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Study on Calculation Method of Parameters in Molecular Calculation Model by Pseudo Chemical Potential Method

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Abstract: There are some parameters in the molecular calculationmodel of the pseudo chemical potential (PCP) method that is a new method that thermodynamic formalization is applied in molecular calculation. These parameters were introduced for decreasing errors caused by hypotheses and approximations during theoretical derivation of calculationmodel and up to now the method for obtaining the parameters was not presented. In this paper, we are going to discuss the determining method of parameters introduced to obtain more correct calculation results. The determining method of these parameters have characters of two categories. One of them is determined by calculating on the basis of ionization energy and electron affinity, and the other is estimated by solving normal equation that makes square of difference of calculation values by ab initio method and PCP method into minimum. In this paper, correctness and reliability of the parameters determined was estimated. By investigating the correlation between the PCP and electronegativity, physical meaning of PCP as the scale of mass migration was confirmed and from this result, the reliability of parameter γ_α was shown. And by inverse calculation of determining equation of interaction parameter $k_{\alpha\beta}$, the correctness of $k_{\alpha\beta}$ was confirmed. Like this, it was shown that the parameters determined can be used enough to PCP method for calculating molecular energy and atomic charge.

Keywords: Pseudo Chemical Potential (PCP), Parameter Calculation, Total Energy, Charge Distribution

1. Introduction

The wave function theory (WFT) [1-3] and the density functional theory (DFT) [4, 5] established on the basis of the formalization of quantum theory are becoming basic means for quantum theoretical study of structures and properties of system and there have been many studies for improving accuracy and speed of calculations by using ab initio method and semi-empirical method [8-20].

In reference [22], we have suggested new pseudo chemical potential (PCP) method, whose efficiency in calculating total energy and atomic charge distribution of molecular is much higher than above methods. We have defined the PCP on the basis of thermodynamic formalization and introduced the method for calculating total energy and charge distribution by using PCP method, but have not referred to the calculation method of parameters in detail.

In this paper, we have studied on the calculating method of parameters introduced in the model for calculating properties of molecule by PCP method.

In the pseudo chemical potential (PCP) method, parameter γ_α is used that is introduced defining Lagrange undetermined multiplier of Euler-Lagrange (EL) equation (1) [4-7] of density functional theory, chemical potential of electron μ (equation (2)).

$$\mu = \left[\frac{\partial E}{\partial N}\right]_{V(r)} \tag{1}$$

$$\mu = \mu_\alpha^0 + \gamma_\alpha \ln \frac{N_\alpha}{N_\alpha^0} \quad (2)$$

On the other hand, interaction parameter between α atom and β atom, $k_{\alpha\beta}$ is used, that is introduced, in Born-Oppenheimer approximation, modeling the total energy of molecule as sum of the energy of atom domain and interaction energy between domains (equation (3)).

$$E^M = \sum_\alpha \left[N_\alpha \left(\mu_\alpha^0 + \gamma_\alpha \ln \frac{N_\alpha}{N_\alpha^0} - \gamma_\alpha \right) + \varepsilon_\alpha \right] + \sum_\alpha \sum_{\beta \neq \alpha} k_{\alpha\beta} \frac{q_\alpha q_\beta}{R_{\alpha\beta}} \quad (3)$$

Chemical potential of electron μ is constant in total space, as in the thermodynamic system that is ground canonical ensemble of finite temperature, that is, macroscopic system and it corresponds to inclination of energy of electron system E for electron number N in given external field V(r). It also has meaning of scale of electron migration in atom, molecule or solid, and meaning of electronegativity, scale of ability attracting electron. Parameter γ_α is a proportional constant between flow of electron system in atom, molecule or solid and driving force dμ and has dimension of energy. In case of neutral atom, $N_\alpha = N_\alpha^0$, $\mu = \mu_\alpha^0$ and it has physical meaning determined by equation (2).

Interaction parameter $k_{\alpha\beta}$ is a correction parameter introduced to reduce error produced by approximation applied when total energy of molecule is calculated with value of quantum mechanical average in reference [22].

Integration constant ε_α is a constant occurring when equation (1) is integrated.

2. Determining Method of the Parameters

To calculate atomic charge in the molecule or total energy of molecule, parameters in the equation must be calculated. In the parameters, there are parameters of neutral atom, μ_0, γ and interaction parmeter, $k_{\alpha\beta}$.

2.1. Parameter of Neutral Atom γ, PCPμ_0 and Integration Constant ε

Integrating equation (1) with respect to electron number N, equations (4) is obtained

$$E(N,V) = N(\mu - \gamma) + \varepsilon \quad (4)$$

From equation (4), equations (5), (6), (7) are obtained

$$E(N_0,V) = N_0(\mu_0 - \gamma) + \varepsilon \text{ (in case of neutralatom)} \quad (5)$$

$$E(N_0 - 1,V) = (N_0 - 1)\left(\mu_0 - \gamma + \gamma ln \frac{N_0 - 1}{N_0}\right) + \varepsilon \quad (6)$$

$$E(N_0 + 1,V) = (N_0 + 1)\left(\mu_0 - \gamma + \gamma ln \frac{N_0 + 1}{N_0}\right) + \varepsilon \quad (7)$$

Ionization energy (I) and electron affinity (A) are presented as follows.

$$I = E(N_0 - 1,V) - E(N_0,V) \quad (8)$$

$$A = E(N_0,V) - E(N_0 + 1,V) \quad (9)$$

From equations (4), (5), (6), (7), and ionization energy (8) and electron affinity (9), correction parameter γ (10) and PCP of neutral atom μ_0 (11) can be calculated.

$$I = -(\mu_0 - \gamma) + \gamma(N_0 - 1) ln \frac{N_0 - 1}{N_0}$$

$$A = -(\mu_0 - \gamma) - \gamma(N_0 + 1) ln \frac{N_0 + 1}{N_0}$$

$$\gamma = \frac{I - A}{(N_0 - 1) ln \frac{N_0 - 1}{N_0} + (N_0 + 1) ln \frac{N_0 + 1}{N_0}} \quad (10)$$

$$\mu_0 = -I + \gamma + \gamma(N_0 - 1) ln \frac{N_0 - 1}{N_0} \quad (11)$$

Integration constant of equation (1) is obtained from condition to be neutral atom, $N_\alpha = N_\alpha^0$

$$\varepsilon_\alpha = E_\alpha^0 - N_\alpha^0(\mu_\alpha^0 - \gamma_\alpha^0) \quad (12)$$

In case of hydrogen atom, equation (12) is obtained.

$$\gamma = \frac{I - A}{(N_0 + 1) ln \frac{N_0 + 1}{N_0}}, \mu_0 = -I + \gamma \quad (13)$$

2.2. Interaction Parameter

PCP of α-atom in molecule is as follows.

$$\mu_\alpha^M = \left(\frac{\partial E^M}{\partial N_\alpha}\right)_{V, N_{\beta \neq \alpha}}, \mu_\alpha^M = \mu_\alpha^0 + \gamma_\alpha \ln \frac{N_\alpha}{N_\alpha^0} - \sum_\beta k_{\alpha\beta} \frac{q_\beta}{R_{\alpha\beta}} \quad (14)$$

From equilibrium condition of electron migration of PCP of α-atom in molecule

$$\mu_1^M = \mu_2^M, \mu_2^M = \mu_3^M, \ldots \mu_{n-1}^M = \mu_n^M$$

charge distribution equation of molecule (15) is obtained [21].

$$\begin{cases} \mu_1^0 + \gamma_1 \ln \frac{N_1}{N_1^0} - \sum_\beta k_{1\beta} \frac{q_\beta}{R_{1\beta}} = \mu^M \\ \mu_2^0 + \gamma_2 \ln \frac{N_2}{N_2^0} - \sum_\beta k_{2\beta} \frac{q_\beta}{R_{1\beta}} = \mu^M \\ \cdots \cdots \cdots \cdots \\ \mu_n^0 + \gamma_n \ln \frac{N_n}{N_n^0} - \sum_\beta k_{n\beta} \frac{q_\beta}{R_{1\beta}} = \mu^M \\ \sum_{\alpha=1}^n q_\alpha = 0 \end{cases} \quad (15)$$

This charge distribution equation just becomes determining equation of interaction parameter $k_{\alpha\beta}$. Unknown numbers of equation (15) are atomic charge q_α and PCP of molecule μ^M, they are n+1 in all.

Because equation (15) is one for calculating atomic charge in molecule, interaction parameter $k_{\alpha\beta}$ must be determined so that values of atomic charges calculated by this equation should reproduce examination results or results calculated by using ab initio method.

In order to determine interaction parameter $k_{\alpha\beta}$ by least square method so that values of atomic charges in molecule should reproduce results of ab initio method (STO-3G), the equation (15) was transformed into normal equation.

Firstly, by transforming equation (15) to equation (16), unknown number μ^M is eliminated.

$$\begin{cases} \left(\sum_{j\neq 1} k_{1j}\frac{q_j}{R_{1j}} - \sum_{j\neq n} k_{nj}\frac{q_j}{R_{nj}}\right) = (\mu_1^0 - \mu_n^0) + \left(\gamma_1 \ln\frac{N_1}{N_1^0} - \gamma_n \ln\frac{N_n}{N_n^0}\right) \\ \left(\sum_{j\neq 2} k_{2j}\frac{q_j}{R_{2j}} - \sum_{j\neq n} k_{nj}\frac{q_j}{R_{nj}}\right) = (\mu_2^0 - \mu_n^0) + \left(\gamma_2 \ln\frac{N_1}{N_2^0} - \gamma_n \ln\frac{N_n}{N_n^0}\right) \\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots \\ \left(\sum_{j\neq n-1} k_{n-1j}\frac{q_j}{R_{n-1j}} - \sum_{j\neq n} k_{nj}\frac{q_j}{R_{nj}}\right) = (\mu_1^0 - \mu_n^0) + \left(\gamma_1 \ln\frac{N_1}{N_1^0} - \gamma_n \ln\frac{N_n}{N_n^0}\right) \end{cases} \quad (16)$$

where n-atomic number in molecule.

Next, because for unknown variable in the equation (16), k_{ij} not only atomic species but also bond mode must be considered, $k_{ijb}$with new subscript is used. Equation (16) is that for any one molecule. For realizing least square method, Sm molecular samples must be taken.

Among Sm molecule samples, the equation (16) for *m*-th molecule is represented as equation (17).

$$\sum_{i=1}^{na}\sum_{j=1}^{na}\sum_{b=1}^{6} k_{ijb}\left(\sum_{\substack{v_m\neq u_m \\ a_{u_m}=a_i \\ a_{v_m}=a_j}}^{n_m}\frac{q_{v_m}}{R_{u_m v_m b}} - \sum_{\substack{v_m\neq n_m \\ a_{n_m}=a_i \\ a_{v_m}=a_j}}^{n_m}\frac{q_{v_m}}{R_{n_m v_m b}}\right) = \left(\mu_{u_m}^0 - \mu_{n_m}^0\right) + \left(\gamma_{u_m}\ln\frac{N_{u_m}}{N_{u_m}^0} - \gamma_{n_m}\ln\frac{N_{n_m}}{N_{n_m}^0}\right),$$

$$(u_m = \overline{1, n_m - 1}, m = \overline{1, S_m}) \quad (17)$$

where *na* is total number of atoms in molecule sample in the table made with atoms in the Sm sample molecules beforehand in which numbers are assigned to atoms, n_m is total number of atoms in m-th molecule and u_m, v_m are atoms binding each other in *m*-th molecule, respectively. Then a_{u_m}, a_{v_m} may respectively become a_i, a_j that are *i, j*-th atoms in the table.

In the above equation, the first term in bracket of the left side is considered when u_m-th atom of *i*-th atom and *m*-th molecule are same and second term is considered when n_m-th atom of *i*-th atom and *m*-th molecule are same. For example, if there are atoms H^1, C^2, O^3, N^4 in database and there are C^1, H^2, O^3 in any molecule 1, and H^1, C^2, N^3 in molecule 2 (superscripts mean numbers assigned to atoms), in case a_1=H, a_2=C, a_3=O, a_4=N and a_{1_1}=C, a_{1_2}=H, a_{1_3}=O, a_{2_1}=H, a_{2_2}=C, a_{2_3}=N. therefore, unknown number is k_{232}, the terms corresponding with doublebond between C and O must be considered. (When possible shapes of bond for atom pairs are regarded as six forms, such as single bond, double bond, triple bond, directional bond, hydrogen bond, and nonbonding, second bonding shape is double bond.)

On the other hand, because the calculation for several molecule samples must be carried out, representing as matrix form in which suffix is accorded with unique number, equation (17) becomes equation (18).

$$QK = \mu \quad (18)$$

In order to obtain calculation equation of the parameters by standard of least square method, the equation (18) was made to regression matrix equation with accuracy of ε.

$$QK = \mu + \varepsilon, s = \varepsilon^T\varepsilon = (\mu - QK)^T(\mu - QK)$$

$$\frac{\partial S}{\partial K} = -2Q(\mu - QK) = 0 \ \rightarrow\ QK = \mu$$

$$K = (Q^TQ)^{-1}Q^T\mu \quad (19)$$

where $Q = \{qn_{ij}\}$, $K = (kn_1, kn_2, \cdots, kn_{np})^T$, $\mu = (\mu n_1, \mu n_2, \cdots, \mu n_{ne})^T$.

$$qn_{ij} = \left(\sum_{\substack{v_m\neq u_m \\ a_{u_m}=a_1 \\ a_{v_m}=a_2}}^{n_m}\frac{q_{v_m}}{R_{u_m v_m b}} - \sum_{\substack{v_m\neq n_m \\ a_{n_m}=a_{d_1} \\ a_{v_m}=a_{d_2}}}^{n_m}\frac{q_{v_m}}{R_{n_m v_m b}}\right)$$

$$kn_j = k_{d_1 d_2 b},$$

$$\mu n_i = \left(\mu_{u_m}^0 - \mu_{n_m}^0\right) + \left(\gamma_{u_m}\ln\frac{N_{u_m}}{N_{u_m}^0} - \gamma_{n_m}\ln\frac{N_{n_m}}{N_{n_m}^0}\right)$$

$$(i = \overline{1, ne};\ j = \overline{1, np};\ b = \overline{1, 6};\ u_m = \overline{1, n_m - 1};\ m = \overline{1, S_m})$$

In above equations, d_1, d_2 are atomic numbers in the table, u_m, n_m correspond to d_1 atom, v_m corresponds to d_2 atom, ne is total number of equationsused for calculation of parameters, np is total number of possible parameters (=3*na*(*na*+1). If the number of atoms in the table is *na*, maximum number that can form bond is $na(na+1)/2$. If bond mode is counted in here, maximum number is $6 \times na(na+1)/2$).

On the other hand, relationship between the atomic numbers in the table, d_1, d_2, bond mode, *b*, and the number of parameter *j* is expressed as equations (20) ~ (23).

$$\text{In case } d_1 = 1: j = 6(d_2 - 1) + b \quad (20)$$

$$\text{In case } d_2 = 1: j = 6(d_1 - 1) + b \quad (21)$$

$$\text{In case } d_1 \geq d_2: j = \sum_{k=1}^{d_2-1} 6(na - k) + 6(d_1 - 1) + b \quad (22)$$

$$\text{In case } d_1 < d_2: j = \sum_{k=1}^{d_1-1} 6(na - k) + 6(d_2 - 1) + b \quad (23)$$

where b is the number according to bonding mode, in case of single bond *b*=1, in case of double bond *b*=2, in case of triple bond *b*=3, in case of aromatic bond *b*=4, in case of hydrogen *b*ond b=5, in case of nonbond*b*=6.

In this way, by using equation (20) ~ (23), parameter kn_j that gave bond mode to between atoms in every molecule is defined in order. Then equation system composed of new variable kn_j is obtained and by solving this equation, interaction parameters containing also bond mode of atoms can be obtained.

3. Results and Discussion

3.1. Calculation Results of Parameters of Neutral Atoms

The calculation results of some neutral atoms obtained by using equation (10), (11) are shown in table 1 and table 2. And in order to confirm physical meaning of PCP as the scale of mass migration, the correlation was considered by comparing it with electronegativity, the scale of ability of attracting electron (table 2).

Table 1. *The relationship between electronegativity and PCPs of some neutral atoms.*

atom	PCPμ_0/eV	electronegativity		γ/eV
		χ_M [7]	χ_P [23]	
H	-4.334	7.18	2.20	9.276 5
Li	-2.740	3.01	0.98	14.067 2
Be	-4.522	4.9	1.57	35.619 4
B	-4.021	4.29	2.04	39.830 1
C	-5.991	6.27	2.55	59.720 4
N	-6.955	7.30	3.04	100.874 1
O	-7.286	7.54	3.44	97.025 7
F	-10.150	10.41	3.98	125.919 6
Na	-2.780	2.85	0.93	50.530 2
P	-5.512	5.62	2.19	146.291 4
S	-6.134	6.22	2.58	132.393 7
R^2		0.869 5	0.930 5	

χ_M –Mullikenelectronegativity, χ_P- Pauling's electronegativity,

Table 2. *The values of PCPs μ0 and parameters γ of neutral atoms.*

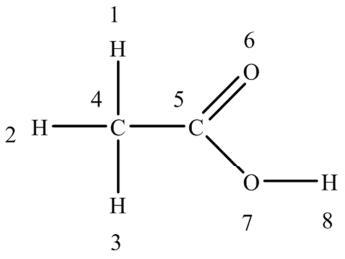
atom	PCP/eV	γ/eV	atom	PCP/eV	γ/eV
H	-4.334	9.276 5	Ni	-4.361	181.961 3
Li	-2.740	14.067 2	Cu	-4.443	188.462 6
Be	-4.522	35.619 4	Zn	-4.395	296.345 1
B	-4.021	39.830 1	Ga	-3.169	179.768 8
C	-5.991	59.720 4	Ge	-4.565	217.564 6
N	-6.955	100.874 1	As	-5.255	296.954 5
O	-7.286	97.025 7	Se	-5.852	263.122 1
F	-10.150	125.919 6	Br	-7.550	295.359 8
Na	-2.780	50.530 2	Rb	-2.323	136.883 3
Mg	-3.642	93.491 5	Sr	-1.968	281.167 5
Al	-3.159	71.948 9	Y	-3.163	248.792 7
Si	-4.690	94.559 4	Zr	-3.613	256.773 3
P	-5.512	146.291 4	Nb	-3.976	245.975 6
S	-6.134	132.393 7	Mo	-3.875	260.375 4
Cl	-8.208	159.028 2	Ru	-4.477	263.977 3
K	-2.386	72.926 3	Rh	-4.277	284.376 6
Ca	-2.133	159.933 3	Pd	-4.422	357.851 8
Sc	-3.289	134.349 2	Ag	-4.418	295.137 7
Ti	-3.399	148.228 9	Cd	-4.298	447.327 6
V	-3.555	142.555 1	In	-3.081	274.381 0
Cr	-3.678	146.837 5	Sn	-4.280	304.979 7
Mn	-3.670	185.950 4	Sb	-4.815	387.575 2
Fe	-4.011	198.071 1	Te	-5.468	366.057 4
Co	-4.256	194.355 5	I	-6.737	391.116 8

Correlation between quantities shows that PCP is the scale attracting or giving electrons, that is, the scale of charge migration. As shown in table 1, sign of PCP is opposite to one of the electronegativity, but absolute value of PCP has the same tendency. From these results, it was again found that as the electronegativity is a scale attracting electron, so PCP can become a scale attracting or giving electron, that is, a scale of migration of charge.

3.2. Calculation Results of Interaction Parameters

3.2.1. Example of Making Equation for Calculating Interaction Parameter

Taking acetic acid for example, let`s try to expand the equation (14). Then equation (24) is obtained.



acetic acid

$$\begin{cases} k_{12}\frac{q_2}{R_{12}}+k_{13}\frac{q_3}{R_{13}}+k_{14}\frac{q_4}{R_{14}}+\cdots+k_{17}\frac{q_7}{R_{17}}+k_{18}\frac{q_8}{R_{18}}- \\ -\left(k_{81}\frac{q_1}{R_{81}}+k_{82}\frac{q_2}{R_{82}}+k_{83}\frac{q_3}{R_{83}}+\cdots+k_{86}\frac{q_6}{R_{86}}+k_{87}\frac{q_7}{R_{87}}\right)=(\mu_1{}^0-\mu_8{}^0)+(\gamma_1 ln\frac{N_1}{N_1^0}-\gamma_8 ln\frac{N_8}{N_8^0}) \\ k_{21}\frac{q_1}{R_{21}}+k_{23}\frac{q_3}{R_{23}}+k_{24}\frac{q_4}{R_{24}}+\cdots+k_{27}\frac{q_7}{R_{27}}+k_{28}\frac{q_8}{R_{28}}- \\ -\left(k_{81}\frac{q_1}{R_{81}}+k_{82}\frac{q_2}{R_{82}}+k_{83}\frac{q_3}{R_{83}}+\cdots+k_{86}\frac{q_6}{R_{86}}+k_{87}\frac{q_7}{R_{87}}\right)=(\mu_2{}^0-\mu_8{}^0)+(\gamma_2 ln\frac{N_2}{N_2^0}-\gamma_8 ln\frac{N_8}{N_8^0}) \\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots \\ k_{71}\frac{q_1}{R_{71}}+k_{72}\frac{q_2}{R_{72}}+k_{73}\frac{q_3}{R_{73}}+\cdots+k_{76}\frac{q_6}{R_{76}}+k_{78}\frac{q_8}{R_{78}}- \\ -\left(k_{81}\frac{q_1}{R_{81}}+k_{82}\frac{q_2}{R_{82}}+k_{83}\frac{q_3}{R_{83}}+\cdots+k_{86}\frac{q_6}{R_{86}}+k_{87}\frac{q_7}{R_{87}}\right)=(\mu_7{}^0-\mu_8{}^0)+(\gamma_7 ln\frac{N_7}{N_7^0}-\gamma_8 ln\frac{N_8}{N_8^0}) \end{cases} \quad (24)$$

Because the interaction parameter relates to atomic species and bond mode, writing parameters together according to the same bond mode and the same atomic species, it is as follows.

k_{14}, k_{24}, k_{34}, k_{41}, k_{42}, k_{43} - single bond between hydrogen and carbon

k_{15}, k_{51}, k_{25}, k_{52}, k_{35}, k_{53}, k_{48}, k_{58}, k_{84}, k_{85}-nonbond between hydrogen and carbon

k_{16}, k_{17}, k_{26}, k_{27}, k_{36}, k_{37}, k_{61}, k_{71}, k_{62}, k_{72}, k_{63}, k_{73}, k_{68}, k_{86} - nonbond between hydrogen and oxygen

k_{45}, k_{54}- single bond between carbon and carbon

k_{46}, k_{47}, k_{74}, k_{64}-nonbond between carbon and oxygen

k_{56}, k_{65} - double bond between carbon and oxygen

k_{57}, k_{75}- single bond between carbon and oxygen

k_{67}, k_{76} -nonbond between oxygen and oxygen

k_{78}, k_{87} - single bond between hydrogen and oxygen

Finally, though they are the interaction parameters for the same atomic species and the same bond mode, subscript relationship in individual molecule is different and also in between molecule and molecule they are represented as if they were different parameters. In this way, because there is no subscript representing bond mode, it is difficult to distinguish them each other, thus to calculate the parameters becomes difficult.

From this, table 3 with the total number of atoms *na*is made and unique numbers are assigned to the atoms in the table so that for various molecules the parameters with the same atomic species and the same bond mode should be expressed as the same subscript. And bond mode between atoms is expressed as subscript b (it is considered that in possible shapes of bond for atom pairs, there are six forms, such as single bond, double bond, triple bond, aromatic bond, hydrogen bond, and nonbond). Then, in order to obtain the interaction parameter, equation system for Sm sample molecules is established. At this time, if in *m*-th molecule (the total number of atoms is n_m) the numbers of atoms considering interaction are expressed as u_m and v_m , respectively, and atomic species is expressed as a, then a_{u_m} and a_{v_m} of *m*-th molecule may be a_i and a_j , respectively, that are *i,j*-th atoms in the table, respectively.

For example, when the Numbers of the atomic species are allotted as in table 3, only for subscripts of the interaction parameters in every molecule, the numbers of the considering atoms are accorded with numbers of this table and, the parameters are expressed as the "k_{ijb}" by introducing also here the bond mode. Then the new equation system could be established with the equations expanded for every sample molecule like the equation (24).

Table 3. *Numbers assigned to atomic species.*

No	1	2	3	4	5	6	7	8	9	…
atom	H	Li	Be	B	C	N	O	F	Cl	…

Concretely, in the equation (24), following relationship is formed.

Because k_{12}, k_{13}, k_{18}, k_{21}, k_{31}, k_{81}, k_{23}, k_{28}, k_{32}, k_{82}, k_{38}, k_{83} are nonbond parameters between hydrogen and hydrogen, if the number of hydrogen in the table is number 1 and value expressing nonbond is 6, they are written as the k_{116}, and because k_{14}, k_{24}, k_{34}, k_{41}, k_{42}, k_{43} are single bond parameters between hydrogen and carbon or carbon and hydrogen, they become k_{151} or k_{511}.

In the equation (24)

k_{12}, k_{13}, k_{18}, k_{21}, k_{31}, k_{81}, k_{23}, k_{28}, k_{32}, k_{82}, k_{38}, k_{83}= k_{116}

k_{14}, k_{24}, k_{34}, k_{41}, k_{42}, k_{43}= k_{151}, k_{511}

k_{15}, k_{51}, k_{25}, k_{52}, k_{35}, k_{53}, k_{48}, k_{58}, k_{84}, k_{85}= k_{156}, k_{516}

k_{16}, k_{17}, k_{26}, k_{27}, k_{36}, k_{37}, k_{61}, k_{71}, k_{62}, k_{72}, k_{63}, k_{73}, k_{68}, k_{86} = k_{176}, k_{716}

k_{45}, k_{54}= k_{551}

k_{46}, k_{47}, k_{74}, k_{64}= k_{576}, k_{756}

k_{56}, k_{65}= k_{572}, k_{752}

k_{57}, k_{75}= k_{571}, k_{751}

k_{67}, k_{76}= k_{776}

k_{78}, k_{87}= k_{171}, k_{711}

Next, rewriting the equation (24) by using parameters with new subscripts, equation (25) is obtained.

$$\begin{cases} k_{116}\left[\left(\frac{q_2}{R_{12}}+\frac{q_3}{R_{13}}+\frac{q_8}{R_{18}}+\right)-\left(\frac{q_1}{R_{81}}+\frac{q_2}{R_{82}}+\frac{q_3}{R_{83}}+\right)\right]+k_{151}\frac{q_4}{R_{14}}+k_{151}\left[\frac{q_5}{R_{15}}-\left(\frac{q_4}{R_{84}}+\frac{q_5}{R_{85}}\right)\right]+ \\ +k_{176}\left(\frac{q_6}{R_{16}}+\frac{q_7}{R_{17}}-\frac{q_6}{R_{86}}\right)-k_{171}\frac{q_7}{R_{87}}=\cdots \\ k_{116}\left[\left(\frac{q_1}{R_{21}}+\frac{q_3}{R_{23}}+\frac{q_8}{R_{28}}+\right)-\left(\frac{q_1}{R_{81}}+\frac{q_2}{R_{82}}+\frac{q_3}{R_{83}}+\right)\right]+k_{151}\frac{q_4}{R_{24}}+k_{156}\left[\frac{q_5}{R_{25}}-\left(\frac{q_4}{R_{84}}+\frac{q_5}{R_{85}}\right)\right]+ \\ +k_{176}\left(\frac{q_6}{R_{26}}+\frac{q_7}{R_{27}}-\frac{q_6}{R_{86}}\right)-k_{171}\frac{q_7}{R_{87}}=\cdots \\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots\ \cdots \\ k_{716}\left(\frac{q_1}{R_{71}}+\frac{q_2}{R_{72}}+\frac{q_3}{R_{73}}\right)+k_{756}\frac{q_4}{R_{74}}+k_{752}\frac{q_5}{R_{75}}+k_{776}\frac{q_6}{R_{76}}+k_{716}\frac{q_8}{R_{78}}- \\ -\left[k_{116}\left(\frac{q_1}{R_{81}}+\frac{q_2}{R_{82}}+\frac{q_3}{R_{83}}+\right)+k_{156}\left(\frac{q_4}{R_{84}}+\frac{q_5}{R_{85}}\right)+k_{176}\frac{q_6}{R_{86}}+k_{171}\frac{q_7}{R_{87}}\right]=\cdots \end{cases} \quad (25)$$

Finally, in the equation (25), according the interaction parameters with the atomic numbers of the table, and in every molecule, rewriting binding atomic species and terms with the same bond mode together, equation (17) in the paper is obtained.

In the equation, in order to emphasize that adding up is possible only in between the atomic species with the same bond mode, "*b*" is written, also in the subscript of the distance R between the atoms.

Next, to obtain the interaction parameter by using the equation (17), simultaneous equations for several molecules must be composed. The equation (18) in the paper is just one in which these simultaneous equations are simply expressed in the form of matrix.

Here, because the interaction parameter must become one column vector, they must be expressed with unique number. Therefore $k_{d_1d_2b}$ is rewritten as knj.

At this time, when two atoms binding in the molecule under consideration are corresponded to the atomic numbers of the table, writing them as d_1, d_2, respectively, relationship between them and unique number of new parameter j is represented as equations (20) ~ (23) in the paper.

In order to confirm this relationship, let's make the interaction parameter according to bond mode correspond with the new parameter marked with the unique number.

Tabulating parameters for some atoms binding with

hydrogen is as follows (table 4).

Table 4. *Correspondence relationship according to bond mode.*

atom1	atom2	bond mode	Interactionparameter	new parameter	atom1	atom2	bond mode	interaction parameter	new parameter
H	H	single bond	k_{111}	kn_1	H	B	aromatic bond	k_{144}	kn_{22}
H	H	double bond	k_{112}	kn_2	H	B	hydrogen bond	k_{145}	kn_{23}
H	H	triple bond	k_{113}	kn_3	H	B	nonbond	k_{146}	kn_{24}
H	H	aromatic bond	k_{114}	kn_4	H	C	single bond	k_{151}	kn_{25}
H	H	hydrogen bond	k_{115}	kn_5	H	C	double bond	k_{152}	kn_{26}
H	H	nonbond	k_{116}	kn_6	H	C	triple bond	k_{153}	kn_{27}
H	Li	single bond	k_{121}	kn_7	H	C	aromatic bond	k_{154}	kn_{28}
H	Li	double bond	k_{122}	kn_8	H	C	hydrogen bond	k_{155}	kn_{29}
H	Li	triple bond	k_{123}	kn_9	H	C	nonbond	k_{156}	kn_{30}
H	Li	aromatic bond	k_{124}	kn_{10}	H	N	single bond	k_{161}	kn_{31}
H	Li	hydrogen bond	k_{125}	kn_{11}	H	N	double bond	k_{162}	kn_{32}
H	Li	nonbond	k_{126}	kn_{12}	H	N	triple bond	k_{163}	kn_{33}
H	Be	single bond	k_{131}	kn_{13}	H	N	aromatic bond	k_{164}	kn_{34}
H	Be	double bond	k_{132}	kn_{14}	H	N	hydrogen bond	k_{165}	kn_{35}
H	Be	triple bond	k_{133}	kn_{15}	H	N	nonbond	k_{166}	kn_{36}
H	Be	aromatic bond	k_{134}	kn_{16}	H	O	single bond	k_{171}	kn_{37}
H	Be	hydrogen bond	k_{135}	kn_{17}	H	O	double bond	k_{172}	kn_{38}
H	Be	nonbond	k_{136}	kn_{18}	H	O	triple bond	k_{173}	kn_{39}
H	B	single bond	k_{141}	kn_{19}	H	O	aromatic bond	k_{174}	kn_{40}
H	B	double bond	k_{142}	kn_{20}	H	O	hydrogen bond	k_{175}	kn_{41}
H	B	triple bond	k_{143}	kn_{21}	H	O	nonbond	k_{176}	kn_{42}

Next, by using the equation (20) ~ (23), rewriting the parameters of acetic acid with the new parameter marked with the unique number, the parameters are as follows.

For the sake of convenience, regarding up to 9-th atom in the table 3, total number of atoms na is 9 and there are k_{116}, k_{151}, k_{511}, k_{156}, k_{516}, k_{176}, k_{716}, k_{551}, k_{576}, k_{756}, k_{572}, k_{752}, k_{571}, k_{751}, k_{776}, k_{171}, k_{711} in interaction parameter.

Because k_{116} is nonbond parameter between the hydrogen and hydrogen, and the atomic number of hydrogen in table 3 is 1, according to the equation (20), the number of new parameter is following.

$$j = 6(1-1)+6 = 6$$

So k_{116}=kn_6.

On the other hand, because in regard to k_{511}, the back atomic number is larger than the front atomic number, according to equation (21), the number is as follows.

$$j = 6(5-1)+1 = 25$$

In the same way, expressing with the unique number for the remaining parameters, the parameters are obtained as follows.

k_{156}=k_{516}=kn_{30}, k_{176}= k_{716}=kn_{42}, k_{171}= k_{711}=kn_{37}

k_{551}=kn_{181}, k_{576}= k_{756}=kn_{198}, k_{572}= k_{752}=kn_{194}

k_{571}= k_{751}=kn_{193}, k_{776}=kn_{240}

Comparing the result with the table 4, it can be found that the values are right, and from this, the interaction parameters can be defined and calculated with the unique numbers.

3.2.2. Calculation Results of Interaction Parameters

The values of interaction parameters obtained by using method described above are given in table 5.

The parameters were obtained from the results of charge calculated for more than 150 organic molecules and more than 50 inorganic molecules by using ab initio (STO-3G) method.

Table 5. *Interaction parameters of some atoms depending on bond mode.*

atom1	atom2	interaction parameter/10^{-10}eVm					
		single bond (s)	double bond (d)	triple bond (t)	aromatic bond (a)	hydrogen bond (h)	nonbond (n)
H	H	-	-	-	-	-	1.757 20
H	C	1.887 43	-	-	-	-	2.410 86
H	N	2.973 17	-	-	-	-	3.799 68
H	O	2.743 34	-	-	-	5.887 61	2.354 99
H	S	7.183 05	-	-	-	-	3.131 37
H	Cl	-0.977 68	-	-	-	-	0.712 04
C	C	4.362 84	4.806 38	1.646 83	4.512 95	-	4.503 86
C	N	4.065 94	-	4.796 24	-	-	4.608 85
C	O	4.557 89	4.958 64	-	-	-	4.433 80
C	F	3.482 99	-	-	-	-	2.201 76
C	P	6.991 55	7.175 76	4.566 63	-	-	8.004 25
C	S	5.656 37	-	-	-	-	6.585 37
C	Cl	3.635 46	-	-	-	-	1.589 47
N	N	3.802 80	6.244 91	-	-	-	5.425 95

atom1	atom2	interaction parameter/10^{-10}eVm					
		single bond (s)	double bond (d)	triple bond (t)	aromatic bond (a)	hydrogen bond (h)	nonbond (n)
N	O	5.278 58	6.478 41	-	-	-	3.919 07
O	O	5.207 27	-	-	-	-	6.218 22
O	S	5.853 82	5.529 71	-	-	-	5.677 84

In order to confirm accuracy and reliability of parameters calculated, we substituted the calculation results of interaction parameters for left-hand side of equation (18), QK and considered relationship between the value and value of right-hand side, μ. (figure 1)

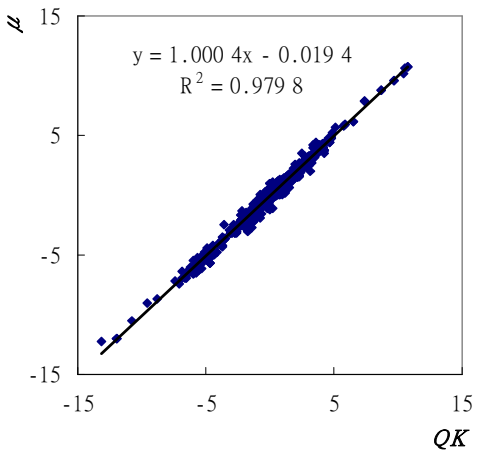


Figure 1. *The result of correlation analysis for calculating parameters.*

As shown in figure 1, in regard to correlation for calculation results, linear relationship was well formed and correlation coefficient R^2=0.979 8, deviation value is 0.005 83.

This shows that our parameters can be used enough for calculating atomic charge of real molecules.

4. Conclusion

1. From the values of ionization energy and electron affinity, the parameters of neutral atoms, μ_0 and γ were defined, and the integration constant ε was also calculated. The physical meaning of PCP as the scale of mass migration was confirmed by comparison with electronegativity, the scale of ability of attracting electron.
2. Calculating method of the parameters depending on bond mode of atoms in molecule was suggested and the parameters were calculated and tabulated.

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