Modified Bond Eigenfunction Method of Constructing Potential Energy Surface of Reaction. II. Application to the Hydrogen Atom-Molecule Reaction

By Iwao YASUMORI

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A new method of constructing the potential energy surface of a chemical reaction was presented in the previous paper and some remarks on the procedure of application were also given. In order to examine its availability, the method is effectively applied to the hydrogen atom-molecule reaction, since much theoretical and experimental knowledge has been accumulated on its component species, H_2 and H.

As is well known, the potential energy surfaces of this reaction have been evaluated by Hirschfelder et al.[1] in a purely theoretical manner and by Eyring et al.[2] semi-empirically. Also, recently several investigators[3] have given some considerations about this system from the standpoint of molecular orbital method.

In this paper, besides the examination of the applicability of the method, surface properties obtained here are discussed comparing them with those obtained in the previous works. Calculation of reaction rate based on the surface is carried out also.

Composite Wave Functions

We denote three hydrogen atoms in the systems, *A*, *B* and *C*, and, for simplicity, confine ourselves to the lowest surface of linear configuration. Therefore, it is assumed that the reaction proceeds by the equation

$$H_AH_B + H_C \rightarrow H_A + H_BH_C$$

on a straight line.

According to the considerations given in Paper 1, the total wave function which expresses the state with the total spin $S=1/2$ and its component $S_z=1/2$ is described as follows:

$$\begin{aligned}\Psi=\sum_{m=1}^{3} C_m\psi_m = {} & C_1\boldsymbol{A}\varphi_{AB}(1,2)\varphi_C(3)\\ & \times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ & +C_2\boldsymbol{A}\varphi_{BC}(1,2)\varphi_A(3)\\ & \times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ & +C_3\boldsymbol{A}\varphi_{CA}(1,2)\varphi_B(3)\\ & \times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\end{aligned} \tag{1}$$

where each term represents the composite functions for bond structures $AB+C$, $BC+A$ and $CA+B$, respectively. In the equation, $\varphi_{AB}(1,2),\cdots$ are $^1\Sigma^+_g$ orbital functions of H_2 and $\varphi_c(3),\cdots$ are atomic 1*s* orbital functions of hydrogen. Spin functions $\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$ and $\alpha(3)$ correspond to singlet state of molecule and doublet state of atom, respectively. There are many higher energy states which correlate to the lowest surface such as $H_2(^{1,3}\Sigma^+)+H(^2S_g, {}^2P_u)$, $H_2(^{1\,3}\Pi)+H(^2P_u)$, etc. But all these composite states were excluded in the present calculation[4], since, apart from the simplification of procedure, their contributions to the energy of the lowest state are rather small and also some of them are hardly available because of the lack of experimental data.

By the operation of antisymmetrizer,

$$\boldsymbol{A}=\frac{1}{\sqrt{3}}\Sigma_t P_t v_t \tag{2}$$

each composite function is expressed as

$$\begin{aligned}\psi_1=&\frac{1}{\sqrt{6}}\varphi_{AB}(1,2)\cdot\varphi_C(3)\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3)\\ &+\frac{1}{\sqrt{6}}\varphi_{AB}(2,3)\cdot\varphi_C(1)\{\alpha(2)\beta(3)-\alpha(3)\beta(2)\}\alpha(1)\\ &+\frac{1}{\sqrt{6}}\varphi_{AB}(3,1)\cdot\varphi_C(2)\{\alpha(3)\beta(1)-\alpha(1)\beta(3)\}\alpha(2)\end{aligned} \tag{3}$$

and so on. The determinant, from which energy values for all configurations of atoms are deduced, is described as

$$\text{Det.}\ |I_{mn}+(\varepsilon_{mn}-\varepsilon)S_{mn}|=0 \qquad m,n=1,2,3 \tag{4}$$

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[1] J. O. Hirschfelder, N. Rosen and H. Eyring, *J. Chem. Phys.*, **4**, 121 (1936).

[2] J. O. Hirschfelder, H. Eyring and B. Topley, ibid., **4**, 170 (1936).

[3] J. M. Walsh and F. A. Matsen, ibid., **19**, 526 (1951); V. Griffing and J. T. Vanderslice, ibid., **23**, 1035 (1955); G. E. Kimball and J. G. Trulio, ibid., **28**, 493 (1958).

[4] However, the composite states $H_2(^3\Sigma_u^+)+H(^2S_g,1s)$, are automatically included in the wave function. See Paper I.

where
$$S_{mn}=\int\bar{\psi}_m\psi_n\mathrm{d}\tau \tag{5}$$

$$I_{mn}=\int\bar{\psi}_m\boldsymbol{I}_n\psi_n\mathrm{d}\tau \tag{6}$$

When we take the lowest state of free atoms 3H as a standard of energy of system, bond energies of species are given by

$$\varepsilon_{m1}=\varepsilon_{\mathrm{H}_2}(AB),\quad \varepsilon_{m2}=\varepsilon_{\mathrm{H}_2}(BC),\quad \varepsilon_{m3}=\varepsilon_{\mathrm{H}_2}(CA)$$
$$m=1,2,3$$

and interaction operators $\boldsymbol{I}_n$'s are also defined as

$$\boldsymbol{I}_1=\boldsymbol{H}-\boldsymbol{H}_{AB}-\boldsymbol{H}_C \tag{7}$$
$$\boldsymbol{I}_2=\boldsymbol{H}-\boldsymbol{H}_{BC}-\boldsymbol{H}_A \text{ and } \boldsymbol{I}_3=\boldsymbol{H}-\boldsymbol{H}_{CA}-\boldsymbol{H}_B$$

where $\boldsymbol{H}$ is the total Hamiltonian of three electrons in the system and $\boldsymbol{H}_{AB}$ and $\boldsymbol{H}_C$ are the partial ones for molecule AB and atom C, respectively, and so on.

Molecular functions taken into the calculation are as follows:

(a) Heitler-London type function,

$$\varphi_{AB}(1,2)=a(1)b(2)+a(2)b(1)$$

where $a(1)$ and $b(2)$ are $1s$ orbital functions of hydrogen,

$$a(1)=(1/\pi)^{1/2}\exp(-r_{A1})$$
and
$$b(2)=(1/\pi)^{1/2}\exp(-r_{B2}),\text{ etc.}$$

(b) Wang type function obtained by introduction of effective nuclear charge z into the atomic orbitals of the function a,

$$a(1)=(z^3/\pi)^{1/2}\exp(-zr_{A1})\quad\text{etc.}$$

(c) Weinbaum type function composed of the above functions, that is, the covalent term, and the ionic term,

$$\varphi^{ion}{}_{AB}(1,2)=a(1)a(2)+b(1)b(2)$$

Since these functions are described by the use of atomic orbital approximation, formulae of elements I_{mn} and S_{mn} given in the Appendix of Paper I are available for the present calculation. In addition to this, it is to be noted that when we estimate the values of $\varepsilon_{\mathrm{H}_2}$ also by the use of these approximate functions, the results are reduced to those of Hirschfelder et al.1) The present method differs from theirs in the point that the interaction energies are evaluated by making use of approximate functions, while the observed values, that is, those deduced from the exact functions, are utilized for the bond energies of H_2.

Details of Calculation and Results

Detailed procedure of energy calculations which were performed by the use of approximate functions are shown below for the respective cases.

(a) Calculation of Symmetrical Linear Configuration with Heitler-London Type Function of H_2.—Making use of the formulae in the Appendix of Paper I, we can express the elements S_{mn} and I_{mn} as the sum of several molecular integrals, i. e., two-center and three-center ones. The values of two-center integrals were obtained from the tables by Kotani et al.5) and by Hirschfelder and Linnett6) (being abbreviated to L.-H. hereafter). For the three-center integrals, values of one electron integrals such as

$$(bc\mid A)=\int b(1)c(1)\frac{1}{r_{A1}}\mathrm{d}\tau_1$$

were taken from the table by Hirschfelder and Weygandt7) and values of two electron ones, for example,

$$(bc\mid a^2)=\int b(1)c(1)\frac{1}{r_{12}}a^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

were calculated in a similar way as those of Hirchfelder's1).

Also some of their values were taken from the table in the paper of Baker et al.8) Therefore, such an approximate calculation as Rudenberg-Mulliken's procedure9),

$$(bc\mid a^2)\cong\frac{1}{2}(bc)\cdot[(b^2\mid a^2)+(c^2\mid a^2)]\quad\text{etc.},$$

was not required in this case.

(b) Calculation with Heitler-London-plus-Ionic Type Function.—Strictly speaking, the coefficient of ionic term added to covalent function must be taken so as to minimize the energy value, since the ionic term is another function contributing ${}^1\Sigma^+$ state of molecule. However, the coefficient was fixed to the value, $C_{ion}=0.1607$ take from L.-H.'s work, in order only to examine the effect of electronic distribution in hydrogen molecular function. In this case, the ionic integrals of two-center type, for example,

$$(ac\mid a^2)=\int a(1)c(1)\frac{1}{r_{12}}a^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2\quad\text{etc.},$$

newly appear. The values were obtained also from the table by Kotani et al.

(c) Calculation with Wang Type Function.—At the values of effective nuclear charge in atomic orbital function, the following values were used for the calculation; (i) the values from original Wang function, $z=1.166$10) and (ii) the values from L.-H.'s work shown in Table I.

When we adopt these functions for the strict procedure of calculation, the molecular integrals which appear, are of unsymmetrical type including the atomic orbital functions with effective nuclear charge, z and $z=1$. The values of these

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5) M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "The Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955); M. Kotani, A. Amemiya and T. Simose, *Proc. Phys.-Math. Soc. Japan*, **20**, Extra 1 (1938); **22**, Extra 1 (1940).

6) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, **18**, 130 (1950).

7) J. O. Hirschfelder and C. N. Weygandt, ibid., **6**, 806 (1938).

8) R. S. Baker, H. Eyring, C. J. Thorne and D. A. Baker, ibid., **22**, 699 (1954).

9) K. Rudenberg, ibid., **19**, 1433 (1951): R. G. Parr and R. S. Mulliken, ibid., **18**, 1338 (1950).

10) S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

TABLE I. VARIATION OF z WITH INTERNUCLEAR SEPARATION IN THE WANG TYPE FUNCTION OF H_2

zR(a. u.)*	1.0	1.5	1.75	2.0	2.5	3.0
z	1.3911	1.2145	1.1388	1.0823	1.0151	1.0000

* 1 a. u. = 0.5292 Å.

unsymmetrical integrals were estimated accurately by James[11] for 1s and 2s orbitals of lithium atom and approximately be Mulligan[12] for carbon dioxide calculation. Here, for simplicity, the effective nuclear charges in all orbitals were assumed to be equally z, so as to utilize the results of calculations a) and b). The effect of this approximation will be discussed later.

(d) Calculation with Wang-plus-Ionic Type Function.—Used values of effective nuclear charge and coefficients of ionic term are as follows: (i) the values used in original Weinbaum's function[13], $z=1.193$ and $C_{ion}=0.256$ and (ii) the values obtained from L.-H's treatment of H_2 which are shown in Table II.

TABLE II. VARIATION OF z AND C_{ion} IN THE WANG-PLUS-IONIC TYPE FUNCTION OF H_2

zR(a. u.)	1.0	1.5	1.75	2.0	2.5	3.0
z	1.3976	1.2411	1.1746	1.1195	1.0472	1.0000
C_{ion}	−0.01603	0.1361	0.1664	0.1780	0.1681	0.1200

Further calculations were performed for the following cases.

(e) Effect of Varying Nuclear Charge z.—For the linear configuration of equi-distance, calculation was carried out varying z in Wang type function as $z=1.0$, 1.166, 1.3, 1.4 and 1.5, respectively.

(f) Comparison of Energy Values on Various Stages of Approximation.—The effects of various approximations such as (i) use of three-center integral values calculated by Rudenberg-Mulliken type approximation, (ii) neglect of these integrals and (iii) ii plus neglect of non-orthogonality of orbitals in S_{mn}'s, were examined utilizing Heitler-London type function for the same configuration as described in e).

(g) Variaton of Energy by Bending.—Increase of energy owing to bend of R_{BC} to R_{AB} was calculated for several equi-distant configurations by the use of Heitler-London and Wang type functions.

(h) Energy Values of Some Unsymmetrical Configuration. — Three-center integrals which appear in this case have need of complicated calculations. However, it is possible that, by an analogy of Mulligan approximation for the unsymmetrical integrals with different z's, these integrals are expressed approximately in terms of symmetrical configurations.

For example, denoting $R_{AB}=R_1$ and $R_{BC}=R_2$, we have

$$(ab \mid bc)_{R_1,R_2}=(ab)_{R_1}\cdot(bc)_{R_2}\times\frac{1}{2}\left[\left(\frac{(ab \mid bc)}{(ab)\,(bc)}\right)_{R_1}+\left(\frac{(ab \mid bc)}{(ab)\,(bc)}\right)_{R_2}\right]$$

Otherwise, these integrals may be resolved into the sum of several two-center integrals by the use of Rudenberg-Mulliken type approximation. Calculation was carried out for the configurations of

$R_{AB}=1.5$ a. u., $R_{BC}=2.0$ a. u.
$R_{AB}=1.75$ a. u., $R_{BC}=2.0$ a. u.
$zR_{AB}=2.00$ a. u., $zR_{BC}=2.50$ a. u.
and $zR_{AB}=2.25$ a. u., $zR_{BC}=2.50$ a. u.

by the use of Heitler-London and Wang ($z=1.4$) type functions and of approximate values of integrals.

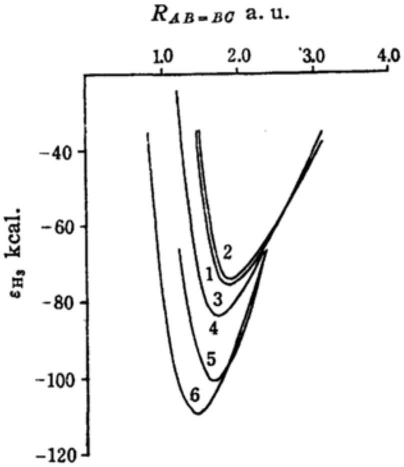

Fig. 1. Energies of symmetrical linea H_3.
1. Heitler-London function
2. H.-L.-plus-Ion function
3. Wang function (L.-H.)
4. Wang-plus-Ion function (L.-H.)
5. Wang function ($z=1.4$)
6. Observed H_2

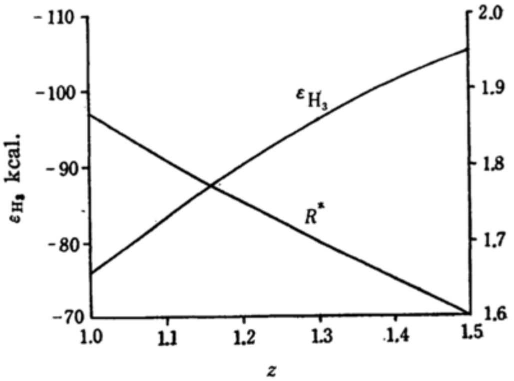

Fig. 2. Variation of energy and nuclear separation of H_3 with increase of z.

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[11] H. M. James, *J. Chem. Phys.*, **2**, 794 (1934).
[12] J. F. Mulligan, ibid., **19**, 347 (1951).
[13] S. Weinbaum, ibid., **1**, 593 (1933).

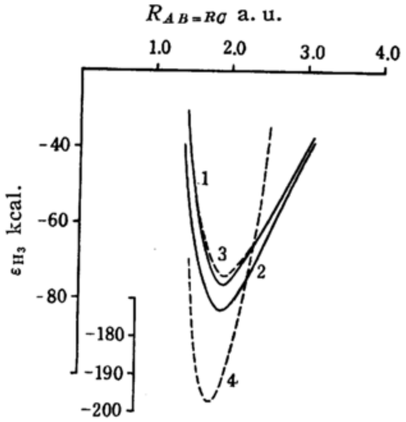

Fig. 3. Energies of H_3 by the use of various approximations.
1. Heitler-London function
2. Three-center integrals by R.-M. approximation
3. Neglect of three-center integrals
4. Neglect of three-center integrals and of non-orthogonality of atomic orbitals

TABLE III. VARIATION OF ENERGY BY BENDING*

(i) $R_{AB}=R_{BC}=2.00$ a. u. (Heitler-London type function)

ϕ (rad.)**	0.000	0.314	0.711
E (kcal.)	−81.8	−81.1	−77.4

(ii) $zR_{AB}=zR_{BC}=2.25$ a. u. (Wang type function $z=1.4$)

ϕ (rad.)	0.000	0.952
E (kcal.)	−100.1	−92.6

(iii) $zR_{AB}=zR_{BC}=2.50$ a. u. (Wang type function $z=1.4$)

ϕ (rad.)	0.000	0.902
E (kcal.)	−101.6	−95.7

* Values of three-center integrals with R.-M. approximation were used.

** ϕ is the angle between lines A-B and B-C.

TABLE IV. ENERGIES OF H_3 FOR UNSYMMETRICAL LINEAR CONFIGURATIONS*

	($z=1$)		($z=1.4$)	
zR_{AB} (a. u.)	1.50	1.75	2.00	2.25
zR_{BC} (a. u.)	2.00	2.00	2.50	2.50
E (kcal.)	−81.1	−83.7	−99.6	−103.4

* Values of three-center integrals with R.-M. approximation were used.

Results obtaind from calculations a)—h) are shown in Figs. 1—3 and Tables III and IV. An example of potential enegy surface constructed from these data is also shown in Fig. 4.

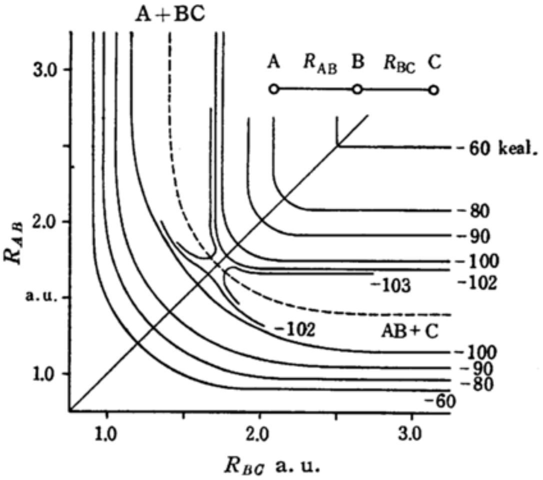

Fig. 4. Potential energy surface of reaction $H_2+H \rightarrow H+H_2$ (Wang type function $z=1.4$).

Discussion

Activation energies obtained by the present method (Table V) are not always satisfactory compared with the observed value⁽¹⁴⁾ or the previous ones by Hirschfelder et al.⁽¹⁾, except the result with Wang

TABLE V. VALUES OF ENERGY OF H_3, E_{H_3}, NUCLEAR SEPARATION, R^*, AT ACTIVATED STATE AND OF ACTIVATION ENERGY, E_a, OBTAINED BY VARIOUS TREATMENTS

Used molecular function	E_{H_3}	(kcal.) E_{H_2}	E_a	(a. u.) R^*
Heitler-London	−76.0	−109.5	33.5	1.87
(R.-M. approx.)	−83.0	−109.5	26.5	1.87
(H.-E.-R.)*	−53.11	− 72.18	19.07	2.00
H.-L.-plus-Ion.	−75.0	−109.5	34.5	1.88
(H.-E.-R.)	−60.39	− 74.02	13.63	2.00
Wang.	−88.0	−109.5	21.5	1.77
(L.-H.)**	−84.0	−109.5	25.5	1.72
(H.-E.-R.)	−56.16	− 86.94	30.78	1.89
Wang-plus-Ion	−88.0	−109.5	21.5	1.73
(L.-H.)	−84.0	−109.5	25.5	1.72
(H.-E.-R)	−67.09	− 92.24	25.15	1.84
Wang. ($z=1.4$)	−101.0	−109.5	8.5	1.65
(R.-M. approx.)	−102.4	−109.5	7.1	1.72
Griffing et al.⁽³⁾***	−63.0	− 71.76	8.76	1.82
Kimball et al.⁽³⁾***	−72.4	—	—	1.93
Observed value⁽¹⁴⁾	—	−109.5	4∼8	—

* Values calculated by Hirschfelder, Eyring and Rosen.

** Values calculated by the use of Hirschfelder-Linnett's coefficients.

*** Values calculated by the LCAO-MO method with configuration interaction.

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14) K. H. Gelb and P. Harteck, *Z. physik. Chem.* (*Bodenstein Festband*), 849(1931); A. Farkas and L. Farkas, *Proc. Roy. Soc.*, **A152**, 124 (1935).

type function in which $z=1.4$. However, marked improvements from their work are found in the absolute energy values of H_3 complex state, that is, the lowering 15~30 kcal. Besides, it is apparent that the activation energies estimated by them are of relative character; the use of improved function of H_2 brings, on the contrary, large increase for the values.

Interesting results are seen for the influence of an added ionic term. The introduction of this term lowers energies of H_3 complex slightly in the case of Hirschfelder et al., while it has almost no effect in the present treatment. These results are owing partly to the small contribution of ionic state to the lowest one and partly to the use of fixed coefficient of that term.

Also the results are explained phenomenally as that addition of this state brought an increase of interaction energy allowing superposition of electrons on the same atom. Considerations shall be done again later relating to the distribution of electrons in the system.

Next, the effect of nuclear charge z is examined. The lowering of energy and the contraction of the dimension of activated complex with increase of z are shown in Fig. 2. When z is increased to 1.4 or larger, the activation energy calculated attains the observed one. This effect may be explained qualitatively as that the use of atomic orbital shrunk by larger z diminishes the interaction between species and then energy of complex and nuclear distance decrease to those of the initial molecule.

If the energies of molecular species are estimated by the use of the same approximate function, this decrease of interaction energy will be compensated by the increase of molecular energy, and then an optimum value of z will be obtained. Accordingly, the variational principle does not always hold in the present method which makes use of the experimental value of molecular energy. However, this "half-theoretical" character of the present method gives an advantage of taking the nuclear charge z as an arbitrary parameter. According to this idea, it becomes possible to choose the z value from such a different point of view as will be discussed below.

When the atom C is separated infinitely from the molecule AB, the energy of the lowest state is apparently equal to that of molecule AB and that of the next higher state belonging to another doublet is expressed, by the use of Wang type function, as follows:

$$E_1=\frac{1}{R_{AB}}+\frac{Q-J}{1-S^2} \tag{8}$$

where

$$S=(ab) \tag{9}$$

$$Q=(a^2 \mid b^2)-(a^2 \mid B)-(b^2 \mid A) \tag{10}$$

and

$$J=(ab \mid ab)-(ab)(ab \mid A+B) \tag{11}$$

This equation corresponds clearly to the theoretical expression of the repulsive ${}^3\Sigma_u^+$ state of H_2.

Since the energy of this state was evaluated accurately by James, Coolidge and Present[15] by the aid of the variation method, we can choose the parameter z so as to coincide the energy by Eq. 8 with the calculated value by them.

The result is satisfactory as shown in Fig. 5; when the nuclear distances R_{AB} and R_{BC} come near the configuration of activated state, z value approaches 1.4. This fact suggests that the use of a composite function which gives better value for the energy of the state correlating strongly to the noticed one, improves the result markedly. Another qualitative reason of taking a larger value of z is in its effect upon the electronic distribution in the molecule. The present results will be improved if we make use of exact molecular function, e. g., James-Coolidge type one[16]. The distinction of J.-C. function from usual orbital ones is in its electronic distribution in which the overlapping of electrons is diminished by the introduction of interelectronic coordinate r_{12}. This effect is

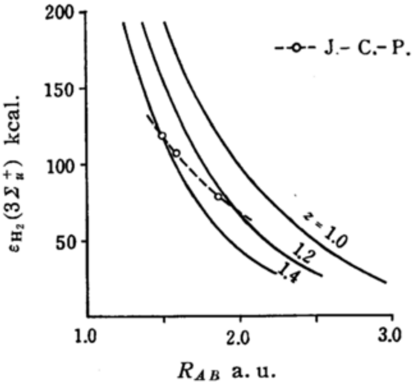

Fig. 5. Energy of triplet state of H_2.

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[15] H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.*, **4**, 187 (1936).

[16] H. M. James and A. S. Coolidge, ibid., **1**, 825 (1933).

attained to some extent by the use of orbital functions with increasing z value. Also the addition of an ionic term, on the contrary, estranges the distribution from J.-C.'s. It is expected, therefore, that the utilization of larger z takes in partly the energy of electronic correlation in molecules, and then in the reacting system. It goes without saying that this correlation is partly included by the use of experimental data for the component species.

Potential Energy Basin

Here, the existence of so-called "potential energy basin" is briefly discussed.

By applying straightforwardly Eyring's semi-empirical method to the H_3 system of linear configuration, the obtained surface has two distinct basins[17], i. e., (a) a markedly deep one occurring where the distances between neighboring atoms, R_{AB} and R_{BC} are smaller than 1.0 a. u. and (b) a shallow one near the activated state.

Neither the results of the present calculation nor that of Hirschfelder et al.[1] show such basins as those above. The fact that these basins are apparent ones, being induced from the assumption of constant coulombic fraction, is explained as follows; for the shrunken configuration where both R_{AB} and R_{BC} are nearly equal to those giving zero bond energies, ε_{AB}, $\varepsilon_{BC} \simeq 0$, the coulombic and exchange parts of these bonds, Q_i and J_i $(i=AB,\ CB)$ are in the relation as

$$Q_i \simeq -J_i \gg 0 \tag{12}$$

while their values by Eyring's procedure are

$$(1-\rho)Q_1 = \rho \cdot J_i \simeq 0 \tag{12'}$$

Therefore, the energy value which is obtained from London's formula,

$$E = Q_{AB} + Q_{BC} + Q_{CA} - [J_{AB}^2 + J_{BC}^2 + J_{CA}^2 - J_{AB}J_{BC} - J_{BC}J_{CA} - J_{CA}J_{AB}]^{1/2} \tag{13}$$

and these Q's and J's, is underestimated extremely as

$$E' = \varepsilon_{AC} = Q_{AC} + J_{AC} \tag{14'}$$

instead of exact value,

$$E = \varepsilon_{AC} + 3Q_{AB} \gg E' \tag{14}$$

This situation is apparently the cause of basin a).

Next, the origin of basin b) is examined. For the equi-distant configuration "P" as shown in Fig. 7, the energy change $\varDelta E$, induced from the small displacements around P is expressed as

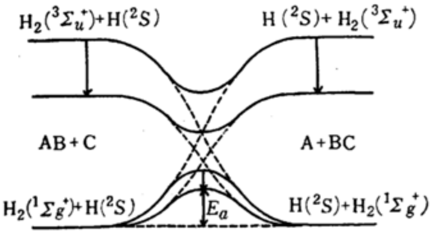

Fig. 6. Variation of activation energy with lowering of upper surface.

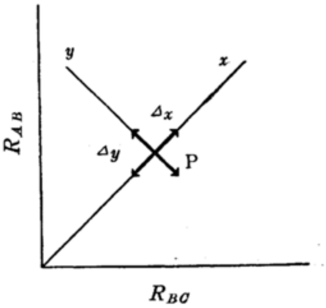

Fig. 7. Displacements around P.

$$\begin{aligned}\varDelta E_x \simeq \sqrt{2}\Bigg[&\left(\frac{\partial Q_{AB}}{\partial R_{AB}}\right)+\frac{1}{2}\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right)\\&+\left(\frac{\partial Q_{AC}}{\partial R_{AC}}\right)-\left(\frac{\partial J_{AC}}{\partial R_{AC}}\right)\Bigg]\cdot(\varDelta x)\\&+\Bigg[\frac{1}{2}\left(\frac{\partial^2 Q_{AB}}{\partial R_{AB}^2}\right)+\frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right)\\&+\left(\frac{\partial^2 Q_{AC}}{\partial R_{AC}^2}\right)-\left(\frac{\partial^2 J_{AC}}{\partial R_{AC}^2}\right)\Bigg]\cdot(\varDelta x)^2\\=&A_1(\varDelta x)+A_2(\varDelta x)^2\end{aligned}$$

along the x axis and

$$\begin{aligned}\varDelta E_y \simeq \Bigg[&\frac{1}{2}\left(\frac{\partial^2 Q_{AB}}{\partial R_{AB}^2}\right)+\frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right)\\&-\frac{3}{4}\cdot\frac{1}{|J_{AB}-J_{AC}|}\cdot\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right)^2\Bigg]\cdot(\varDelta y)^2\\=&B_2(\varDelta y)^2\end{aligned}$$

along the y axis. According to Eyring's assumption of constant ρ, the minimum point appears at the position where the coefficient of $(\varDelta x)$, A_1, is equal to zero and the nuclear separation $R_{AB}^*(=R_{BC}^*)$ is slightly larger than the equilibrium distance r_e of H_2 (1.40 a. u.), for example, $R_{AB}^*=1.6$ and 1.9 a. u. for $\rho=0.2$ and 0.1, respectively. In the case of large coulombic fraction, therefore, this point is apparently in a basin, for $A_2>0$ and B_2, the coefficient of $(\varDelta y)^2$, estimated approximately by the

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[17] S. Sato, This Bulletin, 28, 450 (1955).

use of equation

$$B_2 \simeq \frac{1}{4}\left(\frac{\partial^2 J_{AB}}{\partial R_{AB}^2}\right) - \frac{3}{4}\cdot\frac{1}{|J_{AB}-J_{AC}|}\cdot\left(\frac{\partial J_{AB}}{\partial R_{AB}}\right)^2$$

$$J_{AB} = (1-\rho)\cdot\varepsilon_{H_2}(R_{AB})$$

and of Morse function of H_2, is positive where

$$R_{AB}^* < 1.74\ \text{a. u.}$$

Alternatively, when we give up this assumption of constant ρ, the nuclear distances at the minimum point are somewhat extended. The value of B_2 estimated by making use of the following expression of J_{AB},

$$J_{AB} = D'\left[e^{-2a(r-r_e')} - 2e^{-a(r-r_e')}\right]$$ [18]

where $D' = 0.9\,D_{H_2} = 98.51$ kcal./mol.

$r_e' = 0.9\,r_e = 1.261$ a. u.

and $a = 1.0298$,

is negative where

$$R_{AB}^* > 1.60\ \text{a. u.}$$

This result shows that the surface near the activated state is a saddle-like one or, at least, has not such a depression as was expected by Eyring et al.

Computation of Reaction Rate

Now, we shall evaluate the rate of the reaction on the knowledge of the surface derived here. Such a detailed calculation has been done only by Eyring et al.[19] According to the activated complex theory, the rate v and rate constant k of the elementary reaction $H_2(AB) + H(C) \rightarrow H(A) + H_2(BC)$ are expressed by

$$v = kC_{H_2}\cdot C_H \tag{20}$$

and

$$k = \kappa\frac{I_{H_3}\sigma_{H_2}}{I_{H_2}\sigma_{H_3}}\cdot\frac{h^2}{(4\pi m_H/3)^{3/2}\cdot(kT)^{1/2}} \times\frac{1}{4}\cdot\frac{\sinh\left(\frac{1}{2}\boldsymbol{h}\nu_{H_2}/kT\right)e^{-E_c/\boldsymbol{k}T}}{\sinh\left(\frac{1}{2}\boldsymbol{h}\nu_s/\boldsymbol{k}T\right)\cdot\sinh^2\left(\frac{1}{2}\boldsymbol{h}\nu_\phi/\boldsymbol{k}T\right)} \tag{21}$$

The notations in these equations are as follows:

C; concentration of species.
κ; the transmission coefficient.
I; a moment of inertia.
σ; symmetry number.
m_H; mass of hydrogen atom.
ν_{H_2}; vibrational frequency of H_2.
ν_s and ν_ϕ; stretching and bending vibrational frequencies of activated complex respectively.
E_c; classical energy of activation.

The quantities belonging to molecule or complex are distinguished by the addition of subscripts, e. g., "H_2" or "H_3". Since the complex in the present result is a symmetrical linear one, $\sigma_{H_2} = \sigma_{H_3} = 2$ holds. Constants deduced from the surface constructed by the use of Wang type function ($z=1.4$) are shown in Table VI with Eyring's ones.

TABLE VI. CONSTANTS FOR THE HYDROGEN ATOM-MOLECULE REACTION

	Present result*	Eyring et al.**
R_{AB}^* (Å)	0.88(0.91)	1.354
R_{BC}^* (Å)	0.88	0.753
I_{H_3} (10^{-40} gcm^2)	2.62	3.79
I_{H_2} (〃)	0.458	0.458
$1/2\cdot\boldsymbol{h}\nu_s$ (kcal.)	4.78	5.18
$1/2\cdot\boldsymbol{h}\nu_\phi$ (kcal.)	1.35	0.95
$1/2\cdot\boldsymbol{h}\nu_{H_2}$ (kcal.)	6.27	6.21
E_c (kcal.)	8.5 (7.1)	7.63

* Values obtained by the use of Wang type function with $z=1.4$. In parentheses, those with R.-M. approximation are shown.
** Values obtained from Ref. 19. Coulombic fraction $\rho=0.20$.

TABLE VII. RATE CONSTANTS OF HYDROGEN ATOM-MOLECULE REACTION, k (cc. mol^{-1} sec^{-1})

Temperature °K	300	600	1000
Observed values	9.0×10^7	—	2.2×10^{12}
Present results a.	3.6×10^6	1.0×10^{10}	0.4×10^{12}
〃 b.*	3.9×10^7	3.5×10^{10}	0.7×10^{12}
Eyring et al.	7.3×10^7	7.3×10^{10}	1.5×10^{12}

* Values obtained by the use of constants in parentheses, Table VI.

The evaluated rate values are given in Table VII, with the observed ones by Geib and Harteck and Farkas et al.[14] and also with the calculated ones by Eyring et al. Although detailed comparison is rather difficult because of few experimental data, the agreement with the evaluated ones is reasonably good. The reason why Eyring's values are slightly large compared with the present ones is in the use of larger moment-of-inertia value of the complex deduced from its unsymmetrical form. Accordingly, when we give up the assumption of constant ρ, the moment-of-inertia and therefore rate

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[18] The corresponding coulombic fractions obtained from this function are 0.13, 0.18 and 0.20 at R_{AB}=1.5, 2.0 and 2.5 a. u., respectively.

[19] H. Eyring et al., "The Theory of Rate Processes", McGraw-Hill Book Co. Inc., New York, (1941), p. 203.

also are reduced to those near the present ones.

Besides, it is necessary to use corrected values of transmission coefficient for this reaction consisting of light atoms in low temperatures.

Since it is known that the bending of the reaction path scarcely affects the extent of transmission at all, the evaluation of κ is confined to that through potential energy barrier[20]. Now taking Wigner's correction, $\kappa=1-\frac{1}{24}\left(\frac{h\nu_t}{kT}\right)^2$, where ν_t is the imaginary vibrational frequency of complex along the reaction path, we obtain κ's values to be 6.3, 2.3 and 1.5 at 300, 600 and 1000°K respectively from the value $ih\nu_t=6.8$ kcal. The rate values are then corrected to

$$2.5\times10^8,\ 8.1\times10^{10} \text{ and } 1.1\times10^{12}$$

at respective temperatures. Since Wigner's correction may give upper limit of κ, it is sure that the rate in lower temperatures were well improved.

Conculusion

The method of modified bond eigenfunction was applied to construct the potential energy surface of the hydrogen atom-molecule reaction. Also it was shown that the reaction rates estimated on this surface were in agreement with the observed ones.

In the calculation of surface, we took effective nuclear charge z in orbital function as an arbitrary parameter and showed the propriety of employing a larger z value than unity. Accordingly, it is to be noted that the functions of component species near the configuration of activated state are different from those of "free species" and that, by the use of these deformations, some parts of electronic correlation energy are taken into calculation.

Recently, Arai et al.[21] have developed, in the field of "molecular theory", the method of "deformed-atoms-in-molecules" which differs from the original Moffitt's method by taking deformed atomic orbitals in the molecule. Then, it may be said that the method by the present author corresponds to a further extension of theirs for the reacting system.

Although, the electronic correlation is considered partly in the above-mentioned manner, its full inclusion by the device of more valid approximation for wave function will be the important problem to be studied hereafter.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

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[20] I. Yasumori and K. Fueki, This Bulletin, **29**, 1 (1956). For the effect of curved reaction path, I. Yasumori, ibid.. **32**, 913 (1959).

[21] T. Arai, *J. Chem. Phys.*, **26**, 435, 451 (1957); T. Arai and M. Sakamoto, ibid., **28**, 32 (1958).