

Compliance approach to coupling between electronic and geometric structures of open and closed molecular systems

R. F. Nalewajski · D. Błażewicz · J. Mrozek

Received: 10 July 2007 / Accepted: 14 August 2007 / Published online: 6 March 2008
© Springer Science+Business Media, LLC 2008

Abstract The Density-Functional Theory (DFT) description of equilibria in both the externally *closed* and *open* molecules, controlled by the system overall number of electrons N or the system/reservoir chemical potential μ , respectively, is used to explore within the Born–Oppenheimer approximation the compliance constants reflecting the coupling between molecular electronic and geometric degrees-of-freedom. The ground-state interaction between the electronic and geometrical parameters-of-state in both the externally closed and open molecular systems is explored within the so-called geometrical representations, which use the explicit dependence of the Legendre-transforms of the system Born–Oppenheimer potential-energy-surface on the Cartesian (\mathbf{R}) or internal (\mathbf{Q}) nuclear positions or their energy conjugates, the forces \mathbf{F}_R or \mathbf{F}_Q acting on nuclei. The principal second derivatives of the system electronic energy with respect to both the electronic and nuclear state-variables in the canonical, say, (N , \mathbf{Q}) representation define the system generalized, electronic-nuclear Hessian matrix, including the electronic hardness and geometric force constants as diagonal blocks, as well as the nuclear Fukui function indices determining the coupling between these two aspects of the molecular structure. Its partial or complete inversion subsequently determines the associated compliant matrices in alternative Legendre-transformed representations, in which these principal state-variables have been partly or totally replaced by their respective energy conjugates. Specific coupling-constant descriptors measuring the interplay between molecular electronic and nuclear state-parameters in the geometrically rigid or relaxed systems, are identified and discussed. Their numerical values resulting from the standard *ab initio* calculations (HF, CISD, MP2), with the N -derivatives estimated by finite differences, are compared and discussed for several representative molecules. The minimum-energy coordinates

R. F. Nalewajski (✉) · D. Błażewicz · J. Mrozek
Department of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland
e-mail: nalewajs@chemia.uj.edu.pl

are introduced and discussed within such a combined electronic-nuclear treatment of molecular systems. Other compliant descriptors of the molecule as a whole, generated within the complementary *Electron Following* (EF) and *Electron Preceding* (EP) perspectives on the system global equilibrium, are also reported for illustrative molecules. These compliant quantities are advocated as reactivity criteria, since they directly reflect the system electronic (or geometric) conditions required for the molecule to undergo specific nuclear (or electronic) displacements responsible for the chemical reaction of interest.

Keywords Born-Oppenheimer approximation · Electronic-geometric Hessian · Closed systems · Compliant approach · Geometric representation of molecular states · Molecular equilibria · Open systems · Minimum-energy coordinates · Reactivity criteria · Structure relaxation in molecules · Theory of electronic structure · Thermodynamic potentials

1 Introduction

The atomic units are used throughout the paper; in the adopted notation \mathbf{P} denotes the square (or rectangular) matrix, \mathbf{P} stands for the row or column vector and P represents a scalar quantity. The internal degrees-of-freedom of molecular systems have either electronic or nuclear (geometric) origins. For example, in the Born–Oppenheimer (BO) approximation the equilibrium (ground) state of the externally closed molecule is specified by the system overall number of electrons N (integer) and the external potential $v(\mathbf{r}; \mathbf{R}) = -\sum_{\alpha} Z_{\alpha}/|\mathbf{r} - \mathbf{R}_{\alpha}| \equiv v(\mathbf{r})$ due to the nuclei located at the parametrically specified locations $\mathbf{R} = \{\mathbf{R}_{\alpha}, \alpha = 1, 2, \dots, m\}$ or—alternatively—the nuclear positions themselves. Together they uniquely identify the system (Coulombic) Hamiltonian $\hat{H}(N, v) = \hat{H}(N, \mathbf{R})$ and hence the electronic energy $E[N, v] = \langle \Psi[N, v] | \hat{H}(N, v) | \Psi[N, v] \rangle = E(N, \mathbf{R})$, where $\Psi[N, v]$ denotes the system ground-state wave function. Accordingly, the equilibrium state of an externally open molecule, in contact with the electron reservoir which controls the system chemical potential $\mu = \partial E[N, v]/\partial N$, is uniquely defined by μ and \mathbf{R} [1–7]. In chemistry the mutual interaction between the electronic and geometric (nuclear) structures of molecular or reactive systems plays a vital role in diagnosing the behavior of molecules in different environments. Therefore, designing the adequate measures of this interaction and exploring its structural manifestations constitute a challenging problem in theoretical chemistry [12]. Such coupling rules constitute an important part of the chemical reactivity theory [1–17] and the structural rules reflecting the interplay between the charge transfer (CT) and geometries of molecular subsystems in the Donor–Acceptor (DA) complexes. For example, the familiar Gutmann rules [18] and their semiquantitative extension provided by the mapping relations [3, 7, 9–13] and the Minimum-Energy-Coordinates (MEC) [9–12] of the compliant approach [3, 7, 9–12], in the spirit of the related treatment of nuclear vibrations [19, 20], have been formulated within the Charge-Sensitivity Analysis (CSA) of the molecular systems [3]. They allow one to diagnose the molecular electronic and geometrical relaxations (responses) to hypothetical electronic or nuclear displacements (perturbations).

The recently proposed Legendre-transformed approach to molecular electronic-geometrical structure [11,12] provides a versatile theoretical framework for describing diverse molecular states. It includes all relevant coupling terms between the two aspects of the molecular structure and covers all admissible selections of state-parameters specifying the equilibria in both the externally closed and open systems. The overall number of electrons, N , and its energy-conjugate—the chemical potential, μ , determine the electronic state-parameters in the externally closed and open molecular systems, respectively, with the latter being coupled to a hypothetical electron reservoir. This theoretical framework unites the so-called Electron-Following (EF) and Electron-Preceding (EP) perspectives on molecular changes [3–7,11,12,21], in the spirit of the BO approximation and the Hellmann–Feynman theorem, respectively. In the former the electron distribution responds to the geometrical (nuclear) perturbation, i.e., to a change in the external potential $v(\mathbf{r}; \mathbf{R})$ or geometrical displacement in nuclear positions \mathbf{R} , while the latter implies the system geometrical relaxation following a test displacement in the system electronic state-parameters. Such generalized “polarizabilities” of molecules, e.g., those generated within CSA, provide reliable reactivity criteria [1–12] in the Density-Functional Theory (DFT) [1,22–24].

In the EF perspective of the standard BO approximation the external potential $v(\mathbf{r})$ due to the nuclei carries the information about the system geometry and constitutes the independent *local* parameter of state. The (N, v) variables of the ground-state in the closed molecular system thus constitute the natural set of independent state-variables in the Schrödinger wave-function theory, since they uniquely define the electronic Hamiltonian $\hat{H}(N, v)$. The other set of the global state variables, (μ, v) , identifies uniquely the ground state of the open molecule in contact with an external reservoir of electrons. Therefore, in the EF perspective, in which the external potentials search for their equilibrium (ground-state) electron densities, the electron distribution represents the unconstrained (dependent) local state-variable of molecular systems: $\rho = \rho[v]$. In other words, the electrons “follow” the displacements of the system nuclei. This selection of the dependent (ρ) and independent (v) local state-variables generates the chemical-softness kernel $\sigma(\mathbf{r}, \mathbf{r}')$ of the reactivity theory [1–13] and has been classified as the chemical-softness representation of molecular states [4,12].

These roles of the local state-parameters are reversed in the EP perspective of DFT, which can be also referred to as the chemical-hardness representation [4,12], since it defines another key concept of the electronic-structure and reactivity theories—the chemical-hardness kernel $\eta(\mathbf{r}, \mathbf{r}')$, the inverse of $\sigma(\mathbf{r}, \mathbf{r}')$. In the EP approach the electron density is regarded as the controlling, independent parameter of state, while the external potential responds to the specified redistribution of electrons, thus representing a dependent (unconstrained) state variable: $v = v[\rho]$. In other words, in this reverse perspective the electron densities search for the matching external potentials. The shifts in the electron distribution create conditions for (precede) the movements of nuclei, in the spirit of the Hellmann–Feynman theorem. This way of approaching molecular changes is quite common in the chemical reactivity theory. Indeed, chemists often envisage the key manipulation of the system electronic structure as the primary cause of the desired reconstruction of the molecular geometry, e.g., breaking/forming bonds in the molecule.

One requires both these representations to tackle all issues in the theory of electronic structure of molecules and their chemical reactivity. The wave-function and density-functional formulations of the quantum theory of the electronic structure of molecular systems thus emerge as the complementary descriptions, which together provide theoretical framework of the “complete” theory of chemical reactivity. The emergence of the modern DFT has provided the hitherto missing theoretical framework of the EP perspective and generated new approaches to many classical problems in chemistry. It offers an alternative point of view, from which one can approach the diverse physical/chemical properties and processes involving atomic, molecular and reactive systems. This novel perspective is much in the spirit of the Sanderson’s [25] electronegativity-equalization description of to the equilibrium distribution of electrons in molecular systems.

It is the main purpose of the present work to examine numerical values of coupling constants and MEC components identified in the previous conceptual/qualitative analysis [12]. These quantities will be generated within both the EF and EP perspectives using the standard quantum-mechanical *ab initio* calculations for several representative molecular systems. The reactivity implications of these derivative descriptors of the interaction between the electronic and geometric aspects of the molecular structure will be subsequently examined. Indeed, such coupling indices measure the effect of the hypothetical displacements in the state-parameters of one (independent, perturbation) side of the system structure on the state-variables describing the other (dependent, response) facet. We begin this analysis with a survey of the basic concepts and relations of the generalized compliant description of molecular systems, which simultaneously involves the electronic and nuclear degrees-of-freedom. This short summary opens with a brief interpretation of the important reactivity indices, *viz.*, the electronic Fukui function (FF) [1–3, 26–28] and its nuclear analog [2–8, 11, 12, 29], as examples of the electronic–geometric coupling quantities.

2 Electronic and nuclear Fukui functions as coupling indices

The global state-variables N and μ and the local value of the electron density $\rho(\mathbf{r})$ are all electronic in character, while the row vector of Cartesian coordinates of nuclear positions $\mathbf{R} = \{\mathbf{R}_\alpha\} = \{X_k\}$ or their (negative) energy conjugates—the row vector of components of Cartesian forces acting on nuclei,

$$\begin{aligned} \mathbf{F}_R &= \{\mathbf{F}_\alpha = -(\partial W[N, v(\mathbf{R})]/\partial \mathbf{R}_\alpha)^T\} \equiv -[\partial W(N, \mathbf{R})/\partial \mathbf{R}]^T, \\ W(N, \mathbf{R}) &= E(N, \mathbf{R}) + V_{nn}(\mathbf{R}), \quad V_{nn}(\mathbf{R}) = \sum_\alpha \sum_{\beta > \alpha} Z_\alpha Z_\beta / |\mathbf{R}_\beta - \mathbf{R}_\alpha|, \end{aligned} \quad (1)$$

and the external potential $v(\mathbf{r})$ due to the nuclei in their specified positions, describe the complementary, geometric aspect of the molecular structure. It should be also observed that some important parameters of state exhibit a mixed, electronic-and-nuclear origin. Consider, e.g., the relative external potential of the Euler equation

for the equilibrium electron density $\rho = \rho[N, v]$ in DFT [1,22],

$$u(\mathbf{r}) \equiv v(\mathbf{r}) - \mu = -\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}, \quad (2)$$

which results from the variational principle for the minimum of the density functional for the system electronic energy, $E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + F[\rho]$, subject to the constraint of the system prescribed number of electrons, $N[\rho] = \int \rho(\mathbf{r}) d\mathbf{r} = N^0$:

$$\delta\{E_v[\rho] - \mu N[\rho]\} = 0. \quad (3)$$

Here, the universal functional $F[\rho]$ generates the sum of electronic kinetic and repulsion energies, while the system chemical potential plays the role of the Lagrange multiplier enforcing the global constraint. In the closed molecular system the ground-state energy $E_v[\rho[N, v]] = E[N, v]$ while in the open molecule $E_v[\rho[\mu, v]] = E[\mu, v]$ gives rise to the system grand potential $\Omega[\mu, v] = E - N\mu$.

The Hellmann–Feynman theorem identifies the ground-state electron density $\rho(\mathbf{r})$ as the energy-conjugate of the external potential:

$$\rho(\mathbf{r}) = \left(\frac{\partial E[N, v]}{\partial v(\mathbf{r})} \right)_N = \left(\frac{\partial \Omega[\mu, v]}{\partial v(\mathbf{r})} \right)_\mu. \quad (4)$$

In DFT the Frontier-Electron theory of Fukui [14] has been given a more rigorous foundation in terms of the related density-response index called the electronic Fukui Function (FF) [1–3,26–28]:

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_v = \frac{\partial^2 E[N, v]}{\partial N \partial v(\mathbf{r})} = \left(\frac{\partial \mu}{\partial v(\mathbf{r})} \right)_N, \quad \int f(\mathbf{r}) d\mathbf{r} = 1. \quad (5)$$

It follows from the preceding equation that the electronic FF has a double physical interpretation as the mixed second-derivative (Maxwell relation). On one hand, it reflects the normalized response in the system electron density to a unit shift in the system global average number of electrons; this derivative is calculated for the fixed external potential, i.e., the rigid molecular geometry. On the other hand, it measures the response in the system chemical potential per unit shift in the local value of the external potential; this derivative is calculated for the system fixed number of electrons. The latter interpretation shows that electronic FF reflects the closed-system coupling between the molecular electronic (μ) and nuclear (v) state-variables.

The corresponding row-vector $\boldsymbol{\varphi}_R$ of the nuclear FF (NFF) [2–8,11,12,29] in Cartesian coordinates:

$$\boldsymbol{\varphi}_R(N, \mathbf{R}) = \left(\frac{\partial \mathbf{F}_R(N, \mathbf{R})}{\partial N} \right)_R = - \left(\frac{\partial^2 W(N, \mathbf{R})}{\partial N \partial \mathbf{R}} \right)^T = - \left(\frac{\partial \mu(N, \mathbf{R})}{\partial \mathbf{R}} \right)_N^T, \quad (6)$$

has been introduced to “translate” a given ΔN displacement directly into the conjugate linear responses in the system ground-state forces on nuclei, $\Delta \mathbf{F}_R = \Delta N \boldsymbol{\varphi}_R$.

Therefore, $\varphi_{\mathbf{R}}$ measure the normalized responses in the forces acting on the nuclei per unit displacement in the global number of electrons. The cross-differentiation identity also implies that this index can be alternatively interpreted as the response in the system negative chemical potential (electronegativity) per unit displacements in nuclear positions \mathbf{R} , thus again coupling the electronic (dependent) global variable μ with the (independent) coordinates determining the nuclear positions. In defining these FF quantities we have introduced the so-called *geometric* representation of the molecular ground-state in the externally closed molecule, (N, \mathbf{R}) , for the fixed identity (charges) of the nuclei, in which the nuclear positions \mathbf{R} replace the external potential $v(\mathbf{R})$ in the list of independent state-parameters. The corresponding set of state-variables in the geometric representation of the open molecule reads (μ, \mathbf{R}) .

Therefore, both the electronic and nuclear FF represent the reactivity concepts, which probe the coupling between the geometric and electronic structures of molecules. In fact these two reactivity indices are mutually related through the chain-rule transformation involving the geometric row-kernel $\mathbf{G}(\mathbf{r}; \mathbf{R}) = [\partial v(\mathbf{r}; \mathbf{R})/\partial \mathbf{R}]^T$:

$$\begin{aligned}\varphi_{\mathbf{R}}(N, \mathbf{R}) &= - \left(\frac{\partial^2 W[N, v(\mathbf{R})]}{\partial N \partial \mathbf{R}} \right)^T = - \left(\frac{\partial^2 E[N, v(\mathbf{R})]}{\partial N \partial \mathbf{R}} \right)^T \\ &= - \frac{\partial}{\partial N} \int \left(\frac{\delta E[N, v]}{\delta v(\mathbf{r})} \right)_N \left(\frac{\partial v(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \right)^T d\mathbf{r} \\ &= - \int f(\mathbf{r}) \mathbf{G}(\mathbf{r}; \mathbf{R}) d\mathbf{r}.\end{aligned}\quad (7)$$

It should be emphasized that both these reactivity indices belong to the same chemical-softness representation, of the EF-perspective following the standard BO approach. The electronic FF index depends on the electron-position argument and it discriminates the reactivities of alternative local sites in the molecule with respect to the nucleophilic or electrophilic attack by an approaching agent. The nuclear (geometric) index similarly establishes trends in the system geometry relaxation, which accompany the given test displacement in the system global number of electrons. An alternative way of probing the coupling between the electronic and nuclear degrees-of-freedom in molecular systems is through their direct mapping relations [3, 7, 9–13] implied by the ground-state Euler equation (2).

After this illustrative example we turn to a systematic review of derivative quantities measuring the nuclear-electronic interaction in molecules and of the related compliant analysis of molecular displacements.

3 Electronic-nuclear coupling constants in canonical geometric representation

The direct coupling relations between the electron density $\rho(\mathbf{r})$ and nuclear coordinates \mathbf{R} in the principal representation defined by the total Born–Oppenheimer potential $W[N, v(\mathbf{R})] \equiv W(N, \mathbf{R})$ is obtained by replacing the implicit dependence on \mathbf{R} through the external potential $v(\mathbf{r}; \mathbf{R})$ by the explicit dependence on nuclear coordinates. In order to facilitate a compact vector notation we arrange the nuclear

coordinates $\mathbf{R} = \{\mathbf{R}_\alpha\} = \{X_{\alpha,s}\}$, where index α denotes the nucleus and $s = (x, y, z)$ labels its Cartesian coordinates, in the overall row-vector

$$\begin{aligned} \mathbf{R} &= [\dots, (X_{\alpha,x}, X_{\alpha,y}, X_{\alpha,z}), (X_{\alpha+1,x}, X_{\alpha+1,y}, X_{\alpha+1,z}), \dots] \\ &= (\dots, \mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}, \dots) = \{X_k\}. \end{aligned} \tag{8}$$

Alternatively the relevant set of *internal* nuclear coordinates $\mathbf{Q} = \{Q_s\}$, consisting of bond lengths and angles, can be used to specify the molecular geometry:

$$W(N, \mathbf{R}) \equiv W(N, \mathbf{Q}) \tag{9}$$

The corresponding components of the geometric gradient of the scalar field $g(\mathbf{R}) \equiv g(\mathbf{Q})$, will be similarly arranged in the corresponding row-vectors of partial derivatives:

$$\begin{aligned} \mathbf{g}_R'(\mathbf{R}) &= [\partial g(\mathbf{R})/\partial \mathbf{R}]^T = \{\partial g/\partial X_k\} \text{ or} \\ \mathbf{g}_Q'(\mathbf{Q}) &= [\partial g(\mathbf{Q})/\partial \mathbf{Q}]^T = \{\partial g/\partial Q_s\}. \end{aligned} \tag{10}$$

For example, the force components along the internal coordinates generate the associated gradient vector:

$$\mathbf{F}_Q(N, \mathbf{Q}) = -\partial W(N, \mathbf{Q})/\partial \mathbf{Q} = \{F_s\}. \tag{11}$$

Similarly, the NFF indices in the internal nuclear coordinates form the row-vector

$$\boldsymbol{\varphi}_Q(N, \mathbf{Q}) = \left(\frac{\partial \mathbf{F}_Q(N, \mathbf{Q})}{\partial N} \right)_{\mathbf{Q}} = - \left(\frac{\partial^2 W(N, \mathbf{Q})}{\partial N \partial \mathbf{Q}} \right)^T = - \left(\frac{\partial \mu(N, \mathbf{Q})}{\partial \mathbf{Q}} \right)_{\mathbf{Q}}^T. \tag{12}$$

In the $W(N, \mathbf{R})$ representation the row-vector of forces acting on the system nuclei includes the contribution $\mathbf{F}_n(\mathbf{R})$ due to the repulsion between the system nuclei and the \mathbf{G} -transform of the electronic density:

$$\begin{aligned} \mathbf{F}_R(\mathbf{R}) &= - \left(\frac{\partial W(N, \mathbf{R})}{\partial \mathbf{R}} \right)^T = - \left(\frac{\partial V_{nn}(\mathbf{R})}{\partial \mathbf{R}} \right)^T \\ &\quad - \int \left(\frac{\delta E[N, v]}{\delta v(\mathbf{r})} \right)_N \left(\frac{\partial v(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \right)^T d\mathbf{r} \equiv \mathbf{F}_n(\mathbf{R}) - \int \mathbf{G}(\mathbf{r}; \mathbf{R}) \rho(\mathbf{r}) d\mathbf{r}. \end{aligned} \tag{13}$$

The geometric Hessian of the nuclear force-constants can be similarly expressed as the sum of the relevant nuclear-repulsion term \mathbf{H}_n and the *full* \mathbf{G} -transform of the linear-response function [1–3]:

$$\beta(\mathbf{r}, \mathbf{r}') = \left(\frac{\partial^2 E[N, v]}{\partial v(\mathbf{r}) \partial v(\mathbf{r}')} \right)_N = \left(\frac{\partial \rho(\mathbf{r}')}{\partial v(\mathbf{r})} \right)_N, \quad (14)$$

$$\begin{aligned} \mathbf{H}_R &= \frac{\partial^2 W(N, \mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R}} = - \frac{\partial \mathbf{F}_R(N, \mathbf{R})}{\partial \mathbf{R}} = \frac{\partial^2 V_{nn}(\mathbf{R})}{\partial \mathbf{R} \partial \mathbf{R}} \\ &+ \iint \left(\frac{\partial v(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \right) \left(\frac{\delta^2 E[N, v]}{\delta v(\mathbf{r}) \delta v(\mathbf{r}')} \right)_N \left(\frac{\partial v(\mathbf{r}'; \mathbf{R})}{\partial \mathbf{R}} \right)^T d\mathbf{r} d\mathbf{r}' \\ &\equiv \mathbf{H}_n + \iint \mathbf{G}^T(\mathbf{r}; \mathbf{R}) \beta(\mathbf{r}, \mathbf{r}') \mathbf{G}(\mathbf{r}'; \mathbf{R}) d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (15)$$

The row-vector of the *partial* \mathbf{G} -transform of the linear-response kernel,

$$\mathbf{B}(\mathbf{r}; \mathbf{R}) \equiv \int \beta(\mathbf{r}, \mathbf{r}') \mathbf{G}(\mathbf{r}'; \mathbf{R}) d\mathbf{r}' = \left(\frac{\partial \rho(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \right)_N^T, \quad (16)$$

measures the direct effect of nuclear displacements on electron density $\rho(\mathbf{r}) = \rho[\mathbf{r}; v(\mathbf{R})] \equiv \rho(\mathbf{r}; \mathbf{R})$. It represents in the (N, \mathbf{R}) -representation the nuclear (geometric) equivalent of the “softness” kernel of Eq. 14, describing the externally closed molecular system. A similar transformation of the electronic softness-kernel of an externally open molecule,

$$\sigma(\mathbf{r}, \mathbf{r}') = - \left(\frac{\partial^2 \Omega[\mu, v]}{\partial v(\mathbf{r}) \partial v(\mathbf{r}')} \right)_\mu = - \left(\frac{\partial \rho(\mathbf{r}')}{\partial v(\mathbf{r})} \right)_\mu = - \frac{\delta^2 \Omega[\mu]}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} = - \frac{\delta \rho(\mathbf{r}')}{\delta u(\mathbf{r})}, \quad (17)$$

generates its nuclear analog (a row-vector):

$$\mathbf{S}(\mathbf{r}; \mathbf{R}) \equiv \int \sigma(\mathbf{r}, \mathbf{r}') \mathbf{G}(\mathbf{r}'; \mathbf{R}) d\mathbf{r}' = - \left(\frac{\partial \rho(\mathbf{r}; \mathbf{R})}{\partial \mathbf{R}} \right)_\mu^T. \quad (18)$$

The independent displacements $(\Delta N, \Delta \mathbf{R})$ (perturbations) of this principal geometric representation give rise to the first differential of its thermodynamic potential $W(N, \mathbf{R})$:

$$\begin{aligned} dW(N, \mathbf{R}) &= (\partial W / \partial N)_R \Delta N + \Delta \mathbf{R} (\partial W / \partial \mathbf{R})_N = \mu \Delta N - \Delta \mathbf{R} \mathbf{F}_R^T \\ &\equiv \mu \Delta N - \sum_\alpha \Delta \mathbf{R}_\alpha \mathbf{F}_\alpha^T. \end{aligned} \quad (19)$$

Therefore, the generalized Hessian \mathbf{H}_R transforming the perturbations $(\Delta N, \Delta \mathbf{R})$ into the linear-responses of the conjugate variables $(\Delta \mu, -\Delta \mathbf{F}_R)$,

$$(\Delta \mu, -\Delta \mathbf{F}_R) \equiv \Delta \mathbf{g}_R = (\Delta N, \Delta \mathbf{R}) \mathbf{H}_R, \quad (20)$$

includes the following blocks:

$$\mathbf{H}_R = \begin{bmatrix} \left(\frac{\partial \mu}{\partial N}\right)_R & -\left(\frac{\partial F_R}{\partial N}\right)_R \\ \left(\frac{\partial \mu}{\partial R}\right)_N & -\left(\frac{\partial F_R}{\partial R}\right)_N \end{bmatrix} \equiv \begin{bmatrix} H_{N,N} & \mathbf{H}_{N,R} \\ \mathbf{H}_{R,N} & \mathbf{H}_{R,R} \end{bmatrix} = \begin{bmatrix} \eta & -\boldsymbol{\varphi}_R \\ -\boldsymbol{\varphi}_R^T & \mathbf{H}_R \end{bmatrix}, \quad (21)$$

where \boldsymbol{g}_R denotes the combined electronic-nuclear gradient in Cartesian coordinates, η stands for the rigid-geometry measure of the global hardness, the inverse of the (rigid-geometry) global softness S ,

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_v = \left(\frac{\partial \mu}{\partial N}\right)_R = \left(\frac{\partial \mu}{\partial N}\right)_Q = S^{-1}, \quad (22)$$

and $\boldsymbol{\varphi}_R$ combines the NFF of Eq. 6. The matrix transformation (20) summarizes the two ground-state relations:

$$\Delta \mu = \Delta N \eta - \Delta R \boldsymbol{\varphi}_R^T \quad \text{and} \quad -\Delta F_R = -\Delta N \boldsymbol{\varphi}_R + \Delta R \mathbf{H}_R. \quad (23)$$

The corresponding relations for the internal coordinates in the geometric representation $W(N, Q)$ read:

$$\begin{aligned} dW(N, Q) &= \Delta N (\partial W / \partial N)_Q + \Delta Q (\partial W / \partial Q)_N = \Delta N \mu - \Delta Q \mathbf{F}_Q^T \\ &\equiv \Delta N \mu - \sum_s \Delta Q_s F_s; \end{aligned} \quad (24)$$

$$(\Delta \mu, -\Delta F_Q) \equiv \Delta \boldsymbol{g}_Q = (\Delta N, \Delta Q) \mathbf{H}_Q, \quad (25)$$

$$\mathbf{H}_Q = \begin{bmatrix} \left(\frac{\partial \mu}{\partial N}\right)_Q & -\left(\frac{\partial F_Q}{\partial N}\right)_Q \\ \left(\frac{\partial \mu}{\partial Q}\right)_N & -\left(\frac{\partial F_Q}{\partial Q}\right)_N \end{bmatrix} \equiv \begin{bmatrix} H_{N,N} & \mathbf{H}_{N,Q} \\ \mathbf{H}_{Q,N} & \mathbf{H}_{Q,Q} \end{bmatrix} = \begin{bmatrix} \eta & -\boldsymbol{\varphi}_Q \\ -\boldsymbol{\varphi}_Q^T & \mathbf{H}_Q \end{bmatrix}, \quad (26)$$

$$\Delta \mu = \Delta N \eta - \Delta Q \boldsymbol{\varphi}_Q^T \quad \text{and} \quad -\Delta F_Q = -\Delta N \boldsymbol{\varphi}_Q + \Delta Q \mathbf{H}_Q. \quad (27)$$

where $\boldsymbol{g}_Q = (\mu, -F_Q)$ stands for the combined electronic-nuclear gradient in the internal-coordinate representation.

Since the numerical calculations will be carried out in the internal coordinates, in the remaining part of this survey we shall use these geometric state-parameters and the associated principal derivatives $\mathbf{F}_Q \equiv F$, $\boldsymbol{\varphi}_Q \equiv \boldsymbol{\varphi}$ and $\mathbf{H}_Q = -(\partial F_Q / \partial Q)_N \equiv \mathbf{H}$ in the Legendre-transformed development of the next section.

4 Legendre-transformed representations

The inverse of \mathbf{H} determines the geometric compliance matrix [3, 7, 9–12, 19, 20] describing the open system in the $(\mu, \mathbf{F}\mathbf{Q})$ -representation. The relevant thermodynamic potential is defined by the Legendre transform of the system total Born–Oppenheimer potential, which replaces the state-parameters (N, \mathbf{Q}) with their energy conjugates (μ, \mathbf{F}) , respectively:

$$\Sigma(\mu, \mathbf{F}) = W - N(\partial W/\partial N)_{\mathbf{Q}} - \mathbf{Q}(\partial W/\partial \mathbf{Q})_N = W - N\mu + \mathbf{Q}\mathbf{F}^T, \quad (28)$$

$$d\Sigma = -Nd\mu + \mathbf{Q}d\mathbf{F}^T \quad \text{or} \quad -N = (\partial\Sigma/\partial\mu)_{\mathbf{F}} \quad \text{and} \quad \mathbf{Q} = (\partial\Sigma/\partial\mathbf{F})_{\mu}^T. \quad (29)$$

Setting $\mathbf{F} = \mathbf{0}$ then identifies properties for the equilibrium (relaxed) molecular geometry. The compliance matrix

$$\mathbf{S} = \mathbf{H}^{-1} = \begin{bmatrix} -\left(\frac{\partial N}{\partial\mu}\right)_{\mathbf{F}} & \left(\frac{\partial \mathbf{Q}}{\partial\mu}\right)_{\mathbf{F}} \\ -\left(\frac{\partial N}{\partial\mathbf{F}}\right)_{\mu} & \left(\frac{\partial \mathbf{Q}}{\partial\mathbf{F}}\right)_{\mu} \end{bmatrix} \equiv \begin{bmatrix} \mathbf{S}_{\mu,\mu} & \mathbf{S}_{\mu,\mathbf{F}} \\ \mathbf{S}_{\mathbf{F},\mu} & \mathbf{S}_{\mathbf{F},\mathbf{F}} \end{bmatrix}, \quad (30)$$

relates displacements of the representation independent variables $(\Delta\mu, \Delta\mathbf{F})$ with the conjugate responses $(-\Delta N, \Delta\mathbf{Q})$:

$$(-\Delta N, \Delta\mathbf{Q}) = (\Delta\mu, \Delta\mathbf{F})\mathbf{S}. \quad (31)$$

It summarizes the individual responses in the system (negative) average number of electrons and its geometry:

$$-\Delta N = \Delta\mu\mathbf{S}_{\mu,\mu} + \Delta\mathbf{F}\mathbf{S}_{\mathbf{F},\mu}, \quad \Delta\mathbf{Q} = \Delta\mu\mathbf{S}_{\mu,\mathbf{F}} + \Delta\mathbf{F}\mathbf{S}_{\mathbf{F},\mathbf{F}}. \quad (32)$$

A reference to Eq. 30 shows that the diagonal element $\mathbf{S}_{\mu,\mu}$ represents the relaxed-geometry analog of the negative global softness of Eq. 22, with the latter being defined for the rigid molecular geometry. It follows from the second of Eq. 32 that a change in the open system chemical potential induces an extra relaxation of the molecular frame. This geometric “softness” is measured by derivatives of the row-vector $\mathbf{S}_{\mu,\mathbf{F}} = \{\mathbf{S}_{\mu,s}\} = \mathbf{S}_{\mathbf{F},\mu}^T \equiv S = \{S_s\}$.

One can express the compliance matrix in terms of the elements of the principal charge sensitivities defining the generalized electronic-nuclear “hardness” matrix \mathbf{H} of Eq. 26, by eliminating ΔN and $\Delta\mathbf{Q}$ from Eq. 27:

$$\begin{aligned} -\Delta N &= -\Delta\mu(\eta - B)^{-1} + \Delta\mathbf{F}\mathbf{H}^{-1}\boldsymbol{\varphi}^T(\eta - B)^{-1}, & B &= \boldsymbol{\varphi}\mathbf{H}^{-1}\boldsymbol{\varphi}^T; \\ \Delta\mathbf{Q} &= \Delta\mu\boldsymbol{\varphi}\mathbf{H}^{-1}\mathbf{C} - \Delta\mathbf{F}\mathbf{H}^{-1}\mathbf{C}\boldsymbol{\eta}, & \mathbf{C} &= (\boldsymbol{\eta}\mathbf{I} - \boldsymbol{\varphi}^T\boldsymbol{\varphi}\mathbf{H}^{-1})^{-1}, \end{aligned} \quad (33)$$

or in the combined, matrix form of Eq. 31:

$$\mathbf{S} = \begin{bmatrix} -\left(\frac{\partial N}{\partial \mu}\right)_F = -(\eta - B)^{-1} \equiv -S^{\text{rel}} & \left(\frac{\partial Q}{\partial \mu}\right)_F = \boldsymbol{\varphi} \mathbf{H}^{-1} \mathbf{C} \equiv \mathcal{S} \\ -\left(\frac{\partial N}{\partial F}\right)_\mu = \mathbf{H}^{-1} \boldsymbol{\varphi}^T (\eta - B)^{-1} = S^T & \left(\frac{\partial Q}{\partial F}\right)_\mu = -\mathbf{H}^{-1} \mathbf{C} \eta \equiv \mathbf{G}^{\text{rel}} \end{bmatrix}, \quad (34)$$

where $S^{\text{rel}} = (\eta^{\text{rel}})^{-1}$ stands for the geometrically relaxed softness, inverse of the relaxed hardness, and \mathbf{G}^{rel} denotes the electronically relaxed geometrical compliant matrix, which differs from its closed-system analog $\mathbf{G} = -\mathbf{H}^{-1} = (\partial Q / \partial F)_N$.

Let us now turn to the mixed (N, F) -representation for closed molecular systems. The relevant thermodynamic potential is defined by the Legendre transformation of $W(N, Q)$ which replaces Q by F in the list of the parameters of state:

$$\Theta(N, F) = W - Q(\partial W / \partial Q)_N = W + Q F^T, \quad d\Theta = \mu dN + Q dF^T; \quad (35)$$

$$\mu = (\partial \Theta / \partial N)_F \quad \text{and} \quad Q = (\partial \Theta / \partial F)_N^T. \quad (36)$$

Eliminating $\Delta \mu$ from the first equation(32) and inserting it into the second equation (32) then gives the following transformation of the representation independent displacements $(\Delta N, \Delta F)$ into the linear responses of their conjugates $(\Delta \mu, \Delta Q)$,

$$(\Delta \mu, \Delta Q) = (\Delta N, \Delta F) \mathbf{V}, \quad (37)$$

expressed in terms of the principal compliance coefficients of Eq. 30:

$$\begin{aligned} \mathbf{V} &= \begin{bmatrix} \left(\frac{\partial \mu}{\partial N}\right)_F & \left(\frac{\partial Q}{\partial N}\right)_F \\ \left(\frac{\partial \mu}{\partial F}\right)_N & \left(\frac{\partial Q}{\partial F}\right)_N \end{bmatrix} \equiv \begin{bmatrix} V_{N,N} & V_{N,F} \\ V_{F,N} & V_{F,F} \end{bmatrix} \\ &= \begin{bmatrix} -S_{\mu,\mu}^{-1} & -\mathbf{S}_{\mu,F} S_{\mu,\mu}^{-1} \\ -\mathbf{S}_{F,\mu} S_{\mu,\mu}^{-1} & \mathbf{S}_{F,F} - \mathbf{S}_{F,\mu} \mathbf{S}_{\mu,F} S_{\mu,\mu}^{-1} \end{bmatrix}. \end{aligned} \quad (38)$$

Again, a comparison with Eq. (26) indicates that the diagonal element $V_{N,N}$ represents the molecular hardness for the relaxed geometry of the molecule, a companion parameter for the rigid-geometry hardness of Eq. 22.

The two partial relations combined in Eq. (37),

$$\Delta \mu = \Delta N V_{N,N} + \Delta F V_{F,N} \quad \text{and} \quad \Delta Q = \Delta N V_{N,F} + \Delta F V_{F,F}, \quad (39)$$

again imply that there is an additional geometry relaxation due to the finite external CT between the molecule and the electron reservoir, besides the usual term due to the forces acting on the system nuclei for constant N . This extra relaxation of the molecular frame is described by the coupling blocks $V_{N,F} = V_{F,N}^T$.

The blocks of \mathbf{V} can be also directly expressed in terms of the principal geometric derivatives defining the generalized Hessian of Eq. 26. This can be accomplished by

first expressing $\Delta \mathbf{Q}$ as function of ΔN and $\Delta \mathbf{F}$, using the second equation (27), and then inserting this resulting relation into the first equation (27):

$$\Delta \mu = \Delta N(\eta - B) + \Delta \mathbf{F} \mathbf{H}^{-1} \boldsymbol{\varphi}^T \quad \text{and} \quad \Delta \mathbf{Q} = \Delta N \boldsymbol{\varphi} \mathbf{H}^{-1} - \Delta \mathbf{F} \mathbf{H}^{-1}. \quad (40)$$

A comparison between Eqs. (39) and (40) then gives:

$$\mathbf{V} = \begin{bmatrix} \left(\frac{\partial \mu}{\partial N} \right)_F = (\eta - B) = \eta^{\text{rel}} & \left(\frac{\partial \mathbf{Q}}{\partial N} \right)_F = \boldsymbol{\varphi} \mathbf{H}^{-1} \equiv \mathbf{f} \\ \left(\frac{\partial \mu}{\partial \mathbf{F}} \right)_N = \mathbf{H}^{-1} \boldsymbol{\varphi}^T \equiv \mathbf{f}^T & \left(\frac{\partial \mathbf{Q}}{\partial \mathbf{F}} \right)_N = -\mathbf{H}^{-1} \equiv \mathbf{G} \end{bmatrix}, \quad (41)$$

where the row-vector $\mathbf{f} = \{\mathbf{f}_s\}$ groups the so called Geometric FF (GFF) indices.

Finally, let us examine the (μ, \mathbf{Q}) -representation of an open molecular system. The relevant Legendre transform of the total electronic energy, which replaces N by μ in the list of independent state-parameters, defines the following thermodynamic potential:

$$\Xi(\mu, \mathbf{Q}) = W - N(\partial W / \partial N)_{\mathbf{Q}} = W - N\mu, \quad d\Xi = -Nd\mu - \mathbf{F} d\mathbf{Q}^T; \quad (42)$$

$$-N = (\partial \Xi / \partial \mu)_{\mathbf{Q}} \quad \text{and} \quad -\mathbf{F} = (\partial \Xi / \partial \mathbf{Q})_{\mu}^T. \quad (43)$$

Eliminating $d\mathbf{F}$ from the second equation (32) and inserting the result into the first of these two equations give the following transformation of the representation independent perturbations $(\Delta \mu, \Delta \mathbf{Q})$ into the linear responses of their conjugates $(-\Delta N, -\Delta \mathbf{F})$, expressed in terms of the matrix elements of the compliance matrix \mathbf{S} of Eq. 30:

$$(-\Delta N, -\Delta \mathbf{F}) = (\Delta \mu, \Delta \mathbf{Q}) \mathbf{G}, \quad (44)$$

$$\begin{aligned} \mathbf{G} &= \begin{bmatrix} -\left(\frac{\partial N}{\partial \mu} \right)_{\mathbf{Q}} & -\left(\frac{\partial \mathbf{F}}{\partial \mu} \right)_{\mathbf{Q}} \\ -\left(\frac{\partial N}{\partial \mathbf{Q}} \right)_{\mu} & -\left(\frac{\partial \mathbf{F}}{\partial \mathbf{Q}} \right)_{\mu} \end{bmatrix} \equiv \begin{bmatrix} \mathbf{G}_{\mu, \mu} & \mathbf{G}_{\mu, \mathbf{Q}} \\ \mathbf{G}_{\mathbf{Q}, \mu} & \mathbf{G}_{\mathbf{Q}, \mathbf{Q}} \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{S}_{\mu, \mu} - \mathbf{S}_{\mu, \mathbf{F}} \mathbf{S}_{\mathbf{F}, \mathbf{F}}^{-1} \mathbf{S}_{\mathbf{F}, \mu} & \mathbf{S}_{\mu, \mathbf{F}} \mathbf{S}_{\mathbf{F}, \mathbf{F}}^{-1} \\ \mathbf{S}_{\mathbf{F}, \mathbf{F}}^{-1} \mathbf{S}_{\mathbf{F}, \mu} & -\mathbf{S}_{\mathbf{F}, \mathbf{F}}^{-1} \end{bmatrix}. \end{aligned} \quad (45)$$

The above matrix transformation combines the following partial relations:

$$-\Delta N = \Delta \mu \mathbf{G}_{\mu, \mu} + \Delta \mathbf{Q} \mathbf{G}_{\mathbf{Q}, \mu} \quad \text{and} \quad -\Delta \mathbf{F} = \Delta \mu \mathbf{G}_{\mu, \mathbf{Q}} + \Delta \mathbf{Q} \mathbf{G}_{\mathbf{Q}, \mathbf{Q}}. \quad (46)$$

The elements of this mapping-relation, from the combined electronic–geometric perturbation $(\Delta \mu, \Delta \mathbf{Q})$ of an open molecular system into the linear responses in their Ξ -conjugates $(-\Delta N, -\Delta \mathbf{F})$, can be also expressed in terms of the generalized

“hardness matrix of Eq. 26, by eliminating ΔN from the first equation (27) and by subsequent insertion of the resulting expression into the second of these equations:

$$\begin{aligned} -\Delta N &= -\Delta\mu\eta^{-1} - \Delta\mathbf{Q}\boldsymbol{\varphi}^T\eta^{-1} \equiv -\Delta\mu S - \Delta\mathbf{Q}\mathbf{s}^T, \\ -\Delta\mathbf{F} &= -\Delta\mu\mathbf{s} + \Delta\mathbf{Q}(\mathbf{H} - \boldsymbol{\varphi}^T S \boldsymbol{\varphi}) = -\Delta\mu\mathbf{s} + \Delta\mathbf{Q}(\mathbf{H} - \boldsymbol{\varphi}^T \mathbf{s}). \end{aligned} \quad (47)$$

Here S is the electronic rigid-geometry measure of the system global softness (Eq. 22) and the row-vector \mathbf{s} of the geometric “softnesses” is defined as product of the global softness and NFF vector of Eq. 12:

$$\begin{aligned} \mathbf{s} &= S\boldsymbol{\varphi} = (\partial\mathbf{F}/\partial\mu)\mathbf{Q} = (\partial N/\partial\mathbf{Q})_{\mu}^T = (\partial\mathbf{F}/\partial N)\mathbf{Q}/(\partial\mu/\partial N)\mathbf{Q} \\ &= \{\mathbf{s}_s \equiv (F_s)_{\mu}\} \end{aligned} \quad (48)$$

A reference to the second equation (47) shows that the effective geometrical Hessian of an open molecular system differs from that for the closed system (Eq. 26) by the CT-contribution involving the geometrical softnesses and NFF. Finally, one identifies the corresponding blocks of \mathbf{G} by comparing the general relations of Eq. 46 with the explicit transformations of Eq. 47:

$$\mathbf{G} = \begin{bmatrix} -\left(\frac{\partial N}{\partial\mu}\right)_{\mathbf{Q}} = -S & -\left(\frac{\partial\mathbf{F}}{\partial\mu}\right)_{\mathbf{Q}} = -\mathbf{s} \\ -\left(\frac{\partial N}{\partial\mathbf{Q}}\right)_{\mu} = -S^T & -\left(\frac{\partial\mathbf{F}}{\partial\mathbf{Q}}\right)_{\mu} = \mathbf{H} - \boldsymbol{\varphi}^T \mathbf{s} \equiv \mathbf{H}^{\text{rel}} \end{bmatrix}, \quad (49)$$

where \mathbf{H}^{rel} denotes the electronically relaxed geometrical Hessian, which differs from its closed-system analog $\mathbf{H} = -(\partial\mathbf{F}/\partial\mathbf{Q})_N$.

To summarize, the \mathbf{G} -matrix involves the negative rigid-geometry electronic softness as diagonal element associated with the electronic state-variable μ , the off-diagonal elements defined by the geometric softnesses, and the open-system (electronically relaxed) geometrical Hessian, which differs from the closed-system (electronically rigid) Hessian \mathbf{H} by the LeChâtelier–Braun [30] softening contribution:

$$\begin{aligned} \boldsymbol{\varphi}^T \mathbf{s} &= \boldsymbol{\varphi}^T S \boldsymbol{\varphi} = -(\partial\mu/\partial\mathbf{Q})_N (\partial\mathbf{F}/\partial\mu)\mathbf{Q} = (\partial N/\partial\mathbf{Q})_{\mu} (\partial\mathbf{F}/\partial N)\mathbf{Q} \\ &= (\partial\mathbf{F}/\partial\mathbf{Q})_{\mu} - (\partial\mathbf{F}/\partial\mathbf{Q})_N. \end{aligned} \quad (50)$$

5 Compliance constants and minimum-energy coordinates

In the compliance perspective on nuclear displacements the inverse of the nuclear force-constant matrix \mathbf{H} , defined in the purely geometric \mathbf{Q} -representation (for constant N),

$$\mathbf{H} = \frac{\partial^2 W(N, \mathbf{Q})}{\partial\mathbf{Q}\partial\mathbf{Q}} = \left\{ H_{s,s'} = \frac{\partial W(N, \mathbf{Q})}{\partial Q_s \partial Q_{s'}} = -\left(\frac{\partial F_{s'}}{\partial Q_s}\right)_{Q_{t \neq s}} \right\}, \quad (51)$$

determines the purely geometric compliance matrix [19,20] of the “reverse” purely geometric \mathbf{F} -representation:

$$\mathbf{G} = \frac{\partial^2 \Theta(N, \mathbf{F})}{\partial \mathbf{F} \partial \mathbf{F}} = -\mathbf{H}^{-1} = \left\{ G_{s,s'} = \left(\frac{\partial^2 \Theta(N, \mathbf{F})}{\partial F_s \partial F_{s'}} \right) = \left(\frac{\partial Q_{s'}}{\partial F_s} \right)_{F_t \neq s} \right\}. \quad (52)$$

Here $\Theta(N, \mathbf{F}) = W + \mathbf{Q}\mathbf{F}^T$ (Eq. 35) stands for the Legendre-transform of the total potential-energy surface $W(N, \mathbf{Q})$, in which the nuclear-position coordinates $\mathbf{Q} = \{Q_s\}$ are replaced by the corresponding forces $\mathbf{F} = \{F_s\}$ in the list of parameters of state. Indeed, for the fixed number of electrons N ,

$$[d\Theta(N, \mathbf{F})]_N = \mathbf{Q}d\mathbf{F}^T \quad \text{and} \quad [\partial^2 \Theta(N, \mathbf{F})/\partial F_s \partial F_{s'}]_N = (\partial Q_{s'}/\partial F_s)_{N, \mathbf{F}'}. \quad (53)$$

The constraint of $\mathbf{F}' = \{F_{t \neq s} = 0\}$ in these derivatives implies that the remaining part of the nuclear frame is free to relax the atomic positions until the forces associated with the remaining geometrical degrees of freedom vanish, thus marking the minimum of the system energy with respect to $\{Q_{t \neq s}\}$.

In this section, we shall discuss several concepts of the compliant description of the combined electronic-nuclear degrees-of-freedom of molecular systems [3,7,9–12]. This development is in spirit of the earlier minimum-energy derivatives, for the vanishing forces acting on nuclei, which determine the compliance approach to nuclear motions [19,20].

There are two types of geometrical constraints, which can be imposed on the molecule: that of the rigid geometry \mathbf{Q} and the condition of the vanishing forces $\mathbf{F} = \mathbf{0}$ giving rise to the equilibrium positions of the system nuclei. The latter description amounts to the compliant formalism of nuclear motions [3,9–12,19,20], in which one allows the system to relax all its remaining (electronic and/or nuclear) degrees-of-freedom in response to the probing displacements in the system number of electrons or positions of its constituent atoms. The $\Theta(N, \mathbf{F})$ and $\Sigma(\mu, \mathbf{F})$ representations correspond to such a nuclear-compliant treatment of the molecular geometrical structure, while the $W(N, \mathbf{Q})$ and $\Xi(\mu, \mathbf{Q})$ representations adopt the rigid-geometry approach. The Legendre-transformed approach to geometric representations of molecular states provides the complete set of quantities, which can be used to monitor or index the electronic geometric couplings in molecular systems in both these approaches, covering the externally open and externally closed molecular systems.

Several geometrical quantities introduced in this section provide natural descriptors measuring a coupling between the molecular electronic and geometrical structures. In the canonical geometrical representation $W(N, \mathbf{Q})$ the diagonal blocks of the generalized Hessian \mathbf{H} (Eq. 26), measuring the system rigid-geometry hardness η and force-constants \mathbf{H} , describe the *decoupled* aspects of the electronic and geometric structures, respectively. As we have already observed above, the NFF φ , defining the off-diagonal blocks in \mathbf{H} , reflects the coupling between the electronic and nuclear aspects of the molecular structure. They describe the influence of geometrical displacements in the closed-system on the molecular chemical potential, or the effect of an

external CT on the forces on nuclei. As we have indicated in Eq. 48 the geometrical softnesses $\mathbf{s} = \{\mathbf{s}_\alpha\}$ reflect similar couplings in the externally open molecular systems. It should be stressed, however, that in the geometric compliance matrix \mathbf{S} of Eq. 30 the interaction between these two facets of molecular structure also enters the diagonal blocks, as explicitly shown in Eqs. 33 and 34.

A similar effect of the system electronic or nuclear “softening”, due to its opening relative to a reservoir or a relaxation of its geometry, is seen in the diagonal blocks of the partial compliant matrices \mathbf{V} and \mathbf{G} (see Eqs. 41, 45, and 49). This spontaneous relaxation of the system electronic-nuclear structure reflects the LeChâtelier–Braun principle of “moderation” in the ordinary thermodynamics [30]. Indeed, the extra electronic relaxation $\delta N(\Delta \mathbf{Q})$ induced by the primary nuclear perturbation $\Delta \mathbf{Q}$ in the externally open system, in which a spontaneous CT between the molecule and its reservoir is allowed, effectively lowers the increases in the magnitude of forces on the system nuclei, compared to those in the externally closed system: $[\Delta \mathbf{F}(\Delta \mathbf{Q})]_N > [\Delta \mathbf{F}(\Delta \mathbf{Q})]_\mu$ (see Eq. 50). The indirect effect of the spontaneous geometry relaxation $\delta \mathbf{Q}(\Delta N)$ induced by the primary electronic perturbation ΔN similarly lowers the increase in the system chemical potential, compared to that in the rigid system: $[\Delta \mu(\Delta N)]_{\mathbf{Q}} > [\Delta \mu(\Delta N)]_{F=0}$.

It should be also realized that the generalized softness matrix of Eqs. 30 and 34 also represents the compliant description of the electronic “coordinate” N coupled to the system geometric relaxations. Indeed, the relaxed-geometry global softness of the geometrical representation,

$$\begin{aligned} -S_{\mu,\mu} &= (\partial N / \partial \mu)_F = (\eta - B)^{-1} = (\eta - \boldsymbol{\varphi} \mathbf{H}^{-1} \boldsymbol{\varphi}^T)^{-1} \equiv S^{\text{rel}} \\ &\equiv (\eta^{\text{rel}})^{-1} > \eta^{-1} = S = (\partial N / \partial \mu)_{\mathbf{Q}} > 0, \end{aligned} \quad (54)$$

where the last inequality states the familiar LeChâtelier stability requirement, differs from the conventional definition of the electronic global softness S (Eq. 22), which invokes the rigid-geometry constraint. The geometric-hardness contribution B in Eq. 54 effectively softens the electronic distribution *via* the relaxation of nuclei, reflected by the negative purely geometric compliant \mathbf{H}^{-1} , and the “weighting” factors provided by the NFF $\boldsymbol{\varphi}$ reflecting the relative geometric softnesses of the molecule. The other diagonal block of the generalized geometrical compliants, which contains the electron-nuclear couplings,

$$\mathbf{S}_{F,F} = (\partial \mathbf{Q} / \partial F)_\mu = -\mathbf{H}^{-1} \mathbf{C} \eta = -\mathbf{H}^{-1} (\eta \mathbf{I} - \boldsymbol{\varphi}^T \boldsymbol{\varphi} \mathbf{H}^{-1})^{-1} \eta \neq -\mathbf{H}^{-1} = \mathbf{V}_{F,F}, \quad (55)$$

is also seen to differ from the purely geometrical compliant $\mathbf{V}_{F,F}$ by the additional factor exhibiting both the electronic and nuclear origins. The mixture of the electronic and nuclear inputs is also seen to determine the off-diagonal blocks $\mathbf{S}_{\mu,F}$ and $\mathbf{S}_{F,\mu}$ of the geometric compliant matrix, respectively measuring the effect of the chemical potential on the relaxed nuclear positions ($\mathbf{S}_{\mu,F}$) or the influence of the forces on the effective charge of an open molecule coupled to the external electron reservoir ($\mathbf{S}_{F,\mu}$).

Let us now examine the compliance descriptors of the externally closed system, within the $\Theta(N, \mathbf{F})$ representation, defined by the corresponding blocks of the geometric charge-sensitivities \mathbf{V} (Eq. 38). Again, the first diagonal derivative in this matrix, $V_{N,N} = (\partial\mu/\partial N)_F = \eta - B$ allows the geometry of the system to relax, after an addition/removal of an electron, until the forces on nuclei exactly vanish: $\mathbf{F} = \mathbf{0}$. The electronic–geometric interaction is also detected in the coupling blocks $\mathbf{V}_{N,F} = (\partial\mathbf{Q}/\partial N)_F$ and $\mathbf{V}_{F,N} = (\partial\mu/\partial\mathbf{F})_N$. A reference to Eq. 41 indicates, that they are determined by the purely nuclear compliants $\mathbf{V}_{F,F} = -\mathbf{H}^{-1}$ and NFF.

The electronic-nuclear coupling in molecules is also detected in the other partial Legendre-transformed representation, $\Xi(\mu, \mathbf{Q})$, which defines the combined Hessian \mathbf{G} of Eq. 45. Its first diagonal derivative,

$$\mathbf{G}_{\mu,\mu} = -(\partial N/\partial\mu)_Q = -(\partial N/\partial\mu)_v = -S, \quad (56)$$

represents the purely electronic, global compliant reflecting the negative softness of the rigid system. As shown in Eq. 49, the off-diagonal blocks $\mathbf{G}_{\mu,Q} = -(\partial\mathbf{F}/\partial\mu)_Q$ and $\mathbf{G}_{Q,\mu} = -(\partial N/\partial\mathbf{Q})_\mu$, represent the geometric softnesses of Eq. 48. For the rigid nuclear frame they thus measure the effect of the system chemical potential on forces on nuclei ($\mathbf{G}_{\mu,Q}$) or the influence of nuclear displacements on the effective charge of an open molecule. Since in this representation the molecular system is coupled to an external reservoir, one detects in the geometrical Hessian of this representation the contribution due to external CT triggered by nuclear displacements:

$$\mathbf{G}_{Q,Q} = -(\partial\mathbf{F}/\partial\mathbf{Q})_\mu = \mathbf{H} - \boldsymbol{\varphi}^T \mathbf{s} = \mathbf{H} - \boldsymbol{\varphi}^T S \boldsymbol{\varphi} \neq \mathbf{H} = -(\partial\mathbf{F}/\partial\mathbf{Q})_N. \quad (57)$$

Therefore, this block contains the electronically relaxed force constants in the internal coordinate representation.

The ratio of the matrix elements in s th row of \mathbf{G} (Eq. 52), $\mathbf{G}_s = \{G_{s,s'}, s' = 1, 2, \dots\}$, to the diagonal element $G_{s,s}$ determines k th vector of nuclear (geometric) interaction-constants [19]:

$$(s')_s = G_{s,s'}/G_{s,s} = \left(\frac{\partial Q_{s'}}{\partial F_s}\right)_{F_t \neq s} \left(\frac{\partial Q_s}{\partial F_s}\right)_{F_t \neq s}^{-1} = \left(\frac{\partial Q_{s'}}{\partial Q_s}\right)_{F_t \neq s}, \quad s' = 1, 2, \dots \quad (58)$$

These indices describe the minimum-energy responses, for $\mathbf{F}'_s = \{F_{s' \neq s} = 0\}$, of the remaining nuclear-position variables $\{Q_{s' \neq s}\}$ per unit displacement of s th nuclear coordinate. They thus determine the s th (nuclear) MEC [19,20]. This compliant concept can be used to predict the equilibrium responses of the system geometric structure to a given displacement (perturbation) of the selected s th nuclear coordinate, ΔQ_s , from the initial, equilibrium geometry of the molecule, which accounts for all couplings between the nuclear-position coordinates:

$$d\mathbf{Q}(\Delta Q_s) \Big|_{\mathbf{F}'_s = \mathbf{0}} = \{(s')_s \Delta Q_s\}. \quad (59)$$

Similar concepts can be introduced in the combined electron-nuclear treatment of the geometric representation of the molecular structure [3,7,9–12]. Consider, e.g., the generalized interaction constants defined by the electronic-nuclear softness matrix \mathbf{S} of Eq. 30. The ratios of the matrix elements in $\mathbf{S}_{\mu,F} = \{S_{\mu,s'}\}$ to $S_{\mu,\mu}$ define the following interaction constants between the nuclear coordinates and the system average number of electrons:

$$(s')_N = S_{\mu,s'}/S_{\mu,\mu} = (\partial Q_{s'}/\partial \mu)_{F=0}/(\partial N/\partial \mu)_{F=0} = (\partial Q_{s'}/\partial N)_{F=0} \equiv V_{N,s'}. \quad (60a)$$

They reflect the minimum-energy responses of the system geometrical coordinates to unit displacement in the system number of electrons. The GFF vector (see Eq. 41)

$$\begin{aligned} \mathbf{f} &= \{(s')_N\} = (\partial \mathbf{Q}/\partial N)_{F=0} = \mathbf{V}_{N,F} = (\partial \mu/\partial \mathbf{F})_N^T = \mathbf{V}_{F,N}^T \\ &= (\partial \mathbf{Q}/\partial \mu)_{F=0}/(\partial N/\partial \mu)_{F=0} = \mathbf{S}/S^{\text{rel}} \end{aligned} \quad (60b)$$

can be thus interpreted as an alternative set the NFF indices, which diagnose the normalized effect of changing the oxidation-state of the molecular system as a whole on its geometry. These indices define the following minimum energy coordinate grouping responses in nuclear coordinates due to a finite inflow/outflow of electrons, $\Delta N \neq 0$:

$$d\mathbf{Q}(\Delta N)|_{F=0} = \Delta N \mathbf{f}. \quad (61)$$

It should be realized at this point (see Eq. 48) that NFF of Eq. 12 can be also interpreted as the MEC reflecting the rigid-geometry response in forces per unit displacement in the system number of electrons:

$$\begin{aligned} \boldsymbol{\varphi} &= \{(F_s)_N\} = (\partial \mathbf{F}/\partial N)_{\mathbf{Q}} = -\mathbf{H}_{N,\mathbf{Q}} = -(\partial \mu/\partial \mathbf{Q})_N^T = -\mathbf{H}_{\mathbf{Q},N}^T \\ &= (\partial \mathbf{F}/\partial \mu)_{\mathbf{Q}}/(\partial N/\partial \mu)_{\mathbf{Q}} = \mathbf{s}/S. \end{aligned} \quad (60c)$$

As also indicated in Eq. 48 the geometric softnesses \mathbf{s} also represent the rigid-geometry interaction between forces \mathbf{F} and the system chemical potential. The remaining interaction constants defined in this representation are given by the ratios

$$\begin{aligned} (N)_{s,\mu} &= -S_{\mu,s}/S_{s,s} = (\partial N/\partial Q_s)_{\mu,F'_s=0} \quad \text{and} \\ (s')_{s,\mu} &= S_{s,s'}/S_{s,s} = (\partial Q_{s'}/\partial Q_s)_{\mu,F'_s=0}. \end{aligned} \quad (62)$$

In the open molecule, coupled to an external electron reservoir, which fixes the system chemical potential, they combine the minimum-energy responses in the system number of electrons and the remaining nuclear coordinates, to a unit displacement of Q_s . The associated minimum-energy coordinates,

$$dN(\Delta Q_s) \Big|_{\mu,F'_s=0} = \{(N)_{s,\mu} \Delta Q_s\} \quad \text{and} \quad d\mathbf{Q}(\Delta Q_s) \Big|_{\mu,F'_s=0} = \{(s')_{s,\mu} \Delta Q_s\}, \quad (63)$$

add to a variety of descriptors of the electronic and geometric structures of molecular systems. The $(N)_{s,\mu}$ coupling constants can be used to probe trends in the chemical oxidation/reduction of the open molecule, which follows a given geometrical deformation of the molecule. These probing displacements allow one to identify nuclear changes, which are most effective in bringing about this electronic transformation of the molecule. The other set $\{(s')_{s,\mu}\}$ tests geometrical consequences of a hypothetical nuclear-position perturbation of the molecule, thus facilitating a search for the most effective geometric manipulation of the molecular system in question, which is required to bring about the desired change in the system geometry.

The partial-compliant matrix \mathbf{V} (Eq. 38) of the $\Theta(N, \mathbf{F})$ -representation defines analogous interaction constants for the N -controlled (externally closed) molecules:

$$\begin{aligned}(s')_{\mu} &= V_{N,s'}/V_{N,N} = (\partial Q_{s'}/\partial N)_{\mathbf{F}=\mathbf{0}}/(\partial \mu/\partial N)_{\mathbf{F}=\mathbf{0}} = (\partial Q_{s'}/\partial \mu)_{\mathbf{F}=\mathbf{0}} \\ &= S_{\mu,s'} = S_{s'},\end{aligned}\quad (64)$$

where $\{V_{N,s'}\} = \mathbf{V}_{N,\mathbf{F}}$, and

$$\begin{aligned}(\mu)_{s,N} &= V_{s,N}/V_{s,s} = (\partial \mu/\partial F_s)_N/(\partial Q_s/\partial F_s)_N = (\partial \mu/\partial Q_s)_{N,\mathbf{F}'_s=\mathbf{0}} \quad \text{and} \\ (s')_{s,N} &= V_{s',s}/V_{s,s} = (\partial Q_{s'}/\partial F_s)_{N,\mathbf{F}'_s=\mathbf{0}}/(\partial Q_s/\partial F_s)_{N,\mathbf{F}'_s=\mathbf{0}} \\ &= (\partial Q_{s'}/\partial Q_s)_{N,\mathbf{F}'_s=\mathbf{0}},\end{aligned}\quad (65)$$

with $\{V_{s,N}\} = \mathbf{V}_{\mathbf{F},N}$. The corresponding minimum-energy coordinates

$$\begin{aligned}d\mathbf{Q}(\Delta\mu)|_{\mathbf{F}=\mathbf{0}} &= \{(s')_{\mu}\Delta\mu\}, \quad d\mu(\Delta Q_s)|_{N,\mathbf{F}'_s=\mathbf{0}} = \{(\mu)_{s,N}\Delta Q_s\}, \\ d\mathbf{Q}(\Delta Q_s)|_{\mathbf{F}'_s=\mathbf{0}} &= \{(s')_{s,N}\Delta Q_s\},\end{aligned}\quad (66)$$

reflect the equilibrium responses in the system chemical potential and geometrical coordinates due to finite shifts in the system chemical potential or selected geometrical coordinates, respectively.

Finally, in the $\Xi(\mu, \mathbf{Q})$ representation, in which the generalized partial compliant matrix \mathbf{G} is defined, one obtains the following coupling constants:

$$(F_{s'})_N = \mathbf{G}_{\mu,s'}/\mathbf{G}_{\mu,\mu} = (\partial F_{s'}/\partial \mu)_{\mathbf{Q}}/(\partial N/\partial \mu)_{\mathbf{Q}} = (\partial F_{s'}/\partial N)_{\mathbf{Q}} = \varphi_{s'}, \quad (67)$$

$$\begin{aligned}(N)_{F_s,\mu} &= \mathbf{G}_{s,\mu}/\mathbf{G}_{s,s} = (\partial N/\partial Q_s)_{\mu}/(\partial F_s/\partial Q_s)_{\mu} = (\partial N/\partial F_s)_{\mu,\mathbf{Q}'_s}, \\ (F_{s'})_{F_s,\mu} &= \mathbf{G}_{s',s}/\mathbf{G}_{s,s} = (\partial F_{s'}/\partial Q_s)_{\mu,\mathbf{Q}'_s}/(\partial F_s/\partial Q_s)_{\mu,\mathbf{Q}'_s} = (\partial F_{s'}/\partial F_s)_{\mu,\mathbf{Q}'_s}.\end{aligned}\quad (68)$$

These interaction constants determine the associated minimum-energy trajectories in the force-space:

$$d\mathbf{F}(\Delta N) \Big|_{\mathcal{Q}} = \{(F_s)_N \Delta N\},$$

$$dN(\Delta F_s) \Big|_{\mu, \mathcal{Q}'_s} = \{(N)_{F_s, \mu} \Delta F_s\} \quad \text{and} \quad d\mathbf{F}(\Delta F_s) \Big|_{\mu, \mathcal{Q}'_s} = \{(F_{s'})_{F_s, \mu} \Delta F_s\}.$$
(69)

6 Illustrative calculations

The present application of the joint electronic-nuclear analysis of the generalized sensitivities to external perturbations has been carried out for a selection of polyatomics, H_2O , H_2O_2 , NO_2 , ClF_3 , and formamide, shown in Fig. 1.

These illustrative molecular systems exhibit a variety of internal geometric degrees-of-freedom, bond lengths and angles, which are also specified in the figure. The

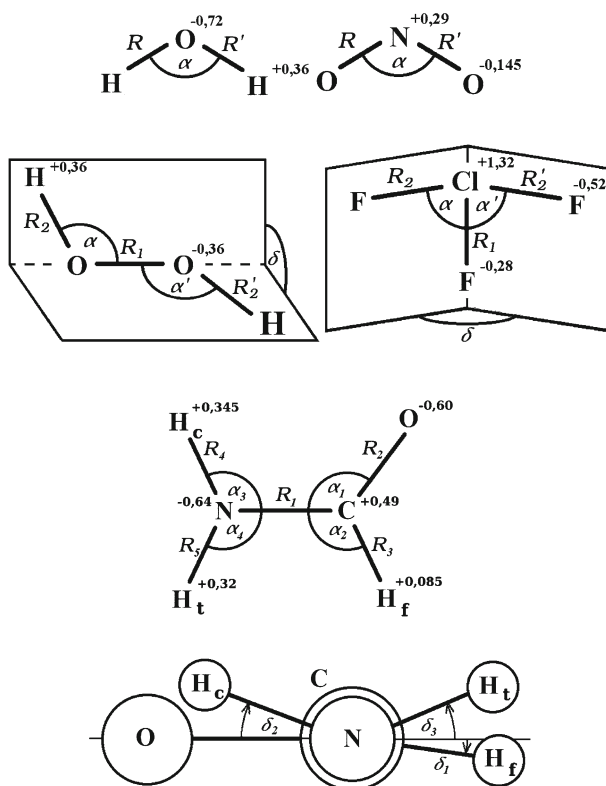


Fig. 1 The internal coordinates in five representative molecular systems (see Table 1 for their equilibrium values) and the Mulliken net-charges of bonded atoms (from HF calculations). The last diagram defines the dihedral angles in formamide, relative to the NCO plane, determining the out-of-plane displacements of the *cis* (H_c), *trans* (H_t) and *formyl* (H_f) hydrogens, respectively

Table 1 Comparison of the predicted and experimental equilibrium geometries for molecules of Fig. 1

Molecule	Coordinate (Fig. 1)	Theoretical method			<i>Exp.</i>
		<i>HF</i>	MP2	CISD	
H ₂ O	$R = R'$	1.782	1.820	1.812	1.811
	α	107.1	105.3	105.6	104.5
H ₂ O ₂	R_1	2.634	2.782	2.725	2.787
	$R_2 = R'_2$	1.788	1.835	1.816	1.795
	$\alpha = \alpha'$	102.6	98.9	100.6	100
	δ^a	116.6	121.4	118.7	119.1
NO ₂	$R = R'$	2.200	2.300	2.249	2.262
	α	136.2	133.7	134.9	134.0
ClF ₃	R_1	2.982	3.101	3.041	3.020
	$R_2 = R'_2$	3.179	3.299	3.226	3.209
	$\alpha = \alpha'$	86.5	87.3	86.6	87.5
	δ^a	180.0	180.0	180.0	180.0
NH ₂ CHO	R_1	2.547	2.578	2.562	2.551
	R_2	2.258	2.321	2.292	2.287
	R_3	2.062	2.077	2.067	2.060
	R_4	1.880	1.905	1.892	1.892
	R_5	1.875	1.901	1.888	1.892
	α_1	124.8	124.5	124.6	124.7
	α_2	113.1	112.8	113.0	112.7
	α_3	119.3	118.4	119.0	118.5
	α_4	121.4	120.5	121.0	120.0
	δ_1^a	0.0	1.7	0.9	0.0
	δ_2^a	0.0	8.4	5.2	0.0
δ_3^a	0.0	9.9	6.3	0.0	

^a Dihedral angle

standard Hartree–Fock (HF) and Configuration–Interaction (CI) MO theories of the electronic structure of molecular systems have been used in numerical calculations (GAUSSIAN software [31]). The former neglects the Coulombic electron-correlation, which is approximately included in the latter. The two variants of the CI approach including the single (S) and double (D) excitations from the HF ground-state configuration have been used: the variational (CISD) scheme and the perturbational (Møller–Plessett, MP2) method. The extended 6-31++G** basis set of Gaussian orbitals, including the split-valence, diffuse and polarization functions, has been used to represent MO. All reported results correspond to the method ground-state equilibrium geometries in the adopted basis set, which are reported in Table 1 with the bond-lengths measured in atomic units and angles in degrees. In all derivative properties of next section the angles will be measured in radians.

The analytical forces and elements of the geometrical Hessian have been determined in all numerical calculations, while the finite difference estimates of the corresponding N -derivatives have been used in the combined electronic-nuclear Hessian. The NFF have been calculated for both the electron-accepting ($\Delta N = +1$) and electron-donating ($\Delta N = -1$) processes, when the system acts as a Lewis acid and base, respectively, relative to the attacking nucleophilic and electrophilic agents. The Mulliken scheme for the neutral system approached by the radical agent, of the unbiased N -derivative given by the arithmetic average of these two estimates, has also been examined. The global hardness, which measures the curvature of the ground-state Born–Oppenheimer potential along the N -coordinate, have been similarly estimated by interpolating the energies for the set of hypothetical electronic displacements $\Delta N = (-1, 0, +1)$.

7 Results and discussion

7.1 H₂O

In Table 2 we have compared the second derivatives of the four electronic thermodynamical potentials for water molecule, which define the corresponding electronic-nuclear Hessians in the alternative Legendre-transformed representations of Sects. 3 and 4. They give rise to the molecular compliants and elements of the MEC reported in Table 3, where some of the compliants of Table 2 have also been repeated to facilitate the comparison. These quantities reflect the effects of both the electronic and nuclear relaxations of the molecular system, due to its opening relative to the external electron reservoir and the equilibrium adjustments in its geometry, in response to the primary perturbations defining the derivative.

We first observe that, in accordance with the LeChâtelier–Braun principle (Eq. 54), the averaged (third entry) geometrically relaxed estimate of the system electronic softness S^{rel} is slightly larger than the rigid-geometry measure S . Accordingly, the averaged estimate of the geometrically-relaxed electronic hardness measure η^{rel} is lower than the familiar rigid-geometry value η . These effects differ in the electron-withdrawing (first entry) and electron-addition (second entry) processes, with the former giving rise to a slightly harder distribution of electrons. This should be intuitively expected, since removal of electrons generates a slightly more contracted, harder, less polarizable distribution of electrons, due to less screened nuclei, thus creating a relatively higher response in the system chemical potential, compared to that expected for the electron-inflow process, with better screened nuclei.

A comparison between numerical results for different quantum mechanical methods reveals that the simplest HF approximation already generates realistic estimates of all these coupling derivatives, in semiquantitative agreement with the more refined MP2 and CISD data. It follows from the geometrically rigid hardnesses of Table 2 that in the HF theory the electrons appear to be somewhat “softer” than in the electronically correlated theories; the same trend is exhibited by the geometrically relaxed hardnesses. Obviously, the opposite trend is reflected by their “inverses”, measuring the corresponding electronic softnesses. This difference can be attributed to an, on average,

Table 2 Elements of the electronic-nuclear Hessians in four alternative Legendre-transformed representations of equilibrium states in water molecule (see Fig. 1 for the definition of the internal coordinates and Table 1 for the equilibrium geometries)

Repres. Derivative	HF	MP2	CISD
(N, Q) $H_{N,N} = \eta$	0.448	0.496	0.485
$-H_{N,Q} = \varphi$: φ_R	-0.044, 0.007, -0.018	-0.037, 0.011, -0.013	-0.041, 0.009, -0.016
φ_α	-0.017, -0.008, -0.012	-0.015, -0.007, -0.011	-0.015, -0.077, -0.011
$H_{Q,Q} = H$: $H_{R,R}$	0.636	0.557	0.573
$H_{R,R'}$	-0.006	-0.010	-0.008
$H_{R,\alpha}$	0.028	0.031	0.030
$H_{\alpha,\alpha}$	0.170	0.157	0.162
(μ, Q) $-G_{\mu,\mu} = S$	2.231	2.018	2.063
$-G_{\mu,Q} = s$: s_R	-0.097, 0.016, -0.040	-0.074, 0.022, -0.026	-0.085, 0.019, -0.033
s_α	-0.037, -0.018, -0.028	-0.031, -0.014, -0.023	-0.031, -0.015, -0.023
$G_{Q,Q} \equiv H^{rel}$: $G_{R,R}$	0.632, 0.636, 0.636	0.554, 0.557, 0.557	0.569, 0.573, 0.572
$G_{R,R'}$	-0.011, -0.007, -0.007	-0.014, -0.011, -0.011	-0.011, -0.008, -0.008
$G_{R,\alpha}$	0.026, 0.028, 0.027	0.029, 0.031, 0.030	0.029, 0.030, 0.030
$G_{\alpha,\alpha}$	0.169, 0.170, 0.170	0.157, 0.157, 0.157	0.162, 0.162, 0.162
(N, F) $V_{N,N} \equiv \eta^{rel}$	0.441, 0.448, 0.446	0.490, 0.495, 0.494	0.478, 0.484, 0.483
$V_{N,F} = f$: f_R	-0.066, 0.014, -0.026	-0.063, 0.023, -0.020	-0.069, 0.019, -0.025
f_α	-0.077, -0.052, -0.064	-0.074, -0.053, -0.063	-0.067, -0.051, -0.059
$V_{F,F} = G$: $G_{R,R}$	-1.583	-1.817	-1.764
$G_{R,R'}$	-0.028	-0.056	-0.041
$G_{R,\alpha}$	0.265	0.364	0.336
$G_{\alpha,\alpha}$	-5.975	-6.512	-6.290
(μ, F) $-S_{\mu,\mu} \equiv S^{rel}$	2.267, 2.234, 2.240	2.041, 2.021, 2.023	2.092, 2.067, 2.070
$S_{\mu,F} \equiv S$: S_R	-0.149, 0.031, -0.058	-0.129, 0.046, -0.041	-0.145, 0.040, -0.052
S_α	-0.174, -0.115, -0.144	-0.150, -0.107, -0.128	-0.141, -0.105, -0.122
$S_{F,F} \equiv G^{rel}$: $S_{R,R}$	-1.593, -1.584, -1.585	-1.825, -1.818, -1.817	-1.774, -1.765, -1.766
$S_{R,R'}$	-0.037, -0.028, -0.029	-0.064, -0.057, -0.057	-0.051, -0.042, -0.042
$S_{R,\alpha}$	0.254, 0.267, 0.262	0.355, 0.367, 0.362	0.326, 0.338, 0.333
$S_{\alpha,\alpha}$	-5.988, -5.981, -5.984	-6.523, -6.518, -6.520	-6.299, -6.295, -6.297

The triple-valued entries report the results obtained for the finite-difference NFF obtained using the $\Delta N = -1$, $\Delta N = +1$ displacements, and the arithmetic average of these two estimates, respectively

smaller electron repulsion in the correlated approaches, which makes the electronic “gas” relatively less polarizable (“harder”) in character. Alternatively, the following screening argument can be put forward to physically justify this observation: in the correlated approaches the valence electrons effectively see a somewhat less screened nuclei, thus giving rise to a more compact “harder” electron distribution. Indeed, the global hardness represents a response in the system chemical potential per unit displacement in the number of electrons. Thus, in the correlated approach this response can be expected to be lower, due to a better avoidance by the valence electrons of assuming nearby instantaneous positions.

Next, let us compare in Table 2 the corresponding elements of the geometric Hessians H and H^{rel} , grouping the force constants for the closed and open (electronically relaxed) water molecule, respectively. One again detects a slight manifestation of the LeChâtelier–Braun principle in the diagonal elements, $0 < G_{s,s} \leq H_{s,s}$, although

Table 3 Representative compliance constants and MEC, relaxed electronically and/or geometrically, for H₂O (see Table 2 for the description of triple-entries)

Repres.	Derivative	HF			MP2			CISD		
<i>F</i>	$(R')_R$	0.017			0.031			0.023		
	$(\alpha)_R$	-0.168			-0.201			-0.190		
	$(R)_\alpha$	-0.044			-0.056			-0.053		
(μ, Q)	$(F_R)_N = \varphi_R$	-0.044,	0.007,	-0.018	-0.037,	0.011,	-0.013	-0.041,	0.009,	-0.016
	$(F_\alpha)_N = \varphi_\alpha$	-0.017,	-0.008,	-0.012	-0.015,	-0.007,	-0.011	-0.015,	-0.007,	-0.011
	$(F_R)_\mu = s_R$	-0.097,	0.016,	-0.040	-0.074,	0.022,	-0.026	-0.085,	0.019,	-0.033
	$(F_\alpha)_\mu = s_\alpha$	-0.037,	-0.018,	-0.028	-0.031,	-0.014,	-0.023	-0.031,	-0.015,	-0.023
	$(N)_{F_R,\mu}$	0.154,	-0.025,	0.064	0.134,	-0.039,	0.047	0.149,	-0.034,	0.057
	$(N)_{F_\alpha,\mu}$	0.221,	0.105,	0.163	0.199,	0.089,	0.144	0.192,	0.090,	0.141
	$(F_R)_{F_R,\mu}$	-0.017,	-0.010,	-0.011	-0.025,	-0.020,	-0.021	-0.019,	-0.014,	-0.014
	$(F_\alpha)_{F_R,\mu}$	0.042,	0.044,	0.043	0.053,	0.055,	0.054	0.051,	0.053,	0.052
	$(F_R)_{F_\alpha,\mu}$	0.156,	0.166,	0.162	0.188,	0.196,	0.193	0.179,	0.187,	0.184
(N, F)	$(R)_\mu = s_R$	-0.149,	0.031,	-0.058	-0.129,	0.046,	-0.041	-0.145,	0.040,	-0.052
	$(\alpha)_\mu = s_\alpha$	-0.174,	-0.115,	-0.144	-0.150,	-0.107,	-0.128	-0.141,	-0.105,	-0.122
	$(\mu)_{R,N}$	0.016			0.011			0.014		
	$(\mu)_{\alpha,N}$	0.011			0.010			0.009		
	$(R')_{R,N}$	0.017			0.031			0.023		
	$(\alpha)_{R,N}$	-0.168			-0.201			-0.190		
	$(R)_{\alpha,N}$	-0.044			-0.056			-0.053		
(μ, F)	$(R)_N = f_R$	-0.066,	0.014,	-0.026	-0.063,	0.023,	-0.020	-0.069,	0.019,	-0.025
	$(\alpha)_N = f_\alpha$	-0.077,	-0.052,	-0.064	-0.074,	-0.053,	-0.063	-0.067,	-0.051,	-0.059
	$(N)_{R,\mu}$	-0.093,	0.019,	-0.037	-0.071,	0.025,	-0.022	-0.081,	0.022,	-0.029
	$(N)_{\alpha,\mu}$	-0.029,	-0.019,	-0.024	-0.023,	-0.016,	-0.020	-0.022,	-0.017,	-0.019
	$(R')_{R,\mu}$	0.023,	0.018,	0.018	0.035,	0.032,	0.031	0.029,	0.024,	0.024
	$(\alpha)_{R,\mu}$	-0.159,	-0.168,	-0.165	-0.194,	-0.202,	-0.199	-0.184,	-0.191,	-0.188
	$(R)_{\alpha,\mu}$	-0.042,	-0.045,	-0.044	-0.054,	-0.056,	-0.055	-0.052,	-0.054,	-0.053

the effect of the system electronic opening is seen to create only a minor “softening” effect on the system electronic hardness, compared to that generated by the geometry-relaxation. The positive character of the diagonal elements reflects the stability (LeChâtelier) requirement. Again, the HF approximation generates quite satisfactory account of these geometric couplings in the molecule, as reflected by the MP2 and CISD results, with the diagonal force constants exhibiting the largest deviations at both the closed- and open-system levels.

The geometric softnesses \mathbf{s} of the (μ, Q) -representation (see Eqs. 48 and 49) and the alternative FF indices, NFF (φ) in the canonical (N, Q) -representation (Eqs. 12 and 26) or GFF (\mathbf{f}) of the (N, F) -representation (Eqs. 41 and 60b), provide additional indices of the electronic-nuclear coupling in the externally open or closed molecules. It follows from Table 2 that the signs of the given NFF index and the corresponding softness component are the same. Indeed, the former represents the scaled version of the latter (see Eq. 60b,c), with the relevant global hardness (positive) providing the scaling factor, so that these two sets of coupling quantities carry the same physical

description of molecular responses. As explicitly indicated in Table 3, the \mathbf{s} and $\boldsymbol{\varphi}$ vectors represent the force compliants in the open and closed molecular systems, respectively.

The moderating exchange of electrons between the molecule and its hypothetical electron reservoir determines the effects of the electronic-nuclear coupling in open molecular systems. Let us assume the initial electronic and geometric equilibrium in such an initially open system: $\mu^0 = \mu_{\text{res}}$, and $\mathbf{F}^0 = \mathbf{0}$. The relevant stability (LeChâtelier) criteria of these two (decoupled) facets of the molecular structure require that the conjugate “forces” $\Delta\mu(\Delta N)$ or $\{\Delta F_s(\Delta Q_s)\}$ created by the primary electronic ($\Delta N > 0$) or nuclear $\{\Delta Q_s > 0\}$ displacements, $\Delta\mu(\Delta N) = \eta\Delta N$ and $\Delta F_s(\Delta Q_s) = -H_{s,s}\Delta Q_s$, will subsequently trigger the directly coupled, spontaneous responses of the system, $\delta N(\Delta N)$ and $\delta Q_s(\Delta Q_s)$, which act in the direction to restore the initial equilibrium. Therefore, the latter must diminish the forces created by the primary displacement, when the hypothetical internal and external barriers effecting the displacements are lifted, $\delta\mu[\delta N(\Delta N)] = \eta\delta N(\Delta N) = -\Delta\mu(\Delta N) = -\eta\Delta N$ and $\delta F_s[\delta Q_s(\Delta Q_s)] = -H_{s,s}\delta Q_s(\Delta Q_s) = -\Delta F_s(\Delta Q_s) = H_{s,s}\Delta Q_s$, or $\delta N(\Delta N) = -\Delta N$ and $\delta Q_s(\Delta Q_s) = -\Delta Q_s$. This is assured by the positive character of the electronic hardness and the diagonal nuclear force constants, $\eta > 0$ and $H_{s,s} > 0$, since then $\Delta\mu(\Delta N) > 0$ implies $\delta N(\Delta N) < 0$, while $-\Delta F_s(\Delta Q_s) > 0$ gives rise to $\delta Q_s(\Delta Q_s) < 0$.

However, due to electron-nuclear coupling in molecules a given displacement in one aspect of the molecular structure creates forces in the complementary aspect: $\Delta\mu(\Delta Q_s) = -\varphi_s\Delta Q_s$ and $\Delta F_s(\Delta N) = \varphi_s\Delta N$. They trigger the indirectly coupled, spontaneous relaxations $\delta N(\Delta Q_s)$ and $\delta Q_s(\Delta N)$, which also act towards diminishing the directly coupled forces $\Delta\mu(\Delta N) < 0$ and $\Delta F_s(\Delta Q_s) > 0$ (the LeChâtelier–Braun principle): $\delta\mu[\delta N(\Delta Q_s)] = \varphi_s\Delta Q_s > 0$ and $\delta F_s[\delta Q_s(\Delta N)] = -\varphi_s\Delta N < 0$. Hence, these indirectly induced electronic and/or nuclear relaxations must exhibit the opposite signs with respect to the corresponding NFF indices.

These effects of the electronic and/or nuclear relaxations are quantified in terms of the MEC listed in Table 3, where the \mathbf{F} -representation data reflect the interaction between the geometrical degrees-of-freedom in the absence of any electronic-nuclear coupling. The first of these entries (R')_R reflects the equilibrium linear response in R' per unit displacement in R , (α)_R measures a similar response in the bond-angle created by this “normalized” perturbation, while (R)_α is the linear bond-length readjustment per unit (1 radian) change in the bond angle. It follows from these purely geometric entries that in the ground-state of the water molecule an increase in one bond-length generates a small elongation of the other bond and a decrease in the bond-angle. The latter coupling effect is also reflected by the negative character of the (R)_α index, which implies a bond shortening following the primary increase in the bond angle. A comparison between the three methods used in numerical calculations again indicates that the HF approximation gives a semiquantitative agreement with predictions from the electron-correlated approaches. Obviously, the same purely geometrical compliants are generated in the (N, \mathbf{F})-representation of the externally closed molecule.

As indicated in Table 3 the first two compliants of the (μ, \mathbf{F})-representation represent the GFF indices of Eq. (60a,b) (see the discussion of Table 2). Consider next

the effects of the electronic opening, in the same representation, on these equilibrium responses of geometric parameters to such geometric displacements. The corresponding electronically relaxed compliants of the open molecule are listed in the final three rows of Table 3, which can be compared with the corresponding responses shown in the three opening rows of the table. It follows from this comparison of the HF results that $(s')_{s,\mu} > (s')_s$, $Q_s \neq Q_{s'} = R, R', \alpha$. Therefore, in this approximation an elongation of one bond in response to lengthening of the other bond becomes more emphasized in the open molecule. Indeed, a reference to Table 2 indicates, that $\varphi_R < 0$ and $\varphi_\alpha < 0$ imply inflow of electrons $\delta N(\Delta Q_s > 0) > 0$ from the reservoir, for $Q_s = R, \alpha$, which starts populating the antibonding MO, thus giving an extra weakening of the other bond R' and hence its larger elongation.

Of interests also are the coupling constants reflecting the $N-Q_s$ or $N-F_s$ interactions, in the (μ, \mathbf{F}) - and (N, \mathbf{F}) -representations, respectively. The $\{(N)_{s,\mu}\}$ indices of the former, satisfactorily reproduced already in the HF theory, show that a test bond elongation or increase in the bond angle both create an outflows of electrons from the system to the reservoir, in accordance with the sign of the respective NFF indices. Clearly, the corresponding $\{(N)_{F_s,\mu}\}$ quantities must exhibit the opposite sign, since a positive displacement of the bond length (angle) implies a negative shift in the corresponding force component.

Consider next the $(\mu)_{s,N}$ indices defined in the (N, \mathbf{F}) -representation (Eq. 65), which reflect a direct effect of a hypothetical shift in the coordinate Q_s of the closed-system on its chemical potential, when the remaining geometrical degrees-of-freedom are fully relaxed. As shown in Table 3 both these indices, for $Q_s = (R, \alpha)$, are positive. It should be realized that in DFT the system chemical potential (Fermi-level) is determined by the highest occupied Kohn–Sham (KS) MO [1, 22, 23] (HOMO), in H_2O describing the lone electron pairs on oxygen. In the closed system it depends solely on the system geometry Q . Thus, elongating the chemical bonds implies less attraction of these non-bonding electrons by the not fully screened hydrogen atoms, and hence the increase in their orbital energies, which justifies $(\mu)_{R,N} > 0$. Alternatively, an orbital hybridization argument can be put forward to rationalize the positive character of this quantity. Namely, it should be realized that a more $2s$ -character in the bonding hybrids implies lower energy levels of these promoted atomic orbitals, and hence weaker interaction with the $1s$ orbitals of hydrogen atoms and hence longer bonds and larger angles (a displacement from sp^3 hybridization towards sp^2 scheme). At the same time this implies less $2s$ -character of the remaining two non-bonding hybrids describing the lone electron pairs on oxygen. The latter implies the higher HOMO level and thus higher chemical potential. To summarize, the longer bonds and larger angles in water molecule imply an increase in the system chemical potential, as indeed reflected by the positive values of the $(\mu)_{s,N}$ indices in Table 3.

A similar way of reasoning justifies the observed signs of the $(s)_\mu$ indices (Eq. 64), for $Q_s = (R, \alpha)$ in the same (N, \mathbf{F}) -representation. As seen in Table 3, the first, $\Delta N = -1$ estimates are both negative, thus implying that in the electron withdrawing processes, in response to $\Delta\mu_{res.} = \Delta\mu < 0$, both bond length and angle increase their equilibrium values. Such an outflow of electrons, from the nonbonding hybrids, implies a weaker electron repulsion between the lone-“pairs”, and thus their less $2s$ character, and hence more $2s$ content in the localized MO describing two OH

bonds. This further implies longer bonds and larger bond angle, as indeed reflected by the negative coupling constants. Finally, the small, positive value of $(R)_\mu$ in the $\Delta N = 1$ estimate, corresponding to $\Delta\mu_{\text{res.}} = \Delta\mu > 0$, is similarly explained. More specifically, such an inflow of electrons starts populating the antibonding MO, thus weakening (lengthening) the two bonds. Moreover, this electronic displacement diminishes the original CT between atoms, thus decreasing the repulsion between a better-screened hydrogens, which should result in decreasing the bond angle.

Turning now to the equilibrium interaction constants of Table 3 involving the forces, in the (μ, \mathcal{Q}) -representation, one first observes that the first two compliants, $(F_s)_N$, for $\mathcal{Q}_s = (R, \alpha)$, represent the NFF of Eq. 60c (see the discussion of Table 2). The final three indices $\{(F_{s'})_{F_s, \mu}\}$ reflect the interaction between forces in the externally open system. It follows from the first two of these indices that a hypothetical displacement $\Delta F_R > 0$, giving rise to an elongation of this bond compared to the equilibrium value, generates $\Delta F_{R'} < 0$ and $\Delta F_\alpha > 0$, thus acting towards shortening the other bond and increasing the bond angle. These implications agree with the electronically relaxed force constants $G_{R, R'} < 0$ and $G_{R, \alpha} > 0$ reported in Table 2 for the same representation.

7.2 NO₂

The electronic-nuclear “force” constants for alternative representations of equilibrium states in NO₂, which exhibits the π -electron system extending throughout the molecule, are reported in Table 4. The associated compliant quantities determining MEC are listed in Table 5. A general feature of these results is that the magnitude of the electronic and/or nuclear relaxation and the strength of the electronic-geometric interaction are much enhanced in NO₂ compared to those observed in water molecule. In many respects the results for these two triatomic (angular) molecules are similar, but there are also several notable differences, which we shall briefly discuss below. As before, all the diverse couplings in the externally closed and open system are reflected in a quite satisfactory manner already within the HF (exchange-only) approximation. A reference to the hardness and softness data of Table 4 shows that, contrary to the trend observed in H₂O, the correlated calculations predict an increased global softness of NO₂, compared to HF results.

In order to simplify the comparison we shall focus on the HF results. It should be recalled that in the simplest orbital interpretation of the ground-state configuration of NO₂, with all bonded atoms exhibiting approximately sp^2 hybridization in their respective valence states, the singly occupied HOMO represents the non-bonding combination of $2p_\pi$ orbitals on oxygen atoms. Therefore, the addition/removal of electrons to/from the system affects mainly the oxygen “ligands” of the central, nitrogen atom.

In the generalized Hessian of the (N, \mathcal{Q}) -representation one detects the positive $\Delta N = -1$ estimate of the NFF index φ_R . It implies that removing an electron from the molecule, $\Delta N < 0$, results in decreasing the force component along the bond length, $\Delta F_R < 0$, which acts towards shortening the N—O bonds. Indeed, removing the non-bonding π electron effectively reduces the electron accumulation on oxygen atoms thus inducing an enhanced coordination via the bonding σ and π MO. Another

Table 4 Same as in Table 2 for NO₂

Repr.	Derivative	HF			MP2			CISD		
(N, Q)	$H_{N,N} = \eta$	0.422			0.343			0.384		
	$-H_{N,Q}: \varphi_R = (F_R)_N$	0.111,	0.112,	0.112	0.048,	0.072,	0.060	0.087,	0.091,	0.089
	$\varphi_\alpha = (F_\alpha)_N$	-0.164,	-0.177,	-0.171	-0.140,	-0.143,	-0.142	-0.148,	-0.157,	-0.153
	$H_{Q,Q} = H: H_{R,R}$	0.947			0.971			1.158		
	$H_{R,R'}$	0.237			-0.128			-0.139		
	$H_{R,\alpha}$	0.061			0.058			0.060		
	$H_{\alpha,\alpha}$	0.412			0.379			0.389		
(μ, Q)	$-G_{\mu,\mu} = S$	2.369			2.918			2.603		
	$-G_{\mu,Q}: S_R = (F_R)_\mu$	0.264,	0.265,	0.265	0.140,	0.211,	0.175	0.227,	0.237,	0.232
	$S_\alpha = (F_\alpha)_\mu$	-0.389,	-0.420,	-0.405	-0.409,	-0.418,	-0.413	-0.386,	-0.410,	-0.398
	$G_{Q,Q} \equiv H^{rel}: G_{R,R}$	0.918,	0.917,	0.917	0.964,	0.956,	0.961	1.138,	1.136,	1.137
	$G_{R,R'}$	0.208,	0.207,	0.208	-0.135,	-0.143,	-0.139	-0.158,	-0.160,	-0.159
	$G_{R,\alpha}$	0.104,	0.108,	0.106	0.078,	0.089,	0.083	0.094,	0.098,	0.096
	$G_{\alpha,\alpha}$	0.348,	0.338,	0.343	0.322,	0.319,	0.321	0.331,	0.324,	0.328
(N, F)	$V_{N,N} \equiv \eta^{rel}$	0.325,	0.313,	0.319	0.279,	0.267,	0.274	0.303,	0.294,	0.299
	$V_{N,F}: f_R = (R)_N$	0.116,	0.118,	0.117	0.084,	0.114,	0.099	0.110,	0.115,	0.113
	$f_\alpha = (\alpha)_N$	-0.433,	-0.465,	-0.449	-0.395,	-0.413,	-0.404	-0.416,	-0.440,	-0.428
	$V_{F,F} = G: G_{R,R}$	-1.133			-1.061			-0.885		
	$G_{R,R'}$	0.276			-0.151			-0.114		
	$G_{R,\alpha}$	0.127			0.187			0.154		
	$G_{\alpha,\alpha}$	-2.462			-2.696			-2.621		
(μ, F)	$-S_{\mu,\mu} \equiv S^{rel}$	3.076,	3.195,	3.133	3.581,	3.745,	3.656	3.297,	3.402,	3.348
	$S_{\mu,F}: S_R = (R)_\mu$	0.358,	0.378,	0.368	0.301,	0.428,	0.363	0.363,	0.392,	0.377
	$S_\alpha = (\alpha)_\mu$	-1.331,	-1.486,	-1.407	-1.416,	-1.547,	-1.478	-1.371,	-1.498,	-1.433
	$S_{F,F} \equiv G^{rel}: S_{R,R}$	-1.175,	-1.178,	-1.176	-1.086,	-1.110,	-1.097	-0.925,	-0.931,	-0.928
	$S_{R,R'}$	0.234,	0.231,	0.232	-0.177,	-0.200,	-0.187	-0.154,	-0.159,	-0.157
	$S_{R,\alpha}$	0.281,	0.303,	0.292	0.306,	0.363,	0.333	0.305,	0.327,	0.316
	$S_{\alpha,\alpha}$	-3.038,	-3.154,	-3.094	-3.255,	-3.334,	-3.293	-3.191,	-3.280,	-3.234

observed difference, compared to water molecule, is the positive value of the force constant coupling both bond-lengths, $H_{R,R'} > 0$, which implies that $\Delta R > 0$ generates $\Delta F_{R'} < 0$, i.e., a shortening of the other bond. This clearly manifests the effect of π bonds in the system. Indeed, a smaller participation of the nitrogen $2p_\pi$ orbital in the elongated π bond facilitates its stronger participation in the other π bond.

A similar physical interpretation applies to the positive values of the corresponding electronically relaxed quantities S_R and $G_{R,R'}$ of the (μ, Q) -representation. This difference propagates itself into the remaining representations as well, giving rise to a relatively high, positive values of the GFF (f_R) or the related softness (S_R) indices, and the corresponding compliants coupling the two bonds: $G_{R,R'}$ and $S_{R,R'}$.

These differences are also detected in the coupling constants. It follows from its $(R')_R$ entries that the inclusion of the Coulomb-correlation changes the sign of this index. This conforms to a similar sign alternation observed in the $H_{R,R'}$ data. A reference to geometric softnesses S of Table 4 reveals that the perturbation $\Delta\mu_{res.} = \Delta\mu > 0$ increases the bond-length. Indeed, such a displacement generates an inflow of electrons, $\Delta N > 0$, and hence increased occupation of the HOMO, which should

Table 5 Same as in Table 3 for NO₂, with removed compliant data already reported in Table 4

Repr.	Derivative	HF	MP2	CISD
F	$(R')_R$	-0.243	0.143	0.129
	$(\mathcal{O})_R$	-0.112	-0.176	-0.174
	$(R)_\alpha$	-0.051	-0.069	-0.059
(μ, Q)	$(N)_{F_R, \mu}$	-0.288, -0.289, -0.288	-0.145, -0.221, -0.182	-0.199, -0.208, -0.204
	$(N)_{F_\alpha, \mu}$	1.117, 1.245, 1.180	1.270, 1.309, 1.289	1.167, 1.265, 1.215
	$(F_{R'})_{F_R, \mu}$	0.226, 0.226, 0.226	-0.140, -0.150, -0.144	-0.139, -0.141, -0.140
	$(F_\alpha)_{F_R, \mu}$	0.114, 0.118, 0.116	0.081, 0.093, 0.087	0.083, 0.086, 0.084
	$(F_R)_{F_\alpha, \mu}$	0.299, 0.319, 0.309	0.242, 0.277, 0.259	0.284, 0.301, 0.292
(N, F)	$(\mu)_{R,N}$	-0.104	-0.093	-0.127
	$(\mu)_{\alpha,N}$	0.182	0.150	0.163
	$(R')_{R,N}$	-0.243	0.143	0.129
	$(\mathcal{O})_{R,N}$	-0.112	-0.176	-0.174
	$(R)_{\alpha,N}$	-0.051	-0.069	-0.059
(μ, F)	$(N)_{R, \mu}$	0.305, 0.321, 0.313	0.277, 0.386, 0.331	0.392, 0.421, 0.406
	$(N)_{\alpha, \mu}$	-0.438, -0.471, -0.455	-0.435, -0.464, -0.449	-0.430, -0.457, -0.443
	$(R')_{R, \mu}$	-0.199, -0.196, -0.198	0.163, 0.180, 0.171	0.167, 0.171, 0.169
	$(\mathcal{O})_{R, \mu}$	-0.240, -0.257, -0.248	-0.281, -0.327, -0.304	-0.330, -0.351, -0.340
	$(R)_{\alpha, \mu}$	-0.093, -0.096, -0.094	-0.094, -0.109, -0.101	-0.096, -0.100, -0.098

result in higher negative charges on the terminal (oxygen) atoms, and hence weaker N → O coordination via both σ and π bonding MO. The next row of compliant data shows that this primary perturbation decreases the bond angle, as intuitively expected. These observations are also consistent with the $(\mu)_{S,N}$ interactions reported in Table 5, which reflect the response in the closed system chemical potential per unit displacement in the system geometrical variables.

Finally, let us summarize the differences relative to H₂O detected in the compliants of the fully relaxed (μ, F) -representation in Table 5. One detects the sign changes in $(N)_{R, \mu}$ and $(R')_{R, \mu}$ indices of the open NO₂. It thus follows from these interaction constants that elongating one bond results in an inflow of electrons to the system and shortening the other bond.

7.3 H₂O₂

In Tables 6 and 7 the representative results for hydrogen peroxide are displayed, again including the generalized Hessians and compliant derivatives. In view of a large number of couplings between the nuclear parameters only diagonal derivatives of the geometric block are reported in Table 6. As before, some of the molecular compliants, representing the geometric or nuclear FF indices and softnesses are reported in Table 6, while the remaining minimum-energy coupling-constants are shown in Table 7.

Table 6 Same as in Table 2 for H₂O₂, with only diagonal geometrical derivatives being reported

Repr.	Derivative	HF	MP2	CISD
(N, Q)	$H_{N,N} = \eta$	0.468	0.461	0.472
	$-H_{N,Q}: \varphi_{R_1} = (F_{R_1})_N$	0.111, 0.009, 0.060	0.039, 0.026, 0.033	0.073, 0.016, 0.045
	$\varphi_{R_2} = (F_{R_2})_N$	-0.036, 0.006, -0.015	-0.030, 0.008, -0.011	-0.031, 0.007, -0.012
	$\varphi_\alpha = (F_\alpha)_N$	-0.008, 0.008, 0.000	-0.003, 0.012, 0.005	-0.005, 0.010, 0.003
	$\varphi_\delta = (F_\delta)_N$	-0.052, 0.001, -0.025	-0.042, 0.001, -0.021	-0.047, 0.001, -0.023
	$H_{Q,Q} = H: H_{R_1,R_1}$	0.442	0.292	0.342
	H_{R_2,R_2}	0.619	0.524	0.559
	$H_{\alpha,\alpha}$	0.263	0.219	0.236
	$H_{\delta,\delta}$	0.010	0.009	0.010
(μ, Q)	$-G_{\mu,\mu} = S$	2.139	2.167	2.120
	$-G_{\mu,Q}: S_{R_1} = (F_{R_1})_\mu$	0.237, 0.019, 0.128	0.084, 0.057, 0.070	0.156, 0.035, 0.095
	$S_{R_2} = (F_{R_2})_\mu$	-0.076, 0.014, -0.031	-0.065, 0.017, -0.024	-0.066, 0.015, -0.025
	$S_\alpha = (F_\alpha)_\mu$	-0.016, 0.016, 0.000	-0.006, 0.027, 0.011	-0.011, 0.022, 0.005
	$S_\delta = (F_\delta)_\mu$	-0.111, 0.003, -0.054	-0.092, 0.002, -0.045	-0.099, 0.002, -0.048
	$G_{Q,Q} \equiv H^{rel}: G_{R_1,R_1}$	0.416, 0.442, 0.434	0.288, 0.290, 0.289	0.330, 0.341, 0.337
	G_{R_2,R_2}	0.616, 0.619, 0.618	0.522, 0.523, 0.523	0.557, 0.559, 0.559
	$G_{\alpha,\alpha}$	0.263, 0.263, 0.263	0.219, 0.218, 0.218	0.236, 0.236, 0.236
	$G_{\delta,\delta}$	0.004, 0.010, 0.008	0.005, 0.009, 0.008	0.005, 0.010, 0.009
(N, F)	$V_{N,N} = \eta^{rel}$	0.164, 0.467, 0.394	0.252, 0.458, 0.409	0.228, 0.470, 0.411
	$V_{N,F}: f_{R_1} = (R_1)_N$	0.184, 0.014, 0.099	0.026, 0.079, 0.052	0.134, 0.037, 0.086
	$f_{R_2} = (R_2)_N$	-0.041, 0.010, -0.015	-0.041, 0.016, -0.012	-0.037, 0.013, -0.012
	$f_\alpha = (\alpha)_N$	0.100, 0.020, 0.060	0.151, 0.026, 0.089	0.113, 0.027, 0.070
	$f_\delta = (\delta)_N$	-5.433, 0.089, -2.672	-4.860, 0.057, -2.401	-4.986, 0.071, -2.457
	$V_{F,F} = G: G_{R_1,R_1}$	-2.547	-4.124	-3.386
	G_{R_2,R_2}	-1.617	-1.913	-1.789
	$G_{\alpha,\alpha}$	-4.186	-5.209	-4.733
$G_{\delta,\delta}$	-110.9	-118.4	-112.3	
(μ, F)	$-S_{\mu,\mu} = S^{rel}$	6.095, 2.142, 2.541	3.964, 2.182, 2.447	4.394, 2.126, 2.432
	$S_{\mu,F}: S_{R_1} = (R_1)_\mu$	1.124, 0.029, 0.251	0.102, 0.171, 0.128	0.590, 0.080, 0.209
	$S_{R_2} = (R_2)_\mu$	-0.250, 0.022, -0.039	-0.164, 0.036, -0.031	-0.163, 0.028, -0.029
	$S_\alpha = (\alpha)_\mu$	0.612, 0.043, 0.153	0.599, 0.057, 0.217	0.497, 0.057, 0.170
	$S_\delta = (\delta)_\mu$	-33.12, 0.190, -6.789	-19.26, 0.124, -5.877	-21.91, 0.151, -5.976
	$S_{F,F} \equiv G^{rel}: S_{R_1,R_1}$	-2.754, -2.547, -2.572	-4.127, -4.138, -4.131	-3.465, -3.389, -3.404
	S_{R_2,R_2}	-1.628, -1.618, -1.618	-1.919, -1.913, -1.913	-1.795, -1.789, -1.789
	$S_{\alpha,\alpha}$	-4.248, -4.187, -4.196	-5.300, -5.211, -5.229	-4.789, -4.735, -4.745
	$S_{\delta,\delta}$	-290.8, -110.9, -129.0	-212.0, -118.4, -132.5	-221.5, -112.3, -126.9

Table 7 Same as in Table 3 for H₂O₂, with removed compliant data already reported in Table 6

Repr.	Derivative	HF	MP2	CISD
F	$(R_2)_{R_1}$	0.006	0.019	0.007
	$(\alpha)_{R_1}$	-0.301	-0.327	-0.307
	$(\delta)_{R_1}$	0.823	0.781	0.782
	$(R_1)_{R_2}$	0.010	0.042	0.014
	$(R_2')_{R_2}$	0.001	0.003	0.001
	$(\alpha)_{R_2}$	0.006	-0.006	0.008
	$(\alpha')_{R_2}$	0.000	-0.012	0.001
	$(\delta)_{R_2}$	-0.176	-0.161	-0.199
	$(R_1)\alpha$	-0.183	-0.259	-0.220
	$(R_2)\alpha$	0.002	-0.002	0.003
	$(R_2')\alpha$	0.000	-0.004	0.000
	$(\alpha')\alpha$	-0.003	0.019	0.005
	$(\delta)\alpha$	-1.002	-0.981	-0.972
	$(R_1)\delta$	0.019	0.027	0.024
	$(R_2)\delta$	-0.003	-0.003	-0.003
	$(\alpha)\delta$	-0.038	-0.043	-0.041
(μ, Q)	$(N)_{F_{R_1}, \mu}$	-0.571, -0.043, -0.295	-0.292, -0.196, -0.244	-0.471, -0.102, -0.282
	$(N)_{F_{R_2}, \mu}$	0.123, -0.022, 0.050	0.125, -0.033, 0.046	0.118, -0.027, 0.045
	$(N)_{F_{\alpha}, \mu}$	0.062, -0.063, -0.001	0.028, -0.124, -0.048	0.048, -0.093, -0.023
	$(N)_{F_{\delta}, \mu}$	27.49, -0.273, 6.432	17.32, -0.208, 5.437	19.59, -0.250, 5.626
(N, F)	$(\mu)_{R_1, N}$	-0.039	-0.013	-0.025
	$(\mu)_{R_2, N}$	0.009	0.007	0.007
	$(\mu)_{\alpha, N}$	-0.014	-0.017	-0.015
	$(\mu)_{\delta, N}$	0.024	0.020	0.022
(μ, F)	$(N)_{R_1, \mu}$	0.408, 0.011, 0.098	0.025, 0.041, 0.031	0.170, 0.023, 0.061
	$(N)_{R_2, \mu}$	-0.154, 0.014, -0.024	-0.086, 0.019, -0.016	-0.091, 0.016, -0.016
	$(N)_{\alpha, \mu}$	0.144, 0.010, 0.037	0.113, 0.011, 0.041	0.104, 0.012, 0.036
	$(N)_{\delta, \mu}$	-0.114, 0.002, -0.053	-0.091, 0.001, -0.044	-0.099, 0.001, -0.047

An inspection of the rigid-geometry hardnesses and softnesses indicates that the HF estimate compares favourably with predictions from more advanced methods, while the corresponding geometrically relaxed estimates exhibit large Coulomb-correlation contributions. This molecule includes the dihedral-angle δ as one of its internal nuclear coordinates. It follows from the $\varphi_{\delta} = (F_{\delta})_N$ data that in the electron withdrawing ($\Delta N < 0$) process, e.g., during an attack by the electrophilic agent, the response in F_{δ} is negative, which implies a decrease in the dihedral angle. This trend is also reflected by the corresponding GFF. The same entries testify that the the electron donating ($\Delta N > 0$) displacement, e.g., in the nucleophilic attack, has comparatively minor

effect on δ . The positive signs of $f_{R_1} = (R_1)_N$ and $f_\alpha = (\alpha)_N$ further testify that the $\Delta N < 0$ ($\Delta N > 0$) electronic perturbation decreases (increases) the length of the central O—O bond and H—O—O angle.

The purely geometric aspect of coupling between nuclear coordinates is reflected by the first part of Table 7. A comparison between the corresponding predictions from the three methods used in numerical calculations shows that the MEC-coupling between bond lengths and angles is strongly influenced by the Coulomb correlation between electrons. An increase in the central bond length, $\Delta R_1 > 0$, is seen to diminish the bond angle, $(\alpha)_{R_1} < 0$, and enlarge the dihedral angle: $(\delta)_{R_1} > 0$. The opposite effect accompanies a hypothetical lengthening of the peripheral bond, $\Delta R_2 > 0$: $(\delta)_{R_2} < 0$. The geometrical $\Delta R_1 > 0$ displacement is seen to exert a moderate positive effect on the length of the O—H bonds, $(R_2)_{R_1} > 0$, in accordance with $(R_1)_{R_2} > 0$, while $\Delta R_2 > 0$ has practically no influence on bond angles and the other O—H bond. The increase in dihedral angle is predicted to lower the bond angle and lengthen the central bond, with practically vanishing effect on the peripheral bonds.

Of interest also is effect of geometrical perturbations on the exchange of electrons between the molecule and its environment (reservoir), indexed in the last part of Table 7. The positive values of the compliant indices $(N)_{R_1,\mu}$ and $(N)_{\alpha,\mu}$ signify an inflow of electrons following the $\Delta R_1 > 0$ and $\Delta\alpha > 0$ perturbations. The $\Delta R_2 > 0$ displacement and a test opening of the dihedral angle, $\Delta\delta > 0$, are both predicted to generate an outflow of electrons from the molecule in the $\Delta N = -1$ estimate of the N -derivatives, with much weaker opposite effect being diagnosed within the $\Delta N = +1$ estimate. Similar trends are detected in the associated influences of the peripheral bond length.

Finally, let us examine the influence of the molecular geometry on the closed-system chemical potential, reflected by the (N, F) -part of Table 7. These entries reflect an increase in the chemical potential (decrease in electronegativity) due to a lengthening of the O—H bond and an opening of the dihedral angle. The opposite effect is observed for the central O—O bond and the H—O—O angle.

7.4 ClF₃

This molecule represents another molecular system containing a single dihedral angle in the list of its internal geometrical coordinates and an overcrowding of valence electron pairs, both bonding and non-bonding. The simplest localized-MO diagram for ClF₃ predicts two lone electron pairs on the chlorine atom, degenerate in the ground-state (planar) conformation, marking the HOMO level. These hybrid orbitals become split, when the system is distorted towards a “pyramidal” arrangement of the three Cl—F bonds. Therefore, as a result of the electron-withdrawing displacement $\Delta N = -1$ the cation ClF₃⁺ involves one fully occupied and one singly occupied lone pairs on this central atom, with the identity of the fully occupied orbital changing, when crossing from $\delta < 180^\circ$, through $\delta = 180^\circ$ (orbital degeneracy), to $\delta > 180^\circ$. The applied quantum-chemical package does not allow for the fixing the orbital occupations, when crossing the planar conformation, thus generating the vanishing “adiabatic” compliants reflecting the electron-nuclear coupling, which involve the dihedral

angle δ (not listed in Tables 8 and 9). Therefore, to estimate the “diabatic” coupling constants, for the “frozen” orbital occupations, we have determined these interaction constants for the ground-state of ClF_3^+ (non-planar); due to convergence problems a more extended basis set of the triple-zeta quality has been used in these additional HF calculations. The cation results are identified by an asterisk in Tables 8 and 9, where the generalized Hessian data and selected compliance derivatives have been reported, respectively.

A general impression from inspecting the corresponding entries in Table 8 for the three methods used in numerical computations reveals a relatively large contributions due to the electron correlation in this molecular system, although the signs of all appreciable interaction constants are properly reproduced already at the simplest HF level. This Coulomb-correlation error is particularly emphasized in the FF and electronic softness quantities as well as the diagonal elements of the geometric derivatives in each representation, while the global hardness/softness descriptors are seen to remain somewhat less affected by the Coulomb correlation between electrons. A strong electron-correlation component is also detected in several compliant descriptors of Table 9, e.g., in the purely geometric coupling $(R'_2)_{R_2}$ between the two peripheral Cl—F bonds or the $(N)_{F_{\alpha,\mu}}$ index reflecting the coupling between the external CT and the bond-angle force component in open system. However, some trends exhibited by the compliant derivatives can be strongly affected by the way the correlation error is accounted for. For example, the $\Delta N = -1$ estimates in the HF and CISD schemes predict $f_{R_2} = (R_2)_N > f_{R_1} = (R_1)_N$, while the opposite inequality relates these structural responses within the MP2 calculations.

A reference to the adiabatic ($H_{\delta,\delta}$) and diabatic ($H_{\delta,\delta}^*$) estimates of the force constant for the dihedral angle in Table 8 reveals that in cation this geometric coordinate appears less “stiff”: $H_{\delta,\delta} > H_{\delta,\delta}^*$. The same trend is seen in the relaxed moduli $G_{\delta,\delta} > G_{\delta,\delta}^*$. This conclusion also follows from examining the corresponding nuclear-softness moduli: $-G_{\delta,\delta} < -G_{\delta,\delta}^*$ and $-S_{\delta,\delta} < -S_{\delta,\delta}^*$. Of particular interest is the diabatic (fixed-occupation) coupling between the dihedral angle and the electronic degrees-of-freedom, which vanishes in the adiabatic approximation. In Table 8 the positive values of the NFF index $\varphi_{\delta}^* = (F_{\delta})_{N^*}$ and the GFF index $f_{\delta}^* = (\delta)_{N^*}$, predicted for ClF_3^+ (non-planar, $\delta < 180^\circ$), indeed imply that an electron inflow to this system “pushes” the system towards the planar structure of the neutral molecule. The opposite, electron-outflow displacement of ClF_3 also explains the pyramidal deformation of the cation. It also follows from Table 9 that an increase in δ generates an inflow of electrons to the open ClF_3^+ , $(N)_{\delta,\mu^*} > 0$, thus independently confirming the planar preference of the neutral system. This displacement also raises the (negative) level of the closed-system chemical potential.

Finally, let us examine selected, purely geometrical MEC collected in the first part of Table 9. In all three quantum-chemical methods used in numerical calculations increase in the bond length of the central Cl—F bond shortens two peripheral bonds and decreases the bond angles: $(R_2)_{R_1} < 0$ and $(\alpha)_{R_1} < 0$. Elongating the peripheral bond is also seen to be accompanied by a moderating shortening of the two remaining chemical bonds, $(R'_2)_{R_2} < 0$ and $(R_1)_{R_2} < 0$, while different responses in the adjacent (α) and opposite (α') bond angles are diagnosed: $(\alpha)_{R_2} < 0$ and $(\alpha')_{R_2} > 0$. An

Table 8 Same as in Table 6 for ClF_3

Repr.	Derivative	HF	MP2	CISD
(N, Q)	$H_{N,N} = \eta$	0.471	0.422	0.450
	$-H_{N,Q}: \varphi_{R_1} = (F_{R_1})_N$	0.034, 0.259, 0.147	0.070, 0.189, 0.129	0.033, 0.225, 0.129
	$\varphi_{R_2} = (F_{R_2})_N$	0.064, 0.062, 0.063	0.042, 0.043, 0.043	0.053, 0.054, 0.054
	$\varphi_\alpha = (F_\alpha)_N$	-0.002, 0.046, 0.022	-0.031, 0.036, 0.003	-0.008, 0.042, 0.017
	$\varphi_{\delta^*} = (F_\delta)_N$	0.155, 0.151, 0.153	0.104, 0.134, 0.119	0.128, 0.141, 0.134
	$H_{Q,Q} = H: H_{R_1,R_1}$	0.395	0.267	0.335
	H_{R_2,R_2}	0.243	0.189	0.227
	$H_{\alpha,\alpha}$	0.555	0.376	0.479
	$H_{\delta,\delta} (H_{\delta,\delta}^*)$	0.254 (0.208)	0.190 (0.173)	0.223 (0.197)
	(μ, Q)	$-G_{\mu,\mu} = S$	2.125	2.372
$-G_{\mu,Q}: S_{R_1} = (F_{R_1})_\mu$		0.072, 0.551, 0.312	0.166, 0.447, 0.307	0.072, 0.500, 0.286
$S_{R_2} = (F_{R_2})_\mu$		0.136, 0.131, 0.134	0.100, 0.103, 0.102	0.119, 0.121, 0.120
$S_\alpha = (F_\alpha)_\mu$		-0.005, 0.097, 0.046	-0.072, 0.085, 0.006	-0.017, 0.094, 0.038
$S_{\delta^*} = (F_\delta)_\mu$		0.380, 0.369, 0.375	0.303, 0.391, 0.347	0.349, 0.382, 0.365
$G_{Q,Q} \equiv H^{rel}: G_{R_1,R_1}$		0.392, 0.252, 0.349	0.255, 0.182, 0.227	0.333, 0.223, 0.298
G_{R_2,R_2}		0.234, 0.235, 0.234	0.184, 0.184, 0.184	0.220, 0.220, 0.220
$G_{\alpha,\alpha}$		0.555, 0.550, 0.554	0.374, 0.373, 0.376	0.478, 0.475, 0.478
$G_{\delta,\delta}$		0.254, 0.254, 0.254	0.190, 0.190, 0.190	0.223, 0.223, 0.223
$G_{\delta,\delta}^*$		0.149, 0.152, 0.151	0.142, 0.121, 0.132	0.152, 0.143, 0.148
(N, F)	$V_{N,N} \equiv \eta^{rel}$	0.441, 0.284, 0.395	0.382, 0.278, 0.346	0.426, 0.285, 0.384
	$V_{N,F}: f_{R_1} = (R_1)_N$	0.065, 0.633, 0.349	0.263, 0.676, 0.470	0.078, 0.644, 0.361
	$f_{R_2} = (R_2)_N$	0.217, 0.169, 0.193	0.184, 0.163, 0.174	0.202, 0.164, 0.183
	$f_\alpha = (\alpha)_N$	-0.004, 0.019, 0.008	-0.089, 0.033, -0.028	-0.016, 0.023, 0.004
	$f_{\delta^*} = (\delta)_N$	0.732, 0.701, 0.717	0.588, 0.678, 0.633	0.624, 0.648, 0.636
	$V_{F,F} = G: G_{R_1,R_1}$	-2.626	-3.910	-3.099
	G_{R_2,R_2}	-4.389	-5.395	-4.576
	$G_{\alpha,\alpha}$	-1.915	-2.742	-2.193
	$G_{\delta,\delta} (G_{\delta,\delta}^*)$	-3.943 (-4.836)	-5.269 (-6.151)	-4.476 (-5.208)
	(μ, F)	$-S_{\mu,\mu} \equiv S^{rel}$	2.270, 3.525, 2.533	2.617, 3.603, 2.889
$S_{\mu,F}: S_{R_1} = (R_1)_\mu$		0.147, 2.232, 0.884	0.689, 2.435, 1.357	0.183, 2.258, 0.941
$S_{R_2} = (R_2)_\mu$		0.492, 0.597, 0.489	0.482, 0.589, 0.502	0.474, 0.573, 0.476
$S_\alpha = (\alpha)_\mu$		-0.009, 0.068, 0.019	-0.234, 0.119, -0.081	-0.037, 0.082, 0.010
$S_{\delta^*} = (\delta)_\mu$		2.927, 2.959, 2.932	2.158, 3.300, 2.582	2.260, 2.807, 2.480
$S_{F,F} \equiv G^{rel}: S_{R_1,R_1}$		-2.635, -4.039, -2.934	-4.091, -5.556, -4.547	-3.113, -4.554, -3.439
S_{R_2,R_2}		-4.496, -4.490, -4.483	-5.484, -5.492, -5.483	-4.671, -4.669, -4.663
$S_{\alpha,\alpha}$		-1.915, -1.916, -1.915	-2.763, -2.746, -2.744	-2.193, -2.194, -2.193
$S_{\delta,\delta}$		-3.943, -3.943, -3.943	-5.269, -5.269, -5.269	-4.476, -4.476, -4.476
$S_{\delta,\delta}^*$		-6.979, -6.910, -6.937	-7.420, -8.387, -7.785	-6.619, -7.029, -6.786

The asterisk identifies the “diabatic” estimate for ClF_3^+

Table 9 Same as in Table 7 for ClF_3

Repr.	Derivative	HF	MP2	CISD
F	$(R_2)_{R_1}$	-0.078	-0.102	-0.083
	$(\alpha)_{R_1}$	-0.091	-0.095	-0.093
	$(R_1)_{R_2}$	-0.046	-0.074	-0.056
	$(R_2')_{R_2}$	-0.201	-0.030	-0.136
	$(\alpha)_{R_2}$	-0.063	-0.014	-0.047
	$(\alpha')_{R_2}$	0.091	0.071	0.081
	$(R_1)_\alpha$	-0.125	-0.135	-0.132
	$(R_2)_\alpha$	-0.144	-0.027	-0.098
	$(R_2')_\alpha$	0.209	0.141	0.168
	$(\alpha')_\alpha$	-0.162	-0.086	-0.138
(μ, Q)	$(N)_{F_{R_1}, \mu}$	-0.185, -2.187, -0.893	-0.653, -2.454, -1.352	-0.217, -2.242, -0.958
	$(N)_{F_{R_2}, \mu}$	-0.580, -0.560, -0.570	-0.545, -0.560, -0.552	-0.539, -0.548, -0.543
	$(N)_{F_\alpha, \mu}$	0.009, -0.177, -0.083	0.194, -0.227, -0.016	0.036, -0.198, -0.080
	$(N)_{F_\delta, \mu}^*$	-2.553, -2.422, -2.487	-2.135, -3.239, -2.630,	-2.287, -2.668, -2.470
(N, F)	$(\mu)_{R_1, N}$	-0.133	-0.120	-0.117
	$(\mu)_{R_2, N}$	-0.044	-0.032	-0.040
	$(\mu)_{\alpha, N}$	-0.004	0.010	-0.002
	$(\mu)_{\delta, N}^*$	-0.148	-0.103	-0.122
(μ, F)	$(N)_{R_1, \mu}$	0.056, 0.553, 0.301	0.168, 0.438, 0.298	0.059, 0.496, 0.274
	$(N)_{R_2, \mu}$	0.110, 0.133, 0.109	0.088, 0.107, 0.092	0.101, 0.123, 0.102
	$(N)_{\alpha, \mu}$	-0.005, 0.035, 0.010	-0.085, 0.043, -0.030	-0.017, 0.037, 0.004
	$(N)_{\delta, \mu}^*$	0.419, 0.428, 0.423	0.291, 0.393, 0.332,	0.342, 0.399, 0.365

The asterisk identifies the “diabatic” estimate for ClF_3^+

increase in the bond angle is accompanied by a shortening of the adjacent peripheral and central bonds, $(R_1)_\alpha < 0$ and $(R_2)_\alpha < 0$, an elongation of the other peripheral bond, $(R_2')_\alpha > 0$, and a decrease in the other bond angle: $(\alpha')_\alpha < 0$.

7.5 NH_2CHO

Formamide exhibits a variety of dihedral angles determining the out-of-plane bending of the three hydrogen atoms (see Fig. 1). A reference to Table 1 shows that the HF method favours the planar structure, while the electron-correlated approaches gives rise to a slightly non-planar arrangement of protons relative to the reference (NCO) plane. This difference is also reflected in Table 10, where the most appreciable elements of the generalized electronic-nuclear Hessians are reported, by the exactly vanishing geometric softness S and GFF indices f for all dihedral angles in HF approximation. Again, the three methods generate quite close estimates of the global

Table 10 Same as in Table 2 for formamide, with the removed diagonal blocks of geometric derivatives and elements of the off-diagonal row, the magnitudes of which, in all estimates, are below the assumed threshold value $\varepsilon = 0.03$

Repr. Derivative	HF	MP2	CISD
$(N, Q) H_{N,N} = \eta$	0.360	0.414	0.392
$-H_{N,Q}: \varphi_{R_1} = (F_{R_1})_N$	0.061, -0.013, 0.024	0.053, -0.012, 0.020	0.055, -0.013, 0.021
$\varphi_{R_2} = (F_{R_2})_N$	-0.093, 0.023, -0.035	-0.052, 0.019, -0.017	-0.072, 0.021, -0.025
$\varphi_{\alpha_2} = (F_{\alpha_2})_N$	-0.035, -0.002, -0.019	-0.033, -0.001, -0.017	-0.033, -0.002, -0.017
$(\mu, Q) -G_{\mu,\mu} = S$	2.779	2.418	2.549
$-G_{\mu,Q}: S_{R_1} = (F_{R_1})_\mu$	0.171, -0.037, 0.067	0.127, -0.029, 0.049	0.139, -0.033, 0.053
$S_{R_2} = (F_{R_2})_\mu$	-0.260, 0.063, -0.099	-0.127, 0.046, -0.040	-0.182, 0.053, -0.065
$S_{\alpha_1} = (F_{\alpha_1})_\mu$	-0.026, 0.015, -0.005	-0.030, 0.020, -0.005	-0.032, 0.018, -0.007
$S_{\alpha_2} = (F_{\alpha_2})_\mu$	-0.098, -0.006, -0.052	-0.080, -0.002, -0.041	-0.085, -0.004, -0.044
$(N, F) V_{N,N} \equiv \eta^{el}$	0.333, 0.359, 0.355	0.388, 0.412, 0.409	0.362, 0.391, 0.387
$V_{N,F}: f_{R_1} = (R_1)_N$	0.153, -0.033, 0.060	0.181, -0.036, 0.072	0.194, -0.039, 0.077
$f_{R_2} = (R_2)_N$	-0.121, 0.026, -0.048	-0.095, 0.026, -0.034	-0.113, 0.027, -0.043
$f_{\alpha_2} = (\alpha_2)_N$	-0.146, -0.006, -0.076	-0.136, -0.007, -0.071	-0.131, -0.007, -0.069
$f_{\alpha_3} = (\alpha_3)_N$	-0.042, 0.014, -0.014	-0.192, 0.037, -0.078	-0.217, 0.038, -0.089
$f_{\alpha_4} = (\alpha_4)_N$	0.032, 0.005, 0.019	-0.115, 0.021, -0.047	-0.145, 0.025, -0.060
$f_{\delta_1} = (\delta_1)_N$	0.000, 0.000, 0.000	0.124, -0.012, 0.056	0.223, -0.024, 0.099
$f_{\delta_2} = (\delta_2)_N$	0.000, 0.000, 0.000	0.699, -0.053, 0.323	1.343, -0.136, 0.604
$f_{\delta_3} = (\delta_3)_N$	0.000, 0.000, 0.000	0.862, -0.097, 0.382	1.639, -0.186, 0.727
$(\mu, F) -S_{\mu,\mu} \equiv S^{el}$	3.000, 2.789, 2.815	2.577, 2.427, 2.446	2.766, 2.559, 2.585
$S_{\mu,F}: S_{R_1} = (R_1)_\mu$	0.458, -0.092, 0.169	0.466, -0.089, 0.176	0.535, -0.099, 0.200
$S_{R_2} = (R_2)_\mu$	-0.364, 0.072, -0.134	-0.245, 0.064, -0.084	-0.313, 0.068, -0.112
$S_{R_3} = (R_3)_\mu$	0.063, -0.023, 0.018	0.040, -0.019, 0.009	0.037, -0.020, 0.007
$S_{R_4} = (R_4)_\mu$	-0.038, -0.001, -0.018	-0.002, 0.006, 0.002	0.001, 0.001, 0.001
$S_{R_5} = (R_5)_\mu$	-0.047, 0.041, -0.001	-0.004, 0.050, 0.023	0.000, 0.041, 0.021
$S_{\alpha_1} = (\alpha_1)_\mu$	0.048, 0.043, 0.044	0.003, 0.057, 0.031	0.000, 0.052, 0.026
$S_{\alpha_2} = (\alpha_2)_\mu$	-0.437, -0.017, -0.214	-0.350, -0.017, -0.174	-0.362, -0.019, -0.179
$S_{\alpha_3} = (\alpha_3)_\mu$	-0.125, 0.040, -0.038	-0.496, 0.090, -0.190	-0.601, 0.098, -0.231
$S_{\alpha_4} = (\alpha_4)_\mu$	0.097, 0.014, 0.053	-0.297, 0.052, -0.115	-0.401, 0.064, -0.155
$S_{\delta_1} = (\delta_1)_\mu$	0.000, 0.000, 0.000	0.319, -0.029, 0.137	0.616, -0.061, 0.257
$S_{\delta_2} = (\delta_2)_\mu$	0.000, 0.000, 0.000	1.802, -0.129, 0.790	3.715, -0.347, 1.561
$S_{\delta_3} = (\delta_3)_\mu$	0.000, 0.000, 0.000	2.221, -0.236, 0.935	4.532, -0.475, 1.879

hardness and softness, both in the geometrically rigid and relaxed representations. Examining the remaining GFF data also reveals that these three levels of treating the Coulomb correlation give rise to a generally consistent signs of geometrical responses per unit inflow of electrons from the reservoir (environment). For example, within the $\Delta N = -1$ estimate of NFF all three methods predict simultaneous lengthening of N—C bond and shortening of C—O bond, and an accompanying decreases in NCH_f and CNH_c bond angles in such an electronic displacement. For such (electron-donating) NFF measure the HF and correlated theories are seen to predict different response in the CNH_t angle. The same physical interpretation follows from the corresponding geometric softnesses of the (μ, \mathbf{F}) -representation in Table 10, since raising the chemical-potential level of the system reservoir generates the electron inflow to the open molecule. The additional softnesses in the (μ, \mathbf{F}) -representation, compared to the GFF entries reported for the (N, \mathbf{F}) -representation, reveal that this increase in the number of electrons generates, for the NFF from $\Delta N = -1$, a lengthening of C—H_f bond and a shortening of two N—H bonds, as well as an increase in NCO angle. These structural responses agree with the predicted responses in geometrical forces, which follow a given electronic displacement in the closed and open molecular systems. They are measured by the NFF ϕ and geometric softnesses \mathbf{s} of the (N, \mathbf{Q}) - and (μ, \mathbf{Q}) -representations, respectively.

It follows from Table 11 that an elongation of the central N—C bond in the externally closed formamide lowers its chemical potential. Indeed, the simple MO diagram for formamide suggests that the doubly occupied HOMO represents the non-bonding π orbital, which roughly consists of the antibonding combination of the $2p_\pi$ atomic orbitals on the nitrogen and oxygen atoms. Thus, lengthening the central bond diminishes this antibinding effect, thus lowering the HOMO level, which marks the system chemical potential. The most important, electron-correlated $\{(N)_{s,\mu}\}$ -comlicants reported in the table reveal, e.g., that for the $\Delta N = -1$ estimate of NFF a lengthening of the central bond and an increase in the dihedral angle of the formyl hydrogen generate an inflow of electrons from the system environment, while the outflow of electrons is predicted, when H_cNC bond-angle is increased.

Finally, let us briefly examine the most important, purely geometric compliant data in Table 11 for the \mathbf{F} -representation. They again reveal the planar-preference in the HF approximation, as witnessed by the vanishing compliants coupling the dihedral angles with the remaining geometrical coordinates. A comparison between quantum-chemical predictions of the MEC reflecting couplings between bond-angles and distances reveals a strong electron-correlation component in $(\alpha_3)_{R_1}$ and $(R_1)_{\alpha_3}$ indices and in practically all couplings between dihedral angles, especially those determining the positions of H_f hydrogen of the CHO group, and the H_t or H_c atoms in the NH₂ group. These results indicate that an out-of-plane bending in one group generates the strong out-of-plane geometrical response in the other group. These couplings are seen to exhibit relatively strong differences between predictions resulting from the two electron-correlated methods. The opening of the in-plane bond angles is also seen to generate the non-planar distortion of the molecule, as indeed expected from an accompanying displacement in the heavy-atom hybridizations, from sp^2 towards sp^3 . A similar geometry relaxation accompanies a lengthening of the central bond, which is seen to diminish the H_cNC angle.

Table 11 The most important compliants for formamide

Repr.	Derivative	HF	MP2	CISD
F	$(\alpha_3)_{R_1}$	-0.031	-0.346	-0.410
	$(\delta_1)_{R_1}$	0.000	0.296	0.503
	$(\delta_2)_{R_1}$	0.000	1.517	2.937
	$(\delta_3)_{R_1}$	0.000	1.784	3.531
	$(R_1)_{\alpha_3}$	-0.012	-0.099	-0.114
	$(\delta_1)_{\alpha_3}$	0.000	-0.271	-0.439
	$(\delta_2)_{\alpha_3}$	0.000	-1.403	-2.577
	$(\delta_3)_{\alpha_3}$	0.000	-1.839	-3.206
	$(R_1)_{\delta_1}$	0.000	0.053	0.077
	$(\alpha_3)_{\delta_1}$	0.000	-0.168	-0.241
	$(\delta_2)_{\delta_1}$	1.331	1.148	2.143
	$(\delta_3)_{\delta_1}$	0.885	0.663	2.006
	$(R_1)_{\delta_2}$	0.000	0.047	0.036
	$(\alpha_3)_{\delta_2}$	0.000	-0.151	-0.115
	$(\delta_1)_{\delta_2}$	0.154	0.199	0.174
	$(\delta_3)_{\delta_2}$	0.851	0.712	1.011
	$(R_1)_{\delta_3}$	0.000	0.042	0.031
	$(\alpha_3)_{\delta_3}$	0.000	-0.151	-0.102
	$(\delta_1)_{\delta_3}$	0.073	0.088	0.116
	$(\delta_2)_{\delta_3}$	0.606	0.542	0.718
(μ, Q)	$(N)_{F_{R_1}, \mu}$	-0.334, 0.072, -0.128	-0.275, 0.062, -0.105	-0.284, 0.066, -0.107
	$(N)_{F_{\alpha_3}, \mu}$	0.089, -0.032, 0.028	0.078, -0.045, 0.017	0.076, -0.040, 0.018
	$(N)_{F_{\delta_1}, \mu}$	0.000, 0.000, 0.000	0.027, 0.007, 0.017	0.016, 0.005, 0.010
	$(N)_{F_{\delta_2}, \mu}$	0.000, 0.000, 0.000	-0.290, -0.087, -0.189	-0.229, -0.066, -0.148
	$(N)_{F_{\delta_3}, \mu}$	0.000, 0.000, 0.000	-0.443, -0.015, -0.229	-0.404, -0.004, -0.204
(N, F)	$(\mu)_{R_1, N}$	-0.030	-0.030	-0.033
(μ, F)	$(N)_{R_1, \mu}$	0.220, -0.046, 0.083	0.185, -0.036, 0.072	0.215, -0.041, 0.084
	$(N)_{\alpha_3, \mu}$	-0.023, 0.008, -0.007	-0.057, 0.011, -0.022	-0.069, 0.011, -0.027
	$(N)_{\delta_1, \mu}$	0.000, 0.000, 0.000	0.023, -0.002, 0.010	0.039, -0.004, 0.016

The derivative quantities the magnitudes of which, in all estimates, are below the assumed threshold value $\varepsilon = 0.03$ have been removed (see Table 10 for the NFF, GFF, and geometric softness data)

8 Conclusion

All chemical or conformational changes involve both nuclear displacements and the concomitant electron redistributions. By the Hohenberg–Kohn theorem of DFT the non-degenerate ground-state electron density of a molecule is in one-to-one correspondence with the underlying external potential due to the system nuclei. In a given stage of the system displacement, depending on what is considered as “perturbation” and what as the equilibrium “response” to it, the EF or the EP approaches can be adopted. In this work, we have determined numerical values of alternative quantities describing molecular responses to both electronic and nuclear perturbations, within the Legendre-transformed representations defining the EP and EF perspectives on molecular structure. Basic derivative quantities and relations have been summarized for both the externally closed and open molecular systems. The so called geometrical representation, in which the nuclear coordinates \mathbf{Q} replace the external potential $v(\mathbf{r}; \mathbf{Q})$ due to nuclei in the list of the system state-parameters, has been used to determine the molecular compliants, which explicitly take into account a subtle coupling between the ground-state electron distribution and the system geometry within the Born–Oppenheimer approximation. Specific quantities reflecting the interaction between the geometrical and electronic structures of molecular systems, and components of the MEC have been generated for representative polyatomic molecules.

The relaxed (compliance) quantities of both the electronic and/or nuclear origin measure the generalized “softnesses” of molecules, which complement the corresponding “hardness” data. Indeed, the electronic softness (electronically relaxed, defined for the rigid-geometry \mathbf{Q} of an open system) and the purely nuclear compliants (geometrically relaxed, defined for closed systems, at constant N) are examples of such complementary quantities to the more familiar electronic hardness and the nuclear force constant descriptors, respectively. This *decoupled* treatment neglects the mutual interaction between the electronic (N) and nuclear (\mathbf{Q}) degrees-of-freedom or their partial energy conjugates, the electronic chemical potential μ , attributed to an external electron reservoir, and the forces \mathbf{F} acting on the system nuclei, respectively.

This coupling between the electronic and geometrical structures of molecular systems is embodied in the potential energy surface of the adiabatic approximation. In the present development both the molecular compliants reflecting the electronic and/or nuclear adjustments have been determined in the *coupled* treatment of the generalized linear responses of molecular systems, which simultaneously admits the electronic and nuclear relaxation of a molecule. In the principal (N , \mathbf{Q})-representation this interaction is measured by the NFF. Together with the electronic hardness and geometric Hessian it defines the generalized matrix of the system electronic-nuclear “force” constants, by the partial or total inversion of which all the molecular compliance data are determined. Such a coupled description of these complementary aspects of the molecular structure forms the *complete* treatment of the adiabatic linear responses in molecules, which address alternative scenarios in the theory of chemical reactivity. For example, the MEC reflecting the electronic-nuclear interaction provide a semi-quantitative measure of responses in quantities describing one aspect of the molecular structure, per unit displacement in quantities describing the other aspect. In the present numerical calculations the N -derivatives have been estimated by the finite differences,

while the Q -derivatives have been calculated analytically by standard MO methods of quantum chemistry.

We have examined this electronic-nuclear interaction in some detail by comparing the corresponding rigid and relaxed hardness/softness and FF data. Among others, these compliants reflect the influence of the nuclear relaxation on the system electronic hardnesses and softnesses, and the effect of the electronic relaxation on the nuclear force constants and vibration compliance descriptors. Of particular importance are the components of MEC, which provide the ground-state “matching” relations between the hypothetical perturbations of molecular systems and their conjugated equilibrium responses. This should allow one to diagnose the electronic and/or nuclear perturbation, which is the most efficient in facilitating the chemical reaction or conformational change of interest. Such applications of this coupled electronic-nuclear treatment of reactants will be the subject of future investigations.

Acknowledgement Generous allocation of computer time in the Academic Computer Center ACK CYFRONET AGH in Cracow (Grant MNiSW/SGI3700/UJ/135/2006) is gratefully acknowledged.

References

1. R.G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989); P.K. Chattaraj, R.G. Parr, *Structure and Bonding* **80**, 11 (1993)
2. P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* **103**, 1793 (2003)
3. R.F. Nalewajski, J. Korchowiec, *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity* (World-Scientific, Singapore, 1997)
4. R.F. Nalewajski, *Information Theory of Molecular Systems* (Elsevier, Amsterdam, 2006)
5. R.F. Nalewajski, in *Reviews of Modern Quantum Chemistry: A Celebration of the Contributions of Robert G. Parr*, Vol. II., ed. by K.D. Sen (World Scientific, Singapore, 2002), p. 1071
6. R.F. Nalewajski, *Structure and Bonding* **80**, 115 (1993); in *Developments in the Theory of Chemical Reactivity and Heterogeneous Catalysis*, ed. by W.M. Mortier, R.A. Schoonheydt (Research Signpost, Trivandrum, 1997), p.135; *Adv. Quantum Chem.* **43**, 119 (2003)
7. R.F. Nalewajski, J. Korchowiec, A. Michalak, *Topics in Current Chemistry* **183**, 25 (1996)
8. M.H. Cohen, *Topics in Current Chemistry* **183**, 143 (1996)
9. R.F. Nalewajski, in *Proceedings of the NATO ASI on Density Functional Theory*, ed. by E.K.U. Gross, R.M. Dreizler (Plenum Press, New York, 1995), p. 339
10. R.F. Nalewajski, A. Michalak, *Int. J. Quantum Chem.* **56**, 603 (1995); *J. Phys. Chem.* **100**, 20076 (1996); *J. Phys. Chem. A* **102**, 636 (1998)
11. R.F. Nalewajski, *Phys. Chem. Chem. Phys.* **1**, 1037 (1999); in *Recent Advances in Density Functional Methods*, Part III., ed. by V. Barone, A. Bencini, P. Fantucci (World Scientific, Singapore, 2002), p. 257; *Computers Chem.* **24**, 243 (2000); R.F. Nalewajski, O. Sikora, *J. Phys. Chem. A* **104**, 5638 (2000)
12. R.F. Nalewajski, *Adv. Quant. Chem.* **51**, 235 (2006)
13. B.G. Baekelandt, G.O.A. Janssens, H. Toufar, W.J. Mortier, R.A. Schoonheydt, R.F. Nalewajski, *J. Phys. Chem.* **99**, 9784 (1995); G.O.A. Janssens, W.J. Mortier, R.A. Schoonheydt, in *Developments in the Theory of Chemical Reactivity and Heterogeneous Catalysis*, ed. by W.M. Mortier, R.A. Schoonheydt (Research Signpost, Trivandrum, 1997), p. 81
14. K. Fukui, *Theory of Orientation and Stereoselection* (Springer-Verlag, Berlin, 1975); *Science* **218**, 747 (1987); H. Fujimoto, K. Fukui, in *Chemical Reactivity and Reaction Paths*, ed. by G. Klopman (Wiley-Interscience, New York, 1974), p. 23
15. Klopman, G., *J. Am. Chem. Soc.* **90**, 223 (1968); G. Klopman, in *Chemical Reactivity and Reaction Paths*, ed. by G. Klopman (Wiley-Interscience, New York, 1974), p. 55
16. R.F. Nalewajski, *J. Am. Chem. Soc.* **106**, 944 (1984)
17. P.W. Ayers, R.G. Parr, *J. Am. Chem. Soc.* **122**, 2010 (2000); *J. Am. Chem. Soc.* **123**, 2007 (2001)

18. V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions* (Plenum, New York, 1978)
19. J.C. Decius, *J. Chem. Phys.* **38**, 241 (1963); L.H. Jones, R.R. Ryan, *J. Chem. Phys.* **52**, 2003 (1970)
20. B.I. Swanson, *J. Am. Chem. Soc.* **98**, 3067 (1976); B.I. Swanson, S.K. Satija, *J. Am. Chem. Soc.* **99**, 987 (1977)
21. H. Nakatsuji, *J. Am. Chem. Soc.* **95**, 345 (1973); *J. Am. Chem. Soc.* **96**, 24 (1974); *J. Am. Chem. Soc.* **96**, 30 (1974)
22. P. Hohenberg, W. Kohn, *Phys. Rev.* **136B**, 864 (1964); W. Kohn, L.J. Sham, *Phys. Rev.* **140A**, 1133 (1965)
23. R.M. Dreizler, E.K.U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990)
24. R.F. Nalewajski (ed.), *Density Functional Theory I-IV; Topics in Current Chemistry* vol. 180–183 (Springer-Verlag, Berlin, 1996)
25. R.T. Sanderson, *Science* **114**, 670 (1951); *Chemical Bonds and Bond Energy*, 2nd edn. (Academic Press, New York, 1976)
26. R.G. Parr, W. Yang, *J. Am. Chem. Soc.* **106**, 4049 (1984); W. Yang, R.G. Parr, *Proc. Natl. Acad. Sci. USA* **82**, 6723 (1985); W. Yang, R.G. Parr, R. Pucci, *J. Chem. Phys.* **81**, 2862 (1984)
27. A. Michalak, F. De Proft, P. Geerlings, R.F. Nalewajski, *J. Phys. Chem. A* **103**, 762 (1999)
28. J. Korchowiec, T. Uchimaru, *J. Phys. Chem. A* **102**, 10167 (1998)
29. M.H. Cohen, M.V. Ganguglia-Pirovano, J. Kurdnovský, *J. Chem. Phys.* **101**, 8988 (1994); *J. Chem. Phys.* **103**, 3543 (1995)
30. H.B. Callen, *Thermodynamics: an Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics* (Wiley, New York, 1962)
31. Gaussian 03, Revision D.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Wallingford CT, 2004