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THEORY OF ADSORPTION OF HYDROGEN ATOM ON METAL SURFACE II*)

By

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Summary

The energy of the system of hydrogen atom and metal with N conduction electrons was investigated, starting from the wave functions of $N+1$ electrons given by a linear combination of three kinds of SLATER determinants; they were the SLATER determinants of $N+1$ BLOCH's wave functions of metal electrons (the appropriate state was denoted as M^-–H^+ state), the SLATER determinants of N BLOCH's wave functions and a wave function of 1s-state of hydrogen atom (M–H state), and the SLATER determinants of $N-1$ BLOCH's wave functions and two 1s-wave functions (M^+–H^- state). SLATER determinants of each kind stood for the ground and the excited states of the appropriate state. The coefficients of the linear combination were determined by the variation method or by the self-consistent field method. It was, thus, concluded, that there existed in general two different types of adsorption, which were called the r-type adsorption and s-type adsorption respectively.

The r-type adsorption is the resonance state between M–H state and M^-–H^+ as well as M^+–H^- state with the proton outside the metal. The heat of adsorption was evaluated for Ni and Cu at *ca.* 3.0 *eV*/atom, the equilibrium distance at *ca.* 1 Å outside the metal surface. The r-type adsorption was concluded to be associated, on account of the resonance, with a pronouced repulsive interactions between adatoms, which gave rise to the decrease of heat of r-type adsorption with increase of the adsorption. The negative polarization of r-adatom was *ca.* 0.02 in unit of elementary charge at the initial stage of adsorption. The r-type adsorption thus increased the work function.

The s-type adsorption is a sort of the dissolution of hydrogen atom dissociated into proton inside the metal near the surface and electron in the conduction band. The appropriate wave function of $N+1$ electrons was given practically by the linear combination of SLATER determinants of $N+1$ BLOCH's wave functions, and the coefficients were determined by the self-consistent field method, when the proton was in the interior of the metal. The relevant extra electron density around the dissolved proton was thus determined as $\lambda^3/8\pi\cdot\exp(-\lambda r)$, where λ was a constant 1/0.3 Å for Ni and Cu and the heat of dissolution was given by $-I+\phi+\lambda e^2/4$, where I was the ionization energy of hydrogen atom and ϕ the work function of the metal.

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An alternative simple treatment of the dissolution was developed resorting to the expression of kinetic energy of $N+1$ electrons according to THOMAS, FERMI and WEIZSAECKER[1]. The heat of dissolution of hydrogen atom was thus calculated as a function of the distance from surface, and the heat of *s*-type adsorption was found for Ni and Cu *ca.* 0.5 *eV* larger than the heat of dissolution in the interior of the metal, at the equilibrium position 0.5 Å apart from the surface. The heat of *s*-type adsorption amounts in consequence to 2.5 *eV*, which is smaller than that of *r*-type adsorption by *ca.* 0.5 *eV*. The repulsive interactions of adatoms, hence the decrease of heat of adsorption with increase of adsorption, was concluded practically absent on the contrary to the case of *r*-type adsorption. The *s*-type adsorption was shown to decrease the work function slightly.

The *r*-type adsorption predominates in consequence in cases of Ni and Cu at the initial stage of adsorption, whereas the *s*-type may possibly prevail later, owing to the rapid decrease of the heat of *r*-type adsorption as mentioned above. It was henceforth inferred that the integral heat of adsorption at full coverage decreases with rise of temperature.

In the case of Pt with larger work function and atomic radius than those of Ni or Cu, the heat of *r*-type adsorption as well as the degree of polarization was concluded to be smaller, and the heat of *s*-type adsorption nearer to that of *r*-type one at the coverage $\theta=0$, so that *s*-type might predominate except at the very initial stage of adsorption.

The effect of adsorption on the work function of Ni or Pt was deduced theoretically from the above results with conclusions in satisfactory agreement with observations by MIGNOLT[2], GUNDRY, CULVER, PRITCHARD and TOMPKINS.[3]

The predominant effect of scattering of conduction electrons by adatoms on the electric conductivity was pointed out and the relevant cross section of scattering was worked out as 0.3 πr_s^2 or $3\sim4$ πr_s^2 respectivity for *s*-type or *r*-type adsorption, r_s being the radius of atomoic sphere of the metal. The increase of conduction electrons for Ni was, on the other hand, 1 or -0.02 per one *s*- or *r*-type adatom. Consequently, the electrical resistance was increased initially by the decrease of the probability p of specular reflection at surface due to *r*-type adsorption. The increase would come to an end at the coverage $\theta=1/4\sim1/2$, when the specular reflection p was reduced to zero. The total increase ΔR_{max} of resistance thus depended on the initial value of p. It was deduced, further, that ΔR_{max} was inversely proportional to the square of thickness of the film and independent of temperature, and that the relative increase $\Delta R_{max}/R_0$ was given by a definite function of the initial value of p and thickness of the film divided by the mean free path of the bulk metal. If the *s*-type adsorption did not occur, the resistance should remain constant with further increase of coverage. If it did instead, the resistance should decrease with increase of θ, giving a resistance maximum around $\theta=1/4\sim1/2$. The above theoretical conclusions where found coherently to account for observations by SUHRMAN,[4][5] WELDLER,[4][5] GENTSH,[4] HERMANN,[5] MIZUSHIMA[5][6] and SCHLIEPHAKE,[5] SACHTLER and DORGELO[7], and ZWIETERING, KOKS and VAN HEERDEN.[8]

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Introduction

A theory of hydrogen adsorption on metal has been developed in a preceding paper[9]*), suggesting that there existed two types of adsorption, *i.e.* the *r*-type adsorption and *s*-type adsorption. The adsorption of *r*-type is that of the ordinary sense with the equilibrium position of the adatom outside the metal, whereas that of *s*-type is a sort of dissolution of hydrogen atom in the metal but with the equilibrium position of the adatom inside the metal close to the surface.

The present paper is devoted to the developement of the previous work[9]. Both types of adsorption are treated by first principles with some approximations. The results obtained are coherent theoretical conclusions on the equilibrium distance, heat of adsorption and the effects of adsorption on the work function and electric conductivity for the types of adsorption in confirmation of the previous suggestion[9].

The state of *s*-type adsorption has been just briefly outlined in (I). The theory of this type of adsorption is now developed in Chapter 1 of the present work in terms of the wave equation

$$\Phi_s = b_0 \Psi(\mathbf{k}_1 \cdots, \mathbf{k}_N, \mathbf{k}_{N+1}) + \sum_i \sum_{\substack{\alpha \\ (i)}} b_{\alpha i} \Psi(\mathbf{k}_1, \cdots, \mathbf{k}_\alpha, \cdots, \mathbf{k}_{N+1}) \qquad \text{(I. 1)}$$

with the normalization condition

*) This paper will be referred to by (I) in the present paper.

$$|b_0|^2+\sum_i\sum_\alpha|b_{\alpha i}|^2=1$$

The first term of (I. 1), *i. e.*

$$\Psi(\mathbf{k}_1,\cdots,\mathbf{k}_N,\mathbf{k}_{N+1})\equiv\frac{1}{\sqrt{(N+1)!}}\begin{vmatrix}\phi(\mathbf{k}_1,\mathbf{r}_1),\cdots, & \phi(\mathbf{k}_N,\mathbf{r}_1), & \phi(\mathbf{k}_{N+1},\mathbf{r}_1)\\ \phi(\mathbf{k}_1,\mathbf{r}_2),\cdots, & \phi(\mathbf{k}_N,\mathbf{r}_2), & \phi(\mathbf{k}_{N+1},\mathbf{r}_2)\\ \cdots, & \cdots, & \cdots, \quad \cdots\\ \phi(\mathbf{k}_1,\mathbf{r}_{N+1}),\cdots, & \phi(\mathbf{k}_N,\mathbf{r}_{N+1}), & \phi(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\end{vmatrix},\tag{I. 1. a}$$

is relevant to the ground state of the system with hydrogen atom dissolved in the metal providing $N+1$-th electron in the conduction band; $\phi(\mathbf{k}_i,\mathbf{r}_j)$ is the BLOCH's wave function of a metal electron of wave number vector $\mathbf{k}_i$ normalized in the volume V of the metal, $\mathbf{k}_i$ *etc.* with Roman subscripts designate the energy levels below the FERMI surface, $\mathbf{k}_\alpha$ *etc.* with Greek ones those above it and $\mathbf{r}_j$ is the coordinate of the j-th electron, where $j=1,\cdots,N,N+1$, and N the total number of electrons is the conduction band of the metal in the normal state. The terms of the summation in (I. 1), *e. g.*

$$\Psi(\mathbf{k}_1,\cdots,\underset{(i)}{\mathbf{k}_\alpha},\cdots,\mathbf{k}_{N+1})\equiv\frac{1}{\sqrt{(N+1)!}}\begin{vmatrix}\phi(\mathbf{k}_1,\mathbf{r}_1),\cdots, & \phi(\mathbf{k}_\alpha,\mathbf{r}_1),\cdots, & \phi(\mathbf{k}_{N+1},\mathbf{r}_1)\\ \phi(\mathbf{k}_1,\mathbf{r}_2),\cdots, & \phi(\mathbf{k}_\alpha,\mathbf{r}_2),\cdots, & \phi(\mathbf{k}_{N+1},\mathbf{r}_2)\\ \cdots, & \cdots, \quad \cdots, & \cdots\\ \phi(\mathbf{k}_1,\mathbf{r}_{N+1}),\cdots, & \underset{(i\text{-th column})}{\phi(\mathbf{k}_\alpha,\mathbf{r}_{N+1})},\cdots, & \phi(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\end{vmatrix},\tag{I. 1. b}$$

is the excited state with an electron of i-th level in the ground state being promoted to α-th level, as denoted by $\underset{(i)}{\mathbf{k}_\alpha}$.

The constant coefficients b_0, $b_{\alpha i}$ *etc.*, hence the energy of dissolved hydrogen atom is determined by the self-consistent field method as outlined in §1. An alternative simple method of deriving the energy and the appropriate properties of dissolved hydrogen atom is now introduced, which leads to the results in conformity with those by the self-consistent field method, in terms of the kinetic energy expression of THOMAS, FERMI and WEIZSAECKER[1] in §2. The heat of dissolution of hydrogen atom is thus calculated in §3 as a function of the distance from the surface, locating the equilibrium position of dissolved proton at approximately 0.5 Å from the surface inside the metal and henceforth its effects on the electric conductivity and the work function are deduced in the subsequenct sections.

The energy of 1*s* state is very high due to the exchange repulsions from metal electrons[9][10], when the hydrogen atom is situated inside the metal or

just near the metal surface, so that the states with an electron or two electrons in 1*s*-state are practically excluded from the resonance of the *s*-type adsorption. However, they have to be taken into account in general for the hydrogen atom more or less apart from the surface outside the metal, since the exchange repulsions from metal electrons is no more intensive.

The state of the *r*-type adsorption is, hence, described in the present work by the wave function Φ_r, *i.e.*

$$\Phi_r = a_0\Psi(\mathbf{k}_1,\cdots,\mathbf{k}_N,1s)+\sum a_{as,si}\Psi(\mathbf{k}_1,\cdots,\underset{(i)}{\mathbf{k}_a},\cdots,\mathbf{k}_N,1s) + \sum b_{as}\Psi(\mathbf{k}_1,\cdots,\mathbf{k}_N,\mathbf{k}_a)+\sum c_{si}\Psi(\mathbf{k}_1,\cdots,\underset{(i)}{1s},\cdots,\mathbf{k}_N,1s) \qquad \text{(I. 2)}$$

where the first term is appropriate to the ground neutral state of adatom, the second one to the excited neutral states, the third one to the positively charged states of the adatom and the fourth one to its negatively charged states; $\underset{(i)}{1s}$ denotes an electron in 1*s*-state promoted from $\mathbf{k}_i$ state, resulting in the excited state of the system, the summations extending over the respective excited states; a_0, $a_{as,si}$, b_{as} and c_{si} are constant coefficients satisfying the normalization condition $|a_0|^2+\sum|a_{as,si}|^2+\sum|b_{as}|^2+\sum|c_{si}|^2=1$. In (I) the negatively charged states and the excited neutral states were allowed for only crudely. The wave functions $\Psi(\mathbf{k}_1,\cdots,\mathbf{k}_N,1s)$ *etc.* in (I.2) are respectively those of electronic configuration $(\mathbf{k}_1,\cdots,\mathbf{k}_N,1s)$ *etc.* given by SLATER determinant; *e.g.*, as

$$\Psi(\mathbf{k}_1,\cdots,\mathbf{k}_N,1s) \equiv \frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \phi(\mathbf{k}_1,\mathbf{r}_1), & \cdots, & \phi(\mathbf{k}_N,\mathbf{r}_1), & \phi(1s,\mathbf{r}_1) \\ \phi(\mathbf{k}_1,\mathbf{r}_2), & \cdots, & \phi(\mathbf{k}_N,\mathbf{r}_2), & \phi(1s,\mathbf{r}_2) \\ \cdots, & \cdots, & \cdots, & \cdots \\ \phi(\mathbf{k}_1,\mathbf{r}_{N+1}), & \cdots, & \phi(\mathbf{k}_N,\mathbf{r}_{N+1}), & \phi(1s,\mathbf{r}_{N+1}) \end{vmatrix}, \qquad \text{(I. 3)}$$

where $\phi(1s,\mathbf{r}_j)$ is the wave function of 1*s*-state of an isolated hydrogen atom.

The energy at the equilibrium position and the relevant properties of the *r*-adatom are determined on the base of (I.2) as the minimum problem in Chapter 2.

Two types of hydrogen adsorption have recently been suggested, on the other hand, by a number of authors on the ground of the observed effects of adsorption on the work function and electric resistance of evaporated films as follows. One of these types of adsorption occurs rapidly with larger initial heat of adsorption causing both electric resistance and work function to increase, while the other type slowly with smaller heat of adsorption decreasing both electric resistance and work function. The amount of the former type of adsorption is markedly reduced by contaminating the surface especially with

oxygen, whereas that of the latter type practically insensitive to the contamination.

Theory of adsorption developed in the first two Chapters are now applied in Chapter 3 to the explanation of the experimental results on the effect of adsorption of hydrogen on the physical properties of adsorbent such as heat of adsorption, work function and electric conductivity. The above experimental results are satisfactorily accounted for, the former and the latter types of adsorption, experimentally recognized, being necessarily ascribed respectively to the *r*- and *s*-type adsorption theoretically deduced.

Chapter 1. The *s*-type Adsorption.

§ 1. Heat of dissolution—the self-consistent field method*).

Eq. (I.1) is written by (I.1.a) and (I.1.b) as

$$\Phi_s = \frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \psi(\mathbf{k}_1, \mathbf{r}_1), & \underline{\psi}(\mathbf{k}_2, \mathbf{r}_1), & \cdots, \underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_1) \\ \underline{\psi}(\mathbf{k}_1, \mathbf{r}_2), & \underline{\psi}(\mathbf{k}_2, \mathbf{r}_2, & \cdots, \underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_2) \\ \cdots, & \cdots, & \cdots, \quad \cdots \\ \underline{\psi}(\mathbf{k}_1, \mathbf{r}_{N+1}), & \underline{\psi}(\mathbf{k}_2, \mathbf{r}_{N+1}), & \cdots, \underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_{N+1}) \end{vmatrix},$$

$$\equiv \frac{1}{\sqrt{(N+1)!}} \det|\underline{\psi}(\mathbf{k}_i, \mathbf{r}_j)|, \qquad (1.1.a)$$

where**)

$$\underline{\psi}(\mathbf{k}_i, \mathbf{r}_j) = \left\{1 - \sum_\alpha |b_{\alpha i}|^2\right\}^{1/2} \psi(\mathbf{k}_i, \mathbf{r}_j) + \sum_\alpha b_{\alpha i} \psi(\mathbf{k}_\alpha, \mathbf{r}_j). \qquad (1.1.b)$$

The coefficients $b_{\alpha i}$ *etc.* are determined self-consistently in what follosws.

The perturbation potentials to the unperturbed periodic potential of the metal are taken to be the potential V_i due to the proton,

$$V_i(\mathbf{r}) = -e^2/r, \qquad (1.2)$$

as expressed with the proton at origin, the COULOMB potential $V_\rho(\mathbf{r})$ of the extra electron density $\rho(\mathbf{r})$ around the dissolved proton resulting from the redistribution of $N+1$ electrons and the perturbation $V_{ex}(\mathbf{r})$ of the exchange potential due to the redistribution. $V_\rho(\mathbf{r})$ is given as***)

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*) cf. Ref. (11) and (12).

**) It is shown in Appendix B, that the higher order terms, not included in (I.1.b) contribute nil as far as the second order energy of the system is concerned.

***) We have from (1.4) and the POISSON's equation for $V_\rho(r)$

$$\Delta V_\rho(\mathbf{r}) = -4\pi e^2 \rho(\mathbf{r}),$$

$$\text{or} \quad \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr}\right) V_\rho(\mathbf{r}) = -\frac{\lambda^3 e^2}{2} \exp(-\lambda r),$$

which leads to (1.3) on integration with the boundary conditions $dV_\rho/dr = -e^2/r^2$ and $V_\rho(\mathbf{r}) = e^2/r$ for $r \to \infty$.

$$V_p(\mathbf{r}) = e^2/r - \left\{e^2/r + \lambda e^2/2\right\} \exp(-\lambda r)\,, \tag{1.3}$$

as derived from a trial function

$$\rho(\mathbf{r}) = \lambda^3/8\pi \cdot \exp(-\lambda r)\,, \quad \int \rho(\mathbf{r})\, d\mathbf{r} = 1\,, \tag{1.4}$$

where λ is a constant to be determined.

The perturbation $V_{ex}(\mathbf{r})$ of the exchange potential is given, according to the simplified treatment by SLATER[13], as

$$V_{ex}(\mathbf{r}) = -3e^2(3/8\pi)^{1/3} \left\{(\rho_0 + \rho(\mathbf{r}))^{1/3} - \rho_0^{1/3}\right\}\,, \tag{1.5.a}$$

where $\rho_0 = N/V$ is the unperturbed density of metal electrons. The above equation may be written as

$$V_{ex}(\mathbf{r}) = -\eta(\lambda e^2/2) \cdot \exp(-\lambda r), \tag{1.5.b}$$

where

$$\eta = \frac{3}{\lambda}\left(\frac{3}{\pi}\right)^{1/3} \frac{\{(\rho_0 + \rho(\mathbf{r}))^{1/3} - \rho_0^{1/3}\}}{\exp(-\lambda r)}\,. \tag{1.5.c}$$

By substituting $\rho_0 = (4\pi/3 \cdot r_s^3)^{-1}$ for a monovalent metal (r_s: the radius of atomic sphere), we have

$$\eta = \frac{3}{(\lambda r_s)} \left\{\frac{3}{\pi} \cdot \frac{3}{4\pi}\right\}^{1/3} \left\{(1 + (\lambda r_s)^3/6 \cdot \exp(-\lambda r))^{1/3} - 1\right\} \exp(\lambda r), \tag{1.5.d}$$

which is illustrated as a function of λr in Fig. 1, for $\lambda r_s = 4.00$, 4.67 and 5.60.

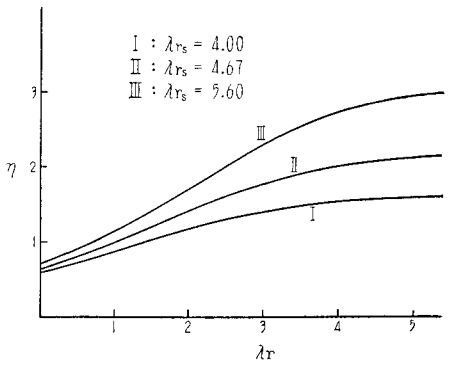

Fig. 1. Values of $\bar{\eta}$ *versus* λr for $\lambda r_s = 4.00$, 4.67 and 5.60.

For the respective values of λr_s the average $\bar{\eta}$ of η

$$\bar{\eta} \equiv \int_0^\infty \eta \exp(-\lambda r) r^2 dr \Big/ \int_0^\infty \exp(-\lambda r) r^2 dr$$

is calculated at 1.32, 1.61 and 2.16 so that $\bar{\eta}$ is expressed approximately as

$$\bar{\eta} \approx 0.34\,\lambda r_s \quad \text{for} \quad 5.6 \geq \lambda r_s \geq 4.0\,, \tag{1.5.e}$$

and $V_{ex}(\mathbf{r})$ similarly by replacing η in (1.5.b) with $\bar{\eta}$,

$$V_{ex}(\mathbf{r}) = -\bar{\eta}(\lambda e^2/2)\exp(-\lambda r)\,. \tag{1.5.f}$$

The resultant perturbation potential $V_p(\mathbf{r})$ is given by (1.2), (1.3) and (1.5.f) as

$$V_p(\mathbf{r}) = V_i(\mathbf{r}) + V_e(\mathbf{r}) + V_{ex}(\mathbf{r}) = -\left\{\frac{e^2}{r} + (1+\bar{\eta})\frac{\lambda e^2}{2}\right\}\exp(-\lambda r)\,, \tag{1.6}$$

which leads by the usual perturbation method to the values of coefficients of (1.1.b)

$$b_{ai} = -V_{ai}/(E(\mathbf{k}_a) - E(\mathbf{k}_i))\,, \tag{1.7}$$

where

$$V_{ai} = \int \psi^*(\mathbf{k}_a, \mathbf{r})\, V_p(\mathbf{r})\psi(\mathbf{k}_i, \mathbf{r})\, d\mathbf{r}\,, \tag{1.8}$$

and $E(\mathbf{k}_a)$ or $E(\mathbf{k}_i)$ is the energy of $\mathbf{k}_a$- or $\mathbf{k}_i$-level.

The value of λ is now determined by the requirement of self-consistency as follows. We have, according to (1.1.b), (1.6), (1.7) and (1.8),

$$\begin{aligned}\rho(\mathbf{r}) &\equiv \sum_{i=1}^{N+1} \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})\underline{\psi}(\mathbf{k}_i, \mathbf{r}) - \sum_{i=1}^{N} \psi^*(\mathbf{k}_i, \mathbf{r})\psi(\mathbf{k}_i, \mathbf{r}) \\ &= \frac{1}{V}\left\{1 - \frac{2k_F}{\pi a_H}\cdot 2\left(\frac{1}{\lambda^2} + \frac{1+\bar{\eta}}{\lambda^2}\right)\right\} + \frac{\lambda}{\pi^2}\,\frac{k_F}{a_H}\left\{1 + \frac{\bar{\eta}}{2}\right\}\exp(-\lambda r), \end{aligned} \tag{1.9}$$

as shown in Appendix A, where k_F is the wave number of an electron at the FERMI surface, and a_H the BOHR radius. By comparing (1.9) with (1.4), λ is given by the condition that the first term should vanish, as

$$\lambda = \left\{\frac{4k_F}{\pi a_H}(2+\bar{\eta})\right\}^{1/2}, \tag{1.10}$$

which converts simultaneonsly, the pre-exponential factor of (1.9) to $\lambda^3/8\pi$, confirming the self-consistency of $\rho(\mathbf{r})$ of (1.4). We have by (1.10) and (1.5.e) $\lambda = 1/0.29$ Å on the base of $r_s = 1.40$ Å and $k_F = 1.92/r_s$.

Footnote of p. 217. The third term on the right side is the same form with the result obtained in Ref. (14), where the perturbation potential is given by lattice vibration, *i.e.*, the first term of (4.11) in the first paper of Ref. (14) is written as the third term of (1.11.a) by making use of (3.9), (3.10), (3.13) (3.14) and (3.15) in the quoted paper.

The heat of dissolution, Q, is now readily derived, as shown in Appendix B, neglecting the potential energy of the proton due to surface double layer, as*)

$$Q = -I + \phi - \frac{1}{2}\int \rho(\mathbf{r})\, V_i(\mathbf{r})\, d\mathbf{r}\,, \qquad (1.11.a)$$

or according to (1.4) and (1.2)

$$Q = -I + \phi + \lambda e^2/4\,, \qquad (1.11.b)$$

where I is the ionization potential of hydrogen atom and ϕ the work function of the metal. The heat of dissolution Q of hydrogen atom into Cu, for which $r_s = 1.40$ Å, is calculated at 3.0 eV/atom by (1.11.b) on the base of $1/\lambda = 0.29$ Å as given by (1.10). The theoretical value may be taken to be in satisfactory agreement with the experimental value 1.6 eV/atom for Cu[15a] in respect that the SLATER's simplified treatment of the exchange effect may be associated with an appreciable error. Reducing $\bar{\eta}$ to $0.20\,\lambda r_s$, for instance, $1/\lambda = 0.325$ Å and Q comes to be 2.0 eV in good agreement with the observed value.**)

The $1/\lambda$ and Q of Ag and Au is evaluated from (1.10) and (1.11.b) at $1/\lambda = 0.34$ Å and $Q = 1.6$ eV on the base of $r_s = 1.58$ Å, $\phi = 4.7$ eV and $\bar{\eta} = 0.20\,\lambda r_s$. This value of Q is smaller than that of Cu by 0.4 eV, in conformity with the observation that Ag or Au does not absorb hydrogen atom appreciablly[15a].

For transition metals with *d*-holes, such as Ni, Pt, Co or Fe, electrons in the *d*-band contribute to the heat of dissolution similar to those in the conduction band or *s*-band.

It will be shown in a later paper that the heat of dissolution of these transition metals may be derived for small amount of dissolved proton, as if they were respectively monovalent metals of the same atomic radii. With this approximation, the heat of dissolution of hydrogen atom into Ni and Pt is larger than that of Cu or Au by 0.1 eV or 0.5 eV respectively, on the base of $\phi_{Ni} - \phi_{Cu} = 0.1$ eV and $(r_s)_{Ni} = (r_s)_{Cu}$ or $\phi_{Pt} - \phi_{Au} = 0.5$ eV and $(r_s)_{Pt} = (r_s)_{Au}$.

§ 2. Heat of dissolution (simplified treatment).

The method outlined in § 1 is now modified for estimating the heat of dissolution. The kinetic energy as well as the potential energy is expressed as a function of electronic density $\varrho(\mathbf{r}) = \rho_0 + \rho(\mathbf{r})$, to give an expression of the total energy as a function of λ according to (1.4). The total energy is now fixed as the minimum problem with λ as a varying parameter.

*) See the footnote in the preceding page.

**) The zero-point vibrational energy is *ca.* 0.3 *eV*, which is neglected in the present derivation.

The kinetic energy of $N+1$ electrons is approximated, according to THOMAS, FERMI and WEIZSACKER[1], as

$$(\Phi_s \bar{T} \Phi_s) = \sum_{i=1}^{N+1} \int \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})(-\hbar^2/2m \cdot \Delta)\underline{\psi}(\mathbf{k}_i, \mathbf{r})\, d\mathbf{r}$$

$$= A \int \underline{\rho}(\mathbf{r})^{5/3} d\mathbf{r} + \kappa B \int |\operatorname{grad} \underline{\rho}|(\mathbf{r})|^2 / \underline{\rho}(\mathbf{r}) d\mathbf{r}\,, \qquad (2.1)$$

where

$$A = \frac{16\pi^3\hbar^2}{5m}\left(\frac{3}{8\pi}\right)^{5/3}, \qquad B = \frac{\hbar^2}{8m}\,, \qquad (2.1.a)$$

$$\underline{\rho}(\mathbf{r}) = \sum_{i=1}^{N+1} \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})\underline{\psi}(\mathbf{k}_i, \mathbf{r}) = \rho_0 + \rho(\mathbf{r})\,, \qquad (2.1.b)$$

and κ is a numerical factor of nearly unity.

Similarly, the kinetic energy of N metal electrons without perturbation is given as

$$(\Psi T \Psi) \equiv \sum_{i=1}^{N} \int \psi^*(\mathbf{k}_i, \mathbf{r})(-\hbar^2/2m \cdot \Delta)\psi(\mathbf{k}_i, \mathbf{r})\, d\mathbf{r} = A \int \rho_0^{5/3} d\mathbf{r}\,, \quad (2.2)$$

where

$$\Psi \equiv \Psi(\mathbf{k}_1, \mathbf{k}_2, \cdots, \mathbf{k}_N) \equiv 1/\sqrt{N!}\det|\psi(\mathbf{k}_i, \mathbf{r}_j)|. \qquad (2.2.b)$$

Hence, the kinetic energy of $N+1$ metal electrons perturbed by the dissolved proton less that of N metal electrons without perturbation is written, according to (2.1) and (2.2), as

$$(\text{K.E.}) = (\Phi_s \bar{T} \Phi_s) - (\Psi T \Psi)$$

$$= A \int \left\{(\rho_0 + \rho(\mathbf{r}))^{5/3} - \rho_0^{5/3}\right\} d\mathbf{r} + \kappa B \int \frac{|\operatorname{grad} \rho(\mathbf{r})|^2}{\rho_0 + \rho(\mathbf{r})}\, d\mathbf{r}\,, \qquad (2.3)$$

By substituting A and B from (2.1.a), $\rho(\mathbf{r})$ from (1.4), and $\rho_0 = (4\pi/3 \cdot r_s^3)^{-1}$, we have

$$(\text{K.E.}) = \zeta_0 \cdot \frac{3}{10} \cdot \frac{6}{(\lambda r_s)^2} \int_0^\infty \left\{\left(1 + (\lambda r_s)^3/6 \cdot \exp(-\lambda r)\right)^{5/3} - 1\right\} (\lambda r)^2 d(\lambda r)$$

$$+ \kappa \frac{\hbar^2}{8m} \frac{\lambda^2}{2} \frac{(\lambda r_s)^3}{6} \int_0^\infty \frac{\exp(-2\lambda r)}{1 + (\lambda r_s)^3/6 \cdot \exp(-\lambda r)} (\lambda r)^2 d(\lambda r)\,. \quad (2.4)$$

The result of numerical integration of (2.4) is shown in Fig. 2 as a function of λr_s. Curve I shows the value of the first term on the right side of (2.4) and II that of the second term there for $\kappa = 1$ respectively in units of $\zeta_0 = (\hbar^2/2m) \cdot k_F^2$, $k_F = (9\pi/4)^{1/3} r_s^{-1}$.

The potential energy of the system of the metal with $N+1$ electrons and a proton dissolved less that of the metal without any perturbation is given by

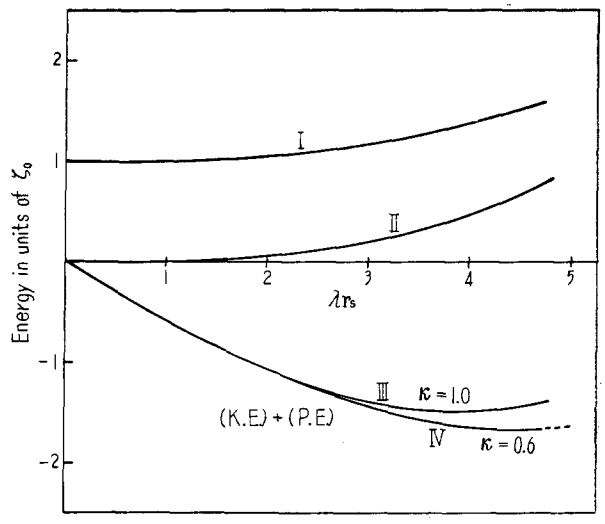

Fig. 2. Kinetic and potential energies as functions of λr_s.
I. THOMAS-FERMI kinetic energy
II. WEIZSAECKER kinetic energy
III. (K.E.)+(P.E.) for $\kappa=1.0$, as measured from $-\phi$
IV. (K.E.)+(P.E.) for $\kappa=0.6$, as measured from $-\phi$
The energy scale is given in units of $\zeta_0=7.0$ eV.

$$(\mathrm{P.E.}) \equiv (\Phi_s \overline{V} \Phi_s) - (\Psi V \Psi)\,, \tag{2.5}$$

where

$$\overline{V} = \sum_{j=1}^{N+1} \sum v(\mathbf{r}_j - \mathbf{R}_l) + \frac{1}{2} \sum_{\substack{j,j'=1 \\ (j \neq j')}}^{N+1} \frac{e}{|\mathbf{r}_j - \mathbf{r}_{j'}|} + \frac{1}{2} \sum_{\substack{l,l' \\ (l \neq l')}} \frac{e}{|\mathbf{R}_l - \mathbf{R}_{l'}|} + \sum_{j=1}^{N+1} V_i(\mathbf{r}_j) + \sum_l \frac{e}{|\mathbf{R}_l|}\,, \tag{2.5.a}$$

and

$$V = \sum_{j=l}^{N} \sum v(\mathbf{r}_j - \mathbf{R}_l) + \frac{1}{2} \sum_{\substack{j,j'=1 \\ (j \neq j')}}^{N} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_{j'}|} + \frac{1}{2} \sum_{\substack{l,l' \\ (l \neq l')}} \frac{e^2}{|\mathbf{R}_l - \mathbf{R}_{l'}|}\,. \tag{2.5.b}$$

The quantity $\mathbf{R}_l$ or $\mathbf{R}_{l'}$ in (2.5.a) or (2.5.b) is the coordinate vector of the l-th or l'-th metal ion and $v(\mathbf{r}_j - \mathbf{R}_l)$ the potential between j-th electron and a metal ion at $\mathbf{R}_l$; the second term is the sum of COULOMB repulsion potentials between $N+1$ or N electrons, the third the sum of those between metal ions, and the fourth or the fifth term of (2.5.a) is the sum of COULOMB potentials of electrons or metal ions due to the proton at the origin respectively.

We have, as shown in Appendix B (ii) (*cf.* (B. 22)),

$$(\text{P.E.}) = \int \rho(\mathbf{r})\,\overline{V}_0 d\mathbf{r} + \int \rho_0 V_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\int \rho(\mathbf{r})\,V_i(\mathbf{r}) d\mathbf{r}$$
$$+ \frac{1}{2}\int \rho(\mathbf{r})\,V_p(\mathbf{r}) d\mathbf{r} + \sum_i \frac{e^2}{|\mathbf{R}_i|}, \qquad (2.6)$$

where we have neglected $\rho'(\mathbf{r})$ in (B. 22), and replaced $V_0(\mathbf{r})$ in (B. 22) by its mean potential $\overline{V}_0 = -(\zeta_0 + \phi)$ of an electron in the metal; $V_i(\mathbf{r}) = -e^2/r$ is the potential of an electron due to proton, and $V_p(\mathbf{r})$ the perturbation potential of an electron due to proton and extra electron density $\rho(\mathbf{r})$ around the proton. The second integral and the last summation of (2.6) practically cancel each other when the proton is situated at the centre of unit cell of cubic lattice.

The (P.E.) is now given, for the proton situated at the centre, as

$$(\text{P.E.}) = -(\zeta_0 + \phi) + \frac{1}{2}\int \rho(\mathbf{r})\,V_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\int \rho(\mathbf{r})\,V_p(\mathbf{r}) d\mathbf{r}$$
$$= -(\zeta_0 + \phi) - \frac{11 + \bar{\eta}}{32}(\lambda r_s)\frac{e^2}{r_s}, \qquad (2.7)$$

since according to (1.2), (1.4) and (1.6),

$$\frac{1}{2}\int \rho(\mathbf{r})\,V_i(\mathbf{r}) d\mathbf{r} = -\frac{1}{2}\int \rho(\mathbf{r})\frac{e^2}{r} d\mathbf{r} = -\frac{\lambda e^2}{4} \qquad (2.8.\text{a})$$

and

$$\frac{1}{2}\int \rho(\mathbf{r})\,V_p(\mathbf{r})\, d\mathbf{r} = -\frac{(3 + \bar{\eta})\lambda e^2}{32}. \qquad (2.8.\text{b})$$

The resultant increase (K.E.)+(P.E.) of the energy of the system is given by (2.4) and (2.7) as shown by curve III or IV in Fig. 2, respectively for $\kappa = 1$ or 0.6. The value of λ at the minimum of the respective curve is 1/0.38 Å or 1/0.30 Å and the appropriate value of $Q = -\{I + (\text{K.E.}) + (\text{P.E.})\}$ is 1.2 eV or 2.7 eV on the base of $\bar{\eta} = 0.2\,(\lambda r_s)$, $\phi = 4.5$ eV, $\zeta_0 = 7.0$ eV and $I = 13.56$ eV. The values of Q and $1/\lambda$ for $\kappa = 0.6$ conforms with these obtained in §1 by the self-consistent method.

§ 3. The *s*-type adsorption.

Surface has two important effects on the distribution of metal electrons, *i.e.*, the spreading effect and the smoothing effect as discussed in detail by BARDEEN[15], HUNTINGTON[16][17], SEITZ[16], SMOLUCHOWSKI[18], and SUGIYAMA[19].

Electrons must spread out of the surface created by splitting the metal, since otherwise the gradient of their density, hence the kinetic energy, must be infinite at the surface due to the second term of (2.1). The spread gives

rise to positive charge inside the surface and negative one outside, or negative double layer, which increases the work function of the metal.

The distribution of electrons is represented approximately as[18]

$$\left.\begin{array}{lll} \rho_0+\rho_s(z) & \text{for} \quad z>0\,, \\ \rho_s(z) & \text{for} \quad z>0\,, \end{array}\right\} \qquad (3.1)$$

where

$$\left.\begin{array}{lll} \rho_s(z)=-1/2\cdot\rho_0\exp(\beta z) & \text{for} \quad z<0\,, \\ \rho_s(z)=\ \ 1/2\cdot\rho_0\exp(-\beta z) & \text{for} \quad z>0\,, \end{array}\right\} \qquad (3.1.a)$$

the coordinate z is perpendicular to the surface toward outside with origin at the surface (*cf.* Fig. 3), and β is a constant approximately equal to$\sim 2/r_s$[18].

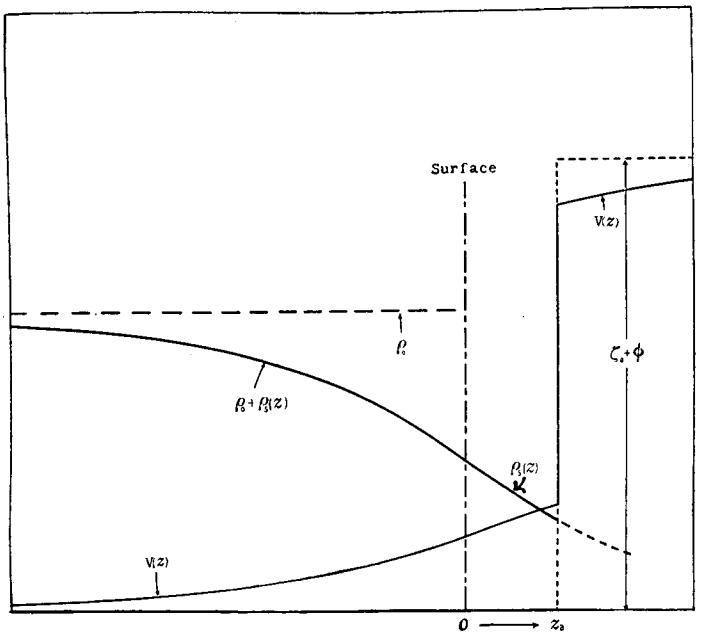

Fig. 3. Spreading of the electron density and resulting negative double layer on a metal surface.

The potential $V_{\rho_s}(z)$ of an electron due to the double layer given by $\rho_s(z)$ is readily derived by integrating the POISSON's equation $d^2V_\rho/dz^2=-4\pi e^2\rho_s(z)$ with boundary conditions $V_{\rho_s}(z)=0$ at $z=+\infty$, $dV_{\rho_s}(z)/dz=0$ at $z=\pm\infty$, and $V_{\rho_s}(z)$ is continuous at $z=0$. We have,

$$\left.\begin{array}{lll} V_{\rho_s}(z)=2\pi e^2/\beta^2\cdot\rho_0\exp(\beta z)-4\pi e^2\rho_0/\beta^2 & \text{for} \quad z<0\,, \\ V_{\rho_s}(z)=-2\pi e^2/\beta^2\cdot\rho_0\exp(-\beta z) & \text{for} \quad z>0\,. \end{array}\right\} \qquad (3.2)$$

The potential appropriate to the metal is expressed as

$$\left.\begin{aligned} V_0(z) &= \bar{V}_0', \quad \bar{V}_0' = -(\zeta_0+\phi)+4\pi e^2\rho_0/\beta^2 \quad \text{for} \quad z<z_B\,, \\ &= 0 \qquad\qquad\qquad\qquad\qquad\quad \text{for} \quad z>z_B\,, \end{aligned}\right\} \tag{3.3}$$

where z_B is assumed to be given by[19]

$$z_B k_F = \frac{3}{4}\left\{\frac{\pi}{2}+\left(\frac{\phi}{\zeta_0}-1\right)\sin^{-1}\sqrt{\frac{\zeta_0}{\zeta_0+\phi}}-\sqrt{\frac{\phi}{\zeta_0}}\right\}. \tag{3.3.a}$$

We have from the above equation $z_B=0.29$ Å or 0.35 Å for $k_F=1.92/r_s$, and either $\phi=5.0$ eV, $\zeta_0=7.0$ eV and $r_s=1.4$ Å appropriate for Cu and Ni or $\phi=4.5$ eV, $\zeta_0=5.0$ eV and $r_s=1.58$ Å appropriate for Pt.

The resultant potential $V(z)$ is thus given by the sum of $V_0(z)$ and $V_{ps}(z)$ as shown in Fig. 3.

The energy $E_s(\beta)$ of the surface formation per unit area or the surface energy as a function of β is derived from (2.1), (3.1), (3.1.a) and (3.3), according to SMOLUCHOWSKI[18], as*)

$$E_s(\beta) = A\frac{\rho_0^{5/3}}{\beta}\left\{\frac{1.2}{2^{5/2}}-1.585\right\}+\kappa B\rho_0\beta\cdot 2\ln 2-\frac{\rho_0\bar{V}_0'}{2\beta}\exp(-\beta z_B)+\frac{\pi e^2\rho_0^2}{2\beta^3}\,,$$

where the first and the second terms are contributions from the kinetic energy and the last two terms those from the potential energy. The value of $1/\beta$ as determined by the minimum condition of $E_s(\beta)$ is $\sim$0.7 Å$\approx r_s/2$, as mentioned before, and the relevant minimum energy is approximately 2.5 eV per one surface metal atom for Cu.

The other effect is the smoothing of the electronic distribution on the surface. This is due to the fact that the energy of electrons is lower when enclosed in flatter surface than in such an angular surface as that of atomic polyhedra[18] as seen from (2.1).

Fig. 4 shows (100) and (110) surface of simple cubic lattice. The electron distribution is originally smooth on the (100) surface (Fig. 4. a), whereas the original angular distribution of the (110) surface illustrated by broken lines should be smoothed as shown by bold curves of Fig. 4. (b) by carrying electrons from hills down to valleys.

This smoothing gives rise to a positive double layer which decreases the work function to an extent depending markedly on the original structure of

*) The first two terms are obtained by replacing B, σ and α in Eq. (14) of Ref. (17) by κB, ρ_0 and β, and putting $r=1$ and $\beta=0$ in Eq. (14) quoted above. The third term is equal to $\bar{V}_0'\int_{(z>z_B)}\rho_s(z)\,dz$ and the last term to $1/2\int V_{\rho_s}(z)\rho_s(z)\,dz$.

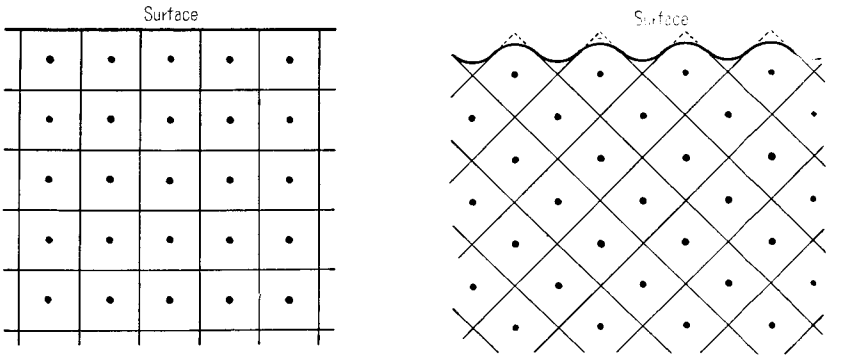

Fig. 4. Smoothing of the electron density and resulting positive double layer (after SMOLUCKOWSKI Ref. 21).
(a) Smoothing does not occure on the 100 plane of simple cubic lattice.
(b) Smoothing occures on the 110 plane.

surface as just exemplified, in distinction from the spreading effect.

We are now ready to discuss the variation of energy caused by bringing the dissolved proton from interior to the surface of metal. The kinetic energy (K.E.) is given, in place of (2.3), as the sum of the two terms in accordance with (2.1), *i.e.*,*)

$$A\Big[\int_{(z<0)}\Big\{(\rho_0+\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0))^{5/3}-(\rho_0+\rho_s(z))^{5/3}\Big\}d\mathbf{r} + \int_{(z>0)}\Big\{(\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0))^{5/3}-\rho_s^{5/3}\Big\}d\mathbf{r}\Big], \tag{3.4.a}$$

and

$$\kappa B\Big[\int_{(z<0)}\frac{|\operatorname{grad}(\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0))|^2}{\rho_0+\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0)}d\mathbf{r}-\int_{(z<0)}\frac{|\operatorname{grad}\rho_s(z)|^2}{\rho_0+\rho_s(z)}d\mathbf{r} + \int_{(z>0)}\frac{|\operatorname{grad}(\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0))|^2}{\rho_s(z)+\rho(\mathbf{r}-\mathbf{r}_0)}d\mathbf{r}-\int_{(z>0)}\frac{|\operatorname{grad}\rho_s(z)|^2}{\rho_s(z)}d\mathbf{r}\Big], \tag{3.4.b}$$

where the origin of coordinate is at the surface, z is the component of $\mathbf{r}\equiv(x,y,z)$ normal to the surface, and $\mathbf{r}_0$ is the coordinate vector of proton; $\rho_0=N/V=(4\pi/3\cdot r_s^3)^{-1}$, $\rho_s(z)$ is given by (3.1.a) and $\rho(\mathbf{r}-\mathbf{r}_0)=\lambda^3/8\pi\cdot\exp(-\lambda|\mathbf{r}-\mathbf{r}_0|)$ according to (1.4).

*) $\int_{(z<0)}$ signifies the integration inside metal surface, $\int_{(z>0)}$ that outside it, and $\int$ withont any indication that over all space.

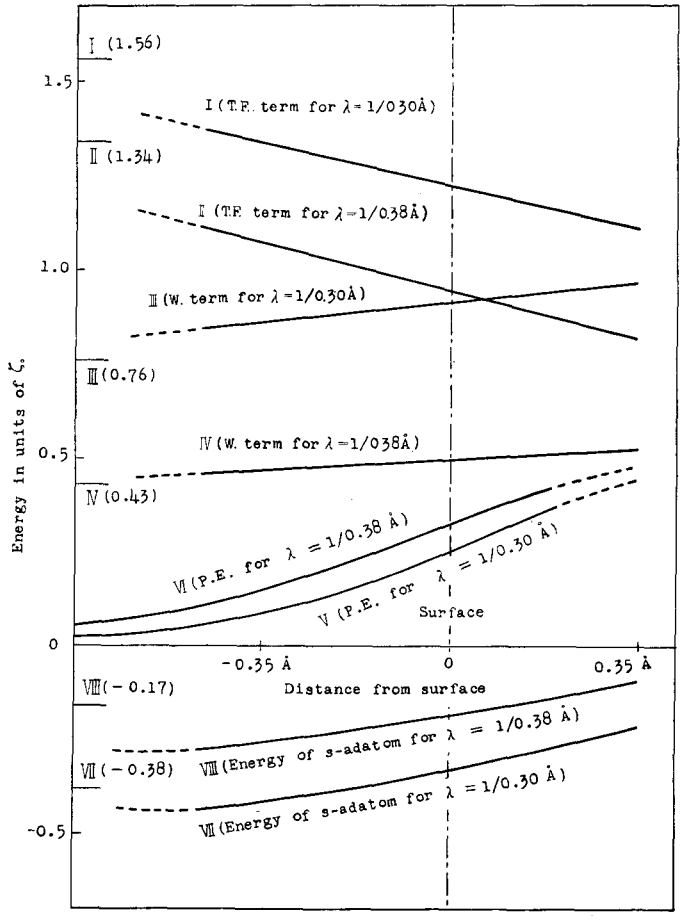

Fig. 5. Kinetic and potential energies as a function of the distance of proton from surface.

I. THOMAS-FERMI kinetic energy for $\lambda=1/0.30$ Å.
II. THOMAS-FERMI kinetic energy for $\lambda=1/0.38$ Å.
III. WEIZSAECKER kinetic energy for $\lambda=1/0.30$ Å and $\kappa=1$.
IV. WEIZSACKER kinetic energy for $\lambda=1/0.38$ Å and $\kappa=1$.
V. P. E. for $\lambda=1/10.30$ Å.
VI. P. E. for $\lambda=1/10.38$ Å.
VII. Energy of s-type adsorption for $\lambda=1/0.30$ Å and $\kappa=0.6$
VIII. Energy of s-type adsorption for $\lambda=1/0.38$ Å and $\kappa=1.0$

The horizontal lines give the respective values in the interior of the metal.

Numerical integration of the above expression gives on the base of $1/\beta=0.7$ Å and $r_s=1.4$ Å, the result shown in Fig. 5. The sum of the values

of (3.4.a) and (3.4.b) equals that given by (2.4) when electron clouds $\rho(\mathbf{r}-\mathbf{r}_0)$ and $\rho_s(z)$ scarcely overlap each other, or when the proton is far inside the metal from the surface. The value of (3.4.a) begins to decrease when they substantially overlap and decreases rapidly near the surface, as much as $0.35\,\zeta_0$ for $1/\lambda=0.30$ Å or $0.4\,\zeta_0$ for $1/\lambda=0.38$ Å at $z=0$ (cf. curves I and II Fig. 5). As $z\to\infty$, the value of (3.4.a) converges to

$$A\int\rho(\mathbf{r}-\mathbf{r}_0)^{5/3}d\mathbf{r}=A\frac{\lambda^2}{(8\pi^2)^{2/3}}\left(\frac{3}{5}\right)^2.$$

The value of (3.4.b) increases when $\rho(\mathbf{r}-\mathbf{r}_0)$ and $\rho_s(z)$ overlap, the magnitude of its increase being about one third of the decrease of (3.4.a) for $\kappa=0.6$ (cf. curves III and IV in Fig. 5). The limiting value of (3.4.b) at $z\to\infty$ is

$$\kappa B\int\frac{|\mathrm{grad}\,\rho(\mathbf{r}-\mathbf{r}_0)|^2}{\rho(\mathbf{r}-\mathbf{r}_0)}d\mathbf{r}=\kappa\frac{\hbar^2}{8m}\lambda^2.$$

The excess (P.E.) of the potential energy of $(N+1)$ electrons perturbed by the field of the proton brought near surface over the potential energy of the unperturbed N electrons is given by replacing $\rho(\mathbf{r})$, ρ_0 and $\overline{V}_0$, which appears on the right side of (2.6), by $\rho(\mathbf{r}-\mathbf{r}_0)$, the electron density given by (3.1) and (3.1.a) and $V(z)=V_0(z)+V_{\rho_s}(z)$ given by (3.2) and (3.3) respectively, as

$$\begin{aligned}(\mathrm{P.E.})=&\int\rho(\mathbf{r}-\mathbf{r}_0)\left\{V_0(z)+V_{\rho_s}(z)\right\}d\mathbf{r}+\int_{(z<0)}\left\{\rho_0+\rho_s(z)\right\}V_i(\mathbf{r}-\mathbf{r}_0)\,d\mathbf{r}\\&+\int_{(z>0)}\rho_s(z)\,V_i(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}+\frac{1}{2}\int\rho(\mathbf{r}-\mathbf{r}_0)\,V_i(\mathbf{r}-\mathbf{r}_0)\,d\mathbf{r}\\&+\frac{1}{2}\int\rho(\mathbf{r}-\mathbf{r}_0)\,V_p(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}+\sum_l\frac{e^2}{|\mathbf{R}_l|},\\=&\int_{(z<z_B)}\rho(\mathbf{r}-\mathbf{r}_0)\overline{V}_0'd\mathbf{r}+\int\rho(\mathbf{r}-\mathbf{r}_0)\,V_{\rho_s}(z)d\mathbf{r}+\int_{(z<0)}\rho_0V_i(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}\\&+\int\rho_s(z)\,V_i(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}+\frac{1}{2}\int\rho(\mathbf{r}-\mathbf{r}_0)\,V_i(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}\\&+\frac{1}{2}\int\rho(\mathbf{r}-\mathbf{r}_0)\,V_p(\mathbf{r}-\mathbf{r}_0)d\mathbf{r}+\sum_l\frac{e^2}{|\mathbf{R}_l|}.\end{aligned}\qquad(3.5)$$

The first term on the third member of (3.5) is readily evaluated from the $\rho(\mathbf{r}-\mathbf{r}_0)$ given by (1.4) as

$$\overline{V}_0'\int_{(z<z_B)}\rho(\mathbf{r}-\mathbf{r}_0)\,d\mathbf{r}=\overline{V}_0'\left[1-\frac{1}{4}\left\{\lambda(z_B-z_0)+2\right\}\exp(-\lambda(z_B-z_0))\right],\qquad(3.6)$$

where z_B is the distance of the potential jump from surface and z_0 the z-

component of $\mathbf{r}_0$. Hence, the increase of potential energy of extra electron density $\rho(\mathbf{r}-\mathbf{r}_0)$ around the dissolved proton at $\mathbf{r}_0=(x_0, y_0, z_0)$ is

$$|\overline{V}_0'|/4\cdot\left\{\lambda(z_B-z_0)+2\right\}\exp(-\lambda(z_B-z_0))\,, \qquad (3.6.a)$$

as compared with its potential energy $\overline{V}_0'$ in the interior of the metal. The second term on the third member of (3.5) represents the potential energy of extra electron density $\rho(\mathbf{r}-\mathbf{r}_0)$ due to the double layer $\rho_s(z)$ produced by the spreading, and the fourth that of proton, since

$$\int\rho_s(z)\,V_i(\mathbf{r}-\mathbf{r}_0)\,d\mathbf{r}=-\int\frac{e^2\rho_s(z)}{|\mathbf{r}-\mathbf{r}_0|}\,d\mathbf{r}=-V_{\rho_s}(z_0)\,.$$

Hence, the second and the fourth term cancel each other approximately. The fifth term on the third member of (3.5) does not vary with distance of proton from the surface according to (2.8.a), assumed that λ remains constant. Under the same assumption the sixth term varies with distance, since η, hence $\bar{\eta}$, varies by replacing ρ_0 in (1.5.c) by (3.1), *e.g.*, the increase of the value of $\bar{\eta}$ is approximately 50%, and the decrease of the value of the sixth term is *ca.* 0.5 eV, when proton is at the surface. The third term gives the COULOMB potential of proton due to metal electrons without any spreading, and the last term the COULOMB potential due to metal ions, hence these two terms compensate each other, for example, for the position of proton along a perpendicular to (110) surface. The (P.E.) is shown by V or VI curve in Fig. 5, and (K.E.) + (P.E.) by VII or VIII for $1/\lambda=0.30$ Å or $1/\lambda=0.38$ Å respectively. The maximum of the resultant energy dectrease is *ca.* 0.5 *eV* at 0.5 Å inside the metal from surface (the *s*-type adsorption).

The energy of dissolved proton is reduced as it approaches the surface to decrease the THOMAS-FERMI kinetic energy as given by the integral (3.4.a) of the terms proportional to the three fifth power of electron density or to lower the peak of the electron density around the proton*). The decrease is the greater the lower λ is as seen from Fig. 5. It is expected as well that the smaller β favours the greater decrease of the energy.

It has been estimated in §1 that λ and β are 1/0.34 Å and 1/0.77 Å for Pt, which are appreciably lower than those 1/0.30 Å and 1/0.70 Å respectively for Ni. It follows that the decrease of the energy for Pt is greater than for Ni.

The proton at the surface is further subjected to the following effects. The spherical distribution $\rho(\mathbf{r})$ of electrons around the proton must be smoothed

*) The energy of proton at kinks or steps of dislocation, or lattice defects at the surface is lowered by *ca.* $1\,eV\sim2\,eV$. Hence, steps, kinks and lattice defects are heterogeneous adsorption sites, different from other normal sites.

similarly to metal electrons at the surface. This smoothing produces on the one hand positive dipole moment, which reduces the work function slightly and results in, on the other hand, a further decrease of energy from that deduced above on the base of spherical distribution. The amount of charge protruded outside the potential barrier at $z_B=0.3$ Å is calculated at 0.08 e on the base of the distance 0.55 Å of proton from the surface, $\lambda=1/0.30$ Å and of the spherical distribution of electron around it. Assuming that half of this amount of charge is smeared over the surface, the dipole moment produced by this effect is 0.06×10^{-18} e.s.u.

Chapter 2. The *r*-type adsorption.

When the proton is at the distance of *ca.* 1 Å outside from the surface, electrons in the metal protrude toward the proton, the wave function of the $\mathbf{k}_i$-level being deformed from $\phi(\mathbf{k}_i, \mathbf{r})$ to

$$\phi(\mathbf{k}_i, \mathbf{r})+c''_{si}\phi(1s, \mathbf{r}),$$

and electron in 1*s*-level intrudes reciprocally into the metal, with the wave function of 1*s*-state modified as

$$\phi(1s, \mathbf{r})+\sum_{\alpha} b''_{\alpha s}\phi(\mathbf{k}_\alpha, \mathbf{r}).$$

Hence, the wave function of the system is generally given by Φ_r or (I. 2), taking the above deformation of the individual wave functions into account. The resonance energy between the neutral state M–H of the first or the second term of (I.2) and the ionic state M^-–H^+ or M^+–H^- given by the third or fourth term plays, as discussed in (I), an important rôle in stabilizing the adsorbed atom (the *r*-type adsorption).

The energy and the degree of polarization are now worked out with Φ_r dealing equally with the third and the fourth terms of (1.1) here, whereas the third term has been just roughly taken into account in (I) as mentioned in the introduction.

§ 4. The energy of *r*-type adsorption.

We first consider the energy decrease of the ground state given by the wave function $\Psi(1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)$ due to its resonance with the ionic states. The appropriate approximate wave function of the system is given, neglecting the excited neutral states expressed by the second term of (I.2), as

$$\Phi'_r = a'_0\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N)+\sum_{\alpha\uparrow} b'_{\alpha s\uparrow}\Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N)$$
$$+\sum_{i\downarrow} c'_{si\downarrow}\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N), \qquad (4.1)$$

where

$$|a'_0|^2+\sum_{\alpha\uparrow}|b'_{\alpha s\uparrow}|^2+\sum_{i\downarrow}|c'_{si\downarrow}|^2=1\,, \tag{4.1.a}$$

the affix $\uparrow$ or $\downarrow$ denotes the spin orientation explicity in case of necessity, the summation $\sum_{\alpha\uparrow}$ covers the terms referred to the levels $\alpha, \beta, \cdots$, above the FERMI surface, with the parallel spin orientation to $1s$ electron, and $\sum_{i\downarrow}$ those referred to the levels $i, i', \cdots$, below the FERMI surface, with the anti-parallel spin orientation to $1s$ electron; $\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N)$ is the wave function of the state, where an electron of $\mathbf{k}_i\downarrow$-level is promoted to the $1s\downarrow$-level.

The equations for a'_0, $b'_{\alpha s}$ and c'_{is} are given by the minimum conditions of $(\Phi'_r\{\mathscr{H}-W'\}\Phi'_r)$, as*)

$$\{E_0-W'\}\,a'_0+\sum_{\alpha\uparrow}V_{s\alpha}b'_{\alpha s\uparrow}+\sum_{i\downarrow}V_{is}c'_{si\downarrow}=0\,, \tag{4.2.a}$$

$$V^*_{s\alpha}a'_0+\{E_{+,s\to\alpha}-W'\}\,b'_{\alpha s\uparrow}=0\,, \tag{4.2.b}$$

$$V^{i*}_{s}a'_0+\{E_{-,i\to s}-W'\}\,c'_{si\downarrow}=0\,, \tag{4.2.c}$$

where W' is the energy to be determined, E_0, $E_{+,s\to\alpha}$ or $E_{-,i\to s}$ the mean energy respectively appropriate to $\Psi(1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)$, $\Psi(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N)$ or $\Psi(1s, \mathbf{k}_1, \cdots, \underset{(i)}{1s}, \cdots, \mathbf{k}_N)$,

$$V_{s\alpha}=\int\Psi^*(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N)\,\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j\,, \tag{4.3.a}$$

and

$$V_{is}=\int\Psi^*(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N)\,\{\mathscr{H}-W'\}\times \times\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j\,. \tag{4.3.b}$$

The matrix elements of interaction such as

$$V_{\alpha\beta}=\int\Psi^*(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N)\,\{\mathscr{H}-W'\}\,\Psi(\mathbf{k}_\beta, \mathbf{k}_1, \cdots, \mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j\,, \tag{4.4.a}$$

$$V_{s\alpha,si}=\Psi^*(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i')}{1s\downarrow}, \cdots, \mathbf{k}_N)\,\{\mathscr{H}-W'\}\times \times\Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j\,, \tag{4.4.b}$$

*) The (4.2.a), (4.2.b) or (4.2.c) is derived from $\partial(\Phi'_r\{\mathscr{H}-W'\}\Phi'_r)/\partial a'^*_0=0$, $\partial(\Phi'_r\{\mathscr{H}-W'\}\Phi'_r)/\partial b'^*_{\alpha s}=0$ or $\partial(\Phi'_r\{\mathscr{H}-W'\}\Phi'_r)/\partial c'^*_{si}=0$ respectively. Overlap integrals such as

$$\int\Psi^*(1s, \mathbf{k}_1, \cdots, \mathbf{k}_N)\,\Psi(\mathbf{k}_\alpha, \mathbf{k}_1, \cdots, \mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j$$

are neglected (cf. Appendix A of (I)).

$$V_{is,si'}=\int\Psi^*(1s\uparrow,\mathbf{k}_1,\cdots,\mathbf{k}_i\downarrow,\cdots,\underset{(i')}{1s\downarrow},\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\times$$
$$\times\Psi(1s\uparrow,\mathbf{k}_1,\cdots,\underset{(i)}{1s\downarrow},\cdots,\mathbf{k}_{i'}\downarrow,\cdots,\mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j,\quad(4.4.c)$$

and

$$V'_{is,si'}=\int\Psi^*(\mathbf{k}_a,\mathbf{k}_1,\cdots,\mathbf{k}_i\downarrow,\cdots,\underset{(i')}{1s\downarrow},\cdots,\mathbf{k}_N)\{\mathscr{H}-W'\}\times$$
$$\times\Psi(\mathbf{k}_a,\mathbf{k}_1,\cdots,\underset{(i)}{1s\downarrow},\cdots,\mathbf{k}_{i'}\downarrow,\cdots,\mathbf{k}_N)\prod_{j=1}^{N+1}d\mathbf{r}_j,\quad(4.4.d)$$

are neglected, since their contributions to the heat of adsorption are small as shown in Appendix A in (I).

We have, eliminating $b'_{as\uparrow}$ and $c'_{si\downarrow}$ from (4.2.a), (4.2.b) and (4.2.c),

$$E_0-W'_g-\sum_{a\uparrow}\frac{|V_{sa}|^2}{E_{+,s\to a}-W'_g}-\sum_{i\downarrow}\frac{|V_{is}|^2}{E_{-,i\to s}-W'_g}=0\,,\qquad(4.5)$$

admitted that the lowest root W'_g of W' satisfies the conditions

$$\left.\begin{aligned}&E_0\;>\;W'_g\,,\\&E_{+,a\to s}>W'_g\,,\\&E_{-,i\to s}>W'_g\,.\end{aligned}\right\}\qquad(4.6)$$

With an approximation

$$\left.\begin{aligned}&|V_{sa}|=|V_{s\beta}|=\cdots=|V_{s,1.14k_F}|\equiv|V_v|\,,\\&|V_{is}|=|V_{i's}|=\cdots=|V_{0.8k_F,s}|\equiv|V_o|\,,\end{aligned}\right\}\qquad(4.7)$$

we have

$$\sum_{a\uparrow}\frac{|V_{sa}|^2}{E_{+,s\to a}-W'_g}=\frac{1}{2}\frac{N_v|V_v|^2}{\bar{E}_+-W'_g}\,,\quad\sum_{i\downarrow}\frac{|V_{is}|^2}{E_{-,i\to s}-W'_g}=\frac{1}{2}\frac{N|V_o|^2}{\bar{E}_--W'_g}\,,$$

(4.7.a), (4.7.b)

hence

$$E_0-W'_g-\frac{1}{2}\frac{N_v|V^v|^2}{E_+-W'_g}-\frac{1}{2}\frac{N|V_o|^2}{\bar{E}_--W'_g}=0\,,\qquad(4.8)$$

where $\{\bar{E}_+-W'_g\}^{-1}$ or $\{\bar{E}_--W'_g\}^{-1}$ is respectively the average of $\{E_{+,s\to a}-W'_g\}^{-1}$ or $\{E_{-,i\to s}-W'_g\}^{-1}$ over N_v vacant or N occupied levels participating in the bond formation; the factor 1/2 of the third and the fourth terms allows for the summation over $\mathbf{k}_a$- or $\mathbf{k}_i$-levels with the spin orientation either parallel or antiparallel to that of the 1*s*-electron.

The lowest root W'_g is given by (4.8) as

$$E_0-W'_g=3.5\text{ eV}\,,\quad\text{or}\quad W'_g=-1.4\text{ eV}\,,\qquad(4.9)$$

for $E_0=2.1$ eV, $D=2.4\,a_H$, $N_v=N$ and $r_s=1.40$ Å, as shown below. Energy

term $\bar{E}_+$ or $\bar{E}_-$ is given, identifying it further with the simple mean of $E_{+,s\to\alpha}$ or $E_{-,i\to s}$, as

$$\bar{E}_+ = E_{+,1s\to k_F} + (\hbar^2/2m)\int_{k_F}^{k_m}(k^2-k_F^2)k^2dk \Big/ \int_{k_F}^{k_m} k^2dk\,,$$
$$= I-\phi+0.31\,\zeta_0\,, \qquad (4.10.a)$$

or

$$\bar{E}_- = E_{-,k_F\to 1s} + (\hbar^2/2m)\int_0^{k_F}(k_F^2-k^2)k^2dk \Big/ \int_0^{k_F} k^2dk$$
$$= \phi-A+2E_0+0.40\,\zeta_0\,, \qquad (4.10.b)$$

where $k_m=2^{1/3}k_F$ and A is the electron affinity of hydrogen atom. The image force potential does not appear in the present approximation.

On the base of the data

$$\zeta_0=7.0\text{ eV},\quad \phi=4.5\text{ eV},\quad A=0.7\text{ eV},\quad I=13.6\text{ eV and } E_0=2.1\text{ eV}^{*)}, \qquad (4.11.a)$$

we have

$$\bar{E}_+=11.3\text{ eV},\qquad \bar{E}_-=10.8\text{ eV}. \qquad (4.11.b)$$

It has previously been worked out for $D=2.4\,a_H$ and $r_s=1.40$ Å that**)

$$\sqrt{N}\,|V_v| = 6.1\text{ eV} \quad \text{and} \quad \sqrt{N}\,|V_o| = 6.9\text{ eV} \qquad (4.11.c)$$

The data of (4.11.a), (4.11.b) and (4.11.c) yields, when substituted into (4.8), the value of (4.9).

We have, further, from (4.2.b), (4.2.c), (4.1.a), (4.7.a) and (4.7.b)

$$\sum_{\alpha\uparrow}|b'_{s\alpha\uparrow}|^2 = \frac{N_v}{2}\frac{|V_v|^2}{(\bar{E}_+-W'_g)^2}|a'_0|^2\,, \qquad (4.12.b)$$

$$\sum_{i\downarrow}|c'_{is\downarrow}|^2 = \frac{N}{2}\frac{|V_o|^2}{(\bar{E}_--W'_g)^2}|a'_0|^2\,, \qquad (4.12.c)$$

and

$$|a'_0|^2 = \left\{1+\frac{N_v}{2}\frac{|V_v|^2}{(\bar{E}_+-W'_g)^2}+\frac{N}{2}\frac{|V_o|^2}{(\bar{E}_--W'_g)^2}\right\}^{-1}. \qquad (4.12.a)$$

The above quantities are evaluated for $D=2.4\,a_H$ as $|a'_0|^2=0.78$, $\sum_{\alpha\uparrow}|b'_{s\alpha\uparrow}|^2=0.09$ and $\sum_{i\downarrow}|c'_{is\downarrow}|^2=0.13$, hence the degree of polarization of adatoms, or the effective charge e^* of adatom, is determined as $e^*=\sum_{\alpha\uparrow}|b'_{s\alpha\uparrow}|^2-\sum_{i\downarrow}|c'_{is\downarrow}|^2=-0.04$ in unit of

*) See Table I in Appendix A in (I). The E_0 was denoted by $A(D)$ in (I).

**) See Eqs. (A. 5), (A. 13), (A. 14), and Table I, (i) and (ii) of Appendix A in (I).

elementary charge.

§ 5. The *r*-type adsorption—higher approximation.

We will now take into account the contributions from the excited neutral states as well as the ionic states in terms of the wave function

$$\Phi_r = a_0\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N) + \sum_{\alpha,i} a_{\alpha s,si}\Psi(1s, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha}, \cdots, \mathbf{k}_N) + \sum_{\alpha\uparrow} b_{\alpha s\uparrow}\Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_N) + \sum_{i\downarrow} c_{si\downarrow}\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N), \quad (5.1)$$

where the second term is expressed as

$$\sum_{\alpha,i} a_{\alpha s,si}\Psi(1s, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha}, \cdots, \mathbf{k}_N) = \sum a_{\alpha s\uparrow,si\uparrow}\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\uparrow}, \cdots, \mathbf{k}_N) + \sum a_{\alpha s\uparrow,si\downarrow}\Psi(1s\downarrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\uparrow}, \cdots, \mathbf{k}_N) + \sum a_{\alpha s\downarrow,si\downarrow}\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\downarrow}, \cdots, \mathbf{k}_N), \quad (5.1.a)$$

i.e., the linear combination of the terms which couple with the ground state through ionic states, as

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\uparrow, \cdots, \mathbf{k}_N) \xrightarrow[\alpha s\uparrow]{} \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\uparrow, \cdots, \mathbf{k}_N) \xrightarrow[si\uparrow]{} \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\uparrow}, \cdots, \mathbf{k}_N) \equiv \pm\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\uparrow}, \cdots, \mathbf{k}_N) \quad (5.1.a.I)$$

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N) \xrightarrow[\alpha s\uparrow]{} \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N) \xrightarrow[si\downarrow]{} \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N) \equiv \pm\Psi(1s\downarrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\uparrow}, \cdots, \mathbf{k}_N) \quad (5.1.a.II)$$

and

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N) \xrightarrow[si\downarrow]{} \Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N) \xrightarrow[\alpha s\uparrow]{} \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s\downarrow}, \cdots, \mathbf{k}_N) \equiv \pm\Psi(1s\downarrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\uparrow}, \cdots, \mathbf{k}_N) \quad (5.1.a.III)$$

or

$$\xrightarrow[\alpha s\downarrow]{} \Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_\alpha\downarrow, \cdots, \mathbf{k}_N) \equiv \pm\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha\downarrow}, \cdots, \mathbf{k}_N) \quad (5.1.a.IV)$$

where arrows with $\alpha s\uparrow$ below denote the transition, in which $1s$ electron with spin orientation $\uparrow$ is transfered to $\mathbf{k}_\alpha$-level in the metal, those with $si\downarrow$ that in which an electron occupying $\mathbf{k}_i$-level with spin orientation $\downarrow$ is transfered to $1s$-level of hydrogen atom, and so on.

The coefficients in (5.1) and (5.1.a) are determined by the minimum conditions of $(\Phi_r\{\mathscr{H} - W\}\Phi_r)$, as

$$\{E_{\cdot}-W_g\}a_0+\sum_{\alpha\uparrow}V_{s\alpha}b_{\alpha s\uparrow}+\sum_{i\downarrow}V_{is}c_{si\downarrow}=0\,, \tag{5.2.a}$$

$$\{E_{0,i\to\alpha}-W_g\}a_{\alpha s\uparrow,si\uparrow}+V_{is}^*b_{\alpha s\uparrow}=0\,, \tag{5.2.b.1}$$

$$\{E_{0,i\to\alpha}-W_g\}a_{\alpha s\uparrow,si\downarrow}+V_{is}^*b_{\alpha s\uparrow}+V_{s\alpha}^*c_{si\downarrow}=0\,, \tag{5.2.b.2}$$

$$\{E_{0,i\to\alpha}-W_g\}a_{\alpha s\downarrow,si\downarrow}+V_{s\alpha}^*c_{si\downarrow}=0\,, \tag{5.2.b.3}$$

$$V_{s\alpha}^*a_0+\sum_{i\downarrow}V_{is}a_{\alpha s\uparrow,si\downarrow}+\sum_{i\uparrow}V_{i\alpha}a_{\alpha s\uparrow,si\uparrow}+\{E_{+,s\to\alpha}-W_g\}b_{\alpha s\uparrow}=0, \tag{5.2.c.1}$$

$$V_{is}^*a_0+\sum_{\alpha\uparrow}V_{s\alpha}a_{\alpha s\uparrow,si\downarrow}+\sum_{\alpha\downarrow}V_{s\alpha}a_{\alpha s\downarrow,si\downarrow}+\{E_{-,i\to s}-W_g\}c_{si\downarrow}=0, \tag{5.2.c.2}$$

where $E_{0,i\to\alpha}$ is the mean energy of the excited neutral state with an electron of $\mathbf{k}_i$-level promoted to the $\mathbf{k}_\alpha$-level, and W_g is the lowest mean energy to be determined.

Substituting $a_{\alpha s\uparrow,si\uparrow}$ *etc.* from (5.2.b.1), (5.2.b.2) and (5.2.b.3) into (5.2.c.1) and (5.2.c.2), we have

$$V_{s\alpha}^*a_0-\sum_{i\downarrow}\frac{V_{is}V_{s\alpha}^*}{E_{0,i\to\alpha}-W_g}c_{si\downarrow}+\left\{E_{+,s\to\alpha}-\sum_{i\uparrow,i\downarrow}\frac{|V_{is}|^2}{E_{0,i\to\alpha}-W_g}-W_g\right\}b_{\alpha s\uparrow}=0\,, \tag{5.3.a}$$

and

$$V_{is}^*a_0-\sum_{\alpha\uparrow}\frac{V_{s\alpha}V_{is}^*}{E_{0,i\to\alpha}-W_g}b_{\alpha s\uparrow}+\left\{E_{-,i\to s}-\sum_{\alpha\uparrow,\alpha\downarrow}\frac{|V_{s\alpha}|^2}{E_{0,i\to\alpha}-W_g}-W_g\right\}c_{si\downarrow}=0\,, \tag{5.3.b}$$

where $\sum_{i\uparrow,i\downarrow}$ or $\sum_{\alpha\uparrow,\alpha\downarrow}$ signifies the summation over both the spin orientations of the electrons on the i-th or α-th level respectively. The coefficient $c_{si\downarrow}$ or $b_{\alpha s\uparrow}$ in the above equations is approximately given as

$$c_{si\downarrow}=-\frac{V_{is}^*a_0}{E_{-,i\to s}-W_g}\,, \tag{5.4.a}$$

or

$$b_{\alpha s\uparrow}=-\frac{V_{s\alpha}^*a_0}{E_{+,s\to\alpha}-W_g}\,, \tag{5.4.b}$$

neglecting the second and the third terms of (5.2.c.2) or (5.2.c.1), which terms are of higher order than the first ones as seen with reference to (4.2.b) or (4.2.c) respectively. Sustituting $c_{si\downarrow}$ or $b_{\alpha s\uparrow}$ from (5.4.a) or (5.4.b) respectively into the second term of (5.3.a) or (5.3.b), which is of higher order than the respective first term is, we have

$$V_{s\alpha}^*\{1+\gamma_{-,\alpha}\}a_0+\{E_{(+),\alpha}-W_g\}b_{\alpha s\uparrow}=0\,, \tag{5.5.a}$$

and

$$V_{is}^{*}\{1+\gamma_{+,i}\}a_0+\{E_{(-),i}-W_g\}c_{si\downarrow}=0\,, \tag{5.5.b}$$

where

$$E_{(+),\alpha}=E_{+,s\to\alpha}-\sum_{i\uparrow,i\downarrow}\frac{|V_{is}|^2}{E_{0,i\to\alpha}-W_g}\,, \tag{5.6.a}$$

$$E_{(-),i}=E_{-,i\to s}-\sum_{\alpha\uparrow,\alpha\downarrow}\frac{|V_{s\alpha}|^2}{E_{0,i\to\alpha}-W_g}\,, \tag{5.6.b}$$

$$\gamma_{-,\alpha}=\sum_{i\downarrow}\frac{|V_{is}|^2}{(E_{0,i\to\alpha}-W_g)(E_{-,i\to s}-W_g)}\,, \tag{5.7.a}$$

and

$$\gamma_{+,i}=\sum_{\alpha\uparrow}\frac{|V_{s\alpha}|^2}{(E_{0,i\to\alpha}-W_g)(E_{+,s\to\alpha}-W_g)}\,. \tag{5.7.b}$$

The equation for W_g, of the form similar to (4.5), is now obtained from (5.2.a), (5.5.a) and (5.5.b), as

$$E_0-W_g-\sum_{\alpha\uparrow}\{1+\gamma_{-,\alpha}\}\frac{|V_{s\alpha}|^2}{E_{(+),\alpha}-W_g}-\sum_{i\downarrow}\{1+\gamma_{+,i}\}\frac{|V_{is}|}{E_{(-),i}-W_g}=0\,, \tag{5.8}$$

or approximately, as

$$E_0-W_g-\frac{1+\gamma_-}{2}\frac{N|V_v|^2}{\bar{E}_{(+)}-W_g}-\frac{1+\gamma_+}{2}\frac{N|V_o|^2}{\bar{E}_{(-)}-W_g}=0\,, \tag{5.9}$$

where N_v is identified with N, $|V_v|$ and $|V_o|$ replaces $|V_{s\alpha}|$ and $|V_{is}|$ respectively according to (4.7) and $\bar{E}_{(+)}$,$\bar{E}_{(-)}$, γ_- and γ_+ are averages of $E_{(+),\alpha}$, $E_{(-),\alpha}$, $\gamma_{-,\alpha}$ and $\gamma_{+,i}$, which are evaluated in turn as below.

The term $E_{(+),\alpha}$ or $E_{(-),i}$ is given, with the same approximation of (4.7), respectively by (5.6.a) or (5.6.b) as

$$E_{(+),\alpha}=E_{+,s\to\alpha}-\frac{N|V_o|^2}{\bar{E}_{0,\alpha}-W_g}\,,\quad E_{(-),i}=E_{-,i\to s}-\frac{N|V_v|^2}{\bar{E}_{0,i}-W_g}\,, \tag{5.10.a), (5.10.b)}$$

where $(\bar{E}_{0,\alpha}-W_g)^{-1}$ or $(\bar{E}_{0,i}-W_g)^{-1}$ is the average of $(E_{0,i\to\alpha}-W_g)^{-1}$ over N occupied k-levels or that of $(E_{0,i\to\alpha}-W_g)^{-1}$ over N unoccupied k_α-levels. The term $\bar{E}_{0,\alpha}$ or $\bar{E}_{0,i}$ is given identifying it with the simple average of $E_{0,i\to\alpha}$, as

$$\begin{aligned}\bar{E}_{0,\alpha}&=E_0+(\hbar^2/2m)k_\alpha^2-(\hbar^2/2m)\langle k_i^2\rangle_{\mathrm{Av}}\\&=E_0+(\hbar^2/2m)k_\alpha^2-(\hbar^2/2m)\int_0^{k_F}k^4dk\Big/\int_0^{k_F}k^2dk\\&=E_0-0.60\zeta_0+(\hbar^2/2m)k_\alpha^2\,,\end{aligned} \tag{5.11.a}$$

or

$$\begin{aligned}\bar{E}_{0,i} &= E_0+(\hbar^2/2m)\langle k_\alpha^2\rangle_{\mathrm{Av}}-(\hbar^2/2m)k_i^2\\ &= E_0+(\hbar^2/2m)\int_{k_F}^{k_m}k^4dk\Big/\int_{k_F}^{k_m}k^2dk-(\hbar^2/2m)k_i^2\\ &= E_0+1.31\,\zeta_0-(\hbar^2/2m)k_i^2,\end{aligned}\qquad(5.11.\mathrm{b})$$

where $\zeta_0=(\hbar^2/2m)k_F^2$ and $k_m=2^{1/3}k_F$ is the maximum wave number for the conduction band of monovalent metals. We have, further, the average $\bar{\bar{E}}_0$ of $\bar{E}_{0,\alpha}$ or $\bar{E}_{0,i}$ over N vacant $\mathbf{k}_\alpha$-levels or over N occupied $\mathbf{k}_i$-levels, as

$$\begin{aligned}\bar{\bar{E}}_0 &\equiv \langle\bar{E}_{0,\alpha}\rangle_{\mathrm{Av}}(=\langle\bar{E}_{0,i}\rangle_{\mathrm{Av}})\\ &= E_0-0.60\,\zeta_0+(\hbar^2/2m)\langle k_\alpha^2\rangle_{\mathrm{Av}}\\ &= E_0-0.60\,\zeta_0+1.31\,\zeta_0\\ &= E_0+0.71\,\zeta_0.\end{aligned}\qquad(5.12)$$

The average $\bar{E}_{(+)}$ of $E_{(+),\alpha}$ or that $\bar{E}_{(-)}$ of $E_{(-),i}$ over N vacant or N occupied levels is expressed approximately, according to (5.10.a) or (5.10.b), by replacing the average of $(\bar{E}_{0,\alpha}-W_g)^{-1}$ with $(\bar{\bar{E}}_0-W_g)^{-1}$, as

$$\bar{E}_{(+)}\equiv\langle E_{(+),\alpha}\rangle_{\mathrm{Av}}=\bar{E}_+-\frac{N|V_o|^2}{\bar{\bar{E}}_0-W_g},\quad \bar{E}_{(-)}\equiv\langle E_{(-),i}\rangle_{\mathrm{Av}}=\bar{E}_--\frac{N|V_v|^2}{\bar{\bar{E}}_0-W_g},\qquad(5.13.\mathrm{a}),\ (5.13.\mathrm{b})$$

where $\bar{E}_+$ or $\bar{E}_-$ is given by (4.10.a) or (4.10.b).

The average γ_- of $\gamma_{-,\alpha}$ or that γ_+ of $\gamma_{+,i}$ respectively over N vacant $\mathbf{k}_\alpha$- or N occupied $\mathbf{k}_i$-levels is now according to (5.7.a) or (5.7.b) by the similar approximation

$$\gamma_-\equiv\langle\gamma_{-,\alpha}\rangle_{\mathrm{Av}}=\frac{1}{2}\,\frac{N|V_o|^2}{(\bar{\bar{E}}_0-W_g)(\bar{E}_--W_g)},\qquad(5.14.\mathrm{a})$$

$$\gamma_+\equiv\langle\gamma_{+,i}\rangle_{\mathrm{Av}}=\frac{1}{2}\,\frac{N|V_v|^2}{(\bar{\bar{E}}_0-W_g)(\bar{E}_+-W_g)}.\qquad(5.14.\mathrm{b})$$

The root W_g for $D=2.4\,a_H$ is now determined at -3.0 eV according to (5.9), (5.12), (5.13.a), (5.13.b), (5.14.a) and (5.14.b) on the base of data given by (4.11.a), (4.11.b) and (4.11.c); we have besides $\gamma_-=0.165$ and $\gamma_+=0.14$. The lowest values of W_g is -4.6 eV for $D=1.8a_H$ on the base of the values of E_0, $|V_v|$ and $|V_o|$ as given by or interpolated from Table 1 in (I).

The lowest value of W_g and the equilibrium distance D_e are increased by taking into account the exchange repulsion $E_0^{(d)}$ due to d-electrons, which is of comparable order of magnitude at $D\lesssim 2.0a_H$ as compared with E_0 in cases of transition metals with d-holes and noble monovalent metals. We have, for

example, $W_g=-2.8$ eV and $D_e=2.2a_H$ by assuming $E_0^{(a)}=E_0\ (a_H/D)^2$.

On the other hand, d-electrons participate in the resonance similarly as discussed above, the contribution being increased by the presence of d-holes.

§ 6. The polarization of r-adatoms.

The degree of polarization is now determined as below. We have from (5.5.a),

$$\sum_{\alpha\uparrow}|b_{as\uparrow}|^2=\sum_{\alpha}(1+\gamma_{-,\alpha})^2\frac{|V_{s\alpha}|^2}{(E_{(+),\alpha}-W_g)^2}a_0^2, \tag{6.1}$$

or, replacing $\gamma_{-,\alpha}$, $E_{(+),\alpha}$, and $|V_{s\alpha}|^2$ respectively with γ_-, $\bar{E}_{(+)}$ and $|V_v|^2$ similarly as in the derivation of (5.9) from (5.8),

$$\sum_{\alpha\uparrow}|b_{as\uparrow}|^2=\frac{(1+\gamma_-)^2}{2}\frac{N|V_v|^2}{(\bar{E}_{(+)}-W_g)^2}a_0^2. \tag{6.1.a}$$

Similarly we have from (5.5.b),

$$\sum_{i\downarrow}|c_{si\downarrow}|^2=\frac{(1+\gamma_+)^2}{2}\frac{N|V_o|^2}{(\bar{E}_{(-)}-W_g)^2}a_0^2. \tag{6,1.b}$$

Eq. (5.2.b.1) yields, on the other hand, with the similar approximation to that for (5.13.a),

$$\begin{aligned}\sum_{\alpha\uparrow,i\uparrow}|a_{as\uparrow,si\uparrow}|^2&=\sum_{\alpha\uparrow,i\uparrow}\frac{|V_{is}|^2}{(E_{0,i\to\alpha}-W_g)^2}|b_{as\uparrow}|^2\\&=\frac{N}{2}\frac{|V_o|^2}{(\bar{E}_0-W_g)^2}\times\sum_{\alpha\uparrow}|b_{as\uparrow}|^2,\end{aligned}$$

hence substituting $\sum_{\alpha\uparrow}|b_{as\uparrow}|^2$ form (6.1.a),

$$\sum_{\alpha\uparrow,i\uparrow}|a_{as\uparrow,si\uparrow}|^2=\frac{(1+\gamma_-)^2}{4}\frac{N|V_o|^2}{(\bar{E}_0-W_g)^2}\frac{N|V_v|^2}{(\bar{E}_{(+)}-W_g)^2}a_0^2. \tag{6.2.a}$$

Eq. (5.2.b.3) and (6.1.b) give similarly

$$\begin{aligned}\sum_{\alpha\downarrow,i\downarrow}|a_{as\downarrow,si\downarrow}|^2&=\sum_{\alpha\uparrow,i\downarrow}\frac{|V_{s\alpha}|^2}{(E_{0,i\to\alpha}-W_g)^2}|c_{si\downarrow}|^2\\&=\frac{N}{2}\frac{|V_v|^2}{(\bar{E}_0-W_g)^2}\times\sum_{i\downarrow}|c_{si\downarrow}|^2\\&=\frac{(1+\gamma_+)^2}{4}\frac{N|V_v|^2}{(\bar{E}_0-W_g)^2}\frac{N|V_o|^2}{(\bar{E}_{(-)}-W_g)^2}a_0^2.\end{aligned} \tag{6.2.b}$$

We have, further, from (5.2.b.2),

$$\sum_{\alpha\uparrow,i\downarrow}|a_{as\uparrow,si\downarrow}|^2=\sum_{\alpha\uparrow,i\downarrow}\frac{(V_{is}^*b_{as\uparrow}+V_{s\alpha}^*c_{si\downarrow})(V_{is}b_{as\uparrow}^*+V_{s\alpha}c_{si\downarrow}^*)}{(E_{0,i\to\alpha}-W_g)^2}$$

$$=\sum_{\alpha\uparrow,i\downarrow}\frac{|V_{is}|^2}{(E_{0,i\to\alpha}-W_g)^2}|b_{as\uparrow}|^2+\sum_{\alpha\uparrow,i\downarrow}\frac{V_{is}^*V_{s\alpha}}{(E_{0,i\to\alpha}-W_g)^2}b_{as\uparrow}c_{si\downarrow}^*$$

$$+\sum_{\alpha\uparrow,i\downarrow}\frac{V_{s\alpha}^*V_{is}}{(E_{0,i\to\alpha}-W_g)^2}b_{as\uparrow}^*c_{si\downarrow}+\sum_{\alpha\uparrow,i\downarrow}\frac{|V_{s\alpha}|^2}{(E_{0,i\to\alpha}-W_g)^2}|c_{si\downarrow}|^2. \tag{6.2.c}$$

The first term of the third member is approximated similarly as in the above cases as,

$$\frac{N}{2}\frac{|V_o|^2}{(\bar{E}_0-W_g)^2}\times\sum_{\alpha\uparrow}|b_{as\uparrow}|^2,$$

or substituting $\sum_{\alpha\uparrow}|b_{as\uparrow}|^2$ from (6.1.a), as

$$\sum_{\alpha\uparrow,i\downarrow}\frac{|V_{is}|^2}{(E_{0,i\to\alpha}-W_g)^2}|b_{as\uparrow}|^2=\frac{(1+\gamma_-)^2}{4}\frac{N|V_o|^2}{(\bar{E}_0-W_g)^2}\frac{N|V_v|^2}{(\bar{E}_{(+)}-W_g)^2}a_0^2. \tag{6.2.c.1}$$

The second term of the same member is transformed by (5.5.a) and (5.5.b) as

$$\sum_{\alpha\uparrow,i\downarrow}\frac{V_{is}^*V_{s\alpha}}{(E_{0,i\to\alpha}-W_g)^2}\frac{(1+\gamma_{-,\alpha})V_{s\alpha}^*}{(E_{(+),\alpha}-W_g)}\frac{(1+\gamma_{+,i})V_{is}}{(E_{(-),i}-W_g)}a_0^2,$$

which is identical with the third term similarly transformed by (5.5.a) and (5.5.b). By the similar approximation to the foregoing one, we have from the above expression of the second as well as of the third term,

$$\sum_{\alpha\uparrow,i\downarrow}\frac{V_{is}^*V_{s\alpha}}{(E_{0,i\to\alpha}-W_g)^2}b_{as\uparrow}c_{si\downarrow}^*=\sum_{\alpha\uparrow,i\downarrow}\frac{V_{s\alpha}^*V_{is}}{(E_{0,i\to\alpha}-W_g)^2}b_{as\uparrow}^*c_{si\downarrow}$$

$$=\frac{(1+\gamma_-)(1+\gamma_+)}{4}\frac{N|V_o|^2\times N|V_v|^2}{(\bar{E}_0-W_g)^2(\bar{E}_{(+)}-W_g)(\bar{E}_{(-)}-W_g)}a_0^2. \tag{6.2.c.2}$$

The last term is given similarly to the first term as,

$$\sum_{\alpha\uparrow,i\downarrow}\frac{|V_{s\alpha}|^2}{(E_{0,i\to\alpha}-W_g)^2}|c_{si\downarrow}|^2=\frac{(1+\gamma_+)^2}{4}\frac{N|V_v|^2}{(\bar{E}_0-W_g)^2}\frac{N|V_o|^2}{(\bar{E}_{(-)}-W_g)^2}a_0^2. \tag{6.2.c.3}$$

Hence, we have from (6.2.c), (6.2.c.1), (6.2.c.2) and (6.2.c.3),

$$\sum_{\alpha\uparrow,i\downarrow}|a_{as\uparrow,si\downarrow}|^2=\frac{1}{4}\frac{N|V_v|^2\cdot N|V_o|^2}{(\bar{E}_0-W_g)^2}\left\{\frac{1+\gamma_-}{\bar{E}_{(+)}-W_g}+\frac{1+\gamma_+}{\bar{E}_{(-)}-W_g}\right\}^2a_0^2. \tag{6.3}$$

The weight $\sum|a_{as,si}|^2$ of the excited neutral states is given in accordance with (5.1.a), as

$$\sum |a_{as,si}|^2 = \sum_{\alpha\uparrow,i\uparrow} |a_{as\uparrow,si\uparrow}|^2 + \sum_{\alpha\uparrow,i\downarrow} |a_{as\downarrow,si\downarrow}|^2 + \sum_{\alpha\downarrow,i\downarrow} |a_{as\uparrow,si\downarrow}|^2, \tag{6.4}$$

or substituting the terms on the right side from (6.2.a), (6.3) and (6.2.b) as

$$\sum |a_{as,si}|^2 = \frac{1}{2} \frac{N|V_v|^2 \cdot N|V_o|^2}{(\bar{E}_o - W_g)^2} \left\{ \left(\frac{1+\gamma_-}{(\bar{E}_{(+)} - W_g)} \right)^2 + \frac{(1+\gamma_-)(1+\gamma_-)}{(\bar{E}_{(+)} - W_g)(\bar{E}_{(-)} - W_g)} + \left(\frac{1+\gamma_+}{\bar{E}_{(-)} - W_g} \right)^2 \right\} a_0^2 . \tag{6.5}$$

We have from (6.1.a), (6.1.b) and (6.5) referring to (5.12)

$$\sum_{\alpha\uparrow} |b_{as\uparrow}|^2 = 0.29\, a_0^2, \quad \sum_{i\downarrow} |c_{si\downarrow}|^2 = 0.32\, a_0^2, \quad \sum |a_{as,si}|^2 = 0.385\, a_0^2,$$

and, according to the normalization condition of Φ_r given by (5.1),

$$a_0^2 + \sum |a_{as,si}|^2 + \sum_{\alpha\uparrow} |b_{as\uparrow}|^2 + \sum_{i\downarrow} |c_{si\downarrow}|^2 = 1 ,$$

$|a_0^2| = 0.50$ for $D = 2.4\, a_H$ on the base of the data given by (4.11.a), (4.11.b), (4.11.c), (5.15) and (5.16). Hence, we have finally $e^* = \sum_{\alpha\uparrow} |b_{as\uparrow}|^2 - \sum_{s\downarrow} |c_{si\downarrow}|^2 = 0.145 - 0.16 = -0.015$. This value of e^* is smaller than that obtained in §4 ignoring excited neutral states. The dipole moment μ_r of a r-adatom on Ni or Cu surface is henceforth evaluated, assuming $D_e = 2.4\, a_H$ as

$$\mu_r = 0.015 \times 2.4\, a_H \times e = 0.08 \times 10^{-18} \quad \text{e.s.u.}, \tag{6.7}$$

which is somewhat smaller than the observed value 0.2×10^{-18} e.s.u.*)

It might be remarked that the effective charge e^* is decreased with increase of coverage θ, inasmuch as the contribution of M^+-H^- states to the r-type adsorption decreases relative to that of the M^--H^+ states because of a rapid increase of the exchange repulsion in the former state, which is altogether absent in the latter, although the electrostatic repulsion is the same both in the cases.

Chapter 3. Experimental results in the light of the present theory.

Conclusions are now derived from the theory of adsorption developed in the preceding chapters on the effect of adsorption and temperature change on the heat of adsorption, work function and electric conductivity of adsorbent metals and compared with relevant experimental results.

*) Estimated from the increase of work function at $\theta \simeq 0$ (cf. Ref. (3)). The theoretical value e^*, hence μ_r, depends markedly on the distance from surface, so that $d\mu_r/dD \gg d\mu_s/dD$, indicating that the infra-red absorption of a r-adatom is more intense than that of a s-adatom.

§7. Change of the state of adsorption and the heat of adsorption.

The existence of the two types of adsorption may reveal itself in the change of differential heat of adsorption with coverage and temperature as illustrated below. The differential heat of adsorption $Q(\theta, T)$ is the excess of the excess of the half of the partial molar enthalpy of gaseous hydrogen H_g over that H_a of adsorbed hydrogen atoms, *i.e.*,

$$Q(\theta, T) = \frac{1}{2} H_g - H_a ,$$

where θ is the fraction of the number n_a of gm atoms of adsorbed hydrogen over its value N_a at the full occupation, when $\theta=1$. It follows that

$$\int_0^{N_a} Q(\theta, T) dn_a = \frac{1}{2} H_g N_a - \int_0^{N_a} H_a dn_a ,$$

or

$$\int_0^1 Q(\theta, T)\, d\theta = \frac{1}{2} H_g - N_a^{-1} \left\{ (\bar{H}_a)_{\theta=1} - (\bar{H}_a)_{\theta=0} \right\} ,$$

where $(\bar{H}_a)_{\theta=0}$ or $(\bar{H}_a)_{\theta=1}$ is the enthalpy respectively of the adsorbent without adsorptive or of adsorbent fully covered by adsorptive. The $(\bar{H}_a)_{\theta=1} - (\bar{H}_a)_{\theta=0}$ may be taken a constant independent of temperature, provided that adatoms are constantly either in the *s*- or in the *r*-state and excited vibrational states ignorable, the energy of the adsorptives at $\theta=1$ thus being kept constant independent of temperature. Expressing H_g as

$$H_g = \varepsilon_0(\mathrm{H_2}) + 7/2\, RT ,$$

it follows from the above two equations that

$$\bar{Q} \equiv \int_0^1 Q(\theta, T)\, d\theta - \frac{7}{4} RT = \frac{\varepsilon_0(\mathrm{H_2})}{2} - N_a^{-1} \left\{ (\bar{H}_a)_{\theta=1} - (\bar{H}_a)_{\theta=0} \right\} = \text{const.} \tag{7.1}$$

is a constant independent of temperature, insofar as $\varepsilon_0(\mathrm{H_2})$ and $(\bar{H}_a)_{\theta=1} - (\bar{H}_a)_{\theta=0}$ are respectively constant, where $\varepsilon_0(\mathrm{H_2})$ is the energy of 1 mol hydrogen gas less its translational and rotational energy; $\varepsilon_0(\mathrm{H_2})$ is practically constant independent of temperature below 1000°C.

If, on the other hand, adatoms transit gradually with rise of temperature from *r*-tpye to *s*-type of adsorption or reversely, $(\bar{H}_a)_{\theta=1} - (\bar{H}_a)_{\theta=0}$ does not in general remain constant resulting in a deviation from the rule (7.1), even if ε_0 is constant and the excited vibrational states of adatoms are neglibible as

assured practically at temperatures up to 300°C.

This rule holds satisfactorily in the case of W, where the *s*-type adsorption may be taken as excluded on account of the practical absence of solubility*).

§ 8. Effect of adsorption on the work function.

The increase of work function by adatoms is given as

$$\Delta\varphi = 4\pi\mu(\theta)N_a\theta\,, \tag{8.1}$$

where $\mu(\theta)$ is the effective dipole moment created by the adatoms, *i.e.* the weighted mean of the dipole moment μ_r of *r*-adatoms and that μ_s of *s*-adatoms with the respective coverage as weights. The μ_r is evaluated in §§4 and 6 at $0.08\times10^{-18}\sim0.24\times10^{-18}$ e.s.u. at $\theta=0$ for Ni or Cu, which decreases with increase of the coverage of *r*-adatoms as shown in §6, while μ_s estimated in §3 is approximately constant at -0.06×10^{-18} e.s.u. irrespective of θ.

The *r*-type adsorption should now predominate at the initial stage of adsorption, while the *s*-type may possibly prevail later, insofar as the energy of *r*-type adsorption is lower than that of *s*-type one, but rises rapidly with increase of coverage owing to a pronounced mutual repulsion through the intermediary of metal electrons**) as discussed qualitatively in (I). It follows that the work function increases steeply at the initial stage, but slowly later or even decreases, on account of the depolarization of *r*-type adsorption referred to above as well as of a possible appearance of the *s*-type adsorption with positive dipole moment.

These theoretical conclusions are in accordance with experimental results obtained by MIGNOLET[2], GUNDRY, TOMPKINS, CULVER and PRITCHARD[3]. The work function decreases actually near $\theta\approx1$ as observed for Ni[5] and Co[3].

The work function of Pt is larger than that of Ni. This increase of work function from Ni to Pt decreases the negative polarization of *r*-adatom as shown in §6, diminishes, as illustrated in §§4 and 5, the heat of adsorption of *r*-adatoms, and increases the heat of the *s*-type adatoms as discussed in §3. These conditions should cause the *s*-type adatom more abundant on Pt than on Ni, hence, the increase of work function of Pt by adsorption should be less than in the case of Ni. If the heat of *r*-type adatom on Pt is higher than that of *s*-type adatom at very low coverage but lower than the latter at higher coverage in accordance with the relative change of the heats of the two types of adatom discussed above, the *r*-type adsorption predominates more or less at the low coverage but the *s*-type adsorption does in its stead at higher coverage. The

*) Two types of adsorption of hydrogen are observed by some authors. One of them may be attributed to *r*-type and the other to $H_2^{(+)}$ instead of *s*-type one.

**) cf. §9 also.

work function then increases with increase of coverage at the low coverage but soon decreases at higher one. This effect on the work function must be the more distinct, the lower the temperature. Actually, SUHRMAN, WEDLER and GENTSH[41] have observed that at 100°K the work function of Pt slightly increases initially and then decreases with increase of coverage, resulting in the overall decrease of work function at $\theta=1$, and that at 273°K the work function remains more or less constant initially with increase of coverage and then decreases at higher coverage. We conclude incorporating the above observations that in the case of Pt the *r*-type one occurs just at the initial stage and then gives place to the *s*-type adsorption.

§ 9. Effect of adsorption on the conductivity.

The electric conductivity σ of a thin metallic film is theoretically derived by FUCHS[20] and SONDHEIMER[21], in terms of the thickness d of the film, the number N of free electrons per unit volume, the mean free path $\bar{l}$, the mean velocity $\bar{v}$ of an electron at the FERMI surface, and the probability p of specular reflection of an electron at the surface of the film, as

$$\sigma = \sigma_0 \Phi_p(d/\bar{l})/(d/\bar{l}), \tag{9. 1}$$

where

$$\frac{x}{\Phi_p(x)} = 1 - \frac{3}{2x}(1-p)\int_0^\infty \left(\frac{1}{t^3} - \frac{1}{t^5}\right)\frac{1-\exp(-xt)}{1-p\cdot\exp(-xt)}\,dt, \tag{9. 1. a}$$

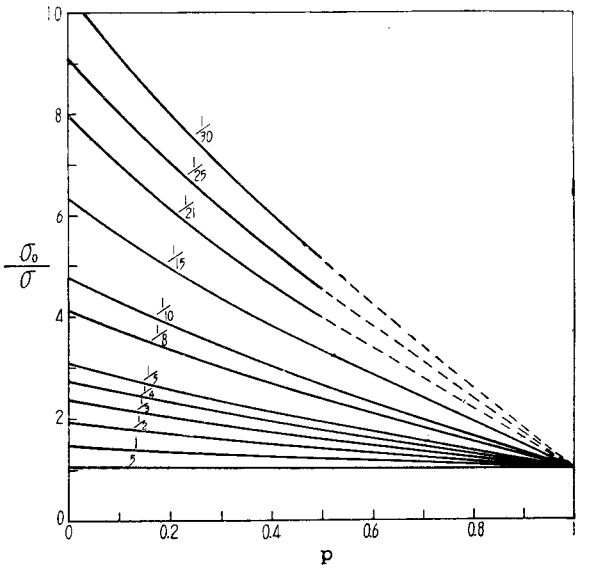

Fig. 6. Theoretical σ_0/σ plotted against p for various $d/\bar{l}$.

and

$$\sigma_0 = \frac{Ne^2\bar{l}}{m\bar{v}} \tag{9.1.b}$$

is the specific conductivity of the bulk metal. Fig. 6 shows σ_0/σ, which is unity for $p=1$, as plotted aginst p for the different values of $(d/\bar{l})$ according to (9.1) and (9.1.a).

The value of p_0 of p at $\theta=0$ of clean metallic film estimated in two ways, assuming that p does not depend on temperature.

The resistance R_0 of a film is proportional to $1/(\sigma\cdot d)$, the proportional constant c' being given by the conditions of the experiment. We have, hence, from (9.1) and (9.1.b),

$$R_0(d) = \frac{c'}{\sigma\cdot d} = \frac{c'}{d^2}\,\frac{m\bar{v}}{Ne^2}\left(\frac{d}{\bar{l}}\right)\left\{\Phi_p(d/\bar{l})/(d/\bar{l})\right\}^{-1},$$

or

$$cR_0(d)d^2 = (d/\bar{l})^2/\Phi_p(d/\bar{l}) \tag{9.2}$$

where c is another constant given by

$$c = (Ne^2)/(c'm\bar{v})\,. \tag{9.2.a}$$

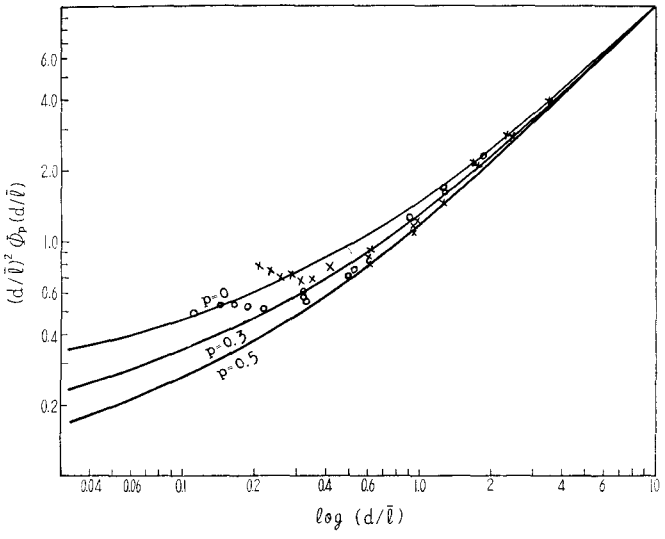

Fig. 7. Theoretical curves of $\log\{(d/\bar{l})^2\Phi_p(d/\bar{l})\}$ *versus* $\log(d/\bar{l})$ for $p=0$, 0.3 and 0.5.
The crosses are observed values[6] at 273°K represented with constants $c=3.6\times10^{-6}/\Omega$ Å^2 and $\bar{l}=150$ Å, and circles are those at 90°K with constants $c=3.6\times10^{-16}/\Omega$ Å^2 and $\bar{l}=270$ Å.

Eq. (9.2) shows that the curve of $\log\{R_0(d)\cdot d^2\}$ *versus* $\log d$ is superposed upon the curve of $\log\{(d/\bar{l})^2/\Phi_p(d/\bar{l})\}$ *versus* $\log(d/\bar{l})$ for the appropriate value of p by a proper selection of $\bar{l}$ and c, so that we may determine p_0 as well as $\bar{l}$ from the observed $R_0(d)$ as a function of d.

MIZUSHIMA[6] has observed $R_0(d)$ of evaporated Ni film for $d=30$ Å$\sim$500 Å at $T=273$°K and 90°K. By comparing the experimental curves of $\log\{R_0(d)\cdot d^2\}$ versus $\log d$ at 273°K and 90°K with the theoretical curves of Fig. 7 for various p, we have according to the above

$$\left.\begin{aligned} &\bar{l}(T=273°\mathrm{K}) = \sim 150\ \text{Å}\,, \\ &\bar{l}(T=90°\mathrm{K}) = \sim 270\ \text{Å}\,, \\ &c \approx 3.6\times 10^{-6}/\Omega\ \text{Å}^2 \\ \text{and}\quad &p_0 = 0\sim 0.3\,. \end{aligned}\right\} \qquad (9.3)$$

We may estimate the extent of "the lattice imperfection" of evaporated Ni film by the magnitude of the mean free paths just estimated. The probability $P=\bar{v}/\bar{l}$ of an electron to be scattered per unit time is given by the sum of the probability $P_{\text{vib.}}$ due to the lattice vibrations and the probability $P_{\text{irr.}}$ due to the lattice imperfection. $P_{\text{vib.}}$ is expressed as $\bar{v}/\bar{l}_0$ where $\bar{l}_0$ is the mean free path in the absence of the lattice imperfection, estimated at $\bar{l}_0=266$ Å for 273°K and $\bar{l}_0=2100$ Å for 90°K[22]. We have,

$$P_{\text{irr.}} = P - P_{\text{vib.}} = \bar{v}(1/\bar{l} - 1/\bar{l}_0)\,,$$

or by (9.3)

$$P_{\text{irr.}} = \bar{v}(1/270 - 1/2100) \approx \bar{v}/330 \text{ at } 90°\mathrm{K},$$

and

$$P_{\text{irr.}} = \bar{v}(1/150 - 1/266) \approx \bar{v}/330 \text{ at } 273°\mathrm{K},$$

which shows that $P_{\text{irr.}}$ is independent of temperatures as it should be provided that the lattice imperfection remains the same.

The value of p_0 is estimated alternatively according to the later conclusion that p_0 is reduced to zero at $\theta=1/4\sim1/2$, where the resistance attains to its maximum. It follows that the increase $\Delta R_{\max}$ of resistance up to the maximum is due to the change of p from p_0 to 0 alone. Eq. (9.2) leads on the other hand to the equation

$$\frac{\Delta R_{\max}}{R_0} = \frac{\Phi_{p_0}(d/\bar{l})}{\Phi_{p=0}(d/\bar{l})} - 1\,, \qquad (9.4)$$

admitting N, d and $\bar{l}$ are respectively unaffected by adsorption. We have, now, from the observed value of $\Delta R_{\max}/R_0$ by SUHRMAN, WEDLER, HERMANN[5], and MIZUSHIMA[6] and from the values of d and $\bar{l}$ estimated as above, $p_0\approx0.04$, which is consistent with the value of p_0 estimated as above (see Fig. 8).

The adsorption of hydrogen atoms affects now the conductivity, along the

line of the present theory, by decreasing the value p besides by varying N, as discussed below respectively in the case of s- and r-type adsorption.

(i) The s-type adsorption increases the number of valence electrons N by dissociation of hydrogen atom into proton dissolved in the metal and electron in the conduction band of the metal; *e.g.*, the number N of conduction electrons of a metallic film of 30 atomic layer is increased by 3.3% at full coverage of s-adatoms, hence the conductivity σ_0 of (9.1.b) approximately by the same relative magnitude*).

The probability p of specular reflection is, on the other hand, nearly unchanged, since the cross section of the proton shielded by metal electrons is $\sim 0.3\,\pi r_s^2$, as shown below, which is fairly small as compared with the cross section $\sim 0.9\,\pi r_s^2$ of the surface atom, corresponding to $p_0 \approx 0.1$ as estimated above.

The cross section of scattering of s-adatom is derived as follows. The matrix element $V_{\alpha i}$ of the transition

$$\Psi(\mathbf{k}_1, \mathbf{k}_2, \cdots, \mathbf{k}_i, \cdots, \mathbf{k}_{N+1}) \to \Psi(\mathbf{k}_1, \mathbf{k}_2, \cdots, \underset{(i)}{\mathbf{k}_\alpha}, \cdots, \mathbf{k}_{N+1})$$

is given by (1.8) and (A.6), as**)

$$V_{\alpha i} = -\frac{4\pi e^2}{V}\left\{\frac{1}{|\mathbf{k}_\alpha - \mathbf{k}_i|^2 + \lambda^2} + \frac{(1+\bar{\eta})\lambda^2}{(|\mathbf{k}_\alpha - \mathbf{k}_i|^2 + \lambda^2)^2}\right\}, \tag{9.4}$$

where $\bar{\eta}$ allows for the exchange effect between electrons.

The transition is however subject to the conservation of energy

$$E(\mathbf{k}_\alpha) - E(\mathbf{k}_i) \leq kT, \tag{9.5}$$

so that $\mathbf{k}_i$ must be at the FERMI surface or just below it, while $\mathbf{k}_\alpha$ just above the FERMI surface, *i.e.*,

$$|\mathbf{k}_\alpha| \approx k_F \approx |\mathbf{k}_i|. \tag{9.5.a}$$

Hence,

$$q(\theta)^2 \equiv |\mathbf{k}_\alpha - \mathbf{k}_i|^2 = 4k_F^2 \sin^2\frac{\theta}{2}. \tag{9.6}$$

By substituting $|\mathbf{k}_\alpha - \mathbf{k}_i|^2$ from (9.6) into (9.4), we have

*) The mean free path $\bar{l}$, the mean velocity $\bar{v}$ or the effective mass m^*, identified with m in (9.1.b), depends in general on N, but we neglect these effects in the present discussions.

**) If we replace $2/\lambda$ in (9.2) by a_H and put $\bar{\eta}=0$, the $V_{\alpha i}$ is reduced to the matrix element of scattering of a free electron from the state $1/\sqrt{V}\cdot\exp(i\mathbf{k}_i\mathbf{r})$ into $1/\sqrt{V}\cdot\exp(i\mathbf{k}_\alpha\mathbf{r}$ by a hydrogen atom.

$$V_{\alpha i} = -\frac{4\pi e^2}{V}\left\{\frac{1}{q(\theta)^2+\lambda^2}+\frac{(1+\bar{\eta})\lambda^2}{(q(\theta)^2+\lambda^2)^2}\right\},$$

$$= -N^{-1}\frac{e^2}{r_s}\left\{\frac{3}{(q(\theta)r_s)^2+(\lambda r_s)^2}+\frac{3(1+\bar{\eta})(\lambda r_s)^2}{\{(q(\theta)r_s)^2+(\lambda r_s)^2\}^2}\right\} \qquad (9.7)$$

inasmuch as

$$V = N(4\pi/3)\,r_s^3\,. \qquad (9.7.\text{a})$$

The order of magnitude of $N|V_{\alpha i}|$ is 4.2 eV for $\theta=0$, and 1.8 eV for $\theta=\pi$ on the base of $r_s=1.4$ Å, $\lambda=1/0.3$ Å and $\bar{\eta}=0.2\,\lambda r_s$.

The transition probability w is given as[23]

$$w = \frac{2\pi}{\hbar}|V_{\alpha i}|^2\rho(\mathbf{k}_\alpha)\,, \qquad (9.8)$$

where $\rho(\mathbf{k}_\alpha)$ is the density of final states and is given as[23]

$$\rho(\mathbf{k}_\alpha) = \rho(k_F) = \frac{mV}{8\pi^3\hbar^2}k_F\,. \qquad (9.8.\text{a})$$

Let now $\sigma_d(\theta,\varphi)$ be the differential scattering cross section for $\mathbf{k}_\alpha$ of the direction within $\theta\sim\theta+d\theta$ and $\varphi\sim\varphi+d\varphi$*). We have now**)

$$\sigma_d(\theta,\varphi) = \frac{mV}{\hbar k_F}w\,, \qquad (9.9)$$

or

$$\sigma_d(\theta,\varphi) = \left(\frac{mV}{2\pi\hbar^2}\right)^2|V_{\alpha i}|^2\,, \qquad (9.10)$$

by (9.7), (9.8) and (9.9).

The total cross section $\sigma_T^{(s)}$ of *s*-adatom relevant to the electric resistance is now the integral of $(1-\cos\theta)\sigma_d(\theta,\varphi)\sin\theta d\theta d\varphi$, where the factor $(1-\cos\theta)$ stands for the condition of steady current in accordance with the BLOCH's equation[24]. The total cross section $\sigma_T^{(s)}$ depends now on the direction of $\mathbf{k}_i$. Let Θ be the angle between $\mathbf{k}_i$ and the normal to the metal surface. We have

*) The φ is taken as the angle between the plane $(\mathbf{k}_i,\mathbf{k}_\alpha)$ comprizing $\mathbf{k}_i$ and $\mathbf{k}_\alpha$, and the metal surface, except in the case of $\mathbf{k}_i$ normal to the surface, where φ specifies the direction of $(\mathbf{k}_i,\mathbf{k}_\alpha)$ around $\mathbf{k}_i$.

**) We have $w=\sigma_d v(\mathbf{k}_i)/V$ by definition, where $v(\mathbf{k}_i)\equiv\frac{\hbar|\mathbf{k}_i|}{m}=\frac{\hbar k_F}{m}$ is the velocity of $\mathbf{k}_i$-electron, hence (9.9).

$$\sigma_T^{(s)}\left(\Theta=\frac{\pi}{2}\right)=\int_0^{\pi}\left\{\int_0^{\pi}(1-\cos\theta)\sigma_a(\theta,\varphi)\sin\theta\,d\theta\right\}d\varphi$$
$$=\left(\frac{mV}{2\pi\hbar^2}\right)^2\int_0^{\pi}\left\{\int_0^{\pi}(1-\cos\theta)|V_{ai}|^2\sin\theta d\theta\right\}d\varphi \qquad (9.\ 11.\ a)$$

and

$$\sigma_T^{(s)}(\Theta=0)=\int_0^{2\pi}\left\{\int_{\frac{\pi}{2}}^{\pi}(1-\cos\theta)\sigma_a(\theta,\varphi)\sin\theta d\theta\right\}d\varphi$$
$$=\left(\frac{mV}{2\pi\hbar^2}\right)^2\int_0^{2\pi}\left\{\int_{\frac{\pi}{2}}^{\pi}(1-\cos\theta)|V_{ai}|^2\sin\theta\,d\theta\right\}d\varphi \qquad (9.\ 11.\ b)$$

Assuming that

$$\sigma_T^{(s)}(\Theta)=\sigma_T\left(\Theta=\frac{\pi}{2}\right)+\cos^2\Theta\left\{\sigma_T(\Theta=0)-\sigma_T\left(\Theta=\frac{\pi}{2}\right)\right\}, \qquad (9.\ 12)$$

we have the average cross section $\langle\sigma_T^{(s)}\rangle_{\mathrm{Av}}$ as

$$\langle\sigma_T^{(s)}\rangle_{\mathrm{Av}}=\sigma_T\left(\Theta=\frac{\pi}{2}\right)+\frac{1}{3}\left\{\sigma_T(\Theta=0)-\sigma_T\left(\Theta=\frac{\pi}{2}\right)\right\}. \qquad (9.\ 13.\ a)$$

or by (9.11.a), (9.11.b)

$$\langle\sigma_T^{(s)}\rangle_{\mathrm{Av}}=2\pi\left(\frac{mV}{2\pi\hbar^2}\right)^2|\bar{V}_{ai}^{(s)}|^2, \qquad (9.\ 13.\ b)$$

where

$$|\bar{V}_{ai}^{(s)}|^2=\frac{1}{2\pi}\left\{\frac{2}{3}\int_0^{\pi}\int_0^{\pi}(1-\cos\theta)|V_{ai}|^2\sin\theta d\theta d\varphi\right.$$
$$\left.+\frac{1}{3}\int_0^{2\pi}\int_{\frac{\pi}{2}}^{\pi}(1-\cos\theta)|V_{ai}|^2\sin\theta d\theta d\varphi\right\}. \qquad (9.\ 14)$$

is the average of $|V_{ai}|^2$. The $|\bar{V}_{ai}^{(s)}|$ is estimated by (9.5), (9.6) and (9.14) at

$$|\bar{V}_{ai}^{(s)}|=N^{-1}\times(2.3\ \mathrm{eV}) \qquad (9.\ 14.\ a)$$

hence $\langle\sigma_T^{(s)}\rangle_{\mathrm{Av}}$ at $\sim 0.3\,\pi r_s^2$ by (9.13.b) and (9.6.a) on the base of $r_s=1.40$ Å, $\lambda=1/0.3$ Å and $\bar{\eta}=0.2\,\lambda r_s$

(ii) In the case of r-type adsorption, the number N of free electrons is practically unaffected; the decrease of N of a metallic film of 30 atomic layer at full coverage is only $(e^*/30)\times 100$ per cent, where the effective charge e^* is of the order of $-0.02\sim-0.04$ as worked out in §§ 4 and 6. The value of p is however markedly decreased by r-type adsorption due to the large value, as shown below, of the matrix element of transition of a free electron into the 1s-state of adatoms or reciprocally of 1s-electron into metal. We consider here such transition of

metal electron from one state to another say from $\mathbf{k}_i$- to $\mathbf{k}_\alpha$-state alone, as an electron in $\mathbf{k}_i$-state is trapped in 1*s*-state, while another electron transits from 1*s*- to $\mathbf{k}_\alpha$-state, ignoring other transition process, *e.g.* a direct one caused by a perturlation field of *r*-adatom not through the intermediary of 1*s*-state. The cross section of *r*-adatom corresponding to the transition specified above must be smaller than the actual one, if other transition processes were not negligible.

The transition $\mathbf{k}_i \to \mathbf{k}_\alpha$ specified above should occur in accordance with the conservation of spin orientation in the following scheme:

(a) In case the spin orientation of $\mathbf{k}_i$- and 1*s*-electrons are anti-parallel, the transition should be*)

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N) \longrightarrow \Psi(1s\uparrow, \mathbf{k}_1, \cdots, 1s\downarrow, \cdots, \mathbf{k}_N)$$

$$\begin{cases} \longrightarrow \Psi(1s\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{\mathbf{k}_\alpha}\downarrow, \cdots, \mathbf{k}_N), & \text{(a. I)} \\ \longrightarrow \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \underset{(i)}{1s}\downarrow, \cdots, \mathbf{k}_N), & \text{(a. II)} \end{cases}$$

or

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N) \longrightarrow \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\downarrow, \cdots, \mathbf{k}_N)$$

$$\longrightarrow \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, 1s\downarrow, \cdots, \mathbf{k}_N) \qquad \text{(a. III)}$$

(b) In case the spin orientation of $\mathbf{k}_i$- and 1*s*-electrons are parallel, the transition should occur as

$$\Psi(1s\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\uparrow, \cdots, \mathbf{k}_N) \longrightarrow \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, \mathbf{k}_i\uparrow, \cdots, \mathbf{k}_N)$$

$$\longrightarrow \Psi(\mathbf{k}_\alpha\uparrow, \mathbf{k}_1, \cdots, 1s\uparrow, \cdots, \mathbf{k}_N) \qquad \text{(b. I)}$$

The ratio of the statistical weight of the case (a) to that of the case (b) is 1 : 3, hence the average $V_{\alpha i}^{(r)}$ of the matrix elements of transition is[23],

$$|V_{\alpha i}^{(r)}|^2 \equiv \frac{1}{4}\left\{\left|\frac{V_{is}V_{s\alpha}}{E_{-,i\to s}-E_0}+\frac{V_{is}V_{s\alpha}}{E_{-,i\to s}-E_0}+\frac{V_{s\alpha}V_{is}}{E_{+,s\to\alpha}-E_0}\right|^2\right\}+\frac{3}{4}\left\{\left|\frac{V_{s\alpha}V_{is}}{V_{+,s\to\alpha}-E_0}\right|^2\right\}$$

$$= \frac{|V_{is}|^2|V_{s\alpha}|^2}{(E_{-,i\to s}-E_0)^2}+\frac{|V_{is}|^2|V_{s\alpha}|^2}{(E_{-,i\to s}-E_0)(E_{+,s\to\alpha}-E_0)}+\frac{|V_{is}|^2|V_{s\alpha}|^2}{(E_{+,s\to\alpha}-E_0)^2}, \qquad (9.15)$$

where the terms in the first bracket of the second member correspond in turn to the transitions of (a. I), (a. II) and (a. III) respectively, and the term in the second bracket to (b. I); $E_{-,i\to s}$, $E_{+,s\to\alpha}$, and E_0 are defined respectively in connection with (4.2.a), (4.2.b) and (4.2.c), while V_{is} and $V_{s\alpha}$ similarly by (4.3.a) and (4.3.b).

Taking the condition of (9.5) or (9.6) into account, we have

*) The (a. I), (a. II), (a. III) and (b. I) correspond to (5.1.a.IV), (5.1.a.III), (5.1.a.II) and (5.1.a.I) respectively.

$$E_{-,i\to s}=E_{-,k_F\to 1s}=\phi-A+2E_0\,,$$

and

$$E_{+,s\to a}=E_{+,1s\to k_F}=I-\phi\,.$$

Hence, the average $|\overline{V}_{ai}^{(r)}|^2$ of $|V_{ai}^{(r)}|^2$ given by (9.15) over the direction of both $\mathbf{k}_i$ and $\mathbf{k}_a$ is estimated according to the approximations of Appendix A in (I), as

$$|\overline{V}_{ai}^{(r)}|=N^{-1}\{8.4\text{ eV}\}\,, \tag{9.16}$$

since $|\overline{V}_{is}|=|\overline{V}_{sa}|=|\overline{V}_{s,k_F}|$ ($=6.3$ eV for $D=2.4\,a_H$) by the condition (9.5.a). The cross section of scattering is similarly derived as in (i), by replacing $|\overline{V}_{ai}^{(s)}|^2$ of (9.13.b) by $|\overline{V}_{ai}^{(r)}|^2$. The result is in accordance with (9.14.a) and (9.16)

$$\langle\sigma_T^{(r)}\rangle_{Av}=2\pi\left(\frac{mV}{2\pi\hbar^2}\right)^2|\overline{V}_{ai}^{(r)}|^2=4.0\,\pi r_s^2 \tag{9.17}$$

which is essentially the lower bound according to the above.

It is concluded that the large cross section of r-adatoms causes p to vanish at $\theta\approx 1/4\sim 1/2$, and besides, it is responsible for the intense repulsion, as remarked in (I), between r-adatoms through the intermediary of metal electrons.

The decrease of p has now a pronounced effect on the resistance as illustrated in Fig. 6 that the resistance increases by *ca.* 3% with decrease of p from 0.04 to 0 for $d/\bar{l}=1/2$.

We are now ready to discuss the effect of adsorption on electric resistance. The electric resistance should increase initially rapidly due to the decrease of the probability p of specular reflection by r-type adsorption which predominates initially as mentioned in the preceding section. The increase will come to an end at $\theta=1/4\sim 1/2$, when p is reduced to zero, the total increase $\Delta R_{\max}$ of resistance depending thus on the initial value p_0 of p. Fig. 8 shows $\Delta R_{\max}/R_0$ as plotted against $d/\bar{l}$ by (9.4), which practically reproduces the experimental results by MIZUSHIMA[6] for $p_0=0.04$.

The present theory leads to a further theorem that $\Delta R_{\max}\cdot d^2$ is independent of temperature as well as of thickness for films with the same p_0 values. We have from (9.2)

$$c\Delta R_{\max}(d)\cdot d^2=\left\{(d/\bar{l})^2\Phi_{p=0}(d/\bar{l})-(d/\bar{l})^2\Phi_{p_0}(d/\bar{l})\right\}\,, \tag{9.18}$$

Table 1 shows the theoretical value of the right side of (9.18), which is approximately constant independent of $d/\bar{l}$, hence that $\Delta R_{\max}(d)\cdot d^2$ is similarly constant independent of T and d. The observations by MIZUSHIMA[6]*) shows that this is actually the case: $\Delta R_{\max}(d)\cdot d^2$ is constantly $\sim 9000\,\Omega\,\text{Å}^2$ according to his

*) MIZUSHIMA has pointed that $\Delta R_{\max}$ is independent on temperature (Cf. Ref. (7)).

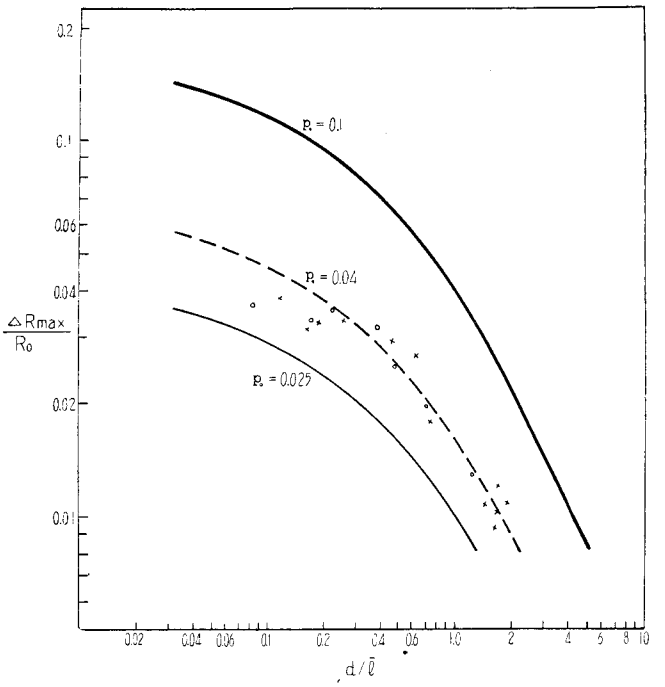

Fig. 8. Theoretical curves of $\log\{\Delta R_{\max}/R_0\}$ *versus* $\log(d/\bar{l})$ for $p_0=0.1$, 0.04 and 0.025. The crosses are observed values[6] at 273°K represented with $\bar{l}=150$Å, and circles are those at 90°K with $\bar{l}=270$ Å.

observation both at 273°K and 90°K, for d-values from 30 Å to 400 Å. From the latter values of $\Delta R_{\max}(d)\cdot d^2$ imcoporated with $c=3.6\times10^{-6}/\Omega$Å^2 of (9.3), we have $c\Delta R_{\max}(d)\cdot d^2\approx0.03$, which determines p_0 at *ca.* 0.05 according to (9.18) and Table I ($d/\bar{l}=1/10\sim5$).

TABLE 1. The values of $\{(d/\bar{l})^2/\Phi_{p=0}(d/\bar{l})-(d/\bar{l})^2/\Phi_{p_0}(d/\bar{l})\}$

p_0 \ $d/\bar{l}$	1/30	1/25	1/15	1/10	1/5	1/2	1	2	5
0.1	0.044	0.044	0.048	0.049	0.054	0.058	0.056	0.052	0.042
0.2	0.082	0.082	0.090	0.095	0.104	0.111	0.110	0.100	0.083
0.3	0.116	0.118	0.129	0.146	0.150	0.164	0.161	0.142	0.127

If the s-type adsorption does not occur, the resistance will remain constant with further increase of coverage. If, on the other hand, the s-type adsorption

should occur, the resistance will decrease with increase of θ giving a resistance maximum around $\theta=1/4\sim1/2$. It has been concluded that*) *s*-type adsorption does occur in the case of Ni. It follows that the resistance maximum should exist in the above range of θ as actually confirmed by experiments by SUHRMAN, WEDLER, MIZUSHIMA, HERMANN and SCHLIEPHAKE[5], SACHTLER and DORGELO[7], and ZWIETERING, KOKS and HEERDEN[8]. Similar maximum has been observed by ZWIETERING, KOKS and HEERDEN[8] with Fe.

For Pt film, however, the resistance should decrease monotonously due to the predominance of the *s*-type adsorption except just at the initial stage of coverageas concluded from the observed decrease of work function**). SUHRMAN, WELDER and GENTSH[4] have actually observed monotonous decrease of resistance for Pt evaporated film.

When the surface is contaminated by, say O^{--}, the initial increase due to the *r*-type adsorption will disappear, while the later decrease will persist, provided that O^{--} adsorption decreases p as an adsorptive of large cross section preferentially excluding the *r*-type adsorption on account of its large ion radius. This conclusion is in conformity with the observations of SACHTLER and DORGELS[7].

Conclusion and Acknowledgment

There exist in general two types of adsorption of hydrogen atoms, *i.e.*, *r*-type adsorption and *s*-type one. The *r*-type adsorption is rather an usually conceived adsorption *i.e.*, the state of the adatom situated outside the surface of metal and bonded to it. The *s*-type adsorption is a sort of dissolution into metal, *i.e.*, the state of adatom situated inside the surface and confined to at *ca.* 0.5 Å distance from the surface.

The variation of physical properties, such as work function and electrical conductivity, caused by adsorption was discussed on the basis of the above theory with conclusions in conformity with experiments.

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*) Cf. §§7 and 8.
**) Cf. §8.

Appendix A. Derivation of Eq. (1.9).

The electron density $\rho_0(\mathbf{r})$ of N electrons of the metal without any perturbation is expressed as

$$\rho_0(\mathbf{r}) = \sum_{i=1}^{N} \phi^*(\mathbf{k}_i, \mathbf{r})\phi(\mathbf{k}_i, \mathbf{r}) , \qquad \text{(A. 1. a)}$$

and the electron density $\underline{\rho}(\mathbf{r})$ of $N+1$ electrons of the metal with proton dissolved, as

$$\underline{\rho}(\mathbf{r}) = \sum_{i=1}^{N+1} \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})\, \underline{\psi}\,(\mathbf{k}_i, \mathbf{r}). \qquad \text{(A. 1. b)}$$

The perturbed wave function $\underline{\psi}(\mathbf{k}_i, \mathbf{r})$ is generally developed in terms of the unperturbed wave functions $\phi(\mathbf{k}_i\,, \mathbf{r})$'s as

$$\underline{\psi}(\mathbf{k}_i, \mathbf{r}) = \Big\{1-(1/2)\sum_{\alpha(\neq i)} |b_{\alpha i}|^2\Big\}\phi(\mathbf{k}_i, \mathbf{r}) + \sum_{\alpha(\neq i)} b_{\alpha i}\phi(\mathbf{k}_\alpha, \mathbf{r}) + \sum_{\gamma(\neq i)} c_{\gamma i}\phi(\mathbf{k}_\gamma, \mathbf{r}) , \qquad \text{(A. 2)}$$

where $b_{\alpha i}$'s are the first order and $c_{i\gamma}$'s are the second order coefficients. The factor $\{1-(1/2)\sum_{\alpha(\neq i)} |b_{\alpha i}|^2\}$ of the first term in the second member of (A. 2) assures the normalization conditions

$$\int \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})\underline{\psi}(\mathbf{k}_i, \mathbf{r})d\mathbf{r} = 1 . \qquad \text{(A. 2. a)}$$

The coefficients $b_{\alpha i}$'s and $c_{\gamma i}$'s must be determined, so that the orthogonal relations,

$$\int \underline{\psi}^*(\mathbf{k}_i, \mathbf{r})\underline{\psi}(\mathbf{k}_{i'}, \mathbf{r})d\mathbf{r} = 0 , \qquad \text{for} \quad i \neq i' , \qquad \text{(A. 2. b)}$$

is satisfied; substituting $\underline{\psi}$ from (A. 2), (A. 2. b) leads to the condition

$$b^*_{\alpha i} + b_{i\alpha} = 0 \qquad \text{for} \quad i \neq \alpha , \qquad \text{(A. 3. a)}$$

and

$$c^*_{i'i} + c_{ii'} + \sum b^*_{\alpha i} b_{\alpha i'} = 0 \qquad \text{for} \quad i \neq i' . \qquad \text{(A. 3. b)}$$

The extra electron density around the dissolved proton is given from (A. 1. a) and (A. 1. b), as

$$\underline{\rho}(\mathbf{r}) - \rho_0(\mathbf{r}) \equiv \rho(\mathbf{r}) + \rho'(\mathbf{r}) , \qquad \text{(A. 4)}$$

where $\rho(\mathbf{r})$ is the sum of the first order terms and $\rho'(\mathbf{r})$ that of the second order terms with respect to $b_{\alpha i}, b^*_{\alpha i}$ *etc.* expressed respectively as

$$\rho(\mathbf{r}) = \phi^*(\mathbf{k}_{N+1}, \mathbf{r})\phi(\mathbf{k}_{N+1}, \mathbf{r}) + \sum_i \sum_{\alpha(\neq i)} \Big\{b^*_{\alpha i}\phi^*(\mathbf{k}_\alpha, \mathbf{r})\phi(\mathbf{k}_i, \mathbf{r}) + b_{\alpha i}\phi(\mathbf{k}_\alpha, \mathbf{r})\phi^*(\mathbf{k}_i, \mathbf{r})\Big\} , \qquad \text{(A. 4. a)}$$

and

$$\rho'(\mathbf{r}) = \sum_i \sum_{\alpha(\neq i)} |b_{\alpha i}|^2 \left\{\psi^*(\mathbf{k}_\alpha, \mathbf{r})\psi(\mathbf{k}_\alpha, \mathbf{r}) - \psi^*(\mathbf{k}_i, \mathbf{r})\psi(\mathbf{k}_i, \mathbf{r})\right\}$$
$$+ \sum_i \sum_{\alpha(\neq i)} \sum_{\beta(\neq \alpha, \neq i)} b^*_{\alpha i} b_{\beta i} \psi^*(\mathbf{k}_\alpha, \mathbf{r})\psi(\mathbf{k}_\beta, \mathbf{r})$$
$$+ \sum_i \sum_{\gamma(\neq i)} \left\{c^*_{\gamma i}\psi^*(\mathbf{k}_\gamma, \mathbf{r})\psi(\mathbf{k}_i, \mathbf{r}) + c_{\gamma i}\psi(\mathbf{k}_\gamma, \mathbf{r})\psi^*(\mathbf{k}_i, \mathbf{r})\right\}. \quad \text{(A. 4. b)}$$

The first term on the second member of (A. 4. b) vanishes approximately, since $\psi^*(\mathbf{k}_\alpha, \mathbf{r})\psi(\mathbf{k}_\alpha, \mathbf{r}) \approx \psi^*(\mathbf{k}_i, \mathbf{r})\psi(\mathbf{k}_i, \mathbf{r}) \approx 1/V$, and the contribution to the second order energy from the second and third terms vanishes as shown in Appendix B. Hence, we will be confined in the evaluation of $\rho(\mathbf{r})$ in this appendix.

The $\rho(\mathbf{r})$ is written by substituting $b_{\alpha i}$ from (1. 7), as

$$\rho(\mathbf{r}) = \psi^*(\mathbf{k}_{N+1}, \mathbf{r})\psi(\mathbf{k}_{N+1}, \mathbf{r})$$
$$- \sum_i \sum_{\alpha(\neq i)} \left\{\frac{V^*_{\alpha i}}{E(\mathbf{k}_\alpha) - E(\mathbf{k}_i)}\psi^*(\mathbf{k}_\alpha, \mathbf{r})\psi(\mathbf{k}_i, \mathbf{r}) + \frac{V_{\alpha i}}{E(\mathbf{k}_\alpha) - E(\mathbf{k}_i)}\psi(\mathbf{k}_\alpha, \mathbf{r})\psi^*(\mathbf{k}_i, \mathbf{r})\right\} \quad \text{(A. 5)}$$

The summation $\sum_i$ extends over the occupied levels inside the FERMI sphere and $\sum_\alpha$ over the unoccupied ones outside it. However, $\sum_\alpha$ may be replaced by the summation over all levels, occupied or unoccupied, except for $\alpha = i$, inasmuch as $\sum_i \sum_{\substack{\alpha(\text{over occupied} \\ \text{levels except } \alpha = i)}} \{\cdots\cdots\} = 0$, on account of the antisymmetry of terms of the sum with respect to the permutation of α and i.

We have from (1. 8)

$$V_{\alpha i} = V^*_{\alpha i} = -\frac{4\pi e^2}{V}\left\{\frac{1}{|\mathbf{k}_\alpha - \mathbf{k}_i|^2 + \lambda^2} + \frac{(1+\bar{\eta})\lambda^2}{(|\mathbf{k}_\alpha - \mathbf{k}_i|^2 + \lambda^2)^2}\right\}, \quad \text{(A. 6)}$$

substituting an approximate wave function,

$$\psi(\mathbf{k}_i, \mathbf{r}) = \frac{1}{\sqrt{V}} U_0(\mathbf{r}) \exp(i\mathbf{k}_i\mathbf{r}), \quad |U_0(\mathbf{r})|^2 \approx 1, \quad \text{(A. 7)}$$

where $U_0(\mathbf{r})$ is a function with the period of the lattice.

The energy of $\mathbf{k}_i$-level is given approximately as

$$E(\mathbf{k}_i) = \epsilon_0 + (\hbar^2/2m)k_i^2, \quad k_i = |\mathbf{k}_i| \quad \text{(A. 8)}$$

where ϵ_0 is the lowest energy of the conduction band.

Now, putting $\mathbf{k}_\alpha = \mathbf{k}_i + q$ and replacing $\sum_i \sum_{(\alpha)}$, where (α) covers unoccupied levels as well as occupied levels by $\sum_{q(\neq 0)} \sum_i$ and the summation $\sum_i \{\cdots\}$ by the

integration*) $2V/(2\pi)^3\int\{\cdots\}d\mathbf{k}$, we have, from (A.5), (A.6), (A.7) and (A.8),

$$\rho(\mathbf{r})=\psi^*(\mathbf{k}_{N+1},\mathbf{r})\psi(\mathbf{k}_{N+1},\mathbf{r})+\frac{4\pi e^2}{V^2}\cdot\frac{2V}{(2\pi)^3}\cdot \times\sum_{q(\neq 0)}\int\left[\left\{\frac{|U_0(\mathbf{r})|^2(\exp(i\mathbf{qr})+\exp(-i\mathbf{qr}))}{(\hbar^2/2m)(q^2+2qk_i\cos\mathbf{qk}_i)}\right\}\left\{\frac{1}{q^2+\lambda^2}+\frac{(1+\bar{\gamma}_i)\lambda^2}{(q^2+\lambda^2)^2}\right\}\right]d\mathbf{k}_i\,,$$

or

$$\rho(\mathbf{r})=\psi^*(\mathbf{k}_{N+1},\mathbf{r})\psi(\mathbf{k}_{N+1},\mathbf{r}) +\frac{2k_F}{V\pi a_H}\sum_{q(\neq 0)}|U_0|^2\left\{\exp(i\mathbf{qr})+\exp(-i\mathbf{qr})\right\}\left\{\frac{1}{q^2+\lambda^2}+\frac{(1+\bar{\gamma}_i)\lambda^2}{(q^2+\lambda^2)^2}\right\}f(q/2k_F), \tag{A.9}$$

with

$$f(x)=\frac{1}{2}+\frac{1-x^2}{4x}\log\frac{1+x}{1-x}\,,$$

where $q=|\mathbf{q}|$, $k_F=(3\pi^2N/V)^{1/3}$ is the wave number of an electron at the FERMI surface and $a_H=\hbar^2/me^2$ the BOHR radius. The function $f(q/2k_F)$ is 1 for $q=0$, 1/2 for $q=2k_F$, decreases monotonously like $(1/3)(2k_F/q)^2$ for $q\gg 2k_F$, and is replaced by $\lambda^2/q^2+\lambda^2$ for $\lambda\approx 2k_F$ with good approximation except for $q\gg 2k_F$.

Eq. (A.9) is written, inasmuch as $\psi^*(\mathbf{k}_{N+1},\mathbf{r})\psi(\mathbf{k}_{N+1},\mathbf{r})=|U_0|^2/V$ according to (A.7), as

$$\rho(\mathbf{r})=\frac{|U_0|^2}{V}\left[1-\frac{2k_F}{\pi a_H}\cdot 2\left\{\frac{1}{\lambda^2}+\frac{1+\bar{\gamma}_i}{\lambda^2}\right\}\right] +\frac{2k_F}{V\pi a_H}\sum_q\left[|U_0|^2\left\{\exp(i\mathbf{qr})+\exp(-i\mathbf{qr})\right\}\left\{\frac{1}{q^2+\lambda^2}+\frac{(1+\bar{\gamma}_i)\lambda^2}{(q^2+\lambda^2)^2}\right\}f(q/2k_F)\right], \tag{A.10}$$

where the summation of second term includes, now, the term $q=0$. Replacing $\sum_q[\cdots]$ by the integration

$$\frac{V}{(2\pi)^3}\int[\cdots]d\mathbf{q}\equiv\frac{V}{(2\pi)^3}\int_0^\infty\left\{\int_{\cos\vartheta=-1}^{\cos\theta=1}\left(\int_0^{2\pi}[\cdots]d\varphi\right)d(\cos\theta)\right\}q^2dq\,,$$

and putting $\cos\theta=u$ and $|U_0|^2=1$ according to (A.7), the second term of (A.10), is now

$$\frac{2}{\pi}\frac{k_F}{a_H}\frac{2\pi}{(2\pi)^3}\int_0^\infty\left[\left\{\int_{-1}^{1}(\exp(iqru)+\exp(-iqru))du\right\}\times \left\{\frac{1}{q^2+\lambda^2}+\frac{(1+\bar{\gamma}_i)\lambda^2}{(q^2+\lambda^2)^2}\right\}f(q/2k_F)\right]q^2dq\,,$$

*) The factor 2 is due to the spin weight.

$$= \frac{2k_F}{\pi^3 a_H}\frac{1}{r}\int_0^\infty \left(\frac{q}{q^2+\lambda^2}+\frac{(1+\bar{\eta})q\lambda^2}{(q^2+\lambda^2)^2}\right)\sin qr\cdot f(q/2k_F)\,dq\ .$$

Approximating $f(q/2k_F)$ by $\lambda^2/q^2+\lambda^2$, the above expression is given as*)

$$\frac{k_F\lambda}{2\pi^2 a_H}\left\{1+\frac{1+\bar{\eta}}{4}(1+\lambda r)\right\}\cdot\exp(-\lambda r)\,.$$

Replacing r in the bracket { } by its mean value

$$3/\lambda=\int_0^\infty r\exp(-\lambda r)r^2dr\Big/\int_0^\infty \exp(-\lambda r)r^2dr,$$

we have $\rho(\mathbf{r})$ of (1.9), *i.e.*,

$$\rho(\mathbf{r})=\frac{1}{V}\left[1-\frac{2k_F}{\pi a_H}\cdot 2\left\{\frac{1}{\lambda^2}+\frac{1+\bar{\eta}}{\lambda^2}\right\}\right]+\frac{k_F\lambda}{\pi^2 a_H}\left\{1+\frac{\bar{\eta}}{2}\right\}\exp(-\lambda r)\,. \quad \text{(A. 11)}$$

Appendix B. Derivation of Eq. (1.11.a).

The heat of disolution Q, as given by (1.11), is derived in what follows in four steps (i), (ii), (iii) and (iv).

(i): The kinetic energy of N metal electrons without perturbation is expressed as

$$(\Psi T\Psi)\equiv\int\Psi^*\left\{\sum_{j=1}^{N}(-\hbar^2/2m\cdot\Delta_j)\right\}\Psi\prod_{j=1}^{N}d\mathbf{r}_j\,, \qquad \text{(B. 1)}$$

where Ψ is given by (2.2.b), or

$$\Psi\equiv(N!)^{-\frac{1}{2}}\sum_P\varepsilon(P)P\left\{\psi(\mathbf{k}_1,\mathbf{r}_1)\psi(\mathbf{k}_2,\mathbf{r}_2)\cdots\psi(\mathbf{k}_N,\mathbf{r}_N)\right\}, \qquad \text{(B. 1. a)}$$

by the definition of determinant. In the above expression, P is the permutations of the N electron coordinates, $\varepsilon(P)=1$ for even permutations and $\varepsilon(P)=-1$ for odd ones, and $\sum_P$ extends over all $N!$ permutations. We have, substituting Ψ from (B.1.a) into (B.1),

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*) The integrals involved are given as

$$\int_0^\infty\frac{q\sin qr}{(q^2+\lambda^2)^2}dq=\frac{r^2}{2}\int_0^\infty\frac{\cos(qr)}{(qr)^2+(\lambda r)^2}d(qr)=\frac{r\pi}{4\lambda}e^{-\lambda r}\,,$$

and

$$\int_0^\infty\frac{q\sin qr}{(q^2+\lambda^2)^3}dq=\frac{r}{4}\int_0^\infty\frac{\cos(qr)}{(q^2+\lambda^2)^2}dq=\frac{1+\lambda r}{4\lambda^2}\cdot\frac{r\pi}{4\lambda}e^{-\lambda r}\,.$$

(Cf. WHITTAKER & WATSON, *Modern Analysis* (Cambridge), 1935, p. 116, Examples 1, 3 and 5).

$$(\Psi T\Psi) = (N!)^{-1}\int \sum_P \varepsilon(P) P\{\phi^*(\mathbf{k}_1,\mathbf{r}_1)\phi^*(\mathbf{k}_2,\mathbf{r}_2)\cdots\phi^*(\mathbf{k}_N,\mathbf{r}_N)\}$$
$$\times\left\{\sum_{j=1}^{N}(-\hbar^2/2m\cdot\Delta_j)\right\}\sum_P \varepsilon(P)P\{\phi(\mathbf{k}_1,\mathbf{r}_1)\phi(\mathbf{k}_2,\mathbf{r}_2)\cdots\phi(\mathbf{k}_N,\mathbf{r}_N)\}\prod_{j=1}^{N} d\mathbf{r}_j$$
$$= \int \sum_P \varepsilon(P) P\{\phi^*(\mathbf{k}_1,\mathbf{r}_1)\phi^*(\mathbf{k}_2,\mathbf{r}_2)\cdots\phi^*(\mathbf{k}_N,\mathbf{r}_N)\}$$
$$\times\left\{\sum_{j=1}^{N}(-\hbar^2/2m\cdot\Delta_j)\right\}\phi(\mathbf{k}_1,\mathbf{r}_1)\phi(\mathbf{k}_2,\mathbf{r}_2)\cdots\phi(\mathbf{k}_N,\mathbf{r}_N)\prod_{j=1}^{N} d\mathbf{r}_j \quad \text{(B. 2)}$$

or, using the normalization conditions and orthogonal relations,

$$\left.\begin{aligned}\int\phi^*(\mathbf{k}_i,\mathbf{r})\phi(\mathbf{k}_{i'},\mathbf{r})\,d\mathbf{r} &= 1 \quad \text{for} \quad i=i',\\ &= 0 \quad \text{for} \quad i\neq i',\end{aligned}\right\} \quad \text{(B. 3)}$$

$$(\Psi T\Psi) = \sum_{i=1}^{N}\int\phi^*(\mathbf{k}_i,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\phi(\mathbf{k}_i,\mathbf{r})\,d\mathbf{r}\,. \quad \text{(B. 4)}$$

The kinetic energy of $N+1$ metal electrons perturbed by proton dissolved and extra electron density around it is expressed as

$$(\Phi_s\bar{T}\Phi_s) \equiv \int\Phi_s^*\left\{\sum_{j=1}^{N+1}(-\hbar^2/2m\cdot\Delta_j)\right\}\Phi_s\prod_{j=1}^{N+1} d\mathbf{r}_j\,, \quad \text{(B. 5)}$$

where Φ_s is given by (1.1.a), or

$$\Phi_s \equiv \left\{(N+1)!\right\}^{-\frac{1}{2}}\sum_P \varepsilon(P) P\{\underline{\phi}(\mathbf{k}_1,\mathbf{r}_1)\underline{\phi}(\mathbf{k}_2,\mathbf{r}_2)\cdots\underline{\phi}(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\}\,, \quad \text{(B.5.a)}$$

P is the permutations of the $N+1$ electron coordinates, and $\sum_P$ extends over $(N+1)!$ permutations.

We have from (B.5) and (B.5.a)

$$(\Phi_s\bar{T}\Phi_s) \equiv \left\{(N+1)!\right\}^{-1}\int\sum_P \varepsilon(P) P\{\underline{\phi}^*(\mathbf{k}_1,\mathbf{r}_1)\underline{\phi}^*(\mathbf{k}_2,\mathbf{r}_2)\cdots\underline{\phi}^*(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\}$$
$$\times\left\{\sum_{j=1}^{N+1}(-\hbar^2/2m\cdot\Delta_j)\right\}\sum_P \varepsilon(P) P\{\underline{\phi}(\mathbf{k}_1,\mathbf{r}_1)\underline{\phi}(\mathbf{k}_2,\mathbf{r}_2)\cdots\underline{\phi}(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\}\prod_{j=1}^{N+1} d\mathbf{r}_j$$
$$= \int\sum_P \varepsilon(P) P\{\underline{\phi}^*(\mathbf{k}_1,\mathbf{r}_1)\underline{\phi}^*(\mathbf{k}_2,\mathbf{r}_2)\cdots\underline{\phi}^*(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\}$$
$$\times\left\{\sum_{j=1}^{N+1}(-\hbar^2/2m\cdot\Delta_j)\right\}\underline{\phi}(\mathbf{k}_1,\mathbf{r}_1)\underline{\phi}(\mathbf{k}_2,\mathbf{r}_2)\cdots\underline{\phi}(\mathbf{k}_{N+1},\mathbf{r}_{N+1})\prod_{j=1}^{N+1} d\mathbf{r}_j$$

or, using the normalization conditions and orthogonal relations (A.2.a) and (A.2.b),

$$(\Phi_s\bar{T}\Phi_s) = \sum_{i=1}^{N+1}\int\underline{\phi}(\mathbf{k}_i,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\underline{\phi}(\mathbf{k}_i,\mathbf{r})\,d\mathbf{r}\,. \quad \text{(B. 6)}$$

We have from (A.2),

$$(-\hbar^2/2m\cdot\Delta)\underline{\psi}(\mathbf{k}_i,\mathbf{r})=\left\{1-1/2\sum_{\alpha(\neq i)}|b_{\alpha i}|^2\right\}\cdot(-\hbar^2/2m\cdot\Delta)\psi(\mathbf{k}_i,\mathbf{r})$$
$$+\sum_{\alpha(\neq i)}b_{\alpha i}(-\hbar^2/2m\cdot\Delta)\psi(\mathbf{k}_\alpha,\mathbf{r})+\sum_{\gamma(\neq i)}c_{\gamma i}(-\hbar^2/2m\cdot\Delta)\psi(\mathbf{k}_\gamma,\mathbf{r}),\qquad\text{(B. 7)}$$

so that the total increase (K.E.) of kinetic energy by the first and the second order perturbations is given by (B.4), (B.6), and (B.7), as

$$(\text{K.E.})\equiv(\Phi_s\overline{T}\,\Phi_s)-(\Psi T\Psi)$$
$$=\int\psi^*(\mathbf{k}_{N+1},\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_{N+1},\mathbf{r})d\mathbf{r}$$
$$+\sum_{i=1}^{N+1}\sum_{\alpha(\neq i)}\left[b_{\alpha i}^*\int\psi^*(\mathbf{k}_\alpha,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_i,\mathbf{r})d\mathbf{r}+\text{comp. conj.}\right]$$
$$+\sum_{i=1}^{N+1}\sum_{\alpha(\neq i)}|b_{\alpha i}|^2\Big[\int\psi^*(\mathbf{k}_\alpha,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_\alpha,\mathbf{r})d\mathbf{r}$$
$$-\int\psi^*(\mathbf{k}_i,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_i,\mathbf{r})\,d\mathbf{r}\Big]$$
$$+\sum_{i=1}^{N+1}\sum_{\alpha(\neq i)}\sum_{\beta(\neq\alpha)}b_{\alpha i}^*b_{\beta i}\int\psi^*(\mathbf{k}_\alpha,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_\beta,\mathbf{r})d\mathbf{r}$$
$$+\sum_{i=1}^{N+1}\sum_{\gamma(\neq i)}\left[c_{\gamma i}^*\int\psi^*(\mathbf{k}_\gamma,\mathbf{r})\{-\hbar^2/2m\cdot\Delta\}\,\psi(\mathbf{k}_i,\mathbf{r})d\mathbf{r}+\text{comp. conj.}\right].\qquad\text{(B. 8)}$$

(ii): The mean potential of the metal with $N+1$ electrons, perturbed by proton dissolved and extra electron density, is given as $(\Phi_s\overline{V}\Phi_s)$. The potential energy $\overline{V}$ of the system is according to (2.4.a),

$$\overline{V}\equiv\sum_{j=1}^{N+1}\sum_{l}v(\mathbf{r}_j-\mathbf{R}_l)+(1/2)\sum_{j=1}^{N+1}\sum_{j'(\neq j)=1}^{N+1}e^2/|\mathbf{r}_j-\mathbf{r}_{j'}|+\sum_{j=1}^{N+1}V_i(\mathbf{r}_j)$$
$$+(1/2)\sum_{l}\sum_{l'(\neq l)}e^2/|\mathbf{R}_l-\mathbf{R}_{l'}|+\sum_{l}e^2/|\mathbf{R}_l|.\qquad\text{(B. 9)}$$

We have from (B.9)

$$(\Phi_s\overline{V}\Phi_s)=\text{I}+\text{II}+\text{III}+\text{IV},\qquad\text{(B. 10)}$$

where

$$\text{I}=\int\Phi_s^*\left\{\sum_{j=1}^{N+1}\sum_{l}v(\mathbf{r}_j-\mathbf{R}_l)\right\}\Phi_s\prod_{j=1}^{N+1}d\mathbf{r}_j,\qquad\text{(B. 10. I)}$$

$$\text{II}=\int\Phi_s^*\left\{(1/2)\sum_{j=1}^{N+1}\sum_{j'=1(\neq j)}^{N+1}e^2/|\mathbf{r}_j-\mathbf{r}_{j'}|\right\}\Phi_s\prod_{j=1}^{N+1}d\mathbf{r}_j,\qquad\text{(B. 10. II)}$$

$$\text{III}=\int\Phi_s^*\left\{\sum_{j=1}^{N+1}V_i(\mathbf{r}_j)\right\}\Phi_s\prod_{j=1}^{N+1}d\mathbf{r}_j,\qquad\text{(B. 10. III)}$$

$$\text{IV}=\frac{1}{2}\sum_{l}\sum_{l'(\neq l)}e^2/|\mathbf{R}_l-\mathbf{R}_{l'}|+\sum e^2/|\mathbf{R}_l|,\ \left(\int\Phi_s^*\Phi_s\prod_{j=1}^{N+1}d\mathbf{r}_j=1\right).\qquad\text{(B. 10. IV)}$$

The integral I is developed as*)

$$\mathrm{I} \equiv \left\{(N+1)!\right\}^{-1} \int \sum_{P'} \varepsilon(P) P\left\{\underline{\psi}^*(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}^*(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}^*(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\}$$
$$\times \left\{\sum_{j=1}^{N+1}\sum_{l} v(\mathbf{r}_j - \mathbf{R}_l)\right\} \sum_{P} \varepsilon(P) P\left\{\underline{\psi}(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\} \prod_{j=1}^{N+1} d\mathbf{r}_j,$$
$$= \int \sum_{P} \varepsilon(P) P\left\{\underline{\psi}^*(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}^*(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}^*(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\}$$
$$\times \left\{\sum_{j=1}^{N+1}\sum_{l} v(\mathbf{r}_j - \mathbf{R}_l)\right\} \underline{\psi}(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_{N+1}) \prod_{j=1}^{N+1} d\mathbf{r}_j.$$

Referring to (A.2.a) and (A.2.b), the above equation is transformed as

$$\sum_{i=1}^{N+1} \int \underline{\psi}^*(\mathbf{k}_i, \mathbf{r}_j) \left\{\sum_{l} v(\mathbf{r}_j - \mathbf{R}_l)\right\} \underline{\psi}(\mathbf{k}_i, \mathbf{r}_j)\, d\mathbf{r}_j$$
$$= \sum_{i=1}^{N+1} \int \underline{\psi}^*(\mathbf{k}_i, \mathbf{r}) \left\{\sum_{l} v(\mathbf{r} - \mathbf{R}_l)\right\} \underline{\psi}(\mathbf{k}_i, \mathbf{r})\, d\mathbf{r},$$

or, changing the order of summation and integration, and referring to (A.1.a), (A.1.b) and (A.4),

$$\mathrm{I} = \int \left\{\rho_0(\mathbf{r}) + \rho(\mathbf{r}) + \rho'(\mathbf{r})\right\} \left\{\sum_{l} v(\mathbf{r} - \mathbf{R}_l)\right\} d\mathbf{r}. \qquad \text{(B. 11)}$$

The integral III is given according to (B.12.III) just similarly as I, *i.e.* as

$$\mathrm{III} = \int \left\{\rho_0(\mathbf{r}) + \rho(\mathbf{r})\right\} V_i(\mathbf{r}) d\mathbf{r}, \qquad \text{(B. 12)}$$

except that $\sum_{l} v(\mathbf{r} - \mathbf{R}_l)$ in (B.11) is replaced by $V_i(\mathbf{r})$, and the higher order term $\int \rho'(\mathbf{r}) V_i(\mathbf{r}) d\mathbf{r}$ is neglected.

The integral II is transformed according to (B.10.II), as

$$\mathrm{II} = \left\{(N+1)!\right\}^{-1} \int \sum_{P} \varepsilon(P) P\left\{\underline{\psi}^*\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}^*(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}^*(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\}$$
$$\times \left\{\frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1(\neq j)}^{N+1} e^2/|\mathbf{r}_j - \mathbf{r}_{j'}|\right\} \sum_{P} \varepsilon(P) P\left\{\underline{\psi}(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\} \prod_{j=1}^{N+1} d\mathbf{r}_j$$
$$= \int \sum_{P} \varepsilon(P) P\left\{\underline{\psi}^*(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}^*(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}^*(\mathbf{k}_{N+1}, \mathbf{r}_{N+1})\right\}$$
$$\times \left\{\frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1(\neq j)}^{N+1} e^2/|\mathbf{r}_j - \mathbf{r}_{j'}|\right\} \underline{\psi}(\mathbf{k}_1, \mathbf{r}_1)\underline{\psi}(\mathbf{k}_2, \mathbf{r}_2)\cdots\underline{\psi}(\mathbf{k}_{N+1}, \mathbf{r}_{N+1}) \prod_{j=1}^{N+1} d\mathbf{r}_j, \qquad \text{(B. 13)}$$

or, by (A.2.a) and (A.2.b),

$$\mathrm{II} = \mathrm{II}_c + \mathrm{II}_x, \qquad \text{(B. 13. a)}$$

where

*) Cf. F. SEITZ, *Modern theory of solids* (McGraw-Hill Company), pp. 236~240 (1940).

$$\mathrm{II}_c = \frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}\int \underline{\psi}^*(\mathbf{k}_j,\mathbf{r}_j)\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r}_{j'})\,(e^2/|\mathbf{r}_j-\mathbf{r}_{j'}|) \times \underline{\psi}(\mathbf{k}_j,\mathbf{r}_j)\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}_{j'})\,d\mathbf{r}_j d\mathbf{r}_{j'}\,, \tag{B. 13. b}$$

and

$$\mathrm{II}_{ex} = -\frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}\int \underline{\psi}^*(\mathbf{k}_j,\mathbf{r}_{j'})\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r}_j)\,(e^2/|\mathbf{r}_j-\mathbf{r}_{j'}|) \times \underline{\psi}(\mathbf{k}_j,\mathbf{r}_j)\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}_{j'})\,d\mathbf{r}_j d\mathbf{r}_{j'}\,. \tag{B. 13. c}$$

The II_c is the COULOMB interactions between electrons, and II_{ex} the exchange interaction between them. The summation $\sum_{j=1}^{N+1}\sum_{j=1(\neq j)}^{N+1}$ in (B. 13) is replaced by $\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}$ in (B. 13. b) and (B. 13. c), since the term of summation for $j=j'$ in (B. 13. b) and that in (B. 13. c) cancel each other in (B. 13. a).

The II_c is written as

$$\mathrm{II}_c = \frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}\int \underline{\psi}^*(\mathbf{k}_j,\mathbf{r})\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r}')(e^2/|\mathbf{r}-\mathbf{r}'|)\underline{\psi}(\mathbf{k}_j,\mathbf{r})\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$
$$= \frac{1}{2}\int\left\{\sum_{j=1}^{N+1}\underline{\psi}^*(\mathbf{k}_j,\mathbf{r})\underline{\psi}(\mathbf{k}_j,\mathbf{r})\right\}(e^2/|\mathbf{r}-\mathbf{r}'|)\left\{\sum_{j'=1}^{N+1}\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r}')\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}')\right\}d\mathbf{r}\,d\mathbf{r}'\,,$$

or by (A. 1. a), (A. 1. b) and (A. 4),

$$\mathrm{II}_c = \frac{1}{2}\int\left\{\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}(e^2/|\mathbf{r}-\mathbf{r}'|)\left\{\rho_0(\mathbf{r}')+\rho(\mathbf{r}')+\rho'(\mathbf{r}')\right\}d\mathbf{r}\,d\mathbf{r}'$$
$$= \frac{1}{2}\int\rho_0(\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\rho_0(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' + \int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}(e^2/|\mathbf{r}-\mathbf{r}'|)\,\rho_0(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$
$$+ \frac{1}{2}\int\rho(\mathbf{r})(e^2/\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'\,, \tag{B. 14}$$

where

$$\int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}(e^2/|\mathbf{r}-\mathbf{r}'|)\rho_0(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$
$$= \frac{1}{2}\int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}(e^2/|\mathbf{r}-\mathbf{r}'|)\rho_0(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$$
$$+ \frac{1}{2}\int\rho_0(\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\left\{\rho(\mathbf{r}')+\rho'(\mathbf{r}')\right\}d\mathbf{r}\,d\mathbf{r}'\,;$$

the higher order terms $\int\rho(\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\rho'(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' = \int\rho'(\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$ and $\int\rho'(\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\rho'(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'$ are neglected.

By putting

$$V_{\rho 0}(\mathbf{r}) = \int\frac{e^2\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\,, \tag{B. 15. a}$$

and

$$V_\rho(\mathbf{r}) = \int \frac{e^2\rho(\mathbf{r}')}{\mathbf{r}-\mathbf{r}'}\,d\mathbf{r}' , \qquad \text{(B. 15. b)}$$

we have

$$\mathrm{II}_c = \frac{1}{2}\int \rho_0(\mathbf{r})\,V_{\rho 0}(\mathbf{r})d\mathbf{r} + \int \left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\} V_{\rho 0}(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \rho(\mathbf{r})\,V_\rho(\mathbf{r})d\mathbf{r} . \qquad \text{(B. 16)}$$

The II_{ex} is written as

$$\begin{aligned}
\mathrm{II}_{ex} &= -\frac{1}{2}\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}\int \underline{\psi}^*(\mathbf{k}_j,\mathbf{r}')\underline{\psi}(\mathbf{k}_j,\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r})\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \\
&= -\frac{1}{2}\sum_j\sum_{j'}\int \psi^*(\mathbf{k}_j,\mathbf{r}')\psi(\mathbf{k}_j,\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\psi^*(\mathbf{k}_{j'},\mathbf{r})\psi(\mathbf{k}_{j'},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \\
&\quad -\sum_j\sum_{j'}\int \left\{\underline{\psi}^*(\mathbf{k}_j,\mathbf{r}')\underline{\psi}(\mathbf{k}_j,\mathbf{r})-\psi^*(\mathbf{k}_j,\mathbf{r}')\psi(\mathbf{k}_j,\mathbf{r})\right\} \\
&\qquad \times (e^2/|\mathbf{r}-\mathbf{r}'|)\psi^*(\mathbf{k}_{j'},\mathbf{r})\psi(\mathbf{k}_{j'},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}' \\
&\quad -\frac{1}{2}\sum_j\sum_{j'}\int \left\{\underline{\psi}^*(\mathbf{k}_j,\mathbf{r}')\underline{\psi}(\mathbf{k}_j,\mathbf{r})-\psi^*(\mathbf{k}_j,\mathbf{r}')\psi(\mathbf{k}_j,\mathbf{r})\right\} \\
&\qquad \times (e^2/|\mathbf{r}-\mathbf{r}'|)\left\{\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r})\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}')-\psi^*(\mathbf{k}_{j'},\mathbf{r})\psi(\mathbf{k}_{j'},\mathbf{r}')\right\} d\mathbf{r}\,d\mathbf{r}' .
\end{aligned} \qquad \text{(B. 17)}$$

The first term on the third member of (B. 17) is given, according to the simplified tratment by SLATER[13], as

$$\text{the first term} = \frac{1}{2}\int \rho_0(\mathbf{r})\,V_{ex0}(\mathbf{r})d\mathbf{r} , \qquad \text{(B. 17. a)}$$

where

$$V_{ex0}(\mathbf{r}) = -3e^2(3/8\pi)^{1/3}\rho_0(\mathbf{r})^{1/3} .$$

The second term on the third member of (B. 17) is given approximately as,

$$\text{the second term} = \int \left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\} V_{ex0}(\mathbf{r})d\mathbf{r} , \qquad \text{(B. 17. b)}$$

by making use of (B. 17. a) and of the approximate relation,

$$\begin{aligned}
&-\sum_j\sum_{j'}\int \left\{\underline{\psi}^*(\mathbf{k}_j,\mathbf{r}')\underline{\psi}(\mathbf{k}_j,\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\psi^*(\mathbf{k}_{j'},\mathbf{r})\psi(\mathbf{k}_{j'},\mathbf{r}')\right\} d\mathbf{r}\,d\mathbf{r}' \\
&= \int \left\{\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r})\right\} V_{ex0}(\mathbf{r})d\mathbf{r} .
\end{aligned}$$

The third term on the third member of (B. 17) is given similarly as

$$\text{the third term} = \frac{1}{2}\int \rho(\mathbf{r})\,V_{ex}(\mathbf{r})d\mathbf{r} , \qquad \text{(B. 17. c)}$$

where

$$V_{ex}(\mathbf{r}) = \bar{V}_{ex}(\mathbf{r}) - V_{ex\,0}(\mathbf{r}),$$
$$\bar{V}_{ex}(\mathbf{r}) = -3e^2(3/8\pi)^{1/3}(\rho_0(\mathbf{r})+\rho(\mathbf{r}))^{1/3},$$

by making use of the relations (B.17.a), (B.17.c) and

$$-\sum_{j=1}^{N+1}\sum_{j'=1}^{N+1}\int\left\{\underline{\psi}^*(\mathbf{k}_j,\mathbf{r}')\underline{\psi}(\mathbf{k}_j,\mathbf{r})(e^2/|\mathbf{r}-\mathbf{r}'|)\underline{\psi}^*(\mathbf{k}_{j'},\mathbf{r})\underline{\psi}(\mathbf{k}_{j'},\mathbf{r}')\right\}d\mathbf{r}\,d\mathbf{r}'$$
$$=\int\left\{\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}\left\{-3e^2(3/8\pi)^{1/3}(\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r}))^{1/3}\right\}d\mathbf{r}\,d\mathbf{r}',$$

and negelecting higher order terms $\int\rho'(\mathbf{r})V_{ex}(\mathbf{r})d\mathbf{r}$ as well as $\int\{\rho(\mathbf{r})+\rho'(\mathbf{r})\}$ $\times[-3e^2(3/8\pi)^{1/3}\{(\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r}))^{1/3}-(\rho_0(\mathbf{r})+\rho(\mathbf{r}))^{1/3}\}]d\mathbf{r}$.

We have, thus, from (B.17), (B.17.a), (B.17.b) and (B.17.c),

$$\mathrm{II}_{ex}=\frac{1}{2}\int\rho_0(\mathbf{r})V_{ex\,0}(\mathbf{r})d\mathbf{r}+\int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}V_{ex\,0}(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\rho(\mathbf{r})V_{ex}(\mathbf{r})d\mathbf{r}. \tag{B.18}$$

The integration II is now expressed by (B.13.a), (B.16) and (B.18), as

$$\mathrm{II}=\mathrm{II}_c+\mathrm{II}_{ex}=\frac{1}{2}\int\rho_0(\mathbf{r})\left\{V_{\rho 0}(\mathbf{r})+V_{ex\,0}(\mathbf{r})\right\}d\mathbf{r}$$
$$+\int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}\left\{V_{\rho 0}(\mathbf{r})+V_{ex\,0}(\mathbf{r})\right\}d\mathbf{r}+\frac{1}{2}\int\rho(\mathbf{r})\left\{V_{\rho}(\mathbf{r})+V_{ex}(\mathbf{r})\right\}d\mathbf{r}, \tag{B.19}$$

and the $(\Phi_s\bar{V}\Phi_s)$ is given by (B.10), (B.10.IV), (B.11), (B 12) and (B.19),

$$(\Phi_s\bar{V}\Phi_t)=\int\left\{\rho_0(\mathbf{r})+\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}\left\{\sum_l v(\mathbf{r}-\mathbf{R}_l)\right\}d\mathbf{r}$$
$$+\frac{1}{2}\int\rho_0(\mathbf{r})\left\{V_{\rho 0}(\mathbf{r})+V_{ex\,0}(\mathbf{r})\right\}d\mathbf{r}+\int\left\{\rho(\mathbf{r})+\rho'(\mathbf{r})\right\}\left\{V_{\rho 0}(\mathbf{r})+V_{ex\,0}(\mathbf{r})\right\}d\mathbf{r}$$
$$+\frac{1}{2}\int\rho(\mathbf{r})\left\{V_{\rho}(\mathbf{r})+V_{ex}(\mathbf{r})\right\}d\mathbf{r}+\int\left\{\rho_0(\mathbf{r})+\rho(\mathbf{r})\right\}V_i(\mathbf{r})d\mathbf{r}$$
$$+\frac{1}{2}\sum_l\sum_{l'(\neq l)}\frac{e^2}{|\mathbf{R}_l-\mathbf{R}_{l'}|}+\sum_l\frac{e^2}{|\mathbf{R}_l|}. \tag{B.20}$$

The mean potential $(\Psi V\Psi)$ of the metal with N electrons without perturbation is readily derived from Ψ given by (B.1.a) and V by (2.5.b), with refence to (B.15.a) and (B.17.a), as

$$(\Psi V\Psi)=\int\rho_0(\mathbf{r})\left\{\sum_l v(\mathbf{r}-\mathbf{R}_l)\right\}d\mathbf{r}$$
$$+\frac{1}{2}\int\rho_0(\mathbf{r})\left\{V_{\rho 0}(\mathbf{r})+V_{ex\,0}(\mathbf{r})\right\}d\mathbf{r}+\frac{1}{2}\sum_l\sum_{l'(\neq l)}\frac{e^2}{|\mathbf{R}_l-\mathbf{R}_{l'}|}. \tag{B.21}$$

The increase of potential energy (P.E.) is now given by (B.20) and (B.21), as

$$(\text{P.E.}) \equiv (\Phi_s \overline{V} \Phi_s) - (\Psi V \Psi)$$
$$= \int \left\{ \rho(\mathbf{r}) + \rho'(\mathbf{r}) \right\} V_0(\mathbf{r}) d\mathbf{r} + \int \rho_0(\mathbf{r}) V_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) V_p(\mathbf{r}) d\mathbf{r}$$
$$+ \frac{1}{2} \int \rho(\mathbf{r}) V_i(\mathbf{r}) d\mathbf{r} + \sum_l \frac{e^2}{|\mathbf{R}_l|} , \qquad \text{(B. 22)}$$

$$V_0(\mathbf{r}) = \sum_l v(\mathbf{r} - \mathbf{R}_l) + V_{\rho 0}(\mathbf{r}) + V_{\text{ex}0}(\mathbf{r}) , \qquad \text{(B. 23. a)}$$

and

$$V_p(\mathbf{r}) = V_i(\mathbf{r}) + V_\rho(\mathbf{r}) + V_{\text{ex}}(\mathbf{r}) . \qquad \text{(B. 23. b)}$$

The $V_0(\mathbf{r})$ is the potential of an electron in the metal without any perturbation and $V_p(\mathbf{r})$ is the first order perturbation potential, givn by (1.6), due to the proton dissolved in the metal and extra electron density around it.

(iii): It is now shown that the sum of (K.E.) of (B.8) and the first integral of (B.22) is simply reduced as

$$(\text{K.E.}) + \int \left\{ \rho(\mathbf{r}) + \rho'(\mathbf{r}) \right\} V_0(\mathbf{r}) d\mathbf{r} = E(\mathbf{k}_{N+1}) + \sum_i \sum_{\alpha(\neq i)} \frac{|V_{\alpha i}|^2}{E(\mathbf{k}_\alpha) - E(\mathbf{k}_i)} . \qquad \text{(B. 24)}$$

Substituting $\rho(\mathbf{r})$ and $\rho'(\mathbf{r})$ from (A.4.a) and (A.4.b) into the second term on the left side of the above equation, we have

$$(\text{K.E.}) + \int \left\{ \rho(\mathbf{r}) + \rho'(\mathbf{r}) \right\} V_0(\mathbf{r}) d\mathbf{r}$$
$$= \int \phi^*(\mathbf{k}_{N+1}, \mathbf{r}) \left(-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r}) \right) \phi(\mathbf{k}_{N+1}, \mathbf{r}) \, d\mathbf{r}$$
$$+ \sum_i \sum_{\alpha(\neq i)} \left\{ b_{\alpha i}^* \int \phi^*(\mathbf{k}_\alpha, \mathbf{r}) (-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r})) \phi(\mathbf{k}_i, \mathbf{r}) d\mathbf{r} + \text{comp. conj.} \right\}$$
$$+ \sum_i \sum_{\alpha(\neq i)} |b_{\alpha i}|^2 \int \left\{ \phi^*(\mathbf{k}_\alpha, \mathbf{r}) (-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r})) \phi(\mathbf{k}_\alpha, \mathbf{r}) \right.$$
$$\left. - \phi^*(\mathbf{k}_i, \mathbf{r}) (-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r})) \phi(\mathbf{k}_i, \mathbf{r}) \right\} d\mathbf{r}$$
$$+ \sum_i \sum_{\alpha(\neq i)} \sum_{\beta(\neq \alpha, \neq i)} b_{\alpha i}^* b_{\beta i} \int \phi^*(\mathbf{k}_\alpha, \mathbf{r}) (-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r})) \phi(\mathbf{k}_\beta, \mathbf{r}) d\mathbf{r}$$
$$+ \sum_i \sum_{\gamma(\neq i)} \left\{ c_{\gamma i}^* \int \phi^*(\mathbf{k}_\gamma, \mathbf{r}) (-\hbar^2/2m \cdot \Delta + V_0(\mathbf{r})) \phi(\mathbf{k}_i, \mathbf{r}) d\mathbf{r} + \text{comp. conj.} \right\}$$
(B. 25. a)

or

$$
\begin{aligned}
&= E(\mathbf{k}_{N+1}) \\
&\quad + \sum_i \sum_{\alpha(\neq i)} \left\{ b_{\alpha i} \int \psi^*(\mathbf{k}_\alpha, \mathbf{r}) E(\mathbf{k}_i) \psi(\mathbf{k}_i, \mathbf{r}) d\mathbf{r} + \text{comp. conj.} \right\} \\
&\quad + \sum_i \sum_{\alpha(\neq i)} |b_{\alpha i}|^2 \int \left\{ \psi^*(\mathbf{k}_\alpha, \mathbf{r}) E(\mathbf{k}_\alpha) \psi(\mathbf{k}_\alpha, \mathbf{r}) - \psi^*(\mathbf{k}_i, \mathbf{r}) E(\mathbf{k}_i) \psi(\mathbf{k}_i, \mathbf{r}) \right\} d\mathbf{r} \\
&\quad + \sum_i \sum_{\alpha(\neq i)} \sum_{\beta(\neq \alpha, \neq i)} b^*_{\alpha i} b_{\beta i} \int \psi^*(\mathbf{k}_\alpha, \mathbf{r}) E(\mathbf{k}_\beta) \psi(\mathbf{k}_\beta, \mathbf{r}) d\mathbf{r} \\
&\quad + \sum_i \sum_{\gamma(\neq i)} \left\{ c^*_{\gamma i} \int \psi^*(\mathbf{k}_\gamma, \mathbf{r}) E(\mathbf{k}_i) \psi(\mathbf{k}_i, \mathbf{r}) d\mathbf{r} + \text{comp. conj.} \right\}, \qquad \text{(B. 25. b)}
\end{aligned}
$$

with reference to the equations, *e. g.*

$$\left\{ -\hbar^2/2m \cdot \Delta + V_0(\mathbf{r}) \right\} \psi(\mathbf{k}_i, \mathbf{r}) = E(\mathbf{k}_i) \psi(\mathbf{k}_i, \mathbf{r}) .$$

By the normalization conditions and orthogonal relations (B.3), (B.25.b) is reduced to the form

$$\text{(K.E.)} + \int \left\{ \rho(\mathbf{r}) + \rho'(\mathbf{r}) \right\} V_0(\mathbf{r}) d\mathbf{r} = E(\mathbf{k}_{N+1}) + \sum_i \sum_{\alpha(\neq i)} |b_{\alpha i}|^2 \left\{ E(k_\alpha) - E(k_i) \right\} . \qquad \text{(B. 26)}$$

Eq. (B.24) is arrived at by substituting $b_{\alpha i}$ in (B.26) from (1.7), which satisfies the condition (A.3.a). Hence, we have by (B.8), (B.22) and (B.24),

$$
\begin{aligned}
\text{(K.E.)} + \text{(P.E.)} &= E(\mathbf{k}_{N+1}) + \sum_i \sum_{\alpha(\neq i)} \frac{|V_{i\alpha}|^2}{E(\mathbf{k}_\alpha) - E(\mathbf{k}_i)} \\
&\quad + \int \rho_0(\mathbf{r}) V_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) V_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \rho(\mathbf{r}) V_p(\mathbf{r}) d\mathbf{r} + \sum_I \frac{e^2}{|\mathbf{R}_I|} . \qquad \text{(B. 27)}
\end{aligned}
$$

(iv): The fifth term on the left side of (B.25) is rewritten by (A.4.a), and (1.8) as

$$
\begin{aligned}
\frac{1}{2} \int \rho(\mathbf{r}) V_p(\mathbf{r}) d\mathbf{r} &= \frac{1}{2} \int \psi^*(\mathbf{k}_{N+1}, \mathbf{r}) V_p(\mathbf{r}) \psi(\mathbf{k}_{N+1}, \mathbf{r}) d\mathbf{r} \\
&\quad + \sum_i \sum_{\alpha(\neq i)} \left\{ b^*_{\alpha i} \int \psi^*(\mathbf{k}_\alpha, \mathbf{r}) V_p(\mathbf{r}) \psi(\mathbf{k}_i, \mathbf{r}) d\mathbf{r} + \text{comp. conj.} \right\} \\
&= (\text{order of } \lambda e^2/N) + \sum_i \sum_{\alpha(\neq i)} \left\{ b^*_{\alpha i} V_{\alpha i} + b_{\alpha i} V^*_{\alpha i} \right\}, \qquad \text{(B. 28)}
\end{aligned}
$$

or by substituting $b_{\alpha i}$ from (1.7) and neglecting the first term on the third member,

$$\frac{1}{2} \int \rho(\mathbf{r}) V_p(\mathbf{r}) d\mathbf{r} = - \sum_i \sum_{\alpha(\neq i)} \frac{|V_{\alpha i}|^2}{E(\mathbf{k}_\alpha) - E(\mathbf{k}_i)} . \qquad \text{(B. 29)}$$

Hence, the second and the fifth term on the left side of (B.27) cancel each other, so that

$$(\text{K.E.})+(\text{P.E.})=E(\mathbf{k}_{N+1})+\int\rho_0(\mathbf{r})\,V_i(\mathbf{r})d\mathbf{r}$$
$$+\frac{1}{2}\int\rho(\mathbf{r})\,V_i(\mathbf{r})d\mathbf{r}+\sum_l\frac{e^2}{|\mathbf{R}_l|}\ . \qquad \text{(B. 30)}$$

The first term $E(\mathbf{k}_{N+1})$ is equal to $-\phi$, admitting that the additional electron from hydrogen atom occupies a level at the FERMI surface. The second and the last term cancels each other for proton situated at the centre of cubic crystal along with the approximation of replacing the atomic polyhedron by atomic sphere, and neglecting the potential of the proton due to the potential of the double layer at the surface.

We have, thus, finally

$$(\text{K.E.})+(\text{P.E.})=-\phi+\frac{1}{2}\int\rho(\mathbf{r})\,V_i(\mathbf{r})d\mathbf{r}\ . \qquad \text{(B. 31)}$$

The heat of dissolution Q is in consequence given by (1.11).

Appendix C.

The values of $\sigma_0/\sigma=\Phi_p(d/\bar{l})/(d/\bar{l})$

$d/\bar{l}$ \ p	0	0.1	0.2	0.3	0.5	0.7
1/30	10.422	9.123	7.987	6.952	5.112	—
1/25	9.065	7.983	7.001	6.115	4.540	—
1/21	7.994	7.056	6.206	5.444	4.072	—
1/15	6.309	5.604	4.961	4.376	3.331	2.403
1/10	4.782	4.285	3.832	3.417	2.669	1.997
1/8	4.134	3.726	3.351	3.006	2.384	1.822
1/5	3.096	2.826	2.577	2.345	1.925	1.545
1/4	2.724	2.503	2.299	2.108	1.760	1.445
1/3	2.333	2.163	2.006	1.858	1.588	1.342
1/2	1.916	1.801	1.693	1.591	1.404	1.234
1	1.462	1.406	1.352	1.301	1.204	1.119
2	1.221	1.195	1.171	1.147	1.101	1.059
3	1.141	1.126	1.110	1.095	1.066	1.039
5	1.081	1.072	1.064	1.055	1.039	1.023

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