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RESEARCH ARTICLE

Resultant gradient information, kinetic energy and molecular virial theorem

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Abstract: Resultant *gradient*-information is introduced and applied to problems in chemical reactivity theory. This local measure of the structural information contained in (complex) wavefunctions of electronic states is related to the system overall kinetic energy combining the modulus (probability) and phase (current) contributions. The grand-ensemble representation of thermodynamic equilibria in open systems demonstrates the physical equivalence of the variational energetic and information principles. It is used and to relate the populational derivatives of *ensemble*-average functionals in both these representations, which represent reactivity criteria for diagnosing the charge-transfer (CT) phenomena. Their equivalence is demonstrated by using the in situ potential and hardness descriptors to predict the direction and optimum amount of CT. The virial theorem is generalized into thermodynamic quantities and used to extract the kinetic energy component from qualitative energy profiles in the bond-formation and (*exo/endo*)-ergic reactions. The role of electronic kinetic energy in such chemical processes is reexamined, the virial theorem implications for the Hammond postulate of reactivity theory are explored, and variations of the *structural*-information in chemical processes are addressed. The maximum thermodynamic information rule is formulated and "production" of the *gradient*-information in chemical reactions is addressed. The Hammond postulate is shown to be indexed by the geometric derivative of resultant *gradient*-information at transition-state complex.

Keywords: bond formation, chemical reactivity, grand ensemble, information theory, resultant information, virial theorem

1 Introduction

The Quantum Information Theory (QIT)[1–4] has been shown to provide a solid, unifying basis for understanding - in chemical terms - the electronic structure of molecules, and explaining general trends in their chemical behavior,[5–8] . Thermodynamic energy principle has been interpreted as physically equivalent rule for the resultant content of the overall *gradient*-information in electronic wavefunction, the dimensionless descriptor related to the state average kinetic energy. In the *grand*-ensemble both these variational principles determine the equilibrium state of an open molecular system. This equivalence parallels the same predictions resulting from the minimum-energy and maximum-entropy principles of the ordinary thermodynamics[9] . It explains the proportionality relations between energetic and informational criteria of chemical reactivity, measured by the corresponding populational derivatives of the *ensemble*-average functionals.

The QIT transcription of the variational principle for the electronic (thermodynamic) energy thus allows one to interpret reactivity criteria as the associated populational derivatives of the state resultant *gradient*-information (dimensionless kinetic energy) content. The latter combines the classical (probability) and nonclassical (current) contributions,due to the modulus and (local) phase components of the molecular wavefunction, respectively. The proportionality between the resultant *gradient*-information and the system kinetic energy also suggests the use of molecular virial theorem[10] in general reactivity considerations[5–8] .

To paraphrase Prigogine[11] , the electron density alone carries the information reflecting a "static" structure of "being", missing a "dynamic" structure of "becoming" contained in the state phase or current distributions. Both these manifestations of the electronic "organization" in molecular systems ultimately contribute to overall measures of the structural entropy or information content in generally complex wavefunctions, reflected

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by the *resultant* QIT concepts[1–4] . Their classical contributions, conceptually rooted in Density Functional Theory (DFT)[12–17] , probe the entropic content of incoherent (disentangled) local "events", while the nonclassical terms provide the information supplement due to the coherence (entanglement) of such local events. The resultant measures allow one to distinguish the information content of states generating the same electron density but differing in their phase/current distributions, *e.g.*, the bonded (entangled) and nonbonded (disentangled) states of molecular fragments[18–27] .

The classical Information Theory (IT) of Fisher and Shannon[28–35] has been successfully applied to generate the chemical interpretation of molecular probability distributions,[36–39] . Information principles have been explored[5–8, 40–45] and density pieces attributed to Atoms-in-Molecules (AIM) have been approached,[36–39, 43–47] providing the information basis for the intuitive (stockholder) division of Hirshfeld[48] . Patterns of chemical bonds in molecules have been extracted from electronic orbital communications,[1, 36–38, 49–59] and entropy/information densities have been explored.[1, 36–38, 60, 61] The nonadditive Fisher information[1, 36–38, 62, 63] has been linked to the Electron Localization Function (ELF)[64–66] of modern DFT. This analysis has also formulated the Contragradience (CG) probe[1, 36–38, 67] for spatial localization of chemical bonds, and the Orbital Communication Theory (OCT) of the chemical bond has identified the *bridge*-bonds originating from the cascade propagations of information between AIM, which involve intermediate orbitals.[1, 38, 68–73] The DFT-based approaches to classical issues in reactivity theory[74–80] use the *energy*-centered arguments in justifying the observed reactivity preferences. It is the main purpose of this work to show that general reactivity rules can be alternatively treated using the *resultant*-information/*kinetic*-energy concepts of QIT.

We begin with a short summary of the overall *gradient*-information concept. The resultant QIT descriptor will be introduced and its classical and nonclassical components identified. Populational derivatives of its thermodynamic, *ensemble*-average value generate alternative indices of chemical reactivity, adequate in predicting both the direction and magnitude of electron flows in donor-acceptor systems[5–8] . The molecular virial theorem will be used to generate the information perspective on the bond-formation and the Hammond[81] postulate of reactivity theory. The theorem will be generalized to cover the *ensemble*-average energy components and the role of electronic kinetic energy or the resultant *gradient*-information in chemical processes will be examined. Physical equivalence of the energy and information reactivity descriptors in the *grand*-ensemble representation of *thermodynamic*-equilibria will be stressed, the relation between energetic and information reactivity indices will be examined, and the "production" of the overall structural information in chemical reactions will be addressed.

2 Resultant *gradient*-information and kinetic energy of electrons

Consider a general (complex) quantum state $|\psi\rangle$ of an electron described by the associated wavefunction in position representation,

$$\psi(r) = \langle r|\psi\rangle = R(r)exp[i\phi(r)] \tag{1}$$

with $R(\boldsymbol{r})$ and $\varphi(\boldsymbol{r})$ denoting its modulus and phase components, respectively. They determine the particle probability distribution,

$$p(r) = \psi(r)^*\psi(r) = R(r)^2 \tag{2}$$

and the current density

$$\begin{aligned} j(r) &= [\hbar/(2mi)][\psi(r)^*\nabla\psi(r) - \psi(r)\nabla\psi(r)^*] \\ &= (\hbar/m)\,p(r)\,\nabla\phi(r) \equiv p(r)V(r) \end{aligned} \tag{3}$$

The effective velocity $\boldsymbol{V}(\boldsymbol{r})$ of this probability "fluid" measures the current-per-particle and reflects the state *phase*-gradient:

$$V(r) = j(r)/p(r) = (\hbar/m)\nabla\phi(r) \tag{4}$$

The average Fisher's[28] measure of the *classical gradient*-information for locality events contained in the electronic probability density $p(\boldsymbol{r})$ is reminiscent of von Weizscker's[82] inhomogeneity correction to density-functional for the kinetic-energy:

$$\begin{aligned} I[p] &= \int p(r)[\nabla lnp(r)]^2 dr \equiv \int p(r)I_p(r)dr \\ &= 4\int [\nabla R(r)]^2 dr \equiv I[R] \end{aligned} \tag{5}$$

Here $p(\boldsymbol{r})\ I_p(\boldsymbol{r})$ denotes functional's overall density with $I_p(\boldsymbol{r}) = [\nabla \ln p(\boldsymbol{r})]^2$ standing for the associated density-per-electron. The amplitude form I[R] reveals that this classical descriptor reflects a magnitude of the state *modulus*-gradient. It characterizes an effective "narrowness" of the probability distribution, *i.e.*, a degree of determinicity in particle's position.

This *classical* functional of the *gradient*-information in probability distribution generalizes naturally into the of the quantum state $|\psi\rangle$, which combines the modulus (probability) and phase (current) contributions.[1, 18–22, 62] It is defined by quantum expectation value of the Hermitian operator $\hat{\mathrm{I}}(r)$ of the overall gradient information[62] ,related to electronic *kinetic*-energy operator $\hat{T}(r)$,

$$\begin{aligned}&\hat{I}(r) = -4\Delta \ = (2i\nabla)^2 = \ (8m/\hbar^2)\hat{T}(r) \equiv \sigma\hat{T}(r)\\&\hat{T}(r) = -\left[\hbar^2/\left(2m\right)\right]\nabla^2\end{aligned} \tag{6}$$

The integration by parts then gives the following expression for the average (resultant) *gradient*-information contained in quantum state $|\psi\rangle$:

$$\begin{aligned}I[\psi] &= \langle\psi|\hat{I}|\psi\rangle = -4\int \psi(r)^*\Delta\psi(r)dr\\&= 4\int |\nabla\psi\,(r)\,|^2 dr \equiv \int p(r)I_\psi(r)d\mathbf{r}\\&= I\,[p]\, + 4\int p(r)[\nabla\phi\,(r)]^2 dr\\&\equiv \int p(r)[I_p\,(r)\, + I_\phi\,(r)]d\mathbf{r}\\&\equiv I\,[p]\, + I[\phi] \equiv I[p,\phi]\\&= I\,[p]\, + (2m/h)^2\int p(r)^{-1}j(r)^2 dr\\&\equiv I\,[p]\, + I\,[j] \equiv I\,[p,j]\end{aligned} \tag{7}$$

This quantum *gradient*-information concept $I[\psi] = I[p,\varphi] = I[p,\boldsymbol{j}]$ is seen to combine the classical (probability) contribution $I[p]$ of Fisher and the corresponding nonclassical (phase/current) supplement $I[\varphi] = I[j]$. It also reflects the particle average (dimensionless) kinetic energy $T[\psi]$:

$$I[\psi] = \sigma\langle\psi|\hat{\mathrm{T}}|\psi\rangle T[\psi] = \sigma T[\psi] \tag{8}$$

The above *one*-electron development can be straightforwardly generalized into general N-electron state $|\Psi(N)\rangle$, exhibiting electron density $\rho(\boldsymbol{r}) = Np(\boldsymbol{r})$, where $p(\boldsymbol{r})$ stands for its probability (shape) factor. The corresponding information operator then combines terms due to each electron,

$$\hat{I}(N) = \sum_{i=1}^{N}\hat{I}(r_i) = \sigma\sum_{i=1}^{N}\hat{T}(r_i) \equiv \sigma\hat{T}(N) \tag{9}$$

and determines the (dimensionless) average *gradient*-information as its expectation value proportional to the state average kinetic energy $T(N)$.

$$\begin{aligned}I(N) &= \left\langle\psi\,(N)\,|\hat{I}\,(N)\ |\psi\,(N)\right\rangle\\&= \sigma\,\langle\psi\,(N)\,|\hat{T}\,(N)\,|\ \psi\,(N)\rangle = \sigma T(N)\end{aligned} \tag{10}$$

In the given electron (orbital) configuration specified by a single Slater determinant $\Psi(N) = |\psi_1\psi_2\ldots\psi_N|$, *e.g.*, in the familiar Hartree-Fock of Kohn-Sham theories, these N-electron descriptors combine the additive contributions due to all (singly occupied: $n_s = 1$), molecular orbitals (MO) $\psi = (\psi_1, \psi_2, \ldots, \psi_N) = \{\psi_s\}$:

$$\begin{aligned}T(N) &= \sum\nolimits_s n_s\langle\psi_s|\hat{T}|\psi_s\rangle \equiv \sum\nolimits_s n_sT_S\\&= \sigma^{-1}\sum\nolimits_s n_s\langle\psi_s|\hat{I}|\psi_s\rangle \equiv \sigma^{-1}\sum\nolimits_s n_sI_s\end{aligned} \tag{11}$$

In the analytical LCAO MO representation, when these occupied MO are expressed as linear combinations of the (orthogonalized) atomic orbital (AO) basis $\chi = (\chi_1, \chi_2, \ldots, \chi_k, \ldots)$,

$$|\psi\rangle = |\chi\rangle C, C = \langle\chi|\psi\rangle = \{C_{k,s} = \langle\chi_\kappa|\psi_s\rangle\} \tag{12}$$

the average gradient information contained in $\Psi(N)$, for the unit matrix of MO occupations, $\mathbf{n} = \{n_s\delta_{s,s'} = \delta_{s,s'}\}$, thus reads:

$$\begin{aligned}I(N) &= \sum\nolimits_s n_s\langle\psi_s|\hat{I}|\psi_s\rangle\\&= \sum\nolimits_\kappa\sum\nolimits_l\{\sum\nolimits_s C_{k,s}n_sC_{s,l}^*\}\langle\chi_l|\hat{I}|\chi_\kappa\rangle\\&\equiv \sum\nolimits_k\sum\nolimits_l\gamma_{k,l}\mathrm{I}_{l,k} = tr(\gamma\mathrm{I})\end{aligned} \tag{13}$$

Here, the AO representation of the resultant *gradient*-information operator,

$$\mathrm{I} = \{I_{k,l} = \langle\chi_k|\hat{I}|\chi_l\rangle = \sigma\langle\chi_k|\hat{T}|\chi_l\rangle \equiv \sigma T_{k,l}\} \tag{14}$$

and the Charge/Bond-Order (CBO) (density) matrix of LCAO MO theory,

$$\gamma = CnC^\dagger = \langle\chi|\psi\rangle n\langle\psi|\chi\rangle \equiv \langle\chi|\hat{P}_\psi|\chi\rangle \tag{15}$$

represents the AO-representation of the projection operator onto the occupied MO-subspace,

$$\begin{aligned}\hat{P}_\psi &= N[\sum\nolimits_s|\psi_s\rangle(n_s/N)\langle\psi_s|]\\&\equiv N[\sum\nolimits_s|\psi_s\rangle P_s\langle\psi_s|] \equiv N\hat{\mathrm{d}}\end{aligned} \tag{16}$$

proportional to the density operator $\hat{\mathrm{d}}$ of the configuration MO "ensemble".

This expression for the average overall *gradient*-information assumes thermodynamic-like form, as trace of the product of CBO matrix, the AO representation of the (occupation-weighted) MO projector, which establishes the configuration density operator $\hat{\mathrm{d}}$, and the corresponding AO matrix of the Hermitian operator for the resultant *gradient*-information, related to the system electronic kinetic energy. In this MO "ensemble" averaging the AO information matrix $\mathbf{I}$ constitutes the *quantity*-matrix, while the CBO (density) matrix γ provides the "geometrical" *weighting*-factors reflecting the system electronic state. It has been argued elsewhere that elements of the CBO matrix also generate amplitudes of electronic communications between molecular AO "events".[1,36–38,49–59] This observation adds a new angle to interpreting the average-information expression as the *communication*-weighted (dimentionless) kinetic energy of the system electrons[83] .

A separation of the *modulus*- and *phase*-components of general N-electron states calls for wavefunctions yielding the specified electron density[14] . It can effected using the Harriman-Zumbach-Maschke (HZM)[84,85] construction of DFT, which uses N (complex) *equidensity orbitals*, each separately generating the *molecular* probability distribution $p(\boldsymbol{r})$ and exhibiting the *density*-dependent spatial phase which safeguards the MO orthogonality.

3 Grand-ensemble description of molecular equilibria

In an *open* molecule M(v), identified by the external potential $v(\boldsymbol{Q})$ of the Born-Oppenheimer (BO) approximation for the molecular geometry $\boldsymbol{Q}$ specified by coordinates of the fixed nuclei of the system constituent atoms, the populational derivatives of the average electronic energy or the resultant *gradient*-information call for the *grand*-ensemble representation of thermodynamic equilibria.[5–8,15,86,87] A molecule is then coupled to a hypothetical (macroscopic) electron reservoir R(μ) exhibiting the chemical potential μ, and the heat bath B(T) identified by its absolute temperature T in the composite (macroscopic) system

$$M(\mu,T;v) = [R(\mu)M\,(v)\,B\,(T)] \tag{17}$$

where the vertical *broken* lines separating subsystems symbolize their freedom to exchange electrons or energy. The average number of electrons in such an *externally*-open molecule,

$$\begin{aligned}&\langle \mathrm{N}\rangle_{ens.} \equiv N \;=\; tr(\hat{D}\hat{N}) \;=\sum\nolimits_i P_i N_i\\ &\sum\nolimits_i P_i \;=\; 1, \quad P_\imath \geqslant 0\end{aligned} \tag{18}$$

exhibits a continuous (fractional) spectrum of values, thus justifying the very concept of the populational (N) *derivative* itself. Here,

$$\hat{N} \;=\sum\nolimits_i\sum\nolimits_j |\psi_j\,(N_i)\rangle N_i\langle\psi_j\,(N_i)\,| \tag{19}$$

stands for the particle-number operator in Fock's space and the density operator identifies the equilibrium statistical mixture of the system stationary states $\{|\psi_j[N_i,v]\rangle \equiv |\psi_j{}^i\rangle\}$,

$$\hat{D}(\mu,T;v) = \sum\nolimits_i\sum\nolimits_j |\psi_j\,(N_i)\,\rangle\, P_j{}^i(\mu,T;v)\langle\psi_j\,(N_i)\,| \tag{20}$$

eigenstates of Hamiltonians $\{\hat{\mathrm{H}}(N_i,v) \equiv \hat{\mathrm{H}}_i\}$ for different (integer) numbers of electrons $\{N_i \equiv i\}$ corresponding to energies $\{E_j[N_i,v] \equiv E_j{}^i\}$,

$$\begin{aligned}&\hat{H}(N_i,v)|\psi_j\,[N_i,v]\rangle = E_j(N_i)|\psi_j\,[N_i,v]\rangle\\ &or \quad \hat{H}|\psi_j{}^i\rangle = E_j{}^i|\psi_j{}^i\rangle\end{aligned} \tag{21}$$

these (pure) quantum states appear in the *grand*-ensemble with the (*externally*-imposed) equilibrium thermodynamic probabilities $\{P_j{}^i(\mu,\,T;\,v) \equiv P_j{}^i \geq 0\}$ and the "condensed" probability in Equation 18 is obtained by the partial summation over eigenstates of $\hat{\mathrm{H}}_i$: $P_i = \sum_j P_j{}^i$.

Such electronic N-derivatives are involved in definitions of the system Charge Transfer (CT) criteria of chemical reactivity,[15,74–79] *e.g.*, the chemical potential (negative electronegativity)[15,86–90] or the hardness (softness)[91] and Fukui Function (FF)[92] descriptors of electrons. They are thus definable only for the *mixed*-state of the molecular (microscopic) system M(v), *e.g.*, that corresponding to the thermodynamic equilibrium imposed by intensities (μ, T) characterizing the external (macroscopic) subsystems R(μ) and B(T) in M(μ, T; v), $\mu = \mu_R$ and T=T_B, *i.e.*, for the equilibrium *grand*-canonical density operator of Equation 20: $\hat{\mathrm{D}}_{eq.} \equiv \hat{D}(\mu,T;\,v)$.

The *grand*-canonical intensities determine the ensemble thermodynamic potential, called the *grand*-potential, given by the corresponding Legendre-transform[9] of the *ensemble*-average energy

$$\begin{aligned}\langle E\rangle_{ens.} \equiv\;& E[\hat{D}] \equiv E(N,S;v) = tr(\hat{D}\hat{H})\\ =\;& \sum\nolimits_i\sum\nolimits_j P_j{}^i E_j{}^i\end{aligned} \tag{22}$$

$$\begin{aligned}\Omega =\;& E - ({}^{\partial E}\!/_{\partial N})N - \;({}^{\partial E}\!/_{\partial S})S\\ =\;& E[\hat{D}] - \mu N[\hat{D}] - TS[\hat{D}]\end{aligned} \tag{23}$$

It minimizes at the optimum *state*-probabilities $\{P_j{}^i(\mu,T;v)\} \equiv \boldsymbol{P}_{eq.}(\mu,T;\boldsymbol{Q})$:

$$\begin{aligned}\min_{\hat{\mathrm{D}}} \Omega[\hat{\mathrm{D}}] =\;& \Omega[\hat{\mathrm{D}}(\mu,T;v)]\\ =\;& E[\hat{\mathrm{D}}_{eq.}] - \mu N[\hat{\mathrm{D}}_{eq.}] - TS[\hat{\mathrm{D}}_{eq.}]\\ \equiv\;& \Omega(\mu,T;v) \Rightarrow P_{eq.}(\mu,T;\,Q)\end{aligned} \tag{24}$$

As indicated in the preceding equation, the ensemble parameters μ and T ultimately determine the associated optimum probabilities of the (pure) stationary states $\{|\psi_j[N_i,v]\rangle\}$, eigenstates of Hamiltonians $\{\hat{\mathrm{H}}_i\}$,

$$\begin{aligned}\{P_j{}^i(\mu,\mathrm{T};v) &= \Xi^{-1}exp[\beta(\mu N_i - E_j{}^i)]\}\\ &\equiv P_{eq.}(\mu,T;Q)\end{aligned} \tag{24-1}$$

which define the equilibrium density operator of Equation 20 for the specified geometrical structure $\boldsymbol{Q}$. Here Ξ stands for the *grand*-ensemble partition function, k_B denotes the Boltzmann constant, and $\beta = (k_B T)^{-1}$.

The *electronically*-relaxed, equilibrium ensemble probabilities thus satisfy the following relations between the probability "gradients" for the adopted molecular geometry $\boldsymbol{Q}$:

$$\begin{aligned}&\left.\frac{\partial\Omega(P,Q)}{\partial P}\right|_{P_{eq.}} = 0 \quad \text{or}\\ &\left.\frac{\partial E(P,Q)}{\partial P}\right|_{P_{eq.}} = \mu\left.\frac{\partial N(P)}{\partial P}\right|_{P_{eq.}} + T\left.\frac{\partial S(P)}{\partial P}\right|_{P_{eq.}}\end{aligned} \tag{25}$$

where the explicit dependence of on nuclear coordinates $\boldsymbol{Q}$, resulting from the external potential contribution in the ensemble Hamiltonians $\{\hat{H}_i\}$,also influences eigenvalues$\{E_j{}^i\}$.

The *grand*-potential corresponds to replacing the "extensive" *state*-parameters, of the average values of the particle number $\boldsymbol{N} = N[\hat{\mathrm{D}}]$ and thermodynamic entropy[93]

$$\begin{aligned}S[\hat{D}] = tr(\hat{D}\hat{S}) &= -k_B\sum_i\sum_j P_j{}^i ln P_j{}^i\\ \hat{S} = -k_B\sum_i\sum_j &|\psi_j{}^i\rangle ln P_j{}^i \langle\psi_j{}^i|\end{aligned} \tag{26}$$

bytheir "intensive" conjugates: the chemical potential μ and absolute temperature *T*, respectively. This Legendre-transform includes these "intensities" as Lagrange multipliers enforcing, at the minimum of , the constraints of the specified values of the system *ensemble*-average values of the conjugate "extensive" parameters: the system overall number of electrons,

$$\begin{aligned}\langle N\rangle_{ens.} = N[\hat{D}_{eq.}] &= \sum_i[\sum_j P_j{}^i(\mu,T;v)]N_i\\ &= \sum_i P_i(\mu,T;v)N_i = \langle N(\mu,T;v)\rangle_{ens.}\\ &= N[\mu,T;v] = N\end{aligned} \tag{27}$$

and of thermodynamic (von Neumann's[93]) entropy:

$$\begin{aligned}\langle S\rangle_{ens.} =\ & S[\hat{D}_{eq.}]\\ &= -k_B\sum_i\sum_j P_j{}^i(\mu,T;v) ln P_j{}^i(\mu,T;v)\\ &= \langle S(\mu,T;v)\rangle_{ens.} = S(\mu,T) = S\end{aligned} \tag{28}$$

In equilibrium state the prescribed average extensive descriptors *N* and *S* also uniquely identify the externally-imposed state intensities, $\mu = \mu(N,S)$and$T = T(N,S)$, and hence also the equilibrium energy function

$$\begin{aligned}E[\hat{D}_{eq.}] &= \langle E(\mu,T;v)\rangle_{ens.}\\ &= \sum_i\sum_j P_j{}^i(\mu,T;v)\langle\psi_j{}^i|\hat{H}_i|\psi_j{}^i\rangle\\ &= \sum_i\sum_j P_j{}^i(\mu,T;v)E_j{}^i\\ &= E(\mu,T)\\ &\equiv E(N,S)\end{aligned} \tag{29}$$

It allows one to formally identify the intensive parameters as its partial derivatives with respect to the constrained values of the extensive state-variables:

$$\begin{aligned}\mu &= \left.\left(\frac{\partial E}{\partial N}\right)_S\right|_{\hat{\mathrm{D}}_{eq.}} \quad \text{and}\\ T &= \left.\left(\frac{\partial E}{\partial S}\right)_N\right|_{\hat{\mathrm{D}}_{eq.}}\end{aligned} \tag{30}$$

In the $T \to 0$ limit[15,86,87] only two *ground*-states ($j = 0$), $\{|\psi_0{}^i\rangle, |\psi_0{}^{i+1}\rangle\}$, corresponding to the neighboring integers "bracketing" the given (fractional) $\langle N\rangle_{ens.} = N$, $N_i \leq \langle N\rangle_{ens.} \leq N_i + 1$, appear in the equilibrium statistical mixture. Their ensemble probabilities for the specified

$$\langle N\rangle_{ens.} = iP_i + (i+1)(1-P_i) = N \tag{31}$$

then read:

$$\begin{aligned}P_i &= 1 + i - N \equiv 1 - \omega \ \ and\\ P_{i+1} &= N - i \equiv \omega\end{aligned} \tag{32}$$

The continuous energy function *E*(*N*,*S*) then consists of the straight-line segments between the neighboring integer values of *N*. This implies constant values of the chemical potential in all such admissible ranges of the average electron number and μ-discontinuity at $N = N_i$(integer).[15,86,87]

The *ensemble*-average value of the resultant *gradient*-information,

$$\begin{aligned}\langle I\rangle_{ens.} &\equiv I[\hat{D}_{eq.}] = tr\ [\hat{D}_{eq.}\hat{I}]\\ &= \sum_i\sum_j P_j{}^i(\mu,T;v)\langle\psi_j{}^i|\hat{I}(N_i)|\psi_j{}^i\rangle\\ &\equiv \sum_i\sum_j P_j{}^i(\mu,T;v)I_j{}^i\\ I_j{}^i &= (8m/\hbar^2)\langle\psi_j{}^i|\hat{T}(N_i)|\psi_j{}^i\rangle \equiv \sigma T_j{}^i\end{aligned} \tag{33}$$

is related to the *ensemble*-average kinetic energy $\boldsymbol{T}$:

$$\begin{aligned}\langle T\rangle_{ens.} &\equiv I[\hat{D}_{eq.}] = tr(\hat{D}_{eq.}\hat{T})\\ &= \sum_i\sum_j P_j{}^i(\mu,T;v)\langle\psi_j{}^i|\hat{T}(N_i)|\psi_j{}^i\rangle\\ &\equiv \sum_i\sum_j P_j{}^i(\mu,T;v)T_j{}^i = \sigma^{-1}\langle I\rangle_{ens.}\end{aligned} \qquad (34)$$

The proportionality constant results from relation between the associated electronic operators:

$$\begin{aligned}\hat{T}(N_i) &= \frac{-\hbar^2}{2m}\sum_{k=1}^{N_i}\nabla_k^2 \qquad and\\ \hat{I}(N_i) &= -4\sum_{k=1}^{N_i}\nabla_k^2\end{aligned} \qquad (35)$$

Therefore, the thermodynamic rule of Equation 24, for the minimum of the constrained average value of electronic energy can be alternatively interpreted as the corresponding extremum principle for the *ensemble*-average (resultant) *gradient*-information:[5–8, 36–38, 40]

$$\begin{aligned}&\sigma \min_{\hat{\mathrm{D}}} \Omega[\hat{\mathrm{D}}] = \sigma\Omega[\hat{\mathrm{D}}_{eq.}]\\ &= I[\hat{\mathrm{D}}_{eq.}] + \sigma\{W[\hat{\mathrm{D}}_{eq.}] - \mu N[\hat{\mathrm{D}}_{eq.}] - TS[\hat{\mathrm{D}}_{eq.}]\}\end{aligned} \qquad (36)$$

where the *ensemble*-average value of the system overall potential energy,

$$W[\hat{\mathrm{D}}_{eq.}] = V[\hat{\mathrm{D}}_{eq.}] + U[\hat{\mathrm{D}}_{eq.}] \qquad (37)$$

combines the nuclear-attraction ($V[\hat{\mathrm{D}}_{eq.}]$) and electron-repulsion ($U[\hat{\mathrm{D}}_{eq.}]$) contributions. This information principle is seen to contain an additional constraint of the fixed potential energy, $\langle W\rangle_{ens.} = \boldsymbol{W}$, multiplied by the Lagrange multiplier

$$\lambda_W = -\sigma = \left(\frac{\partial I}{\partial W}\right)_{N,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} \equiv K \qquad (38)$$

besides the remaining constraints, now multiplied by the "scaled" conjugate intensities[5–8] : information "*potential*"

$$\xi \equiv \sigma\mu = \left(\frac{\partial I}{\partial N}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} \qquad (39)$$

information "*temperature*"

$$\tau \equiv \sigma T = \left(\frac{\partial I}{\partial S}\right)_{W,N}\Bigg|_{\hat{\mathrm{D}}_{eq.}} \qquad (40)$$

The conjugate thermodynamic principles, for constrained extrema of the ensemble energy,

$$\delta\Big(E[\hat{\mathrm{D}}] - \mu N[\hat{\mathrm{D}}] - TS[\hat{\mathrm{D}}]\Big)_{\hat{\mathrm{D}}_{eq.}} = 0 \qquad (41)$$

and its overall *gradient*-information,

$$\delta\left(I[\hat{\mathrm{D}}] - \kappa\, W[\hat{\mathrm{D}}] - \xi\, N[\hat{\mathrm{D}}] - \tau\, S[\hat{\mathrm{D}}]\right)_{\hat{\mathrm{D}}_{eq.}} = 0 \qquad (42)$$

have the same optimum-probability solutions of Equation 25. This manifests the physical equivalence of the energetic and "entropic" principles in determining the equilibrium states in thermodynamics[9] .

Several N-derivatives of the *ensemble*-average electronic energy or of the resultant *gradient*-information define useful and adequate CT criteria of chemical reactivity.[15, 74–79] The physical equivalence of the energy and information principles indicates that such concepts are mutually related, being both capable of describing the electron-transfer phenomena in donor-acceptor systems[5–8] . The above ensemble interpretation also applies to diagonal and mixed *second* derivatives of the electronic energy or its kinetic-energy (information) component, which involve the population differentiation.

In *energy*-representation the *chemical hardness*[91] , the "diagonal" populational *second*- derivative of the ensemble energy, reflects the N-derivative ofchemical potential,

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_S\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \left(\frac{\partial \mu}{\partial N}\right)_S\Bigg|_{\hat{\mathrm{D}}_{eq.}} > 0 \qquad (43)$$

while the *information* "hardness" reflects the N-derivative of information "*potential*"[5–8] :

$$\omega = \left(\frac{\partial^2 I}{\partial N^2}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \left(\frac{\partial \xi}{\partial N}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \sigma\eta > 0 \qquad (44)$$

The positive signs of these diagonal population derivatives assure the *external* stability of an open M(v), with respect to hypothetical electron flows between molecular system and its reservoir. They indeed imply an increase (a decrease) of the global energetic and information "intensities" coupled to $\boldsymbol{N}$, μ and ξ, in response to perturbations created by the initial electron inflow (outflow). This accords with the Le Chtelier and Le Chtelier-Braun principles of thermodynamics[9] , that spontaneous responses in system intensities to the initial population displacements diminish effects of the primary perturbations.

By the *cross*-differentiation identity the "*mixed*" *second*-derivative of the ensemble energy, measuring the system global FF[92] , can be alternatively interpreted as either the response in global chemical potential per unit displacement in the external potential, or the density response per unit populational displacement.

$$\begin{aligned} f(r) &= \left(\frac{\partial^2 E}{\partial N \partial v(r)}\right)_S\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \left(\frac{\partial \mu}{\partial v(r)}\right)_S\Bigg|_{\hat{\mathrm{D}}_{eq.}} \\ &= \left(\frac{\partial \rho(r)}{\partial N}\right)_S\Bigg|_{\hat{\mathrm{D}}_{eq.}} \end{aligned} \tag{45}$$

The associated mixed derivative of the resultant gradient information in the *grand*-ensemble similarly reads:

$$\begin{aligned} \varphi r &= \left(\frac{\partial^2 I}{\partial N \partial v(r)}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \left(\frac{\partial \xi}{\partial v(r)}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} \\ &= \ \sigma \left(\frac{\partial \rho(r)}{\partial N}\right)_{W,S}\Bigg|_{\hat{\mathrm{D}}_{eq.}} = \sigma\, f(r) \end{aligned} \tag{46}$$

It has been argued elsewhere[5–8] , that the *in situ* measures of these energy and information derivatives constitute fully equivalent descriptors of electron flows between the polarized subsystems. These CT phenomena in the polarized reactive system $R^+ = (A^+|B^+)$, containing the *mutually*-closed and molecularly polarized *acceptor* (acid, A) and *donor* (basis, B) reactants $\{\alpha^+\}$, are described by populational derivatives: the substrate chemical potentials $\mu_R{}^+ = \{\mu_a{}^+\}$ and elements of the hardness matrix $\eta_R{}^+ = \{\eta\alpha_{,\beta}\}$. These descriptors again call for the *grand*-ensemble representation of the polarized (*externally*-open) reactants, in contact with their separate (macroscopic) electron reservoirs $\{R_a\}$. They represent the electron population $\{N_a \equiv N_a\}$ derivatives of the *ensemble*-average electronic energy in R^+, $E[\{N_\beta\}, v] \equiv E_v(\{N_\beta\})$, the microscopic subsystem in the macroscopic (composite) system,

$$\begin{aligned} M_R{}^+ &= (M_A{}^+|M_B{}^+) \\ &= (R_A A^+|B^+ R_B) \\ &\equiv (R_A M(v)^+ R_B) \end{aligned} \tag{47}$$

where the solid and broken vertical lines separating subsystems again denote their mutual closeness and openness, respectively, with respect to hypothetical flows of electrons. They are calculated for the fixed molecular external potential *v*(***Q***) reflecting the "frozen" molecular geometry ***Q***.

The *in situ* descriptors of CT are thus derived from the corresponding partials of the system *ensemble*-average energy with respect to *ensemble*-average electron populations $\{\mathrm{N}_a\}$ on (*externally*-open) *molecular*-subsystems $\{\alpha^+\}$ in the (*mutually*-closed) *composite* fragments $\{M_a{}^+ = (a^+ R_a)\}\ of\ M_R{}^+$:

$$\begin{aligned} \mu_a &\equiv \partial E_v(\{N_\gamma\})/\partial N_a \\ \eta_{\alpha,\beta} &= \partial^2 E_v(\{N_\gamma\})/\partial N_\alpha \partial N_\beta = \partial \mu_\alpha/\partial \mathrm{N}_\beta \\ &= \partial \mu_\beta/\partial \mathrm{N}_\alpha = \eta_{\beta,\alpha} \end{aligned} \tag{48}$$

The optimum amount of the (fractional) CT is determined by the difference in chemical potentials of the (equilibrium) polarized reactants in R^+,

$$\mu_{CT} = \partial E_v\left(N_{CT}\right)/\partial N_{CT} = \mu_{\mathrm{A}}{}^+ - \mu_{\mathrm{B}}{}^+ < 0 \tag{49}$$

which defines the effective CT-gradient, and the *in situ* hardness (η_{CT}) or softness (S_{CT}) for this process,

$$\begin{aligned} \eta_{CT} &= \partial \mu_{CT}/\partial N_{CT} \\ &= (\eta_{\mathrm{A,A}} - \eta_{\mathrm{A,B}}) + (\eta_{\mathrm{B,B}} - \eta_{\mathrm{B,A+}}) \equiv \eta_{\mathrm{A}}{}^{\mathrm{R}} + \eta_{\mathrm{B}}{}^{\mathrm{R}} \\ &\equiv \Sigma_{CT}{}^{-1} \end{aligned} \tag{50}$$

representing the effective CT-Hessian and its inverse, respectively. The optimum amount of the *inter*-reactant CT,

$$N_{CT} = -\mu_{CT} S_{CT} = -\mu_{CT}/\eta_{CT} \tag{51}$$

then generates the associated (2^{nd}-order) stabilization energy:

$$E_{CT} = {}^{\mu_{CT} N_{CT}}\!/_{2} = {}^{-\mu_{CT}{}^2 S_{CT}}\!/_{2} < 0 \tag{52}$$

The corresponding CT-derivatives of the average *gradient*-information in AB systems similarly involve the *in situ* information potential,

$$\xi_{CT} = \partial I\left(N_{CT}\right)/\partial N_{CT} = \xi_A{}^+ - \xi_B{}^+ = \sigma \mu_{CT} \tag{53}$$

and the associated hardness descriptor, the inverse of the information softness θ_{CT},

$$\omega_{CT} = \partial \xi_{CT}/\partial N_{CT} \equiv \theta_{CT}{}^{-1} = \sigma \eta_{CT} = \sigma\ S_{CT}{}^{-1} \tag{54}$$

In terms of these information descriptors the amount of CT in the acid-base system reads:

$$\begin{aligned} N_{CT} &= -\xi_{CT}/\omega_{CT} = -\xi_{CT}\theta_{CT} \\ &= -\mu_{CT}/\eta_{CT} = -\mu_{CT} S_{CT} \end{aligned} \tag{55}$$

Thus, the *in situ* populational derivatives (ξ_{CT}, $\omega_{CT} = \theta_{CT}{}^{-1}$) of the *ensemble*-average measures of the (resultant) *gradient*-information functionals, provide alternative reactivity descriptors, fully equivalent to the chemical potential and hardness/softness indices (μ_{CT}, $\eta_{CT} = S_{CT}{}^{-1}$) of the energy representation. This demonstrates the physical equivalence of the energy and information treatments of CT phenomena in molecular systems. One thus concludes that the resultant *gradient*-information, the quantum generalization of the classical Fisher measure, indeed constitutes a reliable basis for an "entropic" description of reactivity phenomena.

4 Virial theorem implications

The virial theorem for the stationary electronic states $|\psi_j{}^i\rangle = |\psi_j[N_i,v]\rangle$ in molecules reflects homogeneities of the kinetic and potential energy contributions in such *pure* quantum states,

$$T_j{}^i = \langle\psi_j{}^i|\hat{T}(N_i)|\psi_j{}^i\rangle \text{ and } W_j{}^i = \langle\psi_j{}^i|\hat{W}(N_i,v)|\psi_j{}^i\rangle$$
$$\hat{W}(N_i,v) = \sum_{k=1}^{N_i}[v(k) + \frac{1}{2}\sum_{l\neq k} g(k,l)] = \hat{V}(N_i,v) + \hat{U}(N_i,v) \tag{56}$$

with respect to the uniform scaling of the system electronic and nuclear positions. Here, $g(k,l)$ denotes the repulsion between electrons k and l, and the state electronic energy in $|\psi_j{}^i\rangle$

$$E_j{}^i = \langle\psi_j{}^i|\hat{H}_i|\psi_j{}^i\rangle = T_j{}^i + W_j{}^i \tag{57}$$

In BO approximation both this average energy and its components are parametrically dependent upon molecular geometry specified by the fixed (Cartesian) coordinates $\boldsymbol{Q}$ of the nuclei, and so are the energy differences with respect to the adopted reference, *e.g.*, the Separated Atoms Limit (SAL) or the separated reactants,

$$\begin{aligned} E_j{}^i(Q) &= T_j{}^i(Q) + W_j{}^i(Q) \quad \textit{and} \\ \Delta E_j{}^i(Q) &= \Delta T_j{}^i(Q) + \Delta W_j{}^i(Q) \end{aligned} \tag{58}$$

The molecular virial theorem for the pure stationary state in BO approximation reads[10] :

$$\begin{aligned} &2T_j{}^i(Q) + W_j{}^i(Q) + Q\cdot[\partial E_j{}^i(Q)/\partial Q] \\ &\equiv 2T_j{}^i(Q) + W_j{}^i(Q) + Q\cdot\nabla_Q E_j{}^i(Q) = 0 \end{aligned} \tag{59}$$

It extracts the kinetic and potential components of the overall electronic energy for the current geometrical structure of the molecular system,

$$\begin{aligned} T_j{}^i(Q) &= -E_j{}^i(Q) - Q\cdot\nabla_Q E_j{}^i(Q) \quad \textit{and} \\ W_j{}^i(Q) &= 2E_j{}^i(Q) + Q\cdot\nabla_Q E_j{}^i(Q) \end{aligned} \tag{60}$$

or similarly partitions the relative energies $\Delta E_j{}^i(\boldsymbol{Q})$ of Equation 58.

These relations assume a particularly simple form for the energetical *profiles*, sections of the BO Potential Energy Surface (PES), *e.g.*, the energy function in diatomics, for which the internuclear distance R uniquely specifies the molecular geometry, or along the reaction-coordinate (RC) $\boldsymbol{R}_c$ in chemical processes, with the trajectory arc-length $P = |\boldsymbol{R}_c|$ determining the reaction-progress variable. In diatomics the virial theorem expressed in terms of energy changes relative to SAL reads:

$$\begin{aligned} &2\Delta T_j{}^i(R) + \Delta W_j{}^i(R) + R[d\Delta E_j{}^i(R)/dR] = 0 \quad \textit{or} \\ &\Delta T_j{}^i(R) = -\Delta E_j{}^i(R) - R[d\Delta E_j{}^i(R)/dR] \\ &\qquad = -d[R\Delta E_j{}^i(R)]/dR \quad \textit{and} \\ &\Delta W_j{}^i(R) = 2\Delta E_j{}^i(R) + R[d\Delta E_j{}^i(R)/\partial R] \\ &\qquad = R^{-1}d[R^2\Delta E_j{}^i(R)]/dR \end{aligned} \tag{61}$$

The virial theorem is satisfied in each stationary state $|\psi_j{}^i\rangle$ of the molecular system under consideration. Therefore, it is also obeyed bythe*ensemble*-averagecomponents corresponding to thermodynamic equilibria. Indeed, multiplying Equation 59 and Equation 60 bythe *ensemble*-probabilities $\{P_j{}^i(\mu,T;\ v)\} \equiv \boldsymbol{P}(\mu,T;\boldsymbol{Q})\}$, from the *grand*-canonical equilibrium principle of Equation 24 and Equation 25, and summing over all stationary states involved in this statistical mixture gives directly the associated thermodynamic relations:

$$\begin{aligned} &2T(Q) + W(Q) + Q\cdot\nabla_Q E(Q) = 0 \quad \textit{or} \\ &T(Q) = -E(Q) - Q\cdot\nabla_Q E(Q) \quad \textit{and} \\ &W(Q) = 2E(Q) + Q\cdot\nabla_Q E(Q) \end{aligned} \tag{62}$$

They determine both the system thermodynamic energy,

$$E[\hat{D}_{eq.}] = T[\hat{D}_{eq.}] + W[\hat{D}_{eq.}] \tag{63}$$

its kinetic component $T[\hat{D}_{eq.}] = \sigma^{-1}I[\hat{D}_{eq.}]$ proportional to the associated overall *gradient*-information descriptor $I[\hat{\mathrm{D}}_{eq.}]$, and the *ensemble*-average potential energy

$$\begin{aligned} W[\hat{\mathrm{D}}_{eq.}] &= \langle W\rangle_{ens.} = tr\ (\hat{\mathrm{D}}_{eq.}\hat{\mathrm{W}})Q_{eq.} \\ &= \sum\nolimits_i\sum\nolimits_j P_j{}^i(\mu,T;v)\langle\psi_j{}^i|\hat{\mathrm{W}}(N_i,v)|\psi_j{}^i\rangle \\ &\equiv \sum\nolimits_i\sum\nolimits_j P_j{}^i(\mu,T;v)W_j{}^i \end{aligned} \tag{64}$$

One observes that this generalized, *mixed*-state partitioning also includes the *pure*-state relations of Equation 58 and Equation 59 as the special (*micro*-canonical) case corresponding to $P_j{}^i = 1$ and $\{P_{l\neq j}^{k}{}^{\neq i} = 0\}$.

Let us briefly examine some implications of this general balance between the kinetic and potential components of the thermodynamic value of electronic energy. For the *energy*-minimum geometry $Q_{eq.}(E) = Q_{eq.}$, determined by the vanishing gradient of thermodynamic energy,

$$\nabla_Q E|_{eq.} = 0 \tag{65}$$

the thermodynamic virial relations simplify:

$$T\left(Q_{eq.}\right) \;= -E\left(Q_{eq.}\right) \;= \sigma^{-1} I\left(Q_{eq.}\right) \quad and \quad W\left(Q_{eq.}\right) = 2E\left(Q_{eq.}\right) \tag{66}$$

For such a *geometrically*-relaxed structure the *minimum*-energy principle of thermodynamics thus implies the thermodynamic *maximum*-information rule in QIT:

$$\{min_P[E\left(P\right)]_{\mu,T;Qeq.} \Rightarrow max_P[I\left(P\right)]_{\mu,T;Qeq.}\} \Rightarrow P(\mu,T;Q)\} \tag{67}$$

Inother words, in thermodynamic (*electronically*-relaxed) equilibrium the *geometrically*-relaxed molecular systems assume the maximum resultant *gradient*-information related to its average kinetic energy. This information principle complements the familiar *maximum*-entropy rule of ordinary thermodynamics[9] .

It should be observed that the *energy*-optimum structure $\boldsymbol{Q}_{eq.}(E\;)$ of Equation 65 differs from that determined by the vanishing geometric gradient of the *grand*-potential,

$$\left.\frac{\partial\Omega(P,Q)}{\partial Q}\right|_{\bar{Q}_{eq.}} = 0 \;\Rightarrow\; Q_{eq.}(\Omega) = \bar{Q}_{eq.} \neq Q_{eq.} \tag{68}$$

since then

$$\left.\frac{\partial E(P,Q)}{\partial Q}\right|_{\bar{Q}_{eq.}} = \mu \left.\frac{\partial N(P)}{\partial Q}\right|_{\bar{Q}_{eq.}} + T\left.\frac{\partial S(P)}{\partial Q}\right|_{\bar{Q}_{eq.}} = \left(\mu\frac{\partial N(P)}{\partial P} + T\frac{\partial S(P)}{\partial P}\right)\left.\left(\frac{\partial P}{\partial Q}\right)\right|_{\bar{Q}_{eq.}} \tag{69}$$

Consider now the *pure*-state (*micro*-canonical) case summarized by the virial relations of Eqs. Equation 58-60, which allow to extract the kinetic-energy/gradient-information differences from the corresponding energy profiles. Elsewhere[7,8] we have examined the BO energy profiles corresponding to the *bond*-formation process, A + B = AB (see Figure 1), and the bimolecular chemical-reaction, A + B $\rightarrow$ R^{z} $\rightarrow$ C + D (see Figure 2), where R^{z} denotes the Transition-State (TS) complex, in order to examine the accompanying changes in the resultant gradient information. Let us summarize some general conclusions of this analysis.

Figure 1 presents qualitative plots reflecting variations with internuclear distance of the ground-state *bond*-energy and its *kinetic*-energy contribution. The BO potential $\Delta E(R)$ and its *kinetic*-energy component $\Delta T(R)$ also reflecting variations in (resultant) gradient-information $\Delta I(R) = \sigma\Delta T(R)$, relative to SAL, allow one to examine the energy/information variations with *inter*-nuclear distance R in the bond formation process. It follows from the figure that during a mutual approach by the constituent atoms the kinetic-energy/gradient-information is first diminished relative to the SAL reference, due to the *longitudinal* Cartesian component of the kinetic energy, associated with the "z" direction (along the bond axis).[94,95] At the equilibrium distance R_e the resultant information rises above the SAL value, due to the dominating increase in *transverse* components of the kinetic energy, corresponding to "x" and "y" directions perpendicular to the bond axis. Therefore, at the equilibrium bond length R_e the chemical bond gives rise to a net *increase* in the resultant *gradient*-information relative to SAL, where electrons of each atom experience the external potential of only its own nucleus. This reflects a relatively more compact electron distribution in a molecule, where electrons move in the field of both nuclei.

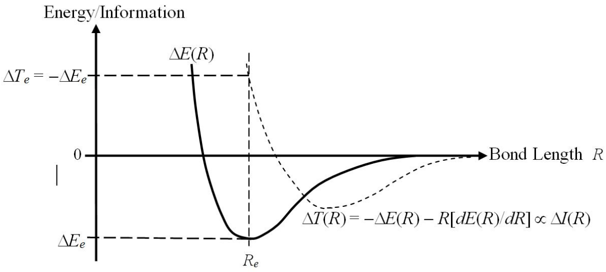

Figure 1. Qualitative diagram of variations in the BO electronic energy $\Delta E(R)$ (solid line) with the internuclear distance R in a diatomic molecule, and of its kinetic energy component from the virial-theorem partitioning, $\Delta T(R) = -d/dR[R\Delta E(R)]$ (broken line), also reflecting the state resultant *gradient*-information $\Delta I(R) = \sigma\Delta T(R)$

Another interesting case of variations in molecular geometry is the (intrinsic) reaction coordinate $\boldsymbol{R}_c$, or equivalently the *progress*-variable (*arc*-length) P along this trajectory, for which the virial relations assume the diatomic-like form (see Figure 2). Let us again examine the virial theorem decomposition of the corresponding energy profile along the $\boldsymbol{R}_c$-section of PES, $\Delta E(\boldsymbol{R}_c) \equiv \Delta E(P)$, in an elementary bimolecular reaction, to which the qualitative Hammond[81] postulate of reactivity theory applies. Again, the *ground*-state *virial*-theorem decomposition can be used to extract qualitative plots of the resultant *gradient*-information from the energy profiles corresponding either to *endo*- or *exo*-ergic reactions (upper panel), or to the energy-*neutral* chemical process on symmetric PES (lower panel).

The qualitative rule of Hammond is seen to be fully indexed by the sign of the geometric, *P*-derivative of the average resultant-information at the TS complex.[5,8–10] More specifically, this postulate emphasizes a relative resemblance of the reaction TS complex $R^{\ddagger}$ to its substrates (products) in the *exo*-ergic (*endo*-ergic) reactions, while for the vanishing reaction energy the position of TS complex is predicted to be located symmetrically between substrates and products. In other words, the activation barrier appears "early" in the *exo*-ergic reactions, *e.g.*, H_2 + F → H + HF, with the reaction substrates being only slightly modified in $R^{\ddagger} \approx [A---B]$, both electronically and geometrically. Accordingly, in the *endo*-ergic bond-breaking-bond-forming process, e.g., H + HF → H_2 + F, the barrier is "late" along the reaction *progress*-variable *P* and the activated complex resembles more the reaction *products*: $R^{\ddagger} \approx [C---D]$. This qualitative statement has been subsequently given several more quantitative formulations and theoretical explanations, based upon both the energetic and entropic arguments[96–103].

The energy profile along the reaction "progress" coordinate *P*,

$$\Delta E(P) = E(P) - E(P_{substrates}) \tag{70}$$

is directly "translated" by the molecular virial theorem into the associated displacement in its kinetic-energy contribution,

$$\Delta T(P) = T(P) - T(P_{substrates}) \tag{71}$$

proportional to the corresponding change in the system resultant *gradient*-information:

$$\Delta I(P) = I(P) - I(P_{substrates}) = \sigma \Delta T(P) \tag{72}$$

$$\begin{aligned} \Delta T(P) &= -\Delta E(P) - P[d\Delta E(P)/dP] \\ &= -d[P\Delta E(P)]/dP \end{aligned} \tag{73}$$

The energy profiles $\Delta E(P)$ in the *endo*- or *exo*-directions, for the positive and negative reaction energy

$$\Delta E_r = E(P_{products}) - E(P_{substrates}) \tag{74}$$

respectively, thus determine uniquely the associated profiles of kinetic-energy (or resultant-information): $\Delta I(P) = \sigma \Delta T(P)$. A reference to qualitative plots in Figure 2 shows that the latter indeed distinguishes these two directions by the sign of its geometrical derivative at $R^{\ddagger}$:

$$\begin{aligned} &endo - direction: \\ &\{(dI/dP)_{\ddagger} > 0 \quad and \quad (dT/dP)_{\ddagger} > 0, \quad \Delta E_r > 0 \\ &energy - neutral: \\ &(dI/dP)_{\ddagger} = 0 \quad and \quad (dT/dP)_{\ddagger} = 0, \quad \Delta E_r = 0 \\ &exo - direction: \\ &(dI/dP)_{\ddagger} < 0 \quad and \quad (dT/dP)_{\ddagger} < 0, \quad \Delta E_r < 0 \end{aligned} \tag{75}$$

This demonstrates that the ground-state RC-derivative $dI/dP|_{\ddagger}$ of the resultant *gradient*-information at TS complex, proportional to $dT/dP|_{\ddagger}$, can serve as an alternative detector of the reaction energetic character: its positive/negative values identify the positive/negative reaction energy ΔE_r in *endo*/*exo*-ergic reactions, exhibiting the late/early activation barriers, respectively; the neutral case ($\Delta E_r = 0$ or $dT/dP|_{\ddagger} = 0$) exhibits an equidistant position of TS between the reaction substrates and products on a symmetrical potential energy surface, e.g., in the hydrogen exchange reaction H + H_2 → H_2 + H.

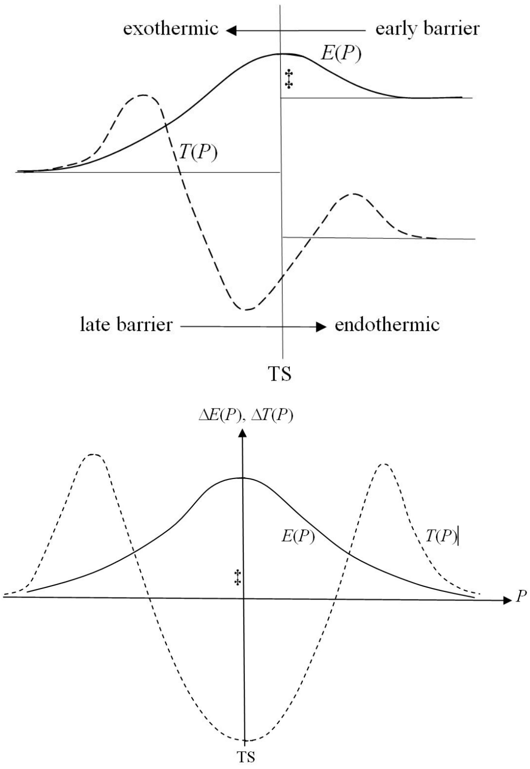

Figure 2. Variations of the BO total electronic energy (ΔE) and its kinetic energy component (ΔT) in the *exo*-ergic ($\Delta E_r < 0$) and *endo*-ergic ($\Delta E_r > 0$) reactions (upper Panel), and for the symmetrical PES ($\Delta E_r = 0$) (lower Panel)

Since the forces acting on nuclei in the equilibrium, separated reactants or products vanish, the reaction energy ΔE_r of Equation 74 determines the corresponding change in the resultant *gradient*-information,

$$\Delta I_r = I(P_{products}) - I(P_{substrates}) = \sigma \Delta T_r \tag{76}$$

proportional to the associated variation in the electronic kinetic energy:

$$\Delta T_r = T\left(P_{products}\right) - T\left(P_{substrates}\right) \;\; = -\Delta E_r \qquad (77)$$

The virial theorem thus implies a net *decrease* of the resultant *gradient*-information in *endo*-ergic processes, $\Delta I_r(endo) \propto$ -$\Delta E_r(endo) < 0$, its increase in *exo*-ergic reactions, $\Delta I_r(exo) \propto$ -$\Delta E_r(exo) > 0$, and a conservation of the overall *gradient*-information in the energy-*neutral* chemical rearrangements: $\Delta I_r(neutral) \propto$ -$\Delta E_r(neutral) = 0$.

One recalls that the classical part of this information displacement probes an average change in the spatial inhomogeneity of electron density. Therefore, the *endo*-ergic processes, requiring a net supply of energy to the reactive system R, give rise to relatively *less*-compact electron distributions in reaction products, compared to substrates. Accordingly, the *exo*-ergic transitions, with a net release of energy from R, generate on average more concentrated electron distributions in products, and no such a change is predicted in energy-*neutral* case.

5 Conclusion

In this overview we have explored qualitative reactivity applications of the resultant information measure in QIT. First, the concept of the overall *gradient*-information in specified quantum state, which combines the classical (probability) and nonclassical (phase/current) contributions, has been introduced as the expectation value of the corresponding (Hermitian) *information*-operator related to that of electronic kinetic energy. We have then explored the *thermodynamic*-average measure and its variational principle in the *grand*-ensemble. The *electron*-population derivatives, information reactivity descriptors of CT phenomena in donor-acceptor systems, have been examined, the physical equivalence of variational principles for *ensemble*-averages of energy and information (*kinetic*-energy) in thermodynamics has been emphasized, and the relation between the *in situ* energy and information CT criteria have been examined.

The proportionality relation between the resultant *gradient*-information and kinetic energy of electrons indicates that the latter plays a more important role in chemical reactivity than previously thought. The electronic energy and information/kinetic-energy represent alternative descriptors of molecular equilibria. They generate physically equivalent and adequate reactivity criteria for describing CT phenomena in the acid-base systems. Since for representative *energy*-profiles this component is readily available from the molecular virial theorem, we have briefly examined the theorem general implications for changes in the overall information content of equilibrium molecular structures, the *bond*-formation process, and the Hammond postulate of reactivity theory. The principle of the maximum thermodynamic information has been formulated and the dependence in chemical processes of the change in the overall *gradient*-information upon the reaction energy has been addressed. The Hammond postulate has been shown to be quantitatively indexed by the geometrical information derivative at TS complex.

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