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Atom−Bond Electronegativity Equalization Method. 1. Calculation of the Charge Distribution in Large Molecules

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On the basis of the principle of electronegativity equalization and density-functional theory, an atom−bond electronegativity equalization method has been developed for the calculation of the charge distribution in large molecules that are connectivity and geometry dependent. The effective electronegativities of an atom and a bond in a molecule are derived and given by equations that contain respective electronegativities, hardness terms, and contributions that come from other atomic and bond charges. The parameters *A*, *B*, *C*, and *D* are the valence-state electronegativity and the valence-state hardnesses. They are obtained by calibrating through calculations of more than 100 model molecules and are transferable and consistently usable. The atom−bond electronegativity equalization method is tested through calculation of the charge distributions in several large organic molecules. It has been shown that there is a very good agreement between the results obtained by the atom−bond electronegativity equalization method and those obtained by the corresponding *ab initio* quantum chemical calculations.

1. Introduction

Electronegativity has been one of the most accepted and used concepts in chemistry for more than 60 years due to the original work by Pauling.[1−3] It is, however, only in recent decades that its physical significance has been elucidated in terms of the density-functional theory. In this respect, Parr et al. have justified that electronegativity is the negative of the chemical potential of an electronic system, such as an atom or a molecule, and simultaneously demonstrated that electronegativity is constant throughout an atom or a molecule, which validates Sanderson's postulate[4,5] that when two or more atoms combine to form a molecule, their electronegativities get equalized.[6−8] This established a new basis for understanding and application of electronegativity and its equalization.

The charge distribution within a large organic or biological molecule is an important characteristic for explanation and prediction of its structure and properties, for instance, reactive sites, ESCA, and NMR shifts.[3,9] Hence the direct calculation of the charge distribution in a molecule without using the traditional quantum chemistry methods has been an active research field in recent years, which mainly relies on thorough understanding of electronegativity and its equalization in the light of density-functional theory. For this purpose, many electronegativity equalization methods or schemes have been formulated and applied.[10−19]

Mortier et al. developed an electronegativity equalization method (EEM) for the calculation of atomic charges and electronic energy in a molecule.[9−12] Within the framework of density-functional theory, they derived an expression of the effective electronegativity of an atom in a molecule, which is equal to the molecular electronegativity. This method has been applied to elucidating some properties of a molecule, even a zeolite system.

York and Yang presented a formulation of the chemical potential equalization principle from the perspective of density-functional theory.[13] Their results provide a linear-response framework for describing the redistribution of electrons upon perturbation by an applied field and the foundation for a promising semiempirical model for polarization and charge transfer in molecular simulations.

Cioslowski and Stefanov showed that the charge-constrained calculations make it possible to rigorously analyze electron flow and electronegativity equalization in the process of bond formation, which provides both the evidence and explanation for the energy derivative discontinuities that are observed in isolated atoms and molecules.[14]

Geerlings et al. formulated a nonempirical electronegativity equalization scheme[15] where an expression for the electronegativity of an atom in a molecule was derived, based on the change upon molecule formulation. Scheraga et al. established a modified partial equalization of orbital electronegativity method for determination of net atomic charges[16] and applied it to neutral molecules as models for polypeptides. Ghosh put forward a semiempirical electronegativity equalization procedure, providing quite accurate predictions of bond energies for simple heteronuclear diatomic molecules.[17]

In this paper, an atom−bond electronegativity equalization method (ABEEM) is developed. First, the theoretical basis for the ABEEM is formulated in light of density-functional theory. Second, the parameters involved in the scheme are discussed and determined through treating a series of model molecules that contain several important organic species with an *ab initio* quantum chemical method. Finally, the ABEEM method is applied to calculation of the charge distribution, the atom charges, and the bond charges, in large organic molecules. Examples are given to show the good agreement between our results and the corresponding *ab initio* quantum chemical calculations.

2. Effective Chemical Potential of an Atom and a Bond in a Molecule

The total electronic energy E_{mol} of a molecule at a certain molecular configuration consists of the kinetic (T), nuclear−electron attraction (V_{ne}), electron−electron interaction (V_{ee}), and

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nuclear−nuclear repulsion (V_{nn}) energies,

$$E_{mol} = T + V_{ne} + V_{ee} + V_{nn} \tag{1}$$

Each component on the right side of eq 1 may be expressed respectively as follows:

$$T = \left\langle \Psi_{mol} \middle| -\frac{1}{2}\sum_i \nabla_i^2 \middle| \Psi_{mol} \right\rangle = \int -\frac{1}{2}\nabla^2 \gamma_{mol}(\vec{r},\vec{r}')|_{\vec{r}=\vec{r}'}\, d\vec{r} \tag{2}$$

$$V_{ne} = \left\langle \Psi_{mol} \middle| -\sum_i \sum_a \frac{Z_a}{|\vec{r}_i - \vec{R}_a|} \middle| \Psi_{mol} \right\rangle = \sum_a \int \frac{-Z_a \varrho(\vec{r})}{|\vec{r} - \vec{R}_a|}\, d\vec{r} \tag{3}$$

$$V_{ee} = \left\langle \Psi_{mol} \middle| \frac{1}{2}\sum_i \sum_{j\neq 1} \left|\frac{1}{|\vec{r}_i - \vec{r}_j|}\right| \Psi_{mol} \right\rangle = \frac{1}{2}\int\int \frac{\varrho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\, d\vec{r}_1\, d\vec{r}_2 \tag{4}$$

$$V_{nn} = \frac{1}{2}\sum_a \sum_{b\neq a} \frac{Z_a Z_b}{R_{a,b}} \tag{5}$$

There Ψ_{mol}, $\gamma_{mol}(\vec{r},\vec{r}')$, $\rho(\vec{r})$, and $\rho_2(\vec{r}_1,\vec{r}_2)$ stand for the molecular wave function, first-order density matrix, electron density, and the two-electron density, respectively. Z_a and $\vec{R}_a$ denote the nuclear charge and coordinates of the *a*th atom, and $R_{a,b}$ is the internuclear separation between atom *a* and atom *b*. The subscripts *i*, 1, and 2 indicate *i*th, first, and second electrons.

In our atom−bond model, the molecular electron density $\rho(\vec{r})$ is partitioned as

$$\rho(\vec{r}) = \sum_a \rho_a(\vec{r}) + \sum_{g-h} \rho_{g-h}(\vec{r}) \tag{6}$$

in which $\rho_a(\vec{r})$ denotes the electron density located on the atom *a*, $\rho_{g-h}(\vec{r})$ 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 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 to N_a, the number of electrons in the atomic fragment *a* in the molecule, and $\rho_{g-h}(\vec{r})$ integrates to 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 6, it can then be deduced that the total electronic energy E_{mol} of a molecule can be expressed as eq 7 if we approximately treat the electronic charges as concentrated at atomic centers (nuclei) and bond centers. The details for this are given in the Appendix of this paper.

$$\begin{aligned} E_{mol} = {} & \sum_a [E_a^* + \mu_a^*(N_a - N_a^*) + \eta_a^*(N_a - N_a^*)^2] + \\ & \sum_{a-b} [E_{a-b}^* + \mu_{a-b}^*(n_{a-b} - n_{a-b}^*) + \eta_{a-b}^*(n_{a-b} - n_{a-b}^*)^2] + \\ & \sum_{a-b}\left[\frac{k_{a,a-b}(-Z_a + N_a)n_{a-b}}{R_{a,a-b}} + \frac{k_{b,a-b}(-Z_b + N_b)n_{a-b}}{R_{b,a-b}}\right] + \\ & k\left[\sum_a \sum_{b(\neq a)} \frac{(1/2)N_a N_b - Z_a N_b}{R_{a,b}} + \right. \\ & \sum_{a-b} \sum_{g-h(\neq a-b)} \frac{(1/2)n_{a-b}n_{g-h}}{R_{a-b,g-h}} + \\ & \left. \sum_{g-h} \sum_{a(\neq g,h)} \frac{-Z_a ng_{-h} + N_a n_{g-h}}{R_{a,g-h}} + \frac{1}{2}\sum_a \sum_{b(\neq a)} \frac{Z_a Z_b}{R_{a,b}}\right] \end{aligned} \tag{7}$$

where *k* is an overall correction coefficient in this approximation.

The chemical potentials of atom *a* and bond *a*−*b* in the molecule are now defined by using eq 7 according to its formalism by means of density functional theory.[10,18] Thus, we obtain eq 8 and eq 9 for the effective chemical potentials μ_a of an atom *a* and μ_{a-b} of a bond *a*−*b*:

$$\begin{aligned} \mu_a = \left(\frac{\partial E_{mol}}{\partial N_a}\right)_{N_b,\ldots R_{a,b}\ldots} = {} & \mu_a^* + 2\eta_a^*(N_a - N_a^*) + \\ & \sum_{a-b} \frac{k_{a,a-b}}{R_{a,a-b}} n_{a-b} + k\left[\sum_{b\neq a} \frac{N_b - Z_b}{R_{a,b}} + \sum_{g-h\neq a-b} \frac{n_{g-h}}{R_{a,g-h}}\right] \end{aligned} \tag{8}$$

$$\begin{aligned} \mu_{a-b} = \left(\frac{\partial E_{mol}}{\partial n_{a-b}}\right)_{N_b,\ldots R_{a,b}\ldots} = {} & \mu_{a-b}^* + 2\eta_{a-b}^*(n_{a-b} - n_{a-b}^*) + \\ & \frac{k_{a,a-b}}{R_{a,a-b}}(N_a - Z_a) + \frac{k_{b,a-b}}{R_{b,a-b}}(N_b - Z_b) + \\ & k\left[\sum_{g\neq a,b} \frac{N_g - Z_g}{R_{a-b,g}} + \sum_{g-h\neq a-b} \frac{n_{g-h}}{R_{a-b,g-h}}\right] \end{aligned} \tag{9}$$

In eq 8, the summation *a*−*b* covers the bonds that connect atom *a* directly, the summation *b* covers all atoms except the atom *a*, and the summation *g*−*h* covers all bonds except the bonds *a*−*b*. In eq 9, the summation *g* covers all atoms except atom *a* and *b*, and the summation *g*−*h* covers all bonds except bond *a*−*b*. The formulas eqs 7−9 are basic and important for application and further development of the ABEEM scheme.

3. Electronegativity Equalization

The existence of a unique chemical potential everywhere in the molecule establishes the electronegativity equalization principle. The effective electronegativity of an atom or a bond is identified as the negative of the corresponding chemical potential. From eq 8, and supposing

$$\frac{k_{a,a-b}}{R_{a,a-b}} = \frac{k_{a,a-c}}{R_{a,a-c}} = \frac{k_{a,a-d}}{R_{a,a-d}} = \frac{k_{a,a-e}}{R_{a,a-d}} = C_a$$

we have eq 10:

$$\chi_a = A_a + B_a q_a + C_a \sum_{a-b} q_{a-b} + k\left(\sum_{b\neq a} \frac{q_b}{R_{a,b}} + \sum_{g-h\neq a-b} \frac{q_{q-h}}{R_{a,g-h}}\right) \tag{10}$$

From eq 9, we have eq 11:

$$\chi_{\rm a-b} = A_{\rm a-b} + B_{\rm a-b}q_{\rm a-b} + C_{\rm a-b,a}q_{\rm a} + D_{\rm a-b,b}q_{\rm b} + k\left(\sum_{g\neq a,b}\frac{q_{\rm g}}{R_{\rm a-b,g}} + \sum_{g-h\neq a-b}\frac{q_{\rm g-h}}{R_{\rm a-b,g-h}}\right) \quad (11)$$

Here $A_{\rm a} = \mu_{\rm a}^*$; $A_{\rm a-b} = \mu_{\rm a-b}^*$, the electronegativities of atom a and bond $a-b$ in the molecule; $B_{\rm a} = 2\eta_{\rm a}^*$and $B_{\rm a-b} = 2\eta_{\rm a-b}^*$, the hardnesses of atom a and bond $a-b$ in the molecule; $q_{\rm a} = N_{\rm a}^* - N_{\rm a} = Z_{\rm a} - N_{\rm a}$ and $q_{\rm a-b} = n_{\rm a-b}^* - n_{\rm a-b} = -n_{\rm a-b}$, the partial charge of atom a and bond $a-b$, i.e., the charge distribution in the molecule. $C_{\rm a-b,a} = k_{\rm a,a-b}/R_{\rm a,a-b}$, $D_{\rm a-b,b} = k_{\rm b,a-b}/R_{\rm b,a-b}$, and $C_{\rm a}$ are regarded as adjustable parameters. The electronegativity equalization principle demands that eq 12 apply for all atoms and all bonds in the molecule:

$$\chi_\alpha = \chi_\beta = ... = \chi_{\alpha-\beta} = \chi_{\gamma-\delta} = ... = \bar{\chi} \quad (12)$$

This yields $n + m$ simultaneous equations for an arbitrary molecule containing m atoms and n bonds; these, along with the constraint equation on its net charge, can be solved to give the molecular electronegativity $\tilde{\chi}$ and the charge distribution on each atom and each bond in the molecule if all parameters in eqs 10 and 11 are known.

Although it is theoretically possible to estimate the parameters involved in eqs 10 and 11 from *ab initio* quantum chemical calculations, it is computationally a difficult task. Since the primary objective of this paper is to calculate the charge distributions in large molecules, it is, of course, desirable to get these parameters in a suitable way such that they are transferable from molecule to molecule and are able to reproduce with the required accuracy the atomic charges and bond charges in a large molecule. For this purpose, more than 100 ordinary molecules, containing various atoms and bonds, were selected as model molecules. The *ab initio* STO-3G SCF method was used to calculate their charge distributions via Mulliken population analysis. (The STO-3G basis set was taken because the Mulliken population analysis is strongly dependent on basis set choice and overestimates the charge transfer between atoms in a molecule when polarization basis sets are used.) Then the charge distributions obtained for the model molecules were brought into eqs 10 and 11 in order to determine the coefficients *A*, *B*, *C*, and *D* through a regression and least-squares optimization procedure.[10,18,19] Three points should be mentioned here. First, the correction factor k is the same value as in the MEEM method.[18,19] Second, the harmonic mean of electronegativity of the neutral atoms that constitute a model molecule is invoked as the initial reference value of its molecular electronegativity. Third, the bond charge $q_{\rm g-h}$ between atoms g and h in a molecule is made equal to the Mulliken interatomic population on the bond $g-h$, by use of a correction factor λ, which is introduced for accommodation of our charge distribution model with the Mulliken population. The remainder of the Mulliken interatomic population for bond $g-h$ is equally allotted to the atoms g and h. The parameter λ is optimized to be 0.15 for all bonds to obtain good and reasonable results. The bond charge $q_{\rm g-h}$ is placed on the point that partitions the bond length according to the ratio of covalent atomic radii of atoms g and h.

The coefficients *A*, *B*, *C*, and *D*, determined in terms of the procedure mentioned above, are listed in Table 1, where the Pauling electronegativity unit is used. The coefficient *A*, the valence-state electronegativity for a neutral atom in a certain molecular environment, has the same order of magnitude as the Pauling electronegativity scale for H, C, N, and O atoms. It was found that the coefficients *A* and *B* converged to the parameters *A* and *B* in the MEEM method[18,19] as the bond charges in molecules decreased to zero. This implies that the ABEEM and the MEEM methods are self-consistent; that is the ABEEM model becomes the MEEM model as the bond charges in molecules are apportioned to their related atoms.

TABLE 1: Atom and Bond Valence Parameters[a]

	A	*B*	*C*	*D*	χ^0
H−	1.832	5.525	0.793		2.2
C−	2.197	3.484	2.237		2.55
N−	2.553	4.513	1.339		3.04
O−	3.176	6.295	1.507		3.55
C═	2.115	3.485	2.006		
N═	2.707	3.851	2.224		
O═	3.422	6.081	5.058		
C−H	3.389	10.064	2.419	2.219	
N−H	2.764	5.597	3.123	2.273	
O−H	5.527	56.426	7.565	0.91	
C−C	2.968	5.391	2.199		
C−N	5.457	28.663	3.74		
C−O	4.565	26.068	2.702		
C═C	3.532	8.346	2.841		
C═N	2.909	4.348	3.113		
C═O	6.832	36.524	3.829		

[a] *A*, *B*, *C*, and *D* are the parameters in eqs 10 and 11; for the bond C−H, the parameter *C* stands for $C_{C-H,H}$, the parameter *D* stands for $D_{C-H,C}$, the same for the bond N-H and the bond O-H; for the other bonds the supposition $C_{\rm a-b,a} = D_{\rm a-b,b}$ has been used. $\chi°$ is the Pauling electronegativity scale.

In Table 1 are listed the Pauling electronegativities χ^0 for some ordinary atoms, as well as their valence-state parameters *A*, *B*, *C*, and *D* (in Pauling units). These parameters are obtained by regression simulation for more than 100 organic molecules such as propane, ethene, propene, methanol, dimethyl ether, methylamine, dimethylamine, and formic acid and hence possess wide transference and applicability. In the table, taking carbon atom as an example, C− denotes that the central carbon has four single bonds linking with other four atoms and C═ stands for the central carbon linking with other three atoms with two single bond and one double bond, etc.

From Table 1, it is seen that the parameter *A* for any bond $g-h$ is always larger than that for the atoms g and h. This reflects the fact that when two or more atoms combine together to form a molecule, the electron density in bond regions has piled up or overlapped in comparison with that in individual isolated atoms.

4. Direct Calculation of the Charge Distribution in a Molecule

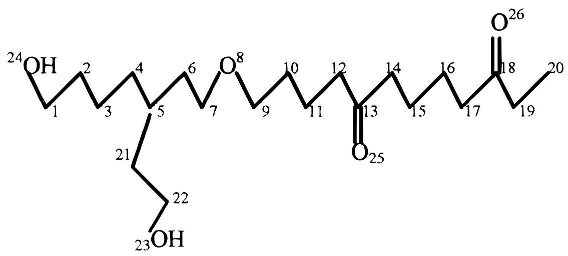
As testing examples, the charge distributions in $C_{20}H_{42}$, $C_{24}O_2N_2H_{52}$, and some other organic molecules have been calculated by our ABEEM method described above. These molecules are quite large and contain a variety of bond types, which demonstrates the possible application to biological molecules of interest in the future and to other large systems. Figure 1 gives the schematic diagram of some molecules studied. For $C_{21}O_5H_{40}$ the charge distributions from the two methods are plotted in Figure 2, in which the linear regression equation is $y = 0.9929x + 6 \times 10^{-7}$ (y are the charge distributions obtained by the ABEEM method and x are those obtained by *ab initio* STO-3G HF-SCF method), the linear correlation coefficient R is 0.9989, and the root-mean-square deviation S is 0.0062. The largest error occurs for C_{13} and C_{18} (0.025), with a relative error of 6.9%. The correlations of charge distributions of other molecules, such as $C_{17}H_{36}$ and $C_{24}O_2N_2H_{52}$, are also very good, like the above one. To enable a better

TABLE 2: Comparison of ABEEM and ab Initio Charge Distribution for $C_{21}O_5H_{40}$[a]

$C_{21}O_5H_{40}$	STO-3G	ABEEM	STO-3G	ABEEM		STO-3G	ABEEM
C1−	0.223	0.222	0.015	0.017	C1−C2	−0.108	−0.101
C2−	0.124	0.117	−0.099	−0.104	C1−O24	−0.081	−0.081
C3−	0.122	0.132	−0.102	−0.095	C1−H011	−0.113	−0.114
C4−	0.123	0.12	−0.1	−0.105	C1−H012	−0.113	−0.114
C5−	0.193	0.202	−0.026	−0.023	C2−C3	−0.109	−0.116
C6−	0.117	0.105	−0.106	−0.117	C2−H021	−0.115	−0.112
C7−	0.215	0.226	0.009	0.022	C2−H022	−0.115	−0.112
C8−	−0.18	−0.177	−0.259	−0.256	C3−C4	−0.109	−0.11
C9−	0.218	0.223	0.012	0.019	C3−H031	−0.115	−0.114
C10−	0.124	0.114	−0.099	−0.107	C3−H032	−0.115	−0.114
C11−	0.127	0.139	−0.096	−0.089	C4−C5	−0.108	−0.111
C12−	0.096	0.087	−0.126	−0.14	C4−H041	−0.115	−0.115
C13═	0.364	0.337	0.192	0.16	C4−H042	−0.115	−0.115
C14−	0.094	0.089	−0.127	−0.138	C5−C6	−0.108	−0.115
C15−	0.13	0.138	−0.093	−0.086	C5−C21	−0.108	−0.112
C16−	0.129	0.136	−0.095	−0.09	C5−H051	−0.115	−0.113
C17−	0.093	0.088	−0.128	−0.139	C6−C7	−0.108	−0.103
C18═	0.365	0.336	0.192	0.16	C6−H061	−0.115	−0.112
C19−	0.096	0.103	−0.125	−0.124	C6−H062	−0.115	−0.113
C20−	0.053	0.058	−0.173	−0.174	C7−O8	−0.079	−0.079
C21−	0.109	0.104	−0.113	−0.121	C7−H071	−0.113	−0.113
C22−	0.222	0.221	0.013	0.015	C7−H072	−0.113	−0.113
O23−	−0.236	−0.234	−0.316	−0.313	C9−O8	−0.079	−0.079
O24−	−0.236	−0.234	−0.316	−0.314	C9−C10	−0.108	−0.104
O25═	−0.165	−0.149	−0.23	−0.214	C9−H091	−0.113	−0.113
O26═	−0.163	−0.149	−0.228	−0.214	C9−H092	−0.113	−0.113
H011	0.101	0.096	0.044	0.039	C10−C11	−0.109	−0.114
H012	0.101	0.096	0.045	0.039	C10−H101	−0.115	−0.113
H021	0.117	0.124	0.06	0.068	C10−H102	−0.115	−0.112
H022	0.118	0.124	0.06	0.068	C11−C12	−0.108	−0.113
H031	0.108	0.112	0.051	0.055	C11−H111	−0.115	−0.114
H032	0.11	0.113	0.052	0.056	C11−H112	−0.115	−0.115
H041	0.11	0.113	0.053	0.055	C12−C13	−0.107	−0.112
H042	0.109	0.113	0.051	0.055	C12−H121	−0.114	−0.116
H051	0.107	0.101	0.049	0.044	C12−H122	−0.115	−0.112
H061	0.119	0.126	0.061	0.069	C13−C14	−0.107	−0.111
H062	0.115	0.123	0.057	0.066	C13═O25	−0.131	−0.131
H071	0.105	0.097	0.049	0.04	C14−C15	−0.107	−0.113
H072	0.105	0.098	0.049	0.042	C14−H141	−0.115	−0.117
H091	0.103	0.097	0.046	0.04	C14−H142	−0.115	−0.113
H092	0.105	0.099	0.048	0.042	C15−C16	−0.109	−0.109
H101	0.118	0.123	0.06	0.067	C15−H151	−0.115	−0.115
H102	0.12	0.125	0.062	0.069	C15−H52	−0.115	−0.112
H111	0.114	0.114	0.056	0.057	C16−C17	−0.108	−0.115
H112	0.109	0.108	0.052	0.051	C16−H161	−0.115	−0.115
H121	0.119	0.118	0.062	0.06	C16−H162	−0.115	−0.113
H122	0.127	0.132	0.07	0.076	C17−C18	−0.107	−0.111
H141	0.113	0.115	0.056	0.057	C17−H171	−0.114	−0.116
H142	0.126	0.128	0.068	0.072	C17−H172	−0.115	−0.112
H151	0.11	0.11	0.053	0.053	C18−C19	−0.107	−0.11
H152	0.12	0.121	0.062	0.066	C18═O26	−0.131	−0.131
H161	0.11	0.11	0.052	0.052	C19−C20	−0.107	−0.116
H162	0.115	0.116	0.057	0.06	C19−H191	−0.114	−0.115
H171	0.119	0.119	0.062	0.061	C19−H192	−0.115	−0.112
H172	0.128	0.132	0.07	0.076	C20−H201	−0.115	−0.116
H191	0.12	0.116	0.063	0.059	C20−H202	−0.115	−0.115
H192	0.128	0.129	0.07	0.073	C20−H203	−0.115	−0.117
H201	0.121	0.122	0.063	0.064	C21−C22	−0.107	−0.108
H202	0.119	0.126	0.061	0.069	C21−H211	−0.115	−0.113
H203	0.114	0.121	0.057	0.062	C21−H212	−0.115	−0.115
H211	0.116	0.122	0.058	0.065	C22−O23	−0.082	−0.081
H212	0.104	0.115	0.047	0.057	C22−H221	−0.115	−0.11
H221	0.125	0.107	0.067	0.052	C22−H222	−0.113	−0.114
H222	0.103	0.097	0.047	0.04	O23−H231	−0.078	−0.078
H231	0.225	0.226	0.186	0.187	O24−H241	−0.078	−0.078
H241	0.225	0.225	0.186	0.186			

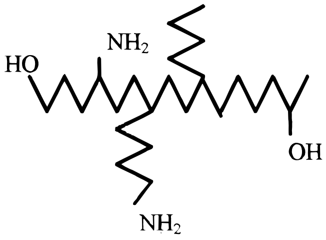
[a] Columns 2, 3, 7, and 8 are the charge distribution results (including the atom charges and the bond charges); columns 4 and 5 are the gross atom charges (the bond charges from the ABEEM method are reallocated to the atoms as is done with Mulliken's bong charges). The symbol H_{xyz} stands for the *z*th hydrogen connecting to the *xy*th heavy atom. For example, H_{011} and H_{012} stand for the first and the second hydrogen atom which bond to the first heavy atom C_1, H_{231} stands for the first hydrogen atom which bonds to the 23th heavy atom, e.g., O_{23}, etc.

comparison, our results are listed with those from *ab initio* STO-3G HF-SCF calculations in Table 2 for $C_{21}O_5H_{40}$. Both the tables and the figure indicate very good agreement between the two methods. This demonstrates that the ABEEM scheme is reasonable and useful. It is believed that the ABEEM method has more flexibility and potential for further development and



(a) $C_{21}O_5H_{40}$

(b) $C_{17}H_{36}$



(c) $C_{24}O_2N_2H_{52}$

Figure 1. Schematic diagrams of molecules $C_{21}O_5H_{40}$, $C_{17}H_{36}$, and $C_{24}O_2H_{52}$.

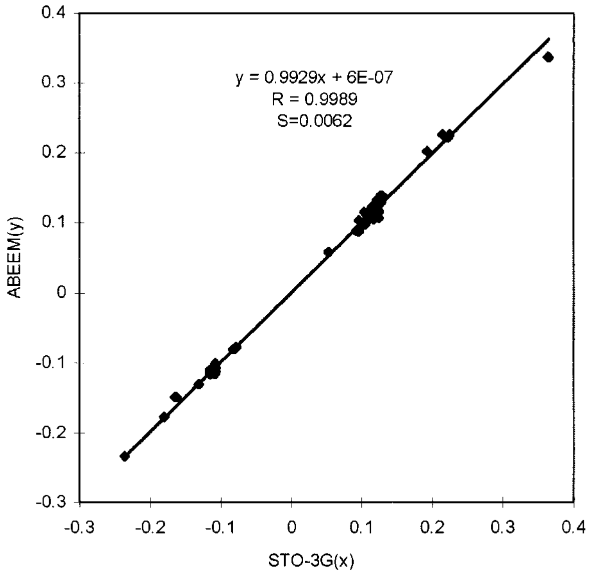


Figure 2. Comparison of ABEEM and ab initio charge distribution for $C_{21}O_5H_{40}$.

application to other chemical problems than the EEM or MEEM schemes because the partition of the molecular electronic density according to the atoms and the bonds contains more suitable parameters than that of EEM or MEEM.

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Appendix: Deduction of Eq 7

Partitioning the molecular electron density according eq 6, the kinetic energy of eq 2 may be expressed formally by a sum contributed by individual partial densities as

$$T = \sum_a \int_{\Omega_\mathrm{a}} -\frac{1}{2}\nabla^2 \gamma(\vec{r};\vec{r}\,')|_{\vec{\mathrm{r}}=\vec{\mathrm{r}}'}\,\mathrm{d}\vec{r} + \sum_{g-h} \int_{\Omega_{\mathrm{g-h}}} -\frac{1}{2}\nabla^2 \gamma(\vec{r};\vec{r}\,')|_{\vec{\mathrm{r}}=\vec{\mathrm{r}}'}\,\mathrm{d}\vec{r} = \sum_a T_\mathrm{a}^\mathrm{mol} + \sum_{g-h} T_{g-h}^\mathrm{mol} \qquad \text{(A1)}$$

Where Ω_a and Ω_{g-h} denote the spatial regions covered by the partial densities $\rho_\mathrm{a}(\vec{\mathrm{r}})$ and $\rho_\mathrm{g-h}(\vec{\mathrm{r}})$, respectively.

Similarly, the V_ne and V_ee energies of eqs 3 and 4 can also be separated into the individual contributions that come from the corresponding partial densities:

$$V_\mathrm{ne} = -\sum_a Z_\mathrm{a} \int_{\Omega_\mathrm{a}} \frac{\rho_\mathrm{a}(\vec{r})}{|\vec{r} - \vec{R}_\mathrm{a}|}\,\mathrm{d}\vec{r} + \sum_a \sum_{b\neq a} \int_{\Omega_\mathrm{g}} \frac{-Z_\mathrm{a}\rho_\mathrm{b}(\vec{r})}{|\vec{r} - \vec{R}_\mathrm{a}|}\,\mathrm{d}\vec{r} + \sum_a \sum_{g-h} \int_{\Omega_\mathrm{g-h}} \frac{-Z_\mathrm{a}\rho_\mathrm{g-h}(\vec{r})}{|\vec{r} - \vec{R}_\mathrm{a}|}\,\mathrm{d}\vec{r}$$

$$= \sum_a \int_{\Omega_\mathrm{a}} \frac{-Z_\mathrm{a}\rho_\mathrm{a}(\vec{r})}{|\vec{r} - \vec{R}_\mathrm{a}|}\,\mathrm{d}\vec{r} + \sum_a \sum_{b\neq a} \frac{-k_\mathrm{a,b} Z_\mathrm{a} N_\mathrm{b}}{R_\mathrm{a,b}} + \sum_a \sum_{g-h} \frac{-k_\mathrm{a,g-h} Z_\mathrm{a} n_\mathrm{g-h}}{R_\mathrm{a,g-h}} \qquad \text{(A2)}$$

$$V_\mathrm{ee} = \frac{1}{2}\sum_a \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_1 \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\sum_{a-b} \int_{\Omega_\mathrm{a-b}} \mathrm{d}\vec{r}_1 \int_{\Omega_\mathrm{a-b}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\sum_a \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_1 \sum_{b\neq a} \int_{\Omega_\mathrm{b}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\sum_{a-b} \int_{\Omega_\mathrm{a-b}} \mathrm{d}\vec{r}_1 \sum_{g-h\neq a-\mathrm{b}} \int_{\Omega_\mathrm{g-h}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \sum_a \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_1 \sum_{g-h} \int_{\Omega_\mathrm{g-h}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{1}{2}\sum_a \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_1 \int_{\Omega_\mathrm{a}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\sum_{a-b} \int_{\Omega_\mathrm{a-b}} \mathrm{d}\vec{r}_1 \int_{\Omega_\mathrm{a-b}} \mathrm{d}\vec{r}_2 \frac{\rho_2(\vec{r}_1,\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2}\sum_a \sum_{b\neq a} \frac{k'_\mathrm{a,b} N_\mathrm{a} N_\mathrm{b}}{R_\mathrm{a,b}} + \frac{1}{2}\sum_{a-b} \sum_{g-h\neq a-b} \frac{k'_\mathrm{a-b,g-h} n_\mathrm{a-b} n_\mathrm{g-h}}{R_\mathrm{a-b,g-h}} + \sum_a \sum_{g-h} \frac{k'_\mathrm{a,g-h} N_\mathrm{a} n_\mathrm{g-h}}{R_\mathrm{a,g-h}} \qquad \text{(A3)}$$

Most of the notations in eqs A2 and A3 are obvious from the previous comments. There are, however, some coefficients, $k_\mathrm{a,b}$, $k_\mathrm{a,g-h}$, $k'_\mathrm{a,b}$, $k'_\mathrm{a-b,g-h}$, and $k'_\mathrm{a,g-h}$, that should be explained. For example, $k_\mathrm{a,b}$ is taken as a correction coefficient, for $Z_\mathrm{a}N_\mathrm{b}/R_\mathrm{a,b}$, because the latter does not exactly equal the corresponding integral of the previous line in eq A2 even though $\rho_b(\vec{r})$ integrates to N_b.

Now the total molecular energy E_{mol} can accordingly be reduced to the following components, each possessing its own explicit meaning, which may be said to be the sum of the intraenergy and the interenergy,

$$E_{mol} = \sum_{a}[T_a^{mol} + V_{ne,a}^{mol} + V_{ee,a}^{mol}] + \sum_{a-b}[T_{a-b} + V_{ee,a-b}^{mol}] + \sum_{a}\sum_{b\neq a}\frac{-k_{a,b}Z_aN_b}{R_{a,b}} + \sum_{a}\sum_{g-h}\frac{-k_{a,g-h}Z_an_{g-h}}{R_{a,g-h}} + \frac{1}{2}\sum_{a}\sum_{b\neq a}\frac{k'_{a,b}N_aN_b}{R_{a,b}} + \frac{1}{2}\sum_{a-b}\sum_{g-h\neq a-b}\frac{k'_{a-b,g-h}n_{a-b}n_{g-h}}{R_{a-b,g-h}} + \sum_{a}\sum_{g-h}\frac{k'_{a,g-h}N_an_{g-h}}{R_{a,g-h}} + \frac{1}{2}\sum_{a}\sum_{b\neq a}\frac{Z_aZ_b}{R_{a,b}} = \sum_{a}E_a^{intra} + \sum_{a-b}E_{a-b}^{intra} + \sum E^{inter} \quad (A4)$$

The total energy is thereby divided into typical "atom" terms and typical"bond" terms (intraatom and intrabond, i.e., the first summation and the second summation in eq A4), atom−atom interaction terms, atom−bond interaction terms, and bond−bond interaction terms. The intraatom contribution and the intrabond contribution depend on the number of electrons as well as the shape factor for the density function. In a molecule, these contributions differ from the isolated atom value due to the change in the number of electrons ($\Delta N_a = N_a - N_a^\circ$) as well as a change of the shape factor due to molecule formation. The latter depends on the details of the electron density profile, i.e., the shape and size or the nature of confinement of the atom and the bond in the molecule.

The value of the $E_{a,mol}^{intra}$ term will not be identical to that for an isolated atom because the extent and the shape of its electron cloud change when an atom is imbedded in a molecule. For an isolated atom *a* the electronic energy can be written as a function of the number of electrons as

$$E_a^{intra} = E_a^\circ + \mu_a^\circ(N_a - N_a^\circ) + \eta_a^\circ(N_a - N_a^\circ)^2 + ... \quad (A5)$$

where E_a° is the value of E_a^{intra} when $N_a = N_a^0$, i.e., the number of electrons in the neutral atom and μ_a° and η_a° are the chemical potential and the absolute hardness. For an ABEEM atom in a molecule we can write an analogous expression by replacing μ_a° and η_a° by μ_a^* and μ_a^*:

$$E_a^{intra} = E_a^* + \int\frac{\delta E_a^*}{\delta\rho_a}\Delta\rho_a(\vec{r})\,d\vec{r} + \frac{1}{2}\int\frac{\delta^2E_a^*}{\delta{\rho_a}^2}(\Delta\rho_a(\vec{r}))^2\,d\vec{r} = E_a^* + \mu_a^*(N_a - N_a^*) + \eta_a^*(N_a - N_a^*)^2 \quad (A6)$$

Similarly, we write eq A7 for an ABEEM bond.

$$E_{a-b}^{intra} = E_{a-b}^* + \int\frac{\delta E_{a-b}^*}{\delta\rho_{a-b}}\Delta\rho_{a-b}(\vec{r})\,d\vec{r} + \frac{1}{2}\int\frac{\delta^2E_{a-b}^*}{\delta{\rho_{a-b}}^2}(\Delta\rho_{a-b}(\vec{r}))^2\,d\vec{r} = E_{a-b}^* + \mu_{a-b}^*(n_{a-b} - n_{a-b}^*) + \eta_{a-b}^*(n_{a-b} - n_{a-b}^*)^2 \quad (A7)$$

There μ_a^* and μ_{a-b}^* are the valence-state chemical potentials of the atom *a* and the bond *a*−*b* in a molecule, respectively; η_a^* and η_{a-b}^* are the valence-state hardnesses in a molecule; and E_a^* and E_{a-b}^* are the valence-state energies in a molecule, respectively. Therefore, we reach the following expression:

$$E_{mol} = \sum_{a}E_a^{intra} + \sum_{a-b}E_{a-b}^{intra} + \sum E^{inter}$$

$$= \sum_{a}[E_a^* + \mu_a^*(N_a - N_a^*) + \eta_a^*(N_a - N_a^*)^2] + \sum_{a-b}[E_{a-b}^* + \mu_{a-b}^*(n_{a-b} - n_{a-b}^*) + \eta_{a-b}^*(n_{a-b} - n_{a-b}^*)^2] + \sum_{a}\sum_{g-h}\frac{-k_{a,g-h}Z_an_{g-h} + k'_{a,g-h}N_an_{g-h}}{R_{a,g-h}} + \sum_{a}\sum_{b(\neq a)}\frac{(1/2)k'_{a,b}N_aN_b - k_{a,b}Z_aN_b}{R_{a,b}} + \sum_{a-b}\sum_{g-h(\neq a-b)}\frac{(1/2)k'_{a-b,g-h}n_{a-b}n_{g-h}}{R_{a-b,g-h}} + \frac{1}{2}\sum_{a}\sum_{b(\neq a)}\frac{Z_aZ_b}{R_{a,b}}$$

$$= \sum_{a}[E_a^* + \mu_a^*(N_a - N_a^*) + \eta_a^*(N_a - N_a^*)^2] + \sum_{a-b}[E_{a-b}^* + \mu_{a-b}^*(n_{a-b} - n_{a-b}^*) + \eta_{a-b}^*(n_{a-b} - n_{a-b}^*)^2] + \sum_{g-h}\left[\frac{-k_{g,g-h}Z_gn_{g-h} + k'_{g,g-h}N_gn_{g-h}}{R_{gg-h}} + \frac{-k_{h,g-h}Z_hn_{g-h} + k'_{h,g-h}N_hn_{g-h}}{R_{h,g-h}}\right] + \sum_{g-h}\sum_{a(\neq g,h)}\frac{-k_{a,g-h}Z_an_{g-h} + k'_{a,g-h}N_an_{g-h}}{R_{a,g-h}} + \sum_{a}\sum_{b(\neq a)}\frac{(1/2)k'_{a,b}N_aN_b - k_{a,b}Z_aN_b}{R_{a,b}} + \sum_{a-b}\sum_{g-h(\neq a-b)}\frac{(1/2)k'_{a-b,g-h}n_{a-b}n_{g-h}}{R_{a-b,g-h}} + \frac{1}{2}\sum_{a}\sum_{b(\neq a)}\frac{Z_aZ_b}{R_{a,b}} \quad (A8)$$

In order to simplify eq A8 and facilitate our algorithm greatly, eq 7 is taken to approximate eq A8.

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