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Studies on the Catalysis by Molten Metal

VII. A Simple MO Treatment on the Dehydrogenation of Alcohols and Amines over the Molten Metal

AKIRA MIYAMOTO, KIYOHISA OKANO
AND YOSHISADA OGINO

Department of Chemical Engineering, Faculty of Engineering, Tohoku University, Aramaki Aoba, Sendai, Japan

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The MO theoretical treatments based on the perturbation theory were made for the catalytic dehydrogenations of alcohols and amines over the molten metals. Namely, the stabilization energy of the liquid metal–adsorbate system was evaluated under the assumption that the delocalizations of electrons from the liquid metal to the adsorbate molecule or vice versa mainly contribute to the stabilization. It was suggested that the smaller work function is necessary for the liquid metal to have a catalytic activity, and that the adsorbate molecule (alcohols and amines) acts as an electron-acceptor in the catalysis over the liquid metal. The comparison of the activity data with the work function data proved the validity of the present theoretical treatment.

INTRODUCTION

In the first paper (*1*) of this series, it was reported that zinc, aluminum, gallium, indium and thallium are active in their molten states for the dehydrogenation of methyl alcohol, whereas cadmium, tin, antimony, lead, bismuth, tellurium and mercury are inactive. Simiarly, *n*-butylamine was found (*2*) to be dehydrogenated by such liquid metals (molten metals) as zinc, gallium, indium and thallium, but the amine can not be dehydrogenated by cadmium, tin, lead and bismuth. Further, the above-mentioned active metals were found to catalyze the dehydrogenation of C_2- to C_7-alcohols as well as C_4- to C_7-amines (*3–6*).

These experimental results raise a question why some liquid metals are active and the other metals are inactive. Although the question is primitive, no existing theories seem to answer the question. In general, the surface catalysis is too complicated to be treated theoretically. However, according to our experimental results (*1–6*), the liquid metal selectively catalyzes the dehydrogenations of alcohols and amines, and the catalyst fouling was found to be scarce. Thus, the liquid metal–alcohol (or amine) is considered to form a simple catalytic system which provides a good foundation to the theoretical work.

The purpose of the present work was to demonstrate that a simple quantum-chemical treatment is successfully applied to solve the problem. The theory gives not only a plausible explanation of the experimental result but also an electronic criterion for the selection of the effective catalysts.

THEORY

In considering the surface catalysis, the interaction energy between the adsorbing molecule or atom and the catalyst surface should be formulated firstly. Thus, we assumed that the interaction energy (*E*) between an adsorbing molecule and the surface of a simple metal will be given by a similar equation representing the interaction energy between two molecules (*7*). Namely, if the interaction energy is small, E is given by

$$E = E_1 + E_2 + E_3 + E_4, \qquad (1)$$

where E_1, E_2, E_3 and E_4 represent the dispersion energy, the exchange energy, the image force potential and the delocalization energy, respectively. The formulation of E_1 was given by many researchers, for instance Lennard-Jones (*8*). Pollard (*8*) gave an expression of E_2 for a simple metal–hydrogen system. Further, the expression of E_3 which is significant only for a polar molecule–metal system was given by Lennard-Jones (*8*). These three terms are responsible mainly for a physical adsorption and, to a first approximation, they may be neglected in the adsorption onto perfectly conducting metals, especially in the chemisorption. Therefore, the remaining term E_4 would play an important role in the chemisorption and catalysis.

We considered that an approximate adsorption energy E_4 for the adsorption model on the liquid metal catalyst given in Fig. 1 may be evaluated by the following equations:

$$E_4 = \Delta E = \sum_{s=1}^{2} [D^{\mathrm{N}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) + D^{\mathrm{E}}(\mathrm{H}_s,\epsilon_{\mathrm{F}})] \sum_{\substack{k \\ \epsilon_k \simeq \epsilon_{\mathrm{F}}}} |\mathrm{H}'_{sk}|^2 \qquad (2)$$

$$= \sum_{s=1}^{2} 2\, D^{\mathrm{R}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) \sum_{\substack{k \\ \epsilon_k \simeq \epsilon_{\mathrm{F}}}} |\mathrm{H}'_{sk}|^2, \qquad (3)$$

$$D^{\mathrm{N}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) = 2 \sum_{i}^{\mathrm{unocc}} \frac{c_{is}^2}{\epsilon_i - \epsilon_{\mathrm{F}}}, \qquad (4)$$

$$D^{\mathrm{E}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) = 2 \sum_{i}^{\mathrm{occ}} \frac{c_{is}^2}{\epsilon_{\mathrm{F}} - \epsilon_i}, \qquad (5)$$

and

$$D^{\mathrm{R}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) = 1/2[D^{\mathrm{N}}(\mathrm{H}_s,\epsilon_{\mathrm{F}}) + D^{\mathrm{E}}(\mathrm{H}_s,\epsilon_{\mathrm{F}})]. \qquad (6)$$

The notations used in these equations are as follows:

ϵ_k	the k-th energy level of the liquid metal,
ϵ_{F}	the Fermi level of the liquid metal,
ϵ_i	the i-th energy level of the adsorbate,
ΔE	delocalization energy,
H_s	the s-th hydrogen atom in the adsorbate ($s = 1, 2$),
$\sum_{i}^{\mathrm{occ}}$	the summation over the occupied levels of the adsorbate molecule,
$\sum_{i}^{\mathrm{unocc}}$	the summation over the unoccupied levels of the adsorbate molecule,
$\sum_{\substack{k \\ \epsilon_k \simeq \epsilon_{\mathrm{F}}}}$	the summation over the levels of the liquid metal near the Fermi level,
$H'_{sk} = \int \chi_s H' \psi_k d\tau$,	
χ_s	the atomic orbital of the s-th hydrogen atom ($s = 1, 2$),
ψ_k	the wave function of the liquid metal corresponding to ϵ_k,
H'	a perturbation potential for the interaction between the adsorbate molecule and the liquid metal,
c_{is}	the LCAO-MO coefficient of the s-th hydrogen atomic orbital of the i-th energy level of the adsorbate molecule.

The proposed equation, viz, Eq. (2), was derived from the one body approximation based on the second order perturbation theory and LCAO-MO approximation. According to Grimley (*15*), even for the

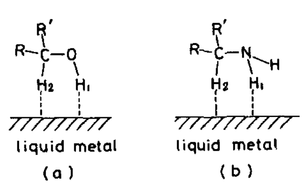

FIG. 1. Adsorption models of alcohol (a) and amine (b) on a liquid metal catalyst.

adsorption with considerably high adsorption energy (~42 kcal/mole for carbon monoxide adsorption on nickel), the perturbation theory is applicable. The adsorption of an alcohol onto the liquid metal had been shown to be ~13 kcal/mole (*5*, *sec*-butyl alcohol–indium system). Thus, it can be said that the application of the perturbation theory to the present problem is plausible. The frontier electron theory proposed by Fukui, Yonezawa and Shingu (*9*) was also taken into consideration to assume that the electronic energy levels near the Fermi level (ϵ_F) of a liquid metal mainly contribute to the delocalization energy. Further, it was also assumed that the variations of the state density and the wave function near the Fermi level would be small. This assumption seems to be valid for the liquid metal, because the electronic state of a liquid metal is represented by the nearly free electron model (*10*). Note that Eq. (2) does not include any cross terms of the delocalization energy including $\mathrm{Re}(H'_{\mathrm{H_1}k}H'^{*}_{\mathrm{H_2}k})$. The validity for the elimination of these terms from Eq. (2) is shown in the Appendix.

In Eqs. (4)–(6), D^N is related to the delocalization of electron from metal to the adsorbing molecule through H_s atom and D^E is related to the delocalization of electron from the adsorbing molecule to metal through H_s atom. Therefore, if we assume that $\Sigma_{k_{\epsilon_k=\epsilon_F}}|H'_{sk}|^2$ takes a constant value irrespective of the species of the adsorbent metal, values of D^N and D^E provide us with the measure of the delocalization energy.

Thus, to evaluate D^N, D^E and D^R, numerical computations were carried out with a NEAC 2200–Model 700 digital computer (Computer Center, Tohoku University). The necessary energy levels and wave functions of alcohols and amines were obtained by applying the extended Hückel molecular orbital theory (*11*), and the molecular parameters given in Table 1 were used.

RESULTS

Methyl alcohol. Relations between ϵ_F and the calculated values of $D^N(H_1,\epsilon_F)$, $D^E(H_1,\epsilon_F)$ and $D^R(H_1,\epsilon_F)$ for the methyl alcohol-liquid metal system are given in Fig. 2. According to the present theory, the characteristic aspects of the electronic interaction between H_1 and the surface of the liquid metal are represented in Fig. 2. For instance, the higher value of $D^N(H_1,\epsilon_F)$ than the value of $D^E(H_1,\epsilon_F)$ at any ϵ_F value means an acidic character of the H_1 atom in the methyl alcohol–liquid metal system. Further, the nearly parallel relation of $D^R(H_1,\epsilon_F)$ with $D^N(H_1,\epsilon_F)$ indicates that the overall interaction between H_1 and the surface is governed by the acidity of the H_1 atom.

Relations between ϵ_F and the calculated values of $D^N(H_2,\epsilon_F)$, $D^E(H_2,\epsilon_F)$ and $D^R(H_2,\epsilon_F)$ are given in Fig. 3. Figure 3 indicates that $D^N(H_2,\epsilon_F)$ is larger than $D^E(H_2,\epsilon_F)$ at any ϵ_F values. On the other hand, $D^R(H_2,\epsilon_F)$ takes the minimum value at $\epsilon_F \simeq -7.5$ eV. From these results it may be pointed out that the acidic character of the H_2 atom is predominant in the range of $\epsilon_F > -7.5$ eV, while the acidity of the liq-

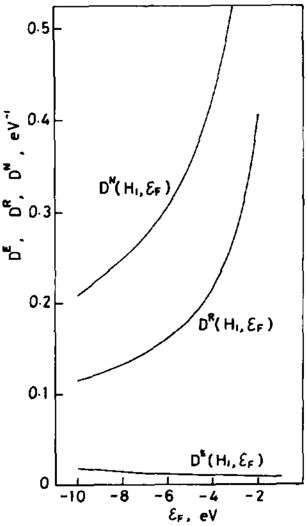

FIG. 2. Calculated values of $D^N(H_1,\epsilon_F)$, $D^E(H_1,\epsilon_F)$ and $D^R(H_1,\epsilon_F)$ for methyl alcohol.

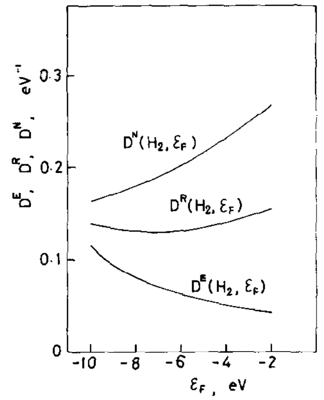

FIG. 3. Calculated values of $D^N(H_2,\epsilon_F)$, $D^E(H_2,\epsilon_F)$ and $D^R(H_2,\epsilon_F)$ for methyl alcohol.

uid metal gradually increases as the ϵ_F value decreases and, in the range of $\epsilon_F < -7.5$ eV, it becomes comparable with the acidity of H_2 atom.

A further remark to be pointed out is that both $D^N(H_1,\epsilon_F)$ and $D^N(H_2,\epsilon_F)$ increase with the increase in ϵ_F. This means that the delocalization of electron from metal to methyl alcohol becomes easier as ϵ_F becomes greater. On the contrary, both $D^E(H_1,\epsilon_F)$ and $D^E(H_2,\epsilon_F)$ decrease with the increase in ϵ_F. This means that the delocalization of electron from methyl alcohol to the liquid metal becomes more difficult as ϵ_F becomes greater.

TABLE 1

PARAMETERS USED FOR THE MO CALCULATION

	Effective nuclear charge Z^*	Ionization potentials		Bond length r (Å)	Bond angle θ (deg)
		Ip(ns) (eV)	Ip(np) (eV)		
H	1.00	13.60	–		
C	3.25	21.43	11.42		
N	3.90	27.50	14.49		
O	4.55	35.30	17.76		
OH				0.96	
CO				1.43	
CH				1.09	
CC				1.53	
CN				1.47	
NH				1.014	
∠COH					110
∠COC					109
∠HCH					109
∠CCO					109
∠CCC					109
∠CCN					110
∠HNH					105.8

Other alcohols. Calculated values of D^N, D^E and D^R for ethyl alcohol, *n*-propyl alcohol, *iso*propyl alcohol, *n*-butyl alcohol and *sec*-butyl alcohol showed that the electronic character of the adsorption of any one of these alcohols onto the liquid metal differs little from that of the adsorption of methyl alcohol.

n-Butylamine. Values of $D^N(H_1,\epsilon_F)$, $D^E(H_1,\epsilon_F)$ and $D^R(H_1,\epsilon_F)$ for *n*-butylamine–liquid metal system are given in Fig. 4. As shown in Fig. 4 the value of $D^N(H_1,\epsilon_F)$ is greater than that of $D^E(H_1,\epsilon_F)$ at any ϵ_F values. This means that the H_1 atom in *n*-butylamine molecule shows an acidic character against the surface of the liquid metal. As mentioned in the previous paragraph, the H_1 atom in methyl alcohol molecule showed the same character as above. Further, the relation between $D^R(H_1,\epsilon_F)$ and ϵ_F for *n*-butylamine differs little from that obtained for methyl alcohol.

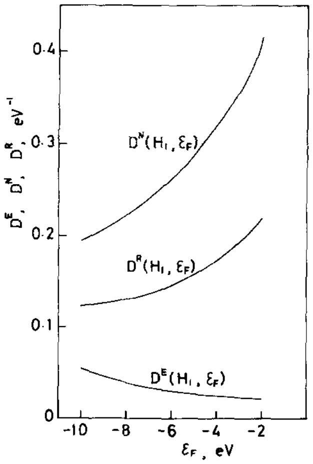

FIG. 4. Calculated values of $D^N(H_1,\epsilon_F)$, $D^E(H_1,\epsilon_F)$ and $D^R(H_1,\epsilon_F)$ for *n*-butylamine.

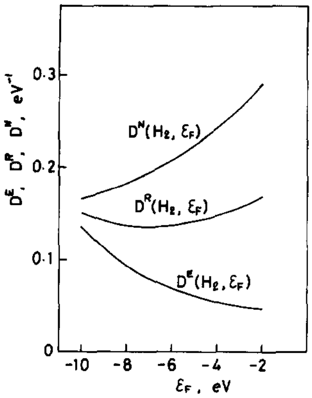

FIG. 5. Calculated values of $D^N(H_2,\epsilon_F)$, $D^E(H_2,\epsilon_F)$ and $D^R(H_2,\epsilon_F)$ for *n*-butylamine.

Values of $D^N(H_2,\epsilon_F)$, $D^E(H_2,\epsilon_F)$ and $D^R(H_2,\epsilon_F)$ for *n*-butylamine are given in Fig. 5. As shown in Fig. 5 D^N is larger than D^E within the range of ϵ_F indicated on the abscissa. On the other hand, D^R takes the minimum value at $\epsilon_F \simeq -7$ eV. These results qualitatively resemble the corresponding results obtained for alcohols including methyl alcohol.

Other Amines. Remarks similar to those made for alcohols and *n*-butylamine were found to be derivable from the calculated values of D^N, D^E and D^R for the other amines (*n*-propylamine, *n*-butylamine, *iso*-butylamine and *n*-hexylamine).

Summary. It seems to be important to point out general dependences of the electronic delocalization energy upon Fermi energy. Two important deductions obtained from the present theory are given below:

1. In the range of $\epsilon_F > -7$ eV, the delocalization energy is an increasing function of ϵ_F irrespective of the species of the adsorbate.
2. Among the four quantities, $D^N(H_1,\epsilon_F)$, $D^N(H_2,\epsilon_F)$, $D^E(H_1,\epsilon_F)$ and $D^E(H_2,\epsilon_F)$, the former two quantities mainly contribute to the total delocalization energy ΔE.

DISCUSSION

The most remarkable result obtained in the present work is that, in the range of $\epsilon_F > -7$ eV, the delocalization energy defined by Eq. (3) increases with the increase in the Fermi energy irrespective of the species of the adsorbate. In other words, owing to the delocalization of the electron, the adsorbed species are more stabilized as the Fermi energy of the liquid metal increases. Therefore, it can be said that the higher the Fermi energy of the liquid metal the stronger is the adsorption on the liquid metal. It is well known that the adsorption plays an important role in the surface catalysis. Then, the Fermi energy of the liquid metal can be considered to have an intimate relation to the catalytic activity of the liquid metal. Further, it can be supposed that the active liquid metal would have a high Fermi energy.

An important deduction from the abovementioned discussion is that the active liquid metal would have a small work function (ϕ). Namely, to a first approximation, the effect of a surface dipole moment upon the work function may be neglected to give

$$\epsilon_F = -\phi, \qquad (7)$$

and it may be understood that the liquid metal of a small work function should have a high ϵ_F value and the adsorption on this metal would be strong. If the work function becomes smaller than a critical value, the adsorption may become strong enough to result in the surface catalysis. The situation becomes clearer by the aid of Fig. 6 which represents relative energy levels of the adsorbate molecule against the Fermi level of the liquid metal. Figure 6 reveals that the delocalization of electron from the occupied electronic energy level near the Fermi level of the liquid metal to the lowest unoccupied level of the adsorbate molecule becomes more feasible as the work function of the liquid metal becomes

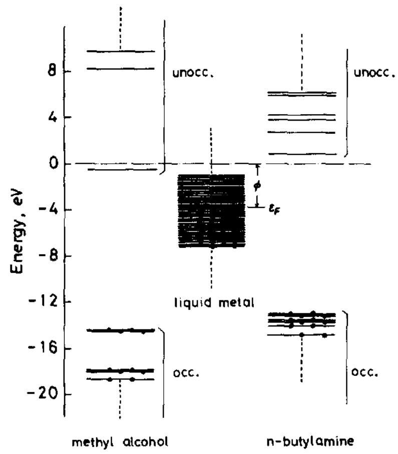

FIG. 6. The respective energy levels of methyl alcohol, *n*-butylamine and liquid metal.

smaller. Thus, the present theory predicts that the activity data would be explained in terms of the work function of the liquid metal.

According to our previous works, Zn, In, Tl, Ga and Al were active in their molten states for the dehydrogenations of alcohols and amines, while Bi, Cd, Sb, Sn, Pb and Hg were inactive. The present theory predicts that the work functions of the former metals should be smaller than those of the latter metals. Unfortunately, however, work function data of liquid metals are scarce in the literature. Therefore, work function data of solid metals (*12,13*) were compared with the catalytic activity and the result is shown in Fig. 7. As shown in Fig. 7, the work function of active metals (Al, Tl, Zn and Ga) have smaller values than those of the inactive metals (Cd, Pb, Sn, Sb, Bi and Hg). This result indicates the validity of the present theoretical treatment though it is rather qualitative. Further, it can be theoretically expected that the catalytic activity may be controlled by alloying suitable metals to reduce the work function.

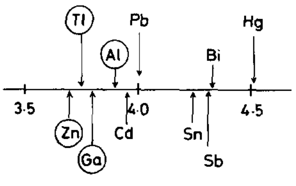

FIG. 7. Work functions of the catalytically active metals (○) and those of the inactive metals. The mean values of data chosen from Refs (*12*) and (*13*).

APPENDIX

1. The purpose of the appendix. An application of the general expression of the delocalization energy to the adsorption model shown in Fig. 1 gives the following equation:

$$\begin{aligned}\Delta E = {} & 2\left[\left(\sum_i^{\text{unocc}} - \sum_i^{\text{occ}}\right)\frac{C_{iH_1}^2}{\epsilon_i - \epsilon_F}\right] \sum_{\substack{k\\ \epsilon_k=\epsilon_F}} |H'_{H_1k}|^2 \\ & + 2\left[\left(\sum_i^{\text{unocc}} - \sum_i^{\text{occ}}\right)\frac{C_{iH_2}^2}{\epsilon_i - \epsilon_F}\right] \sum_{\substack{k\\ \epsilon_k=\epsilon_F}} |H'_{H_2k}|^2 \\ & + 4\left[\left(\sum_i^{\text{unocc}} - \sum_i^{\text{occ}}\right)\frac{C_{iH_1}C_{iH_2}}{\epsilon_i - \epsilon_F}\right] \sum_{\substack{k\\ \epsilon_k=\epsilon_F}} \text{Re}(H'_{H_1k}H'^{*}_{H_2k}),\end{aligned} \tag{A-1}$$

where the suffixes H_1 and H_2 represent the H_1 atom and the H_2 atom in Fig. 1, respectively. The purpose of the present Appendix is to show that the last term is small and negligible compared with the other two terms.

To solve the proposed problem, Eq. (A-1) was replaced by an approximate formula

$$\Delta E = 2DH'(H_1) + 2DH'(H_2) + 4DH'(H_1,H_2), \tag{A-2}$$

because all bracketed quantities in Eq. (A-1) have values of the same order of magnitude and they may be approximated by D. Further, the following abbreviations:

$$\sum_{\substack{k\\ \epsilon_k=\epsilon_F}} |H'_{H_1k}|^2 = H'(H_1),$$

$$\sum_{\substack{k\\ \epsilon_k=\epsilon_F}} |H'_{H_2k}|^2 = H'(H_2), \tag{A-3}$$

$$\sum_k \mathrm{Re}(H'_{\mathrm{H_1}k} H'^{*}_{\mathrm{H_2}k}) = H'(\mathrm{H_1},\mathrm{H_2})$$

were adopted in Eq. (A-2). Thus, the present problem reduces to evaluate $H'(\mathrm{H_1})$, $H'(\mathrm{H_2})$, $H'(\mathrm{H_1},H\mathrm{h_2})$ and to prove the following relation

$$\left|\frac{4DH'(\mathrm{H_1},\mathrm{H_2})}{2DH'(\mathrm{H_1}) + 2DH'(\mathrm{H_2})}\right| \ll 1. \qquad \text{(A-4)}$$

2. *Expressions for* $\mathrm{H}'(H_1)$, $\mathrm{H}'(H_2)$ *and* $\mathrm{H}'(H_1,H_2)$. The extension of the Wolfsberg–Helmholtz approximation (*14*) which is usually employed in the extended Hückel MO calculation gives the following equations;

$$H'_{\mathrm{H_1}k} = \mathrm{const}\cdot S_1(\mathrm{H_1},k_x,k_y,k_z,Z_{\mathrm{H_1}}), \qquad \text{(A-5)}$$

$$H'_{\mathrm{H_2}k} = \mathrm{const}\cdot S_2(\mathrm{H_2},k_x,k_y,k_z,Z_{\mathrm{H_2}}), \qquad \text{(A-6)}$$

where S is an overlap integral between the surface electron and the 1*s* electron of the hydrogen atom in the adsorbed alcohol (or amine), k_x, k_y and k_z are integers (0, 1, 2, . . .), respectively, and Z_H is the distance between the center of the the hydrogen atom and the surface of the liquid metal. Thus, $H'(\mathrm{H_1})$, $H'(\mathrm{H_2})$ and $H'(\mathrm{H_1},\mathrm{H_2})$ can, respectively, be expressed by

$$H'(\mathrm{H_1}) = N(\mathrm{const})^2\langle S_1^2(\mathrm{H_1},k_x,k_y,k_z,Z_{\mathrm{H_1}})\rangle, \qquad \text{(A-7)}$$

$$H'(\mathrm{H_2}) = N(\mathrm{const})^2\langle S_2^2(\mathrm{H_2},k_x,k_y,k_z,Z_{\mathrm{H_2}})\rangle, \qquad \text{(A-8)}$$

$$H'(\mathrm{H_1},\mathrm{H_2}) = N(\mathrm{const})^2 \times \langle S_1(\mathrm{H_1},k_x,k_y,k_z,Z_{\mathrm{H_1}}) \cdot S_2(\mathrm{H_2},k_x,k_y,k_z,Z_{\mathrm{H_2}})\rangle, \qquad \text{(A-9)}$$

where $N = \Sigma_{k_{\epsilon_k=\epsilon_F}}(1)$ and $\langle\ \ \rangle$ means a statistical average.

It is obvious from Eqs. (A-7)–(A-9) that the evaluation of the overlap integral S is required to prove Eq. (A-4). The definition of S is

$$S_1 = \int \psi \cdot \psi_{1s}^{\mathrm{H1}}\, d\tau,\ S_2 = \int \psi \cdot \psi_{1s}^{\mathrm{H2}}\, d\tau, \qquad \text{(A-10)}$$

where ψ is the wave function of the quasi-free electron in the metal and ψ_{1s}^{H} is the wave function of the 1*s* electron in the hydrogen atom. Therefore, exact forms of ψ and ψ_{1s}^{H} become necessary to solve the present problem.

3. *Forms of the wave functions.* (i) ψ. In order to obtain an explicit expression of the wave function ψ, a Cartesian coordinate system shown in Fig. 8 was employed, and it was assumed that a free electron is confined in a cubic potential box ($L \times L \times L$).

The Schrödinger equation for this system can easily be solved to give

$$\psi_x = \left(\frac{2}{L}\right)^{1/2} \sin\,(k_x\pi x/L), \qquad \text{(A-11)}$$

$$\psi_y = \left(\frac{2}{L}\right)^{1/2} \sin\,(k_y\pi y/L), \qquad \text{(A-12)}$$

$$\psi_z^{(1)} = A \sin\left\{\pi\Delta\xi'_n + \pi(k_z - \Delta\xi'_n)\left(\frac{L-z}{L}\right)\right\}, \quad (0 \leqslant z \leqslant L) \qquad \text{(A-13)}$$

$$\psi_z^{(2)} = A \sin\,(\pi\Delta\xi'_n) \exp\left\{-\pi[N_V^2 - (k_z - \Delta\xi'_n)^2]^{1/2}\left(\frac{z-L}{L}\right)\right\}, \quad (z \geqslant L) \qquad \text{(A-14)}$$

where

$$\Delta\xi'_n \doteqdot \cot^{-1}[(N_V^2 - k_z^2)^{1/2}/k_z], \qquad \text{(A-15)}$$

$$N_V = 2mL^2V/\pi^2h^2, \qquad \text{(A-16)}$$

$$A = \left(\frac{2}{L}\right)^{1/2}\left\{1 + \frac{1}{4\pi}\frac{\sin\,(2\pi\Delta\xi'_n)}{(k_z - \Delta\xi'_n)^2} + \frac{1}{2}\frac{\sin^2\,(\pi\Delta\xi'_n)}{[N_V^2 - (k_z - \Delta\xi'_n)^2]^{1/2}}\right\}^{-1/2}. \qquad \text{(A-17)}$$

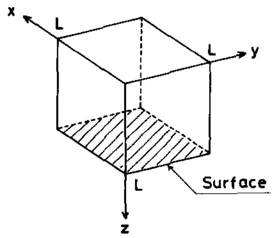

FIG. 8. Cartesian coordinate system for a free electron in a cubic potential box ($L \times L \times L$).

(ii) ψ_{1s}^{H}. If the hydrogen atom H_1 is assumed to locate at $x = x_1$, $y = y_1$ and $z = z_{\mathrm{H}_1}$, then the wave function ψ_1^{H} is given by

$$\psi_{1s}^{\mathrm{H}1} = (\pi a_0^3)^{-1/2} \exp\{-[x_1'^2 + y_1'^2 + (z - Z_{\mathrm{H}_1})^2]^{1/2}/a_0\}, \qquad \text{(A-18)}$$

where a_0 is the Bohr radius, and $x' = x - x_1$, $y' = y - y_1$. Similarly, the wave function of the $1s$ electron of the H_2 atom locating at $x = x_2$, $y = y_2$ and $z = Z_{\mathrm{H}_2}$ is given by

$$\psi_{1s}^{\mathrm{H}^2} = (\pi a_0^3)^{-1/2} \exp\{-[x_2'^2 + y_2'^2 + (z - Z_{\mathrm{H}_2})^2]^{1/2}/a_0\}, \qquad \text{(A-19)}$$

where $x_2' = x - x_2, y_2' = y - y_2$.

4. The overlap integrals S_1 *and* S_2. By putting Eqs. (A-11), (A-12) and (A-18) into Eq. (A-10) we obtain

$$S_1 = K \sin(k_x\pi x_1/L) \sin(k_y\pi y_1/L) J_1(k_x,k_y,k_z,Z_{\mathrm{H}_1}), \qquad \text{(A-20)}$$

where $K = (2/L)(\pi a_0^3)^{-1/2}$ and

$$J_1(k_x,k_y,k_z,Z_{\mathrm{H}_1}) = \int \psi_z \exp\{-[x_1'^2 + y_1'^2 + (z - Z_{\mathrm{H}_1})^2]^{1/2}/a_0\} \times \cos(k_x\pi x'/L) \cos(k_y\pi y'/L)\,dx'dy'dz. \qquad \text{(A-21)}$$

Similarly, the overlap integral S_2 is given by

$$S_2 = K \sin(k_x\pi x_2/L) \sin(k_y\pi y_2/L) J_2(k_x,k_y,k_z,Z_{\mathrm{H}_2}). \qquad \text{(A-22)}$$

5. Evaluations of the statistical averages. From the expressions (A-20) and (A-22), the statistical averages appearing in Eqs. (A-7), (A-8) and (A-9) are given, respectively, by

$$\langle S_1^2(\mathrm{H}_1,k_x,k_y,k_z,Z_{\mathrm{H}_1})\rangle = \frac{K^2}{4} J_1^2(k_x,k_y,k_z,Z_{\mathrm{H}_1}), \qquad \text{(A-23)}$$

$$\langle S_2^2(\mathrm{H}_2,k_x,k_y,k_z,Z_{\mathrm{H}_2})\rangle = \frac{K^2}{4} J_2^2(k_x,k_y,k_z,Z_{\mathrm{H}_2}), \qquad \text{(A-24)}$$

$$\langle S_1(\mathrm{H}_1,k_x,k_y,k_z,Z_{\mathrm{H}_1}) S_2(\mathrm{H}_2,k_x,k_y,k_z,Z_{\mathrm{H}_2})\rangle = \frac{K^2}{4}\left\langle \cos\left(k_x\pi\frac{x_2 - x_1}{L}\right) \cos\left(k_y\pi\frac{y_2 - y_1}{L}\right)\right\rangle \times J_1(k_x,k_y,k_z,Z_{\mathrm{H}_1}) J_2(k_x,k_y,k_z,Z_{\mathrm{H}_2}). \qquad \text{(A-25)}$$

In obtaining Eq. (A-25), the following relation was taken into consideration. That is,

$$\left\langle \cos\left(k_x\pi\frac{x_1 + x_2}{L}\right)\right\rangle = 0 = \left\langle \cos\left(k_y\pi\frac{y_1 + y_2}{L}\right)\right\rangle. \qquad \text{(A-26)}$$

The validity of this relation is easily verified by using Fig. 9, which indicates that the average $\langle\cos(k_x\pi\Delta L/L)\rangle$ reduces to zero as $k_x\Delta L/L$ becomes larger. In Eq. (A-26), both $x_1 + x_2$ and $y_1 + y_2$ have values of the same order of magnitude as L ($\sim 10^8$). Further, k_x (or k_y) takes a value of $\sim 10^8$ provided that only the electron nearest to the Fermi level participates the interaction. Therefore, it can be said that $k_x\pi(x_1 + x_2)/L$ is large enough to make the statistical average reduce to zero.

Further simplification of Eq. (A-25) is achieved by using Fig. 9. Namely, if we take the following values; $L = 1$ cm $= 10^8$ Å, $\Delta L = 2.11$ Å (the distance between H_1 and H_2), $k_{\mathrm{F}} = 1.33 \times 10^8 - 1.65 \times 10^8$ (the lowest and the highest extremes of the k_{F} values for Zn, Ga, Cd, In, Sn, Sb, Hg, Tl, Pb, Bi), then Fig. 9 gives that

$$|\langle\cos(k_x\pi\Delta L/L)\rangle| \leq 0.09. \qquad \text{(A-27)}$$

Therefore, Eq. (A-25) is simplified to give

$$|\langle S_1\cdot S_2\rangle| \leq 0.09(K^2/4)J_1\cdot J_2 = 0.09((\langle S_1^2\rangle\cdot\langle S_2^2\rangle)^{1/2}. \qquad \text{(A-28)}$$

The rearrangement of this equation gives

$$|\langle S_1\cdot S_2\rangle/((\langle S_1^2\rangle\cdot\langle S_2^2\rangle)^{1/2}| \leq 0.09. \qquad \text{(A-29)}$$

By combining this equation with Eqs. (A-7), (A-8) and (A-9), we obtain

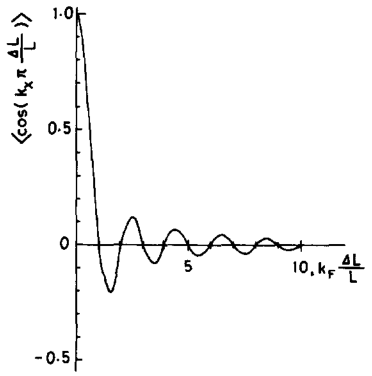

FIG. 9. Calculated values of the statistical average of cos $(k_x\pi\Delta L/L)$ as a function of $k_F\Delta L/L$.

$$|H'(\mathrm{H_1,H_2})/[H'(\mathrm{H_1})H'(\mathrm{H_2})]^{1/2}| \leqslant 0.09. \qquad \text{(A-30)}$$

Since the relation,

$$\{H'(\mathrm{H_1}) + H'(\mathrm{H_2})\}/2 \geqslant [H'(\mathrm{H_1})H'(\mathrm{H_2})]^{1/2}, \qquad \text{(A-31)}$$

generally holds, the following relation

$$|2H'(\mathrm{H_1,H_2})/\{H'(\mathrm{H_1}) + H'(\mathrm{H_2})\}| \leqslant 0.09, \qquad \text{(A-32)}$$

should hold. Thus, Eq. (A-4) is proved to be valid.

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