

## Should We Use Force instead of Energy in the Analysis of Chemical Phenomena? -3 How to Obtain Forces in the Hartree-Fock Theory and Examples of Their Application

There are total differential and partial differential in differentiation. In order to explore the cause of a chemical phenomenon, it is necessary to use partial differential. Here, the reason is explained and the concrete method of calculating the partial differential value for the various forces is introduced. Finally a few examples of application are quoted. As a molecular orbital theory, the Hartree-Fock (HF) method is used. The advantages of the HF method are that it fulfills the virial theorem<sup>1)</sup> theoretically (if one uses the complete system) and that the application to the post-HF methods is easy.

### 1. The Reason Why Partial Differential Must Be Used in Analysis

The word "total" of total differential means summation. Since total differential is the summation of results, one cannot seek the cause of a phenomenon.

To the function  $f(x_1, x_2, \dots, x_n)$  with  $n$  number of differentiable variables,

$$df(x_1, x_2, \dots, x_n) = \sum_{i=1}^n \frac{\partial f(x_1, x_2, \dots, x_n)}{\partial x_i} dx_i \quad 1$$

in which,  $df(x_1, x_2, \dots, x_n)$  is called the total differential. Let us consider the case where  $f$  is  $E$  and  $x$  are only two variables of a nucleus position.

$$dE(x_1, x_2) = \frac{\partial E(x_1, x_2)}{\partial x_1} dx_1 + \frac{\partial E(x_1, x_2)}{\partial x_2} dx_2 \quad 2$$

The above formula means that if  $x_1$  is changed by  $dx_1$ ,  $E$  changes by  $\frac{\partial E(x_1, x_2)}{\partial x_1} dx_1$  and

similarly if  $x_2$  is changed,  $E$  changes by  $\frac{\partial E(x_1, x_2)}{\partial x_2} dx_2$ .  $\frac{\partial E(x_1, x_2)}{\partial x_1}$  and  $\frac{\partial E(x_1, x_2)}{\partial x_2}$  are

proportionality factors of  $dx_1$  and  $dx_2$ . Since  $dE$  depends on those proportionality factors, those factors are the causes. Therefore, the causes of a chemical phenomenon turn out to be  $\frac{\partial E(x_1, x_2)}{\partial x_1}$

and  $\frac{\partial E(x_1, x_2)}{\partial x_2}$ .

### 2. How to Obtain Partial Differential of Total Energy with Respect to Position Variables

The total energy by the HF method consists of the kinetic energy ( $\langle T \rangle$ ), one-electron potential energy ( $\langle V_{eN} \rangle$ ), two-electron potential energy ( $\langle V_{ee} \rangle$ ), and nuclear repulsion energy.

The energy expectation values on physical quantities are denoted by the following general formula.

$$\begin{aligned} \langle X \rangle &= \langle \Psi | \tilde{X} | \Psi \rangle = 2 \sum_i \int \psi_i^*(1) \tilde{X} \psi_i(1) d\tau = 2 \sum_i \sum_r \sum_s c_r^{i*} c_s^i \int \chi_r^*(1) \tilde{X} \chi_s(1) d\tau_1 \\ &= \sum_r \sum_s P_{rs} X_{rs} \end{aligned} \quad 3$$

In Eq. 3,  $\Psi$  is the total wavefunction,  $\tilde{X}$  is the operator for the  $X$  kind of energy,  $\psi_i$  is the  $i$ -th molecular orbital, and  $\chi$  is the atomic orbital.  $P_{rs}$  and  $X_{rs}$  are the bond order and the  $X$  energy between arbitrary atomic orbitals  $r$  and  $s$ .

The formulas which calculate the partial differential values of the various energies with respect to nuclear coordinates are summarized as follows.<sup>2)</sup>

#### Kinetic energy of electrons

$$\frac{\partial \langle T \rangle}{\partial R_a} = \sum_{r,s} P_{rs} \frac{\partial T_{rs}}{\partial R_a} + \sum_{r,s} \frac{\partial P_{rs}}{\partial R_a} T_{rs} + \frac{1}{\zeta} \left[ 2 \langle T \rangle + \sum_b R_b \left( \frac{\partial \langle T \rangle}{\partial R_b} \right)_0 \right] \frac{\partial \zeta}{\partial R_a} \quad 4$$

Here,  $R_a$  is the position variable while  $P_{rs}$  and  $T_{rs}$  are the bond order and the kinetic energy between

orbitals  $r$  and  $s$ .  $\left( \frac{\partial \langle T \rangle}{\partial R_b} \right)_0$  means the partial differential when  $\zeta$  is regarded as a constant.

#### One-electron potential energy

$$\frac{\partial \langle V_{eN} \rangle}{\partial R_a} = \sum_{r,s} \left( P_{rs} \frac{\partial V_{rs}^{eN}}{\partial R_a} + \frac{\partial P_{rs}}{\partial R_a} \right) + \frac{1}{\zeta} \left[ \langle V_{eN} \rangle + \sum_b R_b \left( \frac{\partial \langle V_{eN} \rangle}{\partial R_b} \right)_0 \right] \frac{\partial \zeta}{\partial R_a} \quad 5$$

In the above formula,  $V_{rs}^{eN}$  is the one-electron potential energy between orbitals  $r$  and  $s$ , while

$\left( \frac{\partial \langle V_{eN} \rangle}{\partial R_b} \right)_0$  is the partial differential as  $\zeta$  being a constant.

#### Two-electron potential energy

$$\begin{aligned} \frac{\partial \langle V_{ee} \rangle}{\partial R_a} &= \sum_{r,s} \left( P_{rs} \frac{\partial V_{rs}^{ee}}{\partial R_a} + \frac{1}{2} \sum_{t,u} \frac{\partial}{\partial R_a} \left[ (rs/tu) - \frac{1}{2} (rt/su) \right] + \frac{\partial P_{rs}}{\partial R_a} \left\{ V_{rs}^{ee} + \sum_{t,u} P_{tu} \left[ (rs/tu) - \frac{1}{2} (rt/su) \right] \right\} \right) \\ &+ \frac{1}{\zeta} \left[ \langle V_{ee} \rangle + \sum_b R_b \left( \frac{\partial \langle V_{ee} \rangle}{\partial R_b} \right)_0 \right] \frac{\partial \zeta}{\partial R_a} \end{aligned}$$

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In Eq. 6,  $V_{rs}^{ee}$  is the two-electron potential energy between orbitals  $r$  and  $s$ , and  $\left( \frac{\partial \langle V_{ee} \rangle}{\partial R_b} \right)_0$  is the

partial differential as  $\zeta$  being a constant.

Nuclear repulsion energy

The partial differential of the nuclear repulsion energy with respect to a position variable of the nucleus is obtained by simple classical partial differentiation.

$$\frac{\partial \mathcal{V}_{NN}}{\partial R_a} \quad 7$$

**3. Examples of Application**

1. Role of Kinetic Energy of Electrons in Formation of Chemical Bond

In 1962, Ruedenberg observed the changes of the kinetic energy and the potential energy of the system when  $H^+$  in a far distance approaches to H until they form the covalent bond of hydrogen molecule ion ( $H_2^+$ ), to obtain conclusions as follows<sup>3)</sup>. At first, in far internuclear distance the fall of the kinetic energy takes place by spread of the movement domain due to the relief of the kinetic energy pressure<sup>4)</sup>. Then a fall of the potential energy is brought forth by distortion of the electronic distribution to a bond axis from the spherical distribution of H. In the region where the bond distance is smaller than the equilibrium distance, since movement of the electron is restricted by nuclear potentials, it serves as a rise of the kinetic energy. The rate of the increase in kinetic energy and that of the fall of the potential energy exactly balance at the equilibrium distance.

There is a result of having considered the above result from the viewpoint of "force." <sup>2)</sup>. Table 1 shows the partial differential values of the kinetic energy and the potential energy as a function of the internuclear distance  $R$  in  $H_2^+$ . One must be careful that  $R$  is positive towards the increasing distance.

Table 1. Relationship between nuclear distance and the forces of the kinetic energy or the potential energy (UHF/6-311G\*\*)

[H---H] <sup>+</sup> (bohr)	Total energy (au)	$\frac{\partial \langle T \rangle}{\partial R}$ (hartree / bohr)	$\frac{\partial \langle V \rangle}{\partial R}$ (hartree / bohr)	$\frac{\partial E}{\partial R}$ (hartree / bohr)
1.0	-0.44928	-0.60500	0.08035	-0.52465
1.9834(opt)	-0.60117	-0.20389	0.20389	0
2.0	-0.60116	-0.20042	0.20222	0.00181
3.0	-0.57304	-0.06865	0.10662	0.03797
4.0	-0.53987	-0.00861	0.03486	0.02625
5.0	-0.51999	0.01470	-0.00023	0.01447
6.0	-0.50934	0.01746	-0.01001	0.00745
7.0	-0.50405	0.01239	-0.00885	0.00354
8.0	-5.50162	0.00704	-0.00547	0.00157

In Table 1,  $\frac{\partial \langle T \rangle}{\partial R}$  corresponds to Eq. 4, here we call it “kinetic-energy force”. The kinetic-energy force is the force in which an electron tends to spread according to the uncertainty relationship. That is, it is exactly the same as Ruedenberg’s kinetic-energy pressure. On the other hand,  $\frac{\partial \langle V \rangle}{\partial R}$  is the sum of Eqs. 5, 6, and 7, which is called here “potential-energy force”.

When the internuclear distance is 8au ( $1\text{au} \doteq 0.529\text{\AA}$ ), the kinetic energy force shows the positive values. Since the direction of the increasing distance  $R$  is taken as positive, the kinetic-energy forces are negative towards shortening distance, i.e., attraction, to the direction where the internuclear distance becomes short. Look at the potential-energy force. Conversely to the kinetic-energy force, the potential-energy forces are negative around 8au, i.e., repulsive force. This tendency continues till the distance becomes 5au.

In the internuclear distance shorter than 5au, a completely reverse result is brought. The kinetic energy force shows repulsive against the distance becoming short, and potential energy power shows attraction. And the distance where such forces balance is the optimization structure.

The above results clearly reproduce that of Ruedenberg. The advantage of the method of "force" is that the roles of the kinetic energy and potential energy in the point are known immediately, when the internuclear distance is given. The analysis result about a hydrogen molecule was also performed in the same literature<sup>2)</sup>.

## 2. An Analysis on Conjugation between $\pi$ System and Substituent

The OH group and singlet carbene are used as electron-donating and electron-withdrawing substituents to the vinyl group as a  $\pi$  electron system. When analyzing a chemical reaction theoretically, the potential-energy surfaces from the initial to final states are analyzed. There are several paths considered: IRC (Intrinsic Reaction Coordinate), Steepest Descent Path, and Minimum Energy Path. Since in these processes, the virial theorem ( $\langle V \rangle = -2\langle T \rangle$ ) does not hold except the initial and final states, the roles of the constituents of the total energy are easily known. Contrarily, there is the path called Zero Virial Path (ZVP),<sup>6)</sup> in which the virial ratio ( $\langle V \rangle = -2\langle T \rangle$ ) always holds in the reaction path. This path is shown to exist, at least one, in any reaction.

Since in the ZVP the virial ratio always holds, the role of the energy components cannot be known. However if one uses partial differentials, such an analysis is easily carried. The followings are examples of analysis on ZPV.

### Vinyl alcohol

The angle between the plane of the vinyl group and that of the C-O-H group is expressed by  $\theta$  (Fig. 1). In the *cis* structure ( $0^\circ$ ), the total energy becomes lower than that of the *trans* structure

(180°). The cause is considered to be brought for the by germinal "steric hindrance" of H attached to C<sub>1</sub>. If one analyzes the forces, the cause can be specified easily, but since it is not our purpose here, I will not go deep.

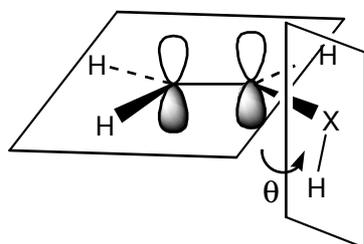


Fig. 1. Definition of the angle between the vinyl group and the XH plane (X=O or C) .

In the angles at 30° and 60°, the forces by the kinetic energy indicate positive values. Since the sign towards increasing is positive, the force works to the direction from which the C-O-H plane returns to 0°. That is, the reason that vinyl alcohol is a planar structure or consequently the reason of conjugation is due to the fall of the electronic-kinetic energy.

Table 2. Partial Differentials of Energy Components as OH rotates along C-O Axis

$\theta$ in degree	$E$ in Hartree	$\langle T \rangle$ in Hartree	$\langle V \rangle$ in Hartree	$\partial \langle T \rangle / \partial \theta$ milliHaree/Rad	$\partial \langle V \rangle / \partial \theta$ milliHaree/Rad	$\partial E / \partial \theta$ milliHaree/Rad
0(cis)	-152.955250	152.953414	-305.908664	0.0	0.0	0.0
30	-152.953340	152.951500	-305.904840	29.2	-22.7	6.5
60	-152.949828	152.948117	-305.897945	26.9	-21.5	5.4
90	-152.948695	152.947116	-305.895811	-7.6	6.5	-1.1
120	-152.950356	152.948909	-305.899265	-34.5	30.2	-4.3
150	-152.952353	152.951198	-305.903551	-29.5	26.7	-2.8
180(trans)	-152.953060	152.952022	-305.905082	0.0	0.0	0.0

### Vinyl Carbene

As for vinyl carbene, the total energy of the *trans* structure (180°) becomes slightly lower than that of the *cis* structure. The forces by the kinetic energy from 30° to 90° show the negative values and the positive values in the forces of the potential energy.

Contrary to the case of vinyl alcohol, it turns out that the force by the potential energy caused the planarity of the molecule. It can also be known by the analysis of population that  $\pi$  electrons flow into carbene from the  $\pi$  electronic system at the time of the plane structure.

Table 3. Partial Differentials along Rotation of the C-C Axis in Vinylcarbene

$\theta$	$E$	$\langle T \rangle$	$\langle V \rangle$	$\partial \langle T \rangle / \partial \theta$	$\partial \langle V \rangle / \partial \theta$	$\partial E / \partial \theta$
in degree	in Hartree	in Hartree	in Hartree	milliHaree/Rad	milliHaree/Rad	milliHaree/Rad
0(cis)	-115.817097	11.814471	-231.631568	0.0	0.0	0.0
30	-115.816601	115.814058	-231.630659	-32.5	36.0	3.5
60	-115.811266	115.808778	-231.620044	-11.8	28.3	16.5
90	-115.806924	115.804590	-231.611513	-29.7	26.4	-3.3
120	-115.813900	115.811802	-231.625702	33.1	-51.6	-18.5
150	-115.819390	115.817032	-231.636422	53.1	-57.1	-4.0
180(trans)	-115.820129	115.817600	-231.637729	0.0	0.0	0.0

Concerning above results, before the idea of the analysis by forces came out, using aniline and nitrobenzene, the relationship between the kinetic energy and, the potential energy when the plane of the substituent groups along the benzene plane are rotated has been analyzed to give the following results: conjugation of aniline is brought forth by lowering the kinetic energy due to the lone electron-pair electrons of N flowing into the benzene ring, and this conjugation is named "conjugation of the kinetic-energy origin." <sup>7)</sup> On the other hand, in nitrobenzene,  $\pi$  electrons of benzene flow into electron-deficient N, lowering the potential energy. This causes the conjugation which is named "the conjugation of potential-energy origin."

- 1) Virial theorem. In a stationary state, the ratio ( $-V/T$ ) of the kinetic energy ( $T$ ) and potential energy ( $V$ ) of the system is exactly 2. This is realized in both quantum mechanical as well as classical systems. In any molecular orbital theory, if the virial theorem is not materialized theoretically, it is deficient as a theory, and it cannot be used for the mechanical analysis of a system. This theorem holds for the HF method if complete system is used as a basis function.
- 2) Tokiwa, H.; Ichikawa, H.; Osamura, Y. J. Chem. Phys. 1992, 96, 6018.
- 3) Ruedenberg, K. Rev. Mod. Phys. 1962, 34, 326.
- 4) Kinetic energy pressure is the concept that Ruedenberg used. If an electron is confined in narrow space, it will try to spread by the uncertainty principle. Probably, this concept was used from the character which resembled gas.
- 5) Tokiwa, H.; Osamura, Y.; Ichikawa, H. Chem. Phys. 1993, 28, 181.
- 6) Nelander, B. J. Chem. Phys. 1969, 51, 469; Nalewajski, R. F. Int. J. Quantum Chem. 1978, 12, 87.
- 7) Ichikawa, H.; Ebisawa, H.; Sameshima, K. Bull. Chem. Soc. Jpn. 1988, 61, 659.