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The Image and Van der Waals Forces at a Metallic Surface

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Calculations based on a model which takes the structure of the metal into account indicate that the force on an electron outside the surface of a metal is just the classical image force, but that the van der Waals force on a neutral molecule may be smaller than that given by a semi-classical calculation based on the method of images. An approximate value for the van der Waals energy between two systems A and B is obtained by calculating the energy of B in the field of A, supposing that the electrons of A are in fixed positions. The result is then averaged over the coordinates of the electrons of A, giving an energy W_A. Systems A and B may be reversed in the above calculation, and an energy W_B be found. The true van der Waals energy is given roughly by $W_AW_B/(W_A+W_B)$. This method gives a new approximate formula for the van der Waals interaction between two molecules, which reduces to a well-known result when further approximations are made. If system A is the molecule and system B a metallic surface, the energy W_A is that found by the image method. The energy W_B is also evaluated, and is shown to be of the same order of magnitude as W_A for ordinary electron densities in the metal. Thus the true energy of interaction may be considerably smaller than that given by the image method.

I. Introduction

The force between an electron or ionized molecule and a metallic surface is usually obtained by the classical method of images. While there can be little doubt that this procedure is justified for a relatively slowly moving ion, there is some question whether correct results will be obtained for the force on an electron whose velocity is comparable to the velocities of the electrons in the metal. Even more doubtful is the use of the image method for the calculation of the van der Waals interaction between a neutral molecule and metallic surface.

Experiments on the Schottky effect indicate that the image law holds for electrons at distances greater than $\sim 10^{-7}$ cm from the metallic surface. Some years ago[1] the author showed that on theoretical grounds one would expect the image law to hold asymptotically at large distances, but it was not possible to find the distance at which the law begins to break down. Since this work has not been reported on in detail, the theory is discussed below in Part II.

The first calculation of the van der Waals interaction between a molecule and a metallic surface, based on the method of images, was made by Lennard-Jones,[2] who showed that the energy depends on the inverse cube of the distance from the surface. Recently Pollard and Margenau[3] have reported a calculation based on a simplified model which indicated that the force should be much smaller than that obtained by Lennard-Jones. The smaller value was found to be in better agreement with the experimental heats of low temperature adsorption. Prosen, Sachs and Teller[4] based their calculation on a straightforward application of the second-order perturbation theory, and found that the energy is inversely proportional to the distance if a free electron gas is assumed in the metal, and is inversely proportional to the square of the distance for a degenerate Fermi gas. In these calculations, the interaction of the electrons in the metal was neglected.

A new approximate method for the calculation of dispersion forces, described below in Part III, shows that while the energy is inversely proportional to the cube of the distance, the magnitude may be in some cases considerably smaller than that given by the image method. The interaction between electrons is taken into account indirectly.

The results of the image method are obtained if it is assumed that the wave function for the

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[1] J. Bardeen, Phys. Rev. **49**, 640 (1936).

[2] J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 334 (1932). Due to a numerical error, the value given for the interaction energy is too large by a factor of two.

[3] W. G. Pollard and H. Margenau, Phys. Rev. **57**, 557 (1940).

[4] E. J. R. Prosen, R. G. Sachs and E. Teller, Phys. Rev. **57**, 1066 (1940).

metal depends parametrically on the coordinates of the external electrons. The expression for the kinetic energy then involves differentiation of the wave function with respect to the parameters. The terms involving these derivatives are neglected in the image treatment. It will be shown that this neglect is justified in the calculation of the force on an electron, but is not justified in the calculation of the van der Waals force on a neutral molecule.

II. Image Force on an Electron

Let the coordinates of the electrons in the metal be denoted by $y_1, y_2, \cdots y_N$, and the coordinates of the electron outside of the surface by $\mathbf{x}\equiv(x, y, z)$. The origin of coordinates is taken at the surface of the metal, with the z axis normal to the surface. The wave equation is

$$(H_M+H_e+V)\Psi(\mathbf{x}; y_1, y_2, \cdots y_N) = (E_M+W)\Psi, \quad (1)$$

in which H_M is the Hamiltonian for the metal, H_e is the Hamiltonian for the external electron, V is the interaction potential, and E_M is the normal energy of the metal. The explicit expression for the interaction potential is

$$V=e^2\sum_{i=1}^{N}|\mathbf{y}_i-\mathbf{x}|^{-1}-e^2\int\rho_+(\mathbf{y}')|\mathbf{y}'-\mathbf{x}|^{-1}d\tau'. \quad (2)$$

The positive charges in the metal are represented by the charge density $e\rho_+(\mathbf{y}')$. If the positive charges were discrete, the integral would be replaced by a sum, but in any case the calculation can be carried through formally with the integral form.

The wave function $\Psi(\mathbf{x}; y_1, \cdots y_N)$ may be written in the approximate form

$$\Psi(\mathbf{x}; y_1, \cdots y_N)=\psi(\mathbf{x}; y_1, \cdots y_N)\varphi(\mathbf{x}), \quad (3)$$

where $\psi(\mathbf{x}, y_1, \cdots y_N)$ is the wave function for the metal in which the coordinates of the external electron enter as parameters. It is a solution of

$$(H_M+V)\psi=(E_M+\omega(\mathbf{x}))\psi. \quad (4)$$

The energy $\omega(\mathbf{x})$ is the image potential $-e^2/4z$, as will be shown explicitly below (cf. Eq. (13)). The function ψ is normalized for all values of $\mathbf{x}$.

$$\int\cdots\int\psi^*\psi d\tau_1\cdots d\tau_N=1 \quad \text{for all } \mathbf{x}. \quad (5)$$

If the function Ψ given by (3) is introduced into (1), we find

$$(H_e+\omega(\mathbf{x}))\psi(\mathbf{x}; y_1, \cdots y_N)\varphi(\mathbf{x})=W\psi\varphi. \quad (6)$$

Now H_e contains a term $-(\hbar^2/2m)\Delta$ which operates on both ψ and φ,

$$H_e\psi\varphi=\psi H_e\varphi-\varphi(\hbar^2/2m)\Delta\psi - (\hbar^2/2m)\,\text{grad}\,\psi\cdot\text{grad}\,\varphi, \quad (7)$$

so that (6) becomes

$$\psi(H_e+\omega(\mathbf{x}))\varphi-\varphi(\hbar^2/2m)\Delta\psi - (\hbar^2/2m)\,\text{grad}\,\psi\cdot\text{grad}\,\varphi=W\varphi\psi. \quad (8)$$

A wave equation for φ may be obtained by taking the diagonal element of (8) with respect to the metallic wave function. Let us multiply through by ψ^* and integrate over the coordinates of the electrons in the metal. Due to the normalization condition, the integral

$$\int\cdots\int\psi^*\text{grad}\,\psi d\tau_1\cdots d\tau_N=0, \quad (9)$$

so that the diagonal element of the last term on the left of (8) is zero. It is true that this term will give a contribution to the energy in the second order, but the magnitude of this contribution[5] is smaller than that obtained from the diagonal element of the second term. We obtain the following equation for the motion of the external electron

$$\left[H_e+\omega(\mathbf{x})-(\hbar^2/2m)\int\cdots \times\int\psi^*\Delta\psi d\tau_1\cdots d\tau_N\right]\varphi=W\varphi. \quad (10)$$

It will be shown that the integral gives an energy of the order of a dispersion force, and so decreases with the cube of the distance from the surface.

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[5] The magnitude of this contribution to the energy can be estimated by a method similar to that used for the diagonal element of the second term of (8).

The image potential, $\omega(\mathbf{x})$ enters just as an ordinary potential into the equation of motion of the electron.

By taking the Laplacian of the normalization integral (5) we find that the integral in Eq. (10) may be expressed in the form:

$$\begin{aligned}-(\hbar^2/2m)&\int\cdots\int\psi^*\Delta\psi d\tau_1\cdots d\tau_N\\ &=(\hbar^2/2m)\int\cdots\int|\text{grad}\,\psi|^2 d\tau_1\cdots d\tau_N. \quad (11)\end{aligned}$$

To evaluate this integral, we start by taking the gradient of Eq. (4), the equation for the wave function of the metal, with respect to the coordinates of the external electron. The resulting equation is:

$$\begin{aligned}(H_M+V)\,&\text{grad}\,\psi+(\text{grad}\,V)\psi\\ &=(E_M+\omega(\mathbf{x}))\,\text{grad}\,\psi+(\text{grad}\,\omega(\mathbf{x}))\psi. \quad (12)\end{aligned}$$

This equation is of just the same form as that obtained in the ordinary first-order perturbation theory. It may be regarded as being obtained by treating $\boldsymbol{\varepsilon}\cdot$ grad V as a small perturbation introduced into Eq. (4). The first-order change in the wave function is then $\boldsymbol{\varepsilon}\cdot$ grad ψ, and Eq. (12) is the equation for grad ψ. In order that this equation have a solution, it follows in the usual way that

$$\text{grad}\,\omega(\mathbf{x})=\int\cdots\int\psi^*(\text{grad}\,V)\psi d\tau_1\cdots d\tau_N. \quad (13)$$

A direct evaluation of this integral, making use of the fact that a charge is induced on the surface of the metal of such a magnitude as to make the tangential components of the electric field vanish on the surface, shows, as one would expect, that $\omega(x)$ is just the ordinary image potential. Some deviation from the formula $\omega=-e^2/4z$ may be expected when the electron is very close to the surface, because the induced charge will not be concentrated on a plane. The amount of the deviation will depend on the structure of the metal.

Grad ψ may be expanded in terms of the proper functions of the metal, ψ_k, which satisfy the equation

$$(H_M+V)\psi_k=E_k\psi_k. \quad (14)$$

By the usual methods, we find

$$\text{grad}\,\psi=\sum a_k\psi_k, \quad (15)$$

where

$$a_k=(\text{grad}\,V)_{k0}/(E_0-E_k). \quad (16)$$

The integral (11) is therefore equal to

$$\begin{aligned}(\hbar^2/2m)&\int\cdots\int|\text{grad}\,\psi|^2 d\tau_1\cdots d\tau_N\\ &=(\hbar^2/2m)\sum a_k^2\\ &=(\hbar^2/2m)\sum|(\text{grad}\,V)_{k0}|^2/(E_0-E_k)^2. \quad (17)\end{aligned}$$

An estimate of the magnitude of $\sum a_k^2$ may be obtained from the sums

$$S_1=\sum a_k^2(E_0-E_k)=(E_0-E_k)_{\text{Av}}\sum a_k^2 \quad (18)$$

and

$$S_2=\sum a_k^2(E_0-E_k)^2=(E_0-E_k)^2_{\text{Av}}\sum a_k^2, \quad (19)$$

both of which may be computed with some accuracy. Thus one would expect that

$$\sum a_k^2\cong S_1^2/S_2, \quad (20)$$

at least as to order of magnitude.

The sum S_2 may be transformed to an integral,

$$\begin{aligned}S_2&=\sum|(\text{grad}\,V)_{k0}|^2\\ &=\int\cdots\int\psi^*(\text{grad}\,V)^2\psi d\tau_1\cdots d\tau_N, \quad (21)\end{aligned}$$

which can be evaluated explicitly. The term with $k=0$ has been included in the sum, but this term is of the order $1/z^4$ and so can be neglected in comparison with the sum of the remaining terms, which is of the order $1/z^3$. The integral depends on the structure of the metal. It is evaluated in part V for a model which should be approximately valid for the monovalent metals, with the result

$$S_2=Ce^4/8r_sz^3, \quad (22)$$

where C is a numerical factor of the order of magnitude unity, r_s is the radius of a sphere whose volume is equal to the volume occupied per electron, and z is the distance from the surface.

The sum S_1 is of the sort which occurs in the second-order perturbation theory:

$$S_1=\sum|(\text{grad}\,V)_{k0}|^2/(E_0-E_k). \quad (23)$$

Let $\boldsymbol{\varepsilon}$ be an arbitrarily small vector and consider Eq. (4) with $\mathbf{x}$ changed to $\mathbf{x}+\boldsymbol{\varepsilon}$. To the order ϵ^2, we have

$$(H_M+V+\boldsymbol{\varepsilon}\cdot\mathrm{grad}\ V+\tfrac{1}{2}(\boldsymbol{\varepsilon}\cdot\mathrm{grad})^2V)\psi = (E_M+\omega(\mathbf{x}+\boldsymbol{\varepsilon}))\psi. \quad (24)$$

If we treat the terms involving $\boldsymbol{\varepsilon}$ as a perturbation, we have, to the order ϵ^2,

$$\omega(\mathbf{x}+\boldsymbol{\varepsilon})=\omega(\mathbf{x})+\int\cdots\int\psi^*(\boldsymbol{\varepsilon}\cdot\mathrm{grad}\ V)\psi d\tau_1\cdots d\tau_N + \frac{1}{2}\int\cdots\int\psi^*\{(\boldsymbol{\varepsilon}\cdot\mathrm{grad})^2V\}\psi d\tau_1\cdots d\tau_N + \sum|(\boldsymbol{\varepsilon}\cdot\mathrm{grad}\ V)_{k0}|^2/(E_0-E_k). \quad (25)$$

We know that $\omega(\mathbf{x}+\boldsymbol{\varepsilon})$ is the image potential, $-e^2/4(z+\epsilon_z)$, which may be expanded in a power series in $\boldsymbol{\varepsilon}$:

$$-e^2/4(z+\epsilon_z)=-e^2/4z+(e^2/4z^2)\epsilon_z-(e^2/4z^3)\epsilon_z^2+\cdots. \quad (26)$$

By taking $\boldsymbol{\varepsilon}$ successively in the x, y, and z directions, and equation the powers of ϵ^2 on the two sides of (25), we find

$$0=\frac{1}{2}\int\cdots\int\psi^*(\partial^2V/\partial x^2)\psi d\tau_1\cdots d\tau_N + \sum|(\partial V/\partial x)_{k0}|^2/(E_0-E_k),$$

$$0=\frac{1}{2}\int\cdots\int\psi^*(\partial^2V/\partial y^2)\psi d\tau_1\cdots d\tau_N + \sum|(\partial V/\partial y)_{k0}|^2/(E_0-E_k),$$

$$-e^2/4z^3=\frac{1}{2}\int\cdots\int\psi^*(\partial^2V/\partial z^2)\psi d\tau_1\cdots d\tau_N + \sum|(\partial V/\partial z)_{k0}|^2(E_0-E_k). \quad (27)$$

The sum of these three equations gives us the value of S_1:

$$S_1=-e^2/4z^3-\frac{1}{2}\int\cdots\int\psi^*(\Delta V)\psi d\tau_1\cdots d\tau_N.$$

Since $\Delta V=0$ inside the metal, the integral vanishes, and

$$S_1=-e^2/4z^3. \quad (28)$$

The approximate value for the integral (11) is finally obtained as

$$(\hbar^2/2m)\int\cdots\int|\mathrm{grad}\ \psi|^2d\tau_1\cdots d\tau_N \sim(\hbar^2/2m)S_1^2/S_2=(\hbar^2/2m)(r_s/2Cz^3). \quad (29)$$

This is a correction to the kinetic energy resulting from the relative motion of the electrons in the metal and the external electron. It decreases with the cube of the distance from the surface, and so is negligible at large distances. This correction term becomes equal to the image potential at a distance

$$z_0=[(\hbar^2/2m)(2r_s/Ce^2)]^{\frac{1}{2}}=(r_s/Ca_0)^{\frac{1}{2}}a_0, \quad (30)$$

where, in the last equation a_0 is the atomic unit of length (0.528×10^{-8} cm). The density of the conduction electrons in sodium is such that $r_s=4a_0$, so that the distance z_0 is of the order a_0. Deviations from the image law due to the fact that the induced charge is not concentrated on a plane will occur before the correction to the kinetic energy is important. For all practical purposes, the latter may be neglected.

III. METHOD FOR CALCULATION VAN DER WAALS ENERGIES

Let us consider the interaction between two systems, A and B, with Hamiltonians H_A and H_B, together with an interaction potential $V(A, B)$. The wave equation is then

$$[H_A+H_B+V(A,B)]\Psi=(E_0^A+E_0^B+W)\Psi, \quad (31)$$

in which E_0^A and E_0^B are the energies of systems A and B in their normal states and W is the interaction energy. Let the proper functions and energies of A and B separately be φ_j^A, φ_k^B, and E_j^A, E_k^B:

$$H_A\varphi_j^A=E_j^A\varphi_j^A;\quad H_B\varphi_k^B=E_k^B\varphi_k^B. \quad (32)$$

The usual second-order perturbation treatment gives

$$W=V_{00,00}+\sum_{j\neq0}\frac{|V_{j0,00}|^2}{(E_0^A-E_j^A)}+\sum_{k\neq0}\frac{|V_{00,k0}|^2}{(E_0^B-E_k^B)} + \sum_{\substack{j\neq0\\k\neq0}}\frac{|V_{j0,k0}|^2}{(E_0^A-E_j^A+E_0^B-E_k^B)}, \quad (33)$$

in which $V_{j0,k0}$ is the matrix element

$$V_{j0,k0}=\int\int \varphi_j{}^{A*}\varphi_k{}^{B*}V(A,B)\varphi_0{}^{A}\varphi_0{}^{B}d\tau_A d\tau_B. \quad (34)$$

In some cases, although difficult to carry out the rigorous treatment, it is possible to carry through the calculation if it is assumed that in calculating the wave function and energy of one system, the coordinates of the other enter as parameters. The calculation of the van der Waals interaction between a molecule and a metal by the image method is an example of this sort.

Let us first assume that the electrons of A are in fixed positions, and calculate the energy, $E(A)$, which is a function of the coordinates of A, from the equation:

$$[H_B+V(A,B)]\psi(B,A) = [E_0{}^B+\epsilon(A)]\psi(B,A). \quad (35)$$

The second-order perturbation treatment gives

$$\epsilon(A)=V_{00}(A)+\sum_{j\neq 0}\frac{|V_{j0}(A)|^2}{(E_0{}^B-E_k{}^B)}, \quad (36)$$

where $V_{j0}(A)$ is the matrix element

$$V_{j0}(A)=\int \varphi_j{}^{B*}V(A,B)\varphi_0{}^B d\tau_B, \quad (37)$$

which depends on the coordinates of A parametrically. Now let $\epsilon(A)$ represent a potential acting on system A:

$$[H_A+\epsilon(A)]\Psi_A=(E_0{}^A+W_A)\Psi_A. \quad (38)$$

Then, again to the second order,

$$W_A=V_{00,00}+\sum_{j\neq 0}\frac{|V_{j0,00}|^2}{(E_0{}^A-E_j{}^A)}+\sum_{k\neq 0}\frac{|V_{00,k0}|^2}{(E_0{}^B-E_k{}^B)} +\sum_{\substack{j\neq 0\\ k\neq 0}}\frac{|V_{j0,k0}|^2}{(E_0{}^B-E_k{}^B)}, \quad (39)$$

which differs from the correct interaction potential, W, (Eq. 33) in the denominator of the last term.

If, instead, we reverse the above procedure and calculate the energy of system A by assuming that the coordinates of B enter parametrically, we find for the interaction energy

$$W_B=V_{00,00}+\sum_{j\neq 0}\frac{|V_{j0,00}|^2}{(E_0{}^A-E_j{}^A)}+\sum_{k\neq 0}\frac{|V_{00,k0}|^2}{(E_0{}^B-E_k{}^B)} +\sum_{\substack{j\neq 0\\ k\neq 0}}\frac{|V_{j0,k0}|^2}{(E_0{}^A-E_j{}^A)}. \quad (40)$$

In the application to the calculation of the van der Waals energy between nonpolar systems, the matrix element $V_{j0,k0}$ is different from zero only when both j and k are different from zero. Only the last terms of (33), (39) and (40) are then nonvanishing. Since $\sum|V_{j0,k0}|^2=(V^2)_{00,00}$ we may express W in the form

$$W=(V^2)_{00,00}/[E_0{}^A-E_j{}^A+E_0{}^B-E_k{}^B]_{\mathrm{Av}}, \quad (41)$$

and also

$$W_A=(V^2)_{00,00}/[E_0{}^B-E_k{}^B]_{\mathrm{Av}},$$
$$W_B=(V^2)_{00,00}/[E_0{}^A-E_j{}^A]_{\mathrm{Av}}. \quad (42)$$

The average energy differences are defined by these equations. One might expect that roughly

$$[E_0{}^A-E_j{}^A+E_0{}^B-E_k{}^B]_{\mathrm{Av}} =[E_0{}^A-E_j{}^A]_{\mathrm{Av}}+[E_0{}^B-E_k{}^B]_{\mathrm{Av}}. \quad (43)$$

With this assumption,

$$W=W_AW_B/(W_A+W_B). \quad (44)$$

While this procedure may be open to some doubt, one can say definitely that W is numerically smaller than either W_A or W_B, and also that if either W_A or W_B is very much smaller than the other, W will be close to the smallest.

IV. VAN DER WAALS FORCES BETWEEN NONPOLAR MOLECULES

The application of the method described in the preceding section to the calculation of the second-order van der Waals interaction between two molecules leads to a different expression from those obtained previously, although if certain further approximations are made, the result reduces to a well-known form.[6]

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[6] For a review of the theory of van der Waals forces, see H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

Let $X^A=\sum x_i^A$, the sum being extended over all the x coordinates of the electrons of molecule A, as measured from the center of gravity of the molecule. Let X^B be defined similarly for molecule B. The interaction potential may then be expressed in the form

$$V(A,B)=(e^2/r^3)(X^AX^B+Y^AY^B-2Z^AZ^B),\qquad(45)$$

where r is the distance between the molecules, and the z axis lies along the line joining them. The normal states of the molecules A and B may be degenerate. If we are interested only in the average value of the interaction energy, W, over all the degenerate states, W may be expressed in terms of the f values:

$$\begin{aligned}f_{j0}&=3f_{j0}{}^{(x)}\\&=(2L+1)^{-1}(2m/\hbar^2)\sum_{\mu\mu'}|X_{j\mu',0\mu}|^2(E_j-E_0),\qquad(46)\end{aligned}$$

where μ and μ' are the magnetic quantum numbers of the initial and final states, respectively, and L is the quantum number of the angular momentum. The expression derived by London[7] for W is

$$W=\frac{3}{2}\frac{e^2}{r^6}\frac{\hbar^2}{m^2}\sum_{j,k}\frac{f_{j0}{}^Af_{k0}{}^B}{(E_0{}^A-E_j{}^A)(E_0{}^B-E_k{}^B)(E_0{}^A-E_j{}^A+E_0{}^B-E_k{}^B)}.\qquad(47)$$

The corresponding expression for W_A, as given by (39) differs from the above in that the last factor in the denominator $(E_0{}^A-E_j{}^A+E_0{}^B-E_k{}^B)$ is replaced by $(E_0{}^B-E_k{}^B)$. For W_B the factor is $(E_0{}^A-E_j{}^A)$. By making use of the static polarizabilities,

$$\begin{aligned}\alpha_A&=(e^2\hbar^2/m)\sum_j f_{j0}{}^A(E_0{}^A-E_j{}^A)^2,\\\alpha_B&=(e^2\hbar^2/m)\sum_k f_{k0}{}^B(E_0{}^B-E_k{}^B)^2,\end{aligned}\qquad(48)$$

and the definition of the f values, W_A and W_B may be expressed in the form

$$\begin{aligned}W_A&=-(e^2/r^6)(R_A{}^2)_{\text{Av}}\alpha_B,\\W_B&=-(e^2/r^6)(R_B{}^2)_{\text{Av}}\alpha_A,\end{aligned}\qquad(49)$$

in which

$$(R^2)_{\text{Av}}=(2L+1)^{-1}\sum_\mu\{(X^2)_{0\mu}+(Y^2)_{0\mu}+(Z^2)_{0\mu}\}.\qquad(50)$$

It is, of course, possible to obtain W_A and W_B without making use of the second-order perturbation theory. Suppose that the electrons of A are in some fixed positions. They will produce a field which will polarize molecule B. The field produced by B will in turn react on A. If the corresponding interaction energy is averaged over the positions of the electrons of A, and also over the degenerate states, Eq. (49) for W_A is obtained.

The approximate value obtained for W is

$$\begin{aligned}W&\sim W_AW_B/(W_A+W_B)\\&=-\frac{e^2}{r^6}\left\{\frac{(R_A{}^2)_{\text{Av}}(R_B{}^2)_{\text{Av}}\alpha_A\alpha_B}{(R_A{}^2)_{\text{Av}}\alpha_B+(R_B{}^2)_{\text{Av}}\alpha_A}\right\}.\qquad(51)\end{aligned}$$

If there is but one term in (48) with an energy difference Δ, we may write

$$(R^2)_{\text{Av}}=3\alpha\Delta/2e^2\qquad(52)$$

and

$$W\sim-(3/2r^6)(\Delta_A\Delta_B\alpha_A\alpha_B/(\Delta_A+\Delta_B)).\qquad(53)$$

This formula, derived in a different way,[8] has been used to get an estimate of the van der Waals energy. The Δ's are often taken equal to the ionization potentials.

The expressions (51) and (53) give the correct values for the interaction between two harmonic oscillators. The van der Waals energy between two hydrogen atoms has been computed very exactly by means of a variational method,[9] with the result

$$W=-6.499(a_0/r)^6(e^2/a_0),\qquad(54)$$

where a_0 is the Bohr orbit radius. This provides a further check on the accuracy of the approximate formula (51). For hydrogen,

$$\begin{aligned}(R^2)_{\text{Av}}&=3a_0{}^2\\\alpha&=9a_0{}^3/2,\end{aligned}$$

so that

$$W\sim-6.75(a_0/r)^6(e^2/a_0),\qquad(55)$$

a result which is not very far from the exact value.

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[7] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

[8] This formula was originally derived by London. Cf. reference 6, Eq. C(10).

[9] L. Pauling and G. Y. Beach, Phys. Rev. **47**, 686 (1935).

V. Van der Waals Force Between a Molecule and a Metallic Surface

The method of Part III may be applied to the calculation of the van der Waals interaction between a molecule and a metallic surface. For simplicity we assume that there is but one electron in the molecule which contributes to the interaction, and that the wave function of this electron has spherical symmetry. It will later be easy to see how the result should be modified for the general case.

The origin of coordinates is taken at the center of the molecule, with the z axis perpendicular to the metallic surface, and D is the distance from the molecule to the surface. The coordinates of the electrons in the metal are again denoted by $y_1, y_2 \cdots y_N$, and those of the electron in the molecule by $x \equiv (x, y, z)$. The positive charges in the metal are represented by a charge density $\rho_+(y')$. The interaction potential, V, is then:

$$V = e^2 \sum_i \frac{\mathbf{x}\cdot\mathbf{y}_i}{y_i^3} - e^2 \int \frac{\mathbf{x}\cdot\mathbf{y}_i}{y'^3} \rho_+(\mathbf{y}') d\tau'. \tag{56}$$

If it is assumed that the electron in the molecule is in some fixed position, the energy may be calculated by the image method.

$$\begin{aligned} \omega(\mathbf{x}) &= -e^2/4D + e^2/(x^2+y^2+(z+2D)^2)^{\frac{1}{2}} \\ &\qquad - e^2/4(z+D) \\ &= -e^2(x^2+y^2+2z^2)/16D^3 + 0(D^{-4}). \end{aligned} \tag{57}$$

To get the van der Waals energy, we must average over all positions of the electron. Since $(x^2)_{\text{Av}} = (y^2)_{\text{Av}} = (z^2)_{\text{Av}} = \frac{1}{3}(r^2)_{\text{Av}}$, we find[10]

$$W_A = -e^2(r^2)_{\text{Av}}/12D^3. \tag{58}$$

The error involved in the application of the image method may be estimated in the same way as was done in Part II. According to Eq. (17), it is

$$\begin{aligned} (\hbar^2/2m) \sum_k |(\text{grad } V)_{k0}|^2/(E_0 - E_k)^2 \\ = (\hbar^2/2m)(S_1^2/S_2), \end{aligned} \tag{59}$$

where the matrix element is taken with respect to the metallic wave functions, and the sum is over all the stationary states of the metallic electrons. The gradient is taken with respect to the coordinates of the external electron. Since grad V is the same for the van der Waals case as it is for the case of a free electron external to the metal, the error involved is the same. According to Eq. (29) it is

$$(\hbar^2/2m)(r_s/2CD^3), \tag{60}$$

which, in many cases, may be as large or larger than the energy (58). Thus the image method cannot be used to calculate the van der Waals energy unless (60) is small compared with (58). The image method gives correct results in the limit of high electron densities in the metal (small r_s).

A more exact expression for the energy may be obtained by use of the method of Part III. We have already obtained W_A; we need further the energy W_B. The electrons in the metal are assumed to be in some fixed positions. These give rise to an electric field outside of the surface. The field vanishes only when averaged over all positions of the electrons in the metal. To obtain W_B, we compute the energy of the molecule in this field, and then average the result over the metallic wave function.

Since the interaction potential (56) is linear in the coordinates of the electron in the molecule, it may be expressed in the form

$$V = \mathbf{x}\cdot\text{grad } V, \tag{61}$$

with grad V independent of $\mathbf{x}$:

$$\text{grad } V = e^2 \sum_i \frac{\mathbf{y}_i}{y_i^3} - e^2 \int \frac{\mathbf{y}'}{y'^3} \rho_+(\mathbf{y}') d\tau'. \tag{62}$$

The change in the energy of the molecule due to this perturbation potential is

$$\epsilon(y_1, \cdots y_N) = \sum_j |(\mathbf{x}\cdot\text{grad } V)_{j0}|^2/(E_0^A - E_j^A). \tag{63}$$

The sum is over all states of the molecule. Replacing the energy denominator by a suitable average, we have:

$$\begin{aligned} \epsilon(y_1, \cdots y_N) &= -\sum_j |(\mathbf{x}\cdot\text{grad } V)_{j0}|^2/\Delta_A \\ &= -(\mathbf{x}\cdot\text{grad } V)_{00}{}^2/\Delta_A \\ &= -(\text{grad } V)^2(r^2)_{\text{Av}}/3\Delta_A \end{aligned} \tag{64}$$

with $\Delta_A = (E_j{}^A - E_0{}^A)_{\text{Av}}$. The last expression results from the assumption that the wave function for the electron in its lowest state is spherically symmetrical. The energy ϵ may also be expressed

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[10] Cf. reference 2.

in terms of the polarizability of the molecule, α_A.

$$\epsilon(y_1, \cdots y_N) = -\alpha_A(\text{grad } V)^2/2e^2. \qquad (65)$$

The van der Waals energy W_B is obtained by averaging $\epsilon(y_1, \cdots y_N)$ over the wave function for the metal.

$$\begin{aligned} W_B &= \int \cdots \int \psi_0^* \epsilon(y_1, \cdots y_N)\psi_0 d\tau_1 \cdots d\tau_N \\ &= -(r^2)_{\text{Av}} S_2/3\Delta_A, \end{aligned} \qquad (66)$$

where S_2 is the same integral as that discussed in Part II.

$$S_2 = \int \cdots \int \psi_0^* (\text{grad } V)^2 \psi_0 d\tau_1 \cdots d\tau_N. \qquad (67)$$

This integral may be evaluated in a straightforward way. Substituting the expression for grad V from Eq. (62), we find

$$S_2 = e^4 \int \cdots \int \psi_0^* \left\{ \sum_{ij} \frac{\mathbf{y}_i \cdot \mathbf{y}_j}{y_i^3 y_j^3} - 2\sum_i \int \frac{\mathbf{y}_i \cdot \mathbf{y}'}{y_i^3 y'^3} \rho_+(\mathbf{y}') d\tau' + \int\int \frac{\mathbf{y}' \cdot \mathbf{y}''}{y'^3 y''^3} \rho_+(\mathbf{y}')\rho_+(\mathbf{y}'') d\tau' d\tau'' \right\} d\tau_1 \cdots d\tau_N. \qquad (68)$$

Let

$$\rho(1, 2) = \int \cdots \int \psi_0^* \psi_0 d\tau_3 \cdots d\tau_N \qquad (69)$$

be the probability density of a given electron at y_1 and another given electron at y_2, and let

$$\rho(1) = \int \rho(1, 2) d\tau_2 \qquad (70)$$

be the probability density for electron (1). The density of electrons is $N\rho(1)$. With this notation, we may write (68) in the form:

$$\begin{aligned} S_2 = e^4 N \int y_1^{-4} \rho(1) d\tau_1 - e^4 \int\int \frac{\mathbf{y}_1 \cdot \mathbf{y}_2}{y_1^3 y_2^3} \{N^2 \rho(1)\rho(2) - N(N-1)\rho(1, 2)\} d\tau_1 d\tau_2 \\ + e^4 \left\{ \int \frac{\mathbf{y}_1}{y_1^3} (N\rho(1) - \rho_+(1)) d\tau_1 \right\}^2. \end{aligned} \qquad (71)$$

The last term vanishes because it is proportional to the square of the field strength due to the metal at a point outside of the surface of the metal.

In order to simplify the above, we may express $\rho(1, 2)$ in the form

$$\rho(1, 2) = (N/(N-1))\rho(1)\rho(2)(1 - g(1, 2)). \qquad (72)$$

If there were no interaction between the electrons $\rho(1, 2)$ would be equal to the product $\rho(1)\rho(2)$. Due to their mutual repulsion, the electrons will tend to have a more or less uniform space charge. Thus if an electron is known to be at $\mathbf{y}_1$, the probability that another electron is close to $\mathbf{y}_1$ is small. There is a hole in the charge distribution about a given electron which is of just sufficient size to accommodate one electron. This hole is represented by the function $g(1, 2)$, which becomes small when the distance $|\mathbf{y}_1 - \mathbf{y}_2|$ is large. It is probable that $g(1, 2)$ drops off exponentially with the distance. The field produced by a given electron is shielded by the neighboring electrons in such a way that at large distances the field has an exponential decrease. The factor $(N/(N-1))$ indicates that the probability of finding the second electron at a large distance from the first is slightly greater than would be expected from the separate probability densities. If the probability of finding the second electron at close distances from the first is less than normal, the probability of finding it at large distances is greater than normal.

If it is assumed that the electrons obey Fermi-Dirac statistics, but are otherwise free, it is found that $\rho(1, 2)$ is of the form (72). The function $g(1, 2)$ for this case has been evaluated by Wigner and Seitz.[11] At large distances of sepa-

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

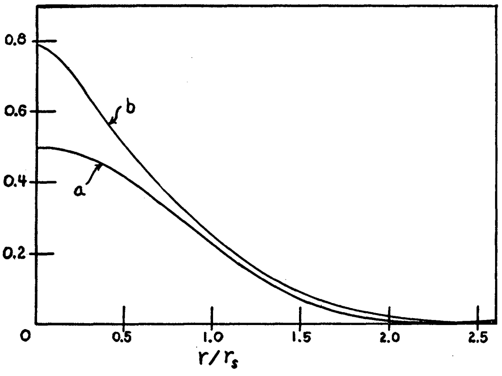

FIG. 1. Plot of the "hole" in the charge distribution about a given electron. (a) The exchange hole for electrons of parallel spin. (b) Assumed curve, taking into account the mutual repulsion of the electrons (after Slater, Rev. Mod. Phys. 6, 209 (1934)).

ration it decreases inversely with the fourth power of the distance between the electrons. For the reasons given in the preceding paragraph, it is probable that if the Coulomb repulsion between the electrons had been taken into account, it would be found that the decrease is actually exponential.

If we substitute (72) into (70), we find that

$$N\int \rho(2)g(1,\,2)d\tau_2=1 \tag{73}$$

for all y_1.

After some simplification, the following expression is obtained for S_2:

$$S_2=\tfrac{1}{2}e^4N^2\int\int\left(\frac{\mathbf{y}_1}{y_1^3}-\frac{\mathbf{y}_2}{y_2^3}\right)^2 \times\rho(1)\rho(2)g(1,\,2)d\tau_1d\tau_2. \tag{74}$$

The equivalence of (74) and (71) follows from (73) and the fact that $g(1,\,2)$ is a symmetric function of its variables.

The integral (74) will now be evaluated for a model which should be approximately valid for the monovalent metals. It is assumed that the density of electrons is uniform, and that $g(1,\,2)$ depends only on the distance $|y_1-y_2|$. Since $g(1,\,2)$ is large only when $|y_1-y_2|$ is small (of the order of atomic dimensions) we may write

$$\frac{\mathbf{y}_2}{y_2^3}=\frac{\mathbf{y}_1+\mathbf{n}}{|y_1+\eta|^3}\sim(\mathbf{y}_1+\mathbf{n})\left\{\frac{1}{y_1^3}-\frac{3(\mathbf{n}\cdot\mathbf{y}_1)}{y_1^5}\right\}, \tag{75}$$

in which $\mathbf{n}=\mathbf{y}_2-\mathbf{y}_1$. Thus, to the order η^2,

$$\left(\frac{\mathbf{y}_1}{y_1^3}-\frac{\mathbf{y}_2}{y_2^3}\right)^2=(\eta^2y_1^2+3(\mathbf{n}\cdot\mathbf{y}_1)^2)/y_1^8. \tag{76}$$

The average value of $3(\mathbf{n}\cdot\mathbf{y}_1)^2$ over all directions of the vector $\mathbf{n}$ is $\eta^2y_1^2$. By inserting the above values into Eq. (74) we find

$$S_2=e^4N^2\rho^2\int\int\frac{\eta^2}{y_1^6}g(\eta)d\tau_1d\tau_\eta. \tag{77}$$

Let[12]

$$N\rho\int\eta^2g(\eta)d\tau_\eta=Cr_s^2, \tag{78}$$

in which r_s is the radius of a sphere whose volume is equal to the volume occupied per electron ($N\rho=3/4\pi r_s^3$) and C is a dimensionless constant of the order of magnitude unity.

In order to evaluate the integral (78), it is necessary to make some assumption about the function $g(\eta)$, as no exact calculation of $g(\eta)$ which takes into account the mutual repulsion of the electrons has been given. For the case of free electrons obeying Fermi-Dirac statistics,[11]

$$g(\eta)=(9/2)(\sin\xi-\xi\cos\xi)^2/\xi^6, \tag{79}$$

where

$$\xi=(9\pi/4)^{\frac{1}{3}}(\eta/r_s)=1.92\eta/r_s.$$

A plot of this function is given in Fig. 1. If the expression (79) is inserted into (78), it is found that the integral diverges. The true function will decrease much more rapidly for large η in such a way as to insure convergence. A possible function is shown schematically in Fig. 1. This function decreases so rapidly that the contribution to the integral for values of η greater than $\sim 2.5\ r_s$ is negligible. A numerical evaluation of the integral using this function gives $C=2.6$. Actually, the shape of the curve will depend on the density of electrons and thus on r_s, so that C will depend on r_s, for ordinary electron densities, the order of magnitude of C will probably not be far from the value given above.

Making use of (78), we find that (77) reduces to:

$$S_2=Ce^4N\rho r_s^2\int\frac{d\tau_1}{y_1^6}=\frac{3C}{4\pi r_s}\cdot 2\pi\int_D^\infty\int_0^\infty\frac{r_1dr_1dz_1}{(r_1^2+z_1^2)^3}.$$

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[12] In order that this integral converge, it is necessary that $g(\eta)$ decrease more rapidly than the inverse fourth power of η when η is large.

The integration is elementary, and gives

$$S_2 = Ce^4/8r_sD^3. \tag{80}$$

Returning to Eq. (66), we find that

$$W_B = -(r^2)_{\text{Av}}Ce^4/24r_s\Delta_AD^3 = -(Ce^2/2r_s\Delta_A)W_A, \tag{81}$$

where W_A is the image value as given by (58). For the case of a general molecule, $(r^2)_{\text{Av}}$ should be replaced by $(R^2)_{\text{Av}}$ as defined by Eq. (50). In terms of the polarizability of the molecule, α_A, W_B is

$$W_B = -C\alpha_Ae^2/16r_sD^3. \tag{82}$$

The approximation (44) gives finally

$$W \sim W_AW_B/(W_A+W_B) = -(e^2(r^2)_{\text{Av}}/12D^3)\cdot\frac{Ce^2/2r_s\Delta_A}{1+Ce^2/2r_s\Delta_A}. \tag{83}$$

W will be smaller than the image value if Δ_A is large or if r_s is large.

For ordinary electron densities in the metal, and with Δ_A equal to about one Rydberg unit (13.5 ev), the factor $Ce^2/2r_s\Delta_A$ is about unity, so that W is about one-half of the image value W_A.

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Theory of the Approach to Magnetic Saturation

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The standard theoretical treatment of magnetization at high fields leads to a formula $J = J_s - b/H^2$; experimentally, a term $-a/H$ is also found. In the standard treatment it is assumed that the internal forces responsible for the incompleteness of saturation are approximately uniform over distances containing a very large number of atoms. If these forces vary rapidly over shorter distances, the interatomic coupling forces prevent the direction of microscopic magnetization from varying with equal rapidity, and the $1/H^2$ law no longer follows. It is shown here that for $H \gg 4\pi J_s$, point, line, and plane concentrations of force lead to laws of the form $J = J_s - a/H^{n/2}$, with $n = 1$, 2, and 3, respectively. For $H \ll 4\pi J_s$ the law is of the same form, but with different apparent values of J_s and a. For $H \overset{\frown}{=} 4\pi J_s$ the behavior is more complicated. The conclusion that the observed a/H term is due to line concentrations of force is supported by the dependence of a on degree of plastic strain, since the mechanism of plastic flow is believed to be a propagation of dislocation lines through the lattice.

§1. INTRODUCTION

At fields much larger than the coercive force, a ferromagnetic material behaves almost reversibly. The theoretical calculation of this part of the magnetization curve is therefore comparatively simple. The conventional treatment leads, at sufficiently high fields, to a formula[1]

$$J = J_s - b/H^2, \tag{1}$$

where H is the magnetic field, J is the magnetization, J_s is the "spontaneous" magnetization predicted by the Weiss-Heisenberg theory at the temperature in question, and b is a constant. In deriving this formula it is assumed that the material is magnetized to a value J_s at each point but that the *direction* of the magnetization varies from one region to another. This is illustrated very crudely in the upper part of Fig. 1. A soft specimen is assumed to consist of unstrained crystals, a hard specimen of regions each under approximately uniform internal stress. Forces due to crystalline anisotropy or to the distortion of the lattice tend to pull the magnetization vector into certain directions, represented by the dotted arrows; these directions are related to the principal axes of the crystal or of the system of internal stresses. As the field is increased, it overcomes these forces and pulls the magnetization vector toward the field direction.

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[1] F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill, 1937), p. 222.