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POLARIZATION OF ATOMS IN THE VICINITY OF SOLID SURFACES BY SURFACE ELECTRIC FIELD: EFFECT OF FIELD INHOMOGENEITY

By

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Abstract

The effect of inhomogeneity of the static electric field produced by a solid in the vicinity of its surface, on the polarization of adsorbed atoms is theoretically discussed. As a typical example, the polarization of rare gas atoms on surfaces of ionic crystals is considered. A few necessary formulas which express the polarization energy, or the energy due to the induction effect, in terms of the dipole and quadrupole polarizabilities of rare gas atoms are derived on the basis of the quantum mechanical perturbation theory, and the magnitude of the above effect is assessed. Some related problems, including the polarization of rare gas atoms on metallic surfaces, are discussed.

§ 1. Introduction

In the vicinity of a surface of an ionic crystal or metal there exists an inhomogeneous, static electric field arising from the array of ions or from peculiar spatial distribution of the electrons of the solid. In surface science, this kind of electric field and its relevance to a variety of surface processes including catalysis have often been discussed. Among others the polarization of physisorbed atoms (or molecules) has been the subject of numerous experimental and theoretical investigations. For one thing, the adsorbed atoms are polarized by the surface electric field and acquire dipole moments, which results in decrease of the work function of the surface on which the atoms are adsorbed. For another thing, the polarization causes lowering of the energy of the system; this energy change is usually given by the simple expression,

$$\Delta E = -\frac{1}{2} \alpha F^2, \quad (1)$$

where α is the polarizability, or the dipole polarizability of the atom and

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F is the electric field strength at the center of the atom. The polarization energy ΔE given by (1) contributes to the interaction energy between the surface and the atom; in other words, it is a part of the adsorption energy. In the theory of intermolecular forces, the interaction energy calculated by (1), or other expressions equivalent to it, is usually called the energy arising from the induction effect.¹⁾ In this case the polarization of one molecule by the static electric field produced by another molecule is dealt with.

In discussing the adsorption energy of rare gas atoms on ionic crystal surfaces²⁻⁵⁾ or on metal surfaces⁶⁻¹⁰⁾ the expression (1) has frequently been used. In deriving (1) we assume the homogeneity of the electric field over the region occupied by the atom as well as linear response of the atom to the field. However, in the very neighborhood of a solid surface the electric field is very often far from being homogeneous, *i. e.*, it rapidly varies over the small region occupied by the atom, which makes Eq. (1) inadequate. This fact was pointed out first by Lenel¹¹⁾ in 1933 and repeatedly by other authors.¹²⁾ The purpose of the present note is to present a method of calculating the correction term to be added to (1) in order to take the inhomogeneity of the electric field into account. In §2 a short preliminary discussion is given. In §3 necessary theoretical formulas are derived on the basis of the quantum mechanical perturbation theory. In §4 the results of a calculation on the argon atom physisorbed on the KBr (001) surface are presented, and a few related problems of current interest in surface physics are discussed. However more detailed calculations on a wider variety of systems and comparison of the results with experiments are left for a forthcoming paper.

§2. Preliminary Consideration

Consider the polarization of a spherical atom by the external electric field F produced by a point charge q_E (see Fig. 1). It can be shown (§3) that the energy change ΔE of the atom due to the polarization is given by

$$\Delta E = \Delta E_1 + \Delta E_2 \quad (2)$$

and

$$\Delta E_1 = -\frac{1}{2} \alpha F_z^2, \quad \Delta E_2 = -\frac{1}{8} \alpha_q F_{zz}^2, \quad (3)$$

where

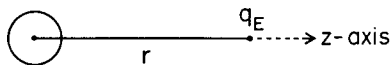


Fig. 1. A rare gas atom and an external point charge q_E .

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$$F_z = -\frac{q_E}{r^2} \text{ and } F_{zz} = \frac{\partial F_z}{\partial z} = -2\frac{q_E}{r^3}$$

are the z -component of the external electric field F at the center of the atom and its gradient in the z -direction, respectively; the direction of the z -axis is taken as shown in Fig. 1 and r is the distance between the atom and the charge. The first term ΔE_1 on the right hand side of (2) is the same thing as the energy given by (1); the second term ΔE_2 is the gradient correction to it and takes care of the inhomogeneity of the electric field around the center of the atom. Equations (3) for ΔE_1 and ΔE_2 are a special case of more general expressions to be derived in the next section. The quadrupole polarizability¹³⁾ α_q occurring there is an atomic property similar to the ordinary polarizability, or the dipole polarizability α . During the last two decades reliable values of quadrupole polarizability have been calculated for a number of atoms by using digital computers and theoretical tools such as the Hartree, the uncoupled Hartree-Fock, and the coupled Hartree-Fock methods.¹³⁾ Selected theoretical values of α_q for rare gas atoms together with those of α are shown in Table 1.

TABLE 1. Dipole and quadrupole polarizabilities,
 α and α_q .

atom	α	α_q
He	0.196* A ³	0.0967* A ⁵
Ne	0.350**	0.268**
Ar	1.493**	1.957**

* ref. 14.

** ref. 16.

Although the energy expression (2) together with (3) is an improvement over (1), it still rests on the assumption of linear response of the atom to the external electric field. If the electric field is very strong, say, 10^8 volt/cm or more, this linearity breaks down. The deviation from the linearity can be calculated by using another atomic property, hyperpolarizability^{13a)} of the atom, but this problem is beyond the scope of this note.

In order to see the relative importance of the term ΔE_2 , we consider the ratio,

$$R = \frac{\Delta E_2}{\Delta E_1} = \frac{1}{4} \frac{\alpha_q}{\alpha} \left(\frac{F_{zz}}{F_z} \right)^2. \quad (4)$$

From (3) and Table 1 we find, for $r=3$ A and the argon atom,

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$$R = \frac{\alpha_q}{\alpha} \frac{1}{r^2} = 0.146,$$

which indicates that ΔE_2 is not quite negligible as compared with ΔE_1 .

An atom in the vicinity of the surface of an ionic crystal, say, an alkali halide crystal, feels the static electric field produced by a large number of cations and anions which constitute the crystal (Fig. 2). Since these ions are spherical, they may be regarded as positive or negative point charges and the resultant electric field \mathbf{F} outside the crystal may be evaluated by summing up respective contributions of the ions.³⁾ In this case, however, the expressions for ΔE_1 and ΔE_2 become more complicated than (3) as will be shown in the next section. In any event the interaction energies ΔE_1 and ΔE_2 , of course, depend on the location of the atom. A numerical calculation made for an argon atom physisorbed on a (001) surface of a KBr crystal will be explained in § 4, and the numerical results will be given in Table 3, where we get an idea of the magnitudes of ΔE_1 and ΔE_2 , and their dependence on the location. Figure 3(I) illustrates the arrangement of ions in the (001) surface plane of an NaCl-type crystal.

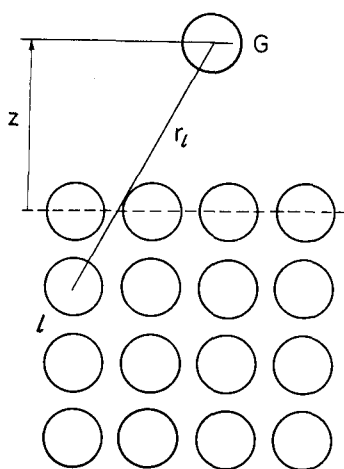


Fig. 2. A rare gas atom (G) interacting with an ionic crystal. The distance between the atom G and the crystal surface is denoted by z and that between the atom G and the ion l by r_l .

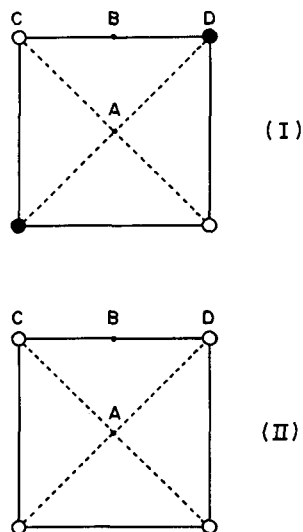


Fig. 3. The arrangement of ions in a (001) surface plane and adatom sites (A, B, C and D).

- : positive ion ●: negative ion
 (I) The case of an NaCl-type ionic crystal.
 (II) The case of a bcc metal.

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If the atom is located at the point A which is above the center of the lattice cell, the energy ΔE_1 becomes zero because the electric field \mathbf{F} vanishes at A owing to the symmetrical arrangement of ions. On the other hand, ΔE_2 does not vanish at A (Table 3) because the gradients of \mathbf{F} are non-zero.

The inhomogeneous electric field in the vicinity of a metal surface arises from the electric double layer formed at the surface. In the last ten years the peculiar electronic distribution in the surface region of metals, which gives rise to the surface double layer, has been the subject of numerous theoretical investigations.^{17,18)} Many of them are based on the density functional formalism¹⁸⁾ (Hohenberg, Kohn and Sham) and the uniform-background model (the jellium model) with planar surface.^{17,18)} In this model the positive charge density $\rho_+(\mathbf{r})$ of the uniform background is assumed to be written as

$$\rho_+(\mathbf{r}) = \begin{cases} 0 & \text{for } z > 0 \\ \rho_0 & \text{for } z < 0 \end{cases} \quad (5)$$

where ρ_0 is the constant density inside the metal. Thus the plane $z=0$ is the surface of the metal, or more exactly the surface of the jellium. Using the variational principle in the density functional formalism, Smith¹⁷⁾ has calculated the electron charge density $\rho_-(\mathbf{r})$ corresponding to (5) and obtained

$$\rho_-(\mathbf{r}) = -\frac{1}{2} \rho_0 e^{-\beta z} \quad \text{for } z > 0, \quad (6)$$

$$\rho_-(\mathbf{r}) = -\rho_0 \left(1 - \frac{1}{2} e^{\beta z}\right) \quad \text{for } z < 0, \quad (7)$$

where β is a variational parameter. The total charge density $\rho(\mathbf{r})$, *i. e.*, the sum of $\rho_+(\mathbf{r})$ and $\rho_-(\mathbf{r})$ is illustrated in Fig. 4. In other words, Fig. 4. depicts the surface double layer calculated by Smith. By considering the Poisson equation for the charge density $\rho(\mathbf{r})$, we can readily calculate the electric field \mathbf{F} arising from the double layer; the electric field \mathbf{F} is in the z -direction, *i. e.*, normal to the metal surface and

$$F_z = \frac{2\pi}{\beta} \rho_0 e^{-\beta z} \quad \text{for } z > 0, \quad (8)$$

$$F_{zz} = \frac{\partial F_z}{\partial z} = -2\pi \rho_0 e^{-\beta z} \quad \text{for } z > 0. \quad (9)$$

In Table 2 the values of the parameter β computed by Smith for various

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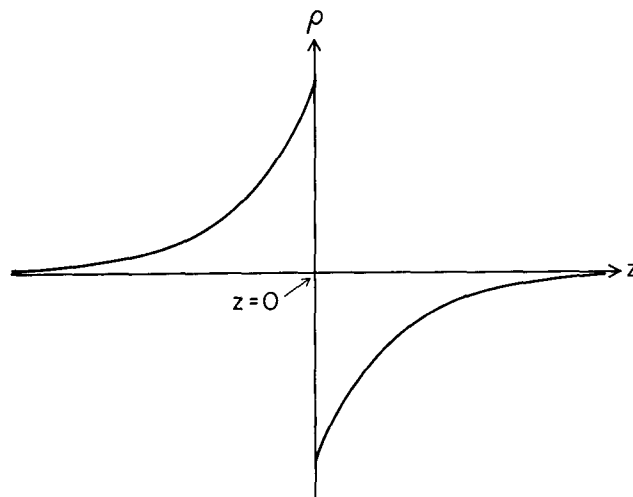


Fig. 4. The change of the charge density ρ with z in the uniform-background model with planar surface, of a metal (after Smith, ref. 17). The positive background terminates at $z=0$.

TABLE 2. The values of the parameters ρ_0 and β for selected metals (Smith, ref. 17)

metal	ρ_0	β
Rb	1.67×10^{-3} a. u.	1.32 a. u.
K	1.95	1.32
Na	3.77	1.27
Li	6.92	1.24
Ag	8.73	1.23
Au	8.80	1.23
Cu	12.6	1.23
Ca	6.90	1.24
Zn	19.5	1.22
Al	26.9	1.24
Pb	19.4	1.22
W	56.2	1.30

metals together with the values of ρ_0 are given. It is to be noticed that whereas ρ_0 varies considerably from one metal to another the value of β varies only slightly. Taking β to be 1.30 a. u., *i. e.*, 2.457 \AA^{-1} , we find

$$\left| \frac{F_{zz}}{F_z} \right| = \beta = 2.457 \text{ \AA}^{-1},$$

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which ratio gives us an idea of the magnitude of the field inhomogeneity and is to be compared with the value of the same ratio in (4) *i. e.*,

$$\frac{F_{zz}}{F_z} = \frac{2}{r} = 0.667 \text{ A}^{-1} \quad \text{for } r = 3 \text{ A}.$$

However the problem of the polarization of physisorbed rare gas atoms on metallic surfaces seems to be much more complicated than that of rare gas atoms on ionic crystals. We will come back to this problem in § 4.

§ 3. Perturbation Calculation

We are interested in the interaction between a rare gas atom [G] and a solid [S]; thus we consider a composite system [G]+[S], such as the one shown in Fig. 2. The perturbation calculation of the interaction energy^{1,19,24)} usually starts with an interaction potential of the form,

$$V = \sum_s^{[G]} \sum_t^{[S]} \frac{q_s q_t}{r_{st}}, \quad (10)$$

where $\sum_s^{[G]}$ is the summation over all the charged particles (electrons and nucleus) making up the atom [G], $\sum_t^{[S]}$ is a similar summation pertaining to the solid [S], q_s and q_t are the charges of particles s and t , and r_{st} is the distance between particles s and t . It is most convenient to introduce the multipole expansion²¹⁾ of V ,

$$V = \sum_{l=0}^{\infty} \left(\sum_{m=-l}^l (-1)^m M_m^{(l)} U_{-m}^{(l)} \right), \quad (11)$$

where the quantity in the parentheses is the scalar products of the tensor $M_m^{(l)}$ and $U_m^{(l)}$ which are defined by

$$M_m^{(l)} = \sum_s^{[G]} q_s r_s^l C_m^{(l)}(s). \quad (12)$$

$$U_m^{(l)} = \sum_t^{[S]} q_t \frac{1}{r_t^{l+1}} C_m^{(l)}(t). \quad (13)$$

In the last two equations, r_s and r_t are the distances from the nucleus of [G] to particle s in [G] and particle t in [S], respectively, and $C_m^{(l)}(s)$ is Racah's spherical harmonic, *i. e.*, $[4\pi/(2l+1)]^{\frac{1}{2}}$ times the ordinary spherical harmonic $Y_m^{(l)}(\theta_s, \phi_s)$. For further details of the above notation, ref. 21 by Pound is referred to. Now $M_m^{(l)}$ is the electric moment operator for the atom [G], $l=0, 1, 2, \dots$ corresponding to monopole, dipole, quadrupole, ...

moments, respectively. Since the atom is neutral (*i. e.*, it is not an ion), the monopole operator $M_0^{(0)}$ vanishes. Hence we have

$$V = \sum_{m=-1}^1 (-1)^m M_m^{(1)} U_{-m}^{(1)} + \sum_{m=-2}^2 (-1)^m M_m^{(2)} U_{-m}^{(2)} + \text{higher order terms.} \quad (14)$$

From the definition (13) we find

$$\begin{aligned} U_0^{(1)} &= \sum_t^{[S]} q_t z_t / r_t^3 = -f_z, \\ U_{\pm 1}^{(1)} &= 2^{-\frac{1}{2}} \sum_t^{[S]} q_t (\mp x_t - i y_t) / r_t^3 = 2^{-\frac{1}{2}} (\pm f_x + i f_y), \\ U_0^{(2)} &= \frac{1}{2} \sum_t^{[S]} q_t (3z_t^2 - r_t^2) / r_t^5 = -\frac{1}{2} f_{zz}, \\ U_{\pm 1}^{(2)} &= (3/2)^{\frac{1}{2}} \sum_t^{[S]} q_t (\mp x_t - i y_t) z_t / r_t^5 = 6^{-\frac{1}{2}} (\pm f_{xz} + i f_{yz}), \\ U_{\pm 2}^{(2)} &= (3/8)^{\frac{1}{2}} \sum_t^{[S]} q_t (x_t \pm i y_t)^2 / r_t^5 = (24)^{-\frac{1}{2}} (-f_{xx} + f_{yy} \mp 2i f_{xy}). \end{aligned} \quad (15)$$

where x_t , y_t and z_t are the coordinates of particle t , the origin of the coordinate system being the center of the atom; and f_α and $f_{\alpha\beta}$ are defined as

$$\begin{aligned} f_x &= - \sum_t^{[S]} \frac{q_t}{r_t^3} x_t, \text{ etc.} \\ f_{xx} &= - \sum_t^{[S]} \frac{q_t}{r_t^5} (3x_t^2 - r_t^2), \text{ etc.} \\ f_{xy} &= - \sum_t^{[S]} \frac{q_t}{r_t^5} 3x_t y_t, \text{ etc.} \end{aligned} \quad (16)$$

Disregarding higher order terms in (14), we use the perturbation theory to calculate the interaction energy arising from the potential (14). By making use of the fact that the electronic state of a rare gas atom in the ground state is spherically symmetric 1S , the calculation is simplified to a considerable extent. We readily find that the first-order energy vanishes because the unperturbed atom [G], which is spherical, possesses no permanent electric moments. The expression for the second-order energy in the perturbation theory involves the summation over intermediate excited states, which are now classified into the following three groups: (a) the states in which both [G] and [S] are being excited; (b) the states in which only [S] is being excited, and (c) the states in which only [G] is being excited. The summation over the intermediate states of group (a) yields

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the energy of the dispersion interaction (the interaction which gives rise to the London dispersion force).^{1,20)*} This interaction energy is usually the most important part of the attractive interaction between a rare gas atom and a solid. However, a considerable number of good theoretical papers on this kind of interaction between an atom (or a molecule) and a solid have been published since the pioneering work of Bardeen,¹⁹⁾ most recent examples being refs. 22~24, and we will not touch on this part of the interaction in the present note. The summation over the states of group (b) or group (c) yields the interaction energy due to the induction effect.¹⁾ However, the summation over the states of group (b) again vanishes because a rare gas atom does not possess any permanent electric moments to polarize the solid. Thus we will now go into the discussion of the summation over the states of group (c).

By virtue of the fact that the tensors $M_m^{(l)}$ and $U_m^{(l)}$ belong to the irreducible representations of the rotation group, the summation over the intermediate states of group (b) is again simplified and yields the interaction energy,

$$\Delta E = \Delta E_1 + \Delta E_2,$$

where

$$\Delta E_1 = -\frac{1}{2} \alpha (F_x^2 + F_y^2 + F_z^2) \quad (17)$$

and

$$\Delta E_2 = -\frac{1}{12} \alpha_q (F_{xx}^2 + F_{yy}^2 + F_{zz}^2 + 2F_{xy}^2 + 2F_{yz}^2 + 2F_{zx}^2). \quad (18)$$

In (17) and (18), F_α and $F_{\alpha\beta}$ are the expectation values of the operators f_α and $f_{\alpha\beta}$, respectively, and α and α_q are the dipole and quadrupole polarizabilities of the atom, which are given by¹³⁾

$$\alpha = 2 \sum_j \frac{1}{\epsilon_j - \epsilon_0} \langle 0 | M_0^{(1)} | j \rangle \langle j | M_0^{(1)} | 0 \rangle \quad (19)$$

and

$$\alpha_q = 2 \sum_j \frac{1}{\epsilon_j - \epsilon_0} \langle 0 | M_0^{(2)} | j \rangle \langle j | M_0^{(2)} | 0 \rangle, \quad (20)$$

where $\epsilon_j - \epsilon_0$ is the energy of the excitation from the ground state 0 to the excited state j of the atom [G] and the summation is over all the excited states of [G].

*) This interaction is very often called the van der Waals interaction. However we avoid using this name because it is not one of very precise usage (see ref. 1).

The above-mentioned expectation values of f_α and $f_{\alpha\beta}$ are to be calculated by using the ground state wave function of the unperturbed solid [S]. Hence we readily find from the definition (16) that F_α is the α -component ($\alpha=x, y, z$) of the electric field which the charged particles in [S] produce at the center of [G] and $F_{\alpha\beta}$ is the field gradient defined as

$$F_{\alpha\beta} = \frac{\partial F_\alpha}{\partial \beta} \quad (\alpha, \beta = x, y, z)$$

The gradients F_{xx} , F_{yy} and F_{zz} satisfy the Laplace equation,

$$F_{xx} + F_{yy} + F_{zz} = 0. \quad (21)$$

Now suppose that by virtue of the symmetry of a system under consideration the following relations hold;

$$F_x = F_y = 0, \quad F_{xx} = F_{yy} \quad \text{and} \quad F_{\alpha\beta} = 0 \quad \text{for} \quad \alpha \neq \beta. \quad (22)$$

Then (17) and (18) reduce to (3) in § 2 since the second equation of (22) implies that both F_{xx} and F_{yy} are equal to $-\frac{1}{2}F_{zz}$ owing to the Laplace equation (21).

§ 4. Numerical Results and Discussion

As a typical example, a numerical calculation has been carried out on the interaction between an argon atom and KBr crystal. The latter is a typical ionic crystal having the NaCl structure and consisting of spherical K^+ and Br^- ions. In order to calculate for such a crystal the electric field and its gradients to be used in (17) and (18), it should be a good approximation to work with a model crystal (point-ion model) which is obtained by replacing the cations in the real crystal by point charges each with charge $+e$ and the anions by point charges each with charge $-e$.* Then the electric field arising from these point charges and its gradients are calculated by a purely classical method^{2~5)} as has been mentioned in § 2. We have calculated ΔE_1 and ΔE_2 by (17) and (18) for an argon atom on the (001) surface of KBr crystal, whose lattice constant has been taken to be 6.59 Å. The results are given in Table 3, where the values have been obtained for four different locations or sites of the argon atom. These four sites A, B, C and D are illustrated in Fig. 3(I):

*) The charge transfer in lithium halide crystals, among alkali halide crystals, has been reported to be incomplete. For example, the ions in LiF crystal have been found to have charge $\pm 0.88e$ rather than $\pm e$ (ref. 25).

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- site A, above the center of the lattice cell ;
- site B, above the mid-point of a lattice edge ;
- site C, above a K^+ ion ;
- site D, above a Br^- ion.

Of course, the calculated values of ΔE_1 and ΔE_2 depend also on z , the distance between the atom and the surface lattice plane of KBr (Fig. 2). The second column of Table 3 gives the values of z used for the calculation (see below.).

TABLE 3. Calculated values of the energies ΔE_1 and ΔE_2 for the argon atom on the KBr (001) surface.

site	z	ΔE_1	ΔE_2
A	2.95 A	0.000 kcal/mole	0.087 kcal/mole
B	3.39	0.069	0.054
C	3.42	0.129	0.079
D	3.77	0.050	0.030

We can obtain from Table 3 an idea of the relative magnitudes of ΔE_1 and ΔE_2 , in which we are most interested in the present note. Perhaps, of more general interest is the total interaction energy between Ar and KBr. As the perturbation theoretical treatment in § 3 indicates the total interaction energy is obtained by adding ΔE_1 and ΔE_2 to the energy of the dispersion interaction provided that the atom is not too close to the solid surface. As the atom gets close to the surface the atom begins to feel the exchange repulsion force from the surface besides the long-range attractive interactions mentioned above; in this way the well-known minimum occurs in the curve of the total interaction energy as a function of the distance z . The shape of the curve in the neighborhood of the minimum is very important. It determines adsorption energy, "adsorption bond" length, and other quantities of physical and chemical interest. However, from a theoretical point of view, we encounter a difficulty in the calculation of the interaction energies in this region.

The perturbation-theoretical treatment presented in § 3 is based on the assumption that the atom is not too close to the surface, so that the wave function of the atom does not overlap that of the solid appreciably. If the overlap is negligibly small, the multipole expansion used in § 3 converges well and the electron exchange between the atom and the solid may be neglected. On the other hand, the exchange repulsion energy is determined by the wave function overlap and the ensuing electron

exchange.

A similar contradiction exists in the theory of the intermolecular forces.¹⁾ One "easy" way of evading the difficulty is to stop worrying too much about this contradiction and to compute the total interaction energy simply as the sum of independently calculated (or estimated) exchange repulsion energy and the long-range attractive interaction energy calculated by the perturbation method described in § 3 (in other words, the additivity is assumed). Another way of overcoming the difficulty is to develop a new perturbation expansion method which takes the overlap of the wave functions into account. There exist quite a few studies²⁶⁾ in this direction in the theory of intermolecular forces, but no such calculations have been made in connection with gas-solid interactions.²⁷⁾

The above-mentioned "easy" way has been adopted by several authors²⁻⁵⁾ in their calculation of the total interaction energies between rare gases and alkali halides. Among others Hayakawa⁴⁾ has calculated the Ar-KBr interaction but his calculation does not include ΔE_2 . He has shown that the total interaction energy takes its minimum value at the distance z given in Table 3; in other words, the z value there is the equilibrium distance, on each site, between the atom and the surface. Although the equilibrium distances in Table 3 will be slightly changed by adding the effect of ΔE_2 to the results of his calculation, those values have been used just for convenience sake.

More numerical calculations, including those of the total interaction energy, have been performed on a variety of rare gases and alkali halides, but the results will be published and discussed in a separate paper.²⁸⁾

We now turn to the case of a rare gas atom on a metallic surface and discuss a few related problems, which have not been completely solved as yet.

In § 2, a short discussion on the polarization of rare gas atoms on a metal has been given on the basis of the uniform-background model of metals. However the "atomic structure" of metals, which is entirely neglected in this model, might have an appreciable effect. In this connection a paper by Wojciechowski²⁹⁾ should be mentioned. In order to calculate the dispersion interaction energy between a molecule and a metal, perturbation methods as described in § 3 have been applied to the case in which the solid [S] is a metal, by Bardeen,¹⁹⁾ Prosen and Sachs^{29a)} Zaremba and Kohn,²⁴⁾ and others. Wojciechowski²⁹⁾ modified the Prosen-Sachs theory^{29a)} and obtained an energy expression which consists of the energy of dispersion interaction, and the energy due to the induction

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effect ΔE_1 given by (17). In his calculation, the following model for the metal [S] is considered: the metal is made up of positive ions and conduction electrons, and the former are regarded as positive point charges (the point-ion model) and the latter as free electrons confined in the metal by an infinite potential barrier placed at the metallic surface. Thus the electronic charge density $\rho_-(\mathbf{r})$ in the vicinity of the surface is given by^{29b)}

$$\rho_-(\mathbf{r}) = 0 \quad \text{for } z > 0, \quad (23)$$

$$\rho_-(\mathbf{r}) = -\rho_0 \left(1 - 3 \frac{\sin 2k_F z}{(2k_F z)^3} + 3 \frac{\cos 2k_F z}{(2k_F z)^2} \right) \quad \text{for } z < 0, \quad (24)$$

where k_F is the Fermi wave number of the conduction electrons. The expressions (23) and (24) are to be compared with (6) and (7) in § 2. This negative charge density $\rho_-(\mathbf{r})$ and the positive point charges (point-ions) generates a static electric field \mathbf{F} in the vicinity of the metallic surface. The energy ΔE_1 given by (17) is due to the polarization of the atom [G] by this field \mathbf{F} . With such a model having an atomic structure, contrary to the case of the uniform-background model, the calculated energy ΔE_1 evidently depends on the site of the rare gas atom on the surface (cf. Fig. 3 (II)), and also on the Miller indices of the surface. Then Wojciechowski claims that he has derived the dependence of the dispersion interaction on the crystallographical direction (Miller indices) of the surface. However this statement is rather misleading because, as one readily finds, the dispersion force part of his energy expression actually does not depend on the crystallographical direction^{*)} whereas his ΔE_1 part does. Meanwhile the expressions (23) and (24) for the electronic charge distribution is certainly less satisfactory¹⁸⁾ than (6) and (7). In any event he was not able to give any numerical results.

Recently Herbst³⁰⁾ calculated the angular distribution of photoelectrons emitted from rare gas atoms (*e. g.*, xenon) physisorbed on a metallic surface. In the model considered by him, the physisorbed atom lies partially inside the surface double layer of the metal and feels an electric field generated by nearby positive point-ions.^{**)}

Returning to the uniform-background model considered in § 2, we notice that the electric field \mathbf{F} at \mathbf{r} is proportional to the charge density

*) Of course this is due to the fact that the point-ions considered here do not have internal structure and thus can not be excited or polarized. See ref. 24 in this connection.

**) In the case of an atom on site A in Fig. 3(II), they are the four ions shown there plus the fifth ion directly below the atom, the effect of other ions being negligible owing to the shielding effect of the conduction electrons.

$\rho(r)$ there as (5), (6) and (8) indicate. In other words, the atom feels the electric field arising from the electric double layer to an appreciable extent only when the atom resides within the double layer,^{*} *i. e.*, only when the wave function of the atom overlaps with that of the metal to a considerable extent. In such a case the perturbation-theoretical treatment described in § 3 should be modified to include orbital overlap²⁶⁾ (see above), the detail of which will be discussed in a separate paper.²⁷⁾ An important consequence of the inclusion of orbital overlap is, besides the exchange repulsion^{23,31)} mentioned above, the occurrence of charge (electron) transfer from the physisorbed atom to the metal or *vice versa*. This kind of charge transfer and its contribution to physisorption energy and work function lowering have frequently been discussed for rare gas atoms on metal surfaces.³²⁻³⁷⁾

The change in work function arising from the adsorption of rare gas atoms on a metal surface is due to the change in the net surface dipole moment of the metal-atom system.⁴¹⁾ As has been mentioned above, the latter change has been related to the polarization of the atom by the static surface electric field,^{6-10,38)} and to the charge transfer between the atom and the metal.³²⁻³⁶⁾ However it has recently been pointed out³⁹⁻⁴²⁾ from the general theory of dispersion forces (van der Waals forces) that the change in net surface dipole moment is induced partly by the dispersion interaction.^{**)} This is very interesting, but a unified general theory which treats various effects or interactions simultaneously on the same footing^{***)} is highly desirable.

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^{*}) In this situation, the Laplace equation (21) should be replaced by the Poisson equation.

^{***)} Thus such a statement as "With a contribution by dispersion forces is meant here each interaction which does not cause a change in work function." (ref. 35) might cause confusion.

^{***)} In this respect, a recent calculation of the interaction between helium and metal surface by Zaremba and Kohn (ref. 37) is of particular interest although the dispersion interaction is still calculated separately in this work.

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