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Calculation of the linear response function by the atom–bond electronegativity equalization method (ABEEM)

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Abstract

Based on density functional theory (DFT) and atom–bond electronegativity equalization method (ABEEM), the condensed linear response function related to the chemical bond region is defined, determined and calculated for some molecules and the results are in good agreement with the usual chemical knowledge. The strengths among all the couplings between the electron density and the potential are in the order of atom–atom, atom–bond and bond–bond. The effect of a change in the potential of every H atom on the electron density of any chemical bond is almost negligible, and the electron density of all the C–H bonds rarely varies with a shift in the potential of any atoms. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

One important purpose of computational chemistry is to understand and predict chemical reactivity and molecular interactions. By the Hohenberg–Kohn theorem [1], the external potential $v(\vec{r})$ (mainly caused by the nuclear charges and their disposition in space) is determined by the electron density $\rho(\vec{r})$. Since $\rho(\vec{r})$ determines the number of electrons, it follows that $\rho(\vec{r})$ also determines the ground state wave function and all other electronic properties of the system. The first step in a reaction is an interaction, which is a perturbation of the system. There are essentially only two ways to change a system, namely by changing the number of electrons, or by modifying the external potential (or, of course, by

changing both at the same time). Different parts of the system will respond ('react') in different ways.

According to density functional theory (DFT) [2], the electron density $\rho(\vec{r})$ contains all the information about the system in the ground state. Its response to the total number N of electrons or the external potential $v(\vec{r})$ at each point is certainly of fundamental importance. In DFT, the displacement of electron density $\rho(\vec{r})$ from equilibrium, in response to a given shift in the total number N of electrons, is defined as a Fukui function [3]: $f(\vec{r}) = (\partial\rho(\vec{r})/\partial N)_{v(\vec{r})}$. The Fukui function is a chemical reactivity index in the sense of the frontier-electron theory of reactivity as invented by Fukui and collaborators [4–6], and a lot of investigations have been made with regard to it [7–10].

The response of the electron density $\rho(\vec{r})$ to the external potential $v(\vec{r})$ is defined as the linear response function $\beta(\vec{r}, \vec{r}')$ [11] within DFT, i.e.

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$$\beta(\vec{r}, \vec{r}') = \left(\frac{\delta \rho(\vec{r})}{\delta v(\vec{r}')} \right)_N = \left(\frac{\delta \rho(\vec{r}')}{\delta v(\vec{r})} \right)_N, \quad (1)$$

which measures a local change in electron density at \vec{r} for a shift in the local external potential at \vec{r}' , at a constant global number N of electrons in the system. The symmetry represented in definition (1) is important. If a perturbation at point \vec{r} produces a density change at point \vec{r}' , then the same perturbation at point \vec{r}' will produce at point \vec{r} precisely the same density change. The linear response function $\beta(\vec{r}, \vec{r}')$ is a very important quantity in DFT. It contains all the relevant information about the effect of nuclear vibrations on electron density polarization. As known, the acid catalytic reactions have everything to do with a perturbation in external potential $v(\vec{r})$. But few works have been reported about the estimate and application of the linear response function. We propose here a rigorous and internally consistent semi-empirical formalism for estimating this important quantity with satisfactory accuracy and direct applicability.

2. Theoretical method

Considering a system containing n atoms and m chemical bonds, in the atom–bond electronegativity equalization method (ABEEM) [12,13], the molecular electron density $\rho(\vec{r})$ is partitioned as the sum of the atomic regions and the chemical bond regions

$$\rho(\vec{r}) = \sum_a \rho_a(\vec{r}) + \sum_{g-h} \rho_{g-h}(\vec{r}) \quad (2)$$

in which $\rho_a(\vec{r})$ denotes the electron density located in the atom a region, and $\rho_{g-h}(\vec{r})$ denotes the electron density allocated around the $g-h$ bond region between atom g and atom h , the summation a covers all atoms in the molecule, and the summation $g-h$ covers all the bonds in the molecule. Here, it should be emphasized that the $\rho_a(\vec{r})$ represents the single-electron density around the nucleus a which could be concentrated on the a site in our ABEEM model, and $\rho_{g-h}(\vec{r})$ stands for the single-electron density around the $g-h$ bond center

that is chosen by a suitable apportionment of the $g-h$ covalent bond length. It is conventionally assumed that $\rho_a(\vec{r})$ integrates into N_a , the number of electrons in the atomic fragment a in the molecule, and $\rho_{g-h}(\vec{r})$ integrates into n_{g-h} , the number of electrons located at the center of the electron density $\rho_{g-h}(\vec{r})$, the bond $g-h$.

Partitioning the molecular electronic density according to Eq. (2), it can then be deduced that the total electronic energy E_{mol} of a molecule can be expressed as Eq. (3) if we approximately treat the electronic charges as being concentrated at the atomic centers (nuclei) and bond centers [12]

$$\begin{aligned} E_{\text{mol}} = & \sum_a [E_a^* + \chi_a^* q_a + \eta_a^* q_a^2] \\ & + \sum_{a-b} [\chi_{a-b}^* q_{a-b} + \eta_{a-b}^* q_{a-b}^2] \\ & + \sum_{i=a-b} \sum_{a-b} C_{i,a-b} q_i q_{a-b} \\ & + k \left[\sum_a \sum_{b(\neq a)} \frac{q_a q_b}{R_{a,b}} + \sum_{a-b} \sum_{g-h(\neq a-b)} \frac{q_{a-b} q_{g-h}}{R_{a-b,g-h}} \right. \\ & \left. + \sum_{g-h} \sum_{a(\neq g,h)} \frac{q_a q_{g-h}}{R_{a,g-h}} \right]. \quad (3) \end{aligned}$$

Here $q_a = Z_a - N_a$ and $q_{a-b} = -n_{a-b}$ are the charges of atom a and chemical bond $a-b$, respectively. Z_a is the nuclear charge of atom a . $R_{a,b}$, $R_{a-b,g-h}$ and $R_{a,g-h}$ are the separations between atoms a and b , chemical bond $a-b$ and chemical bond $g-h$, atom a and chemical bond $g-h$, respectively. E_a^* , χ_a^* , χ_{a-b}^* , η_a^* , η_{a-b}^* , and $C_{i,a-b}$ are the ABEEM parameters. k is an overall correction coefficient in the ABEEM approximation.

According to the definition of electronegativity [14] in density functional theory: $\chi_i = (\partial E / \partial q_i)_{q_j, R}$, formulae (4) and (5) can be easily obtained from Eq. (3):

$$\begin{aligned} \chi_a = & \chi_a^* + 2\eta_a^* q_a + \sum_{a-b} C_{a,a-b} q_{a-b} \\ & + k \left(\sum_{b(\neq a)} \frac{q_b}{R_{a,b}} + \sum_{g-h(\neq a-b)} \frac{q_{g-h}}{R_{a,g-h}} \right), \quad (4) \end{aligned}$$

$$\chi_{a-b} = \chi_{a-b}^* + 2\eta_{a-b}^* q_{a-b} + \sum_{i=a,b} C_{i,a-b} q_i + k \left(\sum_{g \neq (a,b)} \frac{q_g}{R_{a,b}} + \sum_{g-h(\neq a-b)} \frac{q_{g-h}}{R_{a-b,g-h}} \right). \quad (5)$$

Here χ_a and χ_{a-b} stand for the effective electronegativities of atom a and chemical bond $a-b$ in a molecule, respectively.

The response function describes the change in the electron populations of all regions (all atoms and all chemical bonds) caused by a theoretical change in the potential of an atom c (or a chemical bond $g-h$) only. The dv_c perturbation causes a dv_c shift in the electronegativity expression for atom c

$$\chi_c = \chi_c^* + 2\eta_c^* q_c + \sum_{c-b} C_{c-b} q_{c-b} + k \left(\sum_{b(\neq c)} \frac{q_b}{R_{c,b}} + \sum_{g-h(\neq c-b)} \frac{q_{g-h}}{R_{c,g-h}} \right) + dv_c. \quad (6)$$

At the same time for the other atoms and bonds, the electronegativity equations (4) and (5) remain unchanged.

The Sanderson's electronegativity equalization principle [15,16] demands that Eq. (7) apply to all atoms and all chemical bonds in the molecule

$$\chi_a = \chi_c = \cdots = \chi_{a-b} = \chi_{g-h} = \cdots = \chi, \quad (7)$$

where χ is the molecular electronegativity.

Based on partitioning the electron density distribution functions as atomic regions and chemical bond regions in ABEEM and the definition of the linear response function [11] in DFT, we define the condensed response function in ABEEM as follows:

$$\beta(a, b) = -(\delta q_a / \delta v_b)_N = -(\delta q_b / \delta v_a)_N, \quad (8)$$

$$\beta(a, g-h) = -(\delta q_a / \delta v_{g-h})_N = -(\delta q_{g-h} / \delta v_a)_N, \quad (9)$$

$$\begin{aligned} \beta(a-b, g-h) &= -(\delta q_{a-b} / \delta v_{g-h})_N \\ &= -(\delta q_{g-h} / \delta v_{a-b})_N. \end{aligned} \quad (10)$$

Eq. (8) describes the response of electron charge on atom a (or atom b) to the change in potential of atom b (or atom a). Eqs. (9) and (10) have a similar meaning to Eq. (8). In the same way, ac-

cording to the definition of the Fukui function [3] in DFT

$$f(\vec{r}) = (\partial \rho(\vec{r}) / \partial N)_v = -(\delta \chi / \delta v(\vec{r}))_N, \quad (11)$$

we give Eqs. (12) and (13) as the definitions of the condensed Fukui function in ABEEM:

$$f_a = -(\partial q_a / \partial N)_v = -(\delta \chi / \delta v_a)_N, \quad (12)$$

$$f_{a-b} = -(\partial q_{a-b} / \partial N)_v = -(\delta \chi / \delta v_{a-b})_N. \quad (13)$$

Here Eq. (12) is the definition of the condensed Fukui function for atom a in our ABEEM model, and Eq. (13) is the definition of the condensed Fukui function for chemical bond $a-b$ in our ABEEM model. Using these definitions for the condensed Fukui function, the condensed linear response functions and Sanderson's electronegativity equalization principle, we derive Eq. (14) from Eq. (6)

$$\begin{aligned} f_c &= 2\eta_c^* \beta(c, c) + \sum_{c-b} C_{c-b} \beta(c-b, c) \\ &+ k \left(\sum_{b(\neq c)} \frac{\beta(b, c)}{R_{c,b}} + \sum_{g-h(\neq c-b)} \frac{\beta(g-h, c)}{R_{c,g-h}} \right) - 1. \end{aligned} \quad (14)$$

Similarly, the derivation from Eq. (5) yields a set of m equations (15),

$$\begin{aligned} f_c &= 2\eta_{a-b}^* \beta(a-b, c) + \sum_{i=(a,b)} C_{a-b,i} \beta(i, c) \\ &+ k \left(\sum_{g(\neq a,b)} \frac{\beta(g, c)}{R_{a-b,g}} + \sum_{g-h(\neq a-b)} \frac{\beta(g-h, c)}{R_{a-b,g-h}} \right), \end{aligned} \quad (15)$$

while the derivation of Eq. (4) yields a set of $n-1$ equations (16)

$$\begin{aligned} f_c &= 2\eta_a^* \beta(a, c) + \sum_{a-b} C_{a-b,a} \beta(a-b, c) \\ &+ k \left(\sum_{b(\neq a)} \frac{\beta(b, c)}{R_{a,b}} + \sum_{g-h(\neq a-b)} \frac{\beta(g-h, c)}{R_{a,g-h}} \right). \end{aligned} \quad (16)$$

From the total electron number, N , constraint on the definition of the linear response function, it follows that the sum of the response functions equals zero

$$\sum_{c=1}^n \beta(c, a) + \sum_{g-h=n+1}^{n+m} \beta(g-h, a) = 0. \quad (17)$$

For a molecule consisting of n atoms and m chemical bonds, we can write $n - 1$ equations of type (16) and m equations of type (15). Together with the closure condition (17) and (14) we have a set of $n + m + 1$ equations. Since the ABEEM parameters η_a^* , η_{a-b}^* , and $C_{i,a-b}$ have been calibrated before [12,13,17–19], we can, therefore, easily obtain $n + m + 1$ unknowns, namely the $n + m$ condensed linear response functions and the condensed Fukui function on atom c .

3. Results and discussion

Using the method described in Section 2 and the ABEEM parameters [12,13,17–19], the test calculations have been performed for water, methylamine, methanol, ethanol, propanol, propene, aminoethane, propanone, propanal, dimethyl ether, methyl amino-ethanol, and some other organic molecules. The good agreement with the usual chemical knowledge is demonstrated. Here we give the results of molecules C_2H_5OH , CH_3CHO , and $C_{22}O_2H_{44}$ as examples. Fig. 1 shows their schematic diagrams.

Table 1 shows the ABEEM results of the condensed linear response function of ethanol molecule C_2H_5OH . From Table 1 it can be seen that the change in potential of one atom will mainly affect the electron densities of those atoms that bond directly with this atom. For example, the results of $\beta(C_1, C_2) = 0.227$, $\beta(C_1, H_{011}) = 0.215$, $\beta(C_1, H_{012}) = 0.215$, and $\beta(C_1, H_{013}) = 0.214$ show that the electron densities around atom C_2 and atoms $H_{011}, H_{012}, H_{013}$ will be changed greatly if the potential of atom C_1 is changed. From Fig. 1 we know that these atoms C_2, H_{011}, H_{012} , and H_{013} bond with atom C_1 directly. The results of $\beta(C_1, C_2) = 0.227$, $\beta(C_2, O_3) = 0.154$, $\beta(C_2, H_{021}) = 0.192$, and $\beta(C_2, H_{022}) = 0.193$ reveal that the change in potential of atom C_2 will affect the electron densities of atoms C_1, O_3, H_{021} , and H_{022} obviously. The atoms C_1, O_3, H_{021} , and H_{022} bond with atom C_2 directly, too. The merit of ABEEM

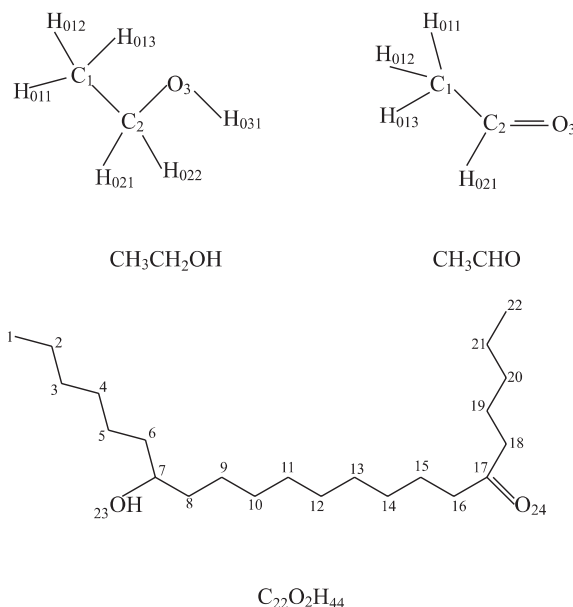


Fig. 1. Schematic diagrams of the CH_3CH_2OH , CH_3CHO and $C_{22}O_2H_{44}$ molecules.

is that the chemical bonds are treated explicitly. One can easily obtain the information related to the chemical bonds by ABEEM. It can be seen from Table 1 that for ethanol molecule, among those quantities related to chemical bonds, only $\beta(C_1, C_1-C_2) = 0.026$, $\beta(C_2, C_1-C_2) = 0.025$, $\beta(C_2, C_2-O_3) = 0.056$, $\beta(O_3, C_2-O_3) = 0.036$, and $\beta(O_3, O_3-H_{031}) = 0.035$ are relatively big. These five condensed linear response functions relate to the three chemical bonds: bond C_1-C_2 , C_2-O_3 , and O_3-H_{031} . It manifests that the electron density of the chemical bond C_1-C_2 changes with respect to a shift in the potentials of atom C_1 or atom C_2 , or both of them simultaneously. The electron density of the chemical bond C_2-O_3 can be affected by modifying the potentials of atom O_3 or atom C_2 or both of them simultaneously. The electron density of the chemical bond O_3-H_{031} varies with the change in the potential of atom O_3 . From Table 1 it can also be seen that the effect of the change in potential of every hydrogen atom on the electron density of any chemical bond is almost negligible. The effect of the change in potential of every chemical bond on the electron density of any other chemical bond in this molecule

Table 1
The ABEM results of the condensed linear response function $\beta(r_1, r_2)$ for C_2H_5OH

	C_1^-	C_2^-	O_3^-	H_{011}	H_{012}	H_{013}	H_{021}	H_{022}	H_{031}	C_1-C_2	C_1-H_{001}	C_1-H_{012}	C_1-H_{013}	C_2-O_3	C_2-H_{021}	C_2-H_{022}	O_3-H_{031}
C_1^-	-0.849																
C_2^-	0.227	-0.773															
O_3^-	-0.020	0.154	-0.419														
H_{011}	0.215	-0.025	0.025	-0.253													
H_{012}	0.215	-0.025	0.014	-0.013	-0.252												
H_{013}	0.214	-0.024	0.017	-0.014	-0.013	-0.254											
H_{021}	-0.023	0.192	0.005	0.022	0.023	0.011	-0.249										
H_{022}	-0.023	0.193	-0.007	0.011	0.023	0.021	-0.010	-0.249									
H_{031}	0.012	-0.004	0.152	0.010	0.008	0.021	0.005	0.019	-0.250								
C_1-C_2	0.026	0.025	0.003	0.005	0.005	0.005	0.005	0.005	0.002	-0.093							
C_1-H_{001}	-0.001	0.002	0.000	0.008	0.003	0.003	0.000	0.000	0.000	0.001	-0.018						
C_1-H_{012}	-0.001	0.002	0.000	0.003	0.008	0.003	0.000	0.000	0.000	0.001	0.000	-0.018					
C_1-H_{013}	-0.001	0.003	0.000	0.003	0.003	0.008	0.000	0.000	0.001	0.001	0.000	0.000	-0.018				
C_2-O_3	0.004	0.056	0.036	0.004	0.000	0.003	0.008	0.005	0.016	0.007	0.000	0.000	0.000	-0.146			
C_2-H_{021}	0.003	-0.001	0.002	0.000	0.000	0.000	0.008	0.002	0.000	0.001	0.000	0.000	0.000	0.002	-0.018		
C_2-H_{022}	0.002	-0.001	0.002	0.000	0.000	0.000	0.002	0.002	0.000	0.001	0.000	0.000	0.000	0.002	0.000	-0.018	
O_3-H_{031}	0.002	-0.002	0.035	0.001	0.001	0.002	0.000	0.002	0.008	0.000	0.000	0.000	0.000	0.005	0.000	0.000	-0.053

is almost negligible, too. It has been known that the change of electron density in a chemical bond means a change of bond strength. So from the results of the condensed linear response function we can obtain quantitative information about the variation in the chemical bond and chemical reactivity.

Table 2 is the condensed linear response function we obtained for the ethanol molecule CH_3CHO . From Table 2 we can also determine that the change in potential of one atom will mainly affect the electron densities of those atoms that bond directly with this atom. If we consider the condensed linear response function related to the chemical bonds only, from the results in Table 2 it can be seen that for the ethanol molecule, only the quantities of $\beta(C_1, C_1-C_2) = 0.023$, $\beta(C_2, C_1-C_2) = 0.031$, $\beta(C_2, C_2=O_3) = 0.101$ and $\beta(O_3, C_2=O_3) = 0.119$ are relatively big. These four condensed linear response functions relate to two chemical bonds: bond C_1-C_2 and bond $C_2=O_3$. This shows that the electron density of chemical bond C_1-C_2 can change with a shift in the potentials of atom C_1 or atom C_2 or both of them simultaneously. The electron density of the chemical bond $C_2=O_3$ varies in accordance with the perturbation in the potentials of atom O_3 or atom C_2 or both of them simultaneously. The fact that $\beta(C_2, C_2=O_3) = 0.101$ and $\beta(O_3, C_2=O_3) = 0.119$ are much larger than $\beta(C_1, C_1-C_2) = 0.023$ and $\beta(C_2, C_1-C_2) = 0.031$ shows that in ethanol, the chemical bond $C_2=O_3$ is a more active site and easier to be affected by changing the potential than the chemical bond C_1-C_2 . From Tables 1 and 2 it can also be seen, like in ethanol, that the effect of the change in the potential of every hydrogen atom on the electron density of any chemical bond is almost negligible. The same conclusion can be obtained about the effect of the change in potential of every chemical bond on the electron density of any other chemical bond and the effect of the shift in potential of any atom on the electron density of any chemical bond C-H.

In summary, from Tables 1 and 2 it can be seen that all the condensed linear response functions can be classed into three groups: the coupling of atom-atom, atom-bond, and bond-bond. The coupling of atom-atom is usually large, that of

Table 2

The ABEEM results of the linear response function $\beta(r_1, r_2)$ for CH_3CHO

	C_1-	$\text{C}_2=$	$\text{O}_3=$	H_{011}	H_{012}	H_{013}	H_{021}	C_1-C_2	$\text{C}_1-\text{H}_{011}$	$\text{C}_1-\text{H}_{012}$	$\text{C}_1-\text{H}_{013}$	$\text{C}_2=\text{O}_3$	$\text{C}_2-\text{H}_{021}$
C_1-	-0.869												
$\text{C}_2=$	0.291	-0.951											
$\text{O}_3=$	-0.071	0.377	-0.522										
H_{011}	0.220	-0.038	0.055	-0.254									
H_{012}	0.218	-0.029	0.038	-0.014	-0.251								
H_{013}	0.218	-0.029	0.038	-0.014	-0.012	-0.251							
H_{021}	-0.040	0.238	-0.035	0.016	0.025	0.025	-0.257						
C_1-C_2	0.023	0.031	-0.001	0.005	0.006	0.006	0.002	-0.093					
$\text{C}_1-\text{H}_{011}$	-0.001	0.003	0.001	0.008	0.003	0.003	0.000	0.001	-0.018				
$\text{C}_1-\text{H}_{012}$	-0.001	0.003	0.000	0.003	0.009	0.003	0.000	0.001	0.000	-0.018			
$\text{C}_1-\text{H}_{013}$	-0.001	0.003	0.000	0.003	0.003	0.009	0.000	0.001	0.000	0.000	-0.018		
$\text{C}_2=\text{O}_3$	0.013	0.101	0.119	0.010	0.004	0.004	0.017	0.016	0.000	0.000	0.000	-0.287	
$\text{C}_2-\text{H}_{021}$	0.002	-0.001	0.003	0.000	0.000	0.000	0.008	0.001	0.000	0.000	0.000	0.004	-0.018

atom–bond is the next, and that of bond–bond is usually negligible. The result that the coupling of atom–atom is larger than that of bond–bond is not unexpected because of their different separations. The result that the coupling of atom–bond is larger than that of bond–bond can be understood in the same way. But the reason that the coupling of atom–atom is larger than that of atom–bond is still unclear because the separation of atom and bond is shorter than the separation of atom and atom.

It has been shown that ABEEM can be used to determine the charge distributions and molecular energies of large molecules [12,17–19]. This test

calculation demonstrates that ABEEM can also be applied to predict another important physical quantity – the linear response function of large molecules. Table 3 shows the ABEEM results of the condensed linear response function of the large molecule, $\text{C}_{22}\text{O}_2\text{H}_{44}$. It should be noted that Table 3 only lists the relatively large quantities and does not include those very small quantities. The same rule as above is shown: the change in potential of one atom will firstly affect the electron densities of those atoms that bond directly with this atom and secondly affect the electron densities of the bonds related to this atom.

Table 3

The ABEEM results of response function $\beta(r_1, r_2)$ for molecule $\text{C}_{22}\text{O}_2\text{H}_{44}$

$\beta(\text{C}_2, \text{C}_1) = 0.231$	$\beta(\text{C}_3, \text{C}_2) = 0.215$	$\beta(\text{C}_4, \text{C}_3) = 0.214$
$\beta(\text{C}_5, \text{C}_4) = 0.214$	$\beta(\text{C}_6, \text{C}_5) = 0.213$	$\beta(\text{C}_7, \text{C}_6) = 0.201$
$\beta(\text{C}_8, \text{C}_7) = 0.201$	$\beta(\text{C}_9, \text{C}_8) = 0.212$	$\beta(\text{C}_{10}, \text{C}_9) = 0.214$
$\beta(\text{C}_{11}, \text{C}_{10}) = 0.214$	$\beta(\text{C}_{12}, \text{C}_{11}) = 0.214$	$\beta(\text{C}_{13}, \text{C}_{12}) = 0.214$
$\beta(\text{C}_{14}, \text{C}_{13}) = 0.214$	$\beta(\text{C}_{15}, \text{C}_{14}) = 0.214$	$\beta(\text{C}_{16}, \text{C}_{15}) = 0.215$
$\beta(\text{C}_{17}, \text{C}_{16}) = 0.249$	$\beta(\text{C}_{18}, \text{C}_{17}) = 0.249$	$\beta(\text{C}_{19}, \text{C}_{18}) = 0.215$
$\beta(\text{C}_{20}, \text{C}_{19}) = 0.214$	$\beta(\text{C}_{21}, \text{C}_{20}) = 0.215$	$\beta(\text{C}_{22}, \text{C}_{21}) = 0.231$
$\beta(\text{O}_{23}, \text{C}_7) = 0.152$	$\beta(\text{O}_{24}, \text{C}_{17}) = 0.329$	$\beta(\text{H}_{011}, \text{C}_1) = 0.209$
$\beta(\text{H}_{012}, \text{C}_1) = 0.210$	$\beta(\text{H}_{013}, \text{C}_1) = 0.209$	$\beta(\text{H}_{021}, \text{C}_2) = 0.194$
$\beta(\text{H}_{022}, \text{C}_2) = 0.194$	$\beta(\text{H}_{031}, \text{C}_3) = 0.193$	$\beta(\text{H}_{031}, \text{C}_3) = 0.193$
$\beta(\text{H}_{041}, \text{C}_4) = 0.193$	$\beta(\text{H}_{042}, \text{C}_4) = 0.193$	$\beta(\text{H}_{051}, \text{C}_5) = 0.193$
$\beta(\text{H}_{052}, \text{C}_5) = 0.192$	$\beta(\text{H}_{061}, \text{C}_6) = 0.192$	$\beta(\text{H}_{062}, \text{C}_6) = 0.192$
$\beta(\text{H}_{071}, \text{C}_7) = 0.179$	$\beta(\text{H}_{081}, \text{C}_8) = 0.192$	$\beta(\text{H}_{082}, \text{C}_8) = 0.192$
$\beta(\text{H}_{091}, \text{C}_9) = 0.192$	$\beta(\text{H}_{092}, \text{C}_9) = 0.192$	–
$\beta(\text{C}_7-\text{O}_{23}, \text{C}_7) = 0.052$	$\beta(\text{C}_7-\text{O}_{23}, \text{O}_{23}) = 0.032$	$\beta(\text{C}_{18}-\text{C}_{17}, \text{C}_{17}) = 0.029$
$\beta(\text{C}_{16}-\text{C}_{17}, \text{C}_{17}) = 0.029$	$\beta(\text{C}_{17}=\text{O}_{24}, \text{C}_{17}) = 0.097$	$\beta(\text{C}_{17}=\text{O}_{24}, \text{O}_{24}) = 0.108$
$\beta(\text{O}_{23}-\text{H}_{231}, \text{O}_{23}) = 0.035$		

4. Conclusion

Based on density functional theory and the atom–bond electronegativity equalization method, a scheme is proposed to quantitatively determine the linear response function – the coupling or interaction between the electron density and the external potential. From the test calculations it can be concluded that among all the responses between the electron density and the potential, the one of atom–atom is the strongest, the one of atom–bond is the next, and the one of bond–bond is almost negligible. The effect of the change in potential of every hydrogen atom on the electron density of any chemical bond is almost negligible, too. The electron density of all the chemical bonds C–H rarely varies with the displacement in the potential of any of the atoms. The change of electron density in a chemical bond means a change of bond strength. So from the results of the condensed linear response function the quantitative information about the variation in chemical bond strength and chemical reactivity may be obtained and applied.

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