

Separability of local reactivity descriptors

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Abstract. The size-dependence of different local reactivity descriptors of dimer A_2 and AB type of systems is discussed. We derive analytic results of these descriptors calculated using finite difference approximation. In particular, we studied Fukui functions, relative electrophilicity and relative nucleophilicity, local softness and local philicity. The results are explained using the example of the dimer of BH_3NH_3 .

Keywords. Local reactivity descriptors; separability; condensed Fukai functions; molecular interactions.

1. Introduction

Understanding molecular interactions has been a great challenge from both experimental and theoretical points of view.¹ Many theoretical models based on molecular orbital density, charge on atoms, bond order etc., have been extensively used in correlating the reactivity of the systems.² In particular, density-based descriptors are known to play key role in determining the stability and reactivity of chemical species. There have been recent studies on the qualitative and quantitative description of these concepts and use of these in the selectivity of reactions in catalysis, adsorption and molecular recognition.

Global reactivity descriptors (GRD), like softness, hardness and chemical potential along with concept of hard soft acid base (HSAB) principle are widely used in describing the reactivity and the stability of chemical systems.^{3–5} On the other hand, local reactivity descriptors (LRD), e.g. Fukui function (FF), local softness^{6–12} etc. have been studied extensively in recent years for characterizing the reactivity and site-selectivity in chemical reactions. These descriptors have been used qualitatively to characterize reactivity of a molecule in chemical reaction. Reactivity to specific agents, e.g. electrophilic, nucleophilic or radical can be described qualitatively using the above descriptors.^{6,13–17}

To describe these reactivity descriptors for atoms in a molecule, condensed definitions of electrophilicity, nucleophilicity etc. have also been proposed

using electronic population of an atom.^{10,18} These condensed local descriptors have also been used to study the site-selectivity in a chemical reaction.^{6,14,15} Among different population analysis^{19,20}, Pal *et al.*²⁰ have shown that the Hirshfeld analysis provides intuitively correct non-negative values of FF. Recently, relative electrophilicity and relative nucleophilicity, which are ratios of electrophilic to nucleophilic FF and vice-versa respectively, have been identified as more reliable criteria for intra-molecular reactivity.¹⁶ More recently, Parr and co-workers have defined a new concept of global philicity²¹ from which Chattaraj and co-workers have defined local philicity indices,²² which have been the subjects of recent study.

The objective of the paper is to study the size dependence of LRD. In particular we study the extensivity or intensivity of these descriptors by having examples of non-interacting dimer. We have used the example of dimer of BH_3NH_3 which has been extensively studied by many groups owing to formation of unusual “dihydrogen bond”.²³ The general case of separability of the descriptors has also been discussed for non-interacting fragments of different types (e.g. $A-B$). Recently, we have discussed the behavior of the reactivity descriptors during complexation of BH_3 and NH_3 using *ab-initio* calculation.²⁴

The paper has been organized as follows. In §2 we present a brief theoretical background defining the local descriptors and how these have been used in the study of reactivity and selectivity. In §3 we discuss separability of different LRDs. Section 4 presents the methodology and computational details, while §5 deals with results and discussion.

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2. Theoretical background

According to the Hohenberg–Kohn (HK) theorem, the ground state energy of an atom or molecule is written as a function of electron density (\mathbf{r}).²⁵

$$E[\mathbf{r}] = \int \mathbf{r}(r)v(r) dr + F_{HK}[\mathbf{r}], \quad (1)$$

with

$$F_{HK}[\mathbf{r}] = T[\mathbf{r}] + V_{ee}[\mathbf{r}], \quad (2)$$

where $v(r)$ is external potential and F_{HK} is universal Hohenberg–Kohn functional comprising the electronic kinetic energy functional, $T[\mathbf{r}]$ and the electron–electron interaction functional, $V[\mathbf{r}]$.

The first and second partial derivatives of $E[\mathbf{r}]$ with respect to the number of electrons N under the constant external potential $v(r)$ are defined as the chemical potential (\mathbf{m}) and the global hardness (\mathbf{h}) of the system respectively.^{3c,5,26,27} The global softness (S) is the half inverse of the hardness. The global descriptor of hardness has been known as an indicator of overall stability of the system.^{3b,28} It is customary to use a finite difference approximation for the computation of \mathbf{m} and \mathbf{h} ⁴

$$\mathbf{m} = -(I + A)/2, \quad (3)$$

$$\mathbf{h} = \frac{1}{2}(I - A). \quad (4)$$

The site-selectivity of a chemical system, cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need be defined. An appropriate definition of local softness $s(r)$ is given by⁷

$$s(r) = (\partial \mathbf{r}(r) / \partial N)_{v(r)} (\partial N / \partial \mathbf{m})_{v(r)} = f(r)S, \quad (5)$$

such that

$$\int s(r)d(r) = S, \quad (6)$$

where, $f(r)$ is defined as the Fukui function.⁷ It can be interpreted (cf. the use of Maxwell’s relation in this scheme) either as the change of electron density $\mathbf{r}(r)$ at each point r when the total number of electrons is changed or as the sensitivity of chemical potential of a system to an external perturbation at a particular point r .

$$f(r) = (\partial \mathbf{r}(r) / \partial N)_{v(r)} = (\partial \mathbf{m} / \partial v(r))_N. \quad (7)$$

The latter point of view, by far the most prominent in the literature, faces the N -discontinuity problem of atoms and molecules,^{29,30} leading to the introduction^{7a} of both right- and left-hand-side derivatives, to be considered at a given number of electrons, $N = N_0$:

$$f^+(r) = (\partial \mathbf{r}(r) / \partial N)_{v(r)}^+, \quad (8)$$

for a nucleophilic attack provoking an electron increase in the system, and

$$f^-(r) = (\partial \mathbf{r}(r) / \partial N)_{v(r)}^-, \quad (9)$$

for an electrophilic attack provoking an electron decrease in the system.

The finite difference method, using the electron densities of N_0 , $N_0 + 1$, $N_0 - 1$, defines

$$f^+(r) \approx \mathbf{r}_{N_0+1}(r) - \mathbf{r}_{N_0}(r), \quad (10)$$

and

$$f^-(r) \approx \mathbf{r}_{N_0}(r) - \mathbf{r}_{N_0-1}(r). \quad (11)$$

A third function describing radical attack, $f^0(r)$, is then obtained as the arithmetic average of $f^+(r)$ and $f^-(r)$,

$$f^0(r) \approx (\mathbf{r}_{N_0+1}(r) - \mathbf{r}_{N_0-1}(r))/2. \quad (12)$$

Atom-condensed Fukui functions were first introduced by Yang *et al*¹⁰, based on the idea of electronic population over atomic regions, similar to procedure followed in population analysis technique.¹⁸ Combined with finite difference approximation, this yields working equations of the type,

$$f_A^+ = q_{A,N_0+1} - q_{A,N_0},$$

$$f_A^- = q_{A,N_0} - q_{A,N_0-1},$$

$$f_A^0 = (q_{A,N_0+1} - q_{A,N_0-1})/2, \quad (13)$$

where, $q_{A,N}$ denotes the electronic population of atom A of a system with N -electrons. Using (5) and

(13), various condensed local softnesses of an atom can be defined.

$$s_A^a = f_A^a S, \quad \forall a = +, -, 0, \quad (14)$$

where +, – and 0 indicate electrophilicity, nucleophilicity and tendency for radical attack respectively.

Several other reactivity descriptors have been proposed. ‘Relative electrophilicity’ (RE) and ‘relative nucleophilicity’ (RN) defined as (f^+/f^-) and (f^-/f^+) respectively have been used successfully by Roy *et al*¹⁶ for describing intra-molecular reactivity. Attempts to use these for inter-molecular reactivity have also been made in recent years. Parr *et al*²¹ proposed a global philicity (W) as $\mathbf{m}^i/2\mathbf{h}$. Using this, Chattaraj *et al*²² proposed the existence of local philicity index $w(r)$ as $Wf(r)$ such that $w(r)$ integrates to global W . The condensed philicity w_A^a in the definition is given by

$$w_A^a = Wf_A^a, \quad \forall a = +, -, 0. \quad (15)$$

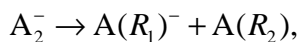
3. Local reactivity descriptors in non-interacting regime

First, we discuss the separation of FF, which is the most important quantity in all other local reactivity descriptors. In this paper, we focus on the special case of a dimer A_2 which dissociates into two identical fragments A. The electron density $\mathbf{r}^{A_2}(r)$ at point r can be written as

$$\mathbf{r}^{A_2}(r) = \mathbf{r}^{A(R_1)}(r) + \mathbf{r}^{A(R_2)}(r), \quad (16)$$

where, $A(R_1)$ and $A(R_2)$ are monomers A at different positions R_1 and R_2

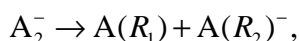
Let us assume that $(N_0 + 1)$ electronic state of A_2 at the geometry of A, i.e. vertical A_2^- fragments as



therefore,

$$\mathbf{r}_{N_0+1}^{A_2}(r) = \mathbf{r}_{N_0+1}^{A(R_1)}(r) + \mathbf{r}_{N_0}^{A(R_2)}(r), \quad (17a)$$

but since $A(R_1)$ and $A(R_2)$ are indistinguishable, therefore there exists another degenerate pathway for the fragmentation,



therefore,

$$\mathbf{r}_{N_0+1}^{A_2}(r) = \mathbf{r}_{N_0}^{A(R_1)}(r) + \mathbf{r}_{N_0+1}^{A(R_2)}(r), \quad (17b)$$

we can now write them as an average,

$$\begin{aligned} \mathbf{r}_{N_0+1}^{A_2}(r) &= \frac{1}{2}([\mathbf{r}_{N_0+1}^{A(R_1)}(r) + \mathbf{r}_{N_0}^{A(R_2)}(r)] \\ &\quad + [\mathbf{r}_{N_0}^{A(R_1)}(r) + \mathbf{r}_{N_0+1}^{A(R_2)}(r)]) \\ &= \frac{1}{2}([\mathbf{r}_{N_0+1}^{A(R_1)}(r) + \mathbf{r}_{N_0}^{A(R_1)}(r)] \\ &\quad + [\mathbf{r}_{N_0+1}^{A(R_2)}(r) + \mathbf{r}_{N_0}^{A(R_2)}(r)]), \end{aligned} \quad (17c)$$

differentiating w.r.t. N , using the finite difference method,

$$\begin{aligned} f_{A_2}^+(r) &\approx \mathbf{r}_{N_0+1}^{A_2}(r) - \mathbf{r}_{N_0}^{A_2}(r), \\ &= \frac{1}{2}([\mathbf{r}_{N_0+1}^{A(R_1)}(r) + \mathbf{r}_{N_0}^{A(R_1)}(r)] + [\mathbf{r}_{N_0+1}^{A(R_2)}(r) \\ &\quad + \mathbf{r}_{N_0}^{A(R_2)}(r)]) - (\mathbf{r}_{N_0}^{A(R_1)}(r) + \mathbf{r}_{N_0}^{A(R_2)}(r)) \\ &= \frac{1}{2}([\mathbf{r}_{N_0+1}^{A(R_1)}(r) - \mathbf{r}_{N_0}^{A(R_1)}(r)] \\ &\quad + [\mathbf{r}_{N_0+1}^{A(R_2)}(r) - \mathbf{r}_{N_0}^{A(R_2)}(r)]) \\ &= \frac{1}{2}(f_{A(R_1)}^+(r) + f_{A(R_2)}^+(r)). \end{aligned} \quad (18)$$

On similar lines, the following can be shown as

$$f_{A_2}^-(r) = \frac{1}{2}(f_{A(R_1)}^-(r) + f_{A(R_2)}^-(r)), \quad (19)$$

and

$$\begin{aligned} f_{A_2}^0(r) &= \frac{1}{2}(f_{A_2}^+(r) + f_{A_2}^-(r)) \\ &= \frac{1}{2}[\frac{1}{2}(f_{A(R_1)}^+(r) + f_{A(R_2)}^+(r)) \\ &\quad + \frac{1}{2}(f_{A(R_1)}^-(r) + f_{A(R_2)}^-(r))] \\ &= \frac{1}{2}[\frac{1}{2}(f_{A(R_1)}^+(r) + f_{A(R_1)}^-(r)) \\ &\quad + \frac{1}{2}(f_{A(R_2)}^+(r) + f_{A(R_2)}^-(r))] \\ &= \frac{1}{2}(f_{A(R_1)}^0(r) + f_{A(R_2)}^0(r)). \end{aligned} \quad (20)$$

From (18)–(20), it can be seen that the FF of the dimer at dissociation is nothing but the sum of the half of FF of the monomer. The results can be generalized to the non-interacting associations of n systems of A i.e; A_n .

It would be interesting to study the behavior of the condensed FF of the atoms for the non interact-

ing dimer. From (18)–(20), the following can be written

$$\begin{aligned} \int f_{A_2}^a(r) d(r) &= \frac{1}{2} \int (f_{A(R_1)}^a(r) + f_{A(R_2)}^a(r)) \\ &= \frac{1}{2} \left(\int f_{A(R_1)}^a(r) d^3r + \int f_{A(R_2)}^a(r) d^3r \right) \\ &= \int f_A^a(r) d^3r, \quad \forall a = +, -, 0. \end{aligned} \quad (21a)$$

The above integral can be written as the sum of atom-condensed FFs. Since the system of A_2 consists of two identical systems A, every atom i of monomer A is represented twice in identical manner,

$$\begin{aligned} \sum_{i=1}^k 2f_{A_i, A_2}^a &= \sum_{i=1}^k f_{A_i, A}^a \\ \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k. \end{aligned} \quad (21b)$$

where k is the number of atoms in the monomer. f_{A_i, A_2}^a and $f_{A_i, A}^a$ denotes the atom condensed FF of atom A_i of dimer and monomer respectively. The following can be deduced from (21),

$$\begin{aligned} f_{A_i, A_2}^a &= f_{A_i, A}^a / 2, \\ \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k. \end{aligned} \quad (22)$$

It may be interesting to note that while the FF of non-interacting dimer at a point r is the sum of the half of FF of the monomer, the atom condensed FFs of the atoms of the non-interacting dimer would be half as that of the monomer. Similarly, for non-interacting A_n , the condensed FF of i th atom in a system A is n times less than that of the atom k in isolated A itself.

$$\begin{aligned} f_{A_i, A_n}^a &= f_{A_i, A}^a / n, \\ \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k. \end{aligned} \quad (23)$$

Let us analyse the behaviour of some other reactivity descriptors. Since both electrophilic- and nucleophilic-condensed FF of an atom in a dimer are half that of the corresponding atom in a monomer, by definition, RE and RN of the atoms of the dimer are the same as those of the corresponding atoms of the monomer. From (22), RE and RN at isolated limit can be derived as

$$\begin{aligned} RE_{A_i, A_2} &= \frac{(f_{A_i}^+ / 2)}{(f_{A_i}^- / 2)} = RE_{A_i, A}, \quad \forall i = 1, 2, \dots, k \\ RN_{A_i, A_2} &= \frac{(f_{A_i}^- / 2)}{(f_{A_i}^+ / 2)} = RN_{A_i, A}, \quad \forall i = 1, 2, \dots, k. \end{aligned} \quad (24)$$

Contrary to atom-condensed FFs, it may be noted that the condensed RE and RN are size-intensive. Equations (22) and (23) result from the artifact of the summation of the condensed Fukui function being unity. However, the sum of the condensed RE and RN of all atoms in a system is not a fixed quantity. Equation (24) implies that the sum of RE or RN for a non-interacting dimer is twice that of the sum for all atoms of the monomer. On similar lines, results can be generalized for non interacting A_n .

Earlier, Pal *et al.*³¹ had shown that for homodiatom molecules, hardness and chemical potential are the same as that of isolated atoms.³¹ It being similar here, we can write for total softness of the dimer of A,

$$S_{A_2} = S_A, \quad \text{and} \quad m_{A_2} = m_A, \quad (25a)$$

therefore,

$$W_{A_2} = W_A. \quad (25b)$$

Using (14), (15), (22), (25a) and (25b) local softness and local philicity of dimer can be derived as

$$\begin{aligned} s_{A_i, A_2}^a &= s_{A_i, A}^a / 2, \quad \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k, \\ w_{A_i, A_2}^a &= w_{A_i, A}^a / 2, \\ \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k. \end{aligned} \quad (26)$$

From the above relations, it can be seen that both local softness and local philicity of dimer behave similar to atom-condensed FFs of the dimer, i.e. all become half of the corresponding values of monomer for all three reactions, viz. electrophilic, nucleophilic and radical. On similar lines, local softness and local philicity of atoms of A_n can be shown as,

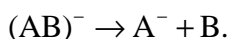
$$\begin{aligned} s_{A_i, A_n}^a &= s_{A_i}^a / n, \quad \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k, \\ w_{A_i, A_n}^a &= w_{A_i}^a / n, \\ \forall a = +, -, 0 \text{ and } i = 1, 2, \dots, k. \end{aligned} \quad (27)$$

If we consider the general case of a complex AB, consisting of two subsystems A and B, which dissociates into fragments A and B, the electron density $\mathbf{r}^{\text{AB}}(r)$ at point r can be written as the sum of electron densities of A and B,

$$\mathbf{r}^{\text{AB}}(r) = \mathbf{r}^{\text{A}}(r) + \mathbf{r}^{\text{B}}(r), \quad (28)$$

where $\mathbf{r}^{\text{A}}(r)$ is the density at r due to atom A. Similarly, $\mathbf{r}^{\text{B}}(r)$ is the electron density at point r due to atom B.

Let us assume that the $(N_0 + 1)$ electronic state of AB at the geometry of AB, i.e. vertical $(\text{AB})^-$ fragments as follows,



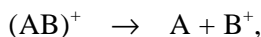
Therefore

$$\mathbf{r}_{N_0+1}^{\text{AB}}(r) = \mathbf{r}_{N_0+1}^{\text{A}}(r) + \mathbf{r}_{N_0}^{\text{B}}(r). \quad (29)$$

Using finite difference method of differentiation with respect to N at the non-interacting limit, we obtain,

$$\begin{aligned} f_{\text{AB}}^+(r) &\approx \mathbf{r}_{N_0+1}^{\text{AB}}(r) - \mathbf{r}_{N_0}^{\text{AB}}(r) \\ &= (\mathbf{r}_{N_0+1}^{\text{A}}(r) + \mathbf{r}_{N_0}^{\text{B}}(r)) - (\mathbf{r}_{N_0}^{\text{A}}(r) + \mathbf{r}_{N_0}^{\text{B}}(r)) \\ &= \mathbf{r}_{N_0+1}^{\text{A}}(r) - \mathbf{r}_{N_0}^{\text{A}}(r) \\ &= f_{\text{A}}^+(r). \end{aligned} \quad (30)$$

Assuming the vertical (N_0-1) electronic state of AB, i.e. $(\text{AB})^+$ fragments as follows,



$$\mathbf{r}_{N_0-1}^{\text{AB}}(r) = \mathbf{r}_{N_0}^{\text{A}}(r) + \mathbf{r}_{N_0-1}^{\text{B}}(r). \quad (31)$$

Again, using a finite difference method of differentiation, we obtain at the non-interacting limit,

$$\begin{aligned} f_{\text{AB}}^-(r) &\approx \mathbf{r}_{N_0}^{\text{AB}}(r) - \mathbf{r}_{N_0-1}^{\text{AB}}(r) \\ &= (\mathbf{r}_{N_0}^{\text{A}}(r) + \mathbf{r}_{N_0}^{\text{B}}(r)) - (\mathbf{r}_{N_0}^{\text{A}}(r) + \mathbf{r}_{N_0-1}^{\text{B}}(r)) \\ &= \mathbf{r}_{N_0}^{\text{B}}(r) - \mathbf{r}_{N_0-1}^{\text{B}}(r) \\ &= f_{\text{B}}^-(r). \end{aligned} \quad (32)$$

The third function describing radical attack, $f_{\text{AB}}^0(r)$, which is the arithmetic average of $f_{\text{AB}}^+(r)$ and $f_{\text{AB}}^-(r)$, is then obtained at the non-interacting limit as

$$f_{\text{AB}}^0(r) = (f_{\text{A}}^+(r) + f_{\text{B}}^-(r))/2. \quad (33)$$

From (30) and (32), it can be seen that as the complex dissociates, the FF of the complex reduces to the FF of the individual fragment depending on whose cation or anion is more stable. Electrophilic FF of the complex at dissociation is the electrophilic FF of the fragment whose anion is more stable, while the nucleophilic FF at dissociation is the nucleophilic FF of the fragment whose cation is more stable.

From (30) and (32), the following can be seen:

$$\sum_{k=1}^{a_k} f_{A_k, \text{AB}}^+ + \sum_{k=1}^{b_k} f_{B_k, \text{AB}}^+ = \sum_{k=1}^{a_k} f_{A_k}^+, \quad (34a)$$

$$\sum_{k=1}^{a_k} f_{A_k, \text{AB}}^- + \sum_{k=1}^{b_k} f_{B_k, \text{AB}}^- = \sum_{k=1}^{b_k} f_{B_k}^-. \quad (35b)$$

where A_k and B_k are the k th atoms of fragment A and fragment B respectively, and a_k and b_k are the total number of atoms in fragments A and B respectively.

One can thus write for condensed FF,

$$\begin{aligned} f_{A_k, \text{AB}}^+ &= f_{A_k}^+, \\ f_{B_k, \text{AB}}^+ &= 0, \\ f_{A_k, \text{AB}}^- &= 0, \\ f_{B_k, \text{AB}}^- &= f_{B_k}^-. \end{aligned} \quad (36)$$

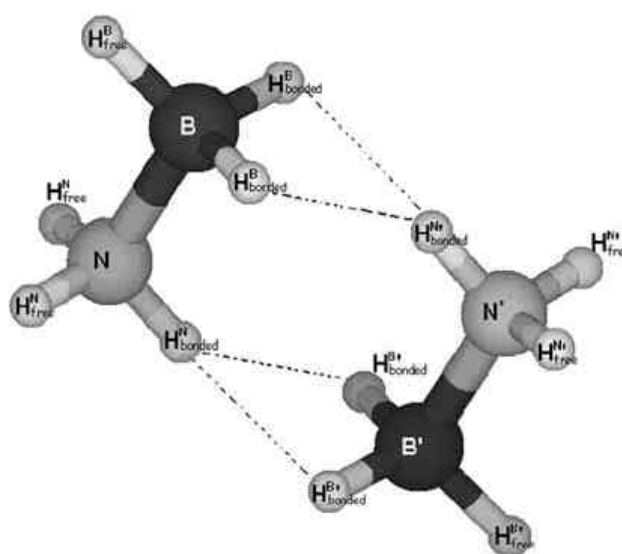


Figure 1. Structure of BH_3NH_3 dimer.

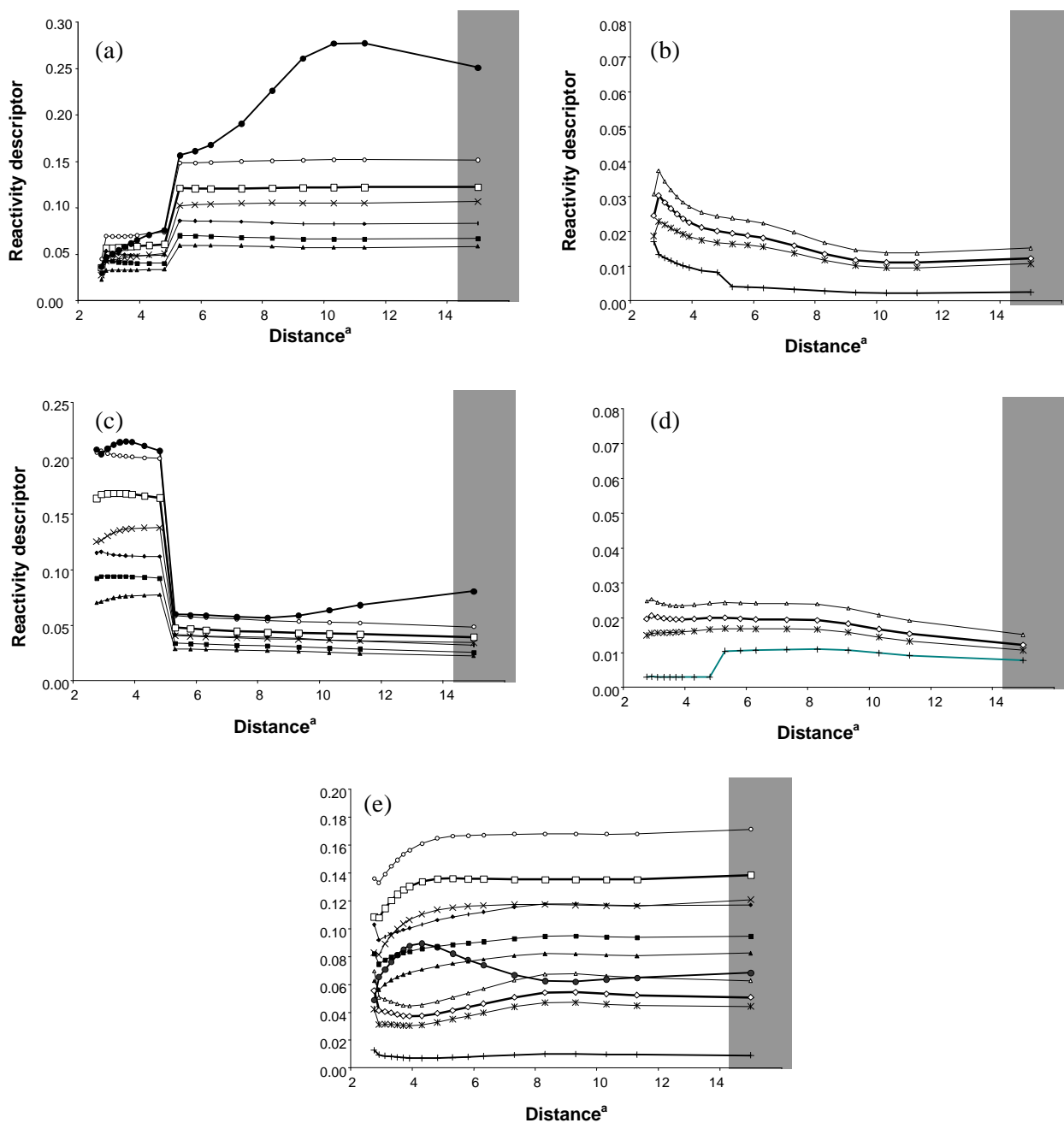


Figure 2. Variation of local reactivity descriptors with BN' distance (a)–(b) H_{bonded}^B , (c)–(d) H_{free}^B , (e) boron. \diamond f^+ , \square f^- , \blacksquare f^0 , \triangle s^+ , \circ s^- , \blacklozenge s^0 , $*$ $w^+(\#)$, \times $w^-(\#)$, \blacktriangle w^0 , $\text{---}+$ $\text{RE}^{(*)}$, \bullet $\text{RN}^{(*)}$ (# scaled up by factor of 10; *scaled down by factor of 40; points in the shaded region correspond to the half value of monomers except for RE and RN where it corresponds to the full value).

Hence, as the complex dissociates, the condensed electrophilic FF of the atoms of the fragment for which the anion is formed, goes towards the condensed electrophilic FF of isolated fragment, while for other atoms it goes towards zero. The condensed nucleophilic FF of the atoms of the fragment for which cation is formed, goes towards the condensed nu-

cleophilic FF of isolated fragment, while for the atoms of the other fragment these values go to zero.

From (22), one can write the following,

$$\sum_{k=1}^{a_k} f_{A_k,AB}^0 + \sum_{k=1}^{b_k} f_{B_k,AB}^0 = \frac{1}{2} \left[\sum_{k=1}^{a_k} f_{A_k}^+ + \sum_{k=1}^{b_k} f_{B_k}^- \right]. \quad (37)$$

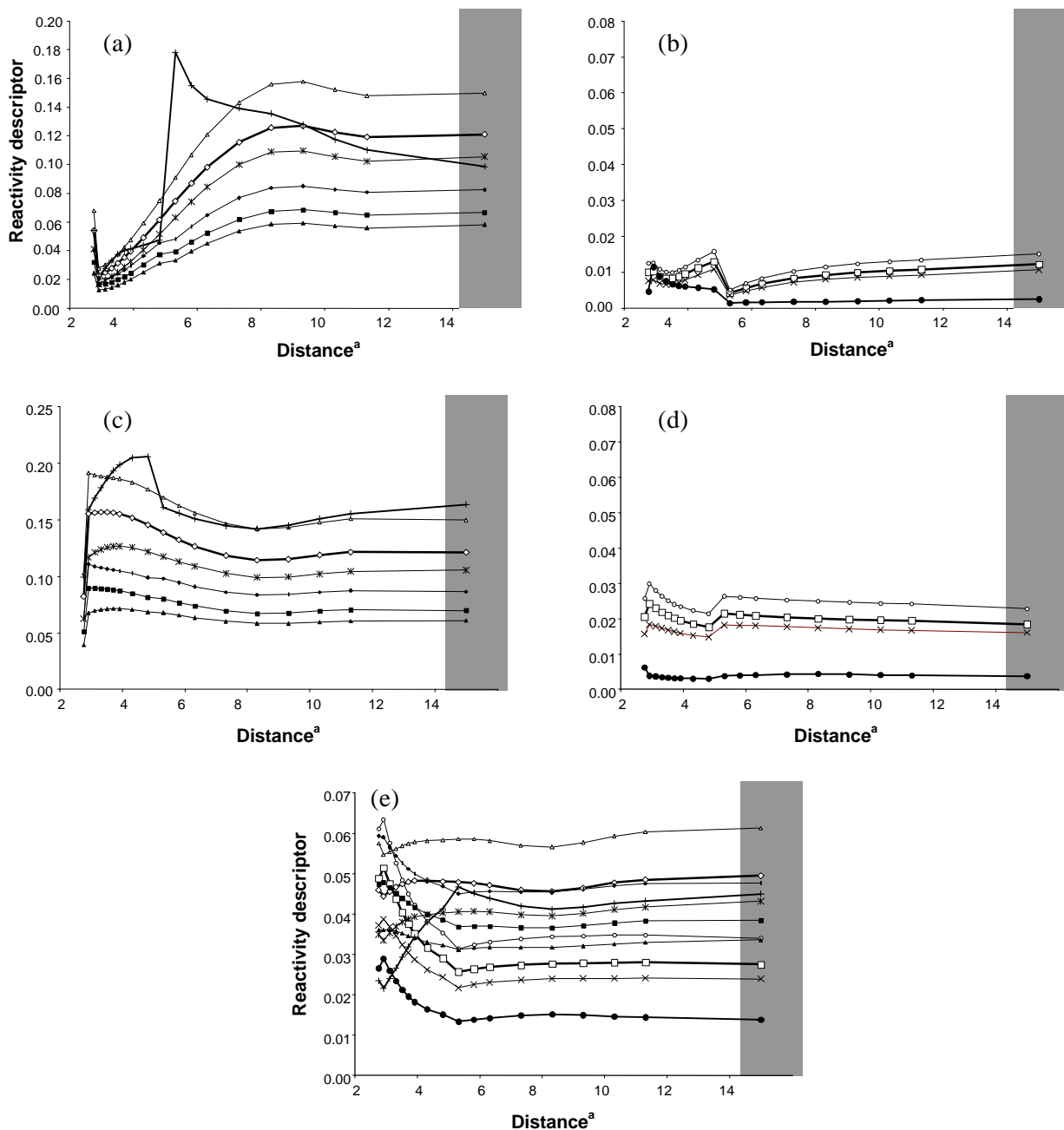


Figure 3. Variation of local reactivity descriptors with BN' distance (a)–(b) $H_{\text{bonded}}^{\text{N}}$, (c)–(d) $H_{\text{free}}^{\text{N}}$, (e) nitrogen. \diamond f^+ , \square f^- , \blacksquare f^0 , \triangle s^+ , \circ s^- , \blacklozenge s^0 , \ast $w^{+(\#)}$, \times $w^{-(\#)}$, \blacktriangle w^0 , --- $\text{RE}^{(*)}$, \blacklozenge $\text{RN}^{(\%)\#}$ (# scaled up by factor of 10; * scaled down by factor of 100 in (a) and by factor of 40 in others; % scaled down by factor of 40; points in the shaded region correspond to the half value of monomers except for RE and RN where it corresponds to the full value).

One can conclude about the condensed FF for radical attack,

$$\begin{aligned} f_{A_k,AB}^0 &= f_{A_k}^+ / 2 \neq f_{A_k}^0, \\ f_{B_k,AB}^0 &= f_{B_k}^+ / 2 \neq f_{B_k}^0. \end{aligned} \quad (38)$$

Though electrophilic- and nucleophilic-condensed FF's of the complex at the isolated limit separate out as those of the isolated fragments depending on the fragmentation of cation or anion of the complex, it is interesting to note that the condensed FF describing radical attack has different behaviour.

It should be noted that throughout the paper, anions or cations referred to are the vertical anions or cations, since the definition of FF demands that external potential be kept constant while calculating the derivatives.

4. Methodology and computational details

For simplicity, the symmetrical (C₂) closed shell system (BH₃NH₃)₂ is chosen, which, on fragmentation, also yields closed shell monomer BH₃NH₃. Geometry optimization of the individual BH₃NH₃ as well as constrained optimization of (BH₃NH₃)₂ were carried out with *ab-initio* Moller–Plesset perturbation (MP2) quantum chemical calculations using 6-31++G(*d*, *p*) basis set. Condensed FF's were calculated via (13) using Lowdin population analysis (LPA)^{19a,b} at MP2 level. The average values are reported for dihydrogen bonded hydrogen connected to boron H_{bonded}^B and free hydrogen connected to nitrogen H_{free}^N.

For obtaining limiting values of the FF of atoms of the complex, calculations were performed on isolated BH₃NH₃ molecules.

The calculations were performed using the GAMESS system of programs.³²

5. Results and discussions

Figure 1 presents the structure of the BH₃NH₃ dimer. The structure corresponds to the fully optimized structure of BH₃NH₃ dimer and the B–N' distance is 3.31469 Å. Figure 2 presents the variation of different reactivity descriptors for the atoms of BH₃ as the B–N' distance is changed. Figure 2a presents nucleophilic and radical reactivity descriptors of H_{bonded}^B. Figure 2b presents electrophilic descriptors of H_{bonded}^B. Figures 2c and d present corresponding reactivity descriptors of H_{free}^N. Figure 2e presents all eleven reactivity descriptors for the boron atom. The local philicity values are scaled up ten times and values for RE and RN are scaled down by factor of 40 for so that they could be shown on the same figure.

Figure 3 presents the variation of different reactivity descriptors for the atoms of NH₃ as the B–N' distance is changed. Figure 3a presents electrophilic and radical reactivity descriptors of H_{bonded}^N. Figure 3b presents nucleophilic descriptors of H_{bonded}^N. Figures 3c and d present corresponding reactivity descriptors of H_{free}^N. Figure 3e presents all eleven

reactivity descriptors for boron atom. The local philicity values are scaled up ten times and values for RE and RN are scaled down by factor of 40 except in figure 3a where RE is scaled down by factor of 100.

Points under the shaded region in figures 2 and 3 correspond to the half values of the reactivity descriptors of the monomer BH₃NH₃ except for relative-electrophilicity and relative-nucleophilicity, where they correspond to the values for the monomer. From figures 2 and 3 it can be seen that the reactivity descriptors do behave as described in the §3. Condensed Fukui functions, local softness and local philicity of dimers separate out as half the monomer values, while relative electrophilicity and relative nucleophilicity approach the corresponding monomer values.

Recently, we discussed the behaviour of reactivity descriptors during complexation of BH₃ and NH₃ using *ab-initio* calculation.²⁴ We have seen that the non-interacting values of *f*⁺ or *f*[–] are approached only by atoms of fragmented species for complex anion or cation respectively. Our discussion in §3 for complex AB analytically justifies the results obtained earlier.

Acknowledgment

AT acknowledges the Council of Scientific and Industrial research, New Delhi, for a research fellowship. The authors thank the anonymous reviewer for their suggestions that improved the manuscript.

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