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Electronic–geometric coupling in model reactive system

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Abstract The equilibria in triatomic (collinear) reactive system are examined. The linear-response treatment of adjustments in the molecular electronic and geometrical degrees-of-freedom, determined from the chemical-potential (electronegativity) equalization principle, are predicted using the previously proposed analytical representation of the chemical hardness matrix in atomic resolution. The system relaxation is determined from the joint electronic–nuclear Hessian in the *electron-following* representation, defined by the corresponding second partials of the system Born–Oppenheimer potential. It includes the diagonal blocks of the electronic hardness tensor and geometric force constants, as well as the *off*-diagonal blocks of the nuclear Fukui function indices, which determine the coupling between the molecular electronic and geometrical structures. The latter are explicitly modelled using the canonical hardness tensor of the constituent atoms. This combined treatment explicitly accounts for the mutual coupling between the system charge distribution and its geometry. The molecular compliant descriptors, which determine the system minimum-energy coordinates, can be also generated using the inverse, *electron-preceding* representation.

The atomic units are used throughout the paper, unless explicitly specified otherwise. In the adopted notation **P** denotes the square (or rectangular) matrix, *P* stands for the row or column vector, and *P* represents the scalar quantity.

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1 Introduction

Each molecular process involves coupled displacements in the distribution of the system electrons and the accompanying shifts in positions of its constituent atoms. In chemistry the mutual interaction between the electronic and geometric structures of molecules or reactive systems plays a vital role in diagnosing their behavior in different environments. Therefore, designing adequate descriptors of this coupling and establishing principles for qualitative predictions of its structural and reactivity manifestations constitutes a challenging problem in theoretical chemistry [1–27]. Indeed, the rules governing a subtle interplay between the electronic and geometric degrees-of-freedom in molecular and reactive systems constitute an important part of the structural chemistry and theory of chemical reactivity, e.g., [28–36]. They reflect effects of the mutual interaction between an internal *polarization* (P) and/or external *charge transfer* (CT) on one side, and the concomitant geometrical relaxation on the other side, e.g., in molecular subsystems of the *donor-acceptor* (DA) complexes.

The *Gutmann rules* [36] of structural chemistry and their extension provided by the so called *Mapping Relations* [5,6,12–18,21–26] formulated within the *Charge-Sensitivity Analysis* (CSA) of molecular systems [5,6,9–12] allow for a qualitative or *semi*-quantitative predictions of such relaxational effects, respectively. Another example is provided by the *Minimum-Energy-Coordinates* (MEC) [12–26] of the compliant approach in CSA [5,6,12], in the spirit of the related treatment of nuclear vibrations [37–40]. All these descriptors allow one to diagnose the molecular responses to hypothetical electronic or nuclear displacements (perturbations). The thermodynamic-like approach using the Legendre-transformed representations [5,6,12–16,18–21] provides a versatile theoretical framework for describing diverse equilibrium states of molecules in different chemical environments.

The internal degrees-of-freedom of molecular systems are of either electronic or nuclear (geometric) origins. In the *Born–Oppenheimer* (BO) approximation the equilibrium (ground) state of the externally-*closed* molecule is specified by its overall (integer) number of electrons N (electronic variable) and the parametric nuclear coordinates $\mathbf{R} = \{\boldsymbol{R}_\alpha\}$. Alternatively, any equivalent set of internal coordinates $\boldsymbol{Q}$ can be used to define the external potential $v(\boldsymbol{r}; \boldsymbol{Q})$ due to the nuclei in their fixed positions. The state parameters $(N, \boldsymbol{Q})$ uniquely identify the system (Coulombic) Hamiltonian

$$\hat{H}(N, v) = \sum_{i=1}^{N} v(\boldsymbol{r}_i; \boldsymbol{Q}) + \hat{F}(N) \equiv \hat{H}(N, \boldsymbol{Q}), \tag{1}$$

where the operator $\hat{F}(N)$ corresponds to the sum of the electron kinetic and repulsion energies, the molecular ground state $\Psi[N, v] = \Psi(N, \boldsymbol{Q})$, the electronic energy

$$E[N, v] = \langle \Psi[N, v]|\hat{H}(N, v)|\Psi[N, v]\rangle = E(N, \boldsymbol{Q}), \tag{2}$$

and the BO potential including the nuclear repulsion energy $V_{nn}(\boldsymbol{Q})$:

$$W(N, \boldsymbol{Q}) = E(N, \boldsymbol{Q}) + V_{nn}(\boldsymbol{Q}). \tag{3}$$

One similarly specifies the equilibrium state of an externally-*open* molecular system, which is characterized by the average (fractional) number of electrons. Such systems are considered to be hypothetically coupled to an external electron reservoir, which fixes the system chemical potential $\mu = \partial E(N, \boldsymbol{Q})/\partial N$. In the geometrically-rigid molecule of the adiabatic treatment this equilibrium state is then identified by the modified set of state-parameters $(\mu, \boldsymbol{Q})$. The corresponding equilibrium (relaxed) geometries exhibit the vanishing forces acting on the nuclear frame, $\boldsymbol{F} = -[\partial W(N, \boldsymbol{Q})/\partial \boldsymbol{Q}]^T = \boldsymbol{0}$, in the associated sets of the state-variables $(N, \boldsymbol{F})$ or $(\mu, \boldsymbol{F})$ describing the geometrically-relaxed, electronically closed and open systems, respectively. The four admissible representations of molecular states [13–16],

$$(N, \boldsymbol{Q}), (\mu, \boldsymbol{Q}), (N, \boldsymbol{F}), \text{ and } (\mu, \boldsymbol{F}), \tag{4}$$

describe all alternative scenarios encountered in the theory of chemical reactivity. Indeed, the closed reactants, geometry—rigid or—relaxed, in the opening stage of a reaction in the gas phase, can be indexed by the derivative properties defined in the $(N, \boldsymbol{Q})$ and $(N, \boldsymbol{F})$ approaches, while the properties of the chemisorbed (externally-open) reactants of the heterogeneous catalysis or the chemical species in solution can be characterized using descriptors generated within the $(\mu, \boldsymbol{Q})$ and $(\mu, \boldsymbol{F})$ theoretical frameworks.

To summarize, the overall number of electrons, N, and its energy conjugate, the chemical potential μ, determine the *electronic* state-variables in the externally closed and open molecular systems, respectively. Accordingly, the internal coordinates $\boldsymbol{Q}$ of the nuclear frame or their energy-conjugates, the (vanishing) forces $\boldsymbol{F}$ acting on the nuclei, describe the rigid or relaxed molecular geometries. This combined linear-response treatment of the electronic and geometric state-variables [13–26] fully accounts for their mutual interactions embodied in the generalized electronic–nuclear Hessian or its inverse grouping the associated molecular complaints. The relevant coupling terms are represented by the *off*-diagonal elements in such generalized "force constant" tensors for admissible selections of the system state-parameters, which uniquely specify the equilibria in the externally closed or open molecules, for both rigid and relaxed system geometries.

This theoretical framework unites the so called *Electron-Following* (EF) and *Electron-Preceding* (EP) perspectives [41–43] on molecular changes. The former is in the spirit of the BO approximation, in which the nuclear frame determines the equilibrium distributions of electrons, while the latter expresses the essence of the Hellmann-Feynman theorem, that electronic distribution determines the forces on nuclei, thus determining conditions for adjustments in molecular geometry. Therefore, in the EF approach the electron distribution responds to geometrical (nuclear) perturbations, displacements in nuclear positions, while in the EP treatment the system geometrical relaxation follows a hypothetical manipulation of the system electronic structure (bonding pattern). The EP and EF perspectives are covered by the *canonical* softness and hardness representations, respectively. The former uses the external potential variable thus corresponding to the $[(N, \boldsymbol{Q}), (\mu, \boldsymbol{Q})$ or $(N, v), (\mu, v)]$ parameters of state, while the latter is linked to inverse specifications of the independent state variables $[(N, \boldsymbol{F}), (\mu, \boldsymbol{F})]$ or $[(N, \rho), (\mu, \rho)]$, where denotes the system electron density [13,16].

Such generalized "polarizabilities" of molecules are generated within CSA of molecular systems [5,6]. They provide reliable criteria in reactivity theories [1–27] based upon the modern *Density-Functional Theory* (DFT) [1,2,44–47]. In the EF outlook the adjustment $\Delta\rho$ in the electron distribution represents the unconstrained (dependent) *local* state-variable of the molecular system in question: $\Delta\rho = \Delta\rho[N, \Delta v] = \Delta\rho(N, \Delta\boldsymbol{Q})$ or $\Delta\rho = \Delta\rho[\mu, \Delta v] = \Delta\rho(\mu, \Delta\boldsymbol{Q})$. In other words, the electron density responds ("follows") the displacements $\Delta\boldsymbol{Q}$ of the system nuclei. This selection of the dependent (ρ) and independent (v) local state-variables has been classified as the *softness representation* of molecular states [7,13,14], since it generates the chemical-softness kernel $\sigma(\boldsymbol{r}, \boldsymbol{r}') = -\delta\rho(\boldsymbol{r}')/\delta u(\boldsymbol{r})$ of reactivity theory, where the relative external potential $u(\boldsymbol{r}) = v(\boldsymbol{r}) - \mu$.

These roles are reversed in the EP perspective of DFT, which can be referred to as the complementary *hardness representation* [7,13,14] defining another key concept of the electronic-structure and reactivity theories—the chemical-hardness kernel $\eta(\boldsymbol{r}', \boldsymbol{r}) = -\delta u(\boldsymbol{r})/\delta\rho(\boldsymbol{r}')$, the inverse of $\sigma(\boldsymbol{r}, \boldsymbol{r}')$. In the EP approach the displacement in the system electron density, $\Delta\rho$, effected either by the controlled change in the system number of electrons $\Delta N = \int \Delta\rho d\boldsymbol{r}$ or the displacement in the chemical potential of the external reservoir, $\Delta\rho = \Delta\rho(\Delta N, \boldsymbol{F} = \boldsymbol{0})$ or $\Delta\rho = \Delta\rho(\Delta\mu, \boldsymbol{F} = \boldsymbol{0})$, respectively, is now 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: $\Delta v = \Delta v[\Delta\rho]$. The shifts in the electron distribution thus "precede" the movements of nuclei, $\Delta\boldsymbol{Q} = \Delta\boldsymbol{Q}(\Delta N, \boldsymbol{F} = \boldsymbol{0})$ or $\Delta\boldsymbol{Q} = \Delta\boldsymbol{Q}(\Delta\mu, \boldsymbol{F} = \boldsymbol{0})$, in the spirit of the Hellmann-Feynman (force) theorem. This way of approaching molecular displacements 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., the breaking/forming of specific bonds in the molecule.

The admissible use of either the electronic or nuclear primary causes of chemical reactions can be thus facilitated by using the generalized development which unites the electronic and nuclear degrees of freedom of molecular or reactive systems in a single theoretical framework. In fact one requires both these perspectives to tackle diverse issues in the theory of electronic structure of molecules and of 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 a more complete theory of chemical reactivity. The emergence of the modern DFT has provided the EP perspective and generated novel treatments of many classical problems in chemistry. It offers an alternative point of view on the physical/chemical properties and processes involving atomic, molecular and reactive systems. This approach is very much in spirit of the Sanderson's [48,49] Electronegativity-Equalization description of the equilibrium distribution of electrons in molecular systems.

Examples of reactivity indices quantifying the electronic–geometric coupling are provided by the electronic *Fukui function* (FF) [1–6,50–54] and its nuclear analog (NFF) [13–21,27,55,56]. These molecular descriptors have been widely discussed in previous works [13–16] and their use as reactivity indices has also been suggested [14]. Illustrative numerical data of these derivative properties for selected polyatomic

molecules have been reported [14–16] and interpreted as manifestations of the LeChâtelier–Braun principle of thermodynamics [57].

In predicting the behaviour of reactants the sybsystem responses can be applied indirectly—by using the respective sets of differential charge sensitivities, or directly—in terms of the relevant geometric *Minimum Energy Coordinates* (MEC) [13–16]. For example, the second derivatives of the molecular electronic energy in the $(N, \boldsymbol{Q})$ representation reflect responses in the system chemical potential and geometric forces to displacements in these canonical state-variables, while components of the fully relaxed MEC defined in the inverted (compliance) representation $(\mu, \boldsymbol{F})$ determine the molecular compliants measuring the equilibrium responses in the effective oxidation state and geometry of the chemisorbed reactants per unit displacements in the electronic chemical potential of the catalyst or in forces behind molecular deformations. This versatility should facilitate an ultimate identification of the crucial electronic/geometrical requirements for the desired reaction pathway, thus aiding a search for the most effective catalyst of the surface reaction.

Typical applications of the DFT-based hardness/softness (FF) descriptors as reactivity criteria are limited to rather simplified *single*-reactant scenarios [1–4], by probing regional preferences of a molecular reactant to an attack by the fixed (small) approaching agent. In such applications the charge sensitivities of the attacked molecule are used, with some success, as reactivity indicators of the preferred site to be attacked. In a more realistic *two*-reactant approach [5,6] one takes into account response properties of both reactants in the bimolecular reactive system, recognizing differences in their matching/coupling for alternative mutual orientations of two molecular reactants. The present work constitutes a first attempt to use this more adequate treatment in describing the simplest atom-exchange reaction in a triatomic (collinear) collision complex.

In this work we derive expressions for quantities measuring the electron-nuclear coupling in the model atom-exchange reaction involving a concerted *bond-breaking-bond-forming* processes in the (collinear) reactive system

$$A\!-\!B + C \rightarrow [A\text{----}B\text{------}C]^{\ddagger} \rightarrow A + B\!-\!C. \tag{5}$$
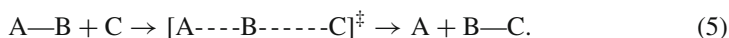
The combined approach to the equilibrium states in this simple reactive system as a whole and in diatomic reactants/products requires adequate analytical representation of the hardness and NFF derivatives of the molecular energy [13–16]. In this work, which examines modelling possibilities of such descriptors, we shall develop explicit expressions for these quantities in the triatomic system of interest.

The resulting theoretical model of this prototype reactive system should allow one to probe several electronic–nuclear coupling processes as functions of the reaction progress variable, say $R \equiv R_{BC}$, e.g., between the equilibrium $A \rightarrow B$ polarization $q = \Delta N_A = N_A - N_A^0 = -\Delta N_B$, where N_i^0 stands for the electron population of the isolated atom $i = A, B$, and the substrate bond length $r \equiv R_{AB}$, or between the equilibrium amount of $AB \rightarrow C$ CT between both reactants, $Q = \Delta N_C = N_C - N_C^0 = -\Delta N_{AB}$, and the diatomic bond length r or the inter-reactant separation R. All these interactions between electronic and geometric aspects of the molecular structure can be approached using both the EP and EF perspectives. In the

former the relations between the system perturbations and responses are determined by the combined electronic/nuclear Hessian, while in the latter this transformation is effected using the generalized softness matrix defined by Hessian's inverse which combines the associated compliants.

The present work mainly focuses on establishing analytical expressions for the key NFF descriptors of this model collision complex, leaving the numerical calculations to future work on the subject. In modeling these crucial coupling quantities we shall neglect the contributions to chemical potentials of bonded atoms due to a change in their effective external potentials introduced by the presence of the remaining *Atoms-in-Molecules* (AIM). In such an approach the geometric influence on charge sensitivities originates solely from the inter-nuclear dependence of the AIM coupling hardnesses and the electron flows they effect at the given stage of the reaction.

2 Derivative descriptors of the collinear reactive system

The molecular complaints, can be directly used as the *one*-reactant reactivity criteria, which allow one to diagnose the preferred attacks by small, prototype agents, when this molecule is a part of the reactive system. Combinations of these molecular descriptors can be also applied in the *inter*-reactant *decoupled* approach to DA complexes, when the relative acidic/basic character of the *donor* (D) and *acceptor* (A) subsystems is known beforehand. Indeed, the $\Delta N_A > 0$ and $\Delta N_D < 0$ displacements of the two reactants are predetermined by their electronegativity differences, and so are the associated responses in the chemical potentials to these primary perturbations: $\Delta \mu_A > 0$ and $\Delta \mu_D < 0$. These displacements can be subsequently applied to predict the geometrical changes of the two mutually open reactants, at the CT stage of the reaction, by using the relevant complaints which fully account for the relaxation of the system remaining (unconstrained) degrees of freedom.

However, the outcome of the bimolecular chemical reactions ultimately depends on the electronic/geometrical structure of both reactants, thus calling for a truly *two*-reactant description in reactivity theory. Such a general, *inter*-subsystem *coupled* approach [5–11] can be also envisaged, but the relevant compliant and MEC data would eventually require calculations on the reactive system $\mathcal{R} = [A\text{-}\text{-}\text{-}B]$ as a whole, with the internal coordinates Q now including those specifying the internal geometries of two subsystems and their mutual orientation/separation in the reactive system. In practical implementations of this combined treatment of the electronic and nuclear state-variables one could use as much as possible the *intra*-reactant data generated in calculations on the separate reactants.

The *two*-reactant Hessian now unites the respective blocks of the molecular tensors introduced in previous, molecular development [13–16]. This principal electronic–nuclear Hessian of the whole reactive system includes as diagonal blocks the hardnesses of the two reactants in $\mathcal{R}$,

$$\eta_{X,Y} = \partial^2 E(N_A, N_B, \boldsymbol{Q})/\partial N_X \partial N_Y = \partial \mu_Y(N_A, N_B, \boldsymbol{Q})/\partial N_X = \eta_{Y,X}$$
$$= \partial \mu_X(N_A, N_B, \boldsymbol{Q})/\partial N_Y \quad X = A, B; \quad Y = A, B, \tag{6}$$

and the geometric Hessian of the second partials of the BO potential with respect to nuclear degrees-of-freedom:

$$\mathbf{H} = \{\partial^2 W(N_A, N_B, \boldsymbol{Q})/\partial \boldsymbol{Q} \partial \boldsymbol{Q}\} = -\partial \boldsymbol{F}(N_A, N_B, \boldsymbol{Q})/\partial \boldsymbol{Q}, \qquad (7)$$

$$\mathbf{H}(A\text{---}B) = \begin{bmatrix} \eta_A & \eta_{A,B} & -\boldsymbol{\varphi}_A^T \\ \eta_{B,A} & \eta_B & -\boldsymbol{\varphi}_B^T \\ -\boldsymbol{\varphi}_A & -\boldsymbol{\varphi}_B & \mathbf{H} \end{bmatrix} \equiv \begin{bmatrix} \boldsymbol{\eta} & -\boldsymbol{\varphi}^T \\ -\boldsymbol{\varphi} & \mathbf{H} \end{bmatrix}. \qquad (8)$$

Here, the rigid-geometry hardness matrix $\boldsymbol{\eta}$ reflects mutual couplings between electronic (populational) state-variables, with the *off*-diagonal hardnesses ($A \neq B$), equal by the cross-differentiation Maxwell relation of Eq. (6),

$$\eta_{A,B} = \partial \mu_B(N_A, N_B, \boldsymbol{Q})/\partial N_A = \partial \mu_A(N_A, N_B, \boldsymbol{Q})/\partial N_B = \eta_{B,A}$$
$$= \partial^2 E(N_A, N_B, \boldsymbol{Q})/\partial N_A \partial N_B, \qquad (9)$$

measuring the rigid-geometry responses in the chemical potential of one reactant per unit shift in the number of electrons on the other reactant. The rectangular matrix $\boldsymbol{\varphi} = [\boldsymbol{\varphi}_A, \boldsymbol{\varphi}_B]$ of the NFF descriptors,

$$\boldsymbol{\varphi}_X = -\partial^2 W(N_A, N_B, \boldsymbol{Q})/\partial N_X \partial \boldsymbol{Q} = -\partial \mu_X(N_A, N_B, \boldsymbol{Q})/\partial \boldsymbol{Q}$$
$$= [\partial \boldsymbol{F}(N_A, N_B, \boldsymbol{Q})/\partial N_X]^T, \quad X = A, B, \qquad (10)$$

determines the interaction between electronic and geometric degrees of freedom in $\mathcal{R}$.

Relations between the perturbations in the basic state variables ($\Delta N_A, \Delta N_B, \Delta \boldsymbol{Q}$) and the coupled responses of their energy ("intensive") conjugates ($\Delta \mu_A, \Delta \mu_B, -\Delta \boldsymbol{F}$) in the canonical geometric representation ($N_A, N_B, \boldsymbol{Q}$) then read:

$$(\Delta \mu_A, \Delta \mu_B, -\Delta \boldsymbol{F}) \equiv (\Delta \boldsymbol{\mu}, -\Delta \boldsymbol{F}) = (\Delta N_A, \Delta N_B, \Delta \boldsymbol{Q})\mathbf{H}(A\text{---}B)$$
$$\equiv (\Delta \boldsymbol{N}, \Delta \boldsymbol{Q})\mathbf{H}(A\text{---}B). \qquad (11)$$

The fully inverted compliance matrix, $\mathbf{S}(A\text{---}B) = \mathbf{H}(A\text{---}B)^{-1}$ similarly determines the inverse transformation of displacements in "intensities" ($\Delta \boldsymbol{\mu}, \Delta \boldsymbol{F}$) into the associated responses in the canonical electronic/geometrical state parameters ($-\Delta \boldsymbol{N}, \Delta \boldsymbol{Q}$):

$$(-\Delta N_A, -\Delta N_B, \Delta \boldsymbol{Q}) \equiv (-\Delta \boldsymbol{N}, \Delta \boldsymbol{Q}) = (\Delta \mu_A, \Delta \mu_B, \Delta \boldsymbol{F})\mathbf{S}(A\text{---}B)$$
$$\equiv (\Delta \boldsymbol{\mu}, \Delta \boldsymbol{F})\mathbf{S}(A\text{---}B). \qquad (12)$$

In the *two*-reactant resolution this generalized softness matrix exhibits the following
block structure [14]:

$$
\mathbf{S}(A\text{---}B) = \begin{bmatrix}
-\left(\frac{\partial N_A}{\partial \mu_A}\right)_F & -\left(\frac{\partial N_B}{\partial \mu_A}\right)_F & \left(\frac{\partial \mathbf{Q}}{\partial \mu_A}\right)_F \\
-\left(\frac{\partial N_A}{\partial \mu_B}\right)_F & -\left(\frac{\partial N_B}{\partial \mu_B}\right)_F & \left(\frac{\partial \mathbf{Q}}{\partial \mu_B}\right)_F \\
-\left(\frac{\partial N_A}{\partial \mathbf{F}}\right)_\mu & -\left(\frac{\partial N_B}{\partial \mathbf{F}}\right)_\mu & \left(\frac{\partial \mathbf{Q}}{\partial \mathbf{F}}\right)_\mu
\end{bmatrix}
\equiv \begin{bmatrix}
-S_A^{\mathrm{rel}} & -S_{A,B}^{\mathrm{rel}} & \tilde{\mathbf{S}}_A \\
-S_{B,A}^{\mathrm{rel}} & -S_B^{\mathrm{rel}} & \tilde{\mathbf{S}}_B \\
\tilde{\mathbf{S}}_A^T & \tilde{\mathbf{S}}_B^T & \mathbf{G}^{\mathrm{rel}}
\end{bmatrix}
$$

$$
\equiv \begin{bmatrix}
-\mathbf{S}^{\mathrm{rel}} & \tilde{\mathbf{S}} \\
\tilde{\mathbf{S}}^T & \mathbf{G}^{\mathrm{rel}}
\end{bmatrix}. \tag{13}
$$

Here, the geometrically-relaxed softness matrix $\mathbf{S}^{\mathrm{rel}}$ groups the equilibrium, fully
relaxed responses in the subsystem numbers of electrons, following the displacements
in the chemical potentials of their (separate) electron reservoirs,

$$
S_X^{\mathrm{rel}} = -\partial N_X(\mu_A, \mu_B, \mathbf{F})/\partial \mu_X, \qquad S_{X,Y}^{\mathrm{rel}} = -\partial N_Y(\mu_A, \mu_B, \mathbf{F})/\partial \mu_X
$$
$$
X, Y = (A, B); \tag{14}
$$

and the relaxed geometric softness matrix $\tilde{\mathbf{S}} = \begin{bmatrix} \tilde{\mathbf{S}}_A \\ \tilde{\mathbf{S}}_B \end{bmatrix}$ groups the related adjustments
in the geometry of the reactive system,

$$
\tilde{\mathbf{S}}_X = \partial \mathbf{Q}(\mu_A, \mu_B, \mathbf{F})/\partial \mu_X = -[\partial N_X(\mu_A, \mu_B, \mathbf{F})/\partial \mathbf{F}_X]^T. \tag{15}
$$

The (relaxed) geometric compliant matrix,

$$
\mathbf{G}^{\mathrm{rel}} = \partial \mathbf{Q}(\mu_A, \mu_B, \mathbf{F})/\partial \mathbf{F}, \tag{16}
$$

similarly collects responses in the internal geometric coordinates to displacements in
forces, of the externally open reactants coupled to their (separate) electron reservoirs.
Obviously, the partly inverted Legendre-transformed representations would similarly
generate descriptors of the partially (electronically or geometrically) relaxed reactive
systems [13–16].

There are two independent geometrical degrees-of-freedom $\mathbf{Q} = (r, R)$ in the col-
linear complex of Eq. (5). The second variable, treated as the *parameter* measuring
the progress of the mutual approach by reactants $A = A - B$ and $B = C$, can be
regarded as the reaction coordinate along the *Minimum-Energy Path* (MEP), for the
fully relaxed reactants in the electronic and internal-geometric degrees-of-freedom. It
can be realistically modelled by the trajectory conserving the overall phenomenolog-
ical "bond-order" of the single bonds being formed and broken, e.g., in the hydrogen
exchange (B = H) reaction AH + C = A + HC,

$$
n_{A,B} + n_{B,C} = 1, \quad n_{X,Y} \to 0 \quad \text{for} \quad R_{X,Y} \to \infty,
$$
$$
n_{X,Y} = 1 \quad \text{for} \quad R_{X,Y} = R_{X,Y}^e, \tag{17}
$$

where $R_{X,Y}^e = R_{X,Y}(n_{X,Y} = 1)$ stands for the equilibrium length of X—Y bond, in the *Bond-Energy-Bond-Order* (BEBO) method [58] using Pauling's logarithmic relation between this bond-order measure and the internuclear distance [59]:

$$R_{X,Y}(n_{X,Y}) = R_{X,Y}(1) - 0.026 \ln n_{X,Y} \quad \text{or}$$
$$R_{X,Y}(n_{X,Y}) - R_{X,Y}(1) \equiv \Delta R_{X,Y}(n_{X,Y}) = -0.026 \ln n_{X,Y}, \qquad (18)$$

predicting an increase $\Delta R_{X,Y}$ (in 10^{-9} m) of the bond length for fractional bond orders $n_{X,Y} < 1$.

Since the collision complex is closed as a whole, there are only two independent electron population variables in the triatomic system: $N = (q, Q)$. For the given value of the reaction coordinate R they respectively measure the *intra*-diatomic polarization $q(R)$ and the *inter*-reactant transfer of electrons $Q(R)$. Thus for the fixed separation R between reactants the list of state-*variables* in the principal geometrical representation in this simple model of a reactive system reads: $[q(R), Q(R), r(R)] = [N(R), r(R)]$. This parametric treatment of the reaction coordinate gives rise to the following combined Hessian of Eq. (8):

$$\mathbf{H}[AB\text{-}\text{-}\text{-}C(R)] \equiv \begin{bmatrix} \eta_q(R) & \eta_{q,Q}(R) & -\varphi_q(R) \\ \eta_{Q,q}(R) & \eta_Q(R) & -\varphi_Q(R) \\ -\varphi_q(R) & -\varphi_Q(R) & k(R) \end{bmatrix}$$
$$\equiv \begin{bmatrix} \boldsymbol{\eta}^{\text{eff.}}(R) & -\boldsymbol{\varphi}^{\text{eff.}}(R)^T \\ -\boldsymbol{\varphi}^{\text{eff.}}(R) & k(R) \end{bmatrix}, \qquad (19)$$

where $k(R) = \partial^2 W[N^{\text{eq.}}, r]/\partial r^2|_R \equiv -\partial F_r[N^{\text{eq.}}, r]/\partial r|_R$ denotes the force constant of the diatomic reactant AB, calculated for the equilibrium charge distribution $N^{\text{eq.}}$. Here, the effective (in situ) hardness matrix associated with these collective charge displacements $N = (q, Q)$,

$$\boldsymbol{\eta}^{\text{eff.}}(R) = \partial^2 E[N, r(R)]/\partial N \partial N\} \equiv -\partial \boldsymbol{\mu}^{\text{eff.}}[N, r(R)]/\partial N, \qquad (20)$$

where $\boldsymbol{\mu}^{\text{eff.}} = (\mu_q = \partial E/\partial q, \mu_Q = \partial E/\partial Q)$ groups the associated chemical potential descriptors.

The effective NFF matrix similarly contains the associated two components:

$$\boldsymbol{\varphi}^{\text{eff.}}(R) = -\partial^2 W[N, r]/\partial r \partial N|_R \equiv -\partial \boldsymbol{\mu}^{\text{eff.}}[N, r]/\partial r|_R = [\partial F_r[N, r(R)]/\partial N]^T$$
$$= [\varphi_q = -\partial \mu_q/\partial r = \partial F_r/\partial q, \quad \varphi_Q = -\partial \mu_Q/\partial r = \partial F_r/\partial Q], \qquad (21)$$

One can use either of the above cross-derivatives to model the bond-length dependence of the two NFF descriptors. However, within reactivity theory the geometric derivative of the chemical potential appears to be more convenient for modeling purposes, since the finite-difference estimate of the geometrical force with respect to the electronic (flow) variables both escapes simple analytical representation and appears computationally forbidding.

It should be realized that the internal flow q in AB determines the in situ chemical potential difference $\mu_q = \mu_A - \mu_B = \mu_{CT}(B \rightarrow A)$, while the second electron transfer Q (internal in ABC) similarly defines the other in situ chemical potential $\mu_Q = \mu_C - \mu_{AB} = \mu_{CT}(AB \rightarrow C)$. These populational "forces" exactly vanish for the equilibrium amounts of CT, when the chemical potentials of the constituent fragments involved are exactly equalized. This *electronic-equilibrium* criterion $\mu_q = \mu_Q = 0$ marks the minimum of the electronic energy with respect to electron flows in the molecular system in question. However, for any point on the MEP of the mutual approach by both reactants, for simplicity assumed as identical with the $R = R_{BC}$ coordinate of the model collision system, one also relaxes the remaining (r) geometrical degrees-of-freedom of the reactive system, which implies $F_r(R) = 0$. Therefore, in the present collinear model system only the geometrical force F_R along R remains unrelaxed for the specified separation between reactants.

To determine effects of the electron-nuclear coupling, which accompany the mutual approach by reactants in this model reactive system, one requires an adequate analytical representation of the R-dependence of elements in the effective condensed matrices of Eqs. (15) and (16). A reference to Eq. (14) also shows that a more realistic approach should also include a dependence of the A—B force constant upon the current position of the approaching atom C, $k(R)$, which can be generated in the BEBO approximation [58]. It is the main objective of the next section to model these dependencies using the relevant *Electronegativity Equalization* (EE) equations and the previously proposed analytical representation [60] of the canonical hardness matrix of AIM, $\boldsymbol{\eta}^{AIM} = \{\eta_{i,j}\}$, modeled by the corresponding tensor of the (valence-shell) electron-repulsion integrals $\{\gamma_{i,j}\}$ from the *semi*-empirical SCF MO theories: $\eta_{i,j} \cong \gamma_{i,j}$.

3 Modelling the electronic and nuclear Fukui functions

In the familiar finite-difference approximation the energy $E_i(N_i)$ of an open atom i is represented as quadratic function of displacements ΔN_i in its number of electrons N_i, or its effective charge $Q_i = Z_i - N_i$, with Z_i standing for the atomic number of the nucleus:

$$E_i(N_i) \cong E_i^0 + (\partial E_i / \partial N_i)|_0 \Delta N_i + 1/2(\partial^2 E_i / \partial N_i^2)|_0 (\Delta N_i)^2$$
$$= E_i^0 + \mu_i^0 \Delta N_i + 1/2\eta_i^0 (\Delta N_i)^2; \tag{22}$$

here the symbol $|_0$ implies that the derivative is taken for the neutral atom, when $N_i = Z_i$. This quadratic (Mulliken) interpolation of the energies of the neutral atom and its singly charged ions then identifies the two atomic derivatives in the preceding equation in terms of the atom ionization potential I_i and its electron affinity A_i:

$$\mu_i^0 = -1/2(A_i + I_i) < 0 \quad \text{and} \quad \eta_i^0 = I_i - A_i > 0. \tag{23}$$

The above Pariser formula for the *one*-center electron-repulsion integral in *semi*-empirical SCF MO theories, $\gamma_{i,i} \approx I_i - A_i$, also provides adequate (diagonal) elements of

the associated AIM hardnesses, $\eta_{i,i} = \eta_i^0 \approx \gamma_{i,i}$, sometimes adjusted for the displaced effective charge of the bonded atom in question in the molecular environment of interest.

The population coupling between a given pair (i, j) of AIM is similarly reflected by the corresponding *off*-diagonal hardness,

$$\eta_{i,j} = \partial^2 E[\{N_k\}, \boldsymbol{Q}]/\partial N_i \partial N_j = \partial \mu_i[\{N_k\}, \boldsymbol{Q}]/\partial N_j$$
$$= \partial \mu_j[\{N_k\}, \boldsymbol{Q}]/\partial N_i = \eta_{j,i}, \tag{24}$$

which was shown elsewhere [60] to be also realistically represented by the valence-shell (*two*-center) electron-repulsion integral of the semiempirical SCF MO theories: $\eta_{i,j} \cong \gamma_{i,j}$. For example, the familiar Ohno [61] interpolation formula gives the following dependence of this coupling hardness on the separation $R_{i,j} = |\boldsymbol{R}_i - \boldsymbol{R}_j|$ between the two AIM,

$$\eta_{i,j}(R_{i,j}) \cong \gamma_{i,j}(R_{i,j}) = [(a_{i,j})^2 + (R_{i,j})^2]^{-1/2}, \tag{25}$$

with the constant $a_{i,j} = 1/2(\eta_{i,i} + \eta_{j,j})$ then recovering the limiting value $\eta_{i,j}(R_{i,j} \to 0) = \eta_{i,i} = \eta_{j,j}$. The associated geometric (distance) derivative then reads:

$$d\eta_{i,j}(R_{i,j})/dR_{i,j} \cong d\gamma_{i,j}(R_{i,j})/dR_{i,j} = -\{R_{i,j}/[(a_{i,j})^2 + (R_{i,j})^2]\}\gamma_{i,j}(R_{i,j})$$
$$\equiv g_{i,j}(R_{i,j})\gamma_{i,j}(R_{i,j}). \tag{26}$$

With this background in modeling the canonical hardness data of AIM we now turn to the effective derivative quantities of Eqs. (19)–(21). One observes that the hardness tensor of the constituent AIM in $\mathcal{R}$ depends on current values of two geometric variables:

$$\boldsymbol{\eta}^{\text{AIM}}(r, R) = \begin{bmatrix} \eta_{A,A} & \eta_{A,B}(r) & \eta_{A,C}(r + R) \\ \eta_{B,A}(r) & \eta_{B,B} & \eta_{B,C}(R) \\ \eta_{C,A}(r + R) & \eta_{C,B}(R) & \eta_{C,C} \end{bmatrix}$$
$$\equiv \begin{bmatrix} \boldsymbol{\eta}_{AB}(r) & \boldsymbol{\eta}_{AB,C}(r, R) \\ \boldsymbol{\eta}_{C,AB}(r, R) & \eta_{C,C} \end{bmatrix}. \tag{27}$$

Consider first the chemical potential (electronegativity) equalization problem in the diatomic reactant AB. The upper diagonal block $\boldsymbol{\eta}_{AB}(r)$ of $\boldsymbol{\eta}^{\text{AIM}}(r, R)$ for this molecular fragment and the initial levels of the chemical potentials $\boldsymbol{\mu}_{AB} = (\mu_A^0, \mu_B^0)$ together determine the resultant chemical potential of the separated AB, equalized due to the *inter*-atomic CT $q(r) = \Delta N_A(r) = -\Delta N_B(r)$,

$$\mu_{AB}(r) = \mu_A(r) = \mu_A^0 + [\eta_{A,A} - \eta_{B,A}(r)]q(r) \equiv \mu_A^0 + \eta_A^{AB}(r)q(r)$$
$$= \mu_B(r) = \mu_B^0 - [\eta_{B,B} - \eta_{A,B}(r)]q(r) \equiv \mu_B^0 - \eta_B^{AB}(r)q(r). \tag{28}$$

These relations also determine the optimum amount of this CT,

$$q(r) = \left(\mu_B^0 - \mu_A^0\right) \Big/ \left[\eta_A^{AB}(r) + \eta_B^{AB}(r)\right] \equiv -\mu_{CT}^0/\eta_{CT}^{AB}(r). \tag{29}$$

The equalized level of the global/AIM chemical potentials in AB can be expressed as the weighted average of the initial chemical potentials of both atoms:

$$\mu_{AB}(r) = \mu_A(r) = \mu_B(r) = \mu_A^0 \left[\eta_B^{AB}(r) \Big/ \eta_{CT}^{AB}(r)\right] + \mu_B^0 \left[\eta_A^{AB}(r) \Big/ \eta_{CT}^{AB}(r)\right]$$
$$\equiv \mu_A^0 f_A^{AB}(r) + \mu_B^0 f_B^{AB}(r). \tag{30}$$

It should be emphasized that the approximation $\mu_{CT} \approx \mu_{CT}^0$ implies a neglect of shifts in the AIM chemical potentials $\{\mu_i^+\}$, relative to the corresponding separated-atom levels $\{\mu_i^0\}$, generated by the effective external potential due to the presence of the bonding partner(s): $\mu_i^+ \approx \mu_i^0$. This implicit assumption is consistently retained in the modelling development of the present work. Inclusion of such contributions would ultimately require the explicit knowledge of the corresponding electronic *Fukui functions* (FF) [1,2,50–52] of interacting atoms,

$$f_i(\mathbf{r}) = \frac{\partial^2 E_i[N_i, v_i]}{\partial N_i \partial v_i(\mathbf{r})} = \frac{\partial \mu_i}{\partial v_i(\mathbf{r})} = \frac{\partial \rho_i(\mathbf{r})}{\partial N_i} \approx \rho_i^F(\mathbf{r})$$

which can be approximated [1,2] by the relevant *Frontier Electron* (FE) densities $\{\rho_i^F(\mathbf{r})\}$ [28–30].

It is also of interest to determine other charge sensitivities of the diatomic reactant. The inverse of the hardness matrix in atomic resolution generates the associated softness matrix [60],

$$\boldsymbol{\sigma}_{AB} = \boldsymbol{\eta}_{AB}^{-1} = \frac{1}{\det \boldsymbol{\eta}_{AB}} \begin{bmatrix} \eta_{B,B} & -\eta_{A,B} \\ -\eta_{B,A} & \eta_{A,A} \end{bmatrix}, \quad \det \boldsymbol{\eta}_{AB} = \eta_{A,A}\eta_{B,B} - \eta_{A,B}\eta_{B,A}, \tag{31}$$

which in turn gives rise to the AIM softnesses:

$$\boldsymbol{S}^{AB} = \left[S_A^{AB} = \frac{\partial N_A}{\partial \mu_{AB}}, S_B^{AB} = \frac{\partial N_B}{\partial \mu_{AB}}\right] = \frac{1}{\det \boldsymbol{\eta}_{AB}} \left[\eta_B^{AB}, \eta_A^{AB}\right], \tag{32}$$

and the system global softness $S_{AB} = \partial N_{AB}/\partial \mu_{AB}$, inverse of the global hardness $\eta_{AB} = \partial \mu_{AB}/\partial N_{AB} = 1/S_{AB}$,

$$S_{AB} = S_A^{AB} + S_B^{AB} = \eta_{CT}^{AB}/\det \boldsymbol{\eta}_{AB}. \tag{33}$$

The corresponding FF of constituent AIM are then given by the corresponding softness ratios:

$$f^{AB} = \left[f_A^{AB} = \frac{\partial N_A}{\partial N_{AB}} = \frac{S_A^{AB}}{S_{AB}}, f_B^{AB} = \frac{\partial N_B}{\partial N_{AB}} = \frac{S_B^{AB}}{S_{AB}} \right]$$
$$= \frac{1}{\eta_{CT}^{AB}} \left[\eta_B^{AB}, \eta_A^{AB} \right], \quad f_A^{AB} + f_B^{AB} = 1. \tag{34}$$

These FF of bonded atoms are seen in Eq. (30) to provide the "weights" in the expression for the equalized chemical potential in terms of the initial chemical potentials of both atoms.

We have thus determined the effective bond-length dependence of the global chemical potential in the diatomic reactant AB generated by the r-dependence of the model *off*-diagonal hardnesses [Eqs. (25), (26)]. This function determines the associated NFF index:

$$\varphi_r(AB) = -\partial \mu_{AB}(r)/\partial r = \left[f_A^{AB}(r) - f_B^{AB}(r) \right] q(r) [\partial \eta_{A,B}(r)/\partial r]$$
$$= \mu_{CT}^0 (\eta_{A,A} - \eta_{B,B}) g_r(r) \eta_{A,B}(r) / \left[\eta_{CT}^{AB}(r) \right]^2 > 0. \tag{35}$$

The positive character of this dependence results from observing that $\eta_{A,B}(r) > 0$ and $g_r(r) < 0$ [Eq. (26)], and recognizing the sign combination of remaining factors. For example, assuming the relative acidic character of A and basic of B, i.e., $q > 0$, implies $\mu_{CT}^0 < 0$, $\eta_{A,A} - \eta_{B,B} > 0$ and hence $f_A^{AB} - f_B^{AB} < 0$; in the last inequality we have additionally recognized the diatomic charge-stability condition: $\eta_{CT}^{AB} > 0$. To summarize, the negative chemical potential (electronegativity) of the diatomic increases with bond elongation, as indeed expected intuitively from diminished effects of the chemical bonding in such species.

Let us now turn to the global equalization of the chemical potential in the whole triatomic collision complex. For definiteness we assume the amount of the additional CT effect, $(AB) \rightarrow C$, $Q = \Delta N_C = -\Delta N_{AB}$. This outflow of electrons from AB redistributes itself inside this diatomic reactant in accordance with the internal FF indices of Eq. (34),

$$\Delta N_A(Q) = -f_A^{AB} Q, \qquad \Delta N_B(Q) = -f_B^{AB} Q, \tag{36}$$

thus establishing the final equilibrium shifts in electron populations of AIM in $\mathcal{R}$ as a whole:

$$\Delta N_A(q, Q) = q - f_A^{AB} Q, \quad \Delta N_B(q, Q) = -q - f_B^{AB} Q, \quad \Delta N_B(q, Q) = Q. \tag{37}$$

Since we have already determined the equalized level of the chemical potential in AB, one can directly apply the previous formulas by treating this diatomic as whole fragment in the reaction complex [(AB)- - -C]. The effective hardness coupling

between these two complementary subsystems of $\mathcal{R}$ is then determined by the *inter-fragment hardnesses* $\eta_{AB,C} = \partial\mu_C/\partial N_{AB} = \eta_{C,AB} = \partial\mu_{AB}/\partial N_C$. They can be obtained by combining the corresponding matrix elements of $\boldsymbol{\eta}^{AIM}(r, R)$ [62]:

$$\eta_{AB,C}(r, R) = \frac{\partial\mu_{AB}}{\partial N_C} = f_A^{AB}\frac{\partial\mu_{AB}}{\partial N_C} + f_B^{AB}\frac{\partial\mu_{AB}}{\partial N_C}$$
$$= f_A^{AB}(r)\eta_{A,C}(r + R) + f_B^{AB}(r)\eta_{B,C}(R). \quad (38)$$

The effective hardnesses of these two molecular fragments in $\mathcal{R}$,

$$\eta_{AB}^{ABC} = \eta_{AB} - \eta_{C,AB}, \quad \eta_C^{ABC} = \eta_{C,C} - \eta_{AB,C}, \quad (39)$$

then determine the effective in situ hardness for the $[(AB) \to C]CT$:

$$\eta_{CT}^{ABC}(r, R) = \eta_{AB}^{ABC}(r, R) + \eta_C^{ABC}(r, R). \quad (40)$$

Finally, the optimum amount of this exchange of electrons,

$$Q(r, R) = -[\mu_C^0 - \mu_{AB}(r)]/\eta_{CT}^{ABC}(r, R) \equiv -\mu_{CT}^{ABC}(r, R)/\eta_{CT}^{ABC}(r, R), \quad (41)$$

determines the equalized level of the chemical potential in $\mathcal{R}$ as a whole:

$$\begin{aligned}
\mu_{ABC}(r, R) = \mu_{AB}(r, R) &= \mu_{AB}(r) - [\eta_{AB}(r) - \eta_{C,AB}(r, R)]Q(r, R) \\
&\equiv \mu_{AB}(r) - \eta_{AB}^{ABC}(r, R)Q(r, R) \\
&= \mu_C(R) = \mu_C^0 + [\eta_{C,C} - \eta_{AB,C}(r, R)]Q(r, R) \\
&\equiv \mu_C^0 + \eta_C^{ABC}(r, R)Q(r, R) \equiv \mu_C(r, R) \\
&= \mu_A(r, R) = \mu_B(r, R). \quad (42)
\end{aligned}$$

These equalization equations can be again formulated in terms of the associated FF for the two complementary fragments involved in the Q exchange of electrons:

$$\begin{aligned}
\mu_{ABC}(r, R) = \mu_{AB}(r)&\left[\eta_{AB}^{ABC}(r, R)\Big/\eta_{CT}^{ABC}(r, R)\right] \\
&+ \mu_C^0\left[\eta_C^{ABC}(r, R)\Big/\eta_{CT}^{ABC}(r, R)\right] \\
&\equiv \mu_{AB}(r)f_{AB}^{ABC}(r, R) + \mu_C^0 f_C^{ABC}(r, R). \quad (43)
\end{aligned}$$

This effective dependence of the triatomic chemical potential upon the two geometric parameters then allows one to derive the relevant NFF in the model collision complex. For example, the triatomic analog of the NFF derivative of Eq. (35), for the diatomic fragment in the triatomic collision complex, now reads:

$$\begin{aligned}
\varphi_r(ABC) = -\partial\mu_{ABC}(r, R)/\partial r &= -\partial\mu_{AB}(r, R)/\partial r \\
&= \varphi_r(AB)f_{AB}^{ABC}(r, R) \\
&- \mu_{AB}(r)\left(\partial f_{AB}^{ABC}(r, R)/\partial r\right) - \mu_C^0\left(\partial f_C^{ABC}(r, R)/\partial r\right). \quad (44)
\end{aligned}$$

The diatomic result is seen to be recovered when the whole system is limited to this diatomic reactant alone, i.e., for $f_{AB}^{ABC} = 1$ and $f_C^{ABC} = 0$.

4 Sensitivities for collective charge displacements

We now turn to molecular sensitivities associated with the collective charge exchanges q and Q [Eqs. (19), (20), (21)]. Above we have already identified the in situ chemical-potential differences, $\mu_{CT}(B \rightarrow A) \equiv \mu_q = \mu_A - \mu_B$ and $\mu_{CT}(AB \rightarrow C) \equiv \mu_Q = \mu_C - \mu_{AB}$, defining the row vector $\boldsymbol{\mu}^{\text{eff.}} = (\mu_q, \mu_Q)$, as the associated partial energy derivatives with respect to these two amounts of the internal CT in the triatomic system in question. They exactly vanish when the two fragments involved in the electron transfer equalize their chemical potentials, i.e., when they reach the mutual equilibrium.

In order to identify the diagonal elements of the effective hardness matrix $\boldsymbol{\eta}^{\text{eff.}}(R)$ [Eqs. (19), (20)] we refer to the EE Eqs. (28) and (42) which directly give:

$$\eta_{q,q} = \partial\mu_q/\partial q = \partial\mu_A/\partial q - \partial\mu_B/\partial q = \eta_A^{AB} + \eta_B^{AB} = \eta_{CT}^{AB},$$
$$\eta_{Q,Q} = \partial\mu_Q/\partial Q = \partial\mu_C/\partial Q - \partial\mu_{AB}/\partial Q = \eta_C^{ABC} + \eta_{AB}^{ABC} = \eta_{CT}^{ABC}. \quad (45)$$

The matrix off-diagonal elements, equal by the Maxwell cross-differentiation relation

$$\eta_{q,Q} = \partial\mu_Q/\partial q = \eta_{Q,q} = \partial\mu_q/\partial Q = \partial^2 E/\partial q \partial Q, \quad (46)$$

also follow from the corresponding expressions for displacements in the underlying chemical potentials. Let us examine the first derivative in the preceding equation. One observes that the shift in μ_C due to the internal CT $q = dN_A = -dN_B$ in AB reads:

$$d\mu_C(q) = q(\eta_{A,C} - \eta_{B,C}). \quad (47)$$

The associated displacement in the *equilibrium* chemical potential of AB, $d\mu_{AB}(q) = \eta_{AB}dN_{AB}(q) = 0$, since internal flows in AB do not modify the fragment overall number of electrons: $dN_{AB}(q) = 0$. Thus, $d\mu_Q(q) = d\mu_C(q)$ and hence

$$\eta_{q,Q} = \eta_{A,C} - \eta_{B,C}. \quad (48)$$

It can be directly verified that the same answer follows from the second derivative in Eq. (46). Let us examine the displacements in the chemical potentials μ_A and μ_B defining $\mu_q = \mu_A - \mu_B$, due to the second CT, $Q = dN_C = -dN_{AB}$. A reference to Eqs. (34) and (36) gives

$$\begin{aligned}
d\mu_A(Q) &= dN_A(Q)\eta_{A,A} + dN_B(Q)\eta_{B,A} + Q\eta_{C,A} \\
&= Q\left(\eta_{C,A} - f_A^{AB}\eta_{A,A} - f_B^{AB}\eta_{B,A}\right), \\
d\mu_B(Q) &= dN_A(Q)\eta_{A,B} + dN_B(Q)\eta_{B,B} + Q\eta_{C,B} \\
&= Q\left(\eta_{C,B} - f_A^{AB}\eta_{A,B} - f_B^{AB}\eta_{B,B}\right),
\end{aligned} \quad (49)$$

Therefore,

$$d\mu_q(Q) = Q\left[\eta_{C,A} - \eta_{C,B} + f_A^{AB}(\eta_{A,B} - \eta_{A,A}) + f_B^{AB}(\eta_{B,B} - \eta_{B,A})\right]$$
$$= Q\left[\eta_{C,A} - \eta_{C,B} - f_A^{AB}\eta_A^{AB} + f_B^{AB}\eta_B^{AB}\right] = Q(\eta_{C,A} - \eta_{C,B}), \quad (50)$$

and hence

$$\eta_{Q,q} = \partial\mu_q/\partial Q = \eta_{C,A} - \eta_{C,B}. \quad (51)$$

Thus, since the two (collective) degrees-of-freedom of the electron distribution in the reactive system ABC are mutually coupled by a non-vanishing hardness $\eta_{Q,q}$, the displacement in one of these variables generates a *non*-vanishing force associated with the other variable. In other words, any of these flows triggers the associated adjustment in the other electron transfer of the reactive system.

Let us now turn to the effective NFF indices of Eq. (21). It follows from the EE equations in AB [Eq. (28)] that, at this level of modeling, the *r*-dependence of the two AIM chemical potentials $\mu_A(r) = \mu_A^0 + \eta_A^{AB}(r)q(r)$ and $\mu_B(r) = \mu_B^0 - \eta_B^{AB}(r)q(r)$, which determine the equilibrium value of $\mu_q(r) = \mu_A(r) - \mu_B(r)$, originates from both the optimum amount $q(r)$ of the B $\to$ A CT and the effective atomic hardnesses of bonded atoms in AB. In the adopted approximation the resulting chemical-potential difference for this *equilibrium* CT $q = q(r)$ in the separated diatomic AB must exactly vanish (the equilibrium criterion),

$$\mu_q^{eq.}(r) = \mu_{CT}^0 + \eta_{CT}^{AB}(r)q(r) = 0. \quad (52)$$

Indeed, for the global equilibrium in AB, when $dN_{AB} = 0$, the hypothetical *internal* flow q does not affect the fragment chemical potential. For the fixed external potential the latter can be modified only by the net inflow/outflow of electrons: $d\mu_{AB} = \eta_{AB}dN_{AB}$. This observation implies the vanishing equilibrium coupling between r and $\mu_q^{eq.}$:

$$\varphi_q^{eq.} = -\partial\mu_q^{eq.}/\partial r = 0. \quad (53)$$

However, when the current CT q is treated as the *independent* charge variable, which can assume any admissible *non*-equilibrium value, as is indeed the case in the defining derivatives of the combined Hessian of Eq. (19), the derivative of $\mu_q(r) = \mu_{CT}^0 + \eta_{CT}^{AB}(r)q$ gives:

$$\varphi_q(q) = -\partial\mu_q/\partial r = -q\left(\partial\eta_{CT}^{AB}/\partial r\right) = 2q(\partial\eta_{A,B}/\partial r). \quad (54)$$

Since $\partial\eta_{A,B}/\partial r < 0$ [Eq. (26)] this derivative implies that this quantity reflecting coupling between the population force and the internuclear distance exhibits the opposite sign to that of the current amount of CT q, thus acting in direction to restore the electronic equilibrium.

Consider next the diatomic AB fragment in the whole, triatomic system. It follows from Eqs. (50) and (51) that the driving force μ_q being the q flow is then additionally shifted by $d\mu_q(Q) = Q\eta_{Q,q}(r, R) = Q[\eta_{C,A}(r + R)_{-}\eta_{C,B}(R)]$. Therefore, when Q is treated as an arbitrary, r-independent populational variable, the coupling NFF index of Eq. (54) is then modified by the derivative of the effective coupling hardness $\eta_{Q,q}(r, R)$ of Eqs. (48) and (51):

$$\varphi_q(q, Q) = \varphi_q(q) - Q[\partial\eta_{Q,q}(r, R)/\partial r] = \varphi_q(q) - Q[\partial\eta_{C,A}(R_{A,C})/\partial R_{A,C}].$$
(55)

Clearly, the equilibrium derivative of Eq. (53), calculated for the equilibrium internal CT $q = q(r,R)$ which equalizes the chemical potentials of A and B in the presence of the third atom C, remains unchanged since then $\mu_q^{eq.}(r, R) = \mu_A(r, R) - \mu_B(r, R)$ identically vanishes for all values of the two geometrical variables.

It should be also stressed that the global chemical potential $\mu_{AB}(r)$ [Eq. (30)] of the isolated AB differs from the corresponding level $\mu_{AB}(r, R, Q = 0)$ characterizing this diatomic fragment in the presence of C, when these complementary parts are considered to be mutually closed in (A¦B|C); here the vertical *broken* line between A and B signifies their freedom to exchange electrons, $q \neq 0$, while the vertical *solid* line separating AB and C prevents such hypothetical flows of electrons, $Q = 0$. Indeed, the presence of C modifies the effective external potential of AB. However, since this direct influence is neglected in the present approximation, only a finite charge flow $Q = -dN_{AB}$ can modify $\mu_{AB}(r, R, Q)$ relative to $\mu_{AB}(r)$ [see Eq. (39)]:

$$\mu_{AB}(r, R, Q) = \mu_{AB}(r) - \eta_{AB}^{ABC}(r, R)Q.$$
(56)

We conclude this section with a short derivation of the remaining effective NFF component in Eq. (19):

$$\varphi_Q = -\frac{\partial\mu_Q}{\partial r} = \frac{\partial F_r}{\partial Q}.$$
(57)

We shall use the first of the defining derivatives to model this quantity, which couples the electronic and nuclear state variables in the whole triatomic system. The Q-dependence of the two chemical potentials defining $\mu_Q = \mu_C - \mu_{AB}$, from Eq. (42), gives

$$\mu_Q(r, R) = \mu_{CT}^{ABC}(r, R) + Q\eta_{CT}^{ABC}(r, R).$$
(58)

The *inter*-reactant equilibrium condition $\mu_Q^{eq.}(r, R) = 0$ then directly gives the associated optimum amount of CT [Eq. (41)]. Clearly, in such a global equilibrium state of (A¦B¦C), for the equilibrium $Q = Q(r, R)$,

$$\varphi_Q^{eq.} = -\partial\mu_Q^{eq.}/\partial r = 0.$$
(59)

However, when Q is regarded as an independent state variable [see Eq. (19)], the defining derivative of Eq. (57) reads [see Eqs. (35) and (56)]:

$$
\begin{aligned}
-\frac{\partial \mu_Q}{\partial r} &= -\frac{\partial \mu_{CT}^{ABC}}{\partial r} - Q\frac{\partial \eta_{CT}^{ABC}}{\partial r} = \frac{\partial \mu_{AB}(r, R, Q)}{\partial r} - Q\frac{\partial \eta_{CT}^{ABC}}{\partial r} \\
&= \frac{\partial \mu_{AB}(r)}{\partial r} + Q\frac{\partial \eta_{AB}^{ABC}}{\partial r} - Q\left(\frac{\partial \eta_{C}^{ABC}}{\partial r} + \frac{\partial \eta_{AB}^{ABC}}{\partial r}\right) \\
&= -\varphi_r(AB) - Q\frac{\partial \eta_{C}^{ABC}}{\partial r} = -\varphi_r(AB) + Q\frac{\partial \eta_{AB,C}}{\partial r}, \quad (60)
\end{aligned}
$$

where [see Eqs. (26) and (38)]:

$$
\frac{\partial \eta_{AB,C}}{\partial r} = \frac{1}{\left(\eta_{CT}^{AB}\right)^2}\left(\frac{\partial \eta_{A,B}}{\partial R_{A,B}}\right)(\eta_{A,A} - \eta_{B,B})(\eta_{B,C} - \eta_{A,C}) + \frac{\eta_B^{AB}}{\eta_{CT}^{AB}}\left(\frac{\partial \eta_{A,C}}{\partial R_{A,C}}\right). \quad (61)
$$

The preceding derivative reflects the *r*-dependence of the hardness coupling between the two reactants. In an attempt to physically interpret this relation one first observes that for the electronically stable diatomic $\eta_{CT}^{AB} > 0$ and $\eta_B^{AB} > 0$. Moreover, the geometric derivatives of diatomic hardnesses are both negative, $d\eta_{i,j}(R_{i,j})/dR_{i,j} < 0$, since the *two*-center electron repulsion diminishes with increasing internuclear distance. In the collinear collision complex $\eta_{B,C} - \eta_{A,C} > 0$, while the hardness difference $(\eta_{A,A} - \eta_{B,B})$ is shaped by the relative acidic/basic character of both atoms in the diatomic reactant. For identical atoms, e.g., in the hydrogen exchange reaction H—H + X → H + H—X, the first term in Eq. (61) identically vanishes, so that the second (negative) term implies that an increase in the bond length *r* of the diatomic reactant decreases its hardness coupling to the approaching atom. A similar prediction follows when A and B respectively denote the *acidic* and *basic* parts of the diatomic reactant, when $\eta_{A,A} - \eta_{B,B} > 0$, since then both contributions in the preceding equation are negative. In both these cases the NFF of Eq. (60) becomes negative [see Eq. (35)]. Therefore, in this approximation the electronegativity difference $\chi_Q = -\mu_Q$, the driving force of the *inter*-reactant charge flow *Q*, diminishes with an elongation of the diatomic reactant.

5 Couplings along the minimum-energy coordinate

In the preceding development we have treated one interatomic distance $R_{AB} = r$ as the internal geometric variable, while the other independent bond length *R* has been regarded as the *reaction coordinate*, of the mutual approach by the reaction substrates in the reactant (*entrance*) valley of the molecular *Potential Energy Surface* (PES) $W(R_{AB} = r, R_{BC} = R, R_{AC} = r + R)$. In the strong interaction region, between the reactant and product (*exit*) valleys, which includes the *transition-state* complex [A---B-----C]‡, these role are reversed with R_{BC} now representing the internal geometric variable of the diatomic product and R_{AB} approximating the reaction coordinate of the product departure.

For many atom exchange reactions, in which the single bond is broken/formed in a concerted fashion, Eqs. (17) and (18) realistically determine the reaction progress

along the *Minimum Energy Path* (MEP) on PES, in the whole region of the reaction progress variable

$$n \equiv n_{B,C} \in [0, 1], \tag{62}$$

where $n = 0$, i.e., $n_{A,B} = 1 - n = 1$, corresponds to separated reactants and $n = 1 (n_{A,B} = 0)$ represents the separated products, respectively. The MEP $Q(n) = [r(n), R(n)]$, parametrically defined by the corresponding Pauling relations [Eq. (18)],

$$r(n) = R^e_{A,B} - 0.026 \ln(1 - n) \quad \text{and} \quad R(n) = R^e_{B,C} - 0.026 \ln n, \text{ (in } 10^{-9} \text{ m)} \tag{63}$$

or the associated trajectory Eq. (17),

$$\exp(-38.46 \Delta R_{A,B}) + \exp(-38.46 \Delta R_{B,C}) = 1, \tag{64}$$

determines the corresponding BEBO energy profile $W(n) \equiv W\{N^{eq\cdot}[Q(n)], Q(n)\}$ along this MEP-cut, which is known to adequately represent the reaction energy curve. Each value of the bond-order n then determines the local (normal) coordinate system $[t(n), p(n)]$ consisting of the *tangent* $[t(n)]$ and *normal* (perpendicular) $[p(n)]$ directions on the BEBO MEP.

It is of interest in the theory of chemical reactivity to examine the coupling between the electronic and geometrical degrees of freedom along this trajectory. In the present collinear collision complex it is determined by the associated 3×3 Hessian matrix [see Eq. (19)]:

$$\mathbf{H}[AB\text{-}\text{-}\text{-}C(n)] = \begin{bmatrix} \eta^{eff\cdot}(n) & -\varphi^{eff\cdot}(n)^T \\ -\varphi^{eff\cdot}(n) & k(n) \end{bmatrix}. \tag{65}$$

Here, $\eta^{eff\cdot}(n) = \partial^2 W / \partial N \partial N |_{Q(n)} = \partial^2 E / \partial N \partial N |_{Q(n)}$ determines the effective populational Hessian of Eq. (20) for the current point $Q(n)$ on the BEBO MEP, while

$$k(n) = \partial^2 W / \partial p^2 |_{Q(n)} = -\partial F_p / \partial p |_{Q(n)}, \tag{66}$$

denotes the force constant of the local *normal* stretching mode p, orthogonal to the reaction coordinate t. Accordingly, the NFF input $\varphi^{eff\cdot}(n)$ in the MEP Hessian of Eq. (65) is then defined by the *normal* derivative of $\mu^{eff\cdot}(n)$:

$$\varphi^{eff\cdot}(n) = -\partial \mu^{eff\cdot} / \partial p |_{Q(n)} = [-\partial \mu_q / \partial p |_{Q(n)}, -\partial \mu_Q / \partial p |_{Q(n)}]. \tag{67}$$

Let us recall, that for the current point $Q^0 = [r^0 = r(n^0), R^0 = R(n^0)]$ on the MEP of Eq. (63) the equations defining in the original geometrical plane $Q = (r, R)$ the (mutually perpendicular) tangent $t(n)$ and normal $p(n)$ directions $P(n) = [t(n), p(n)]$ respectively read:

$$R'(n^0)(r - r^0) - r'(n^0)(R - R^0) = 0 \text{ and}$$
$$r'(n^0)(r - r^0) + R'(n^0)(R - R^0) = 0, \tag{68}$$

where $R'(n^0) = dR(n)/dn|_{n^0}$ and $r'(n^0) = dr(n)/dn|_{n^0}$. These derivative coefficients define the local transformation

$$\mathbf{O}(n) = [\mathbf{O}_t(n), \mathbf{O}_p(n)] \equiv \partial\mathbf{P}(n)/\partial\mathbf{Q} \tag{69}$$

of the original geometrical variables $\mathbf{Q} = (r, R)$ to the associated MEP-based directions $\mathbf{P}(n) = [\mathbb{Q}(n), \mathbf{q}(n)]$ defined by the corresponding columns of $\mathbf{O}(n) = [\mathbf{O}_t(n), \mathbf{O}_p(n)]$:

$$\mathbf{P}(n) = \mathbf{Q} \begin{bmatrix} R'(n) & r'(n) \\ -r'(n) & R'(n) \end{bmatrix} \equiv \mathbf{Q}\mathbf{O}(n) = [\mathbf{Q}\mathbf{O}_t(n), \mathbf{Q}\mathbf{O}_p(n)]$$
$$= [t(n), p(n)]. \tag{70}$$

The inverse transformation,

$$\mathbf{O}^{-1}(n) \equiv \partial\mathbf{Q}/\partial\mathbf{P}(n) = \frac{1}{[R'(n)]^2 + [r'(n)]^2} \begin{bmatrix} R'(n) & -r'(n) \\ r'(n) & R'(n) \end{bmatrix}$$
$$\equiv \begin{bmatrix} \mathbf{O}_t^{-1}(n) = \partial\mathbf{Q}/\partial t(n) \\ \mathbf{O}_p^{-1}(n) = \partial\mathbf{Q}/\partial p(n) \end{bmatrix}, \tag{71}$$

then determines the MEP sensitivities from the corresponding quantities defined in the original (r,R)-representation. For example, the appropriate chain-rule manipulation of derivatives gives:

$$\boldsymbol{\varphi}^{\mathrm{eff.}}(n) = -\partial\boldsymbol{\mu}^{\mathrm{eff.}}/\partial p|_{P(n)} = -(\partial\mathbf{Q}/\partial p)|_{P(n)}(\partial\boldsymbol{\mu}^{\mathrm{eff.}}/\partial\mathbf{Q})|_{P(n)}$$
$$= \mathbf{O}_p^{-1}(n)\boldsymbol{\varphi}^{\mathrm{eff.}}(\mathbf{P}),$$
$$F_p(n) = -\partial W/\partial p|_{P(n)} = -(\partial\mathbf{Q}/\partial p)|_{P(n)}(\partial W/\partial\mathbf{Q})|_{P(n)} = \mathbf{O}_p^{-1}(n)\mathbf{F}(\mathbf{P}),$$
$$k(n) = \partial^2 W/\partial p^2|_{P(n)} = (\partial\mathbf{Q}/\partial p)|_{P(n)}(\partial^2 W/\partial\mathbf{Q}\partial\mathbf{Q})|_{P(n)}(\partial\mathbf{Q}/\partial p)^T|_{P(n)}$$
$$= \mathbf{O}_p^{-1}(n)\mathbf{K}(\mathbf{P})[\mathbf{O}_p^{-1}(n)]^T, \tag{72}$$

where the square matrix of NFF

$$\boldsymbol{\varphi}^{\mathrm{eff.}}(\mathbf{P}) = -\frac{\partial^2 W}{\partial\mathbf{Q}\partial N}\bigg|_{\mathbf{P}} = \left(\frac{\partial\mathbf{F}}{\partial N}\bigg|_{\mathbf{P}}\right)^T$$
$$= -\left(\frac{\partial\boldsymbol{\mu}^{\mathrm{eff.}}}{\partial\mathbf{Q}}\bigg|_{\mathbf{P}}\right)$$
$$= \begin{bmatrix} \varphi_{r,q}(\mathbf{P}) = -(\partial\mu_q/\partial r)|_P & \varphi_{r,Q}(\mathbf{P}) = -(\partial\mu_Q/\partial r)|_P \\ \varphi_{R,q}(\mathbf{P}) = -(\partial\mu_q/\partial R)|_P & \varphi_{R,Q}(\mathbf{P}) = -(\partial\mu_Q/\partial R)|_P \end{bmatrix}, \tag{73}$$

and the force-constant tensor for original geometric variables $\mathbf{Q} = (r, R)$

$$\mathbf{K}(\boldsymbol{P}) = \left.\frac{\partial^2 W}{\partial \boldsymbol{Q} \partial \boldsymbol{Q}}\right|_{\boldsymbol{P}} = -\left.\frac{\partial^2 \boldsymbol{F}}{\partial \boldsymbol{Q}}\right|_{\boldsymbol{P}}$$

$$= \begin{bmatrix} k_{r,r}(\boldsymbol{P}) = -(\partial F_r/\partial r)\,|_{\boldsymbol{P}} & k_{r,R}(\boldsymbol{P}) = -(\partial F_R/\partial r)\,|_{\boldsymbol{P}} \\ k_{R,r}(\boldsymbol{P}) = -(\partial F_r/\partial R)\,|_{\boldsymbol{P}} & k_{R,R}(\boldsymbol{P}) = -(\partial F_R/\partial R)\,|_{\boldsymbol{P}} \end{bmatrix}, \quad (74)$$

where the force vector contains two components:

$$\boldsymbol{F}(\boldsymbol{P}) = [-\partial W/\partial r|_{\boldsymbol{P}} = F_r\,(\boldsymbol{P})\,, \ -\partial W/\partial R|_{\boldsymbol{P}} = F_R\,(\boldsymbol{P})]. \quad (75)$$

In this force constant matrix $k_{R,r} = k_{r,R}$ determines the equilibrium coupling between the electronically-decoupled geometrical degrees of freedom. The inverse of the force constant matrix, the geometrical *softness* matrix [37–40], $\mathbf{K}^{-1}(\boldsymbol{P}) \equiv \mathbf{G}(\boldsymbol{P})$, then combines the system purely geometric compliants [13–16].

Finally, instead of separating one geometric variable $\mathscr{Q}$ as a parametric measure of the reactant/product proximity along the MEP, one could explicitly include the effects of its coupling to the electron-transfer variables $\boldsymbol{N} = (q, Q)$ and the other geometric variable $\boldsymbol{q}$. This generalized approach calls for the full 4×4 Hessian matrix of the collinear reactive system with respect to both the electronic $\boldsymbol{N}$ and geometric $\boldsymbol{Q} = (r, R)$ or $\boldsymbol{P} = (t, p)$ variables in $\mathcal{R}$, e.g.,

$$\mathbf{H}[\mathrm{AB\text{-}\text{-}\text{-}C}(n)] = \begin{bmatrix} \left.\frac{\partial^2 W}{\partial \boldsymbol{N} \partial \boldsymbol{N}}\right|_{\boldsymbol{P}(n)} & \left.\frac{\partial^2 W}{\partial \boldsymbol{N} \partial \boldsymbol{P}}\right|_{\boldsymbol{P}(n)} \\ \left.\frac{\partial^2 W}{\partial \boldsymbol{P} \partial \boldsymbol{N}}\right|_{\boldsymbol{P}(n)} & \left.\frac{\partial^2 W}{\partial \boldsymbol{P} \partial \boldsymbol{P}}\right|_{\boldsymbol{P}(n)} \end{bmatrix} \equiv \begin{bmatrix} \boldsymbol{\eta}^{\mathrm{eff}\cdot}(n) & -[\boldsymbol{\varphi}^{\mathrm{MEP}}(n)]^T \\ -\boldsymbol{\varphi}^{\mathrm{MEP}}(n) & \mathbf{K}^{\mathrm{MEP}}(n) \end{bmatrix}.$$

$$(76)$$

where $\boldsymbol{\varphi}^{\mathrm{MEP}}(n) = \mathbf{O}^{-1}(n)\boldsymbol{\varphi}^{\mathrm{eff}\cdot}(\boldsymbol{P})$ and $\mathbf{K}^{\mathrm{MEP}}(n) = \mathbf{O}^{-1}(n)\mathbf{K}(\boldsymbol{P})[\mathbf{O}^{-1}(n)]^T$.

The derivatives in the first row of $\boldsymbol{\varphi}^{\mathrm{eff}\cdot}(\boldsymbol{P})$ in Eq. (73) constitute the $\boldsymbol{\varphi}^{\mathrm{eff}\cdot}$ vector already discussed before: $\boldsymbol{\varphi}^{\mathrm{eff}\cdot} = (\varphi_{r,q} = \varphi_q, \varphi_{r,Q} = \varphi_Q)$. The remaining derivatives, of the second row in this generalized NFF matrix, can be similarly modeled using the relevant equations for displacements in the fragment chemical potentials, which have been developed already in the preceding section. For example, when Q is regarded as independent state-variable, differentiating Eq. (58) with respect to R gives [see Eqs. (41) and (56)],

$$\varphi_{R,Q} = -\partial \mu_Q(r, R)/\partial R = -\left[\partial \mu_{\mathrm{CT}}^{\mathrm{ABC}}(r, R)/\partial R\right] - Q\left[\partial \eta_{\mathrm{CT}}^{\mathrm{ABC}}(r, R)/\partial R\right]$$

$$= Q\left\{\left[\partial \eta_{\mathrm{AB}}^{\mathrm{ABC}}(r, R)/\partial R\right] - \left[\partial \eta_{\mathrm{CT}}^{\mathrm{ABC}}(r, R)/\partial R\right]\right\}$$

$$= Q\left[\partial \eta_{\mathrm{AB,C}}^{\mathrm{ABC}}(r, R)/\partial R\right], \quad (77)$$

where the final derivative follows from the model expression for the *inter*-reactant coupling hardness of Eq. (38):

$$\partial \eta_{\mathrm{AB,C}}^{\mathrm{ABC}}(r, R)/\partial R = f_{\mathrm{A}}^{\mathrm{AB}}[\partial \eta_{\mathrm{A,C}}/\partial R_{\mathrm{A,C}}] + f_{\mathrm{B}}^{\mathrm{AB}}[\partial \eta_{\mathrm{B,C}}/\partial R_{\mathrm{B,C}}] < 0. \quad (78)$$

Thus, for a positive *inter*-reactant CT, $Q > 0$, when atom C acts as the *acidic* partner of the *basic* diatomic AB, $\mu_Q < 0$, an increase in the inter-reactant separation R lowers the flow electronegativity $\chi_Q = -\mu_Q$. The opposite trend is predicted for the acidic AB with respect to C, when $\mu_Q > 0$ and hence $Q < 0$.

The R-derivative of $\mu_q(q, Q)$ in the second row of $\boldsymbol{\varphi}^{\text{eff}} \cdot (\boldsymbol{P})$ similarly follows from the fragment chemical potential displacements for the specified charges q and Q. It follows from Eq. (28) that the given internal flow q gives rise to

$$\mu_q(q) = \mu_{\text{CT}}^0 + q \eta_{\text{CT}}^{\text{AB}}(r), \tag{79}$$

while the subsequent inter-reactant flow Q [see Eq. (36)] modifies this chemical potential difference by the following terms:

$$\mu_q(q, Q) = \mu_q(q) + Q\big[f_{\text{B}}^{\text{AB}}(r)\eta_{\text{B}}^{\text{AB}}(r) \\ - f_{\text{A}}^{\text{AB}}(r)\eta_{\text{A}}^{\text{AB}}(r) + \eta_{\text{C,A}}(r + R) - \eta_{\text{C,B}}(R)\big]. \tag{80}$$

Hence the model expression for the NFF of interest [see Eqs. (25) and (26)] reads:

$$\varphi_{R,q} = -\partial\mu_q/\partial R = Q\left(\frac{\partial\eta_{\text{C,B}}}{\partial R_{\text{C,B}}} - \frac{\partial\eta_{\text{C,A}}}{\partial R_{\text{C,A}}}\right). \tag{81}$$

Since for the collinear collision complex $\eta_{\text{C,B}}$ decays faster than $\eta_{\text{C,A}}$ with the *inter*-reactant separation one again predicts that in this approximation $\varphi_{R,q} < 0$, so that the driving electronegativity difference in AB, $\chi_q = -\mu_q$, decreases with increasing separation between reactants.

In each of the above approaches the compliant sensitivities of interest are given by the corresponding elements of the Hessian inverse, which defines the generalized softness matrix. Such descriptors give rise to the MEC measuring equilibrium responses in the remaining state-variables, per unit shift in the parameter of interest (electronic or nuclear) [5,6,13–17,37–40].

6 Conclusion

This article explores simple modelling possibilities of the joint electronic–nuclear description of the prototype, collinear triatomic model of the bimolecular atom-exchange reaction. The independent electronic and geometric state parameters have been identified and explicit analytical expressions for the crucial NFF data, which reflect the coupling between the system electronic and geometric degrees-of-freedom, have been derived using the previously proposed *semi*-empirical representation of the atomic hardnesses by the corresponding *valence*-shell electron-repulsion integrals. The present treatment takes into account all physically important interactions between the system electronic and geometrical structures and is capable of generating all relevant *two*-reactant reactivity probes in both the NF and EP perspectives, in the chemical softness and hardness representations, respectively. By using the analytical BEBO trajectory conserving the overall bond-order, which constitutes a realistic

approximation of the collinear MEP, one can also generate response descriptors for this reaction coordinate.

This development explicitly demonstrates that the range of applications of molecular charge sensitivities is not limited to somewhat over-simplified *single*-reactant problems, being fully capable of covering also the prototype *two*-reactant scenarios. Numerical applications of the present model will be reported in future works on this subject.

References

1. R.G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989)
2. P.K. Chattaraj, R.G. Parr, *Structure and Bonding*, vol. 80 (Springer, Berlin, 1993), p. 11
3. P. Geerlings, F. De Proft, W. Langenaeker, Chem. Rev. **103**, 1793 (2003)
4. P.K. Chattaraj (ed.), *Chemical Reactivity Theory—A Density Functional View* (CRC Press, Taylor & Francis, London, 2009)
5. R.F. Nalewajski, J. Korchowiec, *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity* (World-Scientific, Singapore, 1997)
6. R.F. Nalewajski, J. Korchowiec, A. Michalak, Top. Curr. Chem. **183**, 25 (1996)
7. R.F. Nalewajski, *Information Theory of Molecular Systems* (Elsevier, Amsterdam, 2006)
8. R.F. Nalewajski, in *Reviews of Modern Quantum Chemistry: A Cellebration of the Contributions of Robert G. Parr*, vol. 2, ed. by K.D. Sen (World Scientific, Singapore, 2002), p. 1071
9. R.F. Nalewajski, *Structure and Bonding* (Springer, Berlin, 1993), p. 115
10. R.F. Nalewajski, 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
11. R.F. Nalewajski, Adv. Quantum Chem. **43**, 119 (2003)
12. R.F. Nalewajski, Int. J. Quantum Chem. **56**, 453 (1995)
13. R.F. Nalewajski, Adv. Quantum Chem. **51**, 235 (2006)
14. R.F. Nalewajski, in *Chemical Reactivity Theory—A Density Functional View*, ed. by P.K. Chattaraj (CRC Press, Taylor & Francis, London, 2009), p. 453
15. R.F. Nalewajski, Comput. Chem. **24**, 243 (2000)
16. R.F. Nalewajski, D. Błażewicz, J. Mrozek, J. Math. Chem. **44**, 325 (2007)
17. 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
18. R.F. Nalewajski, Phys. Chem. Chem. Phys. **1**, 1037 (1999)
19. R.F. Nalewajski, in *Recent Advances in Density Functional Methods, Part III*, ed. by V. Barone, A. Bencini, P. Fantucci (World Scientific, Singapore, 2002), p. 257
20. R.F. Nalewajski, *Perspectives in Electronic Structure Theory* (Springer, Berlin, 2010)
21. R.F. Nalewajski, O. Sikora, J. Phys. Chem. A **104**, 5638 (2000)
22. B.G. Baekelandt, G.O.A. Janssens, H. Toufar, W.J. Mortier, R.A. Schoonheydt, R.F. Nalewajski, J. Phys. Chem. **99**, 9784 (1995)
23. 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
24. R.F. Nalewajski, A. Michalak, Int. J. Quantum Chem. **56**, 603 (1995)
25. R.F. Nalewajski, A. Michalak, J. Phys. Chem. **100**, 20076 (1996)
26. R.F. Nalewajski, A. Michalak, J. Phys. Chem. A **102**, 636 (1998)
27. M.H. Cohen, Top Curr Chem **183**, 143 (1996)
28. K. Fukui, *Theory of Orientation and Stereoselection* (Springer, Berlin, 1975)
29. K. Fukui, Science **218**, 747 (1987)
30. H. Fujimoto, K. Fukui, in *Chemical Reactivity and Reaction Paths*, ed. by G. Klopman (Wiley-Interscience, New York, 1974), p. 23
31. G. Klopman, J. Am. Chem. Soc. **90**, 223 (1968)

32. G. Klopman, in *Chemical Reactivity and Reaction Paths*, ed. by G. Klopman (Wiley-Interscience, New York, 1974), p. 55
33. R.F. Nalewajski, J. Am. Chem. Soc. **106**, 944 (1984)
34. P.W. Ayers, R.G. Parr, J. Am. Chem. Soc. **122**, 2010 (2000)
35. P.W. Ayers, R.G. Parr, J. Am. Chem. Soc. **123**, 2007 (2001)
36. V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions* (Plenum, New York, 1978)
37. J.C. Decius, J. Chem. Phys. **38**, 241 (1963)
38. L.H. Jones, R.R. Ryan, J. Chem. Phys. **52**, 2003 (1970)
39. B.I. Swanson, J. Am. Chem. Soc. **98**, 3067 (1976)
40. B.I. Swanson, S.K. Satija, J. Am. Chem. Soc. **99**, 987 (1977)
41. H. Nakatsuji, J. Am. Chem. Soc. **95**, 345 (1973)
42. H. Nakatsuji, J. Am. Chem. Soc. **96**, 24 (1974)
43. H. Nakatsuji, J. Am. Chem. Soc. **96**, 30 (1974)
44. P. Hohenberg, W. Kohn, Phys. Rev. **136B**, 864 (1964)
45. W. Kohn, L.J. Sham, Phys. Rev. **140A**, 1133 (1965)
46. R.M. Dreizler, E.K.U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer, Berlin, 1990)
47. R.F. Nalewajski (ed.), *Density Functional Theory I–IV; Top. Curr. Chem.*, vols. 180–183 (Springer-Verlag, Berlin, 1966)
48. R.T. Sanderson, Science **114**, 670 (1951)
49. R.T. Sanderson, *Chemical Bonds and Bond Energy*, 2nd edn. (Academic Press, New York, 1976)
50. R.G. Parr, W. Yang, J. Am. Chem. Soc. **106**, 4049 (1984)
51. W. Yang, R.G. Parr, Proc. Natl. Acad. Sci. USA **82**, 6723 (1985)
52. W. Yang, R.G. Parr, R. Pucci, J. Chem. Phys. **81**, 2862 (1984)
53. A. Michalak, F. De Proft, P. Geerlings, R.F. Nalewajski, J. Phys. Chem. A **103**, 762 (1999)
54. J. Korchowiec, T. Uchimaru, J. Phys. Chem. A **102**, 10167 (1998)
55. M.H. Cohen, M.V. Ganguglia-Pirovano, J. Kurdnovský, J. Chem. Phys. **101**, 8988 (1994)
56. M.H. Cohen, M.V. Ganguglia-Pirovano, J. Kurdnovský, J. Chem. Phys. **103**, 3543 (1995)
57. H.B. Callen, *Thermodynamics: An Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics* (Wiley, New York, 1962)
58. H.S. Johnston, C.J. Parr, J. Am. Chem. Soc. **85**, 2544 (1963)
59. L. Pauling, J. Am. Chem. Soc. **69**, 542 (1947)
60. R.F. Nalewajski, J. Korchowiec, Z. Zhou, Int. J. Quantum Chem. Symp. **22**, 349 (1988)
61. K. Ohno, Adv. Quantum Chem. **3**, 239 (1967)
62. R.F. Nalewajski, J. Phys. Chem. **93**, 2658 (1989)