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Reconsideration of chemical indices in conceptual density functional theory

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Abstract

The chemical indices of conceptual density functional theory are examined from the view point of the fundamental precepts for the chemical indices, i.e., observability, universality and mathematical rigour, for the energy derivatives with respect to the number of electrons and external potential up to the third order. Consequently, it is proposed that the mathematically-rigorous Iczkowski-Margrave electronegativity, which is electron affinity, is more suggestive than the Pauling electronegativity. The second-order energy derivative with respect to the number of electrons, which is exactly zero, is available as an explicit constraint on the universal functional. Furthermore, charge transferability and orbital reactivity indices, which are the second-order energy derivative with respect to the number of electrons and external potential, are newly classified into the chemical indices of conceptual density functional theory.

1 Introduction

Conceptual density functional theory (DFT) is a theory that is constructed to explain chemistry based on the concept of DFT in the manner of statistical mechanics.[1,2] Parr and coworkers initially reinterpreted DFT as a method using the energy functional of four independent variables: i.e., chemical potential μ, external electron-nuclei potential v, the number of electrons N and outermost orbital energy $\epsilon_{\mathrm{outermost}}$.[3] The choice of v and N variables comes from the variational principle,

$$\delta\left\{\langle\Psi\left|\hat{H}(N,v)\right|\Psi\rangle - E\langle\Psi\mid\Psi\rangle\right\} = 0, \tag{1}$$

where Ψ is ground-state wavefunction. Since this indicates that energy E is a function of N and v, other two variables, μ and ρ, appear in the first-order perturbation of energy of the Hellmann-Feynman formula,

$$E = \left(\frac{\partial E}{\partial N}\right)_v dN + \left(\frac{\partial E}{\partial v}\right)_N dv = \mu dN + \rho dv, \tag{2}$$

For this reason, the chemical indices of conceptual DFT have the derivative forms of the four independent variables, N, v, μ and ρ.

The relations of these four independent variables are derived by Nalewajski and Parr in the manner of statistical mechanics.[4] Based on the Legendre transformation for variable transformation from v to ρ, the Hohenberg-Kohn theorem,[5] which is the basic theorem of DFT, means that the energy functional of intensive v is transformed into the energy functional of extensive ρ. This indicates that energy functional becomes independent of external potential v (i.e., structural deformations in reactions). The Legendre transformation also indicates that the Levy constrained search formulation,[6] which establishes the one-to-one correspondence between ρ and Ψ, becomes identical to finding the optimum chemical potential μ. Considering the Schwarz theorem, which is used in the Maxwell relation of statistical mechanics, for energy with respect to the four independent variables,

$$\frac{\partial}{\partial x_j}\left(\frac{\partial E}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial E}{\partial x_j}\right), \tag{3}$$

where x_i and x_j are natural variables, the following theorem is derived using $\mu = (\partial\mu/\partial v)_n$ and $\rho = (\partial E/\partial n)_v$,

$$f = \left(\frac{\Delta\mu}{\Delta v}\right)_N = \left(\frac{\Delta\rho}{\Delta N}\right)_v. \tag{4}$$

This equation indicates that the direction of the energy variance under structural deformation is identical to that of the electron density variance in the increase and decrease of the number of electrons. Therefore, this function f is synonymous with the chemical indices of the frontier orbital theory, as mentioned later. That is, this equation forms the foundation for the frontier orbital theory.

Beginning with electronegativity index,[3] many chemical indices have been derived using the relations between the four independent variables.[7] Several chemical principles based on these indices are, consequently, proposed: e.g., the hard and soft acid and bases principle,[8] maximum hardness principle,[9] and minimum polarizability principle.[10] However, many physically-groundless, highly-dependent-on-calculation-method, or disconfirmable indices have also been suggested. For overcoming this situation, principal researchers in the field of conceptual DFT recently offered three fundamental precepts for the studies on conceptual DFT:[1]

1. Observability: Our understanding of chemical observations should be based on quantum mechanical observables.

2. Universality: the tools we use to understand the results of quantum mechanical calculations should not depend on the type of calculation that is performed.

3. Mathematical Rigour: the tools we use to understand chemistry should fit into a well-

defined mathematical framework.

These fundamental precepts are so strict that we can sort out only physically-grounded useful indices in the chemical indices that have, so far, been suggested. Note that these precepts exclude even well-known classic chemical indices such as aromaticity[11] and nucleofugality.[12] For the progress of conceptual DFT, it is significant to explicitly present the chemical indices obeying these fundamental precepts as the first step of the reformation.

In this study, the chemical indices of conceptual DFT that satisfy all these fundamental precepts are sorted out for the energy derivatives with respect to the number of electrons N and external potential v in the four independent variables.

2 Chemical indices satisfying fundamental precepts

The chemical indices of conceptual DFT are basically represented as the derivatives of energy with respect to the number of electrons N and external potential v. For other two variables, chemical potential μ and electron density ρ, the energy derivative for μ, $\partial E/\partial \mu = N$, is a given constant and that for ρ correspond to the functionals such as exchange and correlation functionals,[13,14] which are not chemical indices. Therefore, the chemical indices corresponding to the mathematically rigorous expressions of the energy derivatives with respect to N and v,[4]

$$\text{Chemical index} = \frac{\partial^{n_N+n_v} E}{\partial N^{n_N} \partial v^{n_v}} \quad \text{or} \quad \frac{\Delta^{n_N+n_v} E}{\Delta N^{n_N} \Delta v^{n_v}}, \tag{5}$$

are compiled in Table 1. Note that chemical indices in this table are classified into two cases: the energy derivative for "local" processes, $\partial^{n_N+n_v} E/\partial N^{n_N} \partial v^{n_v}$, and that for "total" processes, $\Delta^{n_N+n_v} E/\Delta N^{n_N} \Delta v^{n_v}$. That is, local processes target at the derivatives for the infinitesimal variations of the number of electrons N and for the instantaneous potential v variations in reactions, while total processes represent the differences for the increase or decrease of one electron and those for the v variations in the whole reaction processes. This

Table 1: Chemical indices of the first- and second-order energy variance for the number of electrons N and external potential v, which satisfy the fundamental precepts for the indices of conceptual DFT in Ref.[1] , for local (partial differential) and total (finite differential) processes.

Parameter		Chemical index	
n_N	n_v	Local process (∂)	Total process (Δ)
0	0	Energy E	
1	0	Chemical potential $\mu = \epsilon_{\text{outermost}}$	Minus electronegativity $-\chi = -\text{EA}$
0	1	Electron density ρ	No meaningful index
2	0	0	Double global hardness 2η
1	1	Minus reaction electric flux $-J_\mu$, Charge transferability	Fukui function f, Orbital reactivity $\Delta\epsilon$
0	2	Linear response function χ	No meaningful index
2	1	0	Dual descriptor $f^{(2)}$, Double global hardness variation $2\Delta\eta$

classification is obviously required due to the different corresponding chemical indices, though it has not been adopted in the studies of conceptual DFT as far as I know. The requirement of this classification has been confirmed in the reaction analyses using the reactive orbital energy theory (ROET):[15,16] the reaction-driving charge transfer directions agree with those of the electronic theory of organic chemistry only for local processes.[17] In the subsequent sections, the chemical indices corresponding to the mathematically rigorous energy derivatives are introduced. Note that for the total processes, the chemical indices are defined using the variation of the number of electrons ΔN as the derivatives of energy with respect to the increase or decrease of one electron, when the range is not clearly described, and those using the external potential variation Δv in the normalized intrinsic reaction coordinate (IRC), in which the reactant and product points of the IRC are set to be 0 and 1, respectively. following the ROET analysis.[15,16]

2.1 First-order derivative indices w.r.t. the number of electrons

First, the first partial derivative of energy with respect to the number of electrons has its inception from the concept of electronegativity, which is the origin of conceptual DFT.[3] This concept is originated from the Hohenberg-Kohn theorem,[5] which establishes the stationary principle for energy in terms of N-representable electron density ρ. That is, for an approximate electron density ρ', the stationary principle is established for the energy functional of external potential v under the normalization condition of the number of electrons, $N[\rho'] = N$, such as

$$\delta \left\{ E_v[\rho'] - \mu N[\rho'] \right\} = 0. \tag{6}$$

The Lagrangian multiplier of Eq. (6), μ, is defined as chemical potential. Therefore, chemical potential is obtained in definition as

$$\left(\frac{\partial E}{\partial N} \right)_v = \mu. \tag{7}$$

According to the Janak theorem,[18] the first-order partial energy derivative with respect to the number of electrons is identical to the outermost orbital energy, $\epsilon_{\mathrm{outermost}}$,[13]

$$\left(\frac{\partial E}{\partial N} \right)_v = \mu = \epsilon_{\mathrm{outermost}}. \tag{8}$$

This equation is the mathematically rigorous expression for the first energy derivative with respect to the number of electrons for local processes.

For total processes, the energy variance targets at the increase or decrease of one electron, which corresponds to the minus sign of electron affinity (EA) or ionization potential (IP), respectively.

$$\left(\frac{\Delta E}{\Delta N}\right)_v = \begin{cases} -\mathrm{IP}\ (-1 < \Delta N < 0) \\ -\mathrm{EA}\ (0 < \Delta N < 1) \end{cases} \tag{9}$$

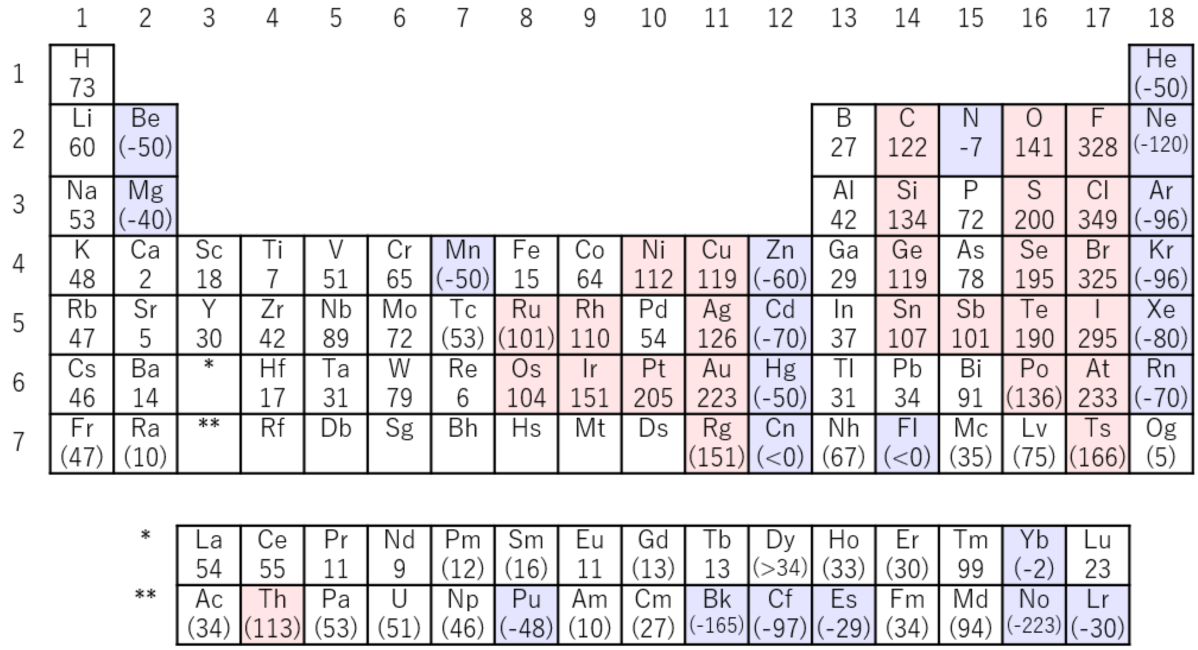
Since the concept of one electron unit is applicable to the experimental situation, the Iczkowski-Margrave electronegativity χ_{en},[19] which comes from the energy variance between neutral and anion, corresponds to the minus EA,

$$\chi_{\mathrm{en}} = -\left(\frac{\Delta E}{\Delta N}\right)_v = \mathrm{EA}. \tag{10}$$

Note that according to the generalized Koopmans theorem,[13,20] this EA is identical to the minus LUMO energy. Therefore, the Iczkowski-Margrave electronegativity is the minus LUMO energy, though it has been often represented as the Mulliken electronegativity,[3]

$$\chi_{\mathrm{en}} = \mathrm{EA} = -\epsilon_{\mathrm{LUMO}} \neq \frac{\mathrm{IP}+\mathrm{EA}}{2}. \tag{11}$$

It is interesting to note that the formulation of total processes consequently agrees with that of local processes in Eq. (8). Since EA is experimentally observable in photoelectron spectroscopy, both these derivative indices, therefore, have the observability, which is a fundamental precept of conceptual DFT mentioned above. Figure 1 shows the periodic table of the experimental EA values of atoms.[21] The figure shows that the following characteristics are different from those of the Pauling electronegativities, which are evaluated from the dissociation energies of dimers: 1. a very low electronegativities are given for nitrogen, group 2, group 12, group 18 and manganese atoms, indicating these tend to be neutral, 2. group 1 atoms have higher electronegativities than those of group 2 atoms, and 3. the electronegativities of actinide-series atoms significantly depend on atomic species. These characteristics of the Iczkowski-Margrave electronegativities are practical from the viewpoint of chemistry: 1. nitrogen is usually cationic as seen in the equilibrium of ammonia and water,



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 73																	He (-50)
2	Li 60	Be (-50)											B 27	C 122	N -7	O 141	F 328	Ne (-120)
3	Na 53	Mg (-40)											Al 42	Si 134	P 72	S 200	Cl 349	Ar (-96)
4	K 48	Ca 2	Sc 18	Ti 7	V 51	Cr 65	Mn (-50)	Fe 15	Co 64	Ni 112	Cu 119	Zn (-60)	Ga 29	Ge 119	As 78	Se 195	Br 325	Kr (-96)
5	Rb 47	Sr 5	Y 30	Zr 42	Nb 89	Mo 72	Tc (53)	Ru (101)	Rh 110	Pd 54	Ag 126	Cd (-70)	In 37	Sn 107	Sb 101	Te 190	I 295	Xe (-80)
6	Cs 46	Ba 14	*	Hf 17	Ta 31	W 79	Re 6	Os 104	Ir 151	Pt 205	Au 223	Hg (-50)	Tl 31	Pb 34	Bi 91	Po (136)	At 233	Rn (-70)
7	Fr (47)	Ra (10)	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg (151)	Cn (<0)	Nh (67)	Fl (<0)	Mc (35)	Lv (75)	Ts (166)	Og (5)

*	La 54	Ce 55	Pr 11	Nd 9	Pm (12)	Sm (16)	Eu 11	Gd (13)	Tb 13	Dy (>34)	Ho (33)	Er (30)	Tm 99	Yb (-2)	Lu 23
**	Ac (34)	Th (113)	Pa (53)	U (51)	Np (46)	Pu (-48)	Am (10)	Cm (27)	Bk (-165)	Cf (-97)	Es (-29)	Fm (34)	Md (94)	No (-223)	Lr (-30)

Figure 1: Experimentally-observed electron affinities of atoms in periodic table as the mathematically-rigorous Iczkowski-Margrave electronegativities in kJ/mol. The values in parentheses indicate the predicted electron affinities. In the table, the atoms of electron affinities less than zero kJ/mol are blue shaded, while those more than 100 kJ/mol are red shaded.

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$, and nitrogen-doped graphene, 2. no anions is observed for group 2 and group 18 atoms in nature, while anions are very unstable for group 12 atoms, as far as we know. These findings indicate that the Iczkowski-Margrave electronegativities are more suggestive than the Pauling ones. Note that there is another candidate for the Iczkowski-Margrave electronegativities in Eq. (10): the IPs for negative ΔN. Interestingly, the experimental IPs bear a close parallel to the Pauling electronegativities. Since the IPs are much larger than the EAs, the electronegativities considering both of them are mostly determined by the IPs, as deduced from the Mulliken electronegativity shown in Eq. (11). Considering the physical meaning of electronegativity, which is the tendency for an atom to attract shared electrons when forming a chemical bond, it is reasonable to adopt the EAs as the electronegativities.

2.2 First-order derivative indices w.r.t. external potential

Next, let us consider the first-order energy derivative with respect to external potential. According to the first-order perturbation of energy of the Hellmann-Feynman formula in Eq. (2), the first-order energy derivative with respect to external potential is given for local processes as[4]

$$\left(\frac{\partial E}{\partial v}\right)_N = \rho. \tag{12}$$

Note that electron density also possesses the observability, because electron density can be observed in, e.g., synchrotron X-ray diffraction experiments.[22]

On the other hand, for total processes, this first-order energy derivative is not identical to the electron density,

$$\left(\frac{\Delta E}{\Delta v}\right)_N \neq \rho, \tag{13}$$

because the density varies before and after reactions. This index consequently provides no meaningful index.

2.3 Second-order derivative indices w.r.t. the number of electrons

In the mathematically-rigorous formula, the second-derivative energy derivative with respect to the number of electrons becomes zero for local processes. This is because according to the first-order derivative in Eq. (8), the second-order energy derivative corresponds to the first-order derivative of the outermost orbital energy with respect to the number of electrons, which is zero due to the Sham-Schlüter theorem,[13,23]

$$\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \left(\frac{\partial \mu}{\partial N}\right)_v = \left(\frac{\partial \epsilon_{\mathrm{outermost}}}{\partial N}\right)_v = 0. \tag{14}$$

The Sham-Schlüter theorem establishes that the outermost orbital energy is independent of fractional occupation number. Since this behavior of the outermost orbital energy significantly depends on the functional used,[24] the relation in Eq. (14) is available even as an explicit constraint on the universal exchange-correlation functional.[25] This index, therefore, implies that it is, so far, required for assuring universality to use long-range corrected functionals that can provide quantitative orbital energies.[24]

The second-order energy derivative with respect to the number of electrons is, contrastingly, nonzero for total processes, because the number of electrons vary by one electron for these processes. Instead, this second-order energy derivative becomes the HOMO-LUMO gap, which is identical to the double global hardness,

$$\left(\frac{\Delta^2 E}{\Delta N^2}\right)_v = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} = 2\eta, \tag{15}$$

where η is global hardness. Note that the HOMO-LUMO gap is observable in state-of-the-art photoelectron spectroscopy. The idea of global hardness, which is the half of the HOMO-LUMO gap, is originated from the concept of hard and soft (Lewis) acids and bases (HSAB)[8] suggesting that soft acids of small global hardnesses have high reactivities and form strong bonds with soft bases, while hard acids of large global hardnesses react fast to form strong bonds with hard bases. However, this concept has never been supported by any experimental study, and it is denied as a necessary condition.[26,27] What we should note is that the pair of HOMO and LUMO are generally not the reactive orbitals driving the reactions.[16] A relationship analogous to the HSAB concept might be found by using the correct reactive orbitals.

2.4 Second-order derivative indices w.r.t. external potential

For local processes, the second-order energy derivative with respect to external potential is the partial derivative of electron density with respect to external potential, which corresponds to linear response function χ,[25]

$$\left(\frac{\partial^2 E}{\partial v^2}\right)_N = \left(\frac{\partial \rho}{\partial v}\right)_N = \chi \tag{16}$$

The linear response function of electron density to external potential[28] at the constant number of electrons is analytically expressed as[25]

$$\begin{aligned} \chi(\mathbf{r},\mathbf{r}') &= -2 \sum_{ia\sigma,jb\tau} \left(M^{-1}\right)_{ia\sigma,jb\tau} \phi^*_{j\tau}(\mathbf{r})\phi_{b\tau}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')\phi^*_{a\sigma}(\mathbf{r}') && (17)\\ (M)_{ia\sigma,jb\tau} &= \delta_{\sigma\tau}\delta_{ij}\delta_{ab}\left(\epsilon_{a\sigma}-\epsilon_{i\sigma}\right) + K_{ia\sigma,jb\tau} + K_{ia\sigma,bj\tau}, && (18) \end{aligned}$$

where matrix $\mathbf{K}$ is the Hartree integral matrix of the Coulomb and exchange-correlation integral kernel containing the elements of

$$\begin{aligned} K_{st\sigma,uv\tau} &= \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \phi^*_{s\sigma}(\mathbf{r}_1)\phi_{t\sigma}(\mathbf{r}_1)\frac{1}{r_{12}}\phi^*_{u\tau}(\mathbf{r}_2)\phi_{v\tau}(\mathbf{r}_2) \\ &\quad + \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \phi^*_{s\sigma}(\mathbf{r}_1)\phi_{t\sigma}(\mathbf{r}_1)\frac{\delta^2 E_{\mathrm{xc}}[\rho_\sigma(\mathbf{r})]}{\delta\rho_\sigma(\mathbf{r}_1)\delta\rho_\tau(\mathbf{r}_2)}\phi^*_{u\tau}(\mathbf{r}_2)\phi_{v\tau}(\mathbf{r}_2), \end{aligned} \tag{19}$$

where $\phi_{i\sigma}$ is the i-th σ-spin orbital, E_{xc} is the exchange-correlation functional, and ρ_σ is the σ-spin electron density. The linear response function of Eq. (17) corresponds to that of the time-dependent response Kohn-Sham theory[29,30] and the coupled-perturbed Kohn-Sham theory.[31,32] Since this linear response function provides very large response to not only electric field for electronic excitations but any kind of external field, it is superior as a chemical index. For example, natural reaction orbitals, which indicate the orbitals of electron transitions in reactions, are obtained as the response to the structural deformation of reactions.[33] Note, however, the linear response function in this formulation is too costly to be directly visualized. The formulation of noninteracting system, which neglects the Hartree integrals in Eq. (17), is, therefore, usually used for the visualization,

$$\chi(\mathbf{r},\mathbf{r}') = -2\sum_{ia\sigma,jb\tau}\left(\epsilon_{a\sigma}-\epsilon_{i\sigma}\right)^{-1}\phi^*_{j\tau}(\mathbf{r})\phi_{b\tau}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')\phi^*_{a\sigma}(\mathbf{r}') \tag{20}$$

As the result of the visualization, it is found that the linear response function has very different distributions for atomic species.[34,35]

In contrast to the significance for the local processes, the second-order energy derivative with respect to external potential has no significant physical meaning for total processes, due to Eq. (13),

$$\left(\frac{\Delta^2 E}{\Delta v^2}\right)_N \neq \left(\frac{\Delta\rho}{\Delta v}\right)_N \neq \chi. \tag{21}$$

This is also a meaningless index.

2.5 Second-order derivative indices w.r.t. the number of electrons and external potential

For the second-order energy derivative with respect to the number of electrons and external potential, the formulation for local processes is given as

$$\left(\frac{\partial^2 E}{\partial N \partial v}\right) = \left(\frac{\partial \mu}{\partial v}\right)_N = \left(\frac{\partial \epsilon_{\mathrm{outermost}}}{\partial v}\right)_N = \left(\frac{\partial \rho}{\partial N}\right)_v . \tag{22}$$

The central two expressions have significant physical meanings, though the rightmost expression, the partial density derivative with respect to the number of electrons at the fixed external potential, is almost meaningless.

First, the partial derivative of chemical potential, $(\partial\mu/\partial v)_N$, is used as a chemical index for electronic flux in reactions, which is called "reaction electronic flux" J_μ,[36]

$$J_\mu = -Q \left(\frac{\partial \mu}{\partial v}\right)_N , \tag{23}$$

where Q is transport coefficient, which is calculated using activation energies, reaction energies and chemical potentials.[37] The reaction electronic flux is confirmed to rapidly increase at transition state regions, though it is almost zero for other regions, in some reaction processes, indicating that this index might be available as a chemical index for searching transition states. Note that since this index assumes that the chemical potential is equal to the global hardness, it is going to be observable in time-resolved photoelectron spectroscopy. However, its application is supposed to be limited, because the chemical potentials contributing to the reactions may not be the pair of HOMO and LUMO, as shown in ROET analyses.[15,16]

Second, the partial derivative of the outermost orbital energy, $(\partial\epsilon_{\mathrm{outermost}}/\partial v)_N$, is taken as "charge transferability" in ROET analyses.[17] Figure 2 shows the normalized reaction diagram for determining the charge transferability indices. This index is also based on the Sham-Schlüter theorem,[13,23] which establishes the orbital energy invariance for the increase

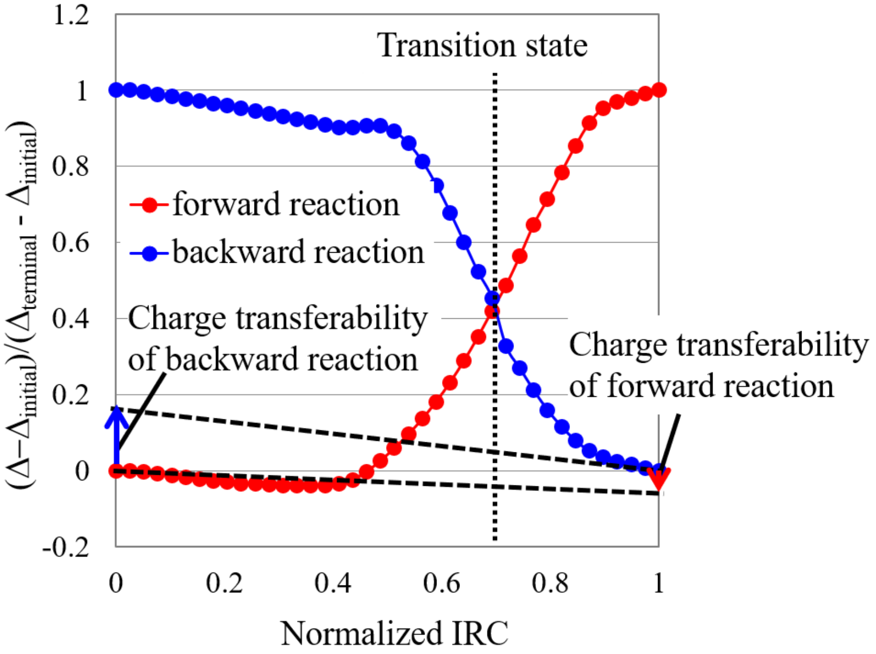


Figure 2: Charge transferability indices of $F^- + CH_3Cl \rightleftharpoons Cl^- + CH_3F$ S_N2 reaction for the forward and backward processes, which are calculated using the normalized gaps between the occupied and unoccupied reactive orbital energies on the normalized intrinsic reaction coordinate.

and decrease of the fractional occupation number of electrons. Actually, it is found for reactions proceeding through the electron transfers between occupied and unoccupied reactive orbitals that the reactive orbital energy gaps hardly vary even under the structural deformations.[15,16] For instance, in the case of the Diels-Alder reaction of 1,3-butadiene and ethylene, the orbital energy gap of the reactive orbitals (HOMO and LUMO) hardly change up to the transition state structure.[38] Charge transferability index, which is a chemical index based on this finding, is set to be more than one indicating that the reaction is charge transfer-driven, when the reactive orbital energy gap gradient on the normalized IRC is lower than the threshold of 0.25 for the initial reaction process such as

$$|\partial\Delta_{\text{gap}}/\partial v|^{-1}/4, \tag{24}$$

where Δ_{gap} is normalized reactive orbital energy gap.[17] Note, therefore, that the quantitative orbital energies of long-range corrected functionals are required to assure the universality.

The second-order energy derivative with respect to the number of electrons and external potential for total processes also have two significant expressions,

$$\left(\frac{\Delta^2 E}{\Delta N \Delta v}\right) = \left(\frac{\Delta\mu}{\Delta v}\right)_N = \left(\frac{\Delta\epsilon_{\mathrm{outermost}}}{\Delta v}\right)_N = \left(\frac{\Delta\rho}{\Delta N}\right)_v . \tag{25}$$

One expression is a most popular chemical index,[4]

$$f = \left(\frac{\Delta\rho}{\Delta N}\right)_v . \tag{26}$$

This function is called "Fukui function", because it corresponds to the reactivity indices of the frontier orbital theory that Fukui and coworkers developed,[39]

$$\text{Electrophilic reactions:} \;\; f^- = (\Delta\rho/\Delta^- N)_v \approx \rho_{\mathrm{HOMO}}(\mathbf{r}), \tag{27}$$

$$\text{Nucleophilic reactions:} \;\; f^+ = (\Delta\rho/\Delta^+ N)_v \approx \rho_{\mathrm{LUMO}}(\mathbf{r}), \tag{28}$$

$$\text{Radical reactions:} \;\; f^0 = (\Delta\rho/\Delta^0 N)_v \approx [\rho_{\mathrm{HOMO}}(\mathbf{r}) + \rho_{\mathrm{LUMO}}(\mathbf{r})]/2, \tag{29}$$

where $\Delta^- N$, $\Delta^+ N$, and $\Delta^0 N$ indicate the decreasing, increasing and $\alpha\beta$-conversion variations of the number of electrons, respectively. Since the frontier orbital theory had not been based on a theorem, it gains the physical foundation from this index. Note, however, that this index is known to be applicable only to a small number of organic reactions, because frontier orbitals, HOMO, LUMO and closely-lying orbitals, do not necessarily drive the reactions as shown in the ROET analyses.[15,16]

Another expression forms the theorem, on which ROET is based, for total processes. ROET is the reaction electronic theory for investigating reactions based on orbital energy variations in the structural deformations of reactions.[15,16] According to the combination of the Janak theorem[18] and the energy linearity theorem that establishes the linear total electronic energy variance with respect to the fractional occupation number for total processes,[20,40]

$$\mu = \frac{\Delta E}{\Delta N} = \epsilon_{\mathrm{outermost}}, \tag{30}$$

the Fukui function in Eq. (26) is transformed to

$$f = \left(\frac{\Delta \mu}{\Delta v}\right)_N = \left(\frac{\Delta \epsilon_{\mathrm{outermost}}}{\Delta v}\right)_N . \tag{31}$$

That is, the Fukui function is statistical-mechanically identical to orbital energy variance with respect to structural deformation with a constant occupation number. This equation forms the foundation for the ROET, because this indicates that reactivity can be analyzed using the orbital energy variance in the structural deformation of reaction. Figure 3 exemplifies the calculated orbital energy variance on the normalized IRC, in which the occupied and unoccupied reactive orbital energies are colored in red and blue, respectively. The ROET analyses indicate that the reactive orbitals, which give the most varied orbital energies, correctly represent the charge transfers of reactions, which are consistent with those of the electronic theory diagrams of organic chemistry.[17]

2.6 Third-order derivative indices w.r.t. the number of electrons and external potential

The third-order energy derivatives with respect to the number of electrons and external potential have four types. Due to Eq. (14), the third-order derivatives with respect to the square and cubic number of electrons are both zero for local processes,

$$\left(\frac{\partial^3 E}{\partial N^2 \partial v}\right) = \left(\frac{\partial^3 E}{\partial N^3}\right)_v = 0. \tag{32}$$

These indices are available as more explicit constraint on the universal exchange-correlation functional than that of the second-order derivative in Eq. (14). The third-order derivatives

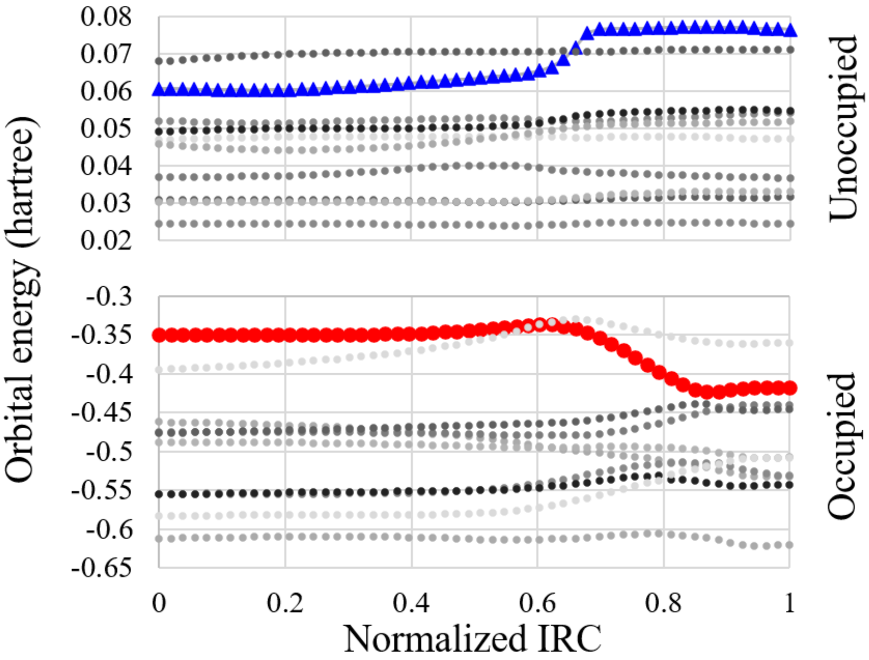


Figure 3: Calculated occupied and unoccupied orbital energies on the normalized intrinsic reaction coordinate of 1,3-butadiene + ethylene $\rightleftharpoons$ cyclohexene Diels-Alder reaction in hartree. The blue orbital energies correspond to the unoccupied reactive orbital energies providing the most destabilized orbital energies, while the red ones correspond to the occupied reactive orbital energies giving the most stabilized orbital energies, for the forward process.

with respect to external potential for local processes correspond to the first-order derivative of the linear response function in Eq. (17) with respect to the number of electrons and external potential, respectively,

$$\left(\frac{\partial^3 E}{\partial N \partial v^2}\right) = \left(\frac{\partial \chi}{\partial N}\right), \tag{33}$$

$$\left(\frac{\partial^3 E}{\partial v^3}\right)_N = \left(\frac{\partial \chi}{\partial v}\right)_N. \tag{34}$$

In Eqs. (33) and (34), the linear response function derivative with respect to the number of electrons correspond to the local response variations for changing the number of electrons and for reaction processes, respectively. However, it is difficult to interpret the physical meaning of these indices at this stage.

Though the third-order energy derivatives for total processes also have four types, the meaningful index is only the derivative with respect to the square number of electrons and external potential. The third-order energy derivatives with respect to square and cubic external potential, $(\Delta^3 E/\Delta v^3)_N$ and $(\Delta^3 E/\Delta v^2 \Delta N)$, are meaningless due to Eqs. (13) and (21). On the other hand, the third-order energy derivative with respect to the number of electrons correspond to the first derivative of double global hardness with respect to external potential,

$$\left(\frac{\Delta^3 E}{\Delta N^3}\right)_v = 2\left(\frac{\Delta \eta}{\Delta N}\right)_v. \tag{35}$$

This index indicates the variance of the HOMO-LUMO gap for the number of electrons, which is difficult to be explained from the physical point of view. For the only meaningful third-order energy derivative, two representations are derived as

$$\left(\frac{\Delta^3 E}{\Delta N^2 \Delta v}\right) = \left(\frac{\Delta f}{\Delta N}\right)_v = 2\left(\frac{\Delta \eta}{\Delta v}\right)_N. \tag{36}$$

One representation is called “dual descriptor”,[41]

$$f^{(2)} = \left(\frac{\Delta f}{\Delta N}\right)_v = |\phi_{\mathrm{LUMO}}|^2 - |\phi_{\mathrm{HOMO}}|^2, \tag{37}$$

which corresponds to the density variation for the transition from HOMO to LUMO. Applying this dual descriptor to Diels-Alder reactions shows that this index explains the Woodward-Hoffmann rule.[42] However, this index has the same application limit as that of the frontier orbital theory.[39] Another representation is the double hardness variation for process,

$$\left(\frac{\Delta \eta}{\Delta v}\right)_N = \eta_{\mathrm{prod}} - \eta_{\mathrm{reac}}. \tag{38}$$

In the application to the Diels-Alder reaction of 1,3-butadiene and ethylene, it is found that the global hardness hardly varies up to the transition state and rapidly increases toward the product when using a long-range corrected DFT.[38] Note, however, that this depends on the calculated reaction, because the reactive orbitals are usually not HOMO and LUMO for other reactions, though they are incidentally HOMO and LUMO for this Diels-Alder reaction. Furthermore, this behavior significantly depends on the functional used due to the very different reproducibility of orbital energies.[24] Since in any case, this hardness variance targets at the total processes, it may not have significant physical meaning as a chemical index.

3 Conclusions

In this study, the chemical indices of conceptual DFT are reconsidered and sorted out on the basis of the fundamental precepts that are required for the chemical indices: i.e., observability, universality and mathematical rigour.[1] This study focuses on the energy derivatives with respect to the number of electrons and external potential up to the third order and classifies them into the local and total processes. As a result, the following views are mainly found for chemical indices:

1. the Iczkowski-Margrave electronegativity, which is the first-order energy derivative with respect to the number of electrons, is identical to the EA, which seems more suggestive than the usual Pauling electronegativity,

2. the second-order energy derivative with respect to the number of electrons for local processes is zero, though it significantly depends on the functional used and therefore is available as an explicit constraint on the universal functional,

3. the second-order energy derivative with respect to the number of electrons and external potential for local processes has two chemical indices: reaction electronic flux for searching transition states and charge transferability for determining charge transfer-driven reactions.

4. the Fukui function, which is one second-order energy derivative with respect to the number of electrons and external potential for total processes, forms the foundation for the chemical indices of the frontier orbital theory,

5. the orbital reactivity, which is another second-order energy derivative with respect to the number of electrons and external potential for total processes, determine the reactive orbitals driving the reactions, and

6. the only meaningful third-order energy derivative is the dual descriptor, which is the

derivative with respect to the number of electrons and external potential for total processes, but it has the same application limit as that of the frontier orbital theory.

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Figure Captions

Fig. 1.

Experimentally-observed electron affinities of atoms in periodic table as the mathematically-rigorous Iczkowski-Margrave electronegativities in kJ/mol. The values in parentheses indicate the predicted electron affinities. In the table, the atoms of electron affinities less than zero kJ/mol are blue shaded, while those more than 100 kJ/mol are red shaded.

Fig. 2.

Charge transferability indices of $F^- + CH_3Cl \rightleftharpoons Cl^- + CH_3F$ S_N2 reaction for the forward and backward processes, which are calculated using the normalized gaps between the occupied and unoccupied reactive orbital energies on the normalized intrinsic reaction coordinate.

Fig. 3.

Calculated occupied and unoccupied orbital energies on the normalized intrinsic reaction coordinate of 1,3-butadiene + ethylene $\rightleftharpoons$ cyclohexene Diels-Alder reaction in hartree. The blue orbital energies correspond to the unoccupied reactive orbital energies providing the most destabilized orbital energies, while the red ones correspond to the occupied reactive orbital energies giving the most stabilized orbital energies, for the forward process.

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