The Interaction Between a Molecule and a Metal Surface

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The interaction between a molecule and a metal surface is discussed from the point of view of the perturbation theory. The interaction energy is found to be inversely proportional to the distance, R, between metal and molecule if the electron degeneracy in the metal is not taken into account and to $R^{-2}\log R$ if this degeneracy is taken into account. The application of the perturbation theory as given here is limited to values of R of the order of magnitude of the Bohr radius because of the neglect of the electron-electron interaction.

1. INTRODUCTION

THE energy of interaction of an atom or molecule with a metal surface has been calculated by Lennard-Jones[1] with the help of a semi-classical picture of the interaction process. He treated the metal classically; that is, its effect on the molecule was assumed to be given by the classical image potential acting on the electrons and nuclei in the molecule. On the other hand, the molecule was treated as a quantum-mechanical system with this image potential acting as a perturbation. The resulting interaction energy turned out to be proportional to R^{-3}, where R is the distance between the molecule and metal surface.

The limitations of this treatment have been discussed by Bardeen[2] who estimated that when the metal as well as the molecule is treated quantum mechanically the resulting interaction energy is still proportional to R^{-3} but it is about half as great as that given by Lennard-Jones. The discrepancy arises from the fact that the Lennard-Jones treatment neglects a term in the kinetic energy of the system of molecule plus metal.

The purpose of the present paper is to treat the problem of the interaction of the molecule and metal directly by means of the perturbation theory. In order to calculate the interaction energy in this way it will be necessary to make specific assumptions about the metal wave functions. In Section 2 these wave functions will be assumed to be products of plane electron waves with the result that the interaction energy is proportional to R^{-1}. Since the exclusion principle has not been taken into account, this result applies only when the density of conduction electrons in momentum space is low; that is, it applies to semiconductors and probably to metals at very high temperatures.

In Section 3 the influence of the exclusion principle is considered. The resulting interaction energy is proportional to $R^{-2}\log R$. Thus, in both cases (Sections 2 and 3) the perturbation theory leads to a smaller interaction energy than the Lennard-Jones and Bardeen treatments for small R. For large R the perturbation method as given here breaks down because of the neglect of the interactions between electrons in the metal. It will be shown in Section 4 that these interactions become important at that value of R for which the perturbation and Lennard-Jones energies become equal. Thus, taking into account the result of Bardeen, it appears that the Lennard-Jones treatment gives an upper limit to the binding energy for all values of R.

It is interesting to note that the R^{-3} dependence of energy on distance is just what would be expected for the interaction of a molecule with the surface of an insulator. The van der Waals interaction between each atom in the insulator and the external molecule is proportional to the inverse sixth power of the distance between them. If this interaction is integrated over all atoms in the insulator, the resulting total interaction is proportional to R^{-3}.

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[1] J. E. Lennard-Jones, Trans. Faraday Soc. **28**, 333 (1932).

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

2. INTERACTION WITH A SEMICONDUCTOR

If the molecule is so far from the metal surface that the wave functions of the molecule and metal electrons do not overlap appreciably, the interaction between the molecule and metal may be treated as a perturbation. In first approximation, this interaction is due to the field of the instantaneous dipole moment of the molecule which acts on the electrons and positive ions in the metal. Since the average value of the dipole moment of the molecule is zero, the first-order perturbation energy vanishes and the energy of interaction of the molecule and metal will be given by the second-order term

$$W=\sum_m{}' \frac{P_{0m}P_{m0}}{E_0-E_m},$$

where $P_{0m}=P^*_{m0}$ are the matrix elements given by

$$P_{0m}=\int \psi_0{}^* P \psi_m d\tau.$$

ψ_0 and ψ_m are the wave functions of the system of molecule plus metal in the initial state and in the mth excited state, respectively. P is the potential energy of the interaction of the electrons and positive ions in the metal with the instantaneous dipole field of the molecule. E_0 and E_m are the energies of the states ψ_0 and ψ_m.

The potential energy P is the sum of three terms:

$$P=P^x+P^y+P^z,$$

where

$$P^x=M^xH^x, \quad P^y=M^yH^y, \quad P^z=M^zH^z.$$

M^x, M^y, and M^z are the components of the dipole moment of the molecule and H^x, H^y, and H^z are quantities depending only on the position of the center of gravity of the molecule and the positions of the electrons and positive ions in the metal. The explicit expressions for H^x, H^y, and H^z will be given below.

Since in zeroth approximation the metal and molecule are independent systems, the wave functions ψ_0 and ψ_m can be written as the product of a molecular wave function, ϕ, and a metal wave function, χ; thus

$$\psi_0=\phi_0\chi_0, \quad \psi_m=\phi_j\chi_k$$

and P^x_{0m}

$$P^x_{0m}=\int \phi_0{}^* M^x \phi_j d\tau \int \chi_0{}^* H^x \chi_k d\tau,$$

or

$$P^x_{0m}=M^x_{0j}H^x_{0k}, \quad P^y_{0m}=M^y_{0j}H^y_{0k}, \quad P^z_{0m}=M^z_{0j}H^z_{0k}.$$

Therefore

$$W=\sum_{x,j,k}{}' \frac{M^x_{0j}M^x_{j0}H^x_{0k}H^x_{k0}}{E_{00}-E_{jk}}. \tag{1}$$

$\sum_{x,j,k}$ indicates a summation over $x=x, y, z$, over all states j of the molecule, and over all states k of the metal. The prime indicates that the term $j=0$ is to be omitted.[3] By definition

$$E_{00}=E_0+E'_0, \quad E_{jk}=E_j+E'_k,$$

where E_0 and E_j refer to the energies of the ground and jth states of the molecule and E'_0, E'_k to the initial and kth states of the metal.

In Eq. (1) cross terms of the type

$$M^x_{0j}M^y_{j0}H^x_{0k}H^y_{k0}$$

do not occur as can be shown by consideration of the symmetry properties of the dipole moment with respect to reflection in planes of symmetry.

The expression $E_{00}-E_{jk}$ which occurs in the denominator of Eq. (1) is equal to $(E_0-E_j)+(E'_0-E'_k)$ where $E'_0-E'_k$ refers to an electron transition in the metal. The positive ions in the metal can also make transitions to new vibrational states but their contribution to the interaction energy can be shown to be small. Electronic transitions corresponding to large energy changes, $E'_0-E'_k$, will contribute little to the interaction energy as compared to those involving small ones because the dipole field varies slowly in the metal so that in the Fourier expansion of this field in the metal the short wave-length terms corresponding to large momentum changes for the electrons have small amplitudes. Thus, for all important terms in Eq. (1), $E'_0-E'_k$ may be neglected as compared to E_0-E_j in the energy denominator. The interaction energy can then be written

$$W=\sum_{x,j\neq 0} \frac{M^x_{0j}M^x_{j0}}{E_0-E_j}(\textstyle\sum_k H^x_{0k}H^x_{k0}).$$

[3] The terms for which $j=0$, $k=0$ do not occur because the diagonal elements of the dipole moment vanish.

This expression can be simplified by observing that

$$\alpha_{xx}=-2\sum{}'_j\frac{M^x_{0j}M^x_{j0}}{E_0-E_j},$$

$$\alpha_{yy}=-2\sum{}'_j\frac{M^y_{0j}M^y_{j0}}{E_0-E_j},$$

$$\alpha_{zz}=-2\sum{}'_j\frac{M^z_{0j}M^z_{j0}}{E_0-E_j}$$

are the diagonal elements of the polarizability tensor of the molecule. Therefore

$$W=-\tfrac{1}{2}\sum_x\alpha_{xx}(\sum_k H^x_{0k}H^x_{k0}).$$

Averaged over all orientations of the molecule, this becomes

$$W=-\tfrac{1}{2}\alpha\sum_{x,k}H^x_{0k}H^x_{k0} \tag{2}$$

with

$$\alpha=\langle\alpha_{xx}\rangle_{Av}=\langle\alpha_{yy}\rangle_{Av}=\langle\alpha_{zz}\rangle_{Av}.$$

The quantities H^x are sums of terms corresponding to the interaction of the dipole field of the molecule with each electron and positive ion in the metal. Thus H^x can be expressed in the form

$$H^x=\sum_e H^x(e)+\sum_n H^x(n)$$

with

$$H^x(e)=\epsilon x_e/r_e^3,\quad H^x(n)=-\epsilon x_n/r_n^3, \tag{3}$$

where $\mathbf{r}_e=(x_e, y_e, z_e)$, $\mathbf{r}_n=(x_n, y_n, z_n)$ are the distances between the molecule and the eth electron and nth positive ion, respectively. ϵ is the electronic charge. Similar equations hold for the terms in y and z. The calculation for just the x term will be carried out until further notice. The x axis is perpendicular to the surface of the metal.

We now have

$$\sum_k H^x_{0k}H^x_{k0}=\sum_k(\sum_e H^x_{0k}(e)+\sum_n H^x_{0k}(n))\times(\sum_e H^x_{k0}(e)+\sum_n H^x_{k0}(n)).$$

Since the positive ions do not undergo transitions, only those positive ion terms with $k=0$ are important. Therefore

$$\sum_k H^x_{0k}H^x_{k0}=\sum_k(\sum_e H^x_{0k}(e)+\sum_n H^x_{00}(n)\delta_{0k})\times(\sum_e H^x_{k0}(e)+\sum_n H^x_{00}(n)\delta_{k0}). \tag{4}$$

The terms $\sum_n H^x_{00}(n)$ just cancel the sums of the electron diagonal matrix elements if we assume a smeared out charge distribution for the positive ions. If the positive ions are properly treated as discrete particles, these terms do not exactly cancel since there is a non-vanishing field outside of the metal. However this field vanishes exponentially over a distance of the order of a lattice spacing in the metal. Therefore, as long as the molecule is at a distance from the metal surface that is great compared to the lattice spacing, the difference between the terms can be neglected and Eq. (4) becomes

$$\sum_k H^x_{0k}H^x_{k0}=\sum_{k\neq 0}(\sum_e H^x_{0k}(e))(\sum_e H^x_{k0}(e)). \tag{5}$$

It is now necessary to make some specific assumption about the wave functions of the electrons in the metal. For the present it will be assumed that these functions are products of plane waves. Thus if $u_\alpha{}^\alpha$ is the plane wave $\exp(-ik_\alpha r_\alpha)$ corresponding to the αth electron in the αth state, the wave function for the initial state will be taken to be

$$\chi_0=\prod_\alpha u_\alpha{}^\alpha. \tag{6a}$$

The only excited states, χ_k, that will be of interest are those for which only one electron, say the βth, is excited to the state β'. The wave functions for these states are assumed to be

$$\chi_{\beta'}=u_\beta{}^{\beta'}\prod_{\alpha\neq\beta}u_\alpha{}^\alpha, \tag{6b}$$

if

$$u_\beta{}^{\beta'}=c\exp(-ik_{\beta'}r_\beta).$$

The quantitative discussion of the effect of the Fermi degeneracy will be taken up in the next section. However if the density of electrons in momentum space is much less than two electrons per h^3/V (V is the volume of the metal), the effect of the Fermi degeneracy is negligible. Therefore the calculations in this section can be applied to semi-conductors and probably to metals at very high temperatures, since in these cases the density of conduction electrons in momentum space is small.

The interaction between electrons is neglected in both this section and next. It will be shown in Section 4 that the relative error introduced by this neglect increases with increasing distance between metal and molecule.

Making use of the wave functions (6), one finds

$$H^x_{0\beta'}(\beta)=\int u_\beta{}^{\beta*}H^x(\beta)u_\beta{}^{\beta'}d\tau_\beta \tag{7}$$

$$H^x_{0\beta'}(\alpha)=0, \quad \alpha\neq\beta,$$

because of the orthogonality of the $u_\beta{}^{\beta*}$ and $u_\beta{}^{\beta'}$. Also because of this orthogonality, all matrix elements $H^x_{0k}(e)$ vanish for which more than one electron makes a transition since the operator $H^x(e)$ involves the coordinates of only one electron. With these results, Eq. (5) may be expressed in the form

$$\sum_k H^x_{0k}H^x_{k0}=\sum_\beta \sum_{\beta'\neq 0} H^x_{0\beta'}(\beta)H^x_{\beta'0}(\beta). \tag{8}$$

It can be seen that

$$\sum_{\beta'} H^x_{0\beta'}(\beta)H^x_{\beta'0}(\beta)=(H^{x^2}(\beta))_{00}$$

or

$$\sum_{\beta'\neq 0} H^x_{0\beta'}(\beta)H^x_{\beta'0}(\beta)=(H^{x^2}(\beta))_{00}-(H^x_{00}(\beta))^2. \tag{9}$$

It is not difficult to show by means of Eqs. (3) and (7) that $(H^x_{00}(\beta))^2$ is proportional to L^{-1} where L is a measure of the linear dimensions of the metal. Thus, if the metal is sufficiently large, this term can be neglected and Eq. (8) becomes

$$\sum_k H^x_{0k}H^x_{k0}=\sum_\beta (H^{x^2}(\beta))_{00}. \tag{10}$$

Now

$$(H^{x^2}(\beta))_{00}=\int u_\beta{}^{\beta*}H^{x^2}(\beta)u_\beta{}^{\beta}d\tau_\beta$$

or since $u_\beta{}^\beta=L^{-\frac{3}{2}}\exp(-ik_\beta r_\beta)$,

$$(H^{x^2}(\beta))_{00}=L^{-3}\int (H^x(\beta))^2 d\tau_\beta=\epsilon^2L^{-3}\int\int\int \frac{x^2}{r^6}dxdydz$$

according to Eq. (3). Summing this over all electrons in the metal is equivalent to multiplying by ρL^3, where ρ is the number of electrons per unit volume in the metal, so

$$\sum_k H^x_{0k}H^x_{k0}=\rho\epsilon^2\int\int\int \frac{x^2dxdydz}{(x^2+y^2+z^2)^3}.$$

The integration is to be carried out over the volume of the metal which will be taken to be an infinite half-space.

If R is the perpendicular distance between the molecule and metal, an elementary integration yields

$$\rho\epsilon^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_R^\infty \frac{x^2dxdydz}{(x^2+y^2+z^2)^3}=\frac{\rho\epsilon^2\pi}{2R}.$$

The corresponding terms involving H^y and H^z are

$$\sum_k H^y_{0k}H^y_{k0}=\rho\epsilon^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_R^\infty \frac{y^2dxdydz}{(x^2+y^2+z^2)^3}=\frac{\rho\epsilon^2\pi}{4R}$$

and

$$\sum_k H^z_{0k}H^z_{k0}=\frac{\rho\epsilon^2\pi}{4R},$$

respectively.

Inserting these results in Eq. (2), one obtains

$$W=-\frac{\alpha}{2}\frac{\pi\rho\epsilon^2}{R}. \tag{11}$$

It is to be noted that in the above derivation no explicit use has been made of the assumption that the electron wave functions are plane waves.

3. THE EFFECT OF ELECTRON DEGENERACY

In order to take into account the Fermi degeneracy of the electrons in the metal, it is necessary to antisymmetrize the wave functions (6). Then the electrons cannot make transitions to those states that are already occupied so the sum on the right-hand side of Eq. (8) is not carried out over a complete set of one-electron states and the completeness theorem, Eq. (9), can no longer be applied. It will therefore be necessary to calculate the sum

$$S_x(\beta)=\sum_{\beta'\neq 0} H^x_{0\beta'}(\beta)H^x_{\beta' 0}(\beta),$$

where β' runs through all values corresponding to only unoccupied states.

Since, insofar as the calculation of matrix elements is concerned, the only important part of the function $H^x(\beta)$ is that part for which the wave functions of the metal electrons do not vanish, we introduce the function $f_x(x, y, z)$ which is equal to $H^x(\beta)$ within the metal and zero outside of the metal. Thus, according to Eq. (3),

$$f_x=\epsilon x/r^3, \quad f_y=\epsilon y/r^3, \quad f_z=\epsilon z/r^3$$

for $x>R$, and

$$f_x=f_y=f_z=0$$

for $x<R$ if the x axis is perpendicular to the surface of the metal and its origin is taken to be at the molecule.

The functions f_x, f_y, and f_z can be expressed as Fourier integrals;

$$f_x=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a_x(\boldsymbol{\tau})\exp[i(\boldsymbol{\tau}\cdot\mathbf{r})]d\tau_x d\tau_y d\tau_z,$$

where the amplitudes $a_x(\boldsymbol{\tau})$ are determined by

$$a_x(\boldsymbol{\tau})=\frac{1}{2\pi^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_x\exp[-i(\boldsymbol{\tau}\cdot\mathbf{r})]dxdydz.$$

With the wave functions (6), the matrix element is

$$H^x_{0\beta'}(\beta)=L^{-3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f_x\exp[i([\mathbf{k}_\beta-\mathbf{k}_{\beta'}]\cdot\mathbf{r})]dxdydz$$

or

$$H^x_{0\beta'}(\beta)=(2\pi)^3 a_x(\boldsymbol{\tau})L^{-3} \tag{12}$$

with

$$\boldsymbol{\tau}=\mathbf{k}_{\alpha'}-\mathbf{k}_\alpha.$$

The explicit expressions for the Fourier amplitudes are

$$a_x(\boldsymbol{\tau})=\frac{\epsilon}{(2\pi)^3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{R}^{\infty}\frac{x\exp[-i(\boldsymbol{\tau}\cdot\mathbf{r})]}{(x^2+y^2+z^2)^{\frac{3}{2}}}dxdydz.$$

In order to carry out the integration over x, consider the complex integral

$$\oint\frac{\xi\exp(-i\tau_x\xi)}{(\xi^2+a^2)^{\frac{3}{2}}}d\xi=0$$

with $\xi=x+iw$ and $a^2=y^2+z^2$. The path of integration is indicated in Fig. 1. Letting the radius bd of

the arc cd approach infinity, we obtain

$$\int_R^\infty \frac{x\exp(-i\tau_x x)}{(x^2+a^2)^{\frac{3}{2}}}dx = i\exp(-i\tau_x R)\int_0^{-\infty}\frac{(R+iw)\exp(\tau_x w)}{(R^2+2iRw-w^2+a^2)^{\frac{3}{2}}}dw.$$

Integration of the right-hand side of this equation by parts yields

$$\int_R^\infty \frac{x\exp(-i\tau_x x)}{(x^2+a^2)^{\frac{3}{2}}}dx = \frac{i\exp(-i\tau_x R)}{\tau_x}\left[\frac{R}{(R^2+a^2)^{\frac{3}{2}}} - \frac{i}{\tau_x}\frac{a^2-2R^2}{(R^2+a^2)^{\frac{5}{2}}}+\cdots\right]. \tag{13}$$

This expansion is valid only if the changes, τ_x, in momentum of the electron are greater than R^{-1}

If only the first term of the expansion is used,

$$a_x(\tau) = \frac{i\exp(-i\tau_x R)}{(2\pi)^3}\frac{\epsilon}{\tau_x}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{R\exp[-i(\tau_y y+\tau_z z)]}{(R^2+y^2+z^2)^{\frac{3}{2}}}dydz. \tag{14}$$

It can be shown[4] that the integral over y and z behaves like $\exp(-[\tau_y+\tau_z]R)$, so the important amplitudes occur for those changes in momentum that are less than R. Therefore the only important changes, τ, in momentum are those vectors lying in a cylinder which is parallel to the x axis and has a radius equal to R^{-1} (cf. Fig. 2).

The expression that is to be evaluated is, according to Eq. (12)

$$S_x(\beta) = \sum_{\beta'\neq 0} H^x_{0\beta'}(\beta)H^x_{\beta' 0}(\beta) = \frac{(2\pi)^3}{L^3}\int\int\int |a_x(\tau)|^2 d\tau_x d\tau_y d\tau_z. \tag{15}$$

The limits of integration are to be chosen in such a way that $\tau = \mathbf{k}_{\alpha'} - \mathbf{k}_\alpha$ corresponds to a transition from a filled to an unfilled state. According to Fig. 2, this means that, for positive τ_x, the lower limit on τ_x is equal to $k_{mx}-k_{\beta x}$, where the vector $\mathbf{k}_m$ has a magnitude given by the momentum of the electron in the highest occupied state in the metal and a direction such that its end point lies in the cylinder of allowed transitions. For negative τ_x, the upper limit is given by $-(k_{mx}+k_{\beta x})$.

The integration is to be carried out over all values of τ_y and τ_z since the lower limit on τ_x makes it certain that the transition will carry the electron out of the Fermi lake. Therefore Eq. (15) is

$$S_x(\beta) = 2\pi^3 L^{-3}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left[\int_{(k_{mx}-k_{\beta x})}^{\infty}|a_x|^2 d\tau_x + \int_{-\infty}^{-(k_{mx}+k_{\beta x})}|a_x|^2 d\tau_x\right]d\tau_y d\tau_z. \tag{16}$$

The integration over τ_y, τ_z can be replaced by one over y, z by means of Parseval's theorem which can be expressed in the form

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|a_x(\tau)|^2 d\tau_y d\tau_z = \frac{1}{(2\pi)^4}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\epsilon^2 R^2 dydz}{\tau_x^2(R^2+y^2+z^2)^3} = \frac{1}{4(2\pi)^3}\frac{\epsilon^2}{\tau_x^2 R^2},$$

when use is made of Eq. (14). Thus

$$S_x(\beta) = \frac{\epsilon^2}{4L^3R^2}\left[\int_{(k_{mx}-k_{\beta x})}^{\infty}\frac{d\tau_x}{\tau_x^2} + \int_{-\infty}^{-(k_{mx}+k_{\beta x})}\frac{d\tau_x}{\tau_x^2}\right] = \frac{\epsilon^2}{2L^3R^2}\frac{k_{mx}}{(k_{mx}^2 - k_{\beta x}^2)}.$$

Similarly

$$S_y(\beta) = S_z(\beta) = \frac{\epsilon^2}{4L^3R^2}\frac{k_{mx}}{(k_{mx}^2 - k_{\beta x}^2)}; \tag{17}$$

and finally

$$\sum_x S_x(\beta) = \frac{\epsilon^2}{L^3R^2}\frac{k_{mx}}{(k_{mx}^2 - k_{\beta x}^2)}.$$

[4] Cf. E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, 1927), p. 384.

According to Eq. (8), this expression is to be summed over all electrons, i.e., over β. The number of electrons with momenta between $\mathbf{k}$ and $\mathbf{k}+d\mathbf{k}$ is $2(2\pi)^{-3}L^3dk_xdk_ydk_z$ hence the sum over electrons is

$$\sum_{\beta,x} S_x(\beta)=\frac{2\epsilon^2}{(2\pi)^3R^2}\int\int\int \frac{k_{mx}}{k_{mx}^2-k_x^2}dk_xdk_ydk_z.$$

Since the expansion (13) is valid only for changes, τ_x, in momentum that are greater than $1/R$, the upper limit in the integration over k_x will be taken to be $k_{mx}-1/R$. The contribution of those electrons with momenta between k_{mx} and $k_{mx}-1/R$ will be estimated below. Integration over k_x gives

$$\sum_{\beta,x} S_x(\beta)=\frac{2\epsilon^2}{(2\pi)^3R^2}\int\int \log(2Rk_{mx}-1)dk_ydk_z. \tag{18}$$

according to the definition of $\mathbf{k}_m$, $k_{mx}^2=k_m^2-(k_y^2+k_z^2)$. If this is inserted into (18), the double integral can be carried out directly by introducing polar coordinates in the k_y-k_z plane. The limits of integration are to be chosen in such a way that $1/R\leq k_{mx}\leq k_m$. The result is

$$\sum_{\beta,x} S_x(\beta)=\frac{2\epsilon^2}{(2\pi)^3}\frac{\pi k_m^2}{R^2}\log 2k_mR, \tag{19}$$

when R is chosen in such a way that $k_mR\gg 1$.

The contribution of electrons with momenta between k_{mx} and $k_{mx}-1/R$ is still to be added to (19). This contribution is certainly less than that of an equal number of free electrons. The latter can be obtained from the results of Section 2, for according to this section, if all the electrons were free the right-hand side of Eq. (19) should be replaced by $\pi\rho\epsilon^2/R$. Since the ratio of the number of electrons with momenta between k_{mx} and $k_{mx}-1/R$ to the total number is $3/k_mR$, the term that is to be added to (19) is less than $3\pi\rho\epsilon^2/R^2k_m$. By substituting $\rho=k_m^3/3\pi^2$, the ratio of the added term to the term already given is less than $1/4\pi\log 2k_mR$. This quantity is much less than one for $k_mR\gg 1$, so the additional term can be neglected and Eq. (19) is correct as it stands.

The interaction energy can now be obtained from Eq. (2) by making use of Eqs. (8) and (19) and the definition of $S_x(\beta)$. The result is

$$W=-\frac{\alpha\epsilon^2\pi k_m^2}{(2\pi)^3}\frac{\log 2k_mR}{R^2}. \tag{20}$$

The factor πk_m^2 in this expression is just the area of that cross section of the surface of maximum energy in momentum space which passes through the origin and is perpendicular to the x axis.

The assumption that the constant energy surfaces in momentum spaces are spheres is, of course, an idealized one. For a real metal, account should be taken of the true dependence of energy on momentum. However, since Eq. (20) does not depend explicitly on the mass of the electron, the more correct formula can be obtained from Eq. (20) simply by replacing the cross-sectional area πk_m^2 by the corresponding area for the actual surface of maximum energy. If it happens that the surface of maximum energy touches the surface of a Brillouin zone, the area of contact must be subtracted from the cross-sectional area.

4. THE ELECTRON-ELECTRON INTERACTION

In the two foregoing sections, use has been made of metal wave functions that are products of one-electron functions. This implies that the Coulomb interaction between electrons in the metal has been taken into account only insofar as the average effect of all electrons on a given electron in concerned.

When the molecule is near the metal, the wave function of the metal electrons is perturbed. This change in wave function implies a change in charge density near the surface of the metal, which in turn involves a change in the Coulomb interaction between electrons. An estimate of the change in Coulomb energy can be obtained by averaging the electron-electron interaction over

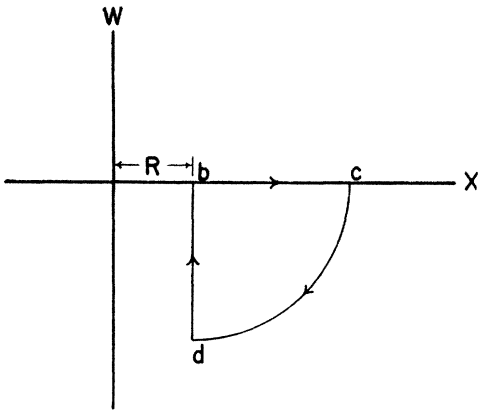

FIG. 1. Path of integration.

the perturbed wave function which is

$$\psi=\phi_0\chi_0+\sum_x\sum_{\beta'}\sum_{j\neq 0}\frac{M^x_{0j}}{E_0-E_j}H^x_{0\beta'}\phi_j\chi_{\beta'}. \quad (21)$$

The notation used here is the same as that given in Section 2.

An estimate of this average can be given for the case of the semi-conductor (Section 2) but is somewhat more difficult to obtain when the Fermi degeneracy is taken into account. In the latter case, the electron-electron interaction is somewhat smaller than in the former because the antisymmetrization of the wave function implies a greater average distance between electrons. Therefore an estimate given for the Coulomb term in the non-degenerate case is an upper limit for that term in the degenerate case, and the limits of validity to be given below for the former result (Eq. 11) are, if anything, too stringent when applied to the latter result (Eq. 20).

The average over the wave function (21) can be carried out by introducing the Fourier analysis of the interaction potential in the same way as in Section 3. When the sum in Eq. (21) is carried out over all one-electron states, the average value of the sum of the electron-electron, electron-positive ion, and positive ion-positive ion interactions is found to be

$$K=\frac{\rho^2}{2}\sum_{j\neq 0}\frac{M^x_{0j}M^x_{j0}}{(E_0-E_j)^2}\int\int\frac{\epsilon^4 x_1x_2d\tau_1d\tau_2}{r_1^3r_2^3|\mathbf{r}_1-\mathbf{r}_2|}. \quad (22)$$

The integration over both sets of variables is to be carried out over the volume of the metal so it is apparent that the integral diverges as the volume approaches infinity.

In order to eliminate this difficulty, the electron-electron interaction should be taken into account in the perturbation calculation. Since the effect of this interaction is to shield the electrons within the metal from the field of the dipole, it can be taken into account in a rough way by introducing a cut-off factor in the interaction potential between molecule and metal. For example, the potential $H^x(\beta)$ can be replaced by $H^x(\beta)\exp(-\mu\cdot\mathbf{r}_\beta)$, where μ is to be chosen large enough to guarantee that the average electron-electron interaction is small compared to the interaction between metal and molecule. It will be shown below that for sufficiently small values of R, this can be done in such a way that the energy W is still given by Eq. (11) to a very good approximation. The validity of the method is questionable for larger values of R since, then, the details of the method used in cutting off the potential become important.

Using the cut-off potential given above, the energy of interaction between metal and molecule becomes

$$W=-\frac{\alpha\rho}{2}\sum_x\int[H^x(\beta)]^2\exp[-2(\mu\cdot\mathbf{r}_\beta)]d\tau_\beta.$$

For $(\mu\cdot\mathbf{r}_\beta)<1$, the exponential can be expanded

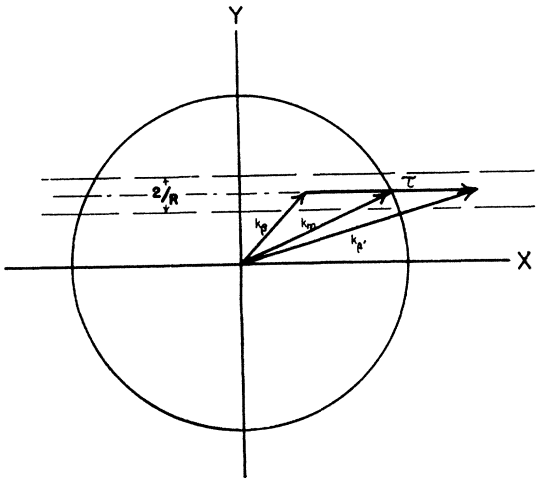

FIG. 2. Momentum vectors.

with the result

$$W=-\frac{\pi}{2}\alpha\rho\epsilon^2\left(\frac{1}{R}+\frac{2}{3}\mu\right)$$
$$+\alpha\rho\int_{(\mu\cdot\mathbf{r}_\beta)\leq 1}[H^z(\beta)]^2(\boldsymbol{\mu}\cdot\mathbf{r}_\beta)d\tau_\beta+\cdots.$$

The first term is just the value of W given by Eq. (11). It is not difficult to show that the term involving the integral becomes appreciable if

$$\mu\approx 1/R. \tag{23}$$

Thus the cut-off potential gives the same energy as the original treatment only if $\mu<1/R$.

Equation (22) is to be replaced by

$$K=\frac{\rho^2}{2}\sum_{j\neq 0}\frac{M^x_{0j}M^x_{j0}}{(E_0-E_j)^2}$$
$$\times\int\int\frac{\epsilon^4x_1x_2\exp\{-(\boldsymbol{\mu}\cdot[\mathbf{r}_1+\mathbf{r}_2])\}}{r_1^3r_2^3|\mathbf{r}_1-\mathbf{r}_2|}d\tau_1d\tau_2.$$

A rough evaluation of the integral yields

$$K\approx\frac{\pi^2\rho^2\epsilon^4}{\mu^5R^4}\sum_{j\neq 0}\frac{M^x_{0j}M^x_{j0}}{(E_0-E_j)^2}=\frac{\pi^2\rho^2\epsilon^4\alpha}{\mu^5R^4\Delta E},$$

where ΔE is some average difference in energy between levels in the molecule. The condition that K be negligible compared to W is

$$\frac{2\pi\rho\epsilon^2}{\mu^5R^3\Delta E}<1.$$

If Eq. (23) is taken into account, it follows that Eq. (11) breaks down for values of R of the order of magnitude of, or greater than $(\Delta E/2\pi\rho\epsilon^2)^{\frac{1}{3}}$. This distance is of the order of magnitude of the Bohr radius if ΔE refers to electronic transitions. The conclusion is, then, that there is, at best, a narrow region for which the Coulomb term can be neglected under the condition that the overlap between the molecular and metal wave functions is sufficiently small to justify a perturbation treatment. For semiconductors this region is much larger than for metals because of the smaller value of ρ for semiconductors.

Finally, the present method should be compared to that of Margenau and Pollard[5] which is also based on the second-order perturbation theory. They computed the interaction of the dipole field of a small element of metal with the molecule. The interaction of the molecule with a half-infinite metal body was then obtained by considering the metal to be made up of many such small elements and adding the contributions of each of them. The details of the metal wave functions were taken into account, at least in part, by introducing the experimentally measurable polarizability of the element of metal.

In order that the field of a metal element be correctly represented by a dipole field, the linear dimensions of the metal elements must be small compared to the distance, R, between the metal and molecule. Otherwise the higher multipole fields of the metal elements become important. On the other hand, the division of the metal into elements cannot be arbitrarily fine since it must be certain that each element behaves like a macroscopic piece of metal (i.e., has an experimentally measurable polarizability). This implies that the linear dimensions of the element must be very large compared to the lattice distance.

When these two conditions are taken together, it is apparent that R must be very large compared to the lattice distance. Thus the treatment of Margenau and Pollard applies for relatively great values of R, while, as we have seen before, the results given here are valid only in the region of small R. The interaction in the treatment given here will be particularly important for the calculation of heats of adsorption when much more becomes known of the repulsion potential between the molecule and metal.

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