

Theory of the Electronic Configuration of a Metallic Surface-Adsorbate System

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The nature of the electronic phenomena involved in the adsorption of alkali atoms on a metallic substrate is discussed. The metal-adsorbate system is treated in terms of a simple model which makes possible a self-consistent calculation of the effective charge on the adsorbed atom. The atom is treated in the Slater approximation and the metal is assumed to be free-electron-like. Numerical results are presented for K, Rb, and Cs adsorbed on W in the presence of various electric fields.

I. INTRODUCTION

A VARIETY of experiments has been performed in which foreign atoms or molecules are adsorbed (or desorbed) on a metal substrate in the presence of very high electric fields. For example, systems consisting of Ba on W,¹ Cs on W,² and CO on W³ have all been studied in some detail.

Qualitatively, three types of adsorption are distinguished⁴: ionic, neutral, and metallic. If the metal is indicated by M and the adsorbate by A , the first type corresponds symbolically to a bond $M^+—A^-$ (or $M^+—A^-$), while the neutral type can be represented by $M^0—A^0$. The third (metallic) type is an intermediate case where only part of an electronic charge has been transferred from the atom to the metal (or vice versa). A quantitative distinction between these three types can be made in terms of the effective electronic charge q localized in the neighborhood of the adsorbate. In this fashion,

$$\begin{aligned} q \cong \mp |e| &\rightarrow \text{ionic adsorption,} \\ q \cong 0 &\rightarrow \text{neutral adsorption,} \\ 0 < |q| < |e| &\rightarrow \text{metallic adsorption.} \end{aligned}$$

Schmidt and Gomer⁵ have recently made a detailed study of the K on W system, and have estimated the electronic charge q as a function of coverage for various exposed crystallographic faces of the W substrate. It is the purpose of this paper to discuss the nature of the electronic phenomena which result in a metallic adsorption of atoms and formulate a simple model which allows an approximate quantitative calculation of q .

We restrict ourselves to electropositive adsorbates in which $q > 0$; in these cases $q \neq 0$ results from the partial emptying of the outermost level of the adsorbed atom. This partial emptying is due to the extended nature of the relevant wave functions.

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¹ E. W. Müller, *Phys. Rev.* **102**, 618 (1956).

² H. Utsugi and R. Gomer, *J. Chem. Phys.* **37**, 1720 (1962).

³ L. W. Swanson and R. Gomer, *J. Chem. Phys.* **39**, 2813 (1963).

⁴ R. Gomer and L. W. Swanson, *J. Chem. Phys.* **38**, 1613 (1963).

⁵ L. D. Schmidt and R. Gomer, *J. Chem. Phys.* **45**, 1605 (1966).

At large separations, when the overlap between metallic wave functions and the atom is very small, the atomic wave function can be considered a good eigenstate, with a well-defined energy E_A . Under these conditions, the occupation of that level is either zero or one, corresponding to the two extreme types of adsorption discussed above. At smaller separations the clear-cut distinction between atomic and metallic states is no longer valid, and, from the point of view of the electronic wave functions, the system should be treated as a whole. The very existence of a charge transfer makes it necessary to include (at least) self-consistency in any theory which hopes to provide a method of calculation.

In what follows we confine our attention to a single adsorbed atom with a single, filled s level in the outermost electronic shell. Since the nature of the problem emphasizes the extended character of the wave functions, we neglect all possible localized surface states.

In Sec. II we define the parameters that are relevant in the calculation. The effective charge q depends on these parameters which are, in turn, functions of q . In Secs. III and IV we arrive at explicit forms for the functional dependence of the parameters and in Sec. V the expressions are combined to obtain a self-consistent solution of the problem.

II. FORMULATION OF THE PROBLEM

The problem under consideration is a many-electron one. The single-electron wave functions which contribute to the many-electron state are, for the metal-atom separations of interest, extended throughout the metal and the atom. In other words, no single electron state is localized around the atom position (as it would be in the case of large separations) giving a finite contribution to the electronic charge q ; thus q is made up from the contributions of an infinitely large number of states, each contributing an infinitesimal amount. In the absence of localized states the Hartree approximation, which neglects exchange as well as correlation effects, is known to be a reasonable one. We then assume that the total wave function of the system Ψ can be expressed as a simple product of one electron functions.

$$\Psi = \prod_i \psi(E_i, l_i, \nu_i; \mathbf{r}_i), \quad (2.1)$$

where each one-electron wave function ψ is determined by three quantum numbers: E , one-electron Hartree energy; l , angular momentum in a direction perpendicular to the surface; ν , a third quantum number which completes the identification of the state. These quantum numbers emphasize the cylindrical symmetry of the problem, the normal to the surface through the atom center defining the axis. It is not necessary to include spin explicitly, since by assuming that not more than one electron can occupy the relevant s state, we have assumed a strong correlation effect between the spins close to the adsorbate and in fact restricted ourselves to only one of the two spin systems.

Each of the ψ functions satisfies a Schrödinger equation of the form

$$H\psi(E, l, \nu) = E\psi(E, l, \nu), \quad (2.2)$$

where H is the self-consistent one-electron Hartree Hamiltonian obtained by minimizing the total energy

$$E_T = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (2.3)$$

with respect to Ψ . In (2.3) \mathcal{H} is the total Hamiltonian for the many-electron system. The Hartree Hamiltonian H will be discussed in detail in the next section.

It is useful at this stage to define an energy density-of-states $n_{l\nu}(E)$ such that any sum over the quantum number E can be replaced by an integral, i.e.,

$$\sum_{El\nu} \rightarrow \sum_{\nu} \int \dots n_{l\nu}(E) dE. \quad (2.4)$$

It is easy now to define the effective charge in a volume V (which is of the order of an atomic volume) around the atom:

$$q = |e| [1 - q^-], \quad (2.5)$$

$$q^- = \sum_{\substack{El\nu \\ \text{occupied} \\ \text{states}}} \int_V |\psi(E, l, \nu; \mathbf{r})|^2 d^3r. \quad (2.6)$$

This last expression can be rewritten as⁶

$$q^- = \int_{-\infty}^{\infty} \frac{\rho(E) dE}{\exp\left[\frac{E - E_F}{kT}\right] + 1} \xrightarrow{T \rightarrow 0} \int_{-\infty}^{E_F} \rho(E) dE, \quad (2.7)$$

where E_F is the Fermi energy (maximum occupied value of E at zero temperature) and

$$\rho(E) \equiv \sum_{\nu} \int_V d^3r |\psi(E, l, \nu; \mathbf{r})|^2 n_{l\nu}(E). \quad (2.8)$$

$\rho(E)$ is the effective electronic charge per unit Hartree energy.

⁶ We restrict ourselves to low temperatures $T \rightarrow 0$; the extension to finite temperatures is straightforward. The effect of finite temperatures on q^- is of the order of kT/Δ , where Δ is the Lorentzian width defined below.

Before attempting a calculation of $\rho(E)$, we present a qualitative discussion of its properties. We first consider the atom at large separations from the metal surface. Because of the negligible overlap the Hartree wave functions are in this case the atomic wave function and the undisturbed electronic wave functions of the metal. The only contribution to the electronic charge in the neighborhood of the atom comes from the atomic level, which has a well-defined energy E_A . This means that

$$\rho(E) = \delta(E - E_A). \quad (2.9)$$

The effective charge is therefore zero or one, depending on whether E_A is below or above the Fermi energy E_F . As the metal-atom separation is reduced, tunneling takes place and the Hartree wave functions become delocalized. The density $\rho(E)$ is no longer a delta function; it spreads and its maximum is shifted. We may assume that $\rho(E)$ can be represented by a Lorentzian distribution

$$\rho(E) = \frac{1}{\pi} \frac{\Delta}{(E - E_\phi)^2 + \Delta^2}, \quad (2.10)$$

where Δ is the (positive definite) width of the level and E_ϕ the position of the maximum.

From Eq. (2.7) we have

$$q^- = \frac{1}{\pi} \left[\tan^{-1} \frac{E_F - E_\phi}{\Delta} + \frac{\pi}{2} \right], \quad (2.11)$$

where we have assumed that the shifted position of the "atomic level" E_ϕ is always well above the bottom of the metallic band (U), i.e.,

$$E_\phi - U \gg \Delta. \quad (2.12)$$

Figure 1 is a graphical representation of Eq. (2.11); the family of curves shown corresponds to various values of Δ .

If this model is correct, E_ϕ and Δ should depend on the external parameters (atomic number of the nucleus, metal-atom separation d , applied external electric field F), as well as on the value of q^- itself, and the equations should then be solved in a self-consistent fashion.

In order to justify Eq. (2.10) [or to find in fact a more accurate form for $\rho(E)$], and to calculate E_ϕ and the width Δ we need first an expression for the one-electron Hartree Hamiltonian H of Eq. (2.2). This Hamiltonian, obtained by a minimization of the total energy of the system, is of the form

$$H = T + V_M + V_A + V_F + V_{ee}, \quad (2.13)$$

where T is the kinetic energy operator, V_M is the potential due to the metal ions, V_A is the potential of the adsorbate ion, V_F is the potential due to an external electric field F , and V_{ee} is the self-consistent potential acting on one electron and due to the average charge distribution of all other electrons. The complete solution

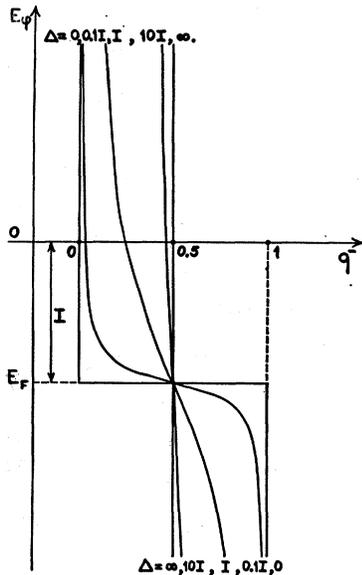


FIG. 1. The effective charge q^- as a function of the position of E_ϕ with respect to the Fermi level E_F .

of the Hartree equations is, if not impossible, certainly an extremely cumbersome numerical problem. We can, however, make some drastic simplifications in the form of (2.13), which, based on the conclusions of previous work, allow an approximate solution to the problem. This solution has the right qualitative features and is also capable of giving fairly accurate quantitative answers for the values of q^- .

It has been shown that:

(a) The potential inside the metal is, for the conduction electrons of simple metals, effectively very smooth⁷; it is a good first approximation to assume that V_M can be replaced by the potential due to a uniform background of positive charge.

(b) The conduction electrons inside the metal screen the effect of any field outside. Except for a rather thin layer where the screening takes place, the total field is zero inside.

(c) The dipole layer at the surface of the metal, which is responsible for the screening discussed in (b), is much narrower than the typical distances involved in our calculations,⁵ and can be consequently assumed to be of zero width.

(d) The effect of V_{ee} for an electron outside the metal due to electrons inside the metal can be approximately replaced by a classical image potential V_{im} , which guarantees a constant potential (taken to be zero) at the surface of the metal.⁸

With these approximations (2.13) can be written as

$$H = T + UP_L + [V_{A'} + V_F + V_{im}]P_R, \quad (2.14)$$

⁷ See, for instance, J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1964).

⁸ J. Bardeen, *Phys. Rev.* **49**, 640 (1936); P. H. Cutler and J. J. Gibbons, *ibid.* **111**, 394 (1958).

where U is the constant potential inside the metal and $V_{A'}$ is the potential due to the adsorbate ion modified by the effective charge q^- of the electrons in its neighborhood. The function $P_L(P_R)$ takes the value one inside (outside) the metal, and the value zero elsewhere, i.e.,

$$\begin{aligned} P_L = 1, \quad P_R = 0, \quad x < 0; \\ P_L = 0, \quad P_R = 1, \quad x > 0. \end{aligned} \quad (2.15)$$

Figure 2 shows a pictorial representation of the potential and defines our energy scale and system of coordinates.

III. PERTURBATION THEORY

A proper solution of the Schrödinger equation (2.2) would entail either a complicated numerical procedure or the matching of analytic wave functions for a variety of points on the metal surface; this calculation would have to be repeated for all values of the relevant external parameters.

We propose here the use of perturbation theory in a scheme similar to that developed by Fano^{9,10} to treat a rather different kind of problem, i.e., the mixing of a discrete atomic level with the continuum due to configuration interaction. This problem resembles the one under consideration in the fact that, in the absence of interaction, a well-defined quantum level and a continuum exist, and the interactions broaden the atomic level into a "resonance" with a characteristic width.

In order to apply Fano's method we restrict ourselves to the following manifold of functions:

(a) An atomic s -like wave function φ which satisfies the Schrödinger equation

$$H_A \varphi \equiv (T + V_{A'}) \varphi = E_A' \varphi. \quad (3.1)$$

(b) A continuum of metallic wave functions $\chi(E, l, \mu)$ which satisfy the Schrödinger equation in the metal

$$H\chi(E, l, \mu) \equiv [T + UP_L]\chi(E, l, \mu) = E\chi(E, l, \mu). \quad (3.2)$$

Here the quantum numbers l and μ are the axial angular momentum and the radial linear momentum; they refer to a cylindrical system of coordinates with axis ($y=0, z=0$) determined by the normal to the surface which passes through the atom. The functions χ are all bound to the metal, i.e., they have a negative energy $E < 0$ and outside the metal ($x > 0$) they decay exponentially. Without loss of generality, it may be assumed that the set $\{\varphi, \chi\}$ is an orthonormal one, i.e., all functions are normalized and φ is orthogonal¹¹ to all χ 's.

⁹ U. Fano, *Phys. Rev.* **124**, 1866 (1961).

¹⁰ P. W. Anderson [*Phys. Rev.* **124**, 41 (1961)] has developed a completely equivalent formulation for treating localized moments; we follow here the notation and nomenclature of Ref. 9.

¹¹ In the actual calculations all χ are orthogonal among themselves, but φ is not orthogonal to the $\{\chi\}$ set; the correction to the lack of orthogonality is straightforward but to avoid unnecessary complications in the formulas we do not include this correction here.

By looking at solutions of our problem which can be expressed as linear combinations of these functions, we neglect all contributions for other atomic states as well as functions which may grow in going from the metal to the ion. This restriction will then result in mixing of metallic wave functions of different energies E ; such a mixing would not occur if the manifold is enlarged to include more functions. For the purpose of studying q^- , i.e., for studying the behavior of wave functions close to the ion, the approximation is a good one and the improper mixing of different E values introduces no significant error.

The one-electron wave functions of the system are now given by

$$\psi(E, l, \nu) = a(E, l, \nu) \varphi$$

$$+ \sum_{\nu'} \int d\mu \int dE' b(E, l, \nu; E', l', \mu) \chi(E', l', \mu) N_{\nu'}(\mu E'), \quad (3.3)$$

Here $N_{\nu'}(\mu E')$ is the density of metallic states with angular momentum l' per unit radial momentum in the plane perpendicular to the metal surface and per unit energy.

Selection rules applied to (3.3) which make use of the fact that φ is an s -like function yield

$$a(E, l, \nu) = 0 \quad \text{for } l \neq 0. \quad (3.4)$$

In addition, only one family of states, say $\nu=0$, contains contributions from φ ,⁹ i.e.,

$$a(E, l, \nu) = 0 \quad \text{for } \nu \neq 0. \quad (3.5)$$

Since the metallic wave functions decay exponentially outside the metal, the only sizeable contribution to (or equivalently the definition of) the density of charge is

$$\rho(E) \equiv |a(E, 0, 0)|^2. \quad (3.6)$$

Straightforward application of perturbation theory as formulated by Fano⁹ yields

$$|a(E, 0, 0)|^2 = \frac{|V_E|^2}{[E - E_\varphi]^2 + \pi |V_E|^4}, \quad (3.7)$$

where

$$|V_E|^2 = \int |\langle \chi(E, 0, \mu) | H | \varphi \rangle|^2 N_0(\mu E) d\mu, \quad (3.8)$$

$$E_\varphi = \langle \varphi | H | \varphi \rangle + G(E), \quad (3.9)$$

$$G(E) = \mathcal{P} \int \frac{|V_{E'}|^2}{E - E'} dE', \quad (3.10)$$

and \mathcal{P} indicates a principal-part integral. It is immediately seen that (3.7) has a form similar to (2.10) if

$$\Delta = \pi |V_E|^2, \quad (3.11)$$

and $|V_E|^2$ is assumed to be a constant independent of

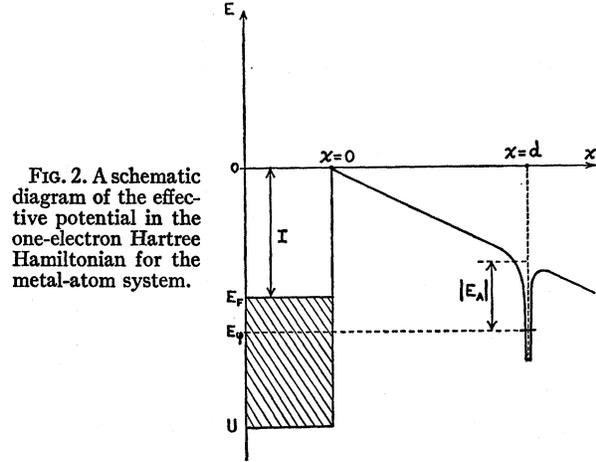


Fig. 2. A schematic diagram of the effective potential in the one-electron Hartree Hamiltonian for the metal-atom system.

E ; in the same approximation the self-energy shift $G(E)$ vanishes because of the odd character of the integrand in (3.10).

IV. CALCULATION OF THE PARAMETERS

In order to find E_φ we rewrite the Hamiltonian (2.14) as

$$H = H_A + [U - V_A'] P_L + [V_F + V_{im}] P_R, \quad (4.1)$$

where H_A is the atomic Hamiltonian of (3.1).

We now make the following approximations:

(i) The self-energy shift $G(E)$ is neglected, i.e.,

$$E_\varphi = \langle \varphi | H | \varphi \rangle. \quad (4.2)$$

(ii) We confine our attention to those separations d (see Fig. 2) for which less than ten percent of the charge associated with $|\varphi|^2$ is inside the metal; it is then reasonable to neglect the second term in (4.1), i.e., the term $[U - V_A'] P_L$.

(iii) We approximate the energy contribution from the external field \mathbf{F} and the image charge by evaluating $(V_F + V_{im})$ at the position of the adsorbate ($x=d$, $y=z=0$). The error involved here is of the order of the small shift of the corresponding atomic s level for the Stark effect.

(iv) The value of the energy of the atomic level E_A' is evaluated by means of the empirical formulas proposed by Slater.¹²

With these approximations,

$$E_\varphi = -R \left[\frac{Z - S_Z - \alpha q^-}{n^*} \right]^2 - |e| F d + \frac{(1 - \beta q^-) e^2}{2d}, \quad (4.3)$$

where R is the Rydberg constant

$$R = 13.6 \text{ eV}, \quad (4.4)$$

¹² J. C. Slater, Phys. Rev. 36, 57 (1930).

TABLE I. Parameters of the calculation.

Metal:	W	$U = -12.0$ eV $I = 4.5$ eV	bottom of the band average ionization potential
Adsorbate:	K	$Z - S_Z = 2.2$	$n^* = 3.7$
	Rb	$Z - S_Z = 2.2$	$n^* = 4$
	Cs	$Z - S_Z = 2.2$	$n^* = 4.2$

and Z is the nuclear charge of the adsorbate; all other symbols will be defined immediately. The first term in (4.3) is the energy of the isolated atom in the Slater approximation, modified by the presence of the effective charge q^- . If for the moment we set $q^- = 0$, that energy corresponds to an approximate (Slater) wave function

$$\varphi = Cr^{(n^*-1)} \exp\{-[(Z - S_Z)/n^*a_0]r\}, \quad (4.5)$$

where a_0 is the Bohr radius, n^* is an effective quantum number related to the usual principal quantum number, S_Z is an effective shielding constant, and C is a normalization constant. The shielding constant S_Z is in fact a sum over the shielding contributions s_i of each of the individual electrons of the same and inner shells of the atom. It is important to note that the relevant electron does not screen itself, but if another electron is present in the same s shell, the latter gives a contribution¹² 0.35 to S_Z . In allowing for the change in E_φ due to the effective charge q^- , we have chosen to increase the shielding by an additional term αq^- . If the effective charge were due to a localized wave function (as it is for large distances d), then α would in fact be zero because of the lack of self-screening. Since, however, the effective electronic charge on the adsorbate is due to a sum over the contribution of many extended wave functions, we assume that an individual electron in the vicinity of the atom feels a screening given by $(S_Z + 0.35 q^-)$, as if the effective charge were equivalent to another electron of charge q^-e in the outer shell. In actual fact α must be a function of the distance d and arises from nontrivial correlation effects which go beyond the Hartree approximation.

The second and third terms in (4.3) are, respectively, the values of V_F and V_{im} at the adsorbate site. The image term V_{im} corresponds to the interaction of the electron with the image of the ion, partly screened by the effective electronic charge q^- ; we take the constant β as equal to one, but its actual value is again a function of distance which depends on detailed correlation effects.

For a given chemical species (i.e., Z and S_Z known) and known values of F and d , E_φ as a function of q^- is a quadratic function with negative quadratic coefficient and a maximum at

$$q_{\max}^- = -\frac{1}{\alpha} [Z - S_Z - \beta e^2 n^{*2} / 4d\alpha R], \quad (4.6)$$

which is independent of F .

The calculation of the width (3.11), (3.8) is a tedious but straightforward process which involves several steps:

- (i) calculation of the metallic wave function $\chi(E, l, \mu)$ in (3.2) with their proper normalization;
- (ii) calculation of the normalization constant C for the atomic function φ (4.5);
- (iii) calculation of the density of states $N_0(\mu, E)$;
- (iv) evaluation of the matrix element

$$\langle \chi(E, 0, \mu) | H | \varphi \rangle;$$
- (v) evaluation of the integral (3.8).

Some details of the calculation are presented in the Appendix.

The parameters used in the calculation for W metal and for K, Rb, and Cs adsorbates are shown in Table I. The calculated widths Δ depend on six variables:

- (1) E , the independent variable of integration as appears in (3.11) and (3.8);
- two parameters which depend on the metal substrate, i.e.,
 - (2) I , the ionization potential,
 - (3) U , the position of the bottom of the conduction band;
- two parameters which depend on the adsorbate and the external field, i.e.,
 - (4) E_φ , the displaced position of the atomic level,
 - (5) Z , the chemical species of the adsorbate;
- and finally
 - (6) d , the metal-adsorbate separation.

In Table II we give various values of Δ as calculated for U and I corresponding to W , and for $E = E_\varphi$. It is seen that the typical widths for reasonable distances ($\sim 3 \text{ \AA}$)

TABLE II. The width Δ .

Metal	d Å	$E = E_\varphi$ eV	Δ eV
K	2.85	-4.5	2.3
	4	-4.5	1.2
	6	-4.5	0.22
	8	-4.5	0.022
Rb	2.85	-4.5	2.4
	4	-4.5	1.5
	6	-4.5	0.42
	8	-4.5	0.050
	4	-5.7	1.6
Cs	2.85	-4.5	3.1
	4	-4.5	2.0
	6	-4.5	0.67
	8	-4.5	0.11
	4	-5.7	2.1

TABLE III. The self-consistent solution for the effective charge q^- and the energy E_φ .

d Å	F V/Å	K		Rb		Cs	
		E_φ eV	q^-	E_φ eV	q^-	E_φ eV	q^-
8	0.00	-2.0	0.00	-1.6	0.00	-1.4	0.00
	0.12	-3.0	0.01	-2.6	0.01	-2.4	0.01
	0.25	-4.0	0.02	-3.6	0.02	-3.4	0.02
	0.31	-4.5	0.12	-4.1	0.03	-3.9	0.05
	0.37	-4.8	0.97	-4.6	0.75	-4.4	0.25
	0.44	-5.3	0.98	-5.1	0.98	-4.9	0.92
	0.50	-5.8	1.00	-5.6	0.99	-5.4	0.96
6	0.00	-1.7	0.02	-1.2	0.04	-1.1	0.06
	0.16	-2.7	0.04	-2.2	0.05	-2.1	0.07
	0.33	-3.7	0.10	-3.3	0.10	-3.1	0.14
	0.42	-4.2	0.22	-3.7	0.17	-3.6	0.22
	0.50	-4.8	0.80	-4.3	0.37	-4.2	0.35
	0.58	-5.3	0.91	-5.0	0.77	-4.8	0.65
	0.66	-5.8	0.94	-5.5	0.86	-5.3	0.77
	0.75	-6.3	0.96	-6.0	0.91	-5.9	0.85
4	0.00	-1.2	0.10	-0.9	0.12	-0.6	0.14
	0.25	-2.3	0.13	-2.0	0.17	-1.6	0.18
	0.50	-3.4	0.27	-3.0	0.26	-2.6	0.26
	0.75	-4.5	0.50	-4.2	0.44	-3.8	0.38
	1.00	-5.6	0.74	-5.4	0.67	-5.0	0.57
	1.25	-6.7	0.85	-6.5	0.78	-6.1	0.70
2.85	0.00	-0.6	0.17				
	0.25	-1.4	0.22				
	0.50	-2.1	0.25				
	1.00	-3.7	0.37				
	1.50	-5.4	0.62				
	2.00	-7.0	0.77				

is of the order of 1.5–3.0 eV. It should be noted, however, that the values calculated for Rb and Cs for $d=2.85$ Å¹³ are unreliable since our approximation (less than 10% of the electronic charge of the atomic function inside the metal) is no longer valid. It is interesting to note that the variation of Δ with E within a shift of about Δ itself is very small, of the order of 5%. It is thus a good approximation to assume the Lorentzian distribution of Eq. (2.10); it should be remembered, however, that the distribution is in fact skewed, and slight departures from the Lorentzian may be detected experimentally.

V. SELF-CONSISTENT SOLUTION

The self-consistent solution of the problem is now obtained graphically. This is done in several steps, illustrated here and in Fig. 3 for the case of K on W at a distance $d=4$ Å.

¹³ The value of 2.85 Å is one of the limits estimated by Schmidt and Gomer (Ref. 5) for K and W.

(1) We choose a value of Δ , as calculated in Sec. IV, which corresponds to the relevant parameters and taken at a value

$$E = E_\varphi = E_F = -I = -4.5 \text{ eV.}$$

From Table II this is $\Delta = 1.2$ eV.

(2) We replace this value in Eq. (2.11) and plot q^- as a function of E_φ (see Fig. 3).

(3) In the same graph we plot Eq. (4.3), i.e., E_φ as a function of q^- for a fixed value of F , repeating the curves for a set of different F values.

(4) Intersection of the curves (2) and (3) gives the self-consistent values of E_φ and q^- , which are tabulated in Table III.

An analysis of the numbers in Table III shows that at a distance of 8 Å the three alkalis K, Rb, and Cs show, for all practical purposes, neutral or completely ionic character, depending on the value of F . In the other extreme, K at a distance of 2.85 Å exhibits always a true metallic character.

One word about the external field F is in order. So far we have assumed that F is due to an externally applied field, but it also may arise from the dipole moment caused by all other atoms ionically or metallically adsorbed at the surface.

The results of Table III are in fair agreement with the experimental values of Schmidt and Gomer⁵ for the values of q^- and its variation with F (or equivalently its variation with coverage of the surface). A more detailed comparison is not rewarding at this stage, since our simplified model does not include a dependence on the crystallographic properties of the surface or other details of the rather complex experiment. It is, however, rewarding to see that the fundamental mechanisms at play can be understood and calculated by means of such a simple scheme.

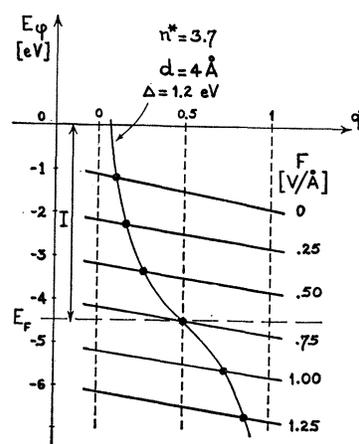


FIG. 3. Diagram for the determination of the self-consistent value of q^- and E_φ for the case of K on W at a distance $d=4$ Å. The family of curves corresponds to various values of the external field F .

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APPENDIX A: DETAILS OF THE CALCULATION OF Δ

(i) We assume the metal to be a very large cylindrical sample of length L_x in the x direction (perpendicular to the surface) and radius L_ρ in the radial ρ direction in the plane parallel to the surface. The metallic wave functions, solutions of (3.2) with $E < 0$, are

$$\chi(E, 0, \mu) = \left(\frac{\mu(E - U - \hbar^2 \mu^2 / 2m)}{L_x L_\rho |U|} \right)^{1/2} \times \begin{cases} -\frac{\kappa}{k_x} \sin k_x x + \cos k_x x & J_0(\mu\rho), \quad x < 0; \\ \left(\frac{\mu(E - U - \hbar^2 \mu^2 / 2m)}{L_x L_\rho |U|} \right)^{1/2} e^{-\kappa x} & \times J_0(\mu\rho), \quad x > 0; \end{cases} \quad (\text{A1})$$

where

$$\hbar^2 k_x^2 / 2m = E - U - \hbar^2 \mu^2 / 2m, \quad k_x > 0, \quad (\text{A2})$$

$$\hbar^2 \kappa^2 / 2m = \hbar^2 \mu^2 / 2m - E, \quad \kappa > 0, \quad (\text{A3})$$

and J_0 is the zeroth-order Bessel function.

(ii) The properly normalized Slater function¹² is

$$\varphi(r) = \left(\frac{(2\gamma)^{2n^*+1}}{4\pi\Gamma(2n^*+1)} \right)^{1/2} r^{n^*-1} e^{-\gamma r}, \quad (\text{A4})$$

where

$$\gamma = (Z - S_Z - \alpha q^-) / n^* a_0. \quad (\text{A5})$$

(iii) The relevant density of metallic states for a single spin is given by

$$N_0(\mu, E) = \frac{L_x L_\rho}{\pi^2} \int_0^\infty \delta[E - U - (\hbar^2/2m)(k_x^2 + \mu^2)] dk_x = \frac{L_x L_\rho m}{\pi^2 \hbar} \frac{1}{[2m(E - U) - \hbar^2 \mu^2]^{1/2}}. \quad (\text{A6})$$

(iv) From (4.1) we obtain with the same approximations of Sec. IV

$$\langle \chi(E, 0, \mu) | H | \varphi \rangle \cong E_\varphi \langle \chi(E, 0, \mu) | \varphi \rangle. \quad (\text{A7})$$

The right-hand side of (A7) has been evaluated by replacing $J_0(\mu\rho)$ in (A1) by one; this is justified by the fact that the major contribution comes from the region $\rho \rightarrow 0$. Consequently,

$$\langle \chi(E, 0, \mu) | H | \varphi \rangle \cong E_\varphi e^{-\kappa d} \left(\frac{\pi \mu^{2n^*+1} (E - U - \hbar^2 \mu^2 / 2m)}{\gamma \Gamma(2n^*+1) L_x L_\rho |U|} \right)^{1/2} \times \left[\int_0^d e^{\kappa x} \Gamma(\gamma x, n^*+1) dx + \int_0^\infty e^{-\kappa x} \Gamma(\gamma x, n^*+1) dx \right], \quad (\text{A8})$$

where $\Gamma(\gamma x, n^*+1)$ is the incomplete gamma function.¹⁴

(v) The integral over x in (A8) as well as the integral over μ which appears in (3.8) were performed numerically with the Titan Computer of the University of Cambridge Mathematical Laboratory. Results are given in Table II.

¹⁴ See, for instance, E. Jahnke, F. Emde, and A. I. Lösch, *Tables of Higher Functions* (McGraw-Hill Book Company, Inc., New York, 1960), p. 13.