Topology of density difference and force analysis

I. Homopolar bond formation

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Abstract. The density difference $\Delta\rho(r)$ of a molecule A–B is defined as the difference of the density $\rho(r)$ of the molecule A–B and the density $\rho_A(r) + \rho_B(r)$ put at the position of the atoms A and B. We investigate here the topological features of the density difference and define electron density flow (EDF) as representing the direction and the amount of the electron density flow in the course of the nuclear displacement processes. As such examples, we study H_2 molecule formation reaction and the interaction of two He atoms. By the topological analysis of $\Delta\rho(r)$, and by using the Hellmann–Feynman force and its partition into the AD, EC, and EGC forces, the characteristic behaviors of the $\Delta\rho(r)$ map are clarified. In particular, the electron cloud preceding and incomplete following are represented by using the concept of the EDF. The natures of the covalent bond are clarified based on the topological properties of the difference density $\Delta\rho(r)$ rather than that of the total density $\rho(r)$.

Key words: Electron density difference – Topological analysis – Hellmann – Feynman force

1. Introduction

The view of chemical bond has been presented in many different standpoints by many chemists and physicists. Among others, one of the present authors established the electrostatic force (ESF) theory for molecular geometry and chemical reaction [1–3] on the basis of the Hellmann–Feynman (H–F) force concept. He also clarified a general behavior of electron density, electron-cloud preceding and incomplete following, in the course of the nuclear rearrangement processes [3, 4]

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like chemical reactions. Bader and his collaborators presented the topological analysis of the electron density [5, 6]. They defined an atom in a molecule and discussed the bond formation in terms of molecular charge distributions $\rho(r)$. Bader and Chandra [7] studied the density difference $\Delta\rho(r)$ along the bond formation process and analyzed the force acting on the nuclei along the process.

This paper concerns with the characters of the density difference during the chemical reaction. We examine the covalent bond formation and its qualitative properties by using the concept of the difference density $\Delta\rho(r)$ and the H–F force. From the $\Delta\rho(r)$ surface, we can obtain many new information about the molecule. This is the reason why we pay more attention to $\Delta\rho(r)$ rather than $\rho(r)$.

2. Density difference and the H–F force

We define *density difference*, or *difference density* $\Delta\rho(r)$ as

$$\Delta\rho(r) = \rho_{AB}(r) - [\rho_A(r) + \rho_B(r)]. \tag{1}$$

$\rho_{AB}(r)$ is the electron density $\rho(r)$ of the molecule A–B at the distance R_{AB}, and $\rho_A(r)$ and $\rho_B(r)$ are the electron density of the separated atoms or the fragments A and B placed at the same positions as in the A–B molecule. We call the density difference $\Delta\rho(r)$ given by Eq. (1) as *molecule formation density difference* (MFDD) and $\rho_A + \rho_B$ as the *density of model system*.

According to the H–F theorem, the force acting on nucleus A is represented by

$$F_A = Z_A \int \rho_{AB}\, r_A/r_A^3\, dr - Z_A Z_B R_{AB}/R_{AB}^3. \tag{2}$$

Nakatsuji partitioned the H–F force into the atomic dipole (AD), exchange, (EC), and extended gross charge (EGC) forces for developing the electrostatic force (ESF) theory for molecular geometries and chemical reactions [1, 3].

$$F_A = \text{AD force} + \text{EC force} + \text{EGC force}. \tag{3}$$

On the other hand, by introducing the "quasi-classical force" (F_A^{cl}) and the "interference force" (F_A^i) [1] from the Ruedenberg partition of the electron density [8], the force F_A is written as

$$F_A = F_A^{cl} + F_A^i, \tag{4}$$

where F_A^{cl} and F_A^i are given by

$$F_A^{cl} = Z_A \left\{ \sum_{\mu_B} N_{\mu_B} \langle \chi_{\mu_B} | r_A/r_A^3 | \chi_{\mu_B} \rangle - Z_B R_{AB}/R_{AB}^3 \right\} \tag{5a}$$

and

$$F_A^i = Z_A \left\{ \sum_{\mu_A} \sum_{\nu_A (\nu \neq \mu)} P_{\mu_A \nu_A} \langle \chi_{\mu_A} | r_A/r_A^3 | \chi_{\nu_A} \rangle + 2 \sum_{\mu_A} \sum_{\nu_A} P_{\mu_A \nu_B} \langle \chi_{\mu_A} | r_A/r_A^3 | \chi_{\nu_B} \rangle \right\}. \tag{5b}$$

Here N_μ is the occupation number of the atomic orbital χ_μ and $P_{\mu\nu}$ is the density matrix element between AO's χ_μ and χ_ν. F_A^{cl} is the EGC force defined by Nakatsuji [1, 4]. Introducing the approximation

$$\langle \chi_{\mu_B} | r_A/r_A^3 | \chi_{\mu_B} \rangle \sim 1/R_{AB}^2$$

F_A^{cl} becomes $Z_A(N_B-Z_B)/R_{AB}^2$. The first term of the interference force is the AD force and the second one the EC force [1, 4]. The AD force is created by the polarization of the electron density belonging to the atom A. The EC force represents the force due to the electrons accumulated or destructed in the A–B region by the exchange interaction.

Now let us define the force for the density of the model system as

$$F_A^m = Z_A \int (\rho_A + \rho_B)r_A/r_A^3 \, dr - Z_A Z_B R_{AB}/R_{AB}^3. \tag{6}$$

The AD force of the model system is zero since ρ_A is spherical around the nucleus A. The EC force is also zero since $P_{\mu_A \nu_B}$ is zero for the model system. Therefore, F_A^m should be identical with the EGC force which is small. This result could be easily understood from its physical meaning. In the model system, there is no exchange and polarization in the electron cloud of the two atoms. Thus,

$$F_A - F_A^m = \int \{\rho_{AB} - (\rho_A + \rho_B)\}r_A/r_A^3 \, dr$$

$$= \int \Delta\rho(r)r_A/r_A^3 \, dr$$

$$= F_A^i. \tag{7}$$

Thus, the MFDD $\Delta\rho$ causes the interference force which represents the AD and EC forces. From the ESF theory the origin of most chemical phenomena is attributed to the AD and EC forces and therefore, in the density approach, the difference density $\Delta\rho(r)$ is important to investigate molecular geometries and chemical reactions.

We can define

$$\Delta\rho(r) = \rho(\text{state } 1) - \rho(\text{state } 0), \tag{8}$$

if two states have the same geometry. For example, state 0 is the ground state and state 1 is a vertical excited state. This $\Delta\rho$ is called state transition density difference (STDD). The MFDD may be viewed as a special example of the STDD: the model molecule may be looked upon as a "ground state" and the real molecule as an "excited state" of the model molecule.

Thus, it is clear that the most essential information for understanding chemistry is involved in the difference density $\Delta\rho(r)$ rather than the density $\rho(r)$ itself. We therefore study the topological feature of the $\Delta\rho(r)$ map in detail.

3. Topology of the difference density surface

Here, we extend the topological analysis of the density $\rho(r)$ given by Bader [5, 6] to the density difference $\Delta\rho(r)$. Similarly to the Laplacian density $L(r)$

$$L(r) = -\nabla^2 \rho(r), \tag{9}$$

we define Laplacian difference density $LD(r)$ by

$$LD(r) = -\nabla^2 \Delta\rho(r), \tag{10}$$

The $\Delta\rho(r)$ surface is more complex than the $\rho(r)$ surface. On the $\Delta\rho(r)$ surface, there are positive and negative areas and there are eight kinds of critical points. The definition of the critical point r_c is given by the condition,

$$|\nabla \Delta\rho(r)|_{r=r_c} = 0. \tag{11}$$

Similar to the critical points on the $\rho(r)$ surface [9], the critical points on the $\Delta\rho(r)$ surface are denoted by $(3, +3)$, $(3, +1)$, $(3, -1)$, and $(3, -3)$ which lie on the positive or negative area. We distinguish such a character of the critical point by $+$ or $-$ sign given as a superscript, for example, $(3, +3)^+$ or $(3, +3)^-$.

Here, we discuss the physical meaning of these critical points.

$(3, -3)^+$: At this point, the value of the density difference is maximal. It means that the electron density is most accumulated at this point as a result of the interaction. If this point precedes beyond the nuclear position in the direction of the reaction coordinate, it is the "electron-cloud preceding" and the reaction is accelerated [4]. On the contrary, if the point is behind the nuclear position along the reaction coordinate, it is the "electron-cloud incomplete following" and the reaction is retarded [4].

$(3, +3)^-$: At this point, the value of the density difference is minimal. It is the most negative point in the negative region. The physical meaning is just opposite to that of the $(3, -3)^-$ point. All the gradient paths starting from the $(3, -3)^+$ point can be linked to the $(3, -3)^-$ point, if the two regions containing the two critical points are in a neighbourhood. We define *electron density flow* (*EDF*) to be the gradient paths connecting from $(3, +3)^-$ to $(3, -3)^+$. The EDF paths could be understood as showing an imaginative description how the electron density flows in the course of the reaction.

$(3, -1)^+$: This is a saddle point on the $\Delta\rho$ surface. In the topological theory of $\rho(r)$, the $(3, -1)$ critical point means the existence of bonding. We use this saddle point on the $\Delta\rho(r)$ surface to clearly describe the characteristics of the homopolar bond as discussed in Section 5.

$(3, +1)^-$: this saddle point lies in the negative region and the meaning is just opposite to that of the $(3, -1)^+$ point.

4. Force and $\Delta\rho$ for homopolar system

In this section, we apply the topological analysis of the $\Delta\rho$ map to the homopolar systems, H_2 and He_2, the most primitive systems. Two atoms approach from an infinite separation to a small distance. We investigate the $\Delta\rho$ map, the force acting on the nuclei, and the bonding nature.

The H–H and He–He systems were calculated by the full CI method with the following basis sets. H: [3s1p] STO's with $\zeta_{1s} = 0.965$, $\zeta_{2s} = 2.430$, $\zeta_{3s} = 1.160$, and $\zeta_{1p} = 1.870$ [10] and at $R_{HH} > 6$ a.u., $\zeta_{1s} = 1$; He: [3s] STO-6G with $\zeta_{1s} = 1.450$, $\zeta_{2s} = 2.641$, and $\zeta_{3s} = 1.723$ [11]. The derivative bases are added to these AO's, so that the H–F theorem is essentially satisfied [12] as the full CI method is used. We therefore perform the force analysis as proposed previously [1].

The atoms A and B are put on the z-axis with $+z$ being the direction of the reaction coordinate for the atom A.

Hydrogen molecule formation

We calculate the energy and the density of the hydrogen molecule H_2 for several H–H distances from 10 a.u. to 1 a.u. The reaction coordinate Q is the internuclear distance R_{AB} in the direction of A → B. We obtained the $(3, -3)^+$ and $(3, +3)^-$ critical points on the $\Delta\rho(r)$ surface at different coordinates and the results are listed in Table 1. Figure 1 shows the EDF on the $\Delta\rho$ map of the H–H system. The graphs could be divided into five kinds.

At $R_{AB} = 10$ a.u., the $(3, +3)^-$ point is behind the nucleus A and the $(3, -3)^+$ point exists ahead the nucleus A, though the value of $\Delta\rho$ is very small. At the center of the two atoms, no accumulation of the density occurs; the center is not a critical point. The EDF is from the point closely back of the nucleus to the point closely ahead of the nucleus. The EDF occurs within each hydrogen atom to produce a polarization of the atomic density in the direction of the reaction coordinate, i.e., to produce the electron cloud preceding within the atomic region as clearly seen from the $\Delta\rho$ map shown in Fig. 1a. Therefore, the AD force is created by this small separation of the $(3, -3)^+$ and $(3, +3)^-$ points, which is the polarization of the atomic density. This is just the origin of the long-range force between the two hydrogen atoms as previously shown by Nakatsuji and Koga [2]. The AD force drives the nucleus A to go forward along the reaction coordinate Q.

As the reaction proceeds further ($R_{HH} = 6$ a.u., 3 a.u.), the $(3, -3)^+$ point moves toward the center of the two H atoms and the $(3, +3)^-$ point toward a little distance *ahead* of the nucleus A as seen from Table 1. At $R = 6$ a.u., the $(3, -3)^+$ point is close to the center, but not at the center: the center is $(3, -1)^+$ point. At $R = 3$ a.u., the center is $(3, -3)^+$ point. Thus, the density at $R = 6$ a.u. have the transient nature between say the Van der Waals nature and the covalent bond nature. The EDF is from the point closely ahead of the nucleus to these $(3, -3)^+$ points in the mid of the two nuclei. The total direction of the EDF is to the mid of the system which shows the electron cloud proceeding. This EDF and proceeding cause an accumulation of the electron density in the atomic and overlap regions within the two protons and the AD and the EC forces increase up. At $R = 6$ a.u., the $\Delta\rho$ increases both in the atomic and overlap regions and the AD and EC forces are comparable. At $R = 3$ a.u., the value of $\Delta\rho$ increases in the overlap region, so that the EC force becomes dominant.

At $R = 2$ a.u., both $(3, -3)^+$ and $(3, +3)^-$ points exist behind the nucleus A as seen in Table 1; the $(3, +3)^-$ point moves away from the nucleus by about 1.3 a.u. Then the EDF divides itself into two branches, one to the center of the molecule, and the other to the point behind the nucleus by 0.138 a.u. This structure is the transition structure of the EDF. However, the direction from $(3, +3)^-$ to $(3, -3)^+$ is positive, and therefore the AD force is positive. Also, in the mid of the molecule, the $(3, -3)^+$ point exists and $\Delta\rho$ value is larger so that it contributes to the attractive EC force which is dominant. These clearly show the occurrence of the electron cloud proceeding.

The situation at $R_{AB} = 1.4$ a.u., which is just nearby the equilibrium geometry, is similar to that at $R = 2$ a.u. The $(3, +3)^-$ point is outside and separated by 1.463 a.u. from the nucleus. The $(3, -3)^+$ point behind the nucleus is very close to the nucleus. The critical point at the center of the bond is $(3, -1)^+$ for the distance smaller than $R = 1.4$ a.u. Therefore the EDF is a preceding but it is not so evident. As the two H atoms close up, the repulsive EGC force increases. The total H–F force acting on proton is close to zero.

Table 1. $\Delta\rho(r)$ and its critical points for the H–H system and the H–F force (a.u.)[a]

R_{AB}	$(3, -3)^+ (3, +)^-$ critical points						H–F force			
	z_A	$\Delta\rho$	z_A	$\Delta\rho$	z_A^b	$\Delta\rho^b$	AD	EC	EGC	Total
10	-0.0007	-0.5E-5	+1.1174	+0.28E-6	+3.0	+0.0001	0.5E-5	0.5E-6	0.0	0.5E-5
6	+0.0910	-0.0008			+1.5	+0.0067	0.0004	0.0005	-0.2E-4	0.0009
3	+0.0412	-0.0024			+1.0	+0.0127	0.0151	0.0447	-0.0059	0.0539
2	-0.1384	+0.0090	-1.3057	-0.0021	+0.7	+0.0431[c]	0.0384	0.0909	-0.0418	0.0875
1.40	-0.0017	+0.0824	-1.4630	-0.0028	+0.6	+0.0727[c]	0.0452	0.1222	-0.1733	0.0059
1.20	+0.0088	+0.1340	d		+0.5	+0.1267[c]	0.0486	0.1332	-0.2980	-0.1162
1	+0.0124	+0.2111	e				0.0515	0.1468	-0.5355	-0.3372

[a] z_A is the vector pointing the $(3, -3)^\pm$ point from the nucleus A along the z-direction

[b] This is at the center of the H–H axis

[c] These are the $(3, -1)^+$ critical points

[d] The $(3, +3)^-$ critical point is at $x = 1.364$, $z_A = -0.643$

[e] The $(3, +3)^-$ critical point is at $x = 1.644$, $z_A = +0.500$ $(z = 0)$
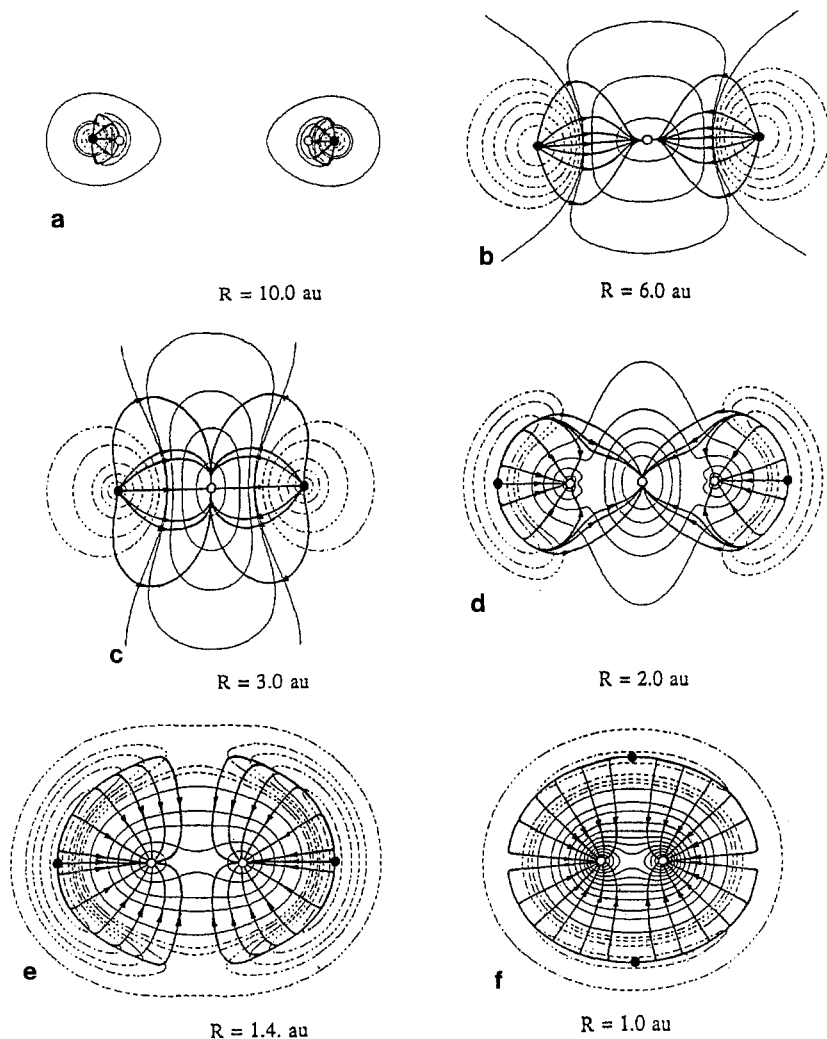
Fig. 1. The EDF curves shown over the density difference $\Delta\rho(r)$ contour map for the H_2 system. Real arrows show the EDF curve, and real and broken lines the positive and negative contours of the $\Delta\rho(r)$ map, respectively. Open and filled circles show the $(3, +3)^+$ and $(3, -3)^-$ positions, respectively. For the position of the H atom see Table 1

At $R_{AB} < 1.4$ a.u., the absolute value of the EGC force becomes greater and greater, due to an increase in the nucleus–nucleus repulsion, but the values of the AD and EC forces are almost constant, so that the total H–F force becomes strongly repulsive. At $R_{HH} = 1$ a.u. the $(3, +3)^-$ point exists interestingly at $z = 0$ (the center of H_2) but vertical to the molecular axis, the distance from the center to the point being $x = 1.644$ a.u. The total EDF becomes opposite to Q and therefore represents the electron-cloud incomplete following. This works to retard the reaction.

Thus, the $\Delta\rho$ map, the critical points on the $\Delta\rho$ map, the EDF, and the AD, EC, and EGC forces clearly show the occurrence of the electron-cloud proceeding in

the range $R_{HH} \geqslant$ Req (1.4 a.u.), and at R smaller than Req, the electron-cloud incomplete following is observed which works to retard the reaction. We note that as the covalent bond is formed the $(3, -3)^+$ point (maximal density point) at the bond center is transformed to the $(3, -1)^+$ point, a saddle point which is also favorable to the EC force. The topological features of the $\Delta\rho$ map and the EDF analysis are thus very valuable for understanding the formation of the homopolar covalent bond.

He–He interaction

We show in Table 2 some topological features of the $\Delta\rho$ map, the H–F force, and its analysis for the He–He system for R from 3 to 1.5 a.u. The EDF curve and the $\Delta\rho$ contour map are shown in Fig. 2.

As the two He atoms approach together from $R = 3$ a.u., the $\Delta\rho$ surfaces are always of the same type. The critical points, the density there and the various forces show monotonous behaviors. The electron density decreases from the internuclear region: the $(3, +3)^-$ point is only at the center of the two atoms. The increase of electron density is observed in the atomic region: the $(3, -3)^+$ points are nearby and behind nuclei. The directions of the EDF are always opposite to the reaction coordinate Q. Thus, the $\Delta\rho$ map represents the electron-cloud incomplete following, which is the density origin of the repulsive force in the He–He system. The decrease of the density in the bond region causes the repulsive EC force (exchange repulsion). All the EDF curves show the electron density incomplete following and causes the AD and EC forces which work to separate the two He atoms.

5. $\Delta\rho(r)$ and the covalent bond

Everyone knows that two hydrogen atoms are combined by a covalent bond. But the evidence of the existence of the covalent bond (EECB) would not be clear from the topological analysis of the total density $\rho(r)$ surface. For example, the existence of the $(3, -1)$ saddle point on the $\rho(r)$ map between the two atoms does not help to describe whether the covalent bond exists or not, because even the model density $\rho A + \rho B$ of H_2 at $R = 1.4$ a.u. has a $(3, -1)$ critical point at the center of the bond. Though this may be thought to satisfy the condition of the covalent bond, there is no bond actually in the model system. Therefore, the EECB should be given in terms of the difference density $\Delta\rho(r)$, not by the total density $\rho(r)$.

We list in Table 3 the topological properties of the critical points r_c at the center of the H_2 and He_2 systems. For H_2, the center r_c is the $(3, -3)^+$ maximal point for R_{AB} larger than and equal to 2 a.u., but it is the $(3, -1)^+$ saddle point for R_{AB} smaller than 1.4 a.u. For He_2, the mid of the atoms is always the $(3, +3)^-$ minimal point. We have plotted in Fig. 3 the curves of the Laplacian difference density $LD(r)$ defined by eq. (10) along the axis of these molecules. For H_2 at $R = 3$ a.u., a small (positive) peak exists on the $LD(r)$ curve at the center of the molecule. At $R = 2$ a.u., the shape of the $LD(r)$ curve has both characteristics of those at $R = 3$ and 1.4 a.u. It has peaks at the center of the bond and at the atomic region. At $R = 1.4$ a.u., there are two peaks of $LD(r)$ between the two nuclei and each of them are close to the nucleus. At both $R = 1.4$ and 1.2 a.u., there is no peak of the $LD(r)$ at the center of the bond.

For He_2, the character of the $LD(r)$ curve is roughly the same for all the separations: we show an example at $R = 2$ a.u. in Fig. 3e. Though there are two

Table 2. $\Delta\rho(r)$ and its critical points for the He–He system and the H–F force[a]

R_{AB}	(3, −3)+ (3, +3)− critical points					H–F force				
	z_A	$\Delta\rho$	z_A	$\Delta\rho$	z_A^b	$\Delta\rho^b$	AD	EC	EGC	Total
3.00	+ 0.0325	+ 0.0251	− 0.0741	+ 0.0158	+ 1.5	− 0.0063	− 0.0013	− 0.0267	− 0.0028	− 0.0308
2.50	+ 0.0338	+ 0.0571	− 0.0896	+ 0.0389	+ 1.25	− 0.0199	− 0.0028	− 0.0781	− 0.0128	− 0.0937
2.00	+ 0.0344	+ 0.1175	− 0.1081	+ 0.0772	+ 1.0	− 0.0590	− 0.0032	− 0.2036	− 0.0576	− 0.2644
1.75	+ 0.0351	+ 0.1537	− 0.1167	+ 0.0986	+ 0.875	− 0.0972	− 0.0091	− 0.3076	− 0.1252	− 0.4419
1.50	+ 0.0355	+ 0.1960	− 0.1242	+ 0.1132	+ 0.75	− 0.1533	− 0.0252	− 0.4211	− 0.2774	− 0.7237

[a] z_A is the vector pointing the (3, −3)± point from the nucleus A along the z-direction
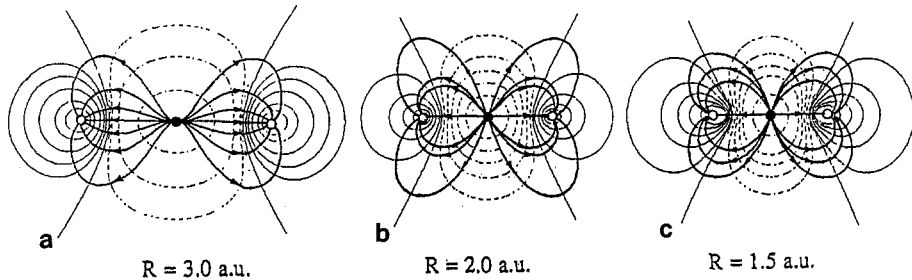[b] This is the center of the H–H axis

Fig. 2. The EDF curve and the $\Delta\rho(r)$ contour map for the He$_2$ system. the definitions of the lines and the circles are the same as those in Fig. 1. The position of the He atom is shown in Table 2

Table 3. Topological properties of the $\Delta\rho(r)$ map at the center of the H$_2$ and He$_2$ systems[a]

System	R_{AB}	$\Delta\rho$	λ_1	λ_2	λ_3	$\nabla^2\Delta\rho$	Nature of the critical point
H$_2$	6	0.0001	0.0008	− 0.0008	− 0.0003	− 0.0019	$(3, -3)^+$
	3	0.0067	− 0.0255	− 0.0255	− 0.0077	− 0.0587	$(3, -3)^+$
	2	0.0127	− 0.0517	− 0.0517	− 0.0332	− 0.1366	$(3, -3)^+$
	1.4	0.0431	− 0.2219	− 0.2219	+ 0.0985	− 0.3453	$(3, -1)^+$
	1.2	0.0727	− 0.4312	− 0.4312	+ 0.2645	− 0.5980	$(3, -1)^+$
	1	0.1267	− 0.9155	− 0.9155	+ 0.5814	− 1.2496	$(3, -1)^+$
He$_2$	2	− 0.0590	+ 0.1668	+ 0.1668	+ 0.1434	+ 0.4770	$(3, +3)^-$

[a] λ_i is the eigenvalue of the Hessian matrix at the center of A–A

peaks of LD(r) between the two nuclei close to the nuclei, the value is negative in the mid area of the two nuclei.

Thus, as the EECB, the following conditions may be listed. First, the value of $\Delta\rho(r)$ must be positive in the mid area of the molecule. Second, there should be a $(3, -1)^+$ in the mid area of the molecule.

The reason of the first condition is self-evident. We discuss the second condition. If we use the total density $\rho(r)$ of H$_2$ to discuss the covalent bond, the characters of the $L(r)$ curve defined by eq. (9) at $R < 3$ a.u. are the same as those of the LD(r) curve at $R = 1.4$ a.u. Actually, Fig. 4 gives the $\rho(r)$ curves of H$_2$ and its model system, and the $\Delta\rho(r)$ curve. When two atoms are bonding, the electron cloud should be accumulated in the bond region. The curve of $\rho(r)$ at the mid $(z = 0)$ of H$_2$ and along the x-direction should also possess larger absolute value of the second derivative. Along the z-direction, the electron cloud should also be accumulated in the mid of the molecule as the two H nuclei approach. As $R_{AB} > 2$ a.u., the covalent bond is forming, but it does not show the EECB. Only as $R_{AB} < 2$ a.u., the EECB appears. This is because the two effects are cooperative: one is the accumulation of the electron cloud in the bond region and the other is the electron cloud contraction towards the nuclei.

In the topological analysis of $\rho(r)$, the peak of L(r) (see Fig. 5) means the electron accumulating point. However, such point exists even in the model density.
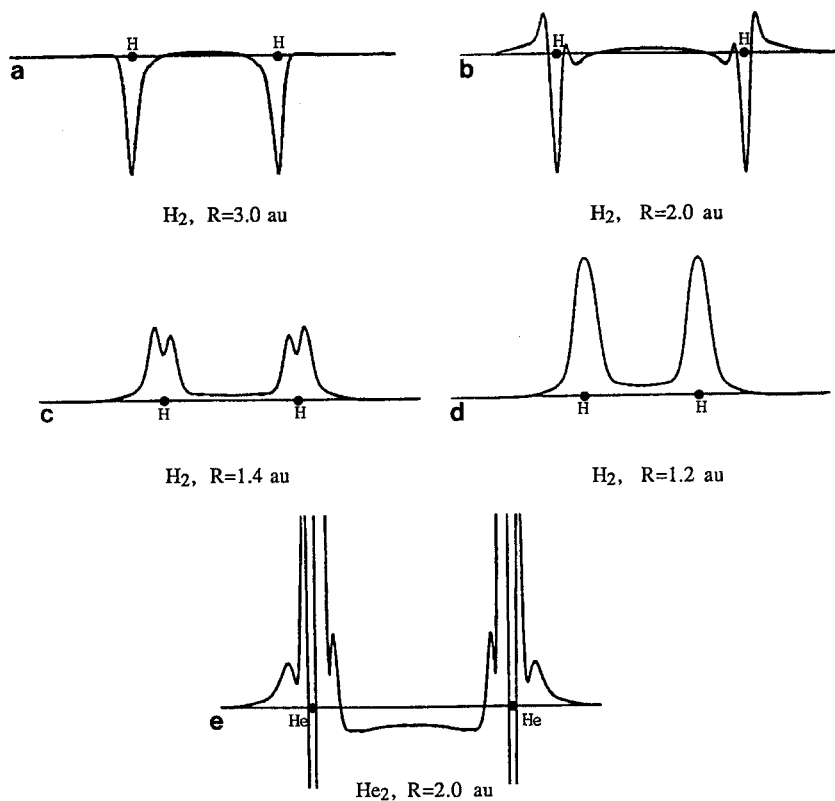
Fig. 3a–e. The LD(r) curves of H_2 at different R, (a) 3 a.u., (b) 2 a.u., (c) 1.4 a.u., and (b) 1.2 a.u., and (e) the LD(r) curve of He_2 at $R = 2$ a.u. Open and filled circles show the $(3, +3)^-$ and $(3, -3)^+$ points, respectively
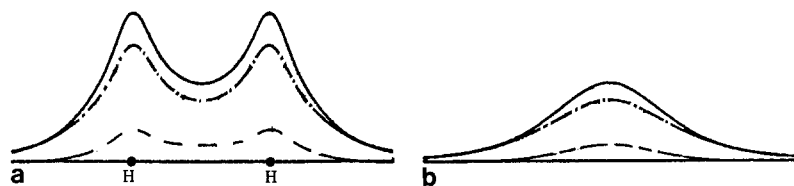

Fig. 4a, b. $\rho(r)$ curve of H_2 molecule (real line), $\rho(r)$ curve of H_2 model system (real dotted line), and $\Delta\rho(r)$ curve of H_2 molecule (broken line) for $R = 1.4$ a.u. (a) along the z-axis (b) along the x-axis passing the center of the bond. Open and filled circles show the $(3, +3)^-$ and $(3, -3)^+$ points, respectively

Therefore, we should subtract the contribution of the model system and the $\Delta\rho(r)$ map reflects the electron exchanging effect more sensitively than the $\rho(r)$ map. In this way, we could judge the EECB from the $\Delta\rho(r)$ map.

6. Summary

In this paper we have studied the topological properties and the behaviors of the difference density $\Delta\rho(r)$ and applied it to the hydrogen molecule formation reaction
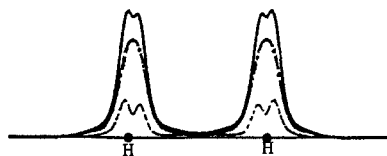
Fig. 5. $L(r)$ curve of H_2 molecule (real line), $L(r)$ curve of H_2 model system (real dotted line), and $LD(r)$ curve of H_2 molecule (broken line) for $R = 1.4$ a.u. Open and filled circles show the $(3, +3)^-$ and $(3, -3)^+$ points, respectively

and to the He–He interacting system. The results may be summarized as follows.
(1) The $(3, +3)^-$ and $(3, -3)^+$ points occurring behind and ahead of the nucleus in the H–H system, at long R, cause the AD force. This polarization of density is the electron-cloud preceding in the atomic region and is the origin of the long-range force.
(2) The $(3, -3)^+$ and $(3, +3)^-$ points appearing in the A–A bond region is the origin of the EC force. If the $(3, +3)^-$ point is at the center of the bond, the exchange repulsion occurs and if the $(3, -3)^+$ point is there, the electron density is accumulated in the bond region by the electron exchange. These behaviors correspond to the electron-cloud incomplete following and preceding, respectively. As the covalent bond is formed, the $(3, -3)^+$ point may be transformed to $(3, -1)^+$, a saddle point which is also favorable to the EC force.
(3) The EDF curve could give a better description for understanding how the electron cloud is reorganized along the reaction, and the total direction of the EDF is the direction of F_A. Then, we can understand the electron-cloud preceding and incomplete following from the EDF curves.
    The evidence of the existence of the covalent bond (EECB) is not necessarily trivial and need to be defined. We have given such definition based on the present analysis of the difference density. We summarize the results as follows.
(4) The density difference $\Delta \rho(r)$ gives a better way of studying the covalent bond and its formation process than $\rho(r)$ itself, since it eliminates the non-bonding factors in the model density.
(5) To define the evidence of the existence of the covalent bond (EECB) it is necessary to study chemical reactions involving covalent bond creation and breaking. This definition is done more clearly with the use of the difference density $\Delta \rho$ than the use of the total density $\rho(r)$.

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