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THEORY OF CHEMISORPTION ON METAL SURFACE[*]

By

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Introduction

The concept of usual valency theory might not be directly applicable to the chemisorption of atoms or molecules on a metal surface. Pollard[1] has suggested that the orbital of surface state, which is localized at the surface, may form one-electron bond with the valence orbital of the adsorbate. This proposition appears, however, to be open to criticism. First, the existence of surface state of adequate energy in a metal is in question[2]; second, the adsorbate should be necessarily positively polarized with an effective charge of *ca.* $e/2$ (e : the elementary charge), not always in conformity with observations; and third, the interactions between the bonding electron and metal electrons might possibly overweigh the bond.

Recently Grimley[3] has investigated the molecular orbital of the combined system of metal and hydrogen atom and found that a few of the surface states originally existed before adsorption are localized about two centers of the proton and the nearest metal atom on the surface, while others remain almost unaffected being slightly hybridized with the orbital of adsorbed hydrogen atom, the localized orbital forming a covalent bond between metal and hydrogen atom, provided that its energy lies below the Fermi level of the metal. Similar conclusions have been arrived at recently by Koutecký[4] by use of Wannier functions to secure orthogonal relations of the molecular orbitals. Grimley and Koutecký have, however, neglected the effect of the perturbation on the other orbitals of metal electrons by the bond electrons. This difficulty might be surmounted by deriving the effective Hamiltonian explicitly for each electron satisfying self-consistency, and

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by calculating the net decrease of the energy of the combined system of metal and hydrogen atom, although this would not be at all simple problem for the combined system, if it be accomplished for an isolated metal.

It might be more general and straightforward to calculate the heat of adsorption without assuming surface states, by representing the electronic state of the combined system with configuration mixing or by configuration interactions. POLLARD[5] has shown recently that a repulsive interaction results from a single configuration of homopolar state M–H composed of the 1s-function of a hydrogen atom and the Bloch wave functions of metal electrons. To do with the attractive state of adsorption, it is required in consequence to include configurations of ionic states M^-–H^+ and M^+–H^-. The M^-–H^+ state is, as shown in the present work carried forward on this line, actually more stable than M–H state, as might be expected from an analogy to the absorption of a hydrogen atom in a metal or heat of formation of alloys[6][7]. Solving the problem of configuration mixing of M–H, M^-–H^+ and M^+–H^-, it is shown as described below that there comes out an orbital localized around the proton and the adjacent metal atoms, which contributes considerably to the adsorption energy, while other electrons together co-operate through perturbation due to adsorption similarly to form the bond.

§ 1. Configurations and Their Energies

The configurations to be taken into account are:

(i) M–H configurations $(n_l, \mathbf{k}_1, \mathbf{k}_2, \cdots, \mathbf{k}_N)$. The wave functions are given as,

$$\Psi(n_l, \mathbf{k}_1, \cdots, \mathbf{k}_N) = \frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \psi(n_l, \mathbf{r}_0), \psi(\mathbf{k}_1, \mathbf{r}_0), \cdots, \psi(\mathbf{k}_N, \mathbf{r}_0) \\ \psi(n_l, \mathbf{r}_1), \psi(\mathbf{k}_1, \mathbf{r}_1), \cdots, \psi(\mathbf{k}_N, \mathbf{r}_1) \\ \cdots \quad \cdots \quad \cdots \quad \cdots \\ \psi(n_l, \mathbf{r}_N), \psi(\mathbf{k}_1, \mathbf{r}_N), \cdots, \psi(\mathbf{k}_N, \mathbf{r}_N) \end{vmatrix}, \qquad (1.1)$$

where $\psi(n_l, \mathbf{r})$, $n_l = 1s, 2s, 2p$, *etc.*, is the wave function of n_l-state of an isolated hydrogen atom, $\psi(\mathbf{k}, \mathbf{r})$ the wave function of a metal electron of wave number vector $\mathbf{k}$ normalized in the volume V of the metal, $\mathbf{r}_i$ the coordinate of the $i+1$-th electrons, $i = 0, 1, \cdots, N$, and N is the total number of metal electrons. Spin variables are not explicitly introduced, taking only the lowest multiplicity into account. We will designate levels above the FERMI level k_F by $\mathbf{k}$ with Greek subscripts as $\mathbf{k}_\alpha$, and those below by that with Roman subscripts as $\mathbf{k}_i$. Thus, the configuration

$$(n_l, \mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_{i-1}, \mathbf{k}_{i+1}, \cdots, \mathbf{k}_N)$$

represents an excited state, an electron initially in $\mathbf{k}_i$-level being promoted to $\mathbf{k}_\alpha$-level.

(ii) M^--H^+ configurations $(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_i, \cdots, \mathbf{k}_N)$, in which an electron of the adsorbate is transferred to occupy the empty $\mathbf{k}_\alpha$-level of the metal. The metal is thus negatively polarized and the adsorbate oppositely.

(iii) M^+-H^- configurations $(n_l, n_l', \mathbf{k}_1, \cdots, \mathbf{k}_{i-1}, \mathbf{k}_{i+1}, \cdots, \mathbf{k}_N)$, in which an electron initially in $\mathbf{k}_i$-level in the metal is transferred to n_l'-state of the adsorbate. The important configuration is only $n_l = n_{l'} = 1s$ (spins being anti-parallel), the others being omitted in this paper.

Energies of the respective configuration will now be investigated before dealing with the interactions among them, which plays an important part in constituting the adsorption energy. The standard of the energy is taken to be that of the metal and the hydrogen atom remote from each other and respectively at their ground states.

The repulsion $A(D)$*) between a hydrogen atom and a metal in the configuration $(1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)$ mentioned above[5] is given as a function of the distance D of an atom from the surface and the density of metal electrons of a given spin as illustrated by the curve I in Fig. 1 for the density $N/2V = \left\{(4\pi/3)\rho_s^3\right\}^{-1}$, where $\rho_s = 3.34 a_H$, a_H being the BOHR radius.

The energy of the configuration $(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N)$, when the proton is at a moderate distance from the metal surface is readily given as

$$I + E(\mathbf{k}_\alpha) - e^2/4D \equiv E_{I+}(\mathbf{k}_\alpha), \tag{1.2}$$

where I is the ionization energy of hydrogen atom, $E(\mathbf{k}_\alpha) \geq -\phi$ (ϕ: work function of the metal) the negative of the ionization energy of $\mathbf{k}_\alpha$-level and the third term is the potential of image force, which modifies the charge distribution of electrons effectively to shield the field of the proton in the interior of the metal. The $E_{I+}(k_\alpha = k_F)$ *versus* D is shown by the curve II in Fig. 1**). As the proton approaches the metal surface so that $\psi(n_l)$ and $\psi(\mathbf{k}_i)$ appreciably overlap, electrons in the metal

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*) The result for $A(D)$ by POLLARD is not correct. $A(D) = (K_1 - K_2 + 2K_3)(1 - \Delta^2)^{-1}$ in place of Eq. (7) in Ref. (5). The numerical values are given in Table I of Appendix A.

**) We assume $\phi = 4.5$ eV and $I = 13.56$ eV.

have chances to move to the proton or, in other words, electrons spread out from the metal surface toward it. The wave function of the state is represented as,

$$\Psi_{\mathrm{ionic}}(\mathbf{k}_\alpha) = d_0 \Psi(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N) + \sum_{(n_l, k_i)} d(n_l, \mathbf{k}_i) \Psi(n_l, \mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_{i-1}, \mathbf{k}_{i+1}, \cdots, \mathbf{k}_N), \qquad (1.3)$$

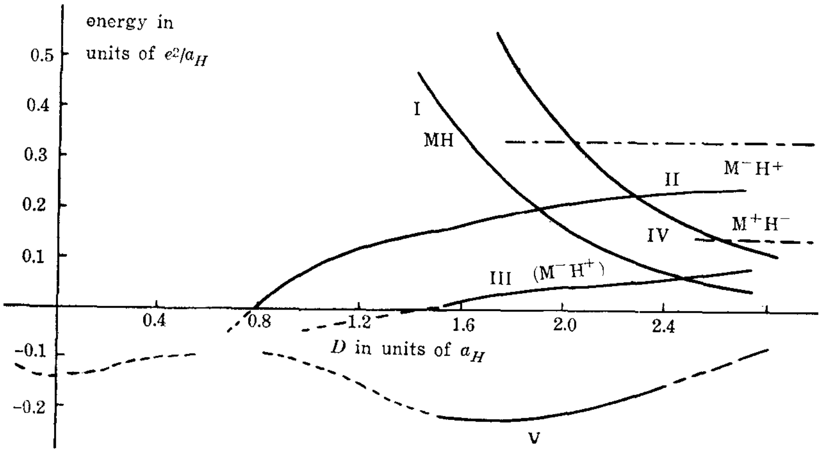

Fig. 1. Energies of various configurations *versus* distance D of hydrogen atom from a metal surface.

Curve I :	the ground state of M-H configuration.
Curve II :	the ground state of M^--H^+ configuration.
Curve III :	the ground state of M^--H^+ configuration, taking into account the deviation from the image force potential $-e^2/4D$ due to the spreading of metal electrons out of metal surface.
Curve IV :	the ground state of M^+-H^- configuration.
Curve V :	the heat of adsorption. The minimum at $D \simeq 0$ is deep enough for adsorption of H_2 for metals with absorbability of hydrogen atom *Cf.*, Concluding remarks.

and the energy $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ of $\Psi_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ will be worked out in the next section; the curve III of Fig. 1 shows the result for $k_\alpha = k_F$. The M^--H^+ state is more stable than M-H state at smaller distance of a proton from metal surface as seen from the curve III. The effective charge of the proton is also estimated in §2. These features are similar to those of absorption of a hydrogen atom in a metal such as Fe, Ni or Cu, where hydrogen atom is ionized, giving off its 1s-electron to the empty $\mathbf{k}_\alpha$-level but being shielded instead by perturbed metal electrons.

The energy of the configuration $(1s, 1s, \mathbf{k}_1, \cdots, \mathbf{k}_{i-1}, \mathbf{k}_{i+1}, \cdots, \mathbf{k}_N)$ is given as,

$$-E(\mathbf{k}_i)-I+R(1s-1s)-e^2/4D+2A(D)\equiv E_{\mathrm{I}-}(\mathbf{k}_i) \qquad (1.4)$$

where the third term is the repulsive energy between the 1*s*-electrons given approximately as $R(1s-1s)\approx I$[8], and the last term represent the exchange interaction of H^- with the metal electrons approximately. The curve IV of Fig. 1 shows $E_{\mathrm{I}-}(k_i)$ for $\mathbf{k}_i=\mathbf{k}_F$ as a function of the distance D.

The wave function of the combined system of metal and hydrogen atom is now given in accordance with the configuration mixing as,

$$\Phi=a_0\Psi(1s,\mathbf{k}_1,\cdots,\mathbf{k}_N)+\sum_\alpha b(\mathbf{k}_\alpha)\Psi_{\mathrm{ionic}}(\mathbf{k}_\alpha)$$
$$+\sum_i c(\mathbf{k}_i)\Psi(1s,1s,\mathbf{k}_1,\mathbf{k}_2,\cdots,\mathbf{k}_{i-1},\mathbf{k}_{i+1},\cdots,\mathbf{k}_N). \qquad (1.5)$$

The first term is the ground state of M–H, the excited ones being included in the second term (*cf.* (1.3)). The energy of the state represented by (1.5) is evaluated in §2 and illustrated by curve V of Fig. 1.

It is interesting to note the similarlity of the present treatment to that of charge-transfer-no-bond binding applied first by MULLIKEN[9] to the interactions between organic compound and to the physical adsorption by MIGNOLET[10], MATSEN, MAKRIDES and HACKERMAN[11]. Xenon and some other inert molecules adsorbed on bare Ni are strongly positively polarized, which phenomena are attributed by MIGNOLET to the charge transfer. Besides, the heats of physical adsorption of such molecules as long chain nitriles, esters, alcoholes and thiols are 10 kcal/mol or more, which are too large for being mere VAN DER WAALS potential. MATSEN *et al.* attributed the anomaly to the charge-transfer-no-bond binding. Eq. (1.7) leads, on the other hand, to the form, by neglecting the contributions of metal electrons, *i.e.*, ignoring the second term of (1.3) and the third of (1.5),

$$\Phi=a_0\Psi(1s,\mathbf{k}_1,\cdots,\mathbf{k}_N)+\sum_\alpha b(\mathbf{k}_\alpha)\Psi(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\mathbf{k}_N),$$

which represent the state of charge transferred partially to the metal.

§ 2. Heat of Chemisorption

In this section, we will evaluate the energy $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ of the state of $\Psi_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ given by (1.3), including the spreading out of metal electrons toward the hydrogen ion (a).[*] With the values $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ thus determined,

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[*] For the sake of brevity, we ignore $d(2s,\mathbf{k}_i)$, $d(2p,\mathbf{k}_j)$, *etc.* in the course of evaluation.

the heat of adsorption is readily determined as will be seen later (b). Some problems concering the present treatment are discussed also (c).

(a) The equation for coefficients d_0 and $d(1s, \mathbf{k}_i)$ of (1.3) are given, by the usual variation method, as,

$$\left.\begin{array}{l} (E_{\mathrm{I}+}(\mathbf{k}_\alpha)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha))d_0+V_{1s,k_1}d(1s,\mathbf{k}_1)+V_{1s,k_2}d(1s,\mathbf{k}_2)+\cdots=0 \\ V^*_{1s,k_1}d_0+(E(1s,\mathbf{k}_1)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha))d(1s,\mathbf{k}_1)+V_{k_1,k_2}d(1s,\mathbf{k}_2)+\cdots=0 \\ V^*_{1s,k_2}d_0+V^*_{k_1,k_2}d(1s,\mathbf{k}_1)+(E(1s,\mathbf{k}_2)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha))d(1s,\mathbf{k}_2)+\cdots=0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{array}\right\} \quad (2.1)$$

where $E_{\mathrm{I}+}(\mathbf{k}_\alpha)$ and $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ is defined in §1, and $E(1s, \mathbf{k}_i)$ is the energy of the configuration $(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_{i-1}, 1s, \mathbf{k}_{i+1}, \cdots, \mathbf{k}_N)$. The matrix elements are given as[†],

$$V_{1s,k_i}=\int\Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\mathbf{k}_i,\cdots,\mathbf{k}_N)\left\{\mathscr{H}-E_{\mathrm{ionic}}\right\}\Psi(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\underset{(i)}{1s},\cdots,\mathbf{k}_N)\prod_j d\mathbf{r}_j, \quad (2.2)$$

$$V_{k_i,k_j}=\int\Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\underset{(j)}{1s},\cdots,\mathbf{k}_N)\left\{\mathscr{H}-E_{\mathrm{ionic}}\right\}\Psi(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\underset{(i)}{1s},\cdots,\mathbf{k}_N)\prod_j d\mathbf{r}_j, \quad (2.3)$$

where $\mathscr{H}$ is the HAMILTONIAN of the combined system. The secular equation for $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ is

$$\begin{vmatrix} E_{\mathrm{I}+}(\mathbf{k}_\alpha)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha) & V_{1s,k_1} & V_{1s,k_2} & \cdots \\ V^*_{1s,k_1} & E(1s,\mathbf{k}_1)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha) & V_{k_1,k_2} & \cdots \\ V^*_{1s,k_2} & V^*_{k_1,k_2} & E(1s,\mathbf{k}_2)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}=0 \quad (2.4)$$

or with an approximation $V_{k_i,k_j}=0$ (see Appendix A),

$$\left\{E_{\mathrm{I}+}(\mathbf{k}_\alpha)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha) - \sum_i\frac{|V_{1s,k_i}|^2}{E(1s,\mathbf{k}_i)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha)}\right\}\prod_j(E(1s,\mathbf{k}_j)-E_{\mathrm{ionic}}(\mathbf{k}_\alpha))=0\,. \quad (2.5)$$

The root $E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$, which converges to $E_{\mathrm{I}+}(\mathbf{k}_\alpha)$ as $|V_{1s,k_i}|$ tends to 0, is given by equating the fiirst factor of (2.5) to zero*). Replacing

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†) V_{1s,k_i} *etc.* ore evaluated in Appendix A. We have neglected terms proportional to $\Delta^2=\int\psi^*(1s,\mathbf{r}_1)\psi(1s,\mathbf{r}_2)f(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1,d\mathbf{r}_2$, where $f(\mathbf{r}_1,\mathbf{r}_2)$ is given by (A. 9) of Appendix A.

*) Cf. Appendix B.

$|V_{1s,k_i}|^2$ with their appropriate mean value $|\overline{V}_{1s,k}|^2$, and the summation $\sum_i \{\cdots\}$ with the integral $N/k_F^3 \int_0^{k_F} \{\cdots\} k^2 dk$, we have

$$E_{\mathrm{I}+}(\mathbf{k}_\alpha) - E_{\mathrm{ionic}}(\mathbf{k}_\alpha) = (N|\overline{V}_{1s,k}|^2/\zeta)\left\{\frac{x}{2}\log\frac{x+1}{x-1} - 1\right\}, \tag{2.6}$$

where $\zeta = (\hbar^2/2m)k_\alpha^2$ is the FERMI energy and

$$x = \left[\left\{A(D) - (\hbar^2/2m)k_\alpha^2 - E_{\mathrm{ionic}}(\mathbf{k}_\alpha)\right\}/\zeta\right]^{1/2}.$$

$E_{\mathrm{ionic}}(\mathbf{k}_\alpha)$ is solved graphically for $k_\alpha = k_F$, $\rho_s = 3.34\,a_H$, $\zeta = 7.0\,\mathrm{eV}$, and $\phi = 4.5\,\mathrm{eV}$. The result is given as,

$$E_{\mathrm{ionic}}(k_F) = E_{\mathrm{I}+}(k_F) - \varepsilon N|\overline{V}_{1s,k}|^2/\zeta\,, \tag{2.7}$$

where $\varepsilon = 0.2$, 0.42 and 0.8, and $\sqrt{N}|\overline{V}_{1s,k}| = 11.3\,\mathrm{eV}$, $8.6\,\mathrm{eV}$ and $6.4\,\mathrm{eV}$ for $D = 1.6$, 2.0 and 2.4 (in units of a_H) respectively (curve III of Fig. 1).

If we take the state $n_l = 2s$ or $2p_z$ into account, the energies will decrease further by some fractions of those given above.

(b) We first determine the coefficients a_0 and $b(\mathbf{k}_\alpha)$'s of (1.5), neglecting the third term or $c(\mathbf{k}_i)$'s. The equations are similar to (2.1) and (2.4); *i.e.*,

$$\left.\begin{array}{l}
\left\{A(D) - W'\right\}a_0 + V_{H,k_\alpha}b(\mathbf{k}_\alpha) + V_{H,k_\beta}b(\mathbf{k}_\beta) + \cdots\cdots\cdots = 0 \\
V^*_{H,k_\alpha}a_0 + \left\{E_{\mathrm{ionic}}(\mathbf{k}_\alpha) - W'\right\}b(\mathbf{k}_\alpha) + V_{k_\alpha,k_\beta}b(\mathbf{k}_\beta) + \cdots = 0 \\
V^*_{H,k_\beta}a_0 + V^*_{k_\alpha,k_\beta}b(\mathbf{k}_\alpha) + \left\{E_{\mathrm{ionic}}(\mathbf{k}_\beta) - W'\right\}b(\mathbf{k}_\beta) + \cdots = 0 \\
\cdot\;\cdot
\end{array}\right\} \tag{2.8}$$

the eigen value W' of (2.8) being given by the secular equation

$$\begin{vmatrix}
A(D) - W' & V_{H,k_\alpha} & V_{H,k_\beta} & \cdots \\
V^*_{H,k_\alpha} & E_{\mathrm{ionic}}(\mathbf{k}_\alpha) - W' & V_{k_\alpha,k_\beta} & \cdots \\
V^*_{H,k_\beta} & V^*_{k_\alpha,k_\beta} & E_{\mathrm{ionic}}(\mathbf{k}_\beta) - W' & \cdots \\
\cdots & \cdots & \cdots & \cdots
\end{vmatrix} = 0\,, \tag{2.9}$$

where

$$\begin{aligned}
V_{H,k_\alpha} = {} & d_0^* \int \Psi^*(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N)\{\mathscr{H} - W'\}\Psi 1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)\prod_{j=0}^{N} d\mathbf{r}_j \\
& + \sum d(n_l, \mathbf{k}_i)^* \int \Psi^*(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \underset{(i)}{n_l}, \cdots, \mathbf{k}_N)\{\mathscr{H} - W'\}\Psi(1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)\prod_{j=0}^{N} d\mathbf{r}\,,
\end{aligned} \tag{2.10}$$

and

$$
\begin{aligned}
V_{k_\alpha,k_\beta} = & \, d^*(n_l,\mathbf{k}_\alpha)d(n_l,\mathbf{k}_\beta)\int \Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\mathbf{k}_N)\prod_{j=0}^{N} d\mathbf{r}_j \\
& + \sum d^*(n_l,\mathbf{k}_i)d_0\int \Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\underset{(i)}{n_l},\cdots,\mathbf{k}_N\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\mathbf{k}_N)\prod_{j=0}^{N} d\mathbf{r}_j \\
& + \sum d_0^* d(n_l,\mathbf{k}_i)\int \Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\underset{(i)}{n_l},\cdots,\mathbf{k}_N)\prod_{j=0}^{N} d\mathbf{r}_j .
\end{aligned}
\tag{2.11}
$$

With an approximation $V_{k_\alpha,k_\beta}=0$, W' is given by the equation,

$$
\left\{A(D)-W'-\sum_{k_\lambda}\frac{|V_{H,k_\lambda}|^2}{E_{\text{ionic}}(\mathbf{k}_\lambda)-W'}\right\}\prod_{k_\mu}\left\{E_{\text{ionic}}(\mathbf{k}_\mu)-W'\right\}=0\,, \tag{2.12}
$$

or, observing that all factors but the first one do not vanish for the lowest energy W'_g of W',

$$
A(D)-W'_g-\sum_{k_\lambda}\frac{|V_{H,k_\lambda}|^2}{E_{\text{ionic}}(\mathbf{k}_\lambda)-W'_g}=0\,. \tag{2.13}
$$

By substituting $\{E_{\text{ionic}}(\mathbf{k}_\lambda)-W'_g\}^{-1}$ with their appropriate average $\{\bar{E}_{\text{ionic}}-W'_g\}^{-1}$, we have

$$
\begin{aligned}
W'_g &= 1/2\left[A(D)+\bar{E}_{\text{ionic}}-\left\{(A(D)-\bar{E}_{\text{ionic}})^2+4\sum_k|V_{H,k}|^2\right\}^{1/2}\right], \qquad (2.14)\\
&\approx \left\{\sum_k |V_{H,k}|^2\right\}^{1/2}\approx d_0\sqrt{N}\,|\bar{V}_{1s,k}| \quad \text{for} \quad A(D)\approx \bar{E}_{\text{ionic}}\,.
\end{aligned}
$$

The energy decrease due to the third term of (1.5) is estimated approximately as

$$
\underset{(k_i \text{ of given spin})}{\sum}|V_{H^-,k_i}|^2\Big/\left\{E_{\text{I}^-}(k_F)+\zeta-W'_g\right\}, \tag{2.15}
$$

where V_{H^-,k_i} is the appropriate matrix element, satisfying

$$
\underset{(k_i \text{ of given spin})}{\sum}|V_{H^-,k_i}|^2\approx(1/2)a_0^2\sum_{(k)}|V_{1s,k}|^2.
$$

The resultant energy W_g of the combined system is now derived approximately with $d_0^2=1/(1+\varepsilon^2N|\bar{V}_{1s,k}|^2/\zeta^2)$, as will be given by (2.18), and numerical values of $\sqrt{N}\,|\bar{V}_{1s,k}|=e^2/a_H(p(\rho_s)-1)q(\rho_s)\sqrt{N}\,|\bar{S}_{1s,k}|$ listed in Table I of Appendix A. The W_g is shown by the curve V in Fig. 1. The heat of chemisorption is *ca.* 5 eV. and the equilibrium distance *ca.* 0.8 Å.

The large density of energy levels of metal electrons favours the adsorption through the second term of (2.7) and through the mean value E_{ionic} of (2.14), similarly as in the case of alloy formation or absorption of a hydrogen atom in metals.

(c) The $|d_0|^2$, which represent the effective charge of adsorbate ion in $\Psi_{\text{ionic}}(\mathbf{k}_\alpha)$-state, is estimated by approximating (cf. Appendix A)

$$d(1s,\mathbf{k}_1)=d(1s,\mathbf{k}_2)=\cdots=d(1s,\mathbf{k}_N)\equiv d\,, \tag{2.16}$$

and

$$|V_{1s,k_1}|=|V_{1s,k_2}|=\cdots=|V_{1s,k_N}|\equiv|V|\,. \tag{2.17}$$

From (2.1) and (2.7), we have

$$(\varepsilon N|V|^2/\zeta)\,d_0+N|V|\,d=0\,,$$

or

$$d=-(\varepsilon|V|/\zeta)\,d_0\,.$$

Hence, $|d_0|^2$ is given as

$$d_0^2=(1+\varepsilon^2N|V|^2/\zeta^2)\,, \tag{2.18}$$

using the normalization condition $d_0^2+Nd^2=1$.

The resultant effective charge of adsorbate is given as,

$$d_0^2\sum_{k_\alpha}|b(\mathbf{k}_\alpha)|^2-\sum_{k_i}|c(\mathbf{k}_i)|^2\,,$$

being more or less neutral[*].

The atomic function of adsorbate is modified by chemisorption, spreading into the interior of the metal or being excited to higher atomic levels. The former effect is readily seen by the similar approximations as (2.16) and (2.17); *i.e.*, the modified term is given,

$$\begin{aligned}\sum d_0\,b(\mathbf{k}_\alpha)\,\psi(\mathbf{k}_\alpha\mathbf{r}) &\sim \text{const.}\sum_{k_\alpha}\exp i\mathbf{k}_\alpha\mathbf{r}\\ &\sim \text{const.}\int k\sin kr/r\,dk\\ &\sim \text{const.}\ \sin k_Fr/r\,,\end{aligned} \tag{2.19}$$

which is localized near metal ions adjacent to the adsorbate. Eq. (2.19) accounts for the long range character of the force between adsorbates as shown in the next section.

§ 3. Repulsion between Adsorbed Hydrogen Atoms

It is known that the heat of adsorption of atoms or molecules

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[*] In rigorous treatment, contributions from $n=2s$ or $2p$ should be taken into account.

on metal surface decreases with covarage. This decrease is sometimes ascribed to the repulsive potential between adsorbed atoms or molecules, which is, however, as given by the valency theory of HEITLER-LONDON, too small to account for the observed decrease.

The pronounced interaction between adsorbed atoms or molecules may be attributed qualitatively to the following two causes in accordance with the present treatment of adsorption with special reference to hydrogen atom.

First, the electronic state of the adsorbed hydrogen atom is given according to the foregoing section as follows:

$1s$ stata presents with probability $|a_0|^2 + \sum_{(k_\alpha, k_i)} |b(\mathbf{k}_\alpha) d_\alpha(1s, k_i)|^2$,

$2s$ state with probability $\sum_{(k_\alpha, k_i)} |b(\mathbf{k}_\alpha) d_\alpha(2s, \mathbf{k}_i)|^2$, *etc.*,

and

$(1s)^2$ state with probability $\sum_{k_i} |c(\mathbf{k}_i)|^2$,

and in consequence the charge cloud spreads out more than in the $1s$-state, resulting in a more intensive overlap of wave functions of the adsorbed atoms, or such exchange repulsion between them.

Second, the interaction between two adsorbed atoms is caused on the part of electrons in metal respectively participating the adsorption bonds as discussed in the foregoing section. The perturbed term of the wave function in metal has been estimated approximately in the foregoing section as

$$\text{const.} \frac{\sin k_F r}{r},$$

which shows that the interaction between adsorbed atoms is of long range character. It is required for more detailed discussion to see whether the interaction is repulsive or attractive. However, it might be expected that the interaction is repulsive when the spins of adsorbed atoms are parallel than when antiparallel, since the available levels to form adsorption bonds are more restricted by PAULI principle than in the case of antiparallel spins, and in consequence, the resultant interaction may be repulsive, when averaged over the triplet and singlet states of respective weights 3 and 1.

The change of work function by adsorption is closely combined with the polarization of adsorbed atoms. If the contribution of the configuration $M^- - H^+$ to the resonance state is larger than that of $M^+ - H^-$, the work function will be depressed and *vice versa*. The mean magnitude of the polarization is also expected to decrease with covarage by the interactions between adsorbed atoms caused by metal electrons.

DE BOER *et al.*[12] have tried to explain the repulsive potential by interactions between dipoles formed by adsorption or by the change of work function by adsorption. However, the interpretations are not always in conformity with the experimental results. Above consideration leads the present author to the view that the double layer formation, which changes the work function, is simple indicative of the excess of the contribution to the resonance state of the configuration either $M^- - H^+$ or $M^+ - H^-$ over the other, but not essentially responsible for the repulsion.

Concluding Remarks

So far, we have been concerned with the energy of a system of metal and atom, the atom being at distance of $\sim 1\,\text{Å}$ from the metal surface. At these distances, energies of homopolar configurations (M-H) and the ionic ones ($M^- - H^+$ or $M^+ - H^-$) are nearly equal, so that the energy decrease of the system is mainly due to interactions between these configurations. The interactions are strong enough to give reasonable heat of chemisorption.

At smaller distances $D \approx 0$, however, only ionic configurations ($M^- - H^+$) including exicited ones are of primary importance, just as in the case of absorption of atom in an ionized form, the V_{k_α, k_i} contributing to the heat of chemisorption. The energy of the system might be lower when the atom is at the surface ($D \approx \pm 0$) than in the interior of the metal, since the potential energy of Coulomb repulsion by metal ions is less at the surface, thus forming stable adsorption.

In the case of Cu, which has absorbability of hydrogen atom (the heat of solution is *ca.* 2 eV), adsorbed hydrogen ion may be equilibrium at distance $D \approx 0$, and the activation energy of chemisorption may be high because of the low density of energy levels. On the other hand, in the case of W, with poorer absorbability and higher energy density, the adsorbate may be stable as $D \approx 1\,\text{Å}$, as discussed in the present paper. Metals such as Ni or Fe, with absorbability and high energy density, may have two types of adsorption state, as discussed by several authors[13].

The present author wishes to express his sincere thanks to Professor J. HORIUTI for his profound interest and valuable discussions on the present work.

Appendix A. Evaluation of the matrix elements

The HAMILTONian $\mathscr{H}$ of the system, which appears in matrix elements to be computed, is given by

$$\mathscr{H} = -(\hbar^2/2m)\sum_{i=0}^{N} \varDelta_i + 1/2 \sum_{i,\, j(i\neq j)} e^2/|\mathbf{r}_i - \mathbf{r}_j| + \sum_{i,\, l} v(\mathbf{r}_i - \mathbf{R}_l)$$

$$-\sum_i e^2/|\mathbf{r}_i - \mathbf{R}_a| + 1/2 \sum_{l,l'(l\neq l')} Z^2e^2/|\mathbf{R}_l - \mathbf{R}_{l'}| + \sum_l Ze^2/|\mathbf{R}_l - \mathbf{R}_a|, \quad \text{(A.1)}$$

where $\mathbf{r}_i$, R_l and R_a are coordinates of electrons ($i=0, 1, \cdots, N$), metal ions ($l=1,2,\cdots,L$), and the ion adsorbed respectively, and Z is the valency of metal ions. The first term respresents the kinetic energy of electrons, the second the sum of potentials between electrons, the third or the fourth the potential energy of electrons in the field of the metal ions or the ion adsorbed. The last two terms are the sum of Coulomb repulsive potentials between metal ions and that between metal ions and an adsorbed ion.

The $\psi(\mathbf{k}, \mathbf{r})$ and $\psi(n_l, \mathbf{r} - \mathbf{R}_a)$ are the wave functions, satisfying the equations,

$$\left\{-\hbar^2/2m\cdot\varDelta + \sum_l v(\mathbf{r} - \mathbf{R}_l) + \sum_i \int e^2 |\psi(\mathbf{k}_i, \mathbf{r}_j)|^2 / |\mathbf{r} - \mathbf{r}_j|\, d\mathbf{r}_j\right\} \psi(\mathbf{k}, \mathbf{r})$$

$$= \left\{E_0 + (\hbar^2/2m)k^2\right\} \psi(\mathbf{k}, \mathbf{r}), \quad \text{(A.2)}$$

$$\int \psi^*(\mathbf{k}', \mathbf{r})\, \psi(\mathbf{k}, \mathbf{r})\, d\mathbf{r} = \delta(\mathbf{k}', \mathbf{k}),$$

and

$$\left\{-\hbar^2/2m\cdot\varDelta - e^2/|\mathbf{r} - \mathbf{R}_a|\right\} \psi(n_l, \mathbf{r} - \mathbf{R}_a) = E(n_l)\, \psi(n_l, \mathbf{r} - \mathbf{R}_a), \quad \text{(A.3)}$$

respectively.

The matrix elements $V_{1s,k}$, $V_{kk'}$ *etc.* are computed as follows:

(a) The $V_{n_l,k}$ of Eq. (2.2) is given as

$$\begin{aligned} V_{n_l,k} &= \int \Psi^*(\mathbf{k}, \mathbf{k}_1, \cdots, \mathbf{k}_N) \left\{ \mathscr{H} - E_{\text{ionic}} \right\} \Psi(n_l, \mathbf{k}_1, \cdots, \mathbf{k}_N) \prod_{i=0}^{N} d\mathbf{r}_i \\ &= \int \sum_P \varepsilon(\mathrm{P}) \mathrm{P} \left\{ \psi(\mathbf{k}, \mathbf{r}_{i0}) \psi(\mathbf{k}_1, \mathbf{r}_{i1}) \cdots \psi(\mathbf{k}_N, \mathbf{r}_{i_N}) \right\} \\ &\quad \times \left\{ \mathscr{H} - E_{\text{ionic}} \right\} \psi(n_l, \mathbf{r}_0) \psi(\mathbf{k}_1, \mathbf{r}_1) \cdots \psi(\mathbf{k}_N, \mathbf{r}_N) d\mathbf{r} \prod_{i=1}^{N} d\mathbf{r}_i , \end{aligned} \tag{A. 4}$$

where P are the permutations of $(\mathbf{r}_0, \mathbf{r}_1, \cdots, \mathbf{r}_N)$ and $\varepsilon(\mathrm{P})$ is $+1$ for even permutations and -1 for odd ones.

We have from (A.1), (A.2) and (A.3),

$$\begin{aligned} V_{n_l,k} &= S(n_l, \mathbf{k}) \left\{ \text{energy of the metal} + E(n_l) - E_{\text{ionic}} \right\} \\ &\quad + S(n_l, \mathbf{k}) \left\{ \sum_l \frac{Ze^2}{|\mathbf{R}_a - \mathbf{R}_l|} - \int \frac{e^2 \sum |\psi(\mathbf{k}_i, \mathbf{r})|^2}{|\mathbf{r} - \mathbf{R}_a|} d\mathbf{r} \right\} \\ &\quad + \int \psi^*(\mathbf{k}, \mathbf{r}) \psi(n_l, \mathbf{r}) \left\{ \int \frac{e^2 \sum |\psi(\mathbf{k}_j, \mathbf{r}_i)|^2}{|\mathbf{r} - \mathbf{r}_i|} d\mathbf{r}_i + \sum_l v(\mathbf{r} - \mathbf{R}_l) \right\} d\mathbf{r} \\ &\quad - \int \psi^*(\mathbf{k}, \mathbf{r}) \psi(n_l, \mathbf{r}_1) \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} f(\mathbf{r}, \mathbf{r}_1) d\mathbf{r} d\mathbf{r}_1 \\ &\quad + \int \psi^*(\mathbf{k}, \mathbf{r}) \psi(n_l, \mathbf{r}_1) \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|} f(\mathbf{r}_1, \mathbf{r}_2) f(\mathbf{r}_2, \mathbf{r}) d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2 , \end{aligned} \tag{A. 5}$$

where

$$S(n_l, \mathbf{k}) = \int \psi^*(\mathbf{k}, \mathbf{r}) \psi(n_l, \mathbf{r}) d\mathbf{r} , \tag{A. 6}$$

and

$$f(\mathbf{r}_1, \mathbf{r}_2) = \sum_{(k \text{ of parallel spins})} \psi^*(\mathbf{k}, \mathbf{r}_1) \psi(\mathbf{k}, \mathbf{r}_2) . \tag{A. 7}$$

With the approximation,

$$\psi(\mathbf{k}, \mathbf{r}) = 1/\sqrt{V} \cdot \exp(i\mathbf{k}\mathbf{r}) , \tag{A. 8}$$

the $f(\mathbf{r}_1, \mathbf{r}_2) \equiv f(|\mathbf{r}_1 - \mathbf{r}_2|)$ is expressed as

$$(N/2V) \left\{ 3(x \cos x - \sin x)/x^3 \right\} , \qquad (= N/2V \text{ as } x \to 0) \tag{A. 9}$$

where $x = k_F r_{12}$ and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The function $f(\mathbf{r}_1, \mathbf{r}_2)$ is closely connected with the correlation of electrons. The probability density $\rho(\mathbf{r}_1, \mathbf{r}_2)$ of an electron at $\mathbf{r}_1$ and another electron at $\mathbf{r}_2$ is given in terms of $f(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{V^2} \left\{ 1 - \frac{1}{2} f(\mathbf{r}_1, \mathbf{r}_2)^2 (2V/N)^2 \right\} ,$$

which implies the exclusion of other electron (2) from (1) of the same spin, as discussed by WIGNER and SEITZ.

We substitute for (A.9) a rectangular function

$$f(\mathbf{r}_1, \mathbf{r}_2) = N/2V \qquad r_{12} \leq \rho_s$$
$$= 0 \qquad r_{12} > \rho_s \tag{A.10}$$

where $\rho_s = 2^{1/3} r_s$ is the radius of a sphere of volume $2V/N$ containing one electron of a given spin.

Eq. (A.5) is evaluated with approximations, beside (A.8) and (A.10), (i) $|\mathbf{r}_1 - \mathbf{R}_a| = |\mathbf{r}_2 - \mathbf{R}_a| - r_{12}\cos\theta$, where θ is the angle between $\mathbf{r}_2 - \mathbf{R}_a$ and $\mathbf{r}_2 - \mathbf{r}_1$, and (ii) the angle between $\mathbf{k}$ and $\mathbf{r} - \mathbf{R}_a$ is equal to that Θ between $\mathbf{k}$ and z-axis perpendicular to the metal surface. These approximations are admissible only when the distance D of the adsorbate from the metal surface is large enough that the overlap integral $S(n_l, \mathbf{k})$ is sufficiently small as compared with $1/\sqrt{N}$.

The $S(1s, \mathbf{k})$ is evaluated as

$$S(1s, \mathbf{k}) = \frac{1}{\sqrt{N}}(6/\rho_s^3)^{1/2}(1+ik\cos\Theta)^{-2}\left\{D + 2(1+ik\cos\Theta)^{-1}\right\}\cdot\exp\{-D\}, \tag{A.11}$$

or as

$$|S(1s, \mathbf{k})|^2 = \frac{1}{N}(6/\rho_s^3)\left\{1+(k\cos\Theta)^2\right\}^{-2}$$
$$\times\left\{D^2 + 4(1+D)(1+(k\cos\Theta)^2)^{-1}\right\}\cdot\exp\{-2D\},$$

with unit length of BOHR radius a_H. Taking the average of $|S(1s, \mathbf{k})|^2$ over various directions of $\mathbf{k}$, we have

$$|\bar{S}(1s, \mathbf{k})|^2 = 3/N\cdot\rho_s^{-3}\Big[(D^2+3D+3)\left\{(1+k^2)^{-1} + \tan^{-1}k/k\right\}$$
$$+ 2(1+D)(1+k^2)^{-2}\Big]\exp\{-2D\}. \tag{A.12}$$

The numerical values of $\sqrt{N}|\bar{S}|$ for $k = 1.04k_F$, $1.25k_F$ and $0.62k_F$ and $\rho_s = 3.30a_H$, $3.34a_H$ and $3.40a_H$ are given in Table I.

The first term of (A.5) is neglected as justified by the results of calculation that $\sqrt{N}|\bar{S}|$ is small compared with unity as seen from Table I, and, that the energy in the bracket amounts only a few electron volts. The second and third terms may be neglected, the contents of the respective brackets being the charge of the adsorbate ion times the potential of the double layer at most and the energy of

TABLE I Numerical values of $\sqrt{N}\,|\bar{S}(1s, \mathbf{k})|$, $p(\rho_s)$ and $q(\rho_s)$, and $A(D)$.
The value of $A(D)$ is given in unit of e^2/a_H, and,
$\rho_s = 2^{1/3} r_s$, D and k^{-1} in unit of a_H.

(i) $\sqrt{N}\,S(s1, \mathbf{k})$

$k = 1.25\,k_F$

D ρ_s	1.6	1.8	2.0	2.2	2.4	2.6
3.30	0.2296	0.1989	0.1718	0.1479	0.1271	0.1090
3.34	0.2265	0.1961	0.1694	0.1462	0.1253	0.1075
3.40	0.2218	0.1921	0.1659	0.1429	0.1228	0.1053

$k = 1.04\,k_F$

D ρ_s	1.6	1.8	2.0	2.2	2.4	2.6
3.30	0.2435	0.2108	0.1820	0.1567	0.1345	0.1154
3.34	0.2400	0.2077	0.1793	0.1544	0.1330	0.1137
3.40	0.2349	0.2033	0.1755	0.1511	0.1298	0.1112

$k = 0.62\,k_F$

D ρ_s	1.6	1.8	2.0	2.2	2.6	2.6
3.30	0.2745	0.2374	0.2048	0.1762	0.1512	0.1293
3.34	0.2679	0.2317	0.1999	0.1719	0.1476	0.1264
3.40	0.2616	0.2262	0.1970	0.1678	0.1440	0.1234

(ii) $p(\rho_s)$ and $q(\rho_s)$

ρ_s	$p(\rho_s)$	$q(\rho_s)$
3.30	2.6095	1.0497
3.34	2.6645	1.0570
3.40	2.7501	1.0685

(iii) $A(D)$

D ρ_s	1.6	1.8	2.0	2.2	2.4	2.6
3.30	0.3341	0.2261	0.1568	0.1088	0.0755	0.0525
3.34	0.3455	0.2355	0.1620	0.1121	0.0779	0.0542
3.40	0.3639	0.2476	0.1712	0.1177	0.0817	0.0569

an electron in the HARTREE field in a metal, with the mean value $-\phi-\zeta+1.2e^2/r_s\approx 0$. The fourth and the last terms are evaluated as,

$$\text{the fourth term} = -(e^2/a_H)\,q(\rho_s)\,S(1s,\mathbf{k}) \tag{A.13}$$

and

$$\text{the fifth term} = (e^2/a_H)\,q(\rho_s)\,p(\rho_s)\,S(1s,\mathbf{k})\,, \tag{A.14}$$

where

$$q(\rho_s) = 3(\cosh\rho_s - 1)/\rho_s^3\,,$$

$$p(\rho_s) = 3(\rho_s\cos\mathrm{h}\,\rho_s - \sinh\rho_s)/\rho_s^3\,.$$

The value of $\sqrt{N}\,|V_{1s,k}|$ for $k=k_F$ and $D=2a_H$ is approximately a few electron volts. (Values of $p(\rho_s)$ and $q(\rho_s)$ are given in Table I. (ii).)

(b) The matrix element V_{k_i,k_j} of (2.1) represents transition of an electron occupying $\mathbf{k}_j$-level to $\mathbf{k}_i$-level by the perturbing field of an adsorbate in a homopolar configuration. The interaction potential is approximately

$$-\frac{e^2}{|\mathbf{r}_i-\mathbf{R}_a|}+\int\frac{e^2|\psi(1s,\mathbf{r})|^2}{|\mathbf{r}_i-\mathbf{r}|}\,d\mathbf{r} = -\frac{e^2}{|\mathbf{r}_i-\mathbf{R}_a|}\exp\left\{-|\mathbf{r}_i-\mathbf{R}_a|\right\}, \tag{A.15}$$

neglecting the perturbation due to other metal electrons. The order of magnitude is estimated as

$$\begin{aligned}|V_{k_i,k_j}| &= \frac{3}{2N}\left(\frac{e^2}{r_s}\right)\frac{\exp\{-D\}}{(r_s^2+r_s^2|\mathbf{k}_i-\mathbf{k}_j|^2\cos^2\theta)}\,,\\ &\approx\frac{1}{N}\left\{\text{less than } 0.2\,\mathrm{eV.}\right\}\,,\end{aligned}$$

where θ is the angle between $\mathbf{k}_i-\mathbf{k}_j$ and z-axis. The neglect of V_{k_i,k_j} in §2 is thus justified.

(c) The integral of the first term of (2.11), *i.e.*,

$$\int\Psi^*(\mathbf{k}_\alpha,\mathbf{k}_1,\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\mathbf{k}_N)\,\Pi\,d\mathbf{r}_i$$

or such integral as

$$\int\Psi^*(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\underset{(i)}{\mathbf{k}_\gamma},\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta,\mathbf{k}_1,\cdots,\mathbf{k}_i,\cdots,\mathbf{k}_N)\,\Pi\,d\mathbf{r}_i$$

represents transition of $\mathbf{k}_\beta$-electron to $\mathbf{k}_\alpha$-level or $\mathbf{k}_i$-electron to $\mathbf{k}_\gamma$-level due to perturbation by the field of adsorbate ion. These interactions are expected to give rise, when the atom is at distance $D \approx 1\text{Å}$, to the image force potential, which induces an extra charge at the surface to make the tangential components of the electric field vanish, and, when $D \approx 0$, to the extra electron distribution, which shields the field of adsorbed ion.

(d) The matrix element of the second or the third term of (2.11), *i.e.*,

$$\int \Psi^*(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \underset{(i)}{n_l}, \cdots, \mathbf{k}_N)\{\mathscr{H} - W'\}\Psi(\mathbf{k}_\beta, \mathbf{k}_1, \cdots, \mathbf{k}_i, \cdots, \mathbf{k}_N)\Pi\, d\mathbf{r}_j, \tag{A.16}$$

or such as

$$\int \Psi^*(\mathbf{k}_\beta, \mathbf{k}_1, \cdots, \underset{(f)}{\mathbf{k}_\gamma}, \cdots, \underset{(i)}{n_l}, \cdots, \mathbf{k}_N)\{\mathscr{H} - W'\}$$
$$\times \Psi(\mathbf{k}_\beta, \mathbf{k}_1, \cdots, \mathbf{k}_f, \cdots, \mathbf{k}_i, \cdots, \mathbf{k}_N)\Pi\, d\mathbf{r}_j, \tag{A.17}$$

correspond to the transition $\mathbf{k}_\beta \to \mathbf{k}_\alpha$ and $\mathbf{k}_i \to n_l$, or $\mathbf{k}_f \to \mathbf{k}_\gamma$ and $\mathbf{k}_i \to n_l$. We have for $nl = 1s$ of (A.16)

$$\delta(s_\alpha s_\beta)\delta(s_{1s}s_i)\frac{6}{N}\left(\frac{e^2}{\rho_s}\right)\left\{\frac{1}{\rho_s^2(\mathbf{k}_\alpha - \mathbf{k}_\beta)^2} + \frac{p(\rho_s) - \delta(s_\alpha s_i)}{\rho_s^2(\mathbf{k}_\alpha - \mathbf{k}_i)^2}\right\} S(1s, \mathbf{k}_\alpha - \mathbf{k}_\beta - \mathbf{k}_i), \tag{A.18}$$

where s_α, s_i or s_{1s} is the spin coordinate and $\delta(s_\alpha s_i) = 1$ for $s_\alpha // s_i$ and $\delta(s_\alpha s_i) = 0$ otherwise. Expression (A.18) becomes infinite as $\mathbf{k}_\alpha$ tends to $\mathbf{k}_\beta$ or $\mathbf{k}_i$, but gives finite contribution to the energy of the system, its magnitude being approximately 1/10 of that from the $V_{1s,k}$ of (a). It might be possible to verify the validity of the expression of (A.17) as well as other matrix elements in this appendix based on the same approximations, by the analysis of the experimental results of electron emission from metals by slow ions of sufficiently large ionization energy, inasmuch as these elements are of primary importance[15] to give rise electron emission by ions.

Appendix B. Derivation of Equation for $E_{\text{ionic}}(\mathbf{k})$

Any root $E_{\text{ionic}}(\mathbf{k})$ of Eq. (2.5) can not be equal to one of $E(1s, \mathbf{k}_i)$ in the absence of degeneracy, *i.e.*,

$$E(1s, \mathbf{k}_1) \neq E(1s, \mathbf{k}_2) \neq \cdots \neq E(1s, \mathbf{k}_N), \tag{B.1}$$

since, if a root $E_{\text{ionic}}(\mathbf{k})$ happens to equal, say, $E(1s, \mathbf{k}_i)$, it follows from (1.9) that

$$\left\{E(1s,\mathbf{k}_1)-E_{\text{ionic}}(\mathbf{k})\right\}\cdots\cdots\left\{E(1s,\mathbf{k}_{i-1})-E_{\text{ionic}}(\mathbf{k})\right\}|\overline{V}_{1s,k_i}|^2$$
$$\times\left\{E(1s,\mathbf{k}_{i+1})-E_{\text{ionic}}(\mathbf{k})\right\}\cdots\cdots\left\{E(1s,\mathbf{k}_N)-E_{\text{ionic}}(\mathbf{k})\right\}=0\,,$$

or that $E_{\text{ionic}}(\mathbf{k})$ should equal one of $E(1s,\mathbf{k}_j)$ other than $E(1s,\mathbf{k}_i)$ in contradiction to the assumption (B.1). Hence, the root $E_{\text{ionic}}(\mathbf{k})$, which converges to $E_{\text{I}+}(\mathbf{k})$ as $|V_{1s,k}|^2$ tends to 0, is given by

$$E_{\text{I}+}(\mathbf{k})-E_{\text{ionic}}(\mathbf{k})-\sum_i\frac{|V_{1s,k_i}|^2}{E(1s,\mathbf{k}_i)-E_{\text{ionic}}(\mathbf{k})}=0\,. \tag{B.2}$$

When $E(1s,\mathbf{k})$'s degenerate, *i.e.*,

$$E(1s,\mathbf{k}_1)=E(1s,\mathbf{k}_2)=\cdots=E(1s,\mathbf{k}_i)\equiv E(1), \qquad (i\text{-fold})$$
$$E(1s,\mathbf{k}_{i+1})=E(1s,\mathbf{k}_{i+2})=\cdots=E(1s,\mathbf{k}_{i+j})\equiv E(i+1), \qquad (j\text{-fold})$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$E(1s,\mathbf{k}_{N-l+1})=E(1s,\mathbf{k}_{N-l+2})=\cdots=E(1s,\mathbf{k}_N)\equiv E(N-l+1), \qquad (l\text{-fold})$$

we have immediately $(i-1)+(j-1)+\cdots+(l-1)$ roots of (1.9), that is, $i-1$ roots are equal to $E(l)$, $j-1$ to $E(i+1),\cdots$, and $l-1$ to $E(N-l+1)$. The equation for the other $N+1-\{(i-1)+(j-1)+\cdots+(l-1)\}$ roots is given as

$$\left\{E_{\text{I}+}(\mathbf{k})-E_{\text{ionic}}(\mathbf{k})\right\}\left\{E(1)-E_{\text{ionic}}(\mathbf{k})\right\}\left\{E(i+1)-E_{\text{ionic}}(\mathbf{k})\right\}\cdots$$
$$\times\left\{E(N-l+1)-E_{\text{ionic}}(\mathbf{k})\right\}+\sum\left\{E(1)-E_{\text{ionic}}(\mathbf{k})\right\}\left\{E(i+1)-E_{\text{ionic}}(\mathbf{k})\right\}\cdots$$
$$\times\left\{|V_{1s,k_{m+1}}|^2+|V_{1s,k_{m+1}}|^2+\cdots+|V_{1s,k_{m+n}}|^2\right\}\times\cdots$$
$$\times\left\{E(N-l+1)-E_{\text{ionic}}(\mathbf{k})\right\}=0\,. \tag{B.3}$$

As $E(1)\not\fallingdotseq E(i+1)\not\fallingdotseq\cdots\not\fallingdotseq E(N-l+1)$, any root of (B.3) can not be equal to one of $E(i+j+1)$ similar as in the case of non-degeneracy, so that the roots are given by the equation

$$E_{\text{I}+}(\mathbf{k})-E_{\text{ionic}}(\mathbf{k})-\sum\frac{|V_{1s,k_{i+1}}|^2+\cdots+|V_{1s,k_{i+j}}|^2}{E(i+1)-E_{\text{ionic}}(\mathbf{k})}=0\,,$$

which is identical with (B.2).

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