A Note on the Intermolecular Orthogonalized Orbital

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The procedure for treating the molecular interaction is simplified by using the intermolecular orthogonalized orbital given by the method of Löwdin, and the accuracy of the approximation is examined, giving examples of the proton spin density of the solvated electron and the delocalization energy between chemically-interacting molecules. The following is then concluded: the intermolecular orthogonalized orbital is a kind of perturbed wavefunction of the molecule interacting with the other system and can most reasonably be applied when the Mulliken-type approximation for the intermolecular integrals can well be used. Its utility with regard to the three-system problem is also briefly discussed.

There have been many investigations[1-3] pointing out the important role of orbital overlapping between chemically-interacting molecules. However, the treatment considering the overlap effect is troublesome, particularly in the perturbation calculation. Consequently, in the present paper, we will try to calculate the electronic state of the composite system of molecules by the use of the intermolecular orthogonalized orbital given by the method of Löwdin[4] and will examine the accuracy of the approximation. An analogous calculation has frequently been performed in obtaining the spin density of a solvated electron on solvent molecules.[5-7] However, the wavefunction of the electron, ψ°, is orthogonalized only to the occupied orbitals of solvent molecules, ψ_i, as follows:

$$\psi^{\circ} = \Big(\psi_e - \sum_i^{\text{occ}} S_{ei}\psi_i\Big)\Big/\Big(1-\sum_i^{\text{occ}} S_{ei}^2\Big)^{1/2}, \tag{1}$$

where ψ_{e} is the non-orthogonalized orbital of the excess electron and where $S_{\mathrm{e}i} = <\psi_{\mathrm{e}}|\psi_i>$. However, this type of orbital constructs a wavefunction which describes only the electron transfer from the occupied orbitals of solvent molecules to the excess electron orbital; in this sense, it is desirable that ψ° be orthogonal also to the vacant orbitals of solvent molecules. Hence, we employ here a wavefunction satisfying this additional restriction.

Procedure

The basic notations used in this paper are summarized below:

	System A	System B
Fock operator	F_{A}	F_{B}
Occupied orbital	i, j	k, l
Vacant orbital	m, n	p, q
All orbital	a	b
Eigenvalue	ε_{a}	ε_{b}
Total energy in the ground state	W_{A}	W_{B}

Let us assume that the SCF MO's of the closed-shell systems, A and B, have already been obtained as:

$$F_{\mathrm{A}}|a> = \varepsilon_a|a>, \quad F_{\mathrm{B}}|b> = \varepsilon_b|b>. \tag{2}$$

The occupied orbitals orthogonalized to all of the orbitals of the other system and normalized to the second order of overlap integrals are given by:

$$\left.\begin{aligned} |i^{\circ}> &= |i> - \frac{1}{2}\sum_b S_{ib}|b> + \frac{3}{8}\sum_b\sum_a S_{ib}S_{ba}|a> \\ |k^{\circ}> &= |k> - \frac{1}{2}\sum_a S_{ka}|a> + \frac{3}{8}\sum_a\sum_b S_{ka}S_{ab}|b> \end{aligned}\right\} \tag{3}$$

which lead to $<i^{\circ}|j^{\circ}> = \mathrm{O}(\mathrm{S}^3)$ and $<i^{\circ}|k^{\circ}> = \mathrm{O}(\mathrm{S}^4)$, where S implies an intersystem overlap integral. We tentatively construct an antisymmetrized wavefunction using these orbitals in the following manner:

$$\Phi^{\circ} = ||\cdots i^{\circ}\bar{i}^{\circ}\cdots j^{\circ}\bar{j}^{\circ}\cdots k^{\circ}\bar{k}^{\circ}\cdots l^{\circ}\bar{l}^{\circ}\cdots|| \tag{4}$$

where $i^{\circ}\bar{i}^{\circ} = i^{\circ}(\mu)\alpha(\mu)\ i^{\circ}(\nu)\beta(\nu)$ (μ, ν: the numbers of electrons, and α, β: spin functions). At this point of the discussion, we proceed without making definite what this wavefunction stands for. The "energy" corresponding to this wavefunction is given by:

$$W_{\mathrm{T}}^{\circ} = \langle\Phi^{\circ}|H|\Phi^{\circ}\rangle, \tag{5}$$

in which H is the hamiltonian operator of the composite system. Equation (5) is approximately written as follows:

$$\begin{aligned} W_{\mathrm{T}}^{\circ} \approx\ & W_{\mathrm{A}} + W_{\mathrm{B}} + Q_{\mathrm{AB}} \\ & -2\sum_i\sum_k S_{ik}[Q_{\mathrm{A},ik} + Q_{\mathrm{B},ik} - S_{ik}(Q_{\mathrm{A},kk} + Q_{\mathrm{B},ii})] \\ & -\sum_i\sum_p S_{ip}[Q_{\mathrm{A},ip} + Q_{\mathrm{B},ip} - \frac{1}{2}S_{ip}(3Q_{\mathrm{B},ii} + Q_{\mathrm{A},pp}) \\ & +\frac{1}{2}S_{ip}(\varepsilon_p - \varepsilon_i)] \\ & -\sum_k\sum_m S_{km}[Q_{\mathrm{A},km} + Q_{\mathrm{B},km} - \frac{1}{2}S_{km}(3Q_{\mathrm{A},kk} + Q_{\mathrm{B},mm}) \\ & +\frac{1}{2}S_{km}(\varepsilon_m - \varepsilon_k)], \end{aligned} \tag{6}$$

where

$$\begin{aligned} Q_{\mathrm{AB}} = 2\sum_i\langle i|V_{\mathrm{B}}|i\rangle + 2\sum_k\langle k|V_{\mathrm{A}}|k\rangle + 2\sum_i\sum_k\langle k|2J_i - K_i|k\rangle \\ + \text{(repulsions between cores of A and B)}, \end{aligned} \tag{7}$$

$$Q_{\mathrm{A},ik} = \langle i|V_{\mathrm{A}} + \sum_j(2J_j - K_j)|k\rangle \quad etc., \tag{8}$$

in which V is the core field and in which J and K are the Coulomb and exchange operators. In Eq. (6), the

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[1] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, *ibid.*, **A68**, 969 (1955).
[2] K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968).
[3] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1969).
[4] P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).
[5] W. E. Blumberg and T. P. Das, *ibid.*, **30**, 251 (1959).
[6] D. E. O'Reilly, *ibid.*, **41**, 3736 (1964).
[7] K. Fueki, *ibid.*, **45**, 183 (1966).

terms which are of the first and of the second order with regard to the overlap integrals are of the same order of magnitude. If the molecules considered to be non-polar, we may be permitted to put:

$$Q_{\mathrm{AB}} \approx 0, \ Q_{\mathrm{A},ik} \approx Q_{\mathrm{B},ik} \approx \cdots \approx 0. \tag{9}$$

Hence, Eq. (6) is simplified as:

$$\begin{aligned} W_{\mathrm{T}}^{\circ} \approx W_{\mathrm{A}} + W_{\mathrm{B}} - \frac{1}{2}\sum_{i}\sum_{p} S_{ip}^{2}(\varepsilon_p - \varepsilon_i) \\ - \frac{1}{2}\sum_{k}\sum_{m} S_{km}^{2}(\varepsilon_m - \varepsilon_k). \end{aligned} \tag{10}$$

On the right-hand side of this equation, the latter two terms express the stabilization brought about by the delocalization of the electronic charge between two molecules.

Other quantities are also easily obtained as follows. By the interaction with System B, the i-th orbital of A varies to:

$$\begin{aligned} \varepsilon_i^{\circ} \approx \varepsilon_i &+ Q_{\mathrm{B},ii} \\ &- \frac{1}{2}\sum_{b} S_{ib}[Q_{\mathrm{A},ib} + Q_{\mathrm{B},ib} - \frac{1}{2}S_{ib}(\varepsilon_i - \varepsilon_b) \\ &- \frac{1}{2}S_{ib}(3Q_{\mathrm{B},ii} + Q_{\mathrm{A},bb})] \\ &- 2\sum_{i}\sum_{j}\sum_{b} S_{jb}\langle jb|ii\rangle - 2\sum_{i}\sum_{a}\sum_{l} S_{al}\langle al|ii\rangle \\ &+ \frac{1}{2}\sum_{i}\sum_{j}\sum_{b} S_{jb}^{2}(3J_{ij} + J_{ib}) + \frac{1}{2}\sum_{i}\sum_{a}\sum_{l} S_{al}^{2}(3J_{il} + J_{ia}) \\ &+ \frac{1}{2}\sum_{i}\sum_{l}\sum_{b} S_{ib}^{2}(3J_{il} + J_{lb}) \end{aligned} \tag{11}$$

and the matrix elements concerning the charge transfer and the electronic excitation, which should vanish when intermolecular SCF MO's are used, are, respectively:

$$\begin{aligned} \langle \Phi_{i\to p}^{\circ}|H|\Phi^{\circ}\rangle &\approx \frac{1}{2}[Q_{\mathrm{A},ip} + Q_{\mathrm{B},ip} - S_{ip}(Q_{\mathrm{A},pp} + Q_{\mathrm{B},ii})] \\ &\quad - \frac{1}{2}[\sum_{a\neq i} S_{ap}Q_{\mathrm{B},ia} + \sum_{b\neq p} S_{ib}Q_{\mathrm{A},pb}] \\ \langle \Phi_{i\to m}^{\circ}|H|\Phi^{\circ}\rangle &\approx Q_{\mathrm{B},im} - \frac{1}{2}\sum_{b} S_{ib}(Q_{\mathrm{A},mb} + Q_{\mathrm{B},mb}) \\ &\quad - \frac{1}{2}\sum_{b} S_{bm}(Q_{\mathrm{A},ib} + Q_{\mathrm{B},ib}) \\ &\quad + \sum_{b} S_{ib}S_{mb}\Big[\frac{1}{8}(\varepsilon_i + \varepsilon_m) - \frac{1}{4}\varepsilon_b \\ &\quad + \frac{3}{8}(Q_{\mathrm{B},ii} + Q_{\mathrm{B},mm}) + \frac{1}{4}Q_{\mathrm{A},bb}\Big]. \end{aligned} \tag{13}$$

Furthermore, it may be noted that the intermolecular orthogonalized orbital is convenient for treating the three-system (A, B, and C) problem; then:

$$|i^{\circ}\rangle = |i\rangle - \frac{1}{2}\sum_{r} S_{ir}|r\rangle + \frac{3}{8}\sum_{r}\sum_{s} S_{ir}S_{rs}|s\rangle, \tag{14}$$

where r indicates all the molecular orbitals of the two systems except A, and where s indicates all those of the two systems except the system to which r belongs. Here, $<i^{\circ}|i^{\circ}> = 1 + O(S^3)$. The accuracy is inferior to that in the case of two systems. With the use of Eq. (14), the core integral is written as:

$$\begin{aligned} \langle i^{\circ}|H^{\mathrm{c}}|i^{\circ}\rangle = \langle i|H^{\mathrm{c}}|i\rangle &- \sum_{r} S_{ir}\langle i|H^{\mathrm{c}}|r\rangle \\ &+ \frac{1}{4}\sum_{r}\sum_{r'} S_{ir}S_{ir'}\langle r|H^{\mathrm{c}}|r'\rangle \\ &+ \frac{3}{4}\sum_{r}\sum_{s} S_{ir}S_{rs}\langle i|H^{\mathrm{c}}|s\rangle, \end{aligned} \tag{15}$$

where $H^{\mathrm{C}} = T + V_{\mathrm{A}} + V_{\mathrm{B}} + V_{\mathrm{C}}$ (T: the one-electron kinetic operator) and where r and r' belong to the same group of molecules. It is clear in Eq. (15) that the three-center integrals emerge from the second and last terms. Thus, according to the orthogonalization procedure, the three-system problem becomes tractable.

Now, let us compare the above treatment with that of Devaquet,[9] in which the following intermolecular SCF MO for two closed-shell molecules is used:

$$|i^{\mathrm{int}}\rangle = |i\rangle(1 - \gamma_i) - \sum_{b} c_{ib}|b\rangle + \cdots, \tag{16}$$

where:

$$\begin{aligned} \gamma_i &= \frac{1}{2}\sum_{b} c_{ib}(c_{ib} - 2S_{ib}) \\ c_{ib} &= \frac{F_{ib} - S_{ib}F_{ii}}{F_{bb} - F_{ii}} \\ &\approx \frac{\frac{1}{2}S_{ib}(\varepsilon_b - \varepsilon_i) + \left[\frac{1}{2}(Q_{\mathrm{A},ib} + Q_{\mathrm{B},ib}) - S_{ib}Q_{\mathrm{B},ii}\right]}{\varepsilon_b - \varepsilon_i + Q_{\mathrm{A},bb} - Q_{\mathrm{B},ii}} \end{aligned} \tag{17}$$

(F: Fock operator for the composite system of two molecules). If we set:

$$\frac{1}{2}(Q_{\mathrm{A},ib} + Q_{\mathrm{B},ib}) - S_{ib}Q_{\mathrm{B},ii} = 0, \ Q_{\mathrm{A},bb} - Q_{\mathrm{B},ii} = 0, \tag{18}$$

i.e., $$Q_{\mathrm{A},ib} + Q_{\mathrm{B},ib} = S_{ib}(Q_{\mathrm{A},bb} + Q_{\mathrm{B},ii}), \tag{19}$$

c_{ib} and γ_i become:

$$c_{ib} \approx \frac{1}{2}S_{ib} \text{ and } \gamma_i \approx -\frac{3}{8}\sum_{b} S_{ib}^{2} \tag{20}$$

respectively. Equation (16) agrees with Eq. (3) if we take only the i term in the summation with respect to a in Eq. (3). Equation (19) is regarded as a "Mulliken-type approximation" for intermolecular integrals in the case of non-polar molecules.

The interaction energies given by Eqs. (3) and (16) are similar except for the term:

$$\left.\begin{aligned} - 2\sum_{i}\sum_{p}\frac{I_{ip}^{2}}{\varepsilon_p - \varepsilon_i} - 2\sum_{k}\sum_{m}\frac{I_{km}^{2}}{\varepsilon_m - \varepsilon_k} \\ I_{ip} = \frac{1}{2}(Q_{\mathrm{A},ip} + Q_{\mathrm{B},ip}) \ \ etc. \end{aligned}\right\} \tag{21}$$

which appears only in the expression of Devaquet. That is, the intermolecular orthogonalized orbital is a kind of approximate perturbed wavefunction of the molecule interacting with the other system, and the validity depends on the adequacy of the approximation represented by Eq. (19). Under the condition that Eq. (19) is well satisfied, the total wavefunction of the single Slater determinant composed of orthogonalized orbitals (Eq. (4)), which includes the resulting charge-transfer and polarization effects, is considered to describe the electronic state of the composite system appropriately.

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[8] L. Brillouin, *Actualites Sci. et Ind.*, **71**, (1933); 159 (1934).

[9] A. Devaquet, *Mol. Phys.*, **18**, 233 (1970).

TABLE 1. THE CALCULATED RESULTS CONCERNING THE INSIDE PROTON SPIN DENSITY OF THE SOLVATED ELECTRON[a]

Solvent	Previous work[b]		The 1s AO orthogonal to all of the orbitals of solvent molecules (I)	The 1s AO orthogonal only to the occupied orbitals of solvent molecules (II)
	Total	Delocalization term		
NH_3	−0.009	+0.0008	+0.020	+0.009
H_2O	−0.012	+0.00004	+0.021	+0.007

a) The model is formed by four solvent molecules with one OH or NH bond oriented toward the cavity center. The orbital exponent of the 1s AO for the solvated electron is 0.3 a.u.$^{-1}$.

b) Ref. 10.

Examples

Table 1 shows the calculated spin densities of the solvated electron on the proton of solvent molecules. The values of I are larger than those of II; this is because in the former the delocalization, from the 1s AO of the excess electron to the vacant orbitals of solvent molecules, and from the occupied orbitals to the 1s AO, are both included, while in the latter only the delocalization from the occupied orbitals to the 1s AO is included. The discrepancy of this I from that of our previous work[10] is mainly caused by the approximation corresponding to omitting the term of (21). The result of II for the ammoniated electron differs very much from O'Reilly's.[6] This may be brought about by the differences between the wavefunctions applied and the approximation in estimating the molecular integrals. For the hydrated electron, the spin density of II is almost identical with Fueki's,[7] *ca.* 0.01, which is given in the same manner as II by the orbital exponent of the 1s AO for an excess electron, 0.312 a.u.$^{-1}$. At any rate, the spin polarization mechanism contributes dominantly in the case of a solvated electron in polar solvents; therefore, the values obtained by the orthogonalized orbital, which gives only an approximate spin delocalization term through the second order of the overlap integral, are unsatisfactory.

In Table 2, the results concerning the delocalization energies between a hydrogen molecule and carbene, between borane and borane, and between carbene and ethylene are compared with those of Fukui *et al.* For models (1) and (2), the present values are overestimated by a factor of several times.[11] For Model (3), the error is as small as *ca.* 16% and when the intermolecular distance R becomes smaller (Model (4)), the error increases. In Model (3), the perturbation expansion with the overlap is suitable because of the large intermolecular distance; besides, Eq. (19) can be expected to be satisfied successfully.

TABLE 2. THE RESULTS OF THE DELOCALIZATION ENERGY (in eV)

Model	Present value	The value given by Fukui *et al.*
(1)	0.048090	0.013575[a]
(2)	0.603132	0.129753[b]
(3)	0.035370	0.042354[c]
(4)	0.105696	0.281025[c]

a) Calculated by M. Miyagi.

b) Calculated by S. Kato.

c) Ref. 12.

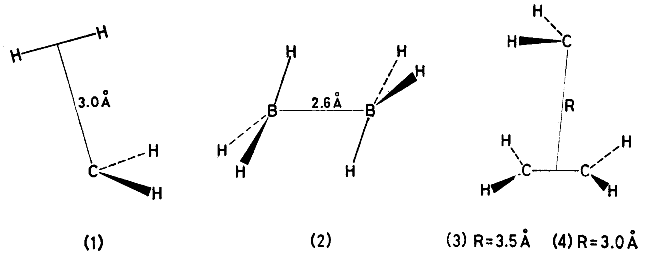

Fig. 1. The models used in the calculation of the delocalization energy.

Conclusion

The intermolecular orthogonalized orbital is a kind of perturbed wavefunction of the molecule interacting with the other system, and, with the use of the orbital, the approximate expression of the interaction energy can easily be derived. It should be noticed, however, that the wavefunction can most reasonably be applied when the Mulliken-type approximation for the intermolecular integrals can be used. This means that, for the case in which the Gaussian-type orbitals are favorably used,[13] it is appropriate to use the intermolecular orthogonalized orbital. Moreover, according to the present procedure, the three-system problem becomes tractable.

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10) S. Ishimaru, H. Kato, T. Yamabe, and K. Fukui, *Chem. Phys. Lett.*, **17**, 264 (1972).

11) For model (1), the value of r.h.s. of Eq. (19) between highest occupied orbitals is −0.605 and that of l.h.s. is −0.327 in eV.

12) H. Fujimoto, S. Yamabe, and K. Fukui, This Bulletin, **45**, 2424, (1972).

13) L. Jansen, "Advances in Quantum Chemistry," Vol. 2, ed. by P. O. Löwdin, Academic Press, New York, (1965), p. 119. H. Margenau and J. Stamper, *ibid.*, Vol. 3, (1967), p. 129.