Theoretical Base of Pseudo Chemical Potential (PCP) Method

Jong Ryong Ju[1], Kim Tong Il[1, 2, *], Jon Yung[1], Yun Hak Sung[2], Kim Gyong Nam[2], Choi Sung Il[2], Han Gwang Bok[2], An Ryong Nam[2]

[1]Collage of Chemistry, University of Science, Pyongyang, D. P. R. Korea

[2]Institute of Catalyst, State Academy of Science, Pyongyang, D. P. R. Korea

Email address:

kimtil@star-co.net.kp (Kim Tong Il)

[*]Corresponding author

Abstract: Pseudo chemical potential (PCP) method is a novel one based on the thermodynamic formalization, and the purpose of this work is to clarify theoretical base of PCP method and to perfect PCP method into a novel method for molecular calculation. Therefore, it is very important to clarify validity of thermodynamic formalization that becomes principle and methodology of this method for achievement of its purpose. The thermodynamic formalization in molecular calculation is to achieve molecular calculation by using principle and methodology of thermodynamics. In order to apply the method of thermodynamic formalization in molecular calculation, it must be clarified that molecule (atom) electron system, computational object of PCP method, can be considered to be "thermodynamic system". In this paper, we have clarified the temperature zero limit (TZL) state of a finite temperature thermal equilibrium system, as physical base of the pseudo chemical potential (PCP) method, having thermodynamic properties and therefore being the research object of thermodynamic formalism. Furthermore, we have proved an existence of energy minimization principle, as the theoretical base of PCP method, and from it derived the variation equation and defined the electron charge distribution equation, and on the basis of it analyzed theoretically the electronegativity equalization principle. Resultantly, herein we have demonstrated theoretical validity of PCP method, as a novel method for calculation of molecular energies and charge distributions.

Keywords: Temperature Zero Limit State, Pseudo Chemical Potential (PCP), Thermodynamic Formalization, Thermodynamic Model of a Molecule

1. Introduction

The wave function theory (WFT) [1–3] in which electron wave function is variable quantity andthe density functional theory (DFT) [4, 5] in which electron density is variable quantity, are a theory and method which were established and principally systemized on the basis of the formalization of quantum theory, and are main means to study the structure and properties of a system on quantum theory.

The pseudo chemical potential (PCP) method proposed by us in the previous work in which electron number is variable quantity [6], as a novel method based on the thermodynamic formalization, has shown much more efficiency in the calculation of a molecular energy and the charge distribution (molecular calculation). In the literature [6], however, the validity of thermodynamic formalization has not principally been substantiated but assumed.

Herein we report the theoretical validity and the base of PCP method applied to molecule electron system.

As mentioned in previous literature [7], temperature zero limit (TZL) state of the finite temperature thermal equilibrium system is very interesting state, furthermore, andis also physical system concerned by us in the study of molecules by means of thermodynamic formalization. The characters of this physical system have been clarified by evaluating resultant equations [8-10] of quantum statistical mechanics on the finite temperature thermal equilibrium system when T→0.

According to the previous research;

First, the free energy of mixture state is expressed in terms of the energy of the ground stateof molecule (atom) electron system, the pure state.

$$A[\hat{\Gamma}_N] = E. \tag{1}$$

Where $\hat{\Gamma}_N$ is a density operator of the mixture state consisting of N electrons (matrix), E is a total energy of the ground state.

Second, the energy minimization principle of the mixture state, $A[\hat{\Gamma}_N^0] \leq A[\hat{\Gamma}_N]$, is expressed in Schrödinger's variation principle [1-3].

$$E_{v0} \leq E_v[\tilde{\rho}]. \tag{2}$$

Third, the chemical potential defined by free energy of the mixture state, $\mu = \left(\frac{\partial A[\hat{\Gamma}]}{\partial N}\right)_{T, v'(r)}$, is defined in terms of the energy of the atomelectron system in the ground state.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v'(r)}. \tag{3}$$

Namely, TZL state is a physical system in which the principles and concepts of the finite temperature state hold true [8-10].

Therefore, we have studied thermodynamic characters of TZL state, from a new viewpoint, with great attention of this fact, from that, we have proved that TZL state has the nature of thermodynamic system and becomes the physical base of PCP method, and application validity of thermodynamic formalism was clarified.

And then, in the paper we demonstrated the existence of the energy minimization principle of molecule (atom) electron system in PCP method established from pseudo chemical potential and defined the phase pseudo chemical potential (PCPP) of molecular composition atoms like in the thermodynamic formalism and on the basis of it, suggested a thermodynamic model of a molecule in which molecule electron system is considered multi-phase (atom) one component (electron) system. On the basis of these results, by derived the variation equation resolving an electron number N^* giving minimum molecule energy, the electron charge distribution equation is obtained, and previous electronegativity equalization principle is analyzed by the variation principle of PCP method.

2. Thermodynamic Properties of TZL State

The TZL state, as quantum-theoretical pure state, has been a research object of wave mechanics, density functional theory and statistic mechanics, but it has not yet been discussed to be a research object of thermodynamics.

1) Appreciation of Thomas-Fermi model

To analyze from other viewpoint previous statistic mechanical studies on TZL state will help in elucidating a new aspect of TZL state.

The object of Thomas-Fermi statistic model widely used in quantum-theoretical research is a micro electron system of TZL state including individual molecule (atom) electron system. Thomas-Fermi statistic model, as a statistic mechanical model, represents the statistic mechanical properties of an object [11-13]. Considering that statistic mechanics is a learning in which quantum mechanics is quantitatively linked with thermodynamics, the model represents not only statistic mechanical properties butthermodynamic properties of an object, so indicates that the individual atom (molecule) electron system has the thermodynamic properties.

2) State variable of limit thermodynamic system (TZL state)

It is important to clarify the existence of state variables in order to indicatethe thermodynamic properties of atom (molecule) electron system.

(1) Entropy [14, 15]

In statistic mechanics, entropy defined by the state realization probability$p_{Ni}$is the following:

$$S = -k_B \sum_i p_{Ni} \ln p_{Ni}. \tag{4}$$

On the other hand, density operator $\hat{\Gamma}_N$ of the finite temperature thermal equilibrium system (mixed state) is equal to Eq. 5;

$$\hat{\Gamma}_N = \sum_i p_{Ni} |\Psi_{Ni}\rangle\langle\Psi_{Ni}| \tag{5}$$

(where $\hat{\Gamma}_N$ is a density operator of mixture state composed of the molecule (pure state) with N same electrons,p_{Ni} is a realization probability of the i-th pure state Ψ_i, N is the number of electrons of the molecule, i is the i-th pure state in the mixture state).

Free energy $A[\hat{\Gamma}_N]$ expressed by the value of diagonal element of $\hat{\Gamma}_N$is as follows;

$$A[\hat{\Gamma}_N] = \sum_i p_{Ni}(\frac{1}{\beta}\ln p_{Ni} + \langle\Psi_{Ni}|\hat{H}|\Psi_{Ni}\rangle). \tag{6}$$

Free energy $A[\hat{\Gamma}_N]$ depends on the variablesp_{Ni} and Ψ_{Ni}, and whenΨ_{Ni} is fixed,p_{Ni} satisfying provability total sum $\sum_i p_{Ni} = 1$ as well as minimizing $A[\hat{\Gamma}_N]$ can be obtained by introducing Lagrange undefined multiplier λ to resolve the following Eq.

$$\frac{\partial}{\partial p_{Ni}} A[\hat{\Gamma}_N] = \frac{\partial}{\partial p_{Ni}}[\sum_i p_{Ni}(\frac{1}{\beta}\ln p_{Ni} + \langle\Psi_{Ni}|\hat{H}|\Psi_{Ni}\rangle + \lambda(\sum_i p_{Ni} - 1)] = 0 \tag{7}$$

$$\frac{\partial}{\partial p_{Ni}}[\sum_i p_{Ni}\left(\frac{1}{\beta}\ln p_{Ni} + \langle\Psi_{Ni}|\hat{H}|\Psi_{Ni}\rangle\right) + \lambda(\sum_i p_{Ni} - 1)] = 0;$$

$$\sum_i(\frac{1}{\beta}\ln p_{Ni} + \langle\Psi_{Ni}|\hat{H}|\Psi_{Ni}\rangle) + p_{Ni}\frac{1}{\beta p_{Ni}} + \lambda) = 0;$$

$$(\tfrac{1}{\beta}\ln p_{Ni} + <\Psi_{Ni}|\hat{H}|\Psi_{Ni}>) + \tfrac{1}{\beta} + \lambda) = 0;$$

$$<\Psi_{Ni}|\hat{H}|\Psi_{Ni}> = E_i;$$

$$\tfrac{1}{\beta}(\ln p_{Ni} + 1) + E_i + \lambda) = 0;$$

$$\ln p_{Ni} = -\beta E_i - \beta\lambda - 1;$$

$$p_{Ni} = e^{-\beta E_i}e^{-\beta\lambda-1} = e^{-\beta E_i}f;$$

$$\sum_i p_{Ni} = \sum_i e^{-\beta E_i}f = f\sum_i e^{-\beta E_i} = 1;$$

$$f = \frac{1}{\sum_i e^{-\beta E_i}};$$

where β is $1/KT$.

Under the thermal equilibrium condition, appearance provability of the *i*-th pure state in the mixture state, $p_{Ni} = p_{Ni}^0$, is equal to;

$$p_{Ni} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}. \qquad (8)$$

For temperature zero limit state $\beta \to \infty(T \to 0)$, Eq. 9 is obtained by calculating probability p_{Ni}.

$$p_{Ni} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{1}{\sum_j e^{-\beta(E_j-E_i)}} = 1;$$

$$p_{Ni} = 1. \qquad (9)$$

As clear from Eq. (9) and Eq. (4), the entropy of system *S* is zero.

(2) Pressure and volume

In TZL state, Fermi-Dirac distribution function makes it possible to determine the thermodynamic variables of the molecule (atom) electron system within the range of Thomas-Fermi model. The electron number of the system N, Fermi energy μ_0, zero point pressure P_0 (pressure of electron gas at $T_0=0$) and zero point energy E_0 are respectively representedas follows [14];

$$N = \frac{8\pi}{3}(\frac{2m}{h^2})^{\frac{3}{2}}V(\mu_0)^{\frac{3}{2}};$$

$$P_0 = \frac{2}{5}\mu_0(\frac{N}{V});$$

$$E_0 = \frac{3}{5}\mu_0 N;$$

which are the results of the statistic mechanical effect in the quantum system rather than the effect of an interaction between electrons or electron and nucleus, indicating the relationship between thermodynamic variables, P_0 and V, in TZL state.

3) Thermodynamic course in a limit thermodynamic system

It is also important to clarify the change of state variable, thermodynamic course, in order to indicate the thermodynamic properties of atom (molecule) electron system.

(1) According to Nernst's theorem of third law of thermodynamics, there is no changeof entropy ($\Delta S = 0$).

(2) Since TZL state is just molecule electron system, there are no changes in volume and pressure ($\Delta V = 0$, $\Delta P = 0$).

(3) As the entropy is zero in TZL state, the free energy and free enthalpy of thermodynamic system are expressed as the internal energy (i.e. energy of molecule electron system) E (E≠0, $\Delta E \neq 0$).

4) Fluctuation in the TZL state (limit thermodynamic system)

Fluctuation is a common indicator of statistical and thermodynamic properties of the system. It is important to clarify the fluctuation property of system in evaluating the thermodynamic properties of moleculeelectron system. As the nature of thermodynamic fluctuation is concerned with the entropy, and according to the previous literature [14-16], the fluctuation in TZL state that we pay attention to is expressed as follows;

$$(\overline{\Delta T})^2 = T^2\Big/C_v , \ (\overline{\Delta V})^2 = -T(\frac{\partial V}{\partial P})_T , (\overline{\Delta S})^2 = C_v ,$$

$$(\overline{\Delta P})^2 = -T(\frac{\partial P}{\partial V})_S$$

where C_v is an equal-volume thermal capacity, T, V, P, S are temperature, volume, pressure and entropy, respectively. From the above equations, it is clear that in the temperature zero limit state the values of fluctuation are all zero and physical meaning of thermodynamic fluctuation disappears. Therefore, temperature zero limit state is a system in which there is nota portion of thermodynamic fluctuation but only the portion of a quantum mechanical uncertainty in the mean square standard deviation of physical quantities.

5) Results and discussion

The conclusion that we had synthesized the previous research results about the TZL state and had analyzed it from a viewpoint of thermodynamic formulation is as follows. Variables are defined determiningthermodynamic properties and their changes of the system including chemical potential and internal energyin an atom (molecule) electron system, furthermore, it is important that there exists the energy minimization principle in the system. An atom (molecule) electron system has the properties of thermodynamic system,

in which the migration of electrons is carried out by chemical potential as thermodynamic driving force, as a result of that, the minimization process of internal energy takes place, resulting in equilibrium of electron migration.

As the physical meaning of chemical potential is thermodynamic potential per electron and its decreasing process is a spontaneous one, the chemical potential serves as thermodynamic driving force. Therefore, the chemical potentialdifference ($\Delta\mu$) causes electron migration. Briefly speaking, an atom (molecule) electron system in TZL state is a physical system having the properties of thermodynamic system in which there exists the concepts of mass migration and equilibrium.

3. Derivation of PCP by Thermodynamic Formalization

From the viewpoint that atom (molecule) electron system is physical system with property of thermodynamic system, we obtained analytic form of Lagrange's undetermined multipliers of density functional theory [7] by thermodynamic formalism.

In general, according to the thermodynamic formalism, mass migration quantity in thermodynamic system is proportional to driving force of mass migration (potential difference $\Delta\mu$, concentration difference Δc) and quantity of mass.

Supposing that differential variation of electron number arising from electron migration, dN, is in proportion to one of chemical potential $d\mu$ and electron number Nand taking proportional constantas $\frac{1}{\gamma}$, then following equation can be obtained.

$$dN = \frac{1}{\gamma} N d\mu. \tag{10}$$

Let`s integrate along the process of charge migration equilibrium.

Namely, supposing that initial chemical potential is μ_α^0, chemical potential after migration equilibrium is μ_α, initial electron number is N_α^0, electron number after migration equilibrium is N_α, because electron number N_α^0 approaches N_α when initial chemical potential μ_α^0 approaches μ_α, integration is as follows.

$$\int_{N_\alpha^0}^{N_\alpha} \frac{1}{N} dN = \int_{\mu_\alpha^0}^{\mu_\alpha} \frac{1}{\gamma} d\mu \tag{11}$$

$$\mu_\alpha = \mu_\alpha^0 + \gamma \ln \frac{N_\alpha}{N_\alpha^0}. \tag{12}$$

We expressedLagrange's undetermined multiplier of density functional theory, μ, as eq. (15) and defined it as pseudo chemical potential adding "pseudo", unlikethe previous researchers named it chemical potential.

To define like this is because the function shape is proportional to log of electron number like state function using in the thermodynamic system usually, and derivation process itself is based on the thermodynamic formalism.

4. Minimization Principle and Variation Equation in PCP Method

1) Minimization principle in PCP method

Firstly, let`s prove the existence of energy minimizationprinciple in PCP method and have variation equation derived from it.

To prove the existence of energy minimization principle in PCP method leads to clarify molecular energy model of this method is to be function giving value of minimum energy. In order to clarify it, it is necessary to investigate and analyze a function shape of a molecular energy model.

Molecular energy has the following function shape;

$$E^M = \sum_\alpha E_\alpha^* - \sum_\alpha \sum_{\beta \neq \alpha} k_{\alpha\beta} \frac{q_\alpha q_\beta}{R_{\alpha\beta}} \tag{13}$$

$$E_\alpha^* = N_\alpha \left(\mu_\alpha^0 + \gamma_\alpha ln \frac{N_\alpha}{N_\alpha^0} - \gamma_\alpha \right) + \varepsilon_\alpha \tag{14}$$

(where N_α -electron number of α atom domain, $k_{\alpha\beta}$ -interaction parameter between α atom and β atom in the molecule)

To find a function shape of E^M, numerical analysis of $\sum_\alpha E_\alpha^*$ and $\sum_\alpha \sum_{\beta \neq \alpha} k_{\alpha\beta} \frac{N_\alpha q_\beta}{R_{\alpha\beta}}$ was carried out for some molecules. The results were shown in table 1.

Table 1. *Components of total energies of some molecules.*

matter	Total energy/eV	energy of atom domain /eV	Interaction energy	
			eV	%
CH_4	-1080.85194	-1080.06053	-0.79141	0.07
C_2H_6	-2129.79075	-2132.93230	3.14154	0.14
C_3H_8	-3180.30810	-3185.76048	5.45238	0.17
C_4H_{10}	-4230.29898	-4238.61895	8.31997	0.19

From the table 1, it can be understood that the main part of numerical value of E^M is just $\sum_\alpha E_\alpha^*$, therefore, the function shape of E^M could be decided by the function shape of $\sum_\alpha E_\alpha^*$, furthermore, one of E_α^*.

Changing Eq. 14,

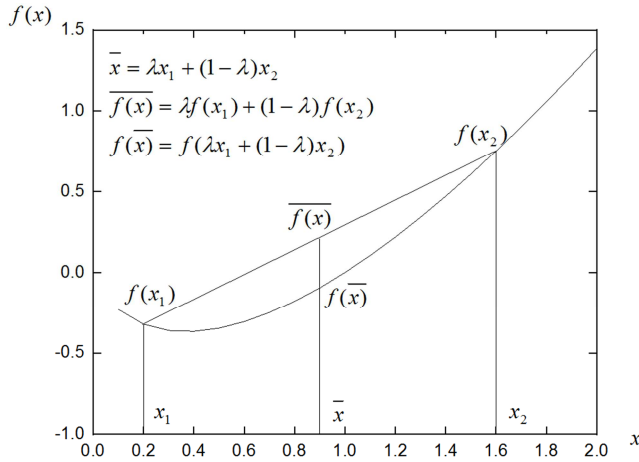$$E_\alpha^* = \gamma_\alpha N_\alpha ln \frac{N_\alpha}{N_\alpha^0} - N_\alpha (\gamma_\alpha - \mu_\alpha^0) + \varepsilon_\alpha \tag{15}$$

is obtained.

From the Eq. above, it canbe found that $\gamma_\alpha N_\alpha ln \frac{N_\alpha}{N_\alpha^0}$ part is main part deciding curve shape of function E_α^* (where γ_α, μ_α^0, ε_α are all constants).

In order to find curve shape of main part, in interval of

variable x [0.2, 1.6], function f(x)=x ln x was represented graphically, considering that main part is function of variable N_α.

Figure 1. *Shape of function f(x)=xlnx in interval of variable x = [0.2, 1.6].*

In our research work, main part is $\gamma_\alpha N_\alpha ln \frac{N_\alpha}{N_\alpha^0}$ part and it has function shape of function f(x)=xlnx.

As is well known, the shape of function *f(x)=xlnx* is convex type.

Figure 1 shows the shape of function *f(x)=xlnx* in interval of variable *x* = [0.2, 1.6].

As shown in Figure 1, function value of average value of *x*, $f(\bar{x})$ is smaller than average value of function value, $\overline{f(x)}$. Namely, between function of variable average, $f(\bar{x})$ and function average, $\overline{f(x)}$, Jensen`s inequality f($\bar{x}$) ≤ $\overline{f(x)}$ is formed.

Resultantly, for main part, Jensen`s inequality f($\bar{x}$) ≤ $\overline{f(x)}$ is formed, therefore, it is clear that a function E_α^* of Eq. 15 is a curve-type ($\frac{\partial^2 f(x)}{\partial^2(x)} > 0$) with a minimal extreme value.

For this reason, it was expected that molecular energy model E^M is also to be function with a minimal extreme value, and investigation was carried out for several molecules such as methane, so it was clarified that Jensen`s inequality is also formed.

For example, a calculation result of methane molecule is shown in table 2.

Table 2. *Calculation results of methane molecule.*

Electron number	Atom					Total energy	Average value
N_i	C	H	H	H	H	$E^M(N)$	$\frac{E^M(N_1)+E^M(N_2)}{2}$
N_1	6.1508	0.9623	0.9623	0.9623	0.9623	-1080.682	-1080.720
N_2	6.2308	0.9423	0.9423	0.9423	0.9423	-1080.758	
$\frac{(N_1)+(N_2)}{2}$	6.1908	0.9523	0.9523	0.9523	0.9523	-1080.852	-1080.852

Demonstrating the molecular total energy model of PCP method is the function shape with the minimal extreme value through the calculation experiments, existence of the minimization principle of PCP method,

$$E_0^M(N^*) \leq E^M(N), \ E_0\left(N^*, \mathcal{v}(r)\right) = \inf_N E(N) \tag{16}$$

is cleared.

In molecule electron system, energy minimization action occurs in the process of forming molecule from neutral atoms.

In PCP method, molecular energy.

$$E^M = \sum_\alpha \left[N_\alpha \left(\mu_\alpha^0 + \gamma_\alpha \ln \frac{N_\alpha}{N_\alpha^0} - \gamma_\alpha \right) + \varepsilon_\alpha \right] - \sum_\alpha \sum_{\beta \neq \alpha} k_{\alpha\beta} \frac{q_\alpha q_\beta}{R_{\alpha\beta}} \tag{17}$$

is a function of electron number N_α, $E^M[N]$, because $q_\alpha = Z_\alpha - N_\alpha$, $q_\beta = Z_\beta - N_\beta$.

According to thermodynamic formalism, partial derivative value of molecular energy.

$$\mu_\alpha^M = \left(\frac{\partial E^M}{\partial N_\alpha} \right)_{\mathcal{v}(r), N_{\beta \neq \alpha}} \tag{18}$$

$$\mu_\alpha^M = \mu_\alpha^0 + \gamma_\alpha \ln \frac{N_\alpha}{N_\alpha^0} - \sum_\beta k_{\alpha\beta} \frac{q_\beta}{R_{\alpha\beta}} \tag{19}$$

is defined as pseudo chemical potential of phase (PCPP). Physical meaning of PCPP is electron migration measure between constituent atoms in molecule electron system.

On the basis of the PCPP concept, we proposed multi-phase one component system, in which component atoms of molecule are regarded as "phases" and electrons as "components", as thermodynamicmodel to replace molecular reality.

The electron migration in molecule formation process, that is, distribution of electrons between component atoms is proceeded so that PCPP of each atom (phase) should be the same, and when the process reaches migration equilibrium to be in bonding state, resultantly, stable molecule with minimum energy is formed.

At this time electron number becomes variable of energy minimization.

2) Variation equation of PCP method

According to the minimization principle, setting up a

variation equation deciding electron number giving minimal molecular energy.

$$\delta E^M [N_1 N_2 \cdots N_n] = 0 \qquad (20)$$

$$dE^M = \sum_{\alpha}^{n} \mu_{\alpha}^{M} dN_{\alpha} = \mu_1^M dN_1 + \mu_2^M dN_2 + \ldots + \mu_n^M dN_n = 0 . \qquad (21)$$

According to the condition that electron number is constant,.

$$\sum_{\alpha}^{n} N_{\alpha} = N_1 + N_2 + N_2 + \ldots + N_n = const \qquad (22)$$

$$d(\sum_{\alpha}^{n} N_{\alpha}) = dN_1 + dN_2 + dN_2 + \cdots + dN_n = 0 \qquad (23)$$

(where n is a number of phase (atom), α is a kind of phase (atom), N_{α} is an electron number of α-th phase (atom), N is an electron number of a molecule.)

$$Eq.\,(20) - Eq.\,(23) \times \mu_1^M = (\mu_2^M - \mu_1^M)dN_2 + (\mu_3^M - \mu_1^M)dN_3 + \cdots (\mu_n^M - \mu_1^M)dN_n = 0. \qquad (24)$$

Since $dN_{\alpha} \neq 0$, equilibrium conditions of PCPP.

$$\mu_1^M = \mu_2^M = \cdots = \mu_{\alpha}^M = \cdots = \mu_n^M \qquad (25)$$

is obtained.

Equilibrium conditions of PCPP (Eq. 25) is obtained from thermodynamic model of molecule electron system. And considering equation (19), Eq. 25 directly obtained from variation equation in PCP method is represented as following simultaneous equation [6].

$$\mu_n^0 + \gamma_n \ln \frac{N_n}{N_n^0} - \sum_{\beta}^{n} k_{n\,\beta} \frac{q_\beta}{R_{n\,\beta}} = \mu^M, \;\; \sum_{\beta}^{n} q_\beta = 0, \;\; (n = 1, 2 \cdots) . \qquad (26)$$

This simultaneous equation is not only an equation for calculation of atomic charge distribution calculating atomic charge of stable molecule in electron migration equilibrium state but also a fundamental equation of PCP method.

Unknown number of the equation for calculation of atomic charge distribution (Eq. 26) are atomic charge q_β and pseudo chemical potential of molecule μ^M, they are (n+1) in all.

In the range of thermodynamic model of molecule electron system proposed by us, electronegativity equalization principle formulated by Sanderson et al. [17, 18], "when atoms (or other combining groups) of different chemical potentials unite to form a molecule with its own characteristic chemical potential, to the extent that the atoms (groups) retain their identity, their chemical potentials must equalize", was derived naturallyby variation principle of PCP method, rather than "principle".

5. Conclusion

In this paper, theoretical fundamental of PCP method have beenclarified.

Firstly, by deepening investigation of temperature zero limit, it`s thermodynamic property as physical baseof the molecule (atom) electron system was clarified, and by application of thermodynamic formalism, function shape of PCP to be itsstarting point was found.

andsolving itfor N, electron number giving minimal molecular energy, N^* is just obtained.

Because E^M is a function of electron number, variation of energy is expressed as total differential equation (21).

Secondly, by demonstrating the molecular total energy model of PCP method is the function of Convex shape with the minimal extreme value through the calculation experiments, the existence of energy minimization principle of PCP method was proved and through deriving a variation equation by using variation (total differential) of the molecular total energy, an atomic charge distribution equation of a molecule was obtained and on the basis of this result, the previous electronegativity equalization principlewas analyzed by variation principle of PCP method.

Acknowledgements

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