formation temperature (the experimental data are not sufficient to determine whether the transformation temperature is ever unique and critical or includes always a span of a number of degrees) a rapid increase in mobility with resultant aggregation of atoms takes place which produces a discontinuous, patch structure of the film. This film then exhibits a decrease in conductance with further temperature (and mobility) increase. The last-mentioned decrease of conductance with increasing temperature is transient; a stable (aged) film in which the agglomeration process has been completed exhibits a negative temperature coefficient of resistance as would be expected for a discontinuous structure. Fukuroi[9] gives a somewhat detailed discussion of the transformation temperature.

A few tests were made of the dependence of the conductance on the voltage applied to the film in measuring the conductance. For the thinner films an increase in conductance with applied voltage was observed in agreement with Foster's[4] results with lead films but this effect disappeared with increasing film thickness and the aged room temperature deposited film of Fig. 2 at 146 atom layers thickness showed no measurable variation of conductance with applied voltage. These results very obviously agree with the agglomeration process explanation since a discontinuous (thinner) film would be expected to exhibit a conductance which is voltage dependent because of the presence of gaps whereas a film approaching bulk metal structure (thicker film) would not.

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Exchange Forces Between Neutral Molecules and a Metal Surface*

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A Heitler-London treatment of the exchange part of the mutual energy of a neutral atom and a metal is developed. The resulting interactions are evaluated on the basis of a simplified model of the metal and lead to a convenient and simple expression for the total exchange energy. In Section III this expression is applied to the interaction of H_2 and He with metals where it is found to represent a repulsion. By adding this exchange interaction to the attractive van der Waals interaction between the molecule and the metal, a potential curve of the usual type possessing a minimum is obtained for each system. The depths of these minima are compared with observed heats of van der Waals adsorption. A discussion is given in an appendix of the effects of some of the simplifications and approximations employed.

At large distances from a solid surface, the mutual energy between an atom or molecule and the solid is predominantly determined by dispersion forces. These forces give rise to the usual $1/R^6$ van der Waals law for the interaction between an element of the solid and the molecule. Summation of this potential over all elements of the solid then leads to a mutual energy decreasing as the inverse third power of the normal distance between the surface and the molecule. This interaction was the subject of study in a previous paper.[1]

At closer distances the shorter range exchange interaction becomes important. For neutral molecules and rare gas atoms this represents a repulsion and its composition with the van der Waals interaction determines a minimum energy from which numerical values for the heat of physical adsorption can be inferred. This interaction is the subject of investigation here. A Heitler-London

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* A preliminary report on some of the work presented here was given at the Washington Meeting, April, 1939.

[1] H. Margenau and W. G. Pollard, Phys. Rev. **60**, 128 (1941).

treatment is developed and the exchange part of the resulting expression is evaluated approximately for a simple free electron model of a metal.

The calculation of the total potential curve for a molecule near a solid surface, which is contemplated here for metals, has been performed fairly adequately in the case of adsorption on ionic crystals.[2] In such problems it is proper to express the interaction of the molecule with the whole crystal as a sum of the interactions with individual ions in it. Such individual interactions can be fairly accurately represented by simple formulae and the summation can be performed without too great difficulty in terms of the known structure of the crystal. These calculations lead to results which show excellent agreement with experimentally determined heats of adsorption at low temperatures. The procedure employed in them is, however, inappropriate for adsorption on metals since interactions with the outer shell electrons of an isolated metal atom would become radically altered when the atom became bound in the metallic state.

I. Heitler-London Treatment

The visiting atom is represented by a core of charge $+e$ above the surface at a point $\mathbf{r}_A$, and an electron with positional coordinate $\mathbf{r}_a$, spin coordinate s_a, and wave function $(c_+\alpha(s_a)+c_-\beta(s_a))\psi(\mathbf{r}_a)$. In the solid we take atomic cores of charge Z_Je at points $\mathbf{r}_J$ together with electrons at points $\mathbf{r}_j$ with wave functions $u_i(\mathbf{r}_j)(i, j=1, 2, \cdots N)$ and spin functions $\alpha(s_j)$ or $\beta(s_j)$. The best antisymmetric wave function of these electrons in the product of individual functions approximation is the familiar determinant

$$\Phi=\frac{1}{(N!)^{\frac{1}{2}}}\begin{vmatrix} u_1(\mathbf{r}_1)\alpha(s_1), & \cdots, & u_n(\mathbf{r}_1)\alpha(s_1), & u_{n+1}(\mathbf{r}_1)\beta(s_1), & \cdots, & u_N(r_1)\beta(s_1) \\ \vdots & & \vdots & \vdots & & \vdots \\ u_1(\mathbf{r}_N)\alpha(s_N), & \cdots, & u_n(\mathbf{r}_N)\alpha(s_N), & u_{n+1}(\mathbf{r}_N)\beta(s_N), & \cdots, & u_N(r_N)\beta(s_N) \end{vmatrix}. \tag{1}$$

The terms have been arranged so that the first n electrons have positive and the next $N-n$ have negative spin functions.

The system solid+atom has $N+1$ electrons which must be described as a single system by a wave function completely antisymmetric in the $N+1$ positional and spin coordinates. Since the spin function of the electron in the visiting atom is represented as a linear combination of the eigenfunctions α and β of the solid, the wave function for the whole system may be taken to be the same linear combination of the two functions

$$\Psi_1=\frac{1}{(N+1)^{\frac{1}{2}}}\left|\begin{array}{c|ccc} \psi(\mathbf{r}_1)\alpha(s_1), & & & \\ & & \Phi & \\ \psi(\mathbf{r}_N)\alpha(s_N), & & & \\ \hline \psi(\mathbf{r}_a)\alpha(s_a), & u_1(\mathbf{r}_a)\alpha(s_a) & \cdots & u_N(\mathbf{r}_a)\beta(s_a) \end{array}\right| \tag{2}$$

and the function Ψ_2 which is obtained from Φ in the same way except that it is bordered on the right with $\psi(\mathbf{r}_i)\beta(s_i)$.

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[2] J. E. Lennard-Jones and B. M. Dent, Trans. Faraday Soc. **24**, 100 (1928); F. V. Lenel, Zeits. f. physik. Chemie **B23**, 379 (1933); J. K. Roberts and W. J. C. Orr, Trans. Faraday Soc. **34**, 1346 (1938); W. J. C. Orr, Proc. Roy. Soc. **A173**, 354 (1939).

The Hamiltonian of this system is given by

$$H=-\frac{\hbar^2}{2m}\nabla_a{}^2-\frac{\hbar^2}{2m}\sum_i \nabla_j{}^2+\tfrac{1}{2}\sum_{J,L}{}' \frac{Z_JZ_Le^2}{r_{JL}}+\sum_L \frac{e^2}{r_{AL}}-\sum_{J,k}\frac{Z_Je^2}{r_{Jk}}-\sum_J\frac{Z_Je^2}{r_{Ja}}$$
$$-\sum_k\frac{e^2}{r_{Ak}}-\frac{e^2}{r_{Aa}}+\tfrac{1}{2}\sum_{jk}{}'\frac{e^2}{r_{jk}}+\sum_j\frac{e^2}{r_{aj}}. \quad (3)$$

The wave function for the whole system is taken to be

$$\Psi=c_+\Psi_1+c_-\Psi_2,$$

where c_+ and c_- depend on the spin function of the electron in the visiting atom. The total energy of the system is given by

$$E=\langle H\rangle_{\text{Av}}=\int\Psi^*H\Psi d\tau\Big/\int\Psi^*\Psi d\tau. \quad (4)$$

The determinant (2) was expanded by minors of the bordered row and column and substituted with (3) in Eq. (4). After summation over spins is carried out in the result it is found that the cross product terms between Ψ_1 and Ψ_2 vanish and the terms in $\Psi_1{}^*\Psi_1$ and $\Psi_2{}^*\Psi_2$ are identical except that the exchange summations in the former which ran from 1 to n are replaced in the latter by summations from $n+1$ to N. Thus the exchange terms refer only to those electrons in the solid having the same spin as that of the electron in the visiting atom. No loss in generality is involved in taking $c_+=1$, $c_-=0$ since expressions for arbitrary c_+ and c_- can always be obtained simply by replacing each

$$\sum_1^n \text{ by } |c_+|^2\sum_1^n+|c_-|^2\sum_{n+1}^N.$$

The evaluation of the total energy (3) is rather involved but quite straightforward. The results are best exhibited in terms of the following expressions

$$f(\mathbf{r}_1,\mathbf{r}_2)=\sum_{i=1}^n u_i{}^*(\mathbf{r}_2)u_i(\mathbf{r}_1), \quad (5a)$$

$$\Delta^2=\int\int\psi^*(1)\psi(2)f(1,2)d\tau_1d\tau_2, \quad (5b)$$

$$K_1=e^2\int\int\frac{\psi^*(1)\psi(2)f(1,2)}{r_{A1}}d\tau_1d\tau_2, \quad (5c)$$

$$K_2=e^2\int\int\frac{\psi^*(1)\psi(2)f(1,2)}{r_{12}}d\tau_1d\tau_2, \quad (5d)$$

$$K_3=e^2\int\int\int\frac{\psi^*(1)\psi(2)f(3,2)f(1,3)}{r_{13}}d\tau_1d\tau_2d\tau_3, \quad (5e)$$

$$G=e\int\int\psi^*(1)\psi(2)f(1,2)\phi(2)d\tau_1d\tau_2, \quad (5f)$$

where ϕ represents the electric potential of the solid

$$\phi(\mathbf{r})=\sum_J\frac{Z_Je}{|\mathbf{r}_J-\mathbf{r}|}-e\int\frac{\sum_{i=1}^N|u_i(\mathbf{r}')|^2}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'. \quad (6)$$

A number of other terms which are of order (surface area of crystal)$^{-1}$ compared with these appear but they were neglected.

The exchange part of the contribution to the total energy (4) representing an interaction between the visiting atom and the solid has the form

$$A(\mathbf{r}_A)=(G+K_1-K_2+K_3)/(1-\Delta^2).$$

The potential ϕ, Eq. (6), arises from the surface double layer and from the polarization of the solid by the visiting atom. In the simplified model used to evaluate this interaction in the next section, both these effects are neglected so that in this approximation the term G vanishes. From a consideration of the relative magnitudes of the various terms when such effects are included, it appears that the term is negligible compared with the others in any case. Thus we may write approximately

$$A(\mathbf{r}_A)=(K_1-K_2+K_3)/(1-\Delta^2). \tag{7}$$

For the case in which the $u_i(\mathbf{r})$ are represented by plane wave functions, the function $f(1, 2)$ defined in Eqs. (5) has been evaluated by Wigner and Seitz.[3] In this case it is a function only of the distance r_{12} between points 1 and 2 and has the form

$$f(1, 2)=3\left(\frac{n}{V}\right)\frac{\sin\xi-\xi\cos\xi}{\xi^3}, \tag{8}$$

where $\xi=k_m r_{12}=[6\pi^2(n/V)]^{\frac{1}{3}}r_{12}$. This function has the value n/V at $\xi=0$ and at large ξ falls off as $1/\xi^2$. The total number of electrons represented by the density f is $\int f(1, 2)d\tau_{12}$. This integral is unfortunately indeterminate but since the function is multiplied in all the interactions (5) by functions of exponentially decreasing character, it seems proper for the present purpose to represent this number as

$$\lim_{c\to 0}\int e^{-cr_{12}}f(1, 2)d\tau_{12}$$

which is equal to unity.

The function $f(1, 2)$ is closely connected with the function $g(1, 2)$ in the expression

$$\rho(1, 2)=\rho(1)\rho(2)[1-g(1, 2)]$$

for the density of particles 1 and 2 in terms of their individual densities. The relation between them is

$$g(1, 2)=\tfrac{1}{2}[f(1, 2)/(n/V)]^2. \tag{9}$$

The properties of this function have been extensively studied by Wigner and Seitz[3] and we may use their results to obtain an interpretation of the role of f in the exchange interactions (5). Each electron in the solid whose spin is the same as that in the visiting atom is surrounded with a "hole" in the total distribution of electrons of like spin. The exclusion of charge from this hole becomes complete as the point occupied by the electron is approached and the total charge excluded is just equal to that of the central electron. The function f represents the density of this excluded charge. The manner in which the excluded density falls off with r_{12} is, however, incorrectly given by (8) as pointed out by Bardeen.[4] In the actual case it must still be n/V for $r_{12}=0$ but should fall off much more rapidly, presumably exponentially, at large r_{12} because of the screening of the field of the central electron by the others in its neighborhood. The total number of electrons excluded must of course in any case be unity.

II. Approximate Calculation for a Metal

In this section a highly simplified and perhaps rather crude evaluation of the interactions in Eqs. (5) will be presented. The method is based on certain approximations, the first of which consists of substituting for the function $f(1, 2)$ a rectangular hole which is such that each of the n metal electrons of the same spin as the visitor is assigned a volume V/n within which the density of electrons of this spin is zero and outside of which it has its normal value n/V. In this scheme the density of the excluded electrons is given by

$$\begin{aligned} f(1, 2)&=n/V, & r_{12}&\leqslant \rho_s,\\ &=0, & r_{12}&>\rho_s, \end{aligned} \tag{10}$$

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

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[3] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).

[4] J. Bardeen, Phys. Rev. **58**, 727 (1940).

TABLE I. *Values and positions of the minima in the potential energy curves for the van der Waals adsorption of* He *and* H_2 *on metals having various values of* r_s.

	He				H_2			
	$-W_m$				$-W_m$			
r_s cm $\times 10^8$	Electron Volts $\times 10^3$	Calories per Mole	D_m cm $\times 10^8$	$\frac{D_m}{\rho_s}$	Electron Volts $\times 10^3$	Calories per Mole	D_m cm $\times 10^8$	$\frac{D_m}{\rho_s}$
1.0	33.0	765	1.9	1.5	38.0	865	2.3	1.8
1.5	14.0	325	2.3	1.2	32.0	730	2.7	1.4
2.0	6.1	140	3.0	1.2	16.0	375	3.3	1.3
2.5	3.0	68	3.7	1.2	8.6	200	3.8	1.2
3.0	1.6	37	4.3	1.2	4.8	110	4.6	1.2

A substitution similar to this of the rectangular for the plane wave form of "hole" has been employed with good success in discussing the cohesive energy of solids.[5] Further consideration of the effect of its use in the present problem is deferred to Section **b** of the Appendix.

The presence of the function (10) in all of the integrals of Eqs. (5) confines the variables $\mathbf{r}_1$ and $\mathbf{r}_2$ to the range $|\mathbf{r}_1-\mathbf{r}_2|\leqslant\rho_s$. When the visiting atom is far from the surface of the metal, both r_{A1} and r_{A2} will be large enough to permit the use of an approximate expansion of r_{A2} in the form

$$r_{A2}=r_{A1}-r_{12}\cos\theta, \tag{11a}$$

where θ is the angle between $\mathbf{r}_{A1}$ and $\mathbf{r}_{12}$. When this is the case it will often be possible to write the wave function of the electron in the visiting atom in the form

$$\psi(2)=\psi(1)\varphi(r_{12}), \tag{11b}$$

which will be valid in this confined region. This procedure may seem inappropriate to the present calculations because the magnitude and behavior of the exchange energy is of greatest interest close to the surface in the region where this approximation is invalid. However, as will be seen, in the case of van der Waals adsorption the minimum in the total potential energy curve will often fall at a great enough distance from the surface to make its use allowable and it is to such cases that the results obtained must be confined. The approximation is discussed further in Section **c** of the Appendix.

If one makes use of (9) and (10) the various terms in Eqs. (5) become

$$\begin{aligned}\Delta^2&=p(\rho_s)F(D),\\ K_1&=e^2p(\rho_s)G(D),\\ K_2&=e^2q(\rho_s)F(D),\\ K_3&=e^2p(\rho_s)q(\rho_s)F(D),\end{aligned} \tag{12}$$

where

$$\begin{aligned}F(D)&=\int_M|\psi(r_{A1})|^2d\tau_1,\\ G(D)&=\int_M|\psi(r_{A1})|^2d\tau_1/r_{A1},\\ p(\rho_s)&=(n/V)\int_s\varphi(r_{12})d\tau_{12},\\ q(\rho_s)&=(n/V)\int_s\varphi(r_{12})d\tau_{12}/r_{12},\end{aligned} \tag{13}$$

and the regions of integration denoted by M and s are defined as follows: The region s is the sphere of radius ρ_s about the point $\mathbf{r}_1$ as center within which the function $f(1, 2)$ defined by Eq. (10) has non-zero values. The region M is the region occupied by the metal and is taken of infinite extent in the x and y directions and extending in the z direction from $z=D$ to $z=\infty$. Substituting the expressions (12) in Eq. (7) we obtain for the total exchange interaction

$$\begin{aligned}A(\rho_s, D)&=e^2[p(\rho_s)G(D)\\ &+q(\rho_s)(p(\rho_s)-1)F(D)]/[1-p(\rho_s)F(D)].\end{aligned} \tag{14}$$

In case the wave function in the visiting atom can be represented by a 1s function of the form

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[5] J. C. Slater, Rev. Mod. Phys. 6, 209 (1934).

$\psi=[1/(\pi a^3)^{\frac{1}{2}}]e^{-r/a}$, the use of Eq. (11a) leads to

$$\psi(r_{A2})=[1/(\pi a^3)^{\frac{1}{2}}]e^{-(r_{A1}-r_{12}\cos\theta)/a},$$

so that, comparing with Eq. (11b), we have

$$\varphi(r_{12})=e^{(r_{12}/a)\cos\theta}.$$

If these functions are substituted into Eqs. (13) the resulting integrals are easily evaluated and lead to the results

$$\begin{aligned} F(D)&=\tfrac{1}{2}(1+D/a)e^{-2D/a},\\ G(D)&=(1/2a)e^{-2D/a},\\ p(\rho_s)&=3[(\rho_s/a)\cosh(\rho_s/a)-\sinh(\rho_s/a)]/(\rho_s/a)^3,\\ q(\rho_s)&=(3/a)[\cosh(\rho_s/a)-1]/(\rho_s/a)^3. \end{aligned} \tag{15}$$

III. ADSORPTION OF HE AND H_2 ON METALS

The total exchange interaction of both electrons in He and in H_2 will be twice that for one of them when the metal contains equal numbers of both spin varieties and when the distance from the metal is large enough to make the double exchange integrals negligible. In the van der Waals case, and particularly in all cases to which the approximation (11) is applicable, the latter condition is fulfilled. For both gases single particle $1s$ functions are used here to describe each of the two electrons. The parameter a in this function may be chosen either from an examination of more elaborate variational wave functions for these systems or from their diamagnetic susceptibilities χ and atomic polarizabilities α calculated on the assumption of $1s$ functions. From the latter method we obtain

$$a\cong[-mc^2\chi/N_0e^2]^{\frac{1}{2}}\cong[\hbar^2\alpha/8me^2]^{\frac{1}{4}}. \tag{16}$$

For He the form of the variational wave function gives $a=0.59a_0$ while from Eq. (16) we get $a=0.64a_0$. In these calculations the value $a=0.62a_0$ was used for He. In the case of H_2, the wave function around each nucleus is best approximated by a $1s$ function with $a=0.84a_0$. But since the nuclei are $1.4a_0$ apart, the resulting configuration is more or less that of a spheroid with major and minor semi-axes $1.54a_0$ and $0.84a_0$. If a is determined from the radius of a sphere whose volume is equal to that of this spheroid, it should be $1.03a_0$. From Eq. (16) we get $a=0.91a_0$. The value $a=0.95a_0$ was used in these calculations for H_2.

In order to obtain the total potential energy of the system in the field of the metal surface, the potential of the attractive forces must be added to the exchange term. These forces are, of course, of the van der Waals type and so occur only in second order. The validity of adding first-order exchange forces to second-order dispersion forces has been investigated by Margenau[6] who finds for the He—He potential that no great error is involved because the contribution from exchange in second order is negligible in the neighborhood of the minimum. Presumably it would also be small in this case and well within the limits of accuracy of Eqs. (14) and (15). The particular form of van der Waals potential used in these calculations was that obtained by Margenau and Pollard.[1]

On adding the exchange potential $A(\rho_s, D)$ of Eq. (14) computed with the functions of Eqs. (15) to the van der Waals potential $W(r_s, D)$ of reference 1, curves possessing minima of the usual type are obtained. In Table I the depths of these minima, W_m, and the corresponding distances D_m at which they occur are shown for He and H_2 at various values of r_s. The ratio D_m/ρ_s of this equilibrium distance to the radius of the sphere in the metal to which the vector r_{12} is confined is also shown. In order for the approximation of Eq. (11) to be valid, this ratio should be large; a condition which unfortunately is not very well fulfilled. This situation will be discussed further in the appendix where it will be shown that the results in Table I are somewhat more reliable for small r_s than this indicates.

The minimum energies expressed in calories per mole are also tabulated in Table I and may be compared roughly with observed heats of adsorption at low temperatures. Such a comparison neglects the vibrational energy of the adsorbed molecule but this will be smaller than the limits of accuracy of the present treatment. Very little experimental data relevant for this comparison is available. Since a large number of investigations of the adsorption of gases on metals have been made (most of them concerning "activated" adsorption or chemisorption), this

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[6] H. Margenau, Phys. Rev. **56**, 1000 (1939).

situation suggests that the binding forces in van der Waals adsorption of H_2 and He on metals are very weak; a condition reflected by the results in Table I. Only one case suitable for comparison with the present results has been found. This is a measurement of the heat of adsorption of H_2 on Ni at 20°K by Eucken and Hunsman.[7] They obtain values of 1200 cal./mole in the initial stages of adsorption which decrease to 400 in the final stages. They give 800 cal./mole as a mean value. With $r_s=1.38$ for Ni, a potential curve for H_2 having a minimum of 0.032 electron volts per molecule corresponding to a heat of adsorption of 795 cal./mole is obtained.

It is of interest to note here the order of magnitude of the heats of van der Waals adsorption of He and H_2 on non-metals. For H_2 it is 1100 cal./mole on Acheson graphite[8] and varies from 1300 to 1700 cal./mole on various charcoals.[9] For He a value of about 140 cal./mole is given by Stout and Giauque[10] for the heat of adsorption on $NiSO_4 \cdot 7H_2O$ at 4°K. These values are comparable with those in Table I for metals.

In conclusion I wish to express my gratitude to Professor Henry Margenau for his continued interest in this work and for a very helpful criticism of the manuscript.

APPENDIX

The evaluation of the exchange integrals (5) which is performed in Section II is based on several approximations and simplifications which are in need of some justification.

TABLE II. *Values of the coefficients $M(\rho_s)$ and $N(\rho_s)$ in Eq. (21) showing the effect of the modification (a) on the exchange interaction.*

ρ_s/a	$f(1, 2)$ FROM EQ. (10) $M(\rho_s)$	$N(\rho_s)$	$f(1, 2)$ FROM EQ. (20) $M(\rho_s)$	$N(\rho_s)$
1.5	0.34	0.065	0.088	−0.021
3.0	0.17	0.062	0.011	−0.0023
6.0	0.12	0.090	0.00027	−0.000039
12.0	1.34	1.35	0.000011	−0.000001

Some of the aspects of the problem which seem to require the most attention may be listed as follows: (a) The metal wave functions $u_i(r)$ obey boundary conditions at the surface so that all electronic densities are much smaller near the surface than in the body of the metal; (b) The use of the rectangular form, Eq. (10), of the function $f(1,2)$ may introduce considerable error when used in integration with an increasing function of r_{12}; (c) The approximation represented by Eq. (11) is valid only for reasonably large values of the ratio D_m/ρ_s. We consider these aspects separately.

a. Effect of boundary conditions on metal wave functions

This effect may be roughly accounted for by choosing the wave functions $u_i(r)$ for a region of constant potential within the metal bounded somewhat beyond its surface by a barrier of infinite height. If the z axis is chosen, as before, normal to the surface and the barrier is taken at $z=0$, the wave functions are given by

$$u_i(r)=(2/V)^{\frac{1}{2}}\sin kz e^{i(k_x x+k_y y)}, \tag{17}$$

where $k_x=2\pi\nu_x/L$, $k_y=2\pi\nu_y/L$, and $k=2\pi\nu/L$ with ν_x, ν_y taking all integral values and ν positive half integral values. If the positive ions in the metal are replaced by a uniform charge distribution of constant density extending from z_0 to infinity, the metal can be made electrically neutral by choosing $z_0=3\pi/8k_m$ where k_m is the maximum wave number in the Fermi distribution.[11] This gives rise to a surface double layer which produces a potential $\phi(z)$, Eq. (6). The resulting exchange interaction G, Eq. (5f), is, however, negligible compared with the others.

The density $f(1, 2)$ computed with the wave functions (17) when there are equal numbers of both spins in the metal is given by [cf. Eq. (5a)]

$$\begin{aligned} f(1, 2) &= \sum_{i=1}^{n} u_i^*(2)u_i(1) \\ &= [2V/(2\pi)^3]\int_0^{k_m} dk\int_0^{(k_m^2-k^2)^{\frac{1}{2}}} \kappa d\kappa \int_{-\pi}^{\pi} u_i^*(2)u_i(1)d\theta \\ &= (z_1^{\frac{1}{2}}z_2^{\frac{1}{2}}/2\pi\rho_{12})\int_0^{k_m} J_1[(k_m^2-k^2)^{\frac{1}{2}}\rho_{12}] \\ &\qquad \times J_{\frac{1}{2}}(kz_1)J_{\frac{1}{2}}(kz_2)(k_m^2-k^2)^{\frac{1}{2}}kdk \end{aligned}$$

with $\rho_{12}=[(x_1-x_2)^2+(y_1-y_2)^2]^{\frac{1}{2}}$. This integral may be evaluated[12] through the substitution $k=k_m\cos\theta$ with the result

$$f(1, 2)=3\frac{n}{V}\left[\frac{\sin\xi-\xi\cos\xi}{\xi^3}-\frac{\sin\eta-\eta\cos\eta}{\eta^3}\right], \tag{18}$$

where $\xi=k_m r_{12}$ has the same meaning as before and $\eta=k_m[\rho_{12}^2+(z_1+z_2)^2]^{\frac{1}{2}}$. At $r_{12}=0$ the function is still equal to the density at the point r_1 but this is no longer n/V; it is replaced by

$$f(1, 2)=3\frac{n}{V}\left[1-\frac{\sin 2k_m z_1-2k_m z_1\cos 2k_m z_1}{(2k_m z_1)^3}\right].$$

The density (18) integrates to a total excluded charge of

$$\int f(1, 2)d\tau_{12}=(2/\pi)Si(k_m z_1), \tag{19}$$

where $Si(x)=\int_0^x \sin x dx/x$ denotes the integral sine function.

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[7] A. Eucken and W. Hunsman, Zeits. f. physik. Chemie, **B44**, 163 (1939).

[8] R. M. Barrer, Proc. Roy. Soc. **A161**, 476 (1937).

[9] R. M. Barrer and E. K. Rideal, Proc. Roy. Soc. **A149**, 231 (1935).

[10] J. W. Stout and W. F. Giauque, J. Am. Chem. Soc. **60**, 393 (1938).

[11] J. Bardeen, Phys. Rev. **49**, 653 (1936).

[12] G. N. Watson, *Theory of Bessel Functions* (Cambridge, 1922), p. 377.

An indication of the effect of this form for $f(1, 2)$ on the results of the present calculation may be obtained by employing an approximation similar to (10) as follows:

$$\begin{aligned} f(1, 2) &= (n/V)(2/\pi)Si(k_m z_1)h(z_1/\rho_s), && r_{12} \leqslant \rho_s \\ &= 0, && r_{12} > \rho_s \end{aligned} \qquad (20)$$

where

$$\begin{aligned} h(z_1/\rho_s) &= 4/[2+3(z_1/\rho_s)-(z_1/\rho_s)^3], && z_1 \leqslant \rho_s \\ &= 1. && z_1 \geqslant \rho_s \end{aligned}$$

The sphere of radius ρ_s about the point z_1 does not extend beyond the barrier and the purpose of the function $h(z_1/\rho_s)$ is to correct for that part of it which is cut off.

Equation (20) has been used in place of Eq. (10) to evaluate the interactions (5). In either case the total exchange energy (7) can be written as

$$A(\rho_s, D) = [M(\rho_s)+(D/a)N(\rho_s)] \exp[-(2D-\rho_s)/a]. \quad (21)$$

The coefficients M and N have been evaluated for several values of the quantity ρ_s/a with both forms of $f(1, 2)$ by numerical integration in this case and the results are given in Table II. It is clear that the introduction of metal wave functions obeying boundary conditions at the surface has a profound effect on the exchange interaction. If this effect were the only one operative, it would completely invalidate the results of Section III but as we shall see in what follows another equally strong effect is present which very nearly counteracts it.

b. Exponential form of $f(1, 2)$

As pointed out at the end of Section I in this paper and in reference 4, the correct form of $f(1, 2)$ should show an exponential decrease with r_{12} at large values. Deep in the body of the metal both of the plane wave forms of this function, Eqs. (8) and (18), are equivalent. In this region a simple function showing the same behavior as these for small r_{12} and representing the same total excluded charge but exhibiting the desired behavior at large r_{12} is given by

$$f(1, 2) = (n/V)[e^{-6.4r_{12}/\rho_s}+(6.4r_{12}/\rho_s)e^{-3.3r_{12}/\rho_s}]. \quad (22)$$

In any scheme employing the approximation of Eqs. (11), this function cannot be used for values of $\rho_s > 3$. The functions $p(\rho_s)$ and $q(\rho_s)$ as defined in Eqs. (13) on the basis of $f(1, 2)$ being given by Eq. (10) may be written for use with Eq. (22)

$$p(\rho_s) = \int \varphi(r_{12})f(1, 2)d\tau_{12}, \quad q(\rho_s) = \int \varphi(r_{12})f(1, 2)d\tau_{12}/r_{12},$$

where the integration now extends throughout space. These integrals are easily evaluated with the form $\varphi(r_{12}) = \exp[(r_{12}/a)\cos\theta]$. If it is assumed that the ratio of values so obtained to those given by Eqs. (15) may be used throughout the metal, including regions near the surface, these new functions may be used in the calculations performed in (a) above to give a new set of exchange interactions. The exchange energy so obtained represents in a rough way the combined effect on the original results of both the modification introduced in (a) and the present one. The coefficients in Eq. (21) obtained in this way are compared in Table III with the original ones. It is evident that the use of Eq. (22) in this way almost cancels the effect of (*a*) shown in Table II.

TABLE III. *Values of the coefficients $M(\rho_s)$ and $N(\rho_s)$ of Eq. (21) showing the combined effect of modifications (a) and (b) on the exchange interactions.*

	$f(1, 2)$ FROM EQ. (10)		$f(1, 2)$ FROM EQ. (20) WITH p AND q FROM EQ. (22)	
ρ_s/a	M	N	M	N
1.0	0.47	0.062	0.34	0.003
1.5	0.34	0.065	0.25	0.032
2.0	0.26	0.065	0.26	0.058
2.5	0.21	0.062	0.57	0.162

c. The approximation of Eqs. (11)

It was pointed out in the discussion of the results of Table I that the smallness of the ratio D_m/ρ_s made the use of the approximation (11) questionable. However, if one takes the refinement introduced in (a) above into account, the situation is somewhat improved. As a result of the behavior of the density $f(1, 2)$ in Eq. (20), the main contribution to the exchange interaction does not come from a sphere centered at the surface and extending beyond it, as in the simple theory, but from a sphere centered within the metal at a depth of order $1/k_m$ and cut off at the surface. This effect adds about 0.4 to the ratios D_m/ρ_s given in Table I so that the use of the approximation seems somewhat better justified.

It is to be noted that all of the difficulties discussed in this appendix are least important at small ρ_s. Thus it appears that the simple theory developed in the body of the paper represents the limiting case of metals with high electronic density fairly reliably but should be used with caution in the case of metals having large values of ρ_s.