | $S_g$ | 3534 | 1.204 | 0.351 |
| **$NH_3$** | $A_1$ | 1090 | 2.052 | 1.266 |
| | $A_1$ | 3462 | 1.096 | 2.584 |
| **$NH_4^+$** | E | 1727 | 2.825 | 2.825 |
| | E | 1727 | 0.424 | 0.424 |
| | $A_1$ | 3369 | 2.330 | 5.760 |
| **$NH_2NH_2$** | $A_g$ | 940 | 3.709 | 2.391 |
| | $A_g$ | 1262 | 1.628 | 1.004 |
| | $A_g$ | 3419 | 0.873 | 1.874 |
| **CHCH** | $S_{gg}$ | 2086 | 0.925 | 4.751 |
| | $S_{gg}$ | 3537 | 0.953 | 0.919 |
| **$CH_2CH_2$** | $A_g$ | 1389 | 0.428 | 1.102 |
| | $A_g$ | 1715 | 3.589 | 0.250 |
| | $A_g$ | 3160 | 2.115 | 1.861 |

Table 3.2 cont.

| | | | | |
|---|---|---|---|---|
| $CH_2F_2$ | $A_1$ | 1131 | 2.291 | 0.600 |
| | $A_1$ | 1553 | 1.209 | 0.197 |
| | $A_1$ | 3042 | 0.905 | 3.158 |
| $CH_3F$ | $A_1$ | 1191 | 1.072 | 1.211 |
| | E | 1219 | 0.255 | 0.255 |
| | E | 1219 | 0.147 | 0.137 |
| | $A_1$ | 1632 | 0.191 | 0.786 |
| | E | 1660 | 0.394 | 0.384 |
| | E | 1660 | 0.676 | 0.676 |
| | $A_1$ | 3196 | 0.905 | 1.485 |
| | E | 3343 | 0.334 | 0.351 |
| | E | 3343 | 0.587 | 0.587 |
| $CH_3Cl$ | $A_1$ | 719 | 5.396 | 4.993 |
| | E | 1035 | 0.131 | 0.131 |
| | $A_1$ | 1398 | 0.160 | 0.239 |
| | E | 1495 | 1.104 | 1.373 |
| | E | 1495 | 0.233 | 0.233 |
| | $A_1$ | 3088 | 3.995 | 4.685 |
| | E | 3192 | 0.222 | 0.223 |
| | E | 3192 | 0.418 | 0.160 |
| $CH_3NH_2$ | A' | 859 | 1.389 | 0.658 |
| | A' | 1067 | 0.291 | 0.370 |
| | A' | 1183 | 1.056 | 0.905 |
| | A' | 2966 | 0.241 | 0.702 |
| | A' | 3072 | 0.372 | 0.193 |
| | A' | 3492 | 0.932 | 1.888 |
| $CH_3OH$ | A' | 1095 | 0.297 | 0.622 |
| | A' | 1385 | 0.290 | 0.209 |
| | A' | 1527 | 0.118 | 0.287 |
| | A' | 2989 | 0.242 | 1.007 |
| | A' | 3122 | 0.301 | 0.118 |
| $CH_3NO_2$ | A' | 672 | 0.952 | 0.394 |
| | A' | 944 | 1.478 | 0.351 |
| | A' | 1168 | 0.363 | 0.263 |
| | A' | 1436 | 2.864 | 4.829 |
| | A' | 3171 | 0.218 | 0.379 |
| $C_6H_6$ | $E_{2g}$ | 621 | 0.239 | 0.570 |
| | $A_{1g}$ | 1020 | 0.316 | 1.501 |
| | $E_{2g}$ | 1653 | 2.868 | 0.273 |
| | $A_{1g}$ | 3210 | 0.240 | 0.038 |

### 3.1.3 Local metallization and the Jahn-Teller effect for the RDX molecule

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a second-order explosive compound, important from a military point of view [A4]. Several theoretical and experimental studies have been carried out on this compound [77]. The main goal was to clarify whether Gilman's concept of local metallization is an adequate way to describe the first stages of RDX dissociation [78]. Based on experimental data, several possible RDX dissociation pathways have been proposed: (i) symmetrical disintegration of the ring into three $CH_2N_2O_2$ radicals or (ii) asymmetric cleavage of the N–$NO_2$ bond. Experimental studies on photoinduced dissociation suggest pathway (ii) [79, 80, 81], while studies with multiphonon collective interaction [82] suggest pathway (i). Theoretical calculations show that the cleavage of the N–$NO_2$ bond is dominant in unimolecular dissociation [83]. A third way was also proposed: successive elimination of radicals as the most exothermic RDX decay channel [77]. These results are of great importance as they show the possibility of testing the method based on renormalized hardness and change of chemical reactivity due to deformation. We were therefore looking for such a deformation of the molecule that most increases its ability to release electrons. It is easy to show that such a state is the one for which the chemical hardness is equal to zero. Th condition $I - A = 0$ was called by Gilman a locally metallic state [78, 84]. In this state, there is no energy barrier to the flow of electrons [62]. This state was selected as the state that is most likely to be the first stage of unimolecular dissociation. All calculations were made in $C_{3v}$ symmetry. The optimized geometry of the molecule is in very good agreement with the results presented by other researchers, both experimental and theoretical [85]. Vibration frequencies and normal modes were determined. The frequencies also agree very well with the experimental data and calculations [86]. The energies of the particle after ionization have been calculated. The forces acting on the atoms in the ionized state $\mathbf{F}_i^{+/-}$ were determined as the negative energy gradient of the ionized molecule. Due to the occurrence of the Jahn-Teller effect, $\mathbf{F}_i^{-}$ does not show $C_{3v}$ symmetry but $C_s$ symmetry. This effect occurs because the HOMO orbital of the RDX molecule consists of two filled e-type orbitals. Removal of an electron from the HOMO orbital therefore causes a two-fold degeneration of the ground state, which is forbidden according to the Jahn-Teller theorem and causes symmetry-breaking forces.

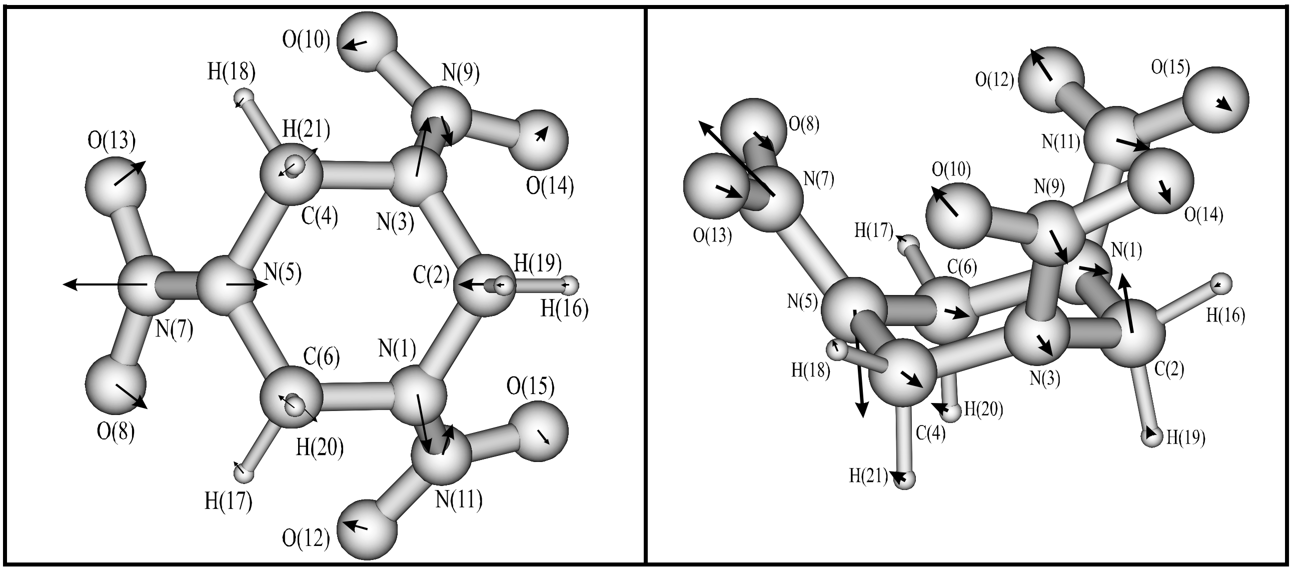

**Fig. 3.3 & 3.4** Nuclear reactivity vectors $\mathbf{\Phi}_i$ for RDX molecule

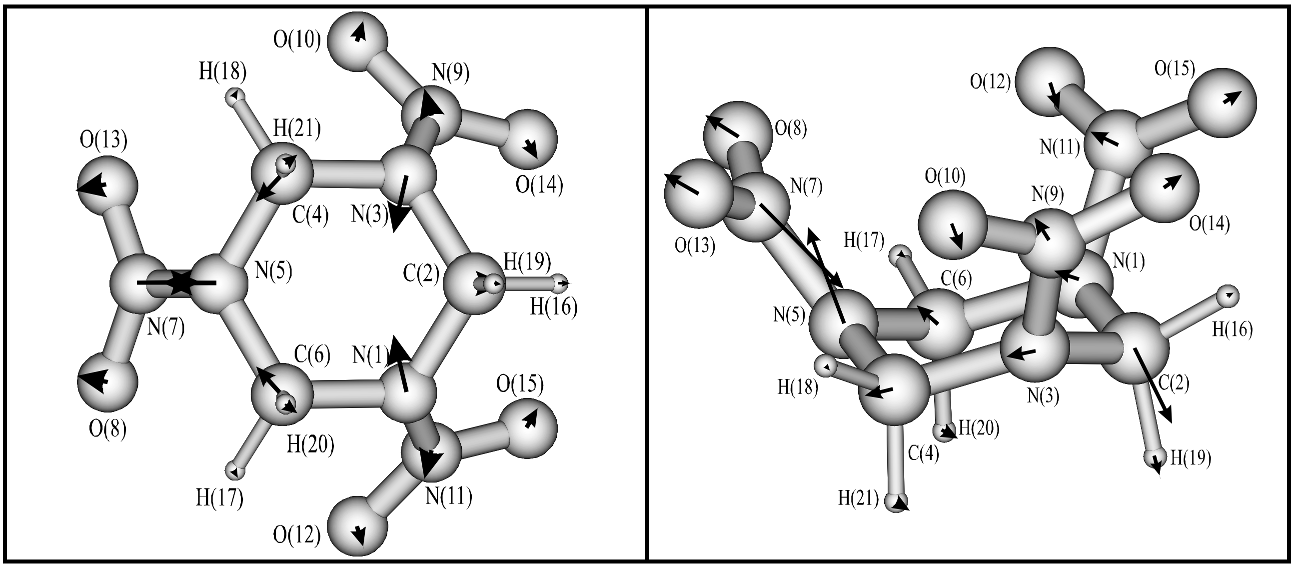

**Fig. 3.5 & 3.6.** Nuclear stiffness vectors $\mathbf{G}_i$ for RDX molecule

Nuclear reactivity indices were determined $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ for each atom (Fig.3.3 to Fig.3.6). The highest value of reactivity indices is obtained along one of the N–NO$_2$ bonds. This suggests that the deformation of the molecule in this direction causes the greatest increase in its reactivity, and therefore breaking the N–NO$_2$ bond can be considered the first stage of the unimolecular disintegration reaction. This is in very good agreement with the results presented by Kuntz and colleagues [87, 88]. The reasoning of these authors follows a very similar track to ours. They prove that the key process is the transfer of the electron from the HOMO orbital to the LUMO and that this process does not require energy input. They calculate the difference between HOMO and LUMO at 5.25 eV, which correlates well with the hardness we have determined $\eta^{\mathrm{o}} = 5.16\,\mathrm{eV}$. They then show that the deformation of the molecule along the N–$NO_2$ bond leads to a decrease in this value. An important addition to our concept from the work of Kuntz and co-workers is the indication that such deformation may take place at points that are defects in the crystal lattice. Nuclear reactivity indices were projected to normal coordinates. The results show the contribution of non-full-symmetric degenerate vibrations with *E* symmetry. This is another aspect of the Jahn-Teller effect. The hardness of the molecule without considering couplings with oscillatory degrees of freedom $\eta^{\mathrm{o}} = 5.16\,\mathrm{eV}$ is renormalized by 7.99 eV. We interpret this fact as the unusual instability of the RDX molecule. The vibrations stretching the N–$NO_2$ bond have the greatest share in this. The hardness is renormalized by such a large value since the concept of renormalization is a very rough approximation and the hardness change calculated in this way is burdened with a large error. However, it can be concluded from this result that the renormalization for RDX is significantly greater than for normal molecules.

**Table 3.3**

Atomic nuclear reactivity indexes in molecule RDX

| **Atom** | $\lvert \mathbf{F}_i^{+} \rvert$ | $\lvert \mathbf{F}_i^{-} \rvert$ | $\lvert \mathbf{G}_i \rvert$ | $\lvert \mathbf{\Phi}_i \rvert$ |
|---|---|---|---|---|
| N1 | 1.655 | 29.561 | 14.774 | 14.834 |
| C2 | 0.862 | 25.331 | 12.567 | 12.777 |
| N3 | 1.655 | 29.561 | 14.774 | 14.834 |
| C4 | 0.981 | 18.027 | 9.192 | 8.859 |
| N5 | 1.854 | 43.410 | 20.804 | 22.608 |
| C6 | 0.981 | 18.027 | 9.192 | 8.859 |
| N7 | 2.285 | 51.656 | 26.967 | 24.690 |
| O8 | 5.395 | 15.273 | 7.910 | 8.284 |
| N9 | 2.390 | 18.799 | 8.362 | 10.471 |
| O10 | 5.469 | 14.024 | 6.675 | 8.291 |
| N11 | 2.390 | 18.799 | 8.362 | 10.471 |
| O12 | 5.469 | 14.024 | 6.675 | 8.291 |
| O13 | 5.395 | 15.273 | 7.910 | 8.284 |
| O14 | 5.360 | 9.023 | 6.282 | 3.951 |
| O15 | 5.360 | 9.023 | 6.282 | 3.951 |
| H16 | 0.501 | 2.508 | 1.480 | 1.039 |
| H17 | 0.540 | 5.646 | 2.857 | 2.815 |
| H18 | 0.540 | 5.646 | 2.857 | 2.815 |
| H19 | 0.648 | 4.029 | 2.328 | 1.705 |
| H20 | 0.621 | 9.967 | 5.131 | 4.851 |
| H21 | 0.621 | 9.967 | 5.131 | 4.851 |

**Table 3.4**

Nuclear reactivity indexes in molecule RDX projected onto the normal modes.

The Jahn–Teller effect is clearly visible.

| α | Symmetry | $\omega_\alpha$ | $G^{o}_{\alpha}$ | $\varphi^{o}_{\alpha}$ | $(\varphi^{o}_{\alpha})^2 / 2k_\alpha$ |
|---|---|---|---|---|---|
| 1 | E | 39.60 | 0.2284 | -0.2298 | 0.3881 |
| 2 | E | 39.60 | 0.5994 | -0.6183 | 2.8093 |
| 3 | $A_2$ | 68.02 | 0.0000 | 0.0000 | 0.0000 |
| 4 | $A_1$ | 69.16 | 0.6531 | -0.6426 | 0.9240 |
| 5 | E | 104.02 | -0.3301 | 0.3255 | 0.1045 |
| 6 | E | 104.02 | -1.1407 | 1.1190 | 1.2353 |
| 7 | E | 228.10 | -0.0015 | 0.0072 | 0.0000 |
| 8 | E | 228.10 | -0.0756 | 0.0766 | 0.0015 |
| 9 | $A_2$ | 304.08 | 0.0000 | 0.0000 | 0.0000 |
| 10 | E | 369.25 | -0.1518 | 0.1546 | 0.0063 |
| 11 | E | 369.25 | 0.3982 | -0.3812 | 0.0385 |
| 12 | E | 416.72 | 0.4373 | -0.4212 | 0.0422 |
| 13 | E | 416.72 | -0.1461 | 0.1454 | 0.0050 |
| 14 | $A_1$ | 442.18 | 1.6701 | -1.6038 | 1.1223 |
| 15 | $A_1$ | 469.60 | -0.7584 | 0.9152 | 0.0570 |
| 16 | E | 589.32 | 0.2378 | -0.2467 | 0.0043 |
| 17 | E | 589.32 | 0.0400 | -0.0517 | 0.0002 |
| 18 | $A_2$ | 592.86 | 0.0000 | 0.0000 | 0.0000 |
| 19 | E | 660.51 | -0.2408 | 0.2353 | 0.0025 |
| 20 | E | 660.51 | -0.9100 | 0.9077 | 0.0369 |
| 21 | $A_1$ | 745.14 | -0.4988 | 0.4987 | 0.0066 |
| 22 | E | 755.08 | 0.0121 | -0.0065 | 0.0000 |
| 23 | E | 755.08 | -0.0368 | 0.0227 | 0.0000 |
| 24 | $A_1$ | 784.51 | 0.6040 | -0.7181 | 0.0102 |
| 25 | E | 860.51 | 1.0335 | -1.0313 | 0.0275 |
| 26 | E | 860.51 | 0.2568 | -0.2593 | 0.0017 |
| 27 | $A_1$ | 893.03 | -0.5822 | 0.4197 | 0.0047 |
| 28 | E | 915.72 | -0.5053 | 0.5054 | 0.0144 |
| 29 | E | 915.72 | 1.8355 | -1.8395 | 0.1904 |
| 30 | $A_1$ | 940.14 | 0.0503 | 0.3247 | 0.0035 |
| 31 | E | 1012.68 | 0.2134 | -0.2223 | 0.0027 |
| 32 | E | 1012.68 | -1.0020 | 1.0279 | 0.0574 |
| 33 | $A_2$ | 1146.90 | 0.0000 | 0.0000 | 0.0000 |
| 34 | $A_1$ | 1247.09 | -0.1516 | 0.3754 | 0.0035 |
| 35 | E | 1258.00 | 0.0068 | -0.0083 | 0.0000 |
| 36 | E | 1258.00 | 0.0103 | -0.0110 | 0.0000 |
| 37 | $A_2$ | 1275.50 | 0.0000 | 0.0000 | 0.0000 |
| 38 | E | 1310.38 | -0.0802 | 0.0735 | 0.0001 |
| 39 | E | 1310.38 | 0.4211 | -0.4285 | 0.0042 |
| 40 | $A_2$ | 1360.84 | 0.0000 | 0.0000 | 0.0000 |
| 41 | $A_1$ | 1368.04 | 0.3772 | 0.2052 | 0.0005 |
| 42 | E | 1383.66 | 0.3816 | -0.3779 | 0.0077 |
| 43 | E | 1383.66 | 1.3695 | -1.3907 | 0.1042 |
| 44 | E | 1407.70 | 3.3250 | -3.3666 | 0.5279 |

| | | | | | |
|---|---|---|---|---|---|
| 45 | E | 1407.70 | 0.8967 | -0.9078 | 0.0384 |
| 46 | E | 1466.84 | -0.4420 | 0.4380 | 0.0109 |
| 47 | E | 1466.84 | -1.7429 | 1.7729 | 0.1790 |
| 48 | $A_1$ | 1487.23 | -0.6911 | 0.4385 | 0.0099 |
| 49 | $A_2$ | 1677.41 | 0.0000 | 0.0000 | 0.0000 |
| 50 | E | 1704.83 | 0.0807 | -0.0813 | 0.0000 |
| 51 | E | 1704.83 | 0.2666 | -0.2735 | 0.0003 |
| 52 | E | 3080.49 | 0.3114 | -0.3129 | 0.0013 |
| 53 | E | 3080.49 | -0.1305 | 0.1283 | 0.0002 |
| 54 | $A_1$ | 3087.24 | -1.2977 | 0.8995 | 0.0108 |
| 55 | E | 3216.85 | -0.0458 | 0.0448 | 0.0000 |
| 56 | E | 3216.85 | -0.0959 | 0.1070 | 0.0001 |
| 57 | $A_1$ | 3218.60 | -0.5099 | 0.2916 | 0.0010 |
| $\sum_\alpha \frac{(\varphi_\alpha)^2}{2k_\alpha}$ | | | | | 7.9972 |

## 3.2 Vibrational softening, renormalization of hardness

The analysis for the harmonic oscillator is extremely simple, the only parameter that depends on the number of electrons in the energy expression is the vibration frequency [A3]:

$$E_v = \hbar\omega\left(\nu + \tfrac{1}{2}\right). \tag{3.2.1}$$

Let: $$\omega' = \left(\frac{\partial \omega}{\partial N}\right)_{v(\mathbf{r})} \tag{3.2.2}$$

and $$\omega'' = \left(\frac{\partial^2 \omega}{\partial N^2}\right)_{v(\mathbf{r})} \tag{3.2.3}$$

Then: $$\chi_v = -\frac{\omega'}{\omega} E_v \tag{3.2.4}$$

and $$\eta_v = \frac{\omega''}{\omega} E_v \, . \tag{3.2.5}$$

Hence: $$\langle \chi_v \rangle = -\frac{\omega'}{\omega}\langle E \rangle = -\frac{\omega'}{\omega}\left(\frac{1}{2}\hbar\omega + \frac{1}{\beta}\frac{u}{e^u - 1}\right) \tag{3.2.6}$$

and $$\langle \eta_v \rangle = \frac{\omega''}{\omega}\langle E \rangle = \frac{\omega''}{\omega}\left(\frac{1}{2}\hbar\omega + \frac{1}{\beta}\frac{u}{e^u - 1}\right) \tag{3.2.7}$$

The average energy of an oscillator is:

$$\langle E \rangle = \frac{1}{2}\hbar\omega + \frac{1}{\beta}\frac{u}{e^u - 1} \tag{3.2.8}$$

Statistical sum in the canonical ensemble is:

$$Q = \frac{e^{-\frac{1}{2}u}}{1-e^{-u}} \tag{3.2.9}$$

where: $u = \frac{\hbar\omega}{k_B T}$ **(**3.2.10)

For the oscillation energy:

$$\left\langle (\delta E_{vib})^2 \right\rangle = \frac{T}{\beta} C_V \tag{3.2.11}$$

and $C_V = k_B \frac{u^2 e^u}{(e^u - 1)^2}$ **(**3.2.12)

$$\left\langle (\delta E_{vib})^2 \right\rangle = \frac{1}{\beta^2} \frac{u^2 e^u}{(e^u - 1)^2} = (\hbar\omega)^2 \frac{e^u}{(e^u - 1)^2} \tag{3.2.13}$$

Now we will use the previously derived expressions for temperature averages $\langle \chi \rangle$ and $\langle \eta \rangle$ for the canonical ensemble. If we compare equation 3.2.6 for electronegativity with 2.8.24 we get:

$$\langle \chi \rangle - \langle \chi_v \rangle = \beta \frac{\omega'}{\omega} \left\langle (\delta E)^2 \right\rangle \tag{3.2.14}$$

and $\langle \chi \rangle = -\frac{\omega'}{\omega} [\langle E \rangle - \beta \left\langle (\delta E)^2 \right\rangle]$ **(**3.2.15)

Hence: $\langle \chi \rangle = -\frac{\omega'}{\omega} [\langle E \rangle - T C_V]$ **(**3.2.16)

By substitution:

$$\langle \chi \rangle = -\hbar\omega \left( \frac{\omega'}{\omega} \right) \left\{ \frac{1}{2} + \frac{1}{e^u - 1} - \frac{u e^u}{\left(e^u - 1\right)^2} \right\} \tag{3.2.17}$$

The derivative exposes the average hardness:

$$\langle \eta \rangle = \frac{\omega''}{\omega} \langle E \rangle - \beta \left\langle (\delta E)^2 \right\rangle \left[ 2\left( \frac{\omega'}{\omega} \right)^2 + \frac{\omega''}{\omega} \right] - \beta^2 \left( \frac{\omega'}{\omega} \right)^2 \frac{\partial \left\langle (\delta E)^2 \right\rangle}{\partial \beta} \tag{3.2.18}$$

or $\langle \eta \rangle = \frac{\omega''}{\omega} [\langle E \rangle - T C_V] + \left( \frac{\omega'}{\omega} \right)^2 T^2 \frac{\partial C_V}{\partial T}$ **(**3.2.19)

Using the analytical relations for the harmonic oscillator we get the important relationship:

$$T^2 \frac{\partial C_V}{\partial T} = -\hbar\omega u f(u) \tag{3.2.20}$$

where *f(u)* is an universal function:

$$f(u) = \frac{2e^u}{\left(e^u - 1\right)^2} - \frac{u e^u \left(e^u + 1\right)}{\left(e^u - 1\right)^3} \tag{3.2.21}$$

Finally, the average hardness $\langle \eta \rangle$ is expressed by three characteristic parameters: *ω, ω'* and *ω''*:

$$\langle \eta \rangle = (\hbar\omega)\left\{ \left(\frac{\omega''}{\omega}\right)\left[\frac{1}{2}+\frac{1}{e^u-1}-\frac{ue^u}{\left(e^u-1\right)^2}\right]-\left(\frac{\omega'}{\omega}\right)^2 uf(u)\right\} \tag{3.2.22}$$

$\langle \eta_v' \rangle$ is expressed by:

$$\langle \eta_v' \rangle = \frac{\omega''}{\omega}\langle E \rangle - \beta\left(\frac{\omega'}{\omega}\right)^2 \left\langle (\delta E)^2 \right\rangle \tag{3.2.23}$$

and $$\langle \eta_v' \rangle = \frac{\omega''}{\omega}\langle E \rangle - \left(\frac{\omega'}{\omega}\right)^2 TC_V \tag{3.2.24}$$

Hence $$\langle \eta_v' \rangle = (\hbar\omega)\left\{ \left(\frac{\omega''}{\omega}\right)\left[\frac{1}{2}+\frac{1}{e^u-1}\right]-\left(\frac{\omega'}{\omega}\right)^2 \frac{ue^u}{\left(e^u-1\right)^2}\right\} \tag{3.2.25}$$

At finite temperatures, there is a set of parameters describing the properties of the molecule: the thermodynamic averages. According to eq. 2.8.25 and eq. 2.8.27 they are not identical to the derivatives of the average energy $\langle \chi_v \rangle$ and $\langle \eta_v' \rangle$. Fig. 3.7 and 3.8 show the functions $\langle \chi \rangle$ and $\langle \eta \rangle$ depending on 1/*u* for the harmonic oscillator model (eq. 3.2.17 and eq. 3.2.22). The significance of these quantities is not obvious. Since the entropy has not been considered, the picture they draw cannot be complete. They show the vibrational contribution to the derivatives of medium energy. In the case of $\langle \chi \rangle$ it is an insignificant contribution, for $\langle \eta \rangle$ it is slightly larger. It is interesting that this contribution is non-zero only at low temperatures – it disappears for temperatures higher than the characteristic temperature: $\frac{kT}{\hbar\omega} > 1$. Functions $\langle \chi_v \rangle$ and $\langle \eta_v' \rangle$ (eq. 3.2.6 eq. 3.2.25) are monotonic. Thermodynamic hardness $\langle \eta_v' \rangle$ decreases with temperature (and becomes negative for high temperatures) regardless of the sign of $\frac{\omega'}{\omega}$ and $\frac{\omega''}{\omega}$. We interpret this phenomenon as vibration softening. Electronegativity $\langle \chi_v \rangle$ decreases with temperature for $\frac{\omega'}{\omega} > 0$ and increases for $\frac{\omega'}{\omega} < 0$, respectively. Bearing in mind that $\langle \chi_v \rangle, \langle \eta_v' \rangle$ determine only the oscillatory contribution to the total electronegativity and hardness (eq. 3.2.6 and eq. 3.2.7), we note that they modify the charge transfer energy - CTA between the investigated molecule and the model gas of free electrons [38]:

$$CTA \cong \frac{\chi^2}{4\eta} = \frac{\left(\chi_{el} + \langle \chi_v \rangle\right)^2}{4\left(\eta_{el} + \langle \eta_v' \rangle\right)} = \frac{\left(I + A + \langle \chi_v \rangle\right)^2}{8\left(I - A + \langle \eta_v' \rangle\right)}$$

The higher derivative may also be analyzed:

$$\frac{1}{2}\frac{\partial^4 E(Q,N)}{\partial Q^2 \partial N^2} = \frac{\partial^2 \eta}{\partial Q^2} = \frac{\partial G}{\partial Q} = \tau \tag{3.2.26}$$

The results for diatomic molecules calculated using the finite difference approximation have been presented in Table 3.5 for a group of diatomic molecules [A2]:

$$\lambda = \frac{\partial^2 \mu}{\partial Q^2} = \frac{\partial}{\partial N}\frac{\partial^2 E}{\partial Q^2} = \frac{\partial k}{\partial N} \cong \frac{1}{2}(k^+ - k^-) \tag{3.2.27}$$

$$\tau = \frac{\partial^2 \eta}{\partial Q^2} = \frac{1}{2}\frac{\partial^2}{\partial N^2}\frac{\partial^2 E}{\partial Q^2} = \frac{1}{2}\frac{\partial^2 k}{\partial N^2} = \frac{1}{2}(k^+ + k^-) - k\ . \tag{3.2.28}$$

**Table 3.5**

Calculated force constants for molecules ($k$) and their ions ($k_+$, $k_-$). The derivatives $\lambda$ and $\tau$ were calculated from eq. 3.2.26 eq. 3.2.27, respectively, in units [eV/Å$^2$] = 0.0624151 [N/m].

| Molecule | $k$ | $k^+$ | $k^-$ | $\lambda$ | $\tau$ | $\hbar\omega$ [eV] | $\omega'/\omega$ [x 10$^2$] | $\omega''/\omega$ [x 10$^2$] |
|---|---|---|---|---|---|---|---|---|
| **LiH** | 8.4235 | 7.3462 | 7.9148 | -0.2843 | -0.7930 | 0.1764 | -8.795 | -11.848 |
| **HF** | 67.8714 | 69.1147 | 51.5993 | 8.7577 | -7.2647 | 0.5173 | 6.860 | -5.946 |
| **F$_2$** | 68.2721 | 29.8298 | 160.833 | -65.5002 | 27.0595 | 0.1213 | -44.118 | 10.863 |
| **Cl$_2$** | 42.9224 | 32.1235 | 48.3226 | 8.0995 | -2.6994 | 0.0716 | -9.792 | -3.735 |
| **Li$_2$** | 2.9684 | 3.4646 | 2.7231 | 0.37074 | 0.1254 | 0.0420 | 1.711 | -2.460 |
| **FCl** | 52.6092 | 135.229 | 49.7169 | 42.7561 | 39.8638 | 0.0985 | 31.523 | 28.729 |
| **CO** | 224.266 | 318.580 | 225.102 | 46.5888 | 47.1503 | 0.2638 | 9.501 | 9.700 |
| **LiF** | 52.7652 | 28.4435 | 23.8230 | 2.3102 | -26.6320 | 0.1096 | 4.583 | 3.497 |
| **BCl** | 36.2379 | 36.2978 | 35.2036 | 0.5472 | 0.4871 | 0.1071 | 0.760 | -0.677 |
| **BH** | 23.8993 | 23.8904 | 22.4986 | 0.6959 | -0.6984 | 0.3022 | 1.479 | -1.466 |
| **CS** | 91.4241 | 55.9846 | 88.1368 | 72.0606 | 19.3634 | 0.1624 | -9.966 | -11.783 |
| **NF** | 92.3158 | 77.0270 | 109.494 | -16.2337 | 0.9094 | 0.1563 | -8.782 | 0.129 |
| **SO** | 75.6626 | 90.2458 | 105.381 | -7.5680 | 22.1512 | 0.1282 | -4.404 | 13.656 |
| **HCl** | 35.6855 | 35.5500 | 9.0719 | 13.2390 | -13.3745 | 0.3792 | 24.691 | -24.897 |
| **LiCl** | 11.7901 | 13.0278 | 11.2808 | 0.8735 | 18.3040 | 0.0779 | 3.653 | 1.505 |
| **BF** | 94.9318 | 98.9950 | 85.4904 | 6.7523 | -2.6892 | 0.1737 | 3.627 | -1.055 |
| **SiO** | 98.1612 | 75.6620 | 97.1819 | -10.7599 | -11.7392 | 0.1470 | -5.853 | -6.356 |

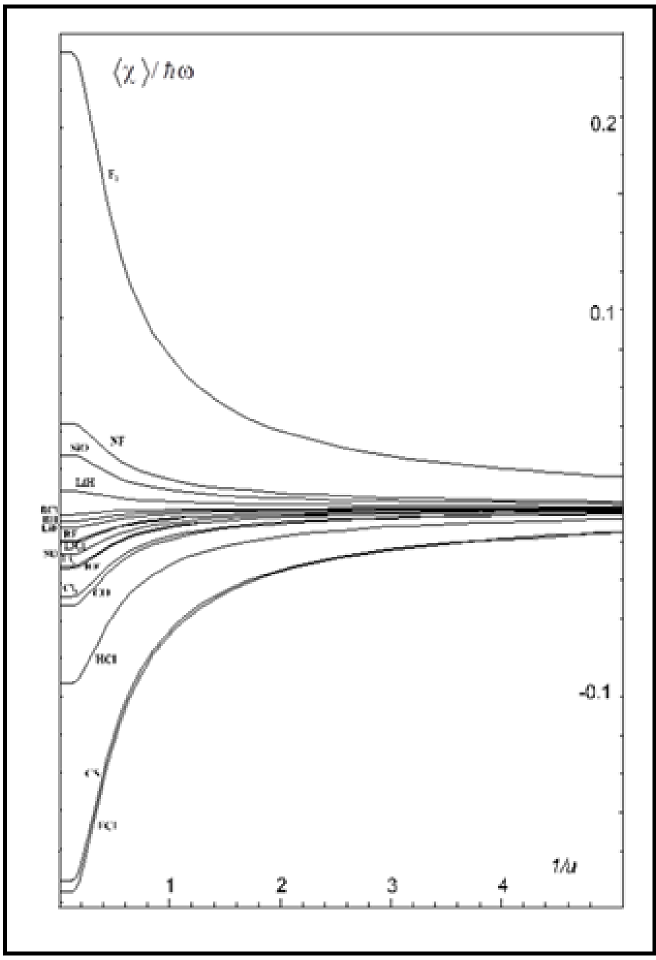

**Fig.3.7** Temperature dependence of the average electronegativity over *1/u* = $k_BT/\hbar\omega$. ($\hbar\omega$ unit)

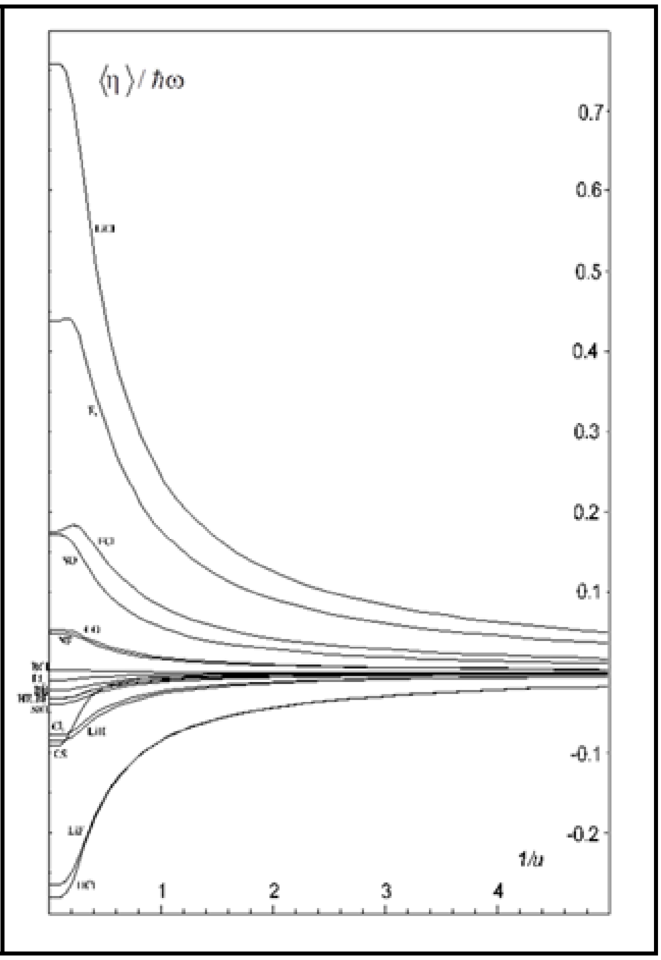

**Fig. 3.8** Temperature dependence of the average hardness over *1/u* = $k_BT/\hbar\omega$. ($\hbar\omega$ unit)

The diagrams have been calculated for the collection of diatomic molecules presented in Table 3.1.

### 3.3 Fluctuations of electronegativity and hardness

The contribution of the real oscillations to the softening of the molecule is represented by fluctuations. Electronegativity and hardness fluctuations for the harmonic oscillator model are determined directly from eq. 3.2.6 and eq. 3.2.7

$$\left\langle (\delta\chi_v)^2 \right\rangle = \left(\frac{\omega'}{\omega}\right)^2 \left\langle (\delta E_{vib})^2 \right\rangle \qquad \textbf{(}3.3.1)$$

and $$\left\langle (\delta\eta_v)^2 \right\rangle = \left(\frac{\omega''}{\omega}\right)^2 \left\langle (\delta E_{vib})^2 \right\rangle \qquad \textbf{(}3.3.2)$$

while the energy fluctuations are represented by eq. 3.2.29.

Hence: $$\left\langle \left(\delta\chi_v\right)^2 \right\rangle = \left(\frac{\omega'}{\omega}\right)^2 \left\langle (\delta E_{vib})^2 \right\rangle = (\hbar\omega')^2 \frac{e^u}{(e^u-1)^2} \qquad \textbf{(}3.3.3)$$

$$\left\langle (\delta\eta_v)^2 \right\rangle = \left(\frac{\omega''}{\omega}\right)^2 \left\langle (\delta E_{vib})^2 \right\rangle = (\hbar\omega'')^2 \frac{e^u}{(e^u-1)^2} \qquad (3.3.4)$$

The derivatives of the energy fluctuations are:

$$\frac{\partial \left\langle (\delta E_{vib})^2 \right\rangle}{\partial N} = -\frac{\omega'}{\omega} k_B T^3 \frac{\partial C_V}{\partial T} = (\hbar\omega)^2 \frac{\omega'}{\omega} f(u) \qquad (3.3.5)$$

$$\frac{\partial^2 \left\langle (\delta E_{vib})^2 \right\rangle}{\partial N^2} = 2k_B T^2 C_V \left(\frac{\omega'}{\omega}\right)^2 + k_B T^3 \frac{\partial C_V}{\partial T}\left[\frac{\omega''}{\omega} - \left(\frac{\omega'}{\omega}\right)^2\right] - k_B T^4 \frac{\partial^2 C_V}{\partial T^2}\left(\frac{\omega'}{\omega}\right)^2 =$$

$$= (\hbar\omega)^2 \left\{ \left(\frac{\omega'}{\omega}\right)^2 \left[ \frac{2e^u}{(e^u-1)^2} - 2f(u) - u\frac{\partial f(u)}{\partial u} \right] - f(u)\frac{\omega''}{\omega} \right\} \qquad (3.3.6)$$

A more reliable way to determine electronegativity and hardness fluctuations is to use expressions 2.8.34 and 2.8.35. Then they are proportional to the fluctuations of the positions of the atoms in harmonic vibrations. These fluctuations will be weighted by the indices $(\varphi_\alpha^{\circ})^2$ and $(G_\alpha^{\circ})^2$. The largest contribution to the change in hardness and electronegativity is potentially made by those vibrations with atoms performing the greatest amplitude. They would be meaningless if $\left|\varphi_\alpha^{\circ}\right|$ or $\left|G_\alpha^{\circ}\right|$ had negligible or zero value. At temperatures T→0 K, the function *ctgh*(*u*/2) →1 (eq. 2.8.40) and the fluctuations reach a minimum. The values of $\Delta\chi$ and $\Delta\eta$ in 0 K are identical with the corresponding fluctuations presented in Table 3.6. At finite temperatures, this effect increases markedly according to the course of the *ctgh* function shown in Fig.3.9. From an experimental point of view, only the temperature averaged values count, the average values $\left(\sum_i (\mathbf{Q}_i^\alpha)^2\right)^{1/2}$ are provided by eq. 2.8.40 [70,71].

$$\left\langle \sum_i (\mathbf{Q}_i^\alpha)^2 \right\rangle = \frac{\hbar\omega_\alpha}{2k_\alpha} \operatorname{ctgh} \frac{\hbar\omega_\alpha}{2k_B T} \qquad (3.3.7)$$

This result will be used to determine the average thermal fluctuations of electronegativity and hardness:

$$\left\langle (\delta\chi)^2 \right\rangle = \sum_\alpha \left\langle (\delta\varphi_\alpha)^2 \right\rangle = \sum_\alpha (\varphi_\alpha^{\circ})^2 \left\langle \sum_i (\mathbf{Q}_i^\alpha)^2 \right\rangle \qquad (3.3.8)$$

$$\left\langle (\delta\eta)^2 \right\rangle = \sum_\alpha \left\langle (\delta G_\alpha)^2 \right\rangle = \sum_\alpha (G_\alpha^{\circ})^2 \left\langle \sum_i (\mathbf{Q}_i^\alpha)^2 \right\rangle \qquad (3.3.9)$$

Indexes $\varphi_\alpha$ and $G_\alpha$ provide information on the possible influence of oscillations on the electronegativity and hardness of the molecule. However, since the average position of atoms during harmonic vibrations does not change, the average electronegativity and hardness do not change; they do fluctuate, though. These fluctuations are proportional to the fluctuations in atomic position, which were discussed earlier in Chapter 2. The magnitude of the fluctuations in electronegativity and hardness provides information on the variations in the reactivity of a molecule that may statistically be expected due to the oscillations. The thermal effect is easy to consider since the thermal fluctuations of the positions of atoms are readily calculated. These fluctuations cause the hardness to become renormalized, and they also are the source of the coupling between the oscillatory and electronic degrees of freedom. Vibration softening is results when the actual particle hardness is reduced by the fluctuation value (the effect of coupling):

$$\tilde{\eta} = \eta - \sum_\alpha \frac{\varphi_\alpha^2}{2k_\alpha} = \eta - \sum_\alpha \hbar\omega_\alpha \frac{(\varphi_\alpha^{\mathrm{o}})^2}{4k_\alpha^2}\,\mathrm{ctgh}\,\frac{\hbar\omega_\alpha}{2k_B T} \qquad 3.3.10$$

This correction is rather small, usually of the order of 0.001 eV. Also, the temperature dependence represented here by the function *ctgh* (eq. 2.8.40) does not bring significant changes. The exception may be soft vibrations, if the value $\varphi_\alpha^{\mathrm{o}}$ is slightly higher. Soft vibration means a large amplitude of atomic vibrations and thus also significant thermal fluctuations. In this way, only the hardness is lowered, while the electronegativity remains unchanged. The second effect leading to the softening of the molecule is the anharmonicity of the molecular vibrations [A2, A4]; this effect affects both the hardness and the electronegativity of the molecule. $\sum_i (\mathbf{Q}_i^\alpha)^2$ has been recalculated by using the Morse potential as a convenient way to describe the anharmonic vibrations in a molecule. The mean deviation in this approximation is given by:

$$\left\langle \bar{Q}_\alpha \right\rangle = -\frac{1}{2a}\ln\left(1 - \frac{E_\alpha(T)}{D_e}\right) > 0 \qquad E_{\mathrm{o}} \le E_\alpha(T) < D_e \qquad (3.3.11)$$

$E_{\mathrm{o}}$ is the energy of a harmonic oscillator, $D_e$ is dissociation energy.

$$E_\alpha(T) = \left\langle E_{vib} \right\rangle + \left\langle (\delta E_{vib})^2 \right\rangle^{1/2} \qquad (3.3.12)$$

But: $$\left\langle E_{vib} \right\rangle = \tfrac{1}{2}\hbar\omega \frac{e^u + 1}{e^u - 1} \qquad (3.3.13)$$

and $$\left\langle (\delta E_{vib})^2 \right\rangle = (\hbar\omega)^2 \frac{e^u}{(e^u - 1)^2} \qquad (3.3.14)$$

Then: $$E_\alpha(T) = \tfrac{1}{2}\hbar\omega_\alpha \frac{\exp(u_\alpha/2)+1}{\exp(u_\alpha/2)-1} \qquad (3.3.15)$$

In the first approximation, the anharmonic reactivity indices for the normal coordinate $\alpha$ are:

$$\varphi_\alpha = \varphi_\alpha^{\mathrm{o}}\left[\left\langle \sum_i (\mathbf{Q}_i^\alpha)^2 \right\rangle + \left\langle \overline{Q_\alpha} \right\rangle^2\right]^{1/2} \qquad (3.3.16)$$

$$G_\alpha = G_\alpha^{\mathrm{o}}\left[\left\langle \sum_i (\mathbf{Q}_i^\alpha)^2 \right\rangle + \left\langle \overline{Q_\alpha} \right\rangle^2\right]^{1/2} \qquad (3.3.17)$$

The renormalized hardness (eq. 3.3.10) will also be modified.

The fluctuations are:

$$\left\langle(\delta\chi)^2\right\rangle_{an} = \left\langle(\delta\chi)^2\right\rangle + \sum_\alpha (\varphi_\alpha^{\mathrm{o}})^2 \left\langle \overline{Q_\alpha} \right\rangle^2 = \sum_\alpha \frac{(\varphi_\alpha^{\mathrm{o}})^2}{2k_\alpha}(\hbar\omega_\alpha)\,p(u_\alpha) \qquad (3.3.18)$$

$$\left\langle(\delta\eta)^2\right\rangle_{an} = \left\langle(\delta\eta)^2\right\rangle + \sum_\alpha (G_\alpha^{\mathrm{o}})^2 \left\langle \overline{Q_\alpha} \right\rangle^2 = \sum \frac{(G_\alpha^{\mathrm{o}})^2}{2k_\alpha}(\hbar\omega_\alpha)\,p(u_\alpha) \qquad (3.3.19)$$

where $p(u_\alpha)$ is universal function:

$$p(u_\alpha) = \mathrm{ctgh}(u_\alpha/2) + \frac{D_e - D_{\mathrm{o}}}{2D_e}\left[\frac{\exp(u_\alpha/2)+1}{\exp(u_\alpha/2)-1}\right]^2 \qquad (3.3.20)$$

The second term is purely anharmonic in nature; $D_o$ and $D_e$ are the dissociation and ground state energies, respectively. Parameter $(D_e - D_o)/2D_e$ was calculated from spectroscopic data [A2] for a series of diatomic molecules. This fraction is of the order of 0.02 for HF, HCl, LiH, BH, $F_2$, and 0.01 - 0.005 for $Li_2$, ClF, $Cl_2$, CO, CS, LiF. To illustrate the possible influence of anharmonism on reactivity indices, a graph of the function was made for $(D_e - D_o)/2D_e = 0.01$. Function $p(u_\alpha)$ determines the temperature dependence of electronegativity and hardness fluctuations. The role of anharmonism is significant, as demonstrated by the comparison of $p(u_\alpha)$ with the *ctgh* function, (Fig.3.9).

The function $p(u_\alpha)$ is increasing much faster than *ctgh*, which will cause the anharmonicity to have a significant effect on electronegativity and hardness at finite temperatures. Both harmonic and anharmonic fluctuations increase with temperature. The zero-temperature limit is shown in Table 3.6; these values are relatively large compared to $\chi$ and $\eta$. When the temperature effect is added, then the fluctuations may reach the critical limit - $\delta X \cong X$. This may be especially important for hardness, the reduction of which leads to instability of the electronic system [43]. Pearson and Palke indicated that the hardness is at its maximum for non-fully symmetric deformations of a molecule [44]. (An exception is the Jahn–Teller effect.) For the fully symmetric vibrations, the chemical reaction - the change in the number of electrons, is supported by softening fluctuations. We therefore expect that large fluctuations in hardness of a given normal vibration indicate the destructive nature of this vibration. This vibration facilitates the chemical reaction.

**Table 3.6**

Calculated hardness and electronegativity with their fluctuations at 0 K calculated from eq. 3.3.2 and 3.3.3. The vibrational softening is shown in column 3.

| Molecule | Global hardness $\eta$ [eV] | $\sum_{\alpha} \frac{(\varphi_{\alpha}^{o})^{2}}{4k_{\alpha}^{2}} \hbar\omega_{\alpha}$ (x $10^3$) [eV] | $\lvert\Delta\eta\rvert = \left\langle (\delta\eta)^{2} \right\rangle^{1/2}$ (T→0), [eV] | Electronegativity $\chi$ [eV] | $\lvert\Delta\chi\rvert = \left\langle (\delta\chi)^{2} \right\rangle^{1/2}$ (T→0), [eV] |
|---|---|---|---|---|---|
| **$H_2O$** | 8.46 | 0.1345 | 0.2555 | 3.92 | 0.0709 |
| **$H_3O^+$** | 10.10 | 6.8973 | 0.4258 | 14.58 | 0.2003 |
| **$H_2S$** | 6.83 | 1.5271 | 0.2255 | 3.56 | 0.1868 |
| **$H_2CO$** | 6.42 | 0.4587 | 0.1240 | 4.31 | 0.1490 |
| **$BF_3$** | 12.45 | 0.1670 | 0.1359 | 5.37 | 0.1328 |
| **$BCl_3$** | 5.82 | 0.0830 | 0.0419 | 5.43 | 0.0689 |
| **$BH_3$** | 6.60 | 2.2650 | 0.2580 | 5.98 | 0.1979 |
| **$BH_4^+$** | 26.34 | 25.2756 | 0.5120 | 12.65 | 0.5497 |
| **$HOCl$** | 6.04 | 1.1540 | 0.1512 | 5.10 | 0.2718 |
| **$HOF$** | 7.76 | 1.6454 | 0.2770 | 4.88 | 0.4301 |
| **$HCN$** | 12.19 | 0.0398 | 0.2756 | 8.35 | 0.0692 |
| **$HCNO$** | 7.13 | 0.1948 | 0.1560 | 3.46 | 0.1522 |
| **$NH_3$** | 7.71 | 5.4185 | 0.2295 | 3.05 | 0.2468 |
| **$NH_4^+$** | 11.64 | 3.8953 | 0.4937 | 14.89 | 0.3256 |
| **$NH_2NH_2$** | 6.55 | 2.3168 | 0.2037 | 2.19 | 0.2365 |
| **$CHCH$** | 7.75 | 0.0460 | 0.2259 | 3.37 | 0.0730 |
| **$CH_2CH_2$** | 7.99 | 0.9636 | 0.1718 | 4.68 | 0.2525 |
| **$CH_2F_2$** | 9.01 | 0.9530 | 0.2318 | 3.59 | 0.1716 |
| **$CH_3F$** | 9.00 | 0.4804 | 0.1703 | 3.76 | 0.1273 |
| **$CH_3Cl$** | 7.31 | 5.4307 | 0.4672 | 3.96 | 0.4401 |
| **$CH_3NH_2$** | 7.02 | 5.3286 | 0.1968 | 2.46 | 0.2170 |
| **$CH_3OH$** | 7.59 | 0.1114 | 0.1219 | 3.06 | 0.0505 |
| **$CH_3NO_2$** | 7.23 | 0.4704 | 0.1516 | 5.40 | 0.1362 |
| **$C_6H_6$** | 5.65 | 0.5072 | 0.0891 | 3.37 | 0.1432 |

The presented method of identifying destructive vibrations that lower the global hardness may be effective in predicting the reactivity of the molecule. The influence of electronegativity seems to be less pronounced. $\Delta\chi$ changes the picture of the reaction, but it seems impossible to take it into account without a knowledge on a partner reacting species.

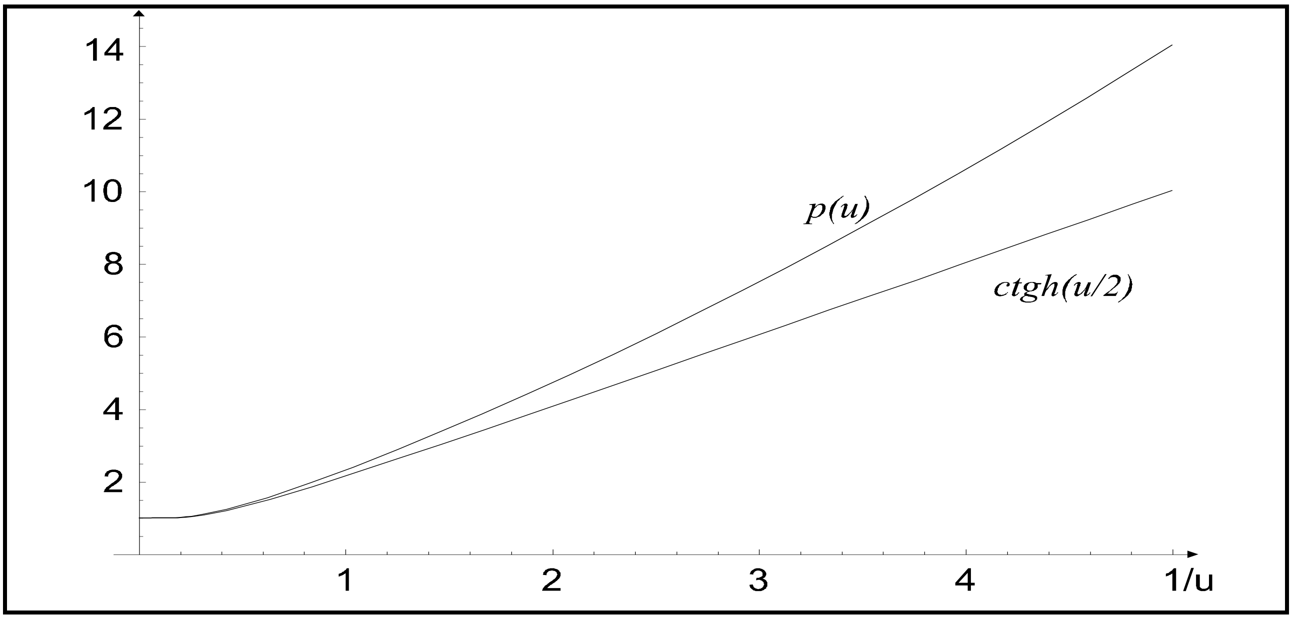

**Fig. 3.4** Functions $p(u)$ and $ctgh(u/2)$ represented with argument $1/u$

# 4

## Summary

This paper has been focused on presentation of the derivatives of energy, potentially playing a role of reactivity indices, with particular emphasis on the role of mixed derivatives. New chemical reactivity index has been proposed - the nuclear stiffness index $\mathbf{G}_i$, the vector quantity reproducing the regional properties of a molecule in terms of modifying the global hardness. Application of that index has been demonstrated to be most practical for the unimolecular dissociation; the phenomenon of detonation is the most famous and evident example of reaction of that kind. The new approach to the molecular mechanism of detonation has been proposed (RDX). The first stage consists in the fact that there is an increase in reactivity induced by mechanical deformation of the molecule. The effect has been known as the local metallization when the chemical hardness tends to zero due to the coupling between the electronic and oscillatory degrees of freedom. Calculations were made that show the dependence of hardness and electronegativity on normal coordinates. As a result, it turns out that breaking the N-N bond (unsymmetrically) is the first step in the dissociation of the molecule RDX.

A method has been proposed for identifying destructive vibrations, that lower the global hardness. It can be effective in predicting the reactivity of a molecule, the effect on electronegativity appears to be minor. The Jahn–Teller effect and the temperature effect on the reactivity of the molecule have been analyzed. The temperature fluctuation of the positions of atoms, and consequently the fluctuations of global hardness and electronegativity have been analyzed in the canonical ensemble. A method for including the anharmonicity of selected vibrations has also been proposed; numerical illustrations of these concepts have been provided. As expected, the modification of hardness or electronegativity due to a coupling with harmonic oscillations is small, typically in the order of the oscillation energy. However, for soft vibrations, the pattern of which is consistent with the nuclear stiffness indices $\mathbf{G}_i$, the change in hardness can be very large.

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