Modified Bond Eigenfunction Method of Constructing Potential Energy Surface of Reaction. I. Theory and General Remarks

By Iwao YASUMORI

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In order to evaluate the chemical reaction rates theoretically, it is necessary to know the detailed feature of the interaction potential between the reacting species, i. e., the potential energy surfaces of the reaction. These surfaces are formed, in principle, from the eigenvalues of the wave equation for all electrons in the system at all orientations of atomic nuclei. Because of mathematical difficulties, however, which are the same as those in the calculation of " molecular energy ", it is extremely difficult to construct the surface with the required accuracy, e. g., 0.1 kcal.

This situation of the problem has been a main cause of the fact that there is no available method for this purpose except Eyring's semi-empirical one[1] which is based on London's formula. Also it has been frequently pointed out by several investigators[2] that this approximate procedure contains many inadequacies, for instance, neglect of non-orthogonality between the orbitals of different atoms, introduction of *s*-electron approximation disregarding the direction of valence and the arbitrary choice of coulombic fraction ρ, etc. Nevertheless, this method has the distinctive character of giving an interpolation formula utilizing the experimental bond energies of component species.

Based on the idea of making use of the observed data for the component species, Moffitt[3] recently developed the " atoms-in-molecules " method in the field of " molecular theory " and succeeded in improving the calculated energy values for oxygen, ethylene, allyl radical, etc. If we regard the reacting system as a " complex molecule " and take molecular species as components, instead of atoms in Moffitt's method, it is possible to develop the corresponding " molecules-in-molecules " or " modified bond eigenfunction " method of constructing potential energy surfaces[4].

According to this idea, the author presents an improved method which stands on a firm basis and has wider applicability. The outline of the method and remarks on its application are given in this paper. The practical application and the inspection of the availability of the method will be made in relation to the hydrogen atom-molecule reaction in the following paper[5].

Theory

Elementary chemical reaction

$$A_1+B_1 \rightarrow A_2+A_2$$

is here considered, where A_1, B_1, A_2 and B_2 denote component molecular species. The potential energy surfaces of this reaction are constructed by the eigenvalues E of the wave equation for all n electrons,

$$\boldsymbol{H}\Psi(1,2,\cdots,n)=E(R_1,R_2,\cdots,R_N)\Psi(1,2\cdots,n) \quad (1)$$

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[1] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc., New York (1941), p. 91.

[2] H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1**, 825 (1933).

[3] W. Moffitt, *Proc. Roy. Soc.*, **A210**, 224, 245 (1951); ibid., **A218**, 464, 486 (1953).

[4] Also this idea has been independently found by Dr. P. Lykos, Argonne National Laboratory, U. S. A., private communication.

[5] This series of papers contains the detailed account of the communication which was presented in *J. Chem. Phys.*, **23**, 1566 (1955).

at every set of fixed orientation of all N nuclei, $R_1, R_2, \cdots R_N$ in the system. Total Hamiltonian $\boldsymbol{H}$ has the usual form as

$$\boldsymbol{H}=-\sum_i \frac{1}{2}\Delta_i+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{p>q}\frac{Z_pZ_q}{R_{pq}}-\sum_p\sum_i\frac{Z_p}{r_{pi}} \tag{2}$$

where p, q, and i, j, denote atomic nuclei and electrons, respectively; Z, nuclear charge, R and r, mutual distances between nuclei and electrons, respectively.

It is almost impossible to solve this equation in general; we must, therefore, be contented with merely some approximate solution. Now, when the distances between each species in the system become infinitely large, the wave function will have the following asymptotic form for any set of reactant or of any product, i. e., A_m+B_m, $A_n+B_n, \cdots$,

$$\Psi=\boldsymbol{A}\psi_{A_m^{\mu}}\cdot\psi_{B_m^{\nu}} \tag{3}$$

or

$$\Psi=\boldsymbol{A}\psi_{A_n^{\mu'}}\cdot\psi_{B_n^{\nu'}} \tag{3'}$$

$\psi_{A_m^\mu}$ and $\psi_{B_m^\nu}$ are the exact eigenfunctions of species A_m and B_m in the states μ and ν, respectively, and satisfy the equations

$$\boldsymbol{H}_{A_m}\psi_{A_m^\mu}=E_{A_m^\mu}\psi_{A_m^\mu} \tag{4}$$

and

$$\boldsymbol{H}_{B_m}\psi_{B_m^\nu}=E_{B_m^\nu}\psi_{B_m^\nu} \tag{4'}$$

where $\boldsymbol{H}_{A_m}$ and $\boldsymbol{H}_{B_m}$ are partial Hamiltonians for A_m and B_m, respectively, having the form of

$$\boldsymbol{H}_{A_m}=-\frac{1}{2}\sum_i\Delta_i+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{p>q}\frac{Z_pZ_q}{R_{pq}}-\sum_p\sum_i\frac{Z_p}{r_{pi}} \tag{5}$$

and

$$\boldsymbol{H}_{B_m}=-\frac{1}{2}\sum_k\Delta_k+\sum_{k>l}\frac{1}{r_{kl}}+\sum_{r>s}\frac{Z_rZ_s}{R_{rs}}-\sum_s\sum_k\frac{Z_s}{r_{sk}} \tag{5'}$$

The nuclei p, q, and electrons i, j, belong to A_m and the nuclei r, s, and electrons k, l, to B_m. Also the eigenvalues $E_{A_m^\mu}$ and $E_{B_m^\nu}$ are those for the states of species, respectively. $\boldsymbol{A}$ in Eq. 3 is an antisymmetrizer[3] which makes the product functions $\psi_{A_m^\mu}\cdot\psi_{B_m^\nu}$ totally antisymmetrical for the exchange between any pair of electrons in the system, and has the form

$$\boldsymbol{A}=\{n!/n_A!\cdot n_B!\}^{1/2}\sum_t P_t v_t \tag{6}$$

where n_A, n_B and n are the numbers of electrons in A_m, B_m and their total respectively, P_t is any operator for inter-species exchange of electrons and $v_t=\pm1$ according to whether P_t gives an even or odd permutation.

Corresponding to all sets of species in their respective electronic states, $A_m^\mu+B_m^\nu$ $(m, \mu, \nu=1, 2, \cdots)$, we take the "composite functions" defined by

$$\psi_{m\mu\nu}=\boldsymbol{A}\psi_{A_m^\mu}\cdot\psi_{B_m^\nu} \tag{7}$$

and we assume that the total wave function is constructed approximately from these sets of composite functions,

$$\Psi=\sum_{m,\mu,\nu}C_{m\mu\nu}\cdot\psi_{m\mu\nu} \tag{8}$$

The eigenvalues $E(R_1, R_2, \cdots, R_N)$ for each orientation of nuclei are given by

$$E=\int\bar{\Psi}\boldsymbol{H}\Psi\mathrm{d}\tau\bigg/\int\bar{\Psi}\Psi\mathrm{d}\tau \tag{9}$$

When the usual variation method is adopted, the above relations are converted into the secular determinant,

$$\mathrm{Det.}\,|H_{m\mu\nu,n\mu'\nu'}-ES_{m\mu\nu,n\mu'\nu'}|=0 \tag{10}$$

where

$$H_{m\mu\nu,n\mu'\nu'}=\int\bar{\psi}_{m\mu\nu}\boldsymbol{H}\psi_{n\mu'\nu'}\mathrm{d}\tau \tag{11}$$

and

$$S_{m\mu\nu,n\mu'\nu'}=\int\bar{\psi}_{m\mu\nu}\psi_{n\mu'\nu'}\mathrm{d}\tau \tag{12}$$

Moreover, when we take an assumption of neglecting the contribution of spin angular momentum to the energy, the whole electronic state is classified with their total spin S and its component S_z values and the determinant is factorized into several smaller ones in which all the elements of H and S are those for the same electronic states $\kappa(S, S_z)$'s,

$$\mathrm{Det.}\,|H^\kappa_{m\mu\nu,\,n\mu'\nu'}-E^\kappa S^\kappa_{m\mu\nu,\,n\mu'\nu'}|=0 \qquad \kappa=1, 2, \cdots \tag{13}$$

Next, let us divide the total Hamiltonian into the partial Hamiltonians $\boldsymbol{H}_{A_n}+\boldsymbol{H}_{B_n}$ for the composite species A_n+B_n and the remaining interaction term $\boldsymbol{I}_n$, that is,

$$\boldsymbol{H}=\boldsymbol{H}_{A_n}+\boldsymbol{H}_{B_n}+\boldsymbol{I}_n \tag{14}$$

where

$$\boldsymbol{I}_n=\sum_i\sum_k\frac{1}{r_{ik}}+\sum_p\sum_s\frac{Z_pZ_s}{R_{ps}}-\sum_p\sum_k\frac{Z_p}{r_{pk}}-\sum_s\sum_i\frac{Z_s}{r_{si}} \tag{15}$$

the nuclei p's and electrons i's belong to A_n and the nuclei s's and electrons k's to B_n. $\boldsymbol{H}_{A_n}$ and $\boldsymbol{H}_{B_n}$ have forms similar to $\boldsymbol{H}_{A_m}$ and $\boldsymbol{H}_{B_m}$, Eqs. 5 and 5'. Accordingly, $H^\kappa_{m\mu\nu,\,n\mu'\nu'}$ is rewritten as

$$H^{\kappa}_{m\mu\nu,\, n\mu'\nu'} = (E_{A^{\mu'}_n} + E_{B^{\nu'}_n}) S^{\kappa}_{m\mu\nu,\, n\mu'\nu'} + I^{\kappa}_{m\mu\nu,\, n\mu'\nu'} \tag{16}$$

where

$$I^{\kappa}_{m\mu\nu,\, n\mu'\nu'} = \int \bar{\psi}_{m\mu\nu} \boldsymbol{I}_n \psi_{n\mu'\nu'} \mathrm{d}\tau \tag{17}$$

The number of bonds which take part in the reaction is usually one or two in each species and if we take an energy scale in which the bond energy of the composite state $A^{\mu'}_n + B^{\nu'}_n$, $\varepsilon_{n\mu'\nu'}$ is measured from the state where all these "reacting bonds" break down and the species A_n and B_n are separated into several fragments (radicals), then the eigenvalues for the composite state is described as a sum of "fragment-state energy" $E_{n\mu'\nu'}$ and "bond energy" $\varepsilon_{n\mu'\nu'}$

$$E_{A^{\mu'}_n} + E_{B^{\nu'}_n} = E_{n\mu'\nu'} + \varepsilon_{n\mu'\nu'} \tag{18}$$

Further, we take conveniently one of these "fragment-states" as a standard state and define its energy, E^{κ}_0. For this standard, the energies of the whole system E and of any composite state which belongs to the same $\kappa(S, S_z)$, $E_{A^{\mu'}_n} + E_{B^{\nu'}_n}$, are rewritten as follows:

$$E^{\kappa} = E^{\kappa}_0 + \varepsilon^{\kappa} \tag{19}$$

and

$$E_{A^{\mu'}_n} + E_{B^{\nu'}_n} = E^{\kappa}_0 + \varepsilon^{\kappa}_{n\mu'\nu'} = E^{\kappa}_0 + (\varepsilon_{A^{\mu'}_n} + \varepsilon_{B^{\nu'}_n}) \tag{20}$$

ε^{κ}, $\varepsilon^{\kappa}_{n\mu'\nu'}$, $\varepsilon_{A^{\mu'}_n}$ and $\varepsilon_{B^{\nu'}_n}$ in Eqs. 19 and 20 are respective "bond energies" of the system, of the composite state and of the species A_n and B_n newly measured from the level E_0. Substituting Eqs. 16, 19 and 20 into 10,

$$\mathrm{Det.}| I^{\kappa}_{m\mu\nu,\, n\mu'\nu'} + (\varepsilon^{\kappa}_{n\mu'\nu'} - \varepsilon^{\kappa}) S_{m\mu\nu,\, n\mu'\nu'} | = 0 \tag{21}$$

is obtained finally. Since $\varepsilon_{A^{\mu'}_n}$ and $\varepsilon_{B^{\nu'}_n}$ in Eq. 20 are bond energies⁶⁾ for molecules, we can frequently utilize their observed values⁷⁾. The remaining unknown quantities, $S_{m\mu\nu,\, n\mu'\nu'}$ and $I_{m\mu\nu,\, n\mu'\nu'}$ can be evaluated, in principle, if we know the exact forms of the composite functions. Unfortunately, this is not the case except for a few states of hydrogen molecule and also the direct use of the function in exact form for the present purpose is unsuitable because of complicated calculations. Therefore, we may use their values calculated by the use of approximate composite functions with a simple analytic form⁸⁾.

Some Limitations for the Composite Functions

According to the above considerations the reactions proceed "adiabatically" on each surface. It is expected that this adiabatic condition brings some limitations on the character of states (wave functions) of species to be combined. Furthermore, when the reacting system has some symmetrical configurations during the reaction, the limitations become finer. This correlation between limited states of species was recently studied by Shuler and Laidler for the polyatomic system by the use of spin and orbital correlation rules⁹,¹⁰⁾.

Their conclusion shows that three or four atomic systems lie frequently on a

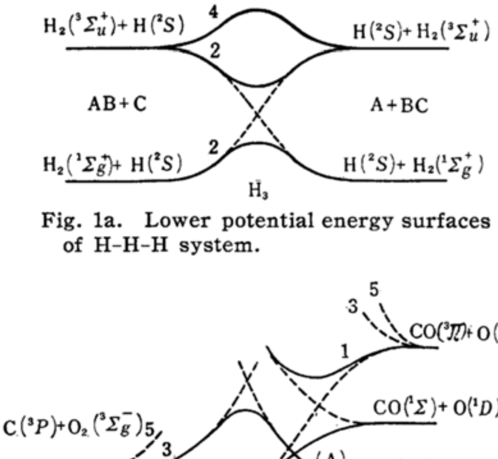

Fig. 1a. Lower potential energy surfaces of H-H-H system.

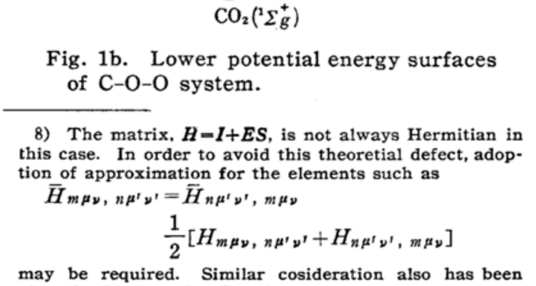

Fig. 1b. Lower potential energy surfaces of C-O-O system.

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6) Here, the definition of "bond energy" is used also for the energy of the repulsive state of a molecule.

7) For example, when A_n is a diatomic molecule, some of its bond energies are given as functions of nuclear distance based on the spectroscopic data. (Morse function etc.)

8) The matrix, $\boldsymbol{H}=\boldsymbol{I}+\boldsymbol{ES}$, is not always Hermitian in this case. In order to avoid this theoretial defect, adoption of approximation for the elements such as

$$\bar{H}_{m\mu\nu,\, n\mu'\nu'} = \bar{H}_{n\mu'\nu',\, m\mu\nu}$$
$$\frac{1}{2}[H_{m\mu\nu,\, n\mu'\nu'} + H_{n\mu'\nu',\, m\mu\nu}]$$

may be required. Similar cosideration also has been given by Moffitt. See Ref. 3.

9) K. E. Shuler, *J. Chem. Phys.*, **21**, 624 (1953).

10) K. J. Laidler, ibid., **22**, 1740 (1954).

straight line or a plane where the orbital correlation may have an important part, while the general polyatomic system scarcely has these constraints at all as long as special symmetry does not exist. These results and the correlation tables given by Shuler[9] are available for the present consideration. Typical examples of correlation for the lower energy surfaces are shown in Fig. 1. In the figure, the numbers on the curves representing adiabatic surfaces are for spin multiplicity, $2S+1$, and the states of reactants and resultants are shown in both ends of each curve. Relative orientation and shapes of the curves are arbitrary.

Some explanations are added to the system H_3 (Fig. 1a). The lowest surface of this reaction is clearly one of doublet. When all the nuclei are orientated on a line, the system has a symmetry of $C_{\infty v}$ and so the lowest state will be classified to ${}^2\Sigma^+$. Then the states of composite species which satisfy this designation are confined

$$H_2({}^{1,3}\Sigma^+)+H({}^2S_g),\quad H_2({}^{1,3}\Sigma^+)+H({}^2P_u)$$
$$H_2({}^{1,3}\Pi)+H({}^2P_u),\ \text{etc.}$$

However, it is known that elements, $S_{m\mu\nu,n\mu'\nu'}$ and $I_{m\mu\nu,n\mu'\nu'}$ which relate to states of higher energy hardly contribute to the lowest state, so we can conveniently neglect these composite states of high energy and can reduce the order of the determinant. Further, when this system has higher symmetries such as equidistance-on-a-line ($D_{\infty h}$) or equilateral triangle (D_{3h}), new relations appear among the coefficients of composite functions $C_{m\mu\nu}$'s, so as to reduce the order of determinant[11].

As for the C-O-O system, the reaction, $CO_2({}^1\Sigma^+)\rightarrow CO({}^1\Sigma)+O({}^3P)$ is a forbidden process in the present treatment. The intersection of the surfaces A and B in Fig. 1b will give, however, the zeroth approximation for the surface of this reaction.

Approximate Estimation of $S_{m\mu\nu,n\mu'\nu'}$ and $I_{m\mu\nu,n\mu'\nu'}$ for the Three-atom System

Discussion is focused here on the reaction, as an example,

$$AB+C\rightarrow A+BC \quad \text{or} \quad AC+B$$

which is composed of three atoms having one valence electron. One of composite functions which express its lowest state with $S=1/2$ and $S_z=1/2$ is

$$\begin{aligned}\psi_1&=\boldsymbol{A}\psi_{AB}(1,2)\cdot\psi_C(3)\\&=\sum_n P_c^n\varphi_{AB}(1,2)\cdot\varphi_C(3)\\&\quad\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\cdot\alpha(3)\end{aligned}\tag{22}$$

where P_c means cyclic exchange of electrons 1, 2 and 3 in this order; φ's are the orbital parts and the bond orbital, $\varphi_{AB}(1,2)$, is symmetrical for the exchange of electrons 1 and 2. Analogous forms are taken for the functions ψ_2 and ψ_3 of other composite states, BC+A and CA+B, respectively.

Now, we neglect the contributions from all higher composite states and assume φ_{AB}, φ_{BC}, $\cdots$, and φ_A, φ_B, $\cdots$, to be the ones of their lowest states, and then the order of determinant can be reduced to three. We take, furthermore, the simplest form of these functions by the use of atomic orbital approximation,

$$\varphi_{AB}(1,2)=a(1)b(2)+a(2)b(1)\tag{23}$$

and
$$\varphi_C(3)=c(3)\tag{24}$$

and so on. In these functions, $a(1)$, $b(2)$ and $c(3)$ express the valence orbitals of atom A, B and C, respectively. By the use of these expressions, the formulae of S_{mn} and I_{mn} ($m, n=1, 2, 3$) are described as shown in the Appendix.

Since the numerical values of molecular integrals including atomic orbitals with the principal quantum number $n=1,2,3$ are available at present[12], it is possible to evaluate the formulae directly except for several multiple-center integrals. Also these integrals are estimated exactly for some simple systems and also are approximately given by, e.g., Rudenberg-Mulliken's procedure[13].

Here, it is interesting to examine the simplification neglecting all these multiple-center integrals in the formulae. In this case, I_{mn} can be described as the function of coulombic energies Q_{AB}, Q_{BC}, $\cdots$, and exchange energies J_{AB}, J_{BC}, $\cdots$, of respective bonds, AB, BC, $\cdots$, for example,

$$I_{11}=2Q_{CA}+Q_{BC}-J_{CA}-J_{BC}$$

where

$$Q_{CA}=\overline{R}_{CA}^{-1}+(c^2|a^2)-(c^2|A)-(a^2|C)$$[14]

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[11] See, for example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1949), Chap. X, p. 172; Chap. XIII, p. 252.

[12] M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, "Table of Molecular Integrals", Maruzen Co., Ltd., Tokyo (1955).

[13] K. Rudenberg, *J. Chem. Phys.*, **19**, 1433 (1951); R. S. Mulliken and R. G. Parr, ibid., **18**, 1338 (1950).

and

$$J_{CA}=(ac)^2\bar{R}_{CA}^{-1}+(ac|ac)-(ac)(ac|A+C),$$

etc.

Moreover, when the non-orthogonality between orbitals of different atoms is disregarded in S_{mn}'s, the expressions for I_{mn}'s and S_{mn}'s exactly correspond to those obtained by the well-known method of bond eigenfunction[15].

Eyring's semi-empirical method is derived readily by the use of these expressions and by taking the values of Q_{AB}, $J_{AB},\cdots$, from the assumption,

$$\varepsilon_{AB}=Q_{AB}+J_{AB},\quad \varepsilon_{BC}=Q_{BC}+J_{BC},\cdots, \qquad (25)$$

and

$$\rho_{AB}=Q_{AB}/\varepsilon_{AB},\qquad \rho_{BC}=Q_{BC}/\varepsilon_{BC},\cdots, \qquad (26)$$

where ε_{AB}, $\varepsilon_{BC},\cdots$ and ρ_{AB}, $\rho_{BC},\cdots$ are bond energies and coulombic fractions of bonds AB, $BC,\cdots$. Therefore, this procedure may be regarded as one of the methods for estimating the elements I_{mn}'s conveniently by the use of ε_{AB}'s and ρ_{AB}'s.

Another basis of the present method will be examined below with respect to this reaction example. It is known theoretically that the wave functions which express the doublet states with $S_z=1/2$ are written as follows, by the use of orbital approximation;

$$\Phi_1=\sum_n P_c^n\{\psi(1,2,3)+\psi(2,1,3)\}$$
$$\times\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3) \qquad (27)$$

and

$$\Phi_2=\sum_n P_c^n\{(\psi 1,2,3)-\psi(2,1,3)\}$$
$$\times\frac{1}{\sqrt{6}}\,[\{\alpha(1)\beta(2)+\alpha(2)\beta(1)\}\alpha(3)$$
$$-2\alpha(1)\alpha(2)\beta(3)] \qquad (28)$$

where $\psi(1,2,3)$ is the orbital function[16]. When we take the simplest form of ψ's, $\psi(1,2,3)=a(1)b(2)c(3)$, etc., Φ_1 is identified with the composite function $\boldsymbol{A}\psi_{AB}\cdot\psi_C$ and Φ_2 is also rewritten as

$$\Phi_2=\sum_n P_c^n\{a(1)b(2)-a(2)b(1)\}c(3)$$
$$\times\frac{1}{\sqrt{6}}\,[\{\alpha(1)\beta(2)+\alpha(2)\beta(1)\}\alpha(3)$$
$$-2\alpha(1)\alpha(2)\beta(3)] \qquad (29)$$

or

$$=\sum_n P_c^n\,[\{b(1)c(2)+b(2)c(1)\}a(3)$$
$$+\{c(1)a(2)+c(2)a(1)\}b(3)]$$
$$\times\frac{1}{\sqrt{6}}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\alpha(3) \qquad (29')$$

These expressions correspond apparently to the state composed of AB in a triplet state and C in a doublet state or the combination of composite states, BC in a singlet state and A in a doublet state, and CA and B in the analogous states.

Since the eigenvalues of these doublet states of the whole system are determined from the wave function,

$$\Psi=c_1\Phi_1+c_2\Phi_2 \qquad (30)$$

the utilization of Φ_1 and Φ_2 as the basic functions is equivalent to the adoption of the set of composite functions, $\boldsymbol{A}\psi_{AB}\cdot\psi_C$, $\boldsymbol{A}\psi_{BC}\cdot\psi_A$ and $\boldsymbol{A}\psi_{CA}\cdot\psi_B$.

The conclusion from the above consideration and also the method of bond-eigenfunction shows that one of these three functions is linearly dependent on the others. But, in the present method, such a relation does not always hold, for the present choice of a functional set is effectively to make use of the observed values of bond energies, ε_{AB}, ε_{BC} and ε_{CA}.

Remarks on the Application to the General System

In several reactions, bonds have frequently a directional character such as *p*-, *d*- orbitals or their hybridization. Also other important cases are the reactions in multielectronic systems with inner-shell and incompleted shell electrons. Any polyatomic system is comprised in the combination of these cases. Some remarks will be made on the application to these systems.

System with Directed Valence Bond. — A typical example is the hydrogen-halogen reaction

$$\mathrm{X}(^2P)+\mathrm{H}_2(^1\Sigma^+)\rightarrow \mathrm{HX}(^1\Sigma^+)+\mathrm{H}(^2S)$$

For simplicity, the halogen atom is assumed to have only a *p*-valence electron. This system has been studied only by Magee with crude approximation[17].

Denoting two independent *p*-orbitals of halogen, which lie on the plane involving three atoms, by p_x and p_y, we can readily see that these *p*-orbitals and *s*-orbitals of two hydrogen atoms form a basis for an

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[14] For these notations, see the definitions given in Appendix.

[15] Ref. 11, Chap. XIII, p. 232.

[16] Ref. 12, p. 15.

[17] J. L. Magee, *J. Chem. Phys.*, 8, 677 (1940).

irreducible representation of the group of surface symmetry C_s. Accordingly, the p-bonding orbital on the plane is expressed by linear combination of p_x and p_y,

$$p_\sigma = \lambda p_x + \mu p_y \tag{31}$$

Since the total wave function is described as

$$\Psi = C_1 \boldsymbol{A}\psi_{\mathrm{XH}_A}\cdot\psi_{\mathrm{H}_B} + C_2 \boldsymbol{A}\psi_{\mathrm{XH}_B}\cdot\psi_{\mathrm{H}_A} + C_3 \boldsymbol{A}\psi_{\mathrm{H}_2}\cdot\psi_{\mathrm{X}} \tag{32}$$

respective bond functions are given by

$$\psi_{\mathrm{XH}_A} = \lambda_1\psi(p_x - h_A) + \mu_1\psi(p_y - h_A)$$

$$\psi_{\mathrm{XH}_B} = \lambda_2\psi(p_x - h_B) + \mu_2\psi(p_y - h_B)$$

and $\psi_{\mathrm{X}} = \lambda_3\psi(p_x) + \mu_3\psi(p_y)$

where h's are the valence orbitals of the hydrogen atom.

Even if all states of higher energy are neglected, the determinant is still so great. But when the ratios λ_i/μ_i's are fixed so as to minimize the energy of each composite state, the order of determinant can be reduced to three and the bond energy of HX is utilized effectively, for the p_σ orbital lies along the line joining H and X in this case[18].

System with Inner-shell Electrons. — The simplest example is the reaction including alkali metal,

$$\mathrm{LiH}(^1\Sigma^+) + \mathrm{H}(^2S) \rightarrow \mathrm{Li}(^2S) + \mathrm{H}_2(^1\Sigma^+)$$

of which one of the composite functions is

$$\psi_1 = \boldsymbol{A}\psi_{\mathrm{LiH}}(1,2,3,4)\cdot\psi_{\mathrm{H}}(5)$$

The orbital part of molecular function, ψ_{LiH} may be factorized by the use of the inner shell orbital ϕ_i[19] and the bond orbital ϕ_{LiH} which are symmetrical for exchange of electrons, respectively. Expressing these orbitals by the introduction of atomic orbital approximation, it is found that I_{mn}'s consist of two parts, (1) integrals with exchange of electrons between inner-shell and bond orbitals of other species and (2) integrals in which inner-shell electrons remain un-exchanged.

Now, we take a simplification neglecting the former because of the small overlapping between inner-shell and valence orbital of different species. The electrons in closed shell distribute almost spherically round the Li nucleus and then contribute to energy only by coulombic repulsion. Since this effect is estimated effectively by adjusting the nuclear charge of Li atom, the system is regarded as the one consisting of three valence electrons only.

The effect of an incomplete shell, lone pair and even that of radicals which are not concerned directly with the reaction, are similar in principle to the above case. However, an important difference between them is that the charge distributions in these cases are not spherically symmetrical for the nuclei noticed. Therefore, it may be necessary to take such an approximation as the replacement of these distributions to several point charges distributed around the nucleus.

Finally, a remark is briefly made on the system having multiple bond. When the bond breaks completely or is newly formed as a result of reaction, all electrons relating to the bond must be taken into the treatment. On the other hand, when the bond is partially subjected to reaction, electrons in the remaining part of the bond behave in the same manner as those of the incompleted shell stated above and then are treated in a similar way too. The above consideration has been taken for the displacement reaction A+BC→AB+C. Conclusions obtained here, however, are readily extended to other types of reaction, for instance, double decomposition, AB+CD→AC+BD.

If the ground states of molecules are all singlet in this case, the lowest surface will also belong to singlet and composite functions, which can be constructed in a way quite analogous to that shown in the previous sections.

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

Appendix

Formulae of S_{mn} and I_{mn} for the System of Three Atoms with One Valence Electron. — In a way similar to ψ_1 of Eq. 22, ψ_2 and ψ_3 for the other composite states are described as follows:

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[18] When the direction of the valence orbital is fixed during the reaction for some reason, for example, the hindrance of atoms or radicals attached to the noticed atom, and it does not accord with the joining line, some correction may be required for full insertion of observed bond energies.

[19] This orbital almost coincides with inner shell orbital of Li atom.

$$\psi_2=\boldsymbol{A}\psi_{BC}(1,2)\cdot\psi_A(3)$$

and $$\psi_3=\boldsymbol{A}\psi_{CA}(1,2)\cdot\psi_B(3)$$

Total Hamiltonian operator and wave function are

$$\boldsymbol{H}=-\frac{1}{2}\sum_{i=1}^{3}\Delta_i+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{p>q}\frac{Z_oZ_q}{R_{pq}}-\sum_p\sum_i\frac{Z_p}{r_{pi}} \qquad \text{(A.1)}$$

and

$$\Psi=C_1\psi_1+C_2\psi_2+C_3\psi_3 \qquad \text{(A.2)}$$

Accordingly, the determinant to be solved is

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

I_{mn}'s are further resolved into several terms for convenience,

$$I_{mn}=K_{mn}-J_{mn}+R_{mn}\cdot S_{mn} \qquad \text{(A.4)}$$

The formulae of ε_{mn}, S_{mn}, R_{mn}, K_{mn} and J_{mn} are shown below. The notation of integrals used in the expressions is as follows:

$$(ab)=\int a(1)b(1)\,\mathrm{d}\tau_1$$

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

$$(ab|ab)=\int a(1)b(1)\frac{1}{r_{12}}\,a(2)b(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$(a^2|B)=\int a^2(1)\cdot\frac{Z_B}{r_{B1}}\,\mathrm{d}\tau_1 \qquad \text{etc.}$$

Also, in the expressions below, ε_{m1} $(A\rightleftarrows C)$ means the exchange of letters "A" and "C" in that of ε_{m1} and so on.

(1) ε_{mn}; $\varepsilon_{m1}=\varepsilon_{AB}$

$\varepsilon_{m2}=\varepsilon_{m1}(A\rightleftarrows C) \qquad m=1,2,3$

$\varepsilon_{m3}=\varepsilon_{m1}(B\rightleftarrows C)$

(2) R_{mn}; $R_{m1}=\bar{R}_{BC}^{-1}+\bar{R}_{AC}^{-1} \quad \bar{R}_{BC}^{-1}=Z_BZ_C\cdot R_{BC}^{-1}$ etc.,

$R_{m2}=R_{m1}(A\rightleftarrows C) \qquad m=1,2,3$

$R_{m3}=R_{m1}(B\rightleftarrows C)$

(3) S_{mn}; $S_{11}=2+2(ab)^2-(bc)^2-(ac)^2-2(ab)(bc)(ca)$

$S_{22}=S_{11}(a\rightleftarrows c)$

$S_{33}=S_{11}(b\rightleftarrows c)$

$S_{12}=S_{21}=-1+2(ac)^2-(ab)^2-(bc)^2$
$\qquad +(ab)(bc)(ca)$

$S_{13}=S_{31}=S_{12}(a\rightleftarrows b)$

$S_{23}=S_{32}=S_{12}(b\rightleftarrows c)$

(4) K_{mn}; $K_{11}=2(a^2|c^2)+2(b^2|c^2)$
$\qquad +4(ab)(ab|c^2)-(ac|ac)$
$\qquad -(bc|bc)-(bc)\cdot\{(a^2|bc)+(ab|ac)\}$
$\qquad -(ac)\{(b^2|ac)+(ab|bc)\}$
$\qquad -2(ab)(ac|bc)$

$K_{22}=K_{11}(a\rightleftarrows c)$

$K_{33}=K_{11}(b\rightleftarrows c)$

$K_{12}=2[(ac|ac)+(ac)(b^2|ac)]$
$\qquad +(bc)(ab|ac)+(ab)(bc|ac)$
$\qquad -[(a^2|c^2)+(b^2|a^2)+(ab|ab)$
$\qquad +(ab)(c^2|ab)+(ac)(bc|ab)$
$\qquad +(bc)\{2(bc|a^2)+(ab|ac)\}]$

$K_{32}=K_{12}(b\rightleftarrows c)$

$K_{21}=K_{12}(a\rightleftarrows c)$

$K_{31}=K_{21}(a\rightleftarrows b)$

$K_{13}=K_{12}(a\rightleftarrows b)$

$K_{23}=K_{13}(a\rightleftarrows c)$

(5) J_{mn}; $J_{11}=\{2-(bc)^2\}\cdot(a^2|C)+\{2-(ac)^2\}\cdot(b^2|C)$
$\qquad +\{4(ab)-2(ac)(bc)\}\cdot(ab|C)$
$\qquad +\{2+2(ab)^2\}\cdot(c^2|A+B)$
$\qquad -\{(bc)+(ab)(ac)\}\cdot(bc|A+B+C)$
$\qquad -\{(ac)+(ab)(bc)\}\cdot(ac|A+B+C)$

$J_{22}=J_{11}(a\rightleftarrows c,\ A\rightleftarrows C)$

$J_{33}=J_{11}(b\rightleftarrows c,\ B\rightleftarrows C)$

$J_{12}=\{2(ac)+2(ab)(bc)\}(ac|B+C)$
$\qquad -\{(ab)+(ac)(bc)\}(ab|B+C)$
$\qquad -\{1+(bc)^2\}(a^2|B+C)$
$\qquad -\{1+(ab)^2\}(c^2|A)$
$\qquad -\{1-2(ac)^2\}(b^2|A)$
$\qquad +\{2(ac)-(ab)(bc)\}(ac|A)$
$\qquad +\{(ac)(ab)-2(bc)\}(bc|A)$
$\qquad +\{2(bc)(ac)-(ab)\}(ab|A)$

$J_{32}=J_{12}(b\rightleftarrows c,\ B\rightleftarrows C)$

$J_{21}=J_{12}(a\rightleftarrows c,\ A\rightleftarrows C)$

$J_{31}=J_{21}(a\rightleftarrows b,\ A\rightleftarrows B)$

$J_{13}=J_{12}(a\rightleftarrows b,\ A\rightleftarrows B)$

$J_{23}=J_{13}(a\rightleftarrows c,\ A\leftrightarrows C)$