

Self-consistent electron theory of a metallic surface

M. B. Partenskii

Ural Forestry Institute, Sverdlovsk
Usp. Fiz. Nauk 128, 69-106 (May 1979)

This is a review of researches on the calculation of the electronic characteristics of a free or perturbed metal surface; these include the electron density, the potential, the spectrum of surface states, the work function, the surface energy, response of the surface to an electric field, the chemisorption of atoms, and the adhesion of two metals. Preference is given to papers that employ the theory of the ground state of an inhomogeneous electron gas, the "density-functional method." The various approximations to the density-functional used in the calculations, and the various models of the lattice ("jelly", pseudopotential), are analyzed as to their applicability. Various sorts of experimental data are discussed on the basis of the theoretical results.

PACS numbers: 73.20.Cw, 73.30.+y, 68.45.-v

CONTENTS

I. Introduction	330
II. Self-consistent theory of an inhomogeneous electron gas (density-functional method)	331
1. Description of the ground state of an inhomogeneous electron gas in terms of the electron density (general formalism)	331
a) The Hohenberg-Kohn theorem	331
b) The linear-response approximation (L.R.A.)	332
2. Approximate expressions for the energy as a density-functional	332
3. Two realizations of the density-functional method	333
a) The Thomas-Fermi method and its perfected form	333
b) The perfected Hartree method	333
III. Electronic properties of an unperturbed metal surface	334
4. Fundamental theoretical relations	334
a) Work function and surface energy (definitions)	334
b) Characteristics of a surface in the uniform-background model ("jelly" model)	334
5. Density, potential, and work function (calculated results)	335
a) "Jelly" model	335
b) Discrete lattice	337
1) "Corrugated background" model	337
2) Use of perturbation theory to take the discrete nature of the lattice into account	338
3) Exact discrete treatment (self-consistent pseudopotential model)	338
6. Surface energy (calculations)	339
a) "Jelly" model	339
b) Discrete lattice	340
c) Effects of nonlocality of exchange and of correlations	340
IV. Influence of an external perturbation on the electron properties of metal surfaces	341
7. Metal surface in an external electric field	341
a) Boundary conditions, asymptotic form of potential	341
b) Electronic properties of a surface in an external field (calculations)	341
1) Thomas-Fermi method	341
2) Many-particle and quantum effects	342
3) Discussion (comparison with experiment)	342
8. Chemisorption of atoms on a metal surface	343
a) Interaction of a point charge with a metal	343
b) Effect of chemisorption on electronic properties of a metal surface	344
1) Chemisorption of isolated atoms	344
2) Effect of adsorbed films on the work function	346
9. Adhesion of metals	347
V. Conclusion	349
References	349

I. INTRODUCTION

During the last thirty years research on surfaces of solids has advanced rapidly. The main features of the "surface boom" have been repeatedly pointed out in the literature and can be summarized as follows: 1) creation and development of experimental methods for obtaining various kinds of information about the properties of a thin ($\sim 5 \text{ \AA}$) surface layer; 2) the development of ultrahigh-vacuum techniques, making

possible new methods for producing and for preserving over long times atomically pure perfect surfaces; 3) the construction of various theoretical models and methods for quantitative interpretation of the experimental data; 4) the remarkable spread and realization of technological applications of surface research (catalysis, solid state microelectronics using thin-film techniques, and many others). Owing to the combined effects of these developments, the physics of surfaces is being transformed before our eyes from

"an art into a quantitative science," and the gap between it and the traditional "bulk" branches of physics is being narrowed. At least two specific causes for the prolonged existence of this gas in the electron theory of metals can be indicated. First, the sharp nonuniformity of the surface layer. In the interior, the discrete nature of the lattice leads to a rather smooth modulation of the density of conduction electrons, whereas near the surface the density falls from the bulk value to zero in distances of the order of atomic dimensions. Second, in surface calculations self-consistency with respect to the electrostatic potential is much more important. Without it we cannot correctly determine the nature of the drop in the electron density, and thus of the parameters of the double layer of charge; it is necessary for the determination of the equilibrium geometry of the surface and in the analysis of the interaction of the metal with the surrounding medium. Any disturbing agent (atom, molecule, or other entity) "adapts itself" to the metal and deforms the electron density near the surface (changes its "environment"). Therefore the use of model (fixed) potentials often leads to error.

It can be understood from these remarks that the state of the theory of a metal surface depends to a large extent on the level of development of the theory of strongly inhomogeneous electronic systems. Remarkable progress in this direction has been achieved rather recently through the creation, in papers by Hohenberg, Kohn, and Sham,^{2,3} of a self-consistent theory of the ground state of an inhomogeneous electron gas, the "density-functional method" (DFM). The purpose of the present review is to acquaint the reader with the applications of the DFM to research on metal surfaces, where they have been extremely fruitful. By providing a unified approach to the quantitative analysis of various processes and phenomena (see Sections III, IV) this method has essentially determined both the present state of the theory of metal surfaces and the most promising directions for its future development. Section II gives a brief introduction to the theory of the method. A more complete exposition can be found in an earlier review.⁴ Various aspects of related questions are considered in other reviews.⁵⁻⁹

Where no statement is made to the contrary, we shall use an atomic system of units: $e = m_e = \hbar = 1$.¹⁾ The unit of length is the Bohr radius $a_H = 0.529$ A, and the unit of energy is 27.2 eV.

II. SELF-CONSISTENT THEORY OF AN INHOMOGENEOUS ELECTRON GAS (IEG) (DENSITY-FUNCTIONAL METHOD)

1. Description of the ground state of an inhomogeneous electron gas in terms of the electron density (general formalism)

a) The Hohenberg-Kohn theorem

Hohenberg and Kohn (H-K)² considered an electron gas in a nonuniform electric field with the potential

¹⁾ e is the charge of the electron; m_e is its mass.

$v(\mathbf{r})$. The Hamiltonian of the system is of the form

$$H = T + V + U, \quad (1.1)$$

where T , V , and U are respectively the kinetic energy of the electrons, their Coulomb interaction with each other, and their interaction with the external field. Let $|\Psi\rangle$ be the ground state vector of the system of particles in the given field, and let $n(\mathbf{r})$ be the corresponding electron density, which satisfies the condition

$$\int n(\mathbf{r}) d\mathbf{r} = N. \quad (1.2)$$

For simplicity it is assumed that the ground state is nondegenerate. Obviously $n(\mathbf{r})$ is uniquely determined by the choice of the external potential $v(\mathbf{r})$. H-K showed that the converse is also true; $v(\mathbf{r})$ is a single-valued functional of the density (up to an additive constant). This result is the starting point for the construction of the density-functional method (DFM). It follows that $|\Psi\rangle$ is also a single-valued functional of $n(\mathbf{r})$ since by the Schrödinger equation $|\psi\rangle$ is uniquely determined by the choice of $v(\mathbf{r})$. Therefore averages calculated with the function $|\Psi\rangle$, for example the kinetic energy and the interaction energy, are single-valued functionals of the density.

Then according to the well-known variational principle for the energy of the ground state (cf., e.g., Sec. 20 in Ref. 10) we have the following theorem (the H-K theorem): There exists a universal functional of the density, $G[n(\mathbf{r})]$, such that the density corresponding to any external potential $v(\mathbf{r})$ must minimize the energy functional

$$E_v[n] = - \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n] \quad (1.3)$$

subject to the subsidiary condition (1.2). The functional $G[n]$ is defined by the relation

$$G[n] = \langle \Psi | T + V | \Psi \rangle - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (1.4)$$

Introducing a Lagrange multiplier μ , we can write the condition for the extremum which follows from the H-K theorem in the form

$$\delta \{ E_v[n] - \mu \int n(\mathbf{r}) d\mathbf{r} \} = 0. \quad (1.5)$$

From this we have

$$\mu = \frac{\delta E_v[n]}{\delta n}. \quad (1.6)$$

For $N \gg 1$, μ is identical with the chemical potential of the system. Let $\varphi(\mathbf{r})$ be the total electrostatic potential energy of an electron (in atomic units it differs from the potential only in sign)

$$\varphi(\mathbf{r}) = \int \frac{n(\mathbf{r}') - n_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'; \quad (1.7)$$

here $n_+(\mathbf{r}')$ is the density of positive charge which produces the potential $v(\mathbf{r})$. Then by means of Eq. (1.3) we can write Eq. (1.5) in the form

$$\varphi(\mathbf{r}) + \frac{\delta G[n]}{\delta n} = \mu. \quad (1.8)$$

We note that Eq. (1.7) follows from the Poisson equation

$$\nabla^2 \varphi(\mathbf{r}) = -4\pi [n(\mathbf{r}) - n_+(\mathbf{r})], \quad (1.9)$$

which assures that the Coulomb potential is self-consistent.

b) The linear-response approximation (L.R.A.)

In some cases it is convenient to represent an external perturbation in the form $v(\mathbf{r}) = v_0(\mathbf{r}) + v_1(\mathbf{r})$, where $v_0(\mathbf{r})$ is the "unperturbed potential" and $v_1(\mathbf{r})$ is a small perturbation. Then, expanding both terms in Eq. (1.8) in powers of the perturbation, we get in the zeroth and linear approximations

$$\varphi_0(\mathbf{r}) + \frac{\delta G[n]}{\delta n} \Big|_{n=n_0(\mathbf{r})} = \mu_0, \quad (1.10)$$

$$\varphi_1(\mathbf{r}) + \int n_1(\mathbf{r}') \frac{\delta^2 G[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Big|_{n=n_0} (d\mathbf{r}') = \mu_1. \quad (1.11)$$

Equations (1.9), (1.10), and (1.11) are the basis of the linear-response approximation (LRA). This finds frequent use in the theory of metal surfaces (cf. Section IV).

2. Approximate expressions for the energy as a density-functional

Equations (1.8) and (1.9) form a self-consistent system, which determines the electron density distribution in the ground state if the explicit form of the functional $G[n]$ is known. The H-K theorem is essentially an existence theorem. Unfortunately, it is still not clear how to obtain the exact forms of the functionals whose existence is assured by this theorem.²⁾ Therefore in carrying out actual calculations it is necessary to approximate $G[n]$ with some "lucky" expression. Hohenberg and Kohn considered two approximations:

1) The first approximation treats the deviations from an average value \bar{n} as small: $|\tilde{n}(\mathbf{r})| \equiv |n(\mathbf{r}) - \bar{n}| \ll \bar{n}$. Then $G[n]$ can be expanded in powers of \tilde{n} :

$$G[n] = G[\bar{n}] + \int K(|\mathbf{r} - \mathbf{r}'|) \tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}') (d\mathbf{r})(d\mathbf{r}') + O(\tilde{n}^3). \quad (2.1)$$

The first term describes a homogeneous electron gas. The linear term drops out because of translational invariance and the normalization condition $\int \tilde{n}(\mathbf{r})(d\mathbf{r}) = 0$. H-K showed that the Fourier transform of the kernel $K(\mathbf{q})$ in the second-order term can be expressed exactly in terms of the static dielectric permittivity $\epsilon(\mathbf{q})$ of a homogeneous electron gas of density \bar{n} : $K(\mathbf{q}) = (2\pi/q^2)[\epsilon(\mathbf{q}) - 1]^{-1}$. An important property of $K(\mathbf{q})$ is that it has a singularity of the form $(q - 2k_F) \ln(q - 2k_F)$ for $q \rightarrow 2k_F$ because of the existence of a sharp boundary of the electron distribution in k -space at $k = k_F$ (k_F is the Fermi momentum). The presence of the singularity leads to Friedel oscillations of the charge density which screens the perturbation acting on the electrons. The general theory of such oscillations in an inhomogeneous electron gas is constructed in Ref. 3. They appear, for example, near a charged impurity in a metal¹² and near the surface of a metal (see subsection 5).

²⁾ An interesting extension of the H-K theorem by Epstein and Rosental¹¹ applies to the "ground state" of an l -rowed Hermitian matrix. With the examples $l=2$ and $l=3$ they showed that in some cases one can also get from the general theorem a recipe for constructing the functionals. However, for practically interesting systems there has so far been no progress in this direction.

2) The other approximation considered by H-K is the case of smoothly varying density: $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$, $r_0 \rightarrow \infty$; they carried out a formal expansion of $G[n]$ in the parameter r_0^{-1} , or, equivalently, in powers of the operator ∇ acting on $n(\mathbf{r})$. By using the symmetry of the functional $g_r[n]$ with $G[n] \equiv \int g_r[n](d\mathbf{r})$ and the ambiguity in its definition³⁾ we can write the series in the form

$$G[n] = \int (d\mathbf{r}) [g_0[n(\mathbf{r})] + g_2[n(\mathbf{r})] |\nabla n(\mathbf{r})|^2 + \dots]. \quad (2.2)$$

The coefficients $g_i[n(\mathbf{r})]$ are ordinary density functions (not functionals). $g_0[n]$, which is the density of non-electrostatic energy in the homogeneous electron gas, is often represented in the form

$$g_0(n) = [t(n) + \epsilon_x(n) + \epsilon_c(n)]_n, \quad (2.3)$$

where t and ϵ_x are respectively the average kinetic energy and the exchange (Hartree-Fock approximation) energy per particle:

$$t(n) = 0.3 (3\pi^2 n)^{2/3} = \frac{1.105}{r_s^2(n)}, \quad (2.4)$$

$$\epsilon_x(n) = -0.75 \left(\frac{3n}{\pi}\right)^{1/3} = -\frac{0.458}{r_s(n)}; \quad (2.5)$$

here $r_s(n) = [(4/3)\pi n]^{-1/3}$. For the correlation energy ϵ_c , in the region of metal densities the Wigner approximation (cf. Ref. 13),

$$\epsilon_c(n) = -\frac{0.44}{r_s(n) + 7.8}, \quad (2.6)$$

is often used, and in the high-density approximation ($r_s \ll 1$) the results of Gell-Mann and Brueckner¹⁴ are applied.

To determine the other coefficients in Eq. (2.2) H-K considered the case in which the density is smooth and also its variations are small. Then the g_i can be expressed in terms of response functions of various orders. For example, $g_2 = 2\pi(-c_2 + c_4^2)$, where the c_i are the coefficients of the expansion of the linear response function in powers of q . There are no odd powers of q in the expansion because the unperturbed system is isotropic. In the random phase approximation the result is

$$g_2(n) = (72n)^{-1}, \quad (2.7)$$

which is identical with the coefficient of the first quantum correction to the kinetic energy of an inhomogeneous gas, which was first calculated by Kompaneets and Pavlovskii¹⁵ (see also Ref. 16). The exchange contribution g_2^x to g_2 was calculated in the high-density limit by Sham,¹⁷ and the correlation contribution was calculated by Ma and Brueckner.¹⁸ Application of these results to calculations for atoms showed that they are essentially insufficient (for example, the exchange contribution found in Ref. 17 turned out to be too small by a factor three). An explanation of this difference was, for example, sought¹⁹ in the neglect of the higher terms in the gradient. However, a later analysis^{20,21} showed that strictly speaking no independent contribu-

³⁾ The functional $g_r[n]$ is the density of nonelectrostatic interaction energy of the inhomogeneous gas, defined up to the divergence of an arbitrary vector functional.

tion of exchange to the gradient expansion exists.⁴⁾ Geldart and Rasolt²³ derived an expression for g_2^{xc} in terms of the one-particle Green's function which is exact to all orders in e^2 . They developed an approximate method by which g_2^{xc} can be calculated in the "intermediate" range of densities ($1 \lesssim r_s \lesssim 6$), which is essential for applications of the theory to metals. The coefficient $g_2^{xc}(n)$ is put in the form

$$g_2^{xc}(n) = c(r_s) n^{-4/3}. \quad (2.8)$$

The function $c(r_s)$ decreases almost linearly with increasing r_s from $c(1) \approx 2.5 \cdot 10^{-3}$ to $c(6) \approx 1.6 \cdot 10^{-3}$. Calculations of surface energies with the nonlocal exchange-correlation correction show better agreement with experiment than those made with other approximations. Papers^{24,25} in which g_2^x and g_2^{xc} have been estimated from empirical considerations may also be mentioned here.

3. Two realizations of the density-functional method

In calculations of surface properties of metals and in other applications of the DFM two calculational schemes are commonly used. One of them involves perfecting the "statistical description" based on the Thomas-Fermi method (TFM) and extending the limits of its applicability.

The second way to realize the DFM involves the formulation of one-particle Schrödinger equations whose self-consistent solution is equivalent to the solution of the variational problem of Eqs. (18), (19).

a) The Thomas-Fermi method and its perfected form

The present state of the statistical theory of matter based on the TFM and its successive modifications, and also the application of the corresponding models to various electron-nuclear systems, have been examined recently in detail.²⁶ We shall concern ourselves here only with the connection of the TFM with the DFM. Our exposition is based on the treatment by Lang.⁴ Substituting Eq. (2.3) in Eq. (1.8), we get

$$\varphi(r) + g_0'(n(r)) = \mu, \quad (3.1)$$

where $g_0'[n(r)] \equiv dg_0(n)/dn|_{n=n(r)}$. If in $g_0(n)$ we keep only the kinetic energy (2.4) and substitute (3.1) in Eq. (1.9), we obtain the well-known Thomas-Fermi equation⁵⁾

$$\nabla^2 \varphi(r) = -\frac{27/2}{3\pi} [\mu - \varphi(r)]^{3/2} + 4\pi n_+(r). \quad (3.2)$$

⁴⁾ The nonexistence of a gradient expansion for the exchange interaction is due to the long-range nature of Coulomb forces. When we go from the Yukawa potential $\nu(q) = (q^2 + \lambda^2)^{-1}$ to the unscreened Coulomb interaction by taking the limit $\lambda \rightarrow 0$, in second order in the interaction parameter e^2 a singularity of the type $\ln^2 \lambda$ appears in g_2^x (Sham erroneously considered only the linear term). Since the dynamical correlation leads to the appearance of effective screening (i.e., $\lambda = \lambda_{\text{eff}} \neq 0$), it can be seen that there is nevertheless a gradient expansion for the sum $g_2^{xc} = g_2^x + g_2^c$. (We note, however, that a static screening of the Coulomb potential does not give a complete description of the effect of correlation; cf., e.g., Ref. 22.)

⁵⁾ For relevant discussion and bibliography see Ref. 27.

Inclusion of the exchange term (2.5) in $g_0(n)$ leads to the Thomas-Fermi-Dirac equation, and a further consideration of correlation gives an equation derived by Gombas.⁵⁾

Inclusion of the gradient terms after substitution of Eq. (2.2) in Eq. (1.16) gives

$$\varphi(r) + g_0'(n(r)) - g_2'(n(r)) |\nabla n(r)|^2 - 2g_2(n(r)) |\nabla^2 n(r)| + \dots = \mu. \quad (3.3)$$

Along with Eq. (1.9), Eq. (3.3) provides an extension of the Thomas-Fermi equation to the case in which exchange-correlation and quantum effects in an inhomogeneous electron gas are taken into account.

b) The perfected Hartree method

Following H-K, we consider a system of N noninteracting fermions, with mass equal to the electron mass, in a static field $v_s(\mathbf{r})$. We denote the wave function of the ground state of the corresponding Hamiltonian $T + V_s$ by $\Psi_s(\mathbf{r})$, and the density of particles by $n(\mathbf{r})$.⁶⁾ From the H-K theorem we can easily derive an equation analogous to Eq. (1.8):

$$v_s(\mathbf{r}) + \frac{\delta T_s[n]}{\delta n} = \mu_s, \quad (3.4)$$

here $T_s[n]$ is the kinetic energy of the system ($T_s[n] = \langle \Psi_s | T | \Psi_s \rangle$). The chemical potential μ_s is given as before by the condition (1.2). Knowing the general form of the functional $T_s[n]$, we can determine $n(\mathbf{r})$ from Eq. (3.4). But we can also obtain $n(\mathbf{r})$ in a more traditional way, by solving a system of N one-particle Schrödinger equations with the potential $v_s(\mathbf{r})$ and determining $\psi_s(\mathbf{r})$ as the Slater determinant formed from one-particle functions. Thus Eq. (3.4) is equivalent to a system of quantum-mechanical equations. Using this fact, and also the fact that Eqs. (1.8) and (3.4) are formally identical when in the latter $v_s(\mathbf{r})$ is replaced by the effective potential

$$v_{\text{eff}}[n, \mathbf{r}] = \varphi(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n}, \quad (3.5)$$

where

$$E_{xc}[n] = G[n] - T_s[n] \quad (3.6)$$

is the exchange-correlation energy ($T_s[n]$ refers to free fermions with the same density as the interacting ones), H-K came to the conclusion that the solution of Eqs. (1.8) and (1.9) is equivalent to the self-consistent solution of the system of N equations

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{eff}}(n, \mathbf{r}) \right) \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}), \quad (3.7)$$

where

$$n(\mathbf{r}) = \sum_{i=1}^N |\Psi_i(\mathbf{r})|^2. \quad (3.8)$$

The realization of the DFM based on Eqs. (3.7), (3.8) and (1.9) is essentially the perfected Hartree method (PHM).

The main difficulties of this approach are associated with the choice of $E_{xc}[n]$. In most papers the local-

⁶⁾ In the general case $v_s(\mathbf{r})$ differs from the external potential $v(\mathbf{r})$ which results in the same density $n(\mathbf{r})$ when interaction is present.

density approximation (LDA)

$$E_{xc}[n] \equiv \int e_{xc}(n) n(\mathbf{r}) d\mathbf{r}, \quad (3.9)$$

$$v_{\text{eff}}(\mathbf{r}) = \varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r})), \quad (3.10)$$

has been used, where

$$\mu_{xc}[n] \equiv [ne_{xc}(n)]' \quad (3.11)$$

is the exchange-correlation part of the chemical potential of a uniform electron gas of density n . This approximation leads to exact results in two limiting cases, mainly when the density changes very slowly, or when the density is very large, $r_s \ll 1$ (in the latter case the exchange energy and correlation energy are much smaller than the kinetic energy, and the error in treating them inaccurately is small). The exchange part of v_{eff} can be calculated from Eq. (2.5):

$$v_{\text{eff}x}(n) = \mu_x(n) = -\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}. \quad (3.12)$$

This formula for the exchange potential was first derived by Dirac.²⁸ Slater proposed the use of a potential obtained by averaging the nonlocal Hartree-Fock exchange potential over the Fermi distribution⁷ and obtained²⁹

$$v_{\text{eff}x}^{\text{Sl}} = \frac{3}{2} \mu_x(n). \quad (3.13)$$

Kohn and Sham³ showed that in the case of smoothly varying density the potential (3.12) is more suitable for calculating $n(\mathbf{r})$; the error in $n(\mathbf{r})$ is $O(|\nabla n|^4)$ when Eq. (3.12) is used, and $O(|\nabla n|^2)$ with Eq. (3.13).

For more exact calculations one can take into account a nonlocal correction of the form $g_2^{xc}(n)|\nabla n|^2$, for example that given by Eq. (2.8). With this approximation for the functional $E_{xc}[n]$ the energy of the ground state can be calculated from Eq. (3.7) with

$$T_s[n] = \sum_{i=1}^N \epsilon_i - \int v_{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (3.14)$$

where the density $n(\mathbf{r})$ must be found from the solution of the self-consistent problem (3.9), (3.10).

III. ELECTRONIC PROPERTIES OF AN UNPERTURBED METAL SURFACE

4. Fundamental theoretical relations

a) Work function and surface energy (definitions)

1) By definition, the work function Φ is the minimum energy that must be expended to remove an electron from the metal at 0°K. It can be put (see Ref. 30) in the form

$$\Phi = \Delta\varphi - \bar{\mu}, \quad (4.1)$$

where

$$\bar{\mu} \equiv \mu - \bar{\varphi}(\mathbf{r}) = \left\langle \frac{\delta G[n]}{\delta n} \right\rangle \quad (4.2)$$

is the chemical potential per unit volume, measured from the level of the mean electrostatic potential $\bar{\varphi} \equiv \langle \varphi(\mathbf{r}) \rangle$ ($\langle \dots \rangle$ denotes averaging over the volume of the metal), and

⁷⁾ That is, over all occupied states in the band in question.

Equation (3.12) corresponds to the occupied state of highest energy.

$$\Delta\varphi(\mathbf{r}) = \varphi(\infty) - \bar{\varphi} \quad (4.3)$$

is the potential difference between the inside and the outside of the metal (the Coulomb barrier). The electrostatic barrier is localized in a microscopic (2–3 Å) neighborhood of the boundary of the metal, so that Eq. (4.1) essentially gives the work function as the sum of a volume component $-\bar{\mu}$ and a surface component $\Delta\varphi$. This separation was first discussed by Wigner and Bardeen.³¹

2) The surface energy is the work required to separate a crystal into two parts along some plane, calculated per unit area of newly formed surface. If the original crystal is macroscopic and the fragments formed are equivalent, then

$$\sigma = (2A)^{-1} \{2(G[n] + E_{es}[n]) - (G[n'] + E_{es}[n'])\}; \quad (4.4)$$

here A is the area of the cleavage boundary, n and n' are the respective electron densities in the fragments and in the original crystal, and E_{es} is the total classical Coulomb energy of the positive and negative charges. Consequently, $G[n] + E_{es}[n]$, unlike the $E_v[n]$ of Eq. (1.3), includes the energies of the ion cores themselves. It is easily verified that

$$E_{es}[n] = (8\pi)^{-1} \int |\nabla\varphi(\mathbf{r})|^2 d\mathbf{r}. \quad (4.5)$$

For what follows it is convenient to separate σ into three parts,

$$\sigma = \sigma + \sigma_{xc} + \sigma_{es}, \quad (4.6)$$

where σ_s and σ_{xc} correspond to using in Eq. (4.4) the $G[n]$ of Eq. (3.6), and σ_{es} is the electrostatic component.

b) Characteristics of a surface in the uniform-background model ("jelly" model)

Most self-consistent calculations of $n(\mathbf{r})$ near a metal surface are based on a simplified model in which the lattice is replaced by a uniform positive background (uniform-background model or "jelly" model).⁸⁾

1) For a crystal occupying the half-space $x < 0$ the density of positive charge in this model is of the form

$$n_+(x) = \bar{n}\theta(-x); \quad (4.7)$$

$$\theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0 \end{cases} \text{ -- Heaviside function.}$$

Because $n_+(x)$ is one-dimensional, the electron

⁸⁾ The "jelly" model describes particularly well "simple" metals, in which the conduction band consists of s and p states, with d states playing no significant part. The question of the applicability of this model is discussed in more detail in Refs. 4 and 13. Here we mention just one feature of the model: On the assumption that the self-energy of the background is purely electrostatic, the total energy of a macroscopic "jelly" metal has a minimum at $r_s = r_s^{(0)} \approx 4$ a.u. (cf. Ref. 32). To make a uniform background with density corresponding to $r_s + r_s^{(0)}$ stable, we must introduce additional nonCoulomb forces ("glue"). The specific form of these forces is highly arbitrary. However, they do not affect the electron distribution.

density also depends only on x . Besides this, it must satisfy the conditions

$$\lim_{|x| \rightarrow +\infty} n(x) = n_+(x) \quad (4.8)$$

and, for a neutral crystal,

$$\int_{-\infty}^{+\infty} [n(x) - n_+(x)] dx = 0. \quad (4.9)$$

Of course $n(x)$ does not break off sharply at the boundary of the background, but extends outside, leading to a lower kinetic energy of the electrons. The smearing out of the electron density is limited by the accompanying increase of the potential energy. The result is that near the boundary a double layer of charge is formed, of atomic dimensions. We find the corresponding electrostatic barrier from Eq. (1.9):

$$\Delta\varphi = \varphi(+\infty) - \varphi(-\infty) = 4\pi \int_{-\infty}^{+\infty} x |n(x) - n_+(x)| dx. \quad (4.10)$$

This definition of $\Delta\varphi$ agrees with Eq. (4.3), since in the "jelly" model $\bar{\varphi} = \varphi(-\infty)$. The Coulomb barrier is not the only obstacle to an electron leaving the metal. Inside the metal each electron lowers its energy through the formation of an exchange-correlation "hole." Therefore the total effective potential inside the metal approaches a value $v_{\text{eff}}[n, -\infty] = \varphi(-\infty) + \mu_{xc}(\bar{n})$, where $\mu_{xc}(\bar{n}) < 0$ is the amount by which the energy of an electron on the Fermi surface is lowered owing to exchange and correlations [see Eqs. (3.10) and (3.11)]. From this, using Eqs. (2.4), (4.1)–(4.3) and the fact that $n(x)$ is constant inside the "jelly" metal, we can obtain the following expression for the work function Φ :

$$\Phi = \{v_{\text{eff}}(n, \infty) - v_{\text{eff}}(n, -\infty)\} - \frac{1}{2} k_F^2, \quad (4.11)$$

where $k_F = (3\pi^2 n)^{1/3}$ is the Fermi momentum. Equation (4.11) allows us to interpret the work function as the additional kinetic energy that must be given to a Fermi electron in order for it to surmount the total barrier that keeps it in the metal (Fig. 1).

2) We now discuss in the framework of the "jelly" model the various contributions to the surface energy in Eq. (4.6). For this purpose we consider a homogeneous unbounded crystal of density \bar{n} . Let us mentally divide it along a plane and pull the halves apart to a macroscopic distance. The electron density in each half extends beyond the boundary of the background, distributing itself so as to minimize the total (and thus the surface) energy. Moreover, the total kinetic energy of the electrons in the two parts becomes smaller than in the original crystal so that $\sigma_s < 0$. The electrostatic energy itself increases: $\sigma_{es} > 0$. There is also an in-

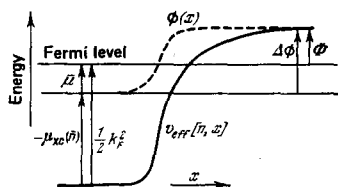


FIG. 1. Schematic representation of the potential near the surface of a "jelly" metal. The volume chemical potential, $\bar{\mu}$, is shown here positive, but can have either sign.

crease of the exchange-correlation energy ($\sigma_{xc} > 0$), since in the neighborhood of the boundary the electrons are further from their neighbors, on the average, than well inside the metal, and the exchange-correlation hole is a less effective mechanism for lowering the energy than it is in the original crystal. In the "jelly" model the electrostatic component of the surface energy can be represented, by using Eqs. (4.4)–(4.6), in the form

$$\sigma_{es} = \frac{1}{2} \int_{-\infty}^{+\infty} \varphi(x) |n(x) - n_+(x)| dx.$$

No analogous simple expressions for σ_s and σ_{xc} can be derived, since the exact expressions for $T_s[n]$ and $E_{xc}[n]$ are not known. In the "jelly" model there is an additional contribution to σ owing to the work done against the aforesaid non-Coulomb forces (the "glue"). These forces are arbitrary in our treatment. In subsection 6, Point a) we shall carry out a calculation without taking them into account, since such a calculation is a good basis for the subsequent analysis [subsection 6, Point b)], in which allowance is made for the discreteness of the lattice.

5. Density, potential, and work function (calculated results)

a) "Jelly" model

The first calculation of the electron distribution at a metal-vacuum boundary in the framework of the TFM was made by Frenkel.³³ The Thomas-Fermi equation has the property of self-similarity and can be put in a universal form which does not contain the characteristics of any particular metal. To do this we must change to dimensionless variables: $\bar{x} = x/\lambda$, $\bar{\varphi} = \varphi/\bar{\mu}$, $\bar{n} = n/\bar{n}$. Here $\lambda = (3\pi/8k_F)^{1/2}$, $\bar{\mu} = [\mu(\bar{n})/\bar{\mu}]' = k_F^2/2$ [cf. Eqs. (4.2) and (2.4)]. Then, when we also use Eq. (4.7), Eq. (3.2) takes the form

$$\bar{\varphi}''(\bar{x}) = -|\bar{\varphi}(\bar{x})|^{3/2} + \theta(-\bar{x}). \quad (5.1)$$

The electron density is connected with the potential by the relation

$$n(\bar{x}) = |\bar{\varphi}(\bar{x})|^{3/2}. \quad (5.2)$$

The solution of Eq. (5.1) must satisfy the boundary conditions

$$\bar{\varphi}(\infty) = 0, \quad \bar{\varphi}(-\infty) = 1, \quad \bar{\varphi}'(\pm\infty) = 0. \quad (5.3)$$

Equation (5.1) can be solved analytically for $\bar{x} \geq 0$. For $\bar{x} < 0$ numerical calculations are necessary. They were first done by Frenkel³³ and improved by Samoilovich³⁴ (see also Ref. 35). As has already been pointed out, the TFM is a special case of the DFM, corresponding to neglect of many-particle and quantum-mechanical effects (quasiuniformity principle). From dimensional considerations it could be expected² that the quasiuniformity approximation is correct if the conditions

$$\frac{|\nabla n(r)|}{n(r)}, \quad \frac{|\nabla^2 n(r)|}{|\nabla n(r)|}, \quad \dots \ll k_F [n(r)], \quad (5.4)$$

are satisfied, since in this case the gradient terms in the expansion (2.2) are small in comparison with the locally homogeneous term. It is easy to show that for

an actual electron distribution, which falls off exponentially outside the metal, the condition (5.4) is violated at even a small distance from the surface. Besides this, outside the metal it is not correct to neglect the exchange-correlation contribution to $g_0(n)$ in comparison with the kinetic part; this is justified inside metals with high electron densities.

Owing to these shortcomings the TFM gives an electron density which falls off too smoothly outside the metal; instead of an exponential decrease, it falls off as (distance)⁻⁶ (in analogy with the case of the Thomas-Fermi atom²⁷). This in turn leads to too large a value of the dipole barrier, which according to Eq. (5.3) is $\Delta\varphi = \frac{1}{2}k_F^2$. (We have here gone back to dimensional variables.) Also, neglect of exchange and correlation decidedly underestimates the value of the volume component of the work function: $\mu = \frac{1}{2}k_F^2$. From this, recalling that in the TFM $v_{\text{eff}} = \varphi$, we get from Eq. (4.12)

$$\Phi_{\text{TF}} = 0. \quad (5.5)$$

The zero value of the work function, and also the negative value of the surface energy, which is obtained in the TFM for all r_s (subsection 6), show that it is not suitable for calculations of energy characteristics of the surface. It follows from Eq. (5.5) that the TFM is incapable of giving a correct picture of the interaction of a positive charge with a metal; electrons, being unhindered from leaving the metal ($\Phi_{\text{TF}} = 0$) leave it when acted on by the field and neutralize the charge. For similar reasons both a negative ion and a charged capacitor are unstable in this model.³⁶ It can be shown that inclusion of exchange and correlation leads to a work function which is not zero, but is the same for all metals.⁹

To avoid these shortcomings of the TFM, Smith³⁷ used the more realistic approximation

$$G[n] = \int (dx) [g_0[n(r)] + g_2[n(r)] |\nabla n(x)|^2], \quad (5.6)$$

where $g_0[n]$ was defined in accordance with Eq. (2.2)–(2.6) and $g_2(n)$ was chosen in the form (2.7). Substitution of Eq. (5.6) in (3.3) leads to a nonlinear differential equation, whose solution requires complicated numerical computations. Smith³⁷ simplified the problem by putting $n(x)$ in the "trial" form

$$n(x) = \bar{n} \left[1 - \frac{1}{2} \exp(\beta x) \right] \theta(-x) + \frac{1}{2} \bar{n} \exp(-\beta x) \theta(x). \quad (5.7)$$

This function satisfies the asymptotic requirement (4.8) and the condition (4.9); β is an adjustable parameter. From Equations (1.5) and (5.7) we have $dE_v(\beta)/d\beta = 0$, or equivalently

$$\frac{d\sigma(\beta)}{d\beta} = 0, \quad (5.8)$$

where $\sigma = E_v[n] - E_v[n\theta(-x)]$ is the surface energy of the semi-infinite metal in question. This last formulation of the condition for a minimum is more convenient,

⁹All the calculations are analogous to those made in Ref. 27 for atoms. When exchange and correlation are taken into account the electron density goes discontinuously to zero at some point $x > 0$, which is determined by the condition that the total energy should be a minimum. Quantum corrections smooth out the discontinuity.

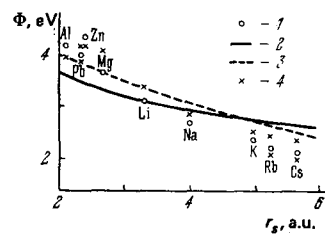


FIG. 2. Work functions of metals, 1—experiment, 2—theory (PTFM, "jelly"³⁷), 3—theory (PHM, "jelly"³⁰), 4—theory (PHM, pseudopotential³⁰).

since σ does not contain the divergences that appear in $E_v[n]$ in the limit $V \rightarrow \infty$ (V is the volume of the specimen). After calculating $\sigma(\beta)$ with the approximation (5.6) for $G[n]$, Smith found from Eq. (5.8) the function $\beta(\bar{n})$. The results calculated for the work function with these values of $\beta(\bar{n})$ are shown in Fig. 2 for a number of metals. In spite of the simplicity of the model, there is reasonable agreement with experiment for most simple metals.

The most accurate description of the electron distribution near the surface is obtained by using the PHM, since the functional $T_s[n]$ is fully taken into account in this method. In particular, in the density $n(x)$ calculated (see Ref. 38) on the basis of a one-dimensional version of Eqs. (3.7), (3.8) (Fig. 3), there is a Friedel oscillation with the characteristic asymptotic form $A \cos(2k_F + \alpha)x^{-2} + O(x^{-3})$, $\alpha = -2\gamma(k_F)$, where $\gamma(k)$ is the phase shift of the asymptotic ($x \rightarrow \infty$) wave function, $\Psi_{k_x, k_y, k_z}(r) = \sin[kx - \gamma(k)] \exp[i(k_y y + k_z z)]$. It is not hard to verify this by substituting Ψ_{k_x, k_y, k_z} in Eq. (3.8) and integrating by parts. It can be seen from Fig. 3 that when the background density is low ($r_s = 5$) the oscillations are large, while for a high density ($r_s = 2$) they are not conspicuous and the density is roughly monotonic and close to the Thomas-Fermi form. This is easily understood; the conditions (5.4) for applying the TFM are better satisfied for larger n . For the exchange-correlation component $\mu_{xc}[n]$ the local-density approximation, (LDA) was used in Ref. 38, as in most subsequent work.

The local approximation gives good results for those characteristics of the surface that depend on integrals over x , namely Φ and σ (see later discussion). Non-integral properties do not behave as well; $v_{\text{eff}}(x)$, for example, does not have the necessary behavior under

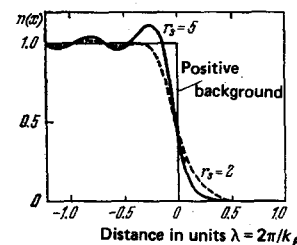


FIG. 3. Normalized electron density at the surface of a "jelly" metal (self-consistent calculation)³⁸. The Friedel oscillations can be seen. They are more pronounced for metals with low electron densities (larger values of r_s).

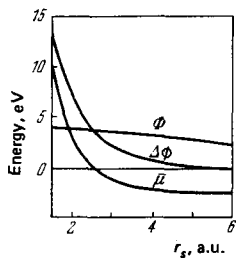


FIG. 4. The work function of a metal and its components.³⁰

reflection outside the metal, and falls off exponentially. The reason is that the LDA does not take into account nonlocal polarization, which is responsible for the appearance of "virtual charge" which leads to the "mirror image" forces.¹⁰⁾

Figure 2 shows the work function calculated by Lang and Kohn³⁰ on the basis of the PHM (dashed curve), and Fig. 4 shows its volume and surface components, $-\bar{\mu}(r_s)$ and $\Delta\varphi(r_s)$. Whereas $\bar{\mu}$ and $\Delta\varphi$ vary by 5.3 and 6.8 eV, respectively, over the range of metallic densities, the total work function varies only from 2.4 to 3.9 eV. It can be seen from Fig. 2 that the results of Lang and Kohn and those of Smith differ by not more than 0.3 eV, although the latter do not take oscillations into account. The reason for the agreement is that in the range of densities where the oscillations are large the surface contribution $\Delta\varphi$ is itself small in comparison with $|\bar{\mu}|$ (Fig. 4). In the comparison of Φ with experiment (see Fig. 2) preference was given to data obtained with the photoelectric method and the contact potential method, which are effective at low temperatures (the references to the original papers are given in Ref. 39). We note that there is a considerable spread of the values of Φ obtained by different methods.⁴⁰ Besides comparison with experiment, there are also "internal" tests of the accuracy of the calculations, based on exact results ("sum rules").

Budd and Vannimenus⁴⁰ derived an exact relation connecting the difference of the potentials at the boundary of the background and in the interior of the "jelly"-metal with the bulk characteristics:

$$\delta\varphi \equiv \varphi(0) - \varphi(-\infty) = \bar{n} \left(\frac{g_0(\bar{n})}{\bar{n}} \right); \quad (5.9)$$

here $g_0(\bar{n})$ is the volume energy density of the homogeneous electron gas, Eq. (2.3). Accordingly, we can calculate $\delta\varphi$ without making any assumptions about the form of the inhomogeneous part of the functional $G[\bar{n}]$. Therefore Eq. (5.9) enables us to estimate the accuracy of numerical calculations based on approximate ways of taking the inhomogeneity into account and carried out on the basis of various versions of the DFM. For example, using exactly the same approximation for $g_0(\bar{n})$ as did Smith³⁷ and Lang and Kohn³⁹

¹⁰⁾This difficulty does not arise when we consider a localized external charge situated outside the metal. In this case the potential of the charge is included as part of the external potential, and virtual charge appears even when exchange and correlation effects between electrons are neglected. (i.e., in the ordinary Hartree self-consistent approach). The corresponding calculations are discussed in subsection 8, a).

TABLE I. Comparison of exact values of $\delta\varphi$ for a metal in the "jelly" model [Eq. (5.10)] with the results of numerical calculations. The values in the second and third columns are taken from Ref. 41 (Table I). The first column gives values of $\delta\varphi$ calculated on the basis of the Smith model.³⁷

r_s , a.u.	$\delta\varphi(r_s)$ Smith	$\delta\varphi(r_s)$ Lang and Kohn	$\delta\varphi(r_s)$ Equation (5.10)
2	0.2651	0.2292	0.2276
3	0.1796	0.1346	0.1329
4	0.1263	0.0273	0.0318
5	0.0935	-0.083	-0.0752
6	0.076	-0.212	-0.1822

we get (in units of $k_F^2/2$)

$$\delta\varphi = 0.4 - 0.0829r_s - \frac{0.0796r_s^2}{(r_s + 7.8)^2}. \quad (5.10)$$

For $r_s \rightarrow 0$ Eq. (5.10) gives $\delta\varphi = 0.4$, corresponding to the TFM. This confirms that the TFM is suitable for use in the limit $n \rightarrow \infty$. Table I shows values of $\delta\varphi$ calculated from Eq. (5.10) and also as calculated in Refs. 37 and 39.

In spite of the local approximation for $E_{xc}[n]$, the results of Lang and Kohn³⁹ agree well with the exact results. The negative values of $\delta\varphi$ at low densities ($r_s \geq 5$) are due to the first oscillation peak of the electron density. The calculations of Smith,³⁷ based on the PTFM, do not take the oscillations into account, and their accuracy in describing the potential decreases with increasing r_s .

We note that comparison with Eq. (5.9) gives a more reliable indication of the accuracy of calculations of electron densities and potentials than does comparison of calculated values of the integral characteristics (Φ and σ) with their experimental values.

b) Discrete lattice

Within the framework of the "jelly" model it is impossible to explain the important experimental fact, that the work functions of single crystals are anisotropic; when the lattice is replaced by a background the nonequivalence of different planes in the lattice disappears. In subsection 6 we shall show that neglect of the discreteness of the lattice also makes it impossible even to predict satisfactorily the numerical values of surface energies, to say nothing of their anisotropy.

1) "Corrugated background" model. The first semiquantitative explanation of the anisotropy of the work function was given by Smoluchowski.⁴² He considered a model in which the positive charge of the lattice was spread uniformly over the Wigner-Seitz cells. Then the distribution inside the metal is the same as in the uniform-background model, but a "relief" appears on the surface, which is different for different faces of a single crystal because of the anisotropy of a Wigner-Seitz cell. With a variation procedure it was shown that the electronic relief (the shape of the surfaces on which the electron density is constant) is smoother than the lattice relief. Complete screening of the background would be accompanied

by nonuniformly distributed amounts of kinetic energy expended (its inhomogeneous part). The smoothing-out effect is especially important for closely packed planes. Owing to the fact that the "peaks" of the deformed background project beyond the "clouds" of the electron density, there is an electrostatic barrier of negative sign, which is larger in absolute value when the closeness of packing on the face in question is smaller. The volume component of the work function of course remains the same as in the "jelly" model. Consequently, it follows from the improved approximate model that a crystal face with closer packing has a larger work function. This rule is verified experimentally. For example, for $W^{43}(\text{bcc})$ we have $\Phi(110)=5.25$ eV, $\Phi(100)=4.63$ eV, $\Phi(111)=4.47$ eV. Data for Cu (fcc) are given in Ref. 44.

This model is now mainly of historical interest. Among its few relatively recent applications we may mention the work of Smith,⁴⁵ who applied the corrugated-background model to calculate the work function of the (110) face of W . Here, relying on Smoluchowski's conclusion that the electron relief is smooth for closely packed planes, Smith used in the calculation an electron distribution corresponding to a plane model with a uniform background.

2) *Use of perturbation theory to take the discrete nature of the lattice into account.* It has already been pointed out that the reason it is hard to deal with the discrete nature of the lattice exactly is that one needs the solution of an essentially three-dimensional system of self-consistent equations. The problem can be greatly simplified by replacing the actual potentials of the ions by pseudopotentials and taking their effect on electrons into account using perturbation theory. Here we must take as the perturbation $\delta V(r)$ the difference between the total pseudopotential of the ions and the potential of the uniform background. Lang and Kohn³⁰ have shown that the resulting contribution from discreteness to the work function can be put in the form

$$\delta\Phi = \int \delta V(x) n_o(x) dx \int n_o(x) dx,$$

where

$$\delta V(x) = \frac{1}{L_y L_z} \iint \delta V(r) dy dz$$

is the perturbing potential averaged over the yz plane, and $n_o(x)$ is the surface density of electrons in the metal from which one electron has been removed.

It will be shown in Section IV that for small values of the electric field F the density of charge $n_r(x)$ induced by it depends linearly on the field. This allows us to express $n_o(x)$ in terms of a linear response to the external field. Calculating the density of the screening charge in the LRA and using the local pseudopotential proposed by Ashcroft⁴⁶ to determine $\delta V(r)$, Lang and Kohn found $\delta\Phi$ for various faces of a number of metals. For example, for the bcc metals Na (Cs) the respective calculated values of $\delta\Phi$ are 0.05 (-0.25) for the (110) face, -0.3 (-0.6) for (100), and -0.4 (-0.65) for (111) (all in eV). These results demonstrate the tendency for the work function to increase with the density of packing of the face, which we

discussed earlier. For the alkali metals the average $\delta\Phi$ turned out to be negative, which led to better agreement with experiment for polycrystalline metals (Fig. 2).

3) *Exact discrete treatment (self-consistent pseudo-potential model).* The first self-consistent calculation in which the discreteness of the lattice was taken into account without the use of perturbation theory was made by Appelbaum and Hamann⁴⁷ for a (100) face of a semi-infinite crystal of Na. The potential used was of the form $v_T(r) = v_{\text{eff}}(r) + v_{\text{ion}}(r)$, where $v_{\text{eff}}(r)$ is the effective potential in the "jelly" model, as defined by Eqs. (3.10) and (1.7), and $v_{\text{ion}}(r)$ describes the nonelectrostatic electron-ion interaction. Owing to the two-dimensional spatial periodicity, the energy ϵ and the two-dimensional wave vector k_{\parallel} can serve as the quantum numbers for the problem.

Appelbaum and Hamann⁴⁷ divided space into three parts: 1) the volume part, extending from $x = -\infty$ to $x = -a$, 2) the surface layer, from $x = -a$ to $x = +b$, and 3) the vacuum, from $+b$ to ∞ . In the first layer the potential is assumed to have its volume value. The corresponding wave functions are known, being ordinary Bloch wave functions. In the vacuum region the potential is independent of the coordinates, and the wave functions decrease exponentially as x increases.

The solutions of the Schrödinger equation in the surface layer are matched with the volume functions at $x = -a$ and with the vacuum functions at $x = b$. Ashcroft's model potential was used for v_{ion} . The boundary at $x = -a$ between the surface and volume regions was chosen between the second and third planes of atoms. Shifting it to a position between the third and fourth planes made only a trifling change in the results. The work function of Na came out 0.3 eV lower than in the "jelly" model, in good agreement with the results of Lang and Kohn³⁰ and with experiment. The calculation of the electron distribution showed that the Friedel oscillations in the surface combine additively with the volume oscillations caused by the discreteness of the lattice. This is not surprising, since neither contribution exceeds 10 percent of the average value of the density.

The self-consistent potential along some axes normal to the surface is shown in Fig. 5.

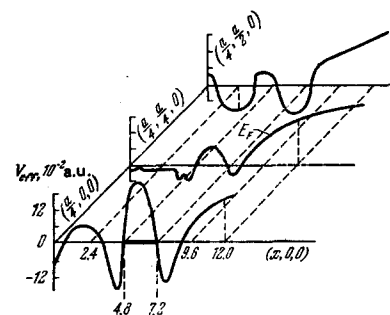


FIG. 5. Variation of the effective potential along three axes normal to the surface Na(100).⁴⁷ The lowest axis goes through the center of a surface atom (distinguished by thickening), and the top axis, halfway between two adjacent surface atoms.

An analogous approach has been used in a number of papers on the electron structure of semiconductor surfaces. References and discussion can be found in the review by Appelbaum and Hamann⁸ and in later papers.⁴⁸⁻⁵¹ A somewhat different approach to the analysis of a surface involves the solution of the three-dimensional self-consistent Schrödinger equation for a crystal plate containing N atomic layers. The first calculation with this geometry was made by Alldredge and Kleinman⁵² for Li, using a plate parallel to the (100) face containing 13 planes of atoms. The boundary conditions were given by placing an infinite step barrier at a distance l of several times the lattice constant from the outermost atomic planes, so that its effect on the actual surface barrier is negligible. The wave functions were found as sums of harmonics falling off along the normal to the value zero at distance l .

By diagonalizing the matrix of the Hamiltonian one can obtain a discrete spectrum of allowed values of $\epsilon_{s\parallel}$ for any value of k_{\parallel} . With increasing thickness of the layer the distance between most of the successive levels decreases, forming a continuous band in the limit. The levels which remain isolated from the band are surface states. They always appear in pairs and are spatially localized near the surface. In their calculations Alldredge and Kleinman⁵² used a nonlocal pseudopotential.⁸ Improved calculations for Li and Na were given by Hardy and Allen.⁵³ Other calculations of this kind deal with electron states at surfaces of Al(111),⁵⁴ Nb(100),⁵⁵ Fe(100),⁵⁶ and Cu(100).⁵⁷

Advantages of the plate geometry are that all of the states, volume and surface, are discrete, and they are all treated in the same way. However, the difficulties in the calculation increase very rapidly with the thickness of the plate. At present there are few papers in which both exact treatment of the discrete lattice and full self-consistency are achieved. Nevertheless, in the opinion of Bennet,⁷ it is the appearance and further development of these researches that mark the entrance into "a new era in the theory of electron properties of surfaces." It is remarkable that these self-consistent calculations automatically include the development of a theory of surface (Tamm) states. An exposition of these (model) approaches and results, and also references to the original papers are given in a review by Davison and Levin.⁵⁸

6. Surface energy (calculations)

The problem of surface energy has played an important part in the development of the applied theory of the DFM. The peculiar "ultradensity catastrophe," in which the "jelly" model value of σ becomes negative for small r_s , posed very sharply the problem of dealing with the discreteness of the lattice, and also stimulated an intensive analysis of the applicability of the gradient expansion and the LDA to calculations of $E_{xc}[n]$.

a) "Jelly" model

The simplest self-consistent calculation of the surface energy of a "jelly" metal was first carried out by

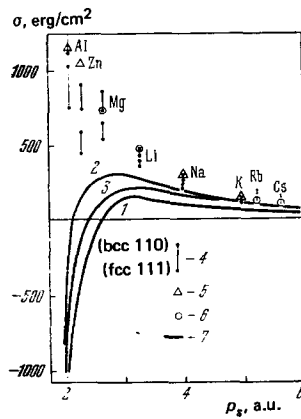


FIG. 6. Comparison of theoretical and experimental values of the surface energy. Curves 1-3, theory: 1—PTFM, LDA,³⁷ 2—PTFM with nonlocality taken into account⁶⁰ (g_2^{xc} calculated from the data of Ref. 59), 3—PHM, LDA.³⁹ The vertical segments (4) describe the theoretical values obtained using a pseudopotential (lower value with LDA, upper with nonlocal $E_{xc}[n]$). 5—experimental values for solid metals,^{65,66} 6—found by extrapolating to 0° K the data on surface tensions of liquid metals (given in cases where no data were found for the solid state), 7—homogeneous background model.

Smoluchowski³⁴ by means of the TFM, in which only the kinetic and electrostatic components of σ are considered. Using Eqs. (4.5), (4.6), (2.4), and (5.1), one can show that

$$\sigma_{\text{TFM}} = -\lambda \bar{\mu} \bar{n} \int_{-\infty}^{+\infty} \psi'^2(\tilde{x}) d\tilde{x} = -0.0763 r_s^{-9/2}.$$

This result is absurd; the experimental values of σ are of course positive and increase rapidly as r_s becomes smaller. Smith³⁷ used the PTFM in calculating surface energies [cf. Eqs. (5.6)–(5.8)]. The functional form of $\sigma(r_s)$ which he found is shown in Fig. 6 (curve 1). In the series of alkali metals (Cs, Rb, K, Na, Li) the calculated σ is positive and increases with density like the experimental value, although the theoretical values are too low. For $r_s \approx 3.1$ they begin to drop, and they become negative at $r_s \approx 2.6$, which indicates that the model used becomes unsuitable at high densities. If, remaining within the framework of the "jelly" model, we include the first gradient correction to $E_{xc}[n]$, using the results of Ref. 59 to calculate g_2^{xc} , the theoretical values of σ become larger,^{60,61} and the agreement with experiment for the light metals is improved (curve 2). For small r_s , however, the behavior of $\sigma(r_s)$ is still "pathological."

A quantum-mechanical calculation (PHM)³⁹ (Fig. 6, curve 3) also does not rectify the behavior of $\sigma(r_s)$ for high background densities, in spite of the exact treatment of the functional $T_s[n]$, Eq. (3.14) (the LDA was used for E_{xc} in Ref. 39). The correctness of Lang and Kohn's analysis³⁹ within the framework of the model employed ("jelly", LDA) can be confirmed by means of an exact relation between the one-particle (σ_s) and the total surface energy of a "jelly" metal.⁶² As was pointed out in subsection 4, Point b), σ_s is the only negative contribution to the surface energy. Consequently, the disagreement with experiment is due to

an underestimate of the electrostatic and/or the exchange-correlation components of σ . Lang and Kohn³⁹ proposed that the cause of the discrepancy lies in the neglect of the discreteness of the lattice.¹¹⁾

b) Discrete lattice

The lattice contribution to the surface energy is calculated in Ref. 39 in first-order perturbation theory [see subsection 5, Point b), 2)]. We denote by σ_0 and n_0 the surface energy and electron density calculated in the uniform-background model. In view of the stationarity condition (1.5) the change of the surface energy in first-order perturbation theory can be expressed in terms of the density $n_0(x)$. Therefore the values of $T_s[n]$ and $E_{xc}[n]$ remain the same as in the "jelly" model, and the change $\delta\sigma \equiv \sigma - \sigma_0$ in the surface energy is completely due to the difference between the energies of interaction of all positive and negative charges in the discrete lattice model in question and in the "jelly" model. Lang and Kohn³⁹ carried out the calculation of $\delta\sigma$ for the closely packed planes fcc (111) and bcc (110), using Ashcroft's pseudopotential⁴⁸ and neglecting the relaxation of the surface density. The lattice contribution leads to positive values of σ even for small r_s and improves the agreement with experiment (see subsection 6). In the cleaving of the crystal there may be a displacement in the x direction of lattice planes parallel to the newly formed surface. It has been shown⁶¹ that the effect of this on σ is small.

A variational procedure has been proposed⁶⁴ which takes into account the averaged effect of lattice discreteness by introducing a term added to the potential inside the metal which depends on the structure of the lattice and the surface considered. Calculations showed that for some metal surfaces the linear approximation is not accurate enough, since the perturbing term $\delta V(r)$ is not always small. A particularly large difference was found for Pb (111); the value $\sigma \sim 550$ erg/cm² found in this way agrees better with experiment⁶⁵ (690 erg/cm²) than the result of the linear approximation³⁹ (1140 erg/cm²). The averaged term $\langle \delta V(r) \rangle$ in this case is about a third of $v_{\text{eff}}(-\infty)$. This method ("variation of the potential") is also effective in the calculation of other characteristics (density, potential, work function).

c) Effects of nonlocality of exchange and of correlations

We have shown that including ionic pseudopotentials can correct shortcomings of the theoretical dependence $\sigma(r_s)$ found in the "jelly" model. It is not obvious, however, that neglect of discreteness is the main and single cause of the discrepancies between theory and experiment and that the theory cannot be improved while remaining within the framework of, say, the "jelly" model. Two papers^{67,68} have considered the contribution to the surface energy of a

"jelly" metal caused by the change of the zero point energy of plasmons owing to the appearance of surface modes when the crystal is split into parts. In a simple model which neglects dispersion of the plasmons this contribution is

$$\sigma_{\text{pl}} = \frac{\omega_0}{16\pi} [V\sqrt{2}(k_c^S)^2 - (k_c^B)^2], \quad (6.1)$$

where k_c^S and k_c^B are the smallest values of the wave vector for which decay into an electron-hole pair (Landau damping) is possible for surface and volume plasmons, respectively, and ω_0 is the frequency of plasma excitation in the volume. Setting, as in Refs. 67, 68, $k_c^S = k_c^B = k_c$, we get

$$\sigma_{\text{pl}} = -\frac{V\sqrt{2}-1}{16\pi} k_c^2 \omega_0. \quad (6.2)$$

Having found good agreement between Eq. (6.2) and the experimental values of σ , the authors of these papers^{67,68} suggested that σ_{pl} be taken as the total surface energy. The assumption was that all other contributions (not included in their calculations) exactly cancel each other. Other papers⁶⁹⁻⁷¹ criticized the result (6.2). It was pointed out that the assumption that k_c^S and k_c^B are equal, which led to agreement of the value (6.2) with experiment, is not justified, since the damping of surface plasmons begins at much larger wavelengths than that of volume plasmons. Feibelman⁷² showed that k_c^S must be smaller than $k_c^B/2^{1/2}$. Then Eq. (6.1) shows that the plasmon contribution is negative and cannot agree with experiment. However, Harris and Jones⁷³ pointed out that these objections bear on details of the calculations in question,^{67,68} but do not fully settle the question of the contribution of the zero-point vibrations to the surface energy. In particular they showed that this contribution is not included in the calculations of Lang and Kohn³⁹; the reason for this is the use of a local approximation for $\mu_{xc}(n)$. The plasmon contribution, caused by large-scale correlations in the electron gas, is of course associated with an essentially nonlocal part of $\mu_{xc}(n)$. For the analysis of the nonlocal effects Harris and Jones, and also Wikborg and Inglesfield,⁷⁴ derived exact expressions for the exchange-correlation energy of a bounded electron gas (see also Ref. 75). For electrons in a potential well with an infinite barrier at the boundary¹²⁾ they calculated the exchange part of the surface energy, σ_x ,⁷³ and also calculations were made in the random phase approximation for both σ_{xc} and σ_c .⁷⁴ These values were compared with $\bar{\sigma}_x$, $\bar{\sigma}_c$, and σ_{xc} calculated in the LDA). It turned out that the difference between $\bar{\sigma}_x$ and σ_{xc} is small (within 10 percent), but the exchange and correlation contributions differ quite significantly. $\bar{\sigma}_x$ exceeds the exact value by about 50 percent, while $\bar{\sigma}_c$, on the contrary, comes out much smaller (by about a factor 6). Accordingly, the LDA provides much better results for the sum of the exchange and correlation energies than for each of them separately. The calculations of

¹¹⁾The discreteness of the lattice has also been taken into account in papers by S. N. Zadumkin and his collaborators (see Ref. 63 and paper cited there). The method used is reminiscent of the PTFM and included a number of empirical parameters.

¹²⁾This model is useful for the analysis of the suitability of various approximate descriptions of an inhomogeneous electron gas, but is too crude for use in calculating surface properties.^{76,77} Much better approximations are given by models with linear⁷⁸ and step (finite height)^{77,79-81} barriers.

Refs. 76, 79–81, 83–85, based on more realistic models of the surface barrier, also confirm that the contribution of the LDA to $\sigma_{xc}[n]$ has a decisive effect. For example, a completely self-consistent analysis⁸¹ in which $g_2^{xc}[n]$ was used²³ (cf. Eq. (2.8) leads to non-local corrections that do not exceed 16 percent of $\sigma_{xc}[n]$, although the relative contribution of nonlocality to the total surface energy can be large (up to 40 percent), since for the majority of metals $\sigma_{xc} > \sigma$ (see Ref. 39). Therefore inclusion of it allows us to bring the theoretical values of σ closer to the experimental values found for solid metals (Fig. 6).

IV. INFLUENCE OF AN EXTERNAL PERTURBATION ON THE ELECTRON PROPERTIES OF METAL SURFACES

In this section we discuss the stationary response of a metal surface to a uniform electric field, and also the interaction of atomic particles with a metal (adsorption) and the interaction of two metals (adhesion). In accordance with the general spirit of this survey, we have not included here many papers in which self-consistency was not considered or was not fully realized (for example, in which the ground state was treated non self-consistently). In some cases it has been necessary to refer to such papers.

7. Metal surface in an external electric field

a) Boundary conditions, asymptotic form of potential

If the ground state is treated non self-consistently, the boundary condition for the field is prescribed on some plane $x=a$ near the surface:

$$\varphi'(a) = F_x; \quad (7.1)$$

here F is the external field, which is directed normal to the surface. For example, $a=0$ if the unperturbed density is approximated by a step function,^{88–89} or if it coincides with the boundary of the “well” in a model with an infinite potential barrier.^{90–92} Actually, because the electron density is “smeared out”, the field near the surface depends both on the external field and on the perturbation of the surface charge that it causes, and it itself subject to definition. The only thing that can be regarded as prescribed is the field at a large distance from the surface:

$$\lim_{x \rightarrow -\infty} \varphi'(x) = F_x. \quad (7.2)$$

Using Eq. (1.9) and the condition

$$\int_{-\infty}^{+\infty} n_F(x) dx = \frac{F_x}{4\pi}, \quad (7.3)$$

which is equivalent to the boundary condition of electrostatics, $F=4\pi\gamma$ (γ is the density of surface charge), and also the fact that $n(x)$ drops rapidly for $x>0$, we can easily show that $\varphi(x)$ has the asymptotic form

$$\varphi(x) = \varphi_0(x) + F_x(x - x_0(F_x)), \quad x \gg 2\text{\AA}, \quad (7.4)$$

where $x_0(F_x) = \int_{-\infty}^{+\infty} n_F(x)x dx / \gamma$ is the “center of gravity” of the charge density induced by the field. Accordingly, $x_0(F_x)$ has the meaning of the “boundary of the metal in the field.” We note that for $F_x > 0$ the motion of the electrons becomes finite, and Eq. (7.2) takes the form

$$\varphi'(x_0) = F_x; \quad (7.5)$$

in this case $x_0(F_x)$ coincides with the classical turning point at which the Fermi level intersects the potential.

b) Electronic properties of a surface in an external field (calculations)

1) *Thomas-Fermi method.* The problem of the penetration of a field into a metal was first solved by Rice⁸⁶ on the basis of approximate Thomas-Fermi equations with the boundary condition (7.1) and $a=0$ (the unperturbed distribution was approximated by a step function). Subsequent papers^{87–89} were devoted to a more accurate solution of the problem with the same boundary conditions, and complete self-consistency in the framework of the TFM was achieved in Ref. 36. According to Eq. (5.5) the TFM does not apply to the description of a surface in a field $F_x < 0$; even an infinitely small field “pulls electrons out” of the metal. Therefore a field $F_x > 0$ was considered in Ref. 36 [cf. Eq. (7.5)]. Calculating the first integral of Eq. (5.1) and using the fact that $\varphi(x)$ and $\varphi'(x)$ are continuous, one can find the value of the potential at the boundary of the background: $\varphi(0, \alpha) = -0.6\bar{\mu}(1 - \alpha^2)$, where $\alpha = F/F_{cr}$ is a dimensionless parameter, and $F_{cr} = (4.8\pi n\bar{\mu})^{1/2} \approx 8.49n^{5/6}$ and lies in the range $2 \cdot 10^8 - 3 \cdot 10^9$ V/cm. The quadratic dependence on the field is due to the external ($x>0$) screening, and neglect of this effect led to a nearly linear relation.^{88,89} It can be easily shown that the field correction found here, $\delta\varphi(0, \alpha) = 0.6\bar{\mu}\alpha^2 \equiv F^2/8\pi\bar{n}$ agrees with the exact result for the “jelly” model, which, when Eqs. (1.9) and (7.3) are used, follows from the “sum rule”

$$\gamma^2 = 2\bar{n} \int_{-\infty}^0 n_F(x) x dx.$$

As was shown in subsection 5, Point a), the value $\varphi_0(0) = -0.6\bar{\mu}$ obtained with the TFM can be very different from the exact value, especially for large r_s . Accordingly, the TFM gives a considerably better description of the field correction to the potential inside the metal than the unperturbed potential. Figure 7 shows the function $x_0(F_x)$ obtained by numerical integration of the TF equation with the condition (7.5). It can be seen that the field, in deforming the electron distribution, shifts its boundary toward the metal and “pushes” electrons into the limits of the background for $\alpha=1$. For large fields ($\alpha \geq 0.7$) the effect of external screening can be neglected; the field, deforming the surface barrier, “makes its way” to the metal.

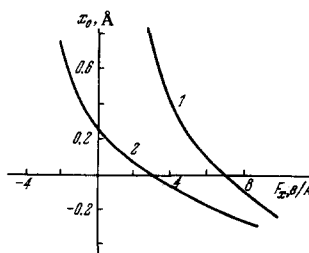


FIG. 7. Shift of the boundary of the electron density under the influence of an electric field. 1—Thomas-Fermi model,⁸⁶ 2—self-consistent quantum-mechanical calculation.⁸⁸

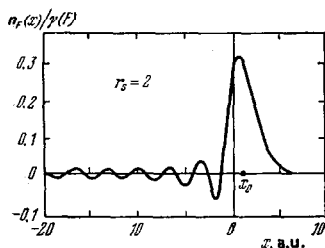


FIG. 8. Normalized density of the screening charge induced by a weak uniform electric field (linear-response approximation)¹¹⁰ x is the coordinate of the "center of mass".

2) *Many-particle and quantum effects.* The TFM, being self-consistent, gives a qualitatively correct picture of the effect of a field $F_x > 0$ on the distribution of the electrons. But this model, as has already been pointed out, describes poorly the quantitative characteristics of the surface and is entirely useless for $F_x < 0$. These shortcomings of the TFM can be overcome by taking into account many-particle and quantum corrections to the energy. Within the framework of linear response (LR) this was done by Lang and Kohn³⁰ in connection with the analysis of the effect of the discreteness of the lattice on the work function [see subsection 5 b)]. It was found that in the region of LR changing the field strength changes only the amplitude of the induced density, and not its shape. In other words, in this region x_0 does not depend on F , and $x_0(0) \neq 0$. The normalized density of the induced charge for $r_s = 2$ is shown in Fig. 8. According to Ref. 30, $x_0(0)$ is positive and ranges from 1.6 atomic units ($r_s = 2$) to 1.2 a.u. ($r_s = 6$). Similar results for $x_0(0)$ are obtained in the limit $F \rightarrow 0$ from calculations that go beyond the framework of the LRA.^{93,94} Theophilou and Modinos⁹³ used a self-consistent quantum-mechanical approach. Empirical considerations were taken into account in choosing the effective potential $v_{\text{eff}}^{(0)}(x)$ of the unperturbed surface,¹³⁾ and the Coulomb part of the induced potential was determined in a self-consistent way. Exchange and correlation were included in the framework of the LDA. The function $x_0(F_x)$ shown in Fig. 7, (curve 2) is an average of values of $x_0^{(1)}(F_x)$ and $x_0^{(2)}(F_x)$ calculated for two approximations to $v_{\text{eff}}^{(0)}(x)$. As the field increases $x_0(F_x)$ shifts toward the metal for $F_x > 0$ [$\delta x_0(F_x) = x_0(F_x) - x_0(0) < 0$] and in the opposite direction for $F_x < 0$. A similar behavior has also been obtained by means of the PTFM.⁹⁴ Conversely, the model with an infinite barrier at the boundary⁹⁰ yields $\delta x(F_x) < 0$ for $F_x < 0$. For $F_x > 0$ the results of Refs. 93 and 94 agree qualitatively with the TFM. The quantitative difference is most important at weak fields, when the significant region for this

¹³⁾ Further from the metal the potential $v_{\text{eff}}^{(0)}(x)$ chosen in Ref. 93 goes over into an image potential, and deep within the metal it takes on a value v_0 , found by considering experimental evidence. Two models were used for the potential in the transition region. The calculations showed that the final results for observable physical quantities (for example, for the current density and the electron energy distribution in cold emission) depend only weakly on the choice of model. This justifies the partial lack of self-consistency in the calculations.

problem includes the vacuum "tail." As has been pointed out [subsection 5, a)], the TFM is least effective in this region. In particular, it gives too smooth a decrease of the electron density, which leads to $x_0(0) = \infty$. For $F_x \geq 7 \cdot 10^8$ V/cm the results of the TFM agree with Ref. 93 to within 0.3 Å.

3) *Discussion (comparison with experiment).* The shift of the boundary in the field leads to a change of the dipole moment of the double layer of charge. Consequently the surface Coulomb barrier changes by the amount $\delta(\Delta\phi) = F_x \delta x_0(F_x)$. According to the calculations in Ref. 93 this amounts to 1.2 eV for $F_x = 5 \cdot 10^8$ V/cm (see Fig. 7). Thus nonlinear effects in strong fields lead to a decided nonadditivity of the "field" ($-F_x x$) and "proper" contributions to the surface barrier. We consider its possible manifestations.

a) Considering that outside the metal $\phi_0(x)$ goes over asymptotically into the image potential, with the plane $x = x_0(0)$ serving as the "mirror" [see subsection 8, a)], we find from Eq. (7.4) that for $x \geq 2$ Å we have $\phi(x) = -|x - x_0(0)|^{-1} + F_x[x - x_0(F_x)]$. The height of the Coulomb barrier in a field $F_x < 0$ is raised by $\delta(\Delta\phi)$ in comparison with the "Schottky barrier" ($x_0 = 0$) and is given by¹⁴⁾ $\phi_{\text{max}} = -F^{1/2} + F \delta x_0(F)$. The shape of the barrier also changes. For sufficiently strong fields ($F > 10^7$ V/cm) this must lead to deviations from the Fowler-Nordheim (F-N) law for cold emission, which predicts that $\lg(j/F^2)$ is a linear function of F^{-1} (j is the emitted current density) and is derived on the assumption that the contributions to the barrier are additive.¹⁵⁾ Deviations of this sort are observed experimentally for $F \geq 5 \cdot 10^7$ V/cm (cf. Ref. 93, Fig. 10). At the present time, however, no unambiguous conclusion can be reached about the true nature of this nonlinearity. First, the calculation of Ref. 93 showed that the experimental deviations cannot be ascribed entirely to the shift of the boundary. Space charge effects, which are important at high current densities,⁹⁶ must also be taken into account, and so must the inhomogeneity of the emitter.⁹⁷ Second, a more rigorous description of the act of emission on the basis of the "threshold" theory (Section 5, subsection 4 in Ref. 95) predicts a deviation from the F-N law independently of all these factors, even for a model with a triangular barrier.

Evidently more unambiguous information about the effect of a field on the surface barrier can be obtained from experiments on thermal self-emission. As was pointed out in Ref. 98, curves of the distribution of the total energy of the emitted electrons $j(\epsilon)$ change slope at an energy $\epsilon_{\text{max}} = \Phi - F^{-1/2} - F \delta x_0$, which is the height of the barrier relative to the Fermi level in the metal. (At $\epsilon = \epsilon_{\text{max}}$ the tunnel mechanism gives way to the thermal one.) Therefore it can be expected that mea-

¹⁴⁾ We recall that $\phi_{\text{max}} = \phi(x_1)$, where x_1 is determined by the condition $\phi'(x)|_{x=x_1} = 0$ for $F_x < 0$.

¹⁵⁾ With the traditional "tunnel" approach the dependence of $\ln(j/F^2)$ on F^{-1} turns out to be linear, both for a triangular barrier and when the Schottky correction for image forces (cf., e.g., Ref. 95, Sections 1, 3) is used.

measurements of $j(\varepsilon)$ at different fields F will give a key to the determination of δx_0 .

b) Owing to the widespread use of the ion projector method, research on surface ionization and on evaporation of surface atoms has become important (see, for example, Ref. 99, Sections 2 and 3). Müller¹⁰⁰ was the first to point out that the shift of the electronic boundary because of a field must change the binding energy of atoms to the surface. Thus the activation energy for evaporation of an ion with charge Z is reduced in a field by the amount $\delta Q_x = ZF\delta x_0$.¹⁶⁾ For evaporation of tungsten ions W^{3+} and W^{4+} from a W surface this quantity amounts to several electron-volts, and provides an explanation of the fact that smaller fields are required to evaporate multiply charged ions than are predicted on the assumption of barrier additivity.

The penetration of the field into the metal also diminishes the critical distance at which an atom at the surface can be ionized,¹⁰² as a result of which the ionic current must be larger and the energy distribution of the ions must be narrower than according to the additive model. These conclusions are in agreement with experiment. Moreover, the narrowing of the ionization zone makes it more probable that ionization will occur without a previous adsorption (scattering with redistribution of charge). The part played by such processes has been emphasized in a number of papers (cf. Ref. 103).¹⁷⁾

c) The different positions of the geometric and "electric" (x_0) boundaries of the metal must affect the capacitance of a parallel-plate capacitor. Let us consider the case in which the two plates are made of the same metal. Suppose plate 1 is given a positive charge of density $\int_{-\infty}^{\infty} n_1(x) dx = \gamma$, and plate 2 receives charge with surface density $\int_{-\infty}^{\infty} n_2(x) dx = -\gamma$.¹⁸⁾ The corresponding potential difference between the plates is then

$$u = 4\pi \int x [n_1(x) + n_2(x)] dx \equiv 4\pi\gamma (x_0^{(1)} - x_0^{(2)}).$$

Using the definition of capacitance (per unit area) $c = \gamma/u$, we get*) $\{c = (x_0^{(1)} - x_0^{(2)})/4\pi = l_c/4\pi$ (sic), where l_c is the effective gap width. Since $x_0^{(1)}(0)$ and $x_0^{(2)}(0)$ are shifted into the gap relative to the geometric boundaries, $c < c_0 \equiv l_0/4\pi$ (sic), where l_0 and c_0 are the "geometrical" gap width and capacitance.} The difference between c and c_0 becomes quite appreciable for $l_0 \lesssim 50$ Å, and can reach 30–40 percent for $l_0 \approx 10$ Å. We know of no direct measurements of capacitance with narrow

*) Note from translation editor: The material in figure brackets is a literal translation of the Russian text which appears to be mathematically incorrect.

¹⁶⁾ In the derivation of the expression for δQ_x it is assumed that the field does not affect the equilibrium position of the surface atoms; this may be untrue for large fields ($\geq 1V/\text{Å}$). Therefore this expression can be used only for crude estimates.

¹⁷⁾ The results of theoretical and experimental research on surface ionization and evaporation are discussed in detail in Ref. 104 (see also references given there).

¹⁸⁾ The thickness of the plate is by hypothesis much larger than the region of localization of the induced charge $n_1(x)$ [$n_2(x)$], which justifies the use of infinite limits of the integrals.

gaps. Indirect confirmation that c and c_0 are different comes from measurements of tunneling characteristics of dielectric gaps, as has been pointed out in Ref. 88.¹⁹⁾ It follows from the calculations of Ref. 93 that c is practically independent of the field, since $\delta x_0^{(1)}(F)$ and $\delta x_0^{(2)}(F)$ have different signs [$F_x < 0 (> 0)$ respectively for the first (second) plate]. This constitutes a serious discrepancy with the results of Refs. 88, 89. Owing to the use in these papers of a model with a sharp break-off of the electron density and consequently a violation of self-consistency, it turns out that $x_0(F_x)$ shifts outward whatever the sign of F_x . Therefore the predicted effect of the field on the capacitance of a narrow gap is enormously exaggerated in Refs. 88, 89.

8. Chemisorption of atoms on a metal surface

The phenomenon of chemisorption has been widely studied with a variety of experimental methods which give information about the states of individual adsorbed particles, and also about the structure and properties of adsorbed films. A brief description of these methods and a bibliography can be found, for example, in a recent review.¹⁰⁵ The first qualitative-theoretical analysis of the electronic state of an adsorbed atom was carried out by Gurney.¹⁰⁶ Subsequently semiempirical methods were widely used in the electron theory of chemisorption, based on quantum-mechanical approximations for molecular orbits and valence bonds. Discussion and bibliography on this work can be found in a number of reviews.¹⁰⁴⁻¹⁰⁹ With these methods various metal-adsorbate systems were studied, dealing both with the chemisorption of individual atoms and with the effects of interaction between atoms adsorbed on a substrate. The result was that a qualitative understanding of the phenomenon of chemisorption was achieved. At the same time, the use of "fitting" parameters and artificial assumptions, and also the partial or complete violation of self-consistency, reduce the heuristic value of these model calculations and hinder the consistent quantitative analysis of chemisorption.

Therefore the use of the DFM, which enables us to start from "first principles" and describe the "self-organization" of the system adsorbed atom-metal, is of undoubted interest even with the crudities associated with the "jelly" model.

a) Interaction of a point charge with a metal (linear response)

The chemical binding of an atom to a surface can be considered on the basis of the DFM if we include in $v(r)$ the electrostatic potential produced by the nucleus of the atom. The direct DFM analysis of chemisorption was preceded by a number of papers in which the interaction of a point charge with a surface was studied on the basis of the LRA (subsection 1, b). Let us briefly consider the results of this work.

The interaction energy of a metal with a positive

¹⁹⁾ In analyzing the results of these experiments, one must allow for the effect of the dielectric on the surface charge distribution. This is discussed in Ref. 104.

charge located at the point x_1 has the form²⁰⁾

$$E_{\text{int}}(q, x_1) = \left[\varphi_0(x_1) + \frac{1}{2} \varphi_1(q, x_1) \right] q, \quad (8.1)$$

when the LRA is used; here $\varphi_0(x)$ is the potential of the unperturbed surface (repulsion), and $\varphi_1(q, x_1)$ is the potential of the screening charge (attraction). Using Eq. (8.1), Lang and Kohn¹¹⁰ showed that

$$E_{\text{int}}(q, x_1) = -\frac{q^2}{4(x_1 - x_0)} + O\left(\frac{q^2}{(x_1 - x_0)^2}\right) \quad \text{for } x_1 \gg 2 \text{ \AA}. \quad (8.2)$$

Here $x_0 \equiv x_0(F=0)$ is as introduced in subsection 7. This relation is confirmed by actual calculations.¹¹¹⁻¹¹² Near the boundary, where the double layer has an effect, there is a deviation from Eq. (8.2). In this region the repulsion begins to prevail over the attraction, and because of their competition $E_{\text{int}}(q, x_1)|_{q=\text{const}}$ has a minimum, corresponding to an equilibrium position of the charge. The dipole moment caused by the point charge is

$$p = q [x_1 - x_0(x_1)]. \quad (8.3)$$

Here allowance has been made for the fact that in general x_0 depends on the position of the charge. It is now not hard to see that in the region of applicability of the linear response approximation (LRA) $x_0(x_1)$ remains unchanged if we replace the point charge by a charged plane $x=x_1$ with a small (LRI) charge density γ . Then it is obvious that $x_0(x_1) \rightarrow x_0(F)$ ($F=4\pi\gamma$) in the limit $x_1 \rightarrow \infty$, i.e., it is determined by the response to an electric field. It follows that for large x_1 the dependence $p(x_1)$ becomes a linear function (as for a plane-plate capacitor), as is confirmed by calculation carried out on the basis of the PTFM¹¹³ and the PHM.¹¹⁰ However, for small x_1 these approaches give decidedly different results; in Ref. 110 $p(x_1)$ goes smoothly to zero for $x_1 \rightarrow 0$, but in Ref. 113 $p(x_1)$ changes sign at $x_1 \approx 0.7$ atomic units and takes on a small negative value for $x_1=0$. We can find out which result is the more accurate by using a "sum rule," which in our notation is of the form

$$x_0(x_1) = \frac{4\pi}{F} \left(\int_0^{x_1} n_F(x) x dx + x_1 \int_{x_1}^{\infty} n_F(x) dx \right)^{-1}, \quad (8.4)$$

where n_F is the charge density induced by the electric field in the LRA. It follows from this rule that $x_0(0) = 0$. Therefore [see Eq. (8.3)] $p(0) = 0$. Consequently, use of the PTFM with the gradient expansion for $T_s[n]$ (Ref. 113) leads to a qualitatively incorrect behavior of $p(x)$. On the other hand, the result based on the PHM, where T_s is taken into account exactly,

²⁰⁾We use the Gell-Mann-Feynman theorem (equation F', R. p. 93)

$$\frac{\partial}{\partial \alpha} \langle \psi | \hat{H}(\alpha) | \psi \rangle = \left\langle \psi \left| \frac{\partial \hat{H}(\alpha)}{\partial \alpha} \right| \psi \right\rangle.$$

Here $\hat{H}(\alpha)$ is the Hamiltonian, which depends on a parameter α . Let α be q , the external charge. Then it can be shown easily that

$$\frac{\partial}{\partial q} \langle \psi | \hat{H}(q, x_1) | \psi \rangle \equiv \frac{\partial E_{\text{int}}(q, x_1)}{\partial q} = \varphi_0(x_1) + \varphi_1(q, x_1).$$

Noting that in the approximation used $\varphi_1(q, x)$ is a linear function of q , and integrating over q , we obtain Eq. (8.1).

agrees very well with Eq. (8.4).¹¹⁴ Consequently, for these problems the PHM has decided advantages.²¹⁾

However, Eq. (8.4) gives no indication as to the applicability of the LRA itself. Lang and Williams¹¹⁵ showed that the response of the metal is nonlinear near the surface even for $q=1$,²²⁾ i.e., the LRA cannot be relied on even for the analysis of the adsorption of hydrogen.

We note that in another paper¹¹⁶ the LRA is applied to the calculation of the effective polarizability of noble-gas atoms adsorbed on a metal surface. In this case the linear approximation is better justified, since, first, the physical adsorption occurs at larger distances than chemisorption, and second, the point dipole which models the adsorbed atom in the field¹¹⁶ produces a much smaller perturbation than a point charge. We also point out a paper¹¹⁷ in which the LRA is used with the TFM. In this form the problem can be solved analytically. The screening of the charge is considered as it moves from $-\infty$ to $+\infty$. As could be expected, for $x_1 \rightarrow \infty$ the screening charge is situated symmetrically with respect to x_1 and is dragged along with q , as a consequence of $\Phi=0$ [see Eq. (5.5)]; i.e., $p=0$. When many-particle and quantum effects are taken into account the screening charge remains near the surface when q recedes from it.

b) Effect of chemisorption on electronic properties of a metal surface.

1) *Chemisorption of isolated atoms.* The first self-consistent calculation of chemisorption was carried out by Smith, Ying, and Kohn.¹¹³ Using the PTFM and the LRA, they considered the chemisorption of hydrogen on the surface of a "jelly" metal. This same approach has been applied to the chemisorption of alkali metals.¹¹⁸ The potential of the ion was modeled by a spherically symmetric pseudopotential. For Na, K, and Cs the calculated values of p and of the binding energy E_a are in reasonable agreement with experiment. Huntington, Turk, and White¹¹⁹ also used the PTFM for the chemisorption of Na, but did not confine themselves to the framework of the LRA. Owing to the fact that the PTFM and LRA are not very suitable for the description of chemisorption (see previous subsection), the most interesting papers for the development of the theory are those in which the interaction of the adsorbed atom with the metal surface is investigated on the basis of the PHM and without restriction to the linear approximation. This was first done by Lang and Williams for the chemisorption of H, Li, and O,¹¹⁵ and subsequently of Si and Cl,¹²⁰ on a

²¹⁾It was pointed out in Section II that the PMTF, in the approximation of Ref. 37, gives a good description of properties which involve averaging over the surface (for example, Φ). The parameters of chemisorption are not of this kind, being determined by the charge distribution in the neighborhood of the adsorbed atom.

²²⁾It was shown that the ratio $p(q, x_1)/q_1$ (for $x_1 = \text{const}$), which should be constant if the LRA holds, changes (at $x_1 = 1$ a.u.) from $0.7 D$ for $q < 1$ to $-0.5 D$ for $q = 1$, i.e., the response to a proton near the surface is decidedly nonlinear.

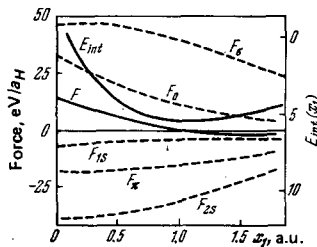


FIG. 9. The energy of interaction of an oxygen atom with a metal [$E_{\text{int}}(x_1)$], the Coulomb force acting on the nucleus (F_K), and its components (F_0, F_{1s}, F_{2s}, F_r , and F_σ). F_0 is the contribution from the unperturbed surface; F_{1s} and F_{2s} are due to the respective polarizations of the wave functions of the 1S and 2S states of the discrete spectrum, and F_r and F_σ are from electrons in states characterized by the respective magnetic quantum numbers $m=0$ and $m=1$ in the continuous spectrum (the classification of the states corresponds to the axial symmetry of the problem).

"jelly" metal. The only parameter in these calculations, besides the charge z of the nucleus, is r_s (or the background density \bar{n}). What was considered was essentially the "self-adaptation" of the adsorbed atom, whose nucleus was placed in the inhomogeneous gas near the boundary of the background. Indeed, no assumptions were made about the form of the perturbing potential, such as introducing a model potential and assuming spherical symmetry near the nucleus,^{118,119} and no artificial distinction was made between "atomic" and "metallic" electron states, such as characterizes semiempirical methods; the Coulomb potential was taken into account in the same way for all the electrons,²³⁾ and the potential was made self-consistent.

In the general case the energy spectrum in the presence of a nucleus contains both discrete and continuous components. In determining the equilibrium position of the atom it turned out to be important to take into account both kinds of states. Only then was it possible to satisfy simultaneously the conditions $dE_{\text{int}}(x_1)/dx_1=0$ and $F_K(x_1)=0$ (F_K is the electrostatic component of the force acting on the nucleus) which are required by the Gell-Mann-Feynman theorem. The various components of F_K for an adsorbed atom o are shown in Fig. 9. The effect of chemisorption on the electron structure of the surface is graphically described by the change of the density of electron states $\Delta N(\epsilon)$, which is shown in Fig. 10 for Cl, Si, and Li. We note that $\Delta N(\epsilon)$ is an experimentally observable quantity. It can be determined, for example, from the energy distribution of photoelectrons.¹²¹ All calculations in Refs. 119 and 120 were made for $r_s=2$, which corresponds to the volume density of electrons in aluminum ($r_s=2.07$). It was shown that as the atom recedes from the surface the peaks of the state density become narrower, are displaced, and go over into discrete atomic states 1s (H), 2s (Li), 2p (O), 3s and 3p (Si), and 3p (Cl). Accordingly we can say that the peaks (or resonances) arise from atomic

²³⁾In calculations made with Anderson's model Hamiltonian¹²¹ (see, e.g., Refs. 122, 123), only the Coulomb interaction between "atomic" electrons is taken into account.

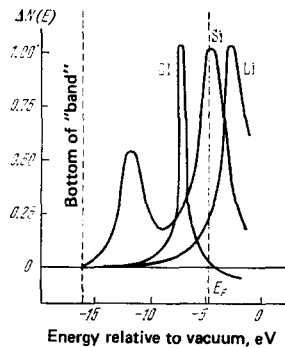


FIG. 10. Change in the density of states in chemisorption. The results shown are for specific equilibrium positions of the nucleus. For Li, $x_1=2.5$ a.u.; for Si, 2.3 a.u.; for Cl, 2.6 a.u.

states, which go over, when the interaction with the metal is "turned on," into a "band"²⁴⁾ of its electron states. The degree of filling of the resonance, and with it the effective charge of the atom, are determined by the position of the peak relative to the Fermi level. It can be seen from Fig. 10 that the 2s resonance of Li lies almost entirely above the Fermi level, while the 3p resonance of Cl lies below it; that is, they provide an example of the chemisorption of a positive and a negative ion, respectively.

In Ref. 120 a calculation of the electron density in the neighborhood of an adsorbed atom is made. It is shown, for example, that the chemisorption bond Si-Me is of markedly directive and covalent character.

Unfortunately an overwhelming majority of the experimental data for the adsorbates considered in these papers relate to chemisorption on transition metals and semiconductors, for which the "jelly" model is an overly crude approximation.²⁵⁾ Therefore the authors of Ref. 127 made a special study of the energy distribution of the photoelectrons for the system O/Al. The functions $p(x_1)$ and $F_{2p}(x_1)$, as calculated for this case in the "jelly" model, are shown in Fig. 11. The equilibrium position $x_1=1.1$ a.u. corresponds to $p(x_1)=-1.7D$, $E_{2p}=-2.2$ eV (relative to E_F). On the other hand it follows from experiment¹²⁷ that $E_{2p}=-7.2$ eV and $p \approx 0$ (for a small concentration of adsorbed atoms). This means that the O^- ions imbed themselves below the boundary of the background (are adsorbed).²⁶⁾ Similar results were obtained earlier for the systems O/Sr¹²⁸ and O/Cs.¹²⁹

An analysis of the causes of the discrepancy between theory and experiment showed that the "jelly" model is quite unsuitable for calculating $E_{\text{int}}(x_1)$, leading to an exaggeration of the distance between the adsorbed atom

²⁴⁾The concept of a "band" is given a conventional meaning in the "jelly" model.

²⁵⁾Appelbaum and Hamann¹²⁵ have given a self-consistent calculation of the chemisorption of atomic H on Si. The discreteness of the lattice was taken into account with a pseudopotential. The effect of monolayers of H and Cl on surface states in Si(111) was studied in Ref. 126.

²⁶⁾We recall that the boundary plane of the crystal lattice passes through $x=-a/2$, which amounts to -2.2 a.u. for Al (111).

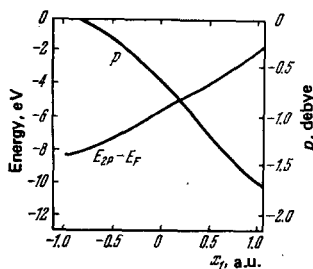


FIG. 11. Energy of the $2p$ resonance $[E_{2p}(x_1)]$ and magnitude of dipole moment $[p(x_1)]$ as functions of the distance from the oxygen atom to the boundary of the background ($r_s = 2$ a.u.).

and the metal. Already in first order in the pseudopotential the position of the minimum is shifted from 1.1 a.u. to 0.3 a.u. Inclusion of higher orders, and also of local lattice distortion near the adsorbed atom, makes it possible to explain the possibility of imbedding. This agrees qualitatively with the results for the adsorption of hydrogen and with a model (cluster) calculation. It has also been shown that taking account of lattice discreteness changes the theoretical forms of $p(x_1)$ and $E_{2p}(x_1)$ only slightly. Accordingly, the position of the resonance and the value of the dipole moment in adsorption can be explained on the basis of the "jelly" model by using the equilibrium position as found by taking the discreteness of the lattice into account. Alternatively, knowing p and E_{2p} from experiment, one can approximately determine the equilibrium position of the adsorbed atom by using the values of $p(x_1)$ and $E_{2p}(x_1)$ calculated in the "jelly" model. We see in Fig. 11 that the equilibrium position indicated by experiment is $x_1 = -0.5$ a.u.

From these considerations it follows that the "jelly" model is a usable foundation for theoretical analysis of chemisorption on metal surfaces, as well as of the characteristics of the unperturbed surface (see Section III). In subsequent papers¹³⁰⁻¹³¹ Lang and Williams related these results to the concept of electronegativity and considered the displacement of resonances with the formation of holes in the valence shell of an adsorbed atom; this has a direct bearing on the interpretation of experimental data on x-ray photoemission. Up to now calculations of chemisorption on transition and noble metals are monopolized by semiempirical methods. However, the very first self-consistent analysis of the electron structure of a monolayer of nitrogen on Cu(100)¹³² showed the effectiveness of the DFM and the importance of self-consistency. Good agreement between the calculated and experimental values of $\Delta N(\epsilon)$ was obtained.

2) Effect of adsorbed films on the work function.

Films of alkali and alkaline-earth elements on refractory metals are of great practical interest for emission electronics, and therefore their influence on the work function has been particularly intensively studied (cf., e.g., Ref. 105). In particular, it has been proved that in most cases the dependence of the work function on the concentration N of adsorbed atoms has a deep minimum corresponding to submonolayer covering (i.e., incomplete filling of a mono-

layer). Langmuir¹³³ gave the first qualitative explanation of this fact. According to the model he proposed, when an atom of an alkali metal (AM) is adsorbed it transfers one electron to the metal (complete ionization) and forms, along with its "mirror image," a dipole of moment p . The adsorption correction to the work function is given by

$$\Delta\Phi = -4\pi p(N)N.$$

The electric field produced by the dipoles leads to their mutual weakening (depolarization). The competition between the increase of N and the accompanying stronger depolarization is the principal reason why the function $\Delta\Phi(N)$ is inherently nonmonotonic.¹³³ The minimum is at the concentration N for which $dp/p = -dN/N$.

We list the main shortcomings of this model: a) The change in the degree of ionization (the shift relative to E_F and broadening of the resonance, is ignored; b) the classical law of image forces is used, although it does not hold near the surface; c) the concept of isolated dipoles loses its meaning when the concentration of adsorbed atoms is high and their wave functions overlap (metallization).

In subsequent researches, the first of which was Ref. 134, these shortcomings were partially overcome by means of various semiempirical models. However, the effects of the interaction of the adsorbed atoms were not taken into account fully enough (even in the most detailed calculations¹³⁵ the exchange interaction between them was neglected), and therefore the applicability of these theoretical results was confined to cases of low concentrations. A paper by Lang,¹³⁶ on the other hand, put the accent on the collective properties of the adsorbed layer. He proposed a model in which the ionic charge of an adsorbed atom is "smeared out" into a step function of positive charge (an analog of the "jelly" model). The thickness of the layer was taken constant, equal to the distance between the closely packed planes in the bulk of the alkali metal, and the charge density \tilde{n} in the layer (the height of the step) was varied, modelling the change of concentration of the adsorbed atoms. The calculation was made with the PHM, so that the Coulomb and exchange interactions between the electrons in the layer were taken into account automatically.

In interpreting the results it is convenient to introduce the distance a between the centers of gravity of the positive charge and of the negative charge screening it (the "moment arm" of the dipole). Then $\Delta\Phi = -4\pi\tilde{n}a$. The calculations showed that $a(\tilde{n})$ decreases nonlinearly. Owing to the competition between the increase of the charge and the decrease of the "moment arm" of the dipole a minimum appears on the curve of $\Delta\Phi(\tilde{n})$, and on the whole the form of the function is like the experimental curve, including the appearance of a maximum at the point where filling of a second adsorbed layer begins (Fig. 12). The calculated minimum values Φ_{\min} for various metals agree well with the experimental values (Fig. 13).

The slope of the curves in the limit $\tilde{n} \rightarrow 0$ is also in passable agreement with experiment, despite the ob-

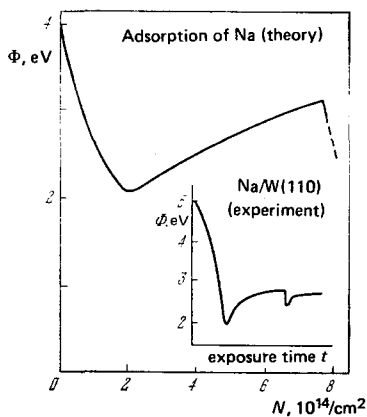


FIG. 12. Change of work function on adsorption of Na. Theoretical curve as obtained in Ref. 136, experimental curve from Ref. 137.

vious crudeness of the model at low concentrations. The reason is that the calculation of Φ involves an averaging of the electron distribution in the plane of the surface, and the average values for the "smeared out" and for the discrete distributions are nearly equal even for small \bar{n} (see Ref. 136, Appendix). Of course this model cannot be used to determine the "local" characteristics of chemisorption, such as the heat of desorption per atom.

The most important shortcoming of this model is that it is hard to relate it to the concept of chemisorption of an individual atom and that it cannot provide a description of the gradual transition from individual properties (of isolated adsorbed atoms) to collective properties. Wojciechowski¹⁴⁷ tried to clarify this matter by considering the effect of a submonolayer of Cs adsorbed on W on the energy and width of the resonance peak of an adsorbed Cs atom. The charge distribution in the submonolayer was modelled, as in Ref. 136, with a step function. A semiempirical approach¹⁴⁸ was used to calculate the width of the res-

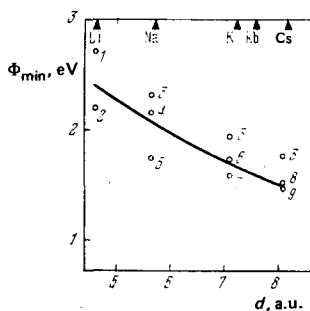


FIG. 13. Minimum values of work function during adsorption. The curve is the theoretical result for $\Phi_{\min}(d)^{136}$ (d is the thickness of the step). The small circles are experimental values. Points 1 to 9 correspond to respective references 138-146. Points 3, 6, 9 are for a (100) surface of Ta, 4 is for Ni (111), and the rest are for W (110). [The corresponding spread in values of n has little effect on the theoretical values of $\Phi_{\min}(d)^{136}$] From the experimental data given in Ref. 136 (when they numbered more than three) we have chosen for each alkali metal the largest, the smallest, and the value closest to the calculated value.

onance. The calculations showed that in a layer of low density, with degree of covering $\theta \leq 0.2$, the Cs is adsorbed in the form of ions, for a larger concentration ($\theta \geq 0.3$) the layer consists mainly of atoms, and at high concentrations ($\theta \geq 0.8$) the coating becomes metallized, and its properties do not differ much from those of metallic Cs. The W then has almost no effect on the work function, its action being nearly completely screened. We note that the quantitative results¹⁴⁷ must be handled with care, since several crude approximations were used. For example, the polarization of an adsorbed atom was not considered, self-consistency was not secured, and no allowance was made for the possibility that the position of an adsorbed atom depends on \bar{n} . Nevertheless the results give an intuitive picture of the "collectivization" and agree qualitatively with experimental data. An indirect confirmation of metallization can be found in the fact that for large \bar{n} the relation $\Phi(\bar{n})$ is analogous to the dependence of the work function on the background density for a number of alkali metals (cf. Fig. 5 in Ref. 147).

In conclusion we present a generalized sum-rule for a "jelly"-metal coated by a submonolayer of adsorbate (the latter is treated by means of the "step" model¹³⁶) which is adjacent to a dielectric medium of permittivity ϵ :

$$\varphi(0) - \varphi(-\infty) + \frac{\bar{n}}{n} [\varphi(d) - \varphi(0)] - \frac{D^2(d)}{8\pi n} \frac{\epsilon - 1}{\epsilon} = \frac{D_0^2}{8\pi n \epsilon} + \frac{1}{8\pi n} \left(\frac{g_0(\bar{n})}{n} \right) \quad (8.5)$$

where $D(x)$ is the electric displacement, D_0 is its value far from the metal (external field) and d is the thickness of the "step." For $\epsilon = 1$, Eq. (8.5) reduces to the rigorous relations obtained by Budd and Vannimenus⁴¹ ($\bar{n} = 0, D_0 = 0$), Bigun¹⁸⁷ ($\bar{n} \neq 0, D_0 = 0$), and Kuzema and Partenskii¹⁸⁸ ($\bar{n} \neq 0, D_0 \neq 0$).

It can also be easily shown that the solution of the TF equation, which has the following form for the system under consideration ($D_{0x} > 0$):

$$\varphi'(x) = -\frac{4\pi n \theta}{1 - (1 - \epsilon) \theta(x-d)} \left[\theta(-x) + \frac{n}{n} \theta(x) \theta(d-x) \right],$$

satisfies relation [Eq. (8.5)] exactly. To do this it is sufficient to evaluate the first integral of the equation and to utilize the continuity of $D(x)$ and $\varphi(x)$.

9. Adhesion of metals

It is known from experiments that when clean metal surfaces are brought into contact considerable forces appear between them (adhesion), which are of great practical importance (friction, deposition of metal films, formation and "collapse" of cracks). Cabrera and Mott¹⁴⁹ were evidently the first to point out the part played by electric contact phenomena in the adhesion of solids. Subsequently electroadhesion phenomena were widely studied, both theoretically and experimentally.¹⁵⁰ In the last five years there have been attempts to construct a self-consistent microscopic theory of adhesion based on the DFM. We shall discuss briefly a number of papers which characterize the level that has been reached in this work. The

boundaries of the interacting metals are assumed to be plane. We can distinguish conventionally three ranges of separation between metals. At small distances d of the order of 2 Å or less the main contribution to the energy of the interaction is due to the overlapping of the "tails" of the electron densities of the metals (range A). At large distances $d \geq 4-5$ Å the interaction is of the van der Waals type (range C). In the intermediate range (B) the transition from a contact interaction to a dispersion interaction occurs. The range C has been well enough investigated, beginning with a pioneer paper by Lifshits¹⁵¹ (see also Refs. 152, 153, and the references given there). Ferrante and Smith,¹⁵⁴ in analyzing the interaction function $E(d)$ (E is the total energy of the interacting metals) approximated the electron density near the surface with a superposition of the distributions $n_1(x)$ and $n_2(x)$ for the separate metals. In this procedure the relaxation of the $n_i(x)$ was neglected; they were taken in the form of Eq. (5.7) with the β derived by Smith³⁷ for an unperturbed surface. The discreteness of the lattice was taken into account to first order in the pseudopotential. For all pairs of metals considered (Al, Mg, Zn) the calculated functions and values of $E(d)$ have a minimum at $d = d_0 \approx 2$ (a.u.). The calculated values of the binding force agree qualitatively and in order of magnitude with experiment. The adhesion binding energy $E_a(d)$ is defined by the relation

$$\bar{E}_a(d) = \frac{E(d) - E(\infty)}{2A}; \quad (9.1)$$

A is the area of contact. For contact between like (same) metals and $d=0$ Eq. (9.1) is identical with the definition (4.4) of surface energy, and in the general case it is accepted procedure to put (9.1) in the form $\bar{E}_a(d_0) = \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_{12})$, where σ_{12} is the "interphase tension" and σ_i is the surface energy of the i th metal. In Ref. 154 \bar{E}_a and its components were calculated, and it was shown that the exchange interaction makes a decisive contribution. The deviation of d_0 from zero, found in Ref. 154 for the case of a like-metal contact, is an erroneous result, associated with the neglect of the relaxation of $n(x)$. For the Al-Al contact it was rectified in a self-consistent calculation based on the PHM (Fig. 14).¹⁵⁷ The self-consistent calculation changes the position of the minimum and increases its depth, bringing $\bar{E}_a(d_0)$ closer to the experimental value of σ_{Al} . Similar results were obtained for Mg, Zn, and Na in Ref. 158, where it was also shown that inclusion of the nonlocality of $E_{xc}[n]$ brings the calculated values of $\bar{E}_a(d_0)$ still closer to the experimental values for a like-metal contact. The curve of $\bar{E}_a(d)$ for Al is shown in Fig. 14.

Budd and Vannimenus⁴¹ derived a very useful "sum rule" showing that in the limit $d \rightarrow 0$ the surface density of repulsive force $F_{12}(d)/A$ for a like-metal contact of "jelly" metal goes to a negative pressure $-P$:

$$\frac{F_{12}(0)}{A} = -P = -\frac{\bar{n}}{n^2} \left(\frac{\epsilon_0 \bar{n}}{n} \right)^2. \quad (9.2)$$

Subsequently¹⁵⁹ these authors made a semi-self-consistent calculation with the PTFM, matching the force with Eq. (9.2) for $d \rightarrow 0$ and with the dispersion force¹⁵² for $d \geq 4$ Å. A similar extrapolation together

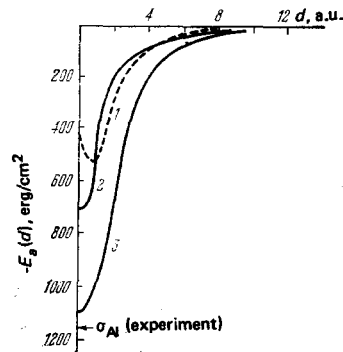


FIG. 14. Energy of Al-Al adhesion bond as a function of the distance between the surfaces (111). Curve 1 is from the calculation in Ref. 154, which does not take relaxation into account; 2 from the self-consistent calculation of Ref. 157 (LDA); 3 from a self-consistent calculation including nonlocality, $E_{xc}[n]$.¹⁵⁸ The experimental value of σ_{Al} for the solid metal is taken from Ref. 65.

with inclusion of a pseudopotential for small d was used¹⁶⁰ for the Al-Al adhesion.

For a more exact analysis of $F_{12}(d)$ in range B one needs to include nonlocal exchange and correlation effects and the plasmon contribution to the energy. However, the position and depth of the minimum of $E(d)$, and along with them also $\bar{E}_a(d_0)$, are determined mainly by the contact interaction (range A).¹⁵⁴⁻¹⁵⁸ Therefore it is easier to calculate $\bar{E}_a(d_0)$ than the force $F_{12}(d)$ for arbitrary d .

Heinrichs and Kumar¹⁶¹ generalized Eq. (9.2) to the case of adhesion of different metals:

$$\frac{F_{12}(0)}{A} = P_2 + \frac{\bar{n}_2}{n_1 - n_2} [\bar{n}_1 (\mu_1 - \mu_2) - (P_1 - P_2)]. \quad (9.3)$$

The second term is equal to the electrostatic force $F(0)^2/8\pi$ ($F(0)$ is the electric field at the boundary), which appears on contact between different metals. Values of the force of adhesion calculated as $E'_a(d)|_{d=0}$ on the basis of the results of Ref. 154 agree well with Eq. (9.3),¹⁶² in spite of the faults that have been pointed out in the method used in Ref. 154.

In Ref. 163 an exact integral relation between σ_{12} and the electrostatic potential $\varphi(x)$, was derived. Approximate calculations^{163, 164} taking lattice discreteness into account show that σ_{12} makes a large contribution to \bar{E}_a when the metals in contact are very dissimilar. For example, for the pair Al-Ag σ_{12} is comparable with σ_{Al} and σ_{Ag} , and for Al-Na $\sigma_{12} \approx 6\sigma_{Na}$ and is nearly equal to σ_{Al} , as calculated in the LDA.³⁹ It must be pointed out that in these papers no allowance is made for defects such as boundary dislocations, which can arise when different lattices are put together (see, e.g., Ref. 165) and which make a considerable contribution to σ_{12} (Refs. 167, 168).²⁷⁾ It has been difficult so far to include their effect in a self-consistent way. Moreover, the problem becomes much more complicated when at least one of the adhesion pair is a

²⁷⁾ Concerning the effect of dislocations on the work function and on the emission of electrons from metals see Ref. 166.

transition metal. An analysis of the difficulties that arise in this case, and also semiempirical calculations with boundary dislocations taken into account, are given in Ref. 168.

V. CONCLUSION

We are convinced that many problems of the physics of surfaces can be successfully solved on the basis of the density-functional method. Starting from a "first principle"—that the energy of the ground state must be a minimum—comparatively simple models of the ion lattice ("jelly," pseudopotential) and of the electron gas (LDA plus the first nonlocal corrections) suffice for the explanation of a wide variety of experimental data relating both to free and to perturbed metal surfaces. We note that the range of problems we have discussed does not exhaust all applications of the DFM to the description of surface phenomena. For a more complete picture we must mention a number of papers on topics close to the subject of this review. For example, there are papers on the electron properties of a surface containing impurity atoms¹⁶⁹ and subject to deformation,¹⁷⁰ the adsorption of inert gases,¹⁷¹ adhesion of a metal and an ionic crystal,¹⁷² surface properties of alloys,¹⁷³ work functions for positrons¹⁷⁴ and for spin-polarized electrons,¹⁷⁵ and the electron structure of vacancies¹⁷⁶ and cavities (internal surfaces).¹⁷⁷ The influence of the transition layer at the boundary of a metal on the dispersion and damping of surface plasmons has been widely discussed.^{178,179} It has been pointed out, for example, that optical spectroscopy of surface plasmons¹⁷⁸ is a promising way to obtain information on the distribution of charge near the surface. For problems of microelectronics the study of the electron structure of a metal-semiconductor boundary¹⁸⁰ or of a semiconductor junction¹⁸¹ is of great practical interest. Papers have appeared in which the DFM is used to study the reconstruction of semiconductor surfaces,¹⁸² i.e., an instability leading to deviation of the structure of the surface from that "prescribed" by the volume. We note in passing that recently there has been a marked increase in the fraction of papers devoted to the self-consistent theory of semiconductor surfaces. Research is also in progress on perfecting the DFM itself. Generalizations of the H-K theorem to the cases of nonzero temperature¹⁸³ and of nonlocal external potential¹⁸⁴ have been derived. An "immanent" self-consistent procedure based on the use of the density-matrix formalism in the framework of the DFM has been developed and tested.¹⁸⁵ A procedure has been proposed¹⁸⁶ for expanding $G[n]$ in terms of correlation functions of various orders.

The self-consistent theory of surfaces is sure to be extensively developed further, and among its next successes may be a consistent inclusion of effects of nonlocality and, in particular, of plasmon effects, in $G[n]$, and also a more exact allowance for lattice discreteness than can be made by using the volume pseudopotential.

In addition to the applications of the DFM to the study of surfaces, which are discussed in this review, this

method is promising for the analysis of volume properties in cases when there is a sharp inhomogeneity in the volume structure. For example, inhomogeneous corrections so calculated may be important in calculations of the structure of single dislocations and aggregations of dislocations, of packing defects, and of grain boundaries in polycrystalline metals.

- ¹C. B. Duke and R. L. Park, *Phys. Today* **25**, 23 (1972). [Russ. Transl. *USP Fiz. Nauk* **111**, 139 (1973)].
- ²P. Hohenberg and W. Kohn, *Phys. Rev.* **B136**, 864 (1964).
- ³W. Kohn and L. J. Sham, *Phys. Rev.* **A140**, 1133 (1965).
- ⁴N. D. Lang, in *Collection: Solid State Physics*, New York, Academic Press, Vol. 28, p. 225, 1973.
- ⁵D. S. Boudreaux and M. J. Sureschke, in *Structure and Properties of Metal Surfaces* (Maruzen Company, Tokyo, 1973) p. 94.
- ⁶S. Lundqvist, in *Surface Science. Lectures presented at an Intern. Course at Trieste from 16 January to 10 April 1974*. IAEA, Vienna **1**, 331.
- ⁷A. Bennet, in *Collection: Novoe v issledovanii poverkhnosti tverdykh tel* (New developments in the study of surfaces of solids), Part 1, Moscow, Mir, 1977, p. 211.
- ⁸J. A. Appelbaum and D. R. Hamann, *Rev. Mod. Phys.* **48**, 479 (1976).
- ⁹N. D. Lang, in *Electron Structure and Reactivity of Metal Surfaces* (Plenum Press, New York, 1976), p. 81.
- ¹⁰L. D. Landau and E. M. Lifshits, *Kvantovaya mekhanika, Nerelyativistskaya teoriya* (Quantum mechanics. Nonrelativistic theory), Moscow, Nauka, 1974. English transl.: Pergamon Press, 1977.
- ¹¹S. T. Epstein and C. M. Rosental, *J. Chem. Phys.* **64**, 247 (1976).
- ¹²J. S. Langer and S. H. Vosko, *J. Phys. and Chem. Sol.* **12**, 196 (1959).
- ¹³D. Pines, *Electronic excitations in Solids*, New York, Benjamin, 1964. [Russ. Transl. Mir, Moscow (1965)].
- ¹⁴M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106**, 364 (1957).
- ¹⁵A. S. Kompaneets and E. S. Pavlovskii, *Zh. Éksp. Teor. Fiz.* **31**, 427 (1956) [*Sov. Phys. JETP* **4**, 328 (1957)].
- ¹⁶D. A. Kirzhnits, *Tr. Fiz. Inst. Akad. Nauk SSSR* **16**, 3 (1961).
- ¹⁷L. J. Sham, in *Computational Methods in Band Theory* (Plenum Press, New York, 1971), p. 458.
- ¹⁸S. K. Ma and K. A. Brueckner, *Phys. Rev.* **165**, 18 (1968).
- ¹⁹J. B. Ortenburger and F. Herman, cited in *Collection of Ref.* **17**, p. 469.
- ²⁰D. J. W. Geldart, M. Rasolt, and C. O. Ambladh, *Sol. State Comm.* **16**, 243 (1975).
- ²¹L. Kleinman, *Phys. Rev. Ser. B* **10**, 2221 (1974).
- ²²A. W. Overhauser *ibid.* **3**, 1888 (1970).
- ²³D. J. W. Geldart and M. Rasolt *ibid.* **13**, 1477 (1976).
- ²⁴K. H. Law and W. Kohn, *J. Phys. and Chem. Sol.* **37**, 99 (1976).
- ²⁵F. Herman, J. P. Van Dyke, and J. B. Ortenburger, *Phys. Rev. Lett.* **22**, 807 (1969); *Intern. J. Quantum Chem.* **35**, 807 (1969).
- ²⁶D. A. Kirzhnits, Yu. E. Lozovik, and G. V. Shpatkovskaya, *Usp. Fiz., Nauk* **117**, 3 (1957) [*Sov. Phys. Uspekhi* **18**, 649 (1976)].
- ²⁷P. Gombas, *Problema mnogikh chastits v kvantovoy mekhaniki* (The many-particle problem in quantum mechanics), Moscow, IL, 1953) (Russian transl. of German original, Verlag Birkhauser, Basel, 1950.)
- ²⁸P. A. M. Dirac, *Proc. Camb. Phil. Soc.* **26**, 376 (1930).
- ²⁹J. C. Slater, *Phys. Rev.* **81**, 365 (1951).
- ³⁰N. D. Lang and W. Kohn *ibid.* **3**, 1215 (1971).
- ³¹E. Wigner and J. Bardeen, *Phys. Rev.* **48**, 84 (1935).
- ³²N. Wiser and M. H. Cohen, *J. Phys. Ser. C* **2**, 193 (1969).

- ³³J. Frenkel, *Zs. Phys. Bd. 51*, 232 (1928).
- ³⁴A. G. Samoïlovich, *Zh. Éksp. Teor. Fiz.* **16**, 135 (1946).
- ³⁵B. Mrowka and A. Recknagel, *Phys. Zs. Bd. 38*, 758 (1937).
- ³⁶M. B. Partenskiĭ, É. I. Popov, and V. E. Kuzema, *Fiz. Met. Metalloved* **41**, 280 (1976).
- ³⁷J. R. Smith, *Phys. Rev.* **181**, p 522 (1969).
- ³⁸N. D. Lang, *Sol. State Comm.* **7**, 1047 (1969).
- ³⁹N. D. Lang and W. Kohn, *Phys. Rev. Ser. B* **1**, 4555 (1970).
- ⁴⁰V. S. Fomenko, *Émissionnye svoïstva materialov* (Emission properties of materials), Kiev, Naukova Dumka, 1970.
- ⁴¹H. F. Budd and J. Vannimemus, *Phys. Rev. Lett.* **31**, 1218 (1973).
- ⁴²R. Smoluchowski, *Phys. Rev.* **60**, 661 (1941).
- ⁴³R. W. Strayer, W. Mackie, and L. W. Swanson, *Surf. Sci.* **34**, 225 (1973).
- ⁴⁴P. O. Gartland, S. Berge, and B. J. Slagsvold, *Phys. Rev. Lett.* **28**, 738 (1972).
- ⁴⁵J. R. Smith, *ibid.* **25**, 1023 (1970).
- ⁴⁶N. W. Ashcroft, *Phys. Lett.* **23**, 48 (1966).
- ⁴⁷J. A. Appelbaum and D. R. Hamann, *Phys. Rev. Ser. B* **6**, 2166 (1972).
- ⁴⁸J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, *ibid.* **14**, 588 (1976).
- ⁴⁹T. Ando *ibid.* **13**, 3468 (1976).
- ⁵⁰G. P. Kerker, S. G. Louie, and M. L. Cohen *ibid.* **17**, 706 (1978).
- ⁵¹J. Ihm, S. G. Louie, and M. L. Cohen *ibid.* p. 769.
- ⁵²G. P. Alldredge and L. Kleinman *ibid.* **10**, 559 (1974); *Phys. Lett. Ser. A* **48**, 337 (1974); *J. Phys. Ser. F* **4**, L207 (1974).
- ⁵³R. W. Hardy and R. E. Allen, *Sol. State Comm.* **19**, 1 (1976).
- ⁵⁴J. R. Chelikowsky, M. Schlüter, and S. G. Cohen *ibid.* **17**, 1103 (1975).
- ⁵⁵S. G. Louie, Ho Kai-Ming, J. R. Chelikowsky, and H. L. Cohen, *Phys. Rev. Lett.* **37**, 1289 (1976); *Phys. Rev. Ser. B* **15**, 5627 (1977).
- ⁵⁶E. Caruthers and L. Kleinman, *Phys. Rev. Lett.* **35**, 738 (1975).
- ⁵⁷J. G. Gay, J. R. Smith, and F. J. Arlinghaus *ibid.* **38**, 561 (1977).
- ⁵⁸S. Dévion and Dzh. Levin, *Poverkhnostnye* (Tammovskie) *sostoyaniya* (Surface [Tamm] states), Moscow, Mir, 1973.
- ⁵⁹P. Vashista and K. S. Singwi, *Phys. Rev. Ser. B* **6**, 875 (1972).
- ⁶⁰G. Paasch and M. Heitschold, *Phys. Stat. Sol. Ser. B* **67**, 743 (1975).
- ⁶¹M. Hietschold, G. Paasch, and P. Ziesche, *ibid.* **70**, 653 (1975).
- ⁶²J. Vannimemus and H. F. Budd, *Phys. Rev. Ser. B* **15**, 5302 (1977).
- ⁶³S. N. Zadumkin and R. M. Digilov, in: *Poverkhnostnye yavleniya v rasplavakh i voznikayushchikh iz nikh tverdykh fazakh* (Surface phenomena in melts and in solid phases arising from them), Kishinev, Shtiintsa, 1974.
- ⁶⁴J. P. Perdew and R. Monnier, *Phys. Rev. Lett.* **37**, 1286 (1976); *Phys. Rev. Ser. B* **17**, 2595 (1978).
- ⁶⁵H. Z. Wawra, *Zs. Metallkunde*, **Bd 66**, S. 395, 492 (1975).
- ⁶⁶Kh. B. Khokonov, in book cited in Ref. 63, p. 190.
- ⁶⁷R. A. Craig, *Phys. Rev. Ser. B* **6**, 1134 (1972).
- ⁶⁸J. Schmit and A. A. Lucas, *Sol. State Comm.* **11**, 415 (1972).
- ⁶⁹P. J. Feibelman, *ibid.* **13**, 319 (1973).
- ⁷⁰W. Kohn, *ibid.* p. 323.
- ⁷¹J. Heinrichs, *ibid.* p. 1599.
- ⁷²P. J. Feibelman, *Phys. Rev.* **176**, 551 (1968).
- ⁷³J. Harris and R. O. Jones, *J. Phys. Ser. F* **4**, 1170 (1974); *Phys. Lett. Ser. A* **46**, 407 (1974).
- ⁷⁴E. Wikborg and J. E. Inglesfield, *Sol. State Commun.* **16**, 335 (1975).
- ⁷⁵M. Jonson and G. Srinivasan, *Phys. Scripta*, **10**, 262 (1974).
- ⁷⁶J. S.-Y. Wang and M. Rasolt, *Phys. Rev. Ser. B* **13**, 5330 (1976).
- ⁷⁸V. Sahni, J. B. Krieger, and J. Gruenebaum, *ibid.* *Ser. B* **15**, 1941 (1977).
- ⁷⁹V. Sahni and J. Gruenebaum, *ibid.* p. 1929.
- ⁸⁰M. Rasolt, J. S.-Y. Wang, and L. M. Kahn, *ibid.* p. 580.
- ⁸¹J. H. Rose, H. B. Shore, D. J. W. Geldart, and M. Rasolt, *Sol. State Comm.* **19**, 619 (1976).
- ⁸²N. D. Lang and L. J. Sham, *ibid.* **17**, 581 (1975).
- ⁸³A. K. Gupta and K. S. Singwi, *Phys. Rev. Ser. B* **15**, 1801 (1977).
- ⁸⁴J. P. Perdew, D. C. Langreth, and V. Sahni, *Phys. Rev. Lett.* **38**, 1030 (1977).
- ⁸⁵D. C. Langreth and J. P. Perdew, *Sol. State Comm.* **17**, 1425 (1975); *Phys. Rev. Ser. B* **15**, 2884 (1977).
- ⁸⁶O. K. Rice, *ibid.* **31**, 1051 (1928).
- ⁸⁷N. F. Mott and R. J., Watts-Tobin, *Electrochem. Acta*, **4**, 79 (1961).
- ⁸⁸N. Y. Ku and F. G. Ullman, *J. Appl. Phys.* **35**, 265 (1964).
- ⁸⁹T. T. Tsong, E. W. Müller, *Phys. Rev.* **181**, 530 (1969).
- ⁹⁰A. V. Sidyakin, *Zh. Éksp. Teor. Fiz.* **58**, 573 (1970) [*Sov. Phys. JETP* **31**, 308 (1970)].
- ⁹¹D. M. Newns, *Phys. Rev. Ser. B* **1**, 3304 (1970).
- ⁹²J. A. Appelbaum and G. A. Baraff, *ibid.* **4**, 1246 (1971).
- ⁹³A. K. Theophilou and A. Modinos, *ibid.* **6**, 801 (1972).
- ⁹⁴M. B. Partenskiĭ and Ya. G. Smorodinskiĭ, *Fiz. Tverd. Tela* **16**, 644 (1974) [*Sov. Phys. Solid State* **16**, 423 (1974)].
- ⁹⁵A. M. Brodskiĭ and Yu. A. Gurevich, *Teoriya elektronnoi emissii iz metallov* (Theory of electron emission from metals), Moscow, Nauka, 1973.
- ⁹⁶J. P. Barbour, W. W. Dolan, J. K. Trolan, E. E. Martin, and W. D. Dyke, *Phys. Rev.* **92**, 45 (1953).
- ⁹⁷A. Modinos, *Surf. Sci.*, **9**, 459 (1968).
- ⁹⁸J. W. Gadzuk and E. W. Plummer, *Phys. Rev. Ser. B* **3**, 2125 (1971).
- ⁹⁹*Avtoionnaya mikroskopiya* (Field-emission microscopy), Moscow, Mir, 1971.
- ¹⁰⁰E. W. Müller, *Adv. Electron. and Electron. Phys.* **13**, 83 (1960).
- ¹⁰¹E. W. Müller, J. Panitz, and S. B. McLane, *Rev. Sci. Instr.* **39**, 83 (1968).
- ¹⁰²T. Tsong and E. W. Müller, *J. Chem. Phys.* **41**, 3279 (1964).
- ¹⁰³D. S. Baudreaux and P. H. Cutter, *Surf. Sci.* **5**, 230 (1966); *Phys. Rev.* **149**, 170 (1966).
- ¹⁰⁴A. V. Kobelev, R. M. Kobeleva, V. E. Kuzema, M. B. Partenskiĭ, O. M. Rosental', and Ya. G. Smorodinskiĭ, *Fiz. Met. Metalloved.* **41**, 493 (1976). M. B. Partenskiĭ and V. E. Kuzema, in: *Tezisy dokladov XVII Vsesoyuznoi konferentsii po emissionnoi elektronike* (Abstracts of reports at the Seventeenth All-Union Conference on emission electronics), Leningrad, 1978, p. 139.
- ¹⁰⁵L. A. Bol'shov, A. P. Napartovich, A. G. Naumovets, and A. G. Fedorus, *Usp. Fiz. Nauk* **122**, 125 (1977) [*Sov. Fiz. Uspekhi* **20**, 432 (1977)].
- ¹⁰⁶R. Gurney, *Phys. Rev.* **47**, 479 (1935).
- ¹⁰⁷K. Wojciechowski, *Progr. Surf. Sci.* **1**, pt. 1, 65 (1971).
- ¹⁰⁸R. Gomer, in *Solid State Physics*. **30** (Academic Press, New York, 1975), p. 93.
- ¹⁰⁹T. B. Grimley, *Progr. Surf. and Membrane Sci.* **9**, 71 (1975).
- ¹¹⁰N. D. Lang and W. Kohn, *Phys. Rev. Ser. B* **7**, 3541 (1973).
- ¹¹¹V. E. Kenner, R. E. Allen, W. M. Saslow, *Phys. Lett.* **38**, 255 (1972).
- ¹¹²J. P. Appelbaum and D. R. Hamann, *Phys. Rev. Ser. B* **6**, 1122 (1972).
- ¹¹³J. R. Smith, S. C. Ying, and W. Kohn, *Phys. Rev. Lett.* **30**, 610 (1973); *Phys. Rev. Ser. B* **11**, 1483 (1975).
- ¹¹⁴H. F. Budd and J. Vannimemus, *ibid.* **12**, 509 (1975).
- ¹¹⁵N. D. Lang and A. R. Williams, *Phys. Rev. Lett.* **34**, 531 (1975).
- ¹¹⁶W. C. Meixner and P. R. Antoniewicz, *Phys. Rev. Ser. B* **13**, 3276 (1976).
- ¹¹⁷S. C. Ying, J. R. Smith, and W. Kohn, *J. Vac. Sci. Technol.*

- 9, 575 (1972).
- ¹¹⁸L. M. Kahn and S. C. Ying, Sol. State Comm. **16**, 799 (1975).
- ¹¹⁹H. B. Huntington, L. A. Turk, and W. W. White, Surf. Sci. **48**, 187 (1975).
- ¹²⁰N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 2120 (1976).
- ¹²¹P. W. Anderson, Phys. Rev. **124**, 41 (1961).
- ¹²²D. M. News, *ibid.* Ser. B **178**, 1123 (1969).
- ¹²³R. Gomer, in: *Novoe v issledovanii poverkhnosti tverdogo tela* (New Developments in the study of surfaces of solids), Moscow, Mir, 1977, p. 189.
- ¹²⁴T. E. Fisher, J. Vac. Sci. Technol. **9**, 860 (1972).
- ¹²⁵J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. **34**, 806 (1975).
- ¹²⁶M. Schlüter and M. L. Cohen, Phys. Rev. Ser. B **17**, 716 (1978).
- ¹²⁷K. Y. Yu, J. N. Miller, P. Chye, W. E. Spicer, N. D. Lang, and A. R. Williams, *ibid.* **14**, 1446 (1976).
- ¹²⁸C. R. Helms and W. E. Spicer, Phys. Rev. Lett. **28**, 565 (1972); **32**, 228 (1974).
- ¹²⁹P. E. Gregory, P. Chye, H. Sunami and W. E. Spicer, J. Appl. Phys. **46**, 3525 (1975).
- ¹³⁰N. D. Lang and A. R. Williams, Phys. Rev. Ser. B **16**, 2408 (1977).
- ¹³¹A. R. Williams and N. D. Lang, Surf. Sci. **65**, 138 (1977).
- ¹³²J. R. Smith, F. S. Arlinghaus, and J. G. Gay, Sol. State Comm. **24**, 279 (1977).
- ¹³³I. Langmuir, L. Am. Chem. Soc. **54**, 2798 (1932).
- ¹³⁴R. W. Gurney, Phys. Rev. **47**, 479 (1935).
- ¹³⁵J. P. Muskat and D. M. News, Sol. State Comm. **11**, 737 (1972); J. Phys. Ser. C **7**, 2630 (1974).
- ¹³⁶N. D. Lang, Phys. Rev. Ser. B **4**, 4234 (1971).
- ¹³⁷A. P. Ovchinnikov and B. M. Tsarev, Fiz. Tverd. Tela **9**, 1927 (1967) [Sov. Phys. Solid State **9**, 1519 (1968)].
- ¹³⁸A. P. Ovchinnikov and B. M. Tsarev, Fiz. Tverd. Tela **9**, 3512 (1967) [Sov. Phys. Solid State **9**, 2766 (1968)].
- ¹³⁹V. M. Gavriluk and V. K. Medvedev, Fiz. Tverd. Tela **8**, 1811 (1966) [Sov. Fiz. Solid State **8**, 1439 (1966)].
- ¹⁴⁰D. L. Ferhs and R. E. Stickney, Surf. Sci. **17**, 32 (1969).
- ¹⁴¹R. L. Gerlach and T. N. Rhodin, *ibid.* **19**, 403 (1970).
- ¹⁴²E. V. Klimenko and V. K. Medvedev, Fiz. Tverd. Tela **10**, 1986 (1968) [Sov. Phys. Solid State **10**, 1562 (1969)].
- ¹⁴³L. D. Schmidt and R. Gomer, J. Chem. Phys. **45**, 1605 (1966).
- ¹⁴⁴A. P. Ovchinnikov, Fiz. Tverd. Tela **9**, 628 (1967) [Sov. Phys. Solid State **9**, 483 (1967)].
- ¹⁴⁵V. M. Gavriluk, A. G. Naumovets, and A. G. Fedorus, Zh. Éksp. Teor. Fiz. **51**, 1332 (1966) [Sov. Phys. JETP **24**, 899 (1967)].
- ¹⁴⁶L. W. Swanson and R. W. Strayer, J. Chem. Phys. **48**, 2421 (1968).
- ¹⁴⁷K. F. Wojciechowski, Surf. Sci. **55**, 246 (1976).
- ¹⁴⁸J. W. Gadzuk, *ibid.* **6**, 133, 159 (1967).
- ¹⁴⁹N. Cabrera and N. F. Mott, Rept. Progr. Phys. **12**, 163 (1948).
- ¹⁵⁰B. V. Deryagin, N. A. Krotova, and V. L. Smilga, Adhezia tverdykh tel (Adhesion of solids), Moscow, Nauka, 1973.
- ¹⁵¹E. M. Lifshits, Zh. Éksp. Teor. Fiz. **29**, 94 (1955) [Sov. Phys. JETP **2**, 73 (1956)].
- ¹⁵²J. Heinrichs, Sol. State Comm. **13**, 1595 (1973).
- ¹⁵³J. E. Inglesfield and E. Wikborg, J. Phys. Ser. F **5**, 1475 (1975).
- ¹⁵⁴J. Ferrante and J. R. Smith, Surf. Sci. **38**, 77 (1973).
- ¹⁵⁵D. M. Rouhani and R. Schuttler, Phys. Stat. Sol. Ser. B **60**, K11 (1973).
- ¹⁵⁶D. M. Rouhani and R. Schuttler, Surf. Sci. **38**, 499, 503 (1973).
- ¹⁵⁷J. Ferrante and J. R. Smith, Sol. State Comm. **20**, 393 (1976).
- ¹⁵⁸J. Ferrante and J. R. Smith, *ibid.* **23**, 527 (1977).
- ¹⁵⁹J. Vannimetus and H. F. Budd, *ibid.* **17**, 1291 (1975).
- ¹⁶⁰J. E. Inglesfield, J. Phys. Ser. F **6**, 68 (1976); R. M. Nieminen, *ibid.* **7**, 375 (1977).
- ¹⁶¹J. Heinrichs and N. Kumar, Sol. State Comm. **18**, 687 (1976).
- ¹⁶²J. R. Smith and J. Ferrante, *ibid.* **21**, 1059 (1977).
- ¹⁶³J. N. Swingler and J. C. Inkson, *ibid.* **24**, 305 (1977).
- ¹⁶⁴J. P. Muskat and G. Allan, J. Phys. Ser. F **7**, 999 (1977).
- ¹⁶⁵J. H. Van der Merve, J. Appl. Phys. **34**, 117 (1963).
- ¹⁶⁶A. A. Andreev and Ya. Paligé, Fiz. Tverd. Tela **3**, 3076 (1962) [Sov. Phys. Solid State **3**, 2238 (1962)]. M. B. Partenskii, Fiz. Met. Metalloved. **32**, 510 (1971); Author's abstract of candidate's dissertation, Sverdlovsk, Ural Polytechnical Institute, 1973. R. I. Mints, V. P. Melekhin, M. B. Partenskii, and I. Yu. Ievlev, Doklady Akad. Nauk SSSR **208**, 814 (1973) [Sov. Phys. Doklady **18**, 143 (1973)]. R. I. Mints, V. P. Melekhin, and M. B. Partenskii, Fiz. Tverd. Tela **16**, 3584 (1974) [Sov. Phys. Solid State **16**, 2330 (1975)]. R. I. Mints, V. P. Melekhin, M. B. Partenskii, and G. I. Rosenman, Fiz. Met. Metalloved. **40**, 886 (1975). S. Yu. Davydov, Fiz. Tverd. Tela **19**, 2418 (1977) [Sov. Phys. Solid State **19**, 1415 (1977)]. F. G. Bass and É. P. Fel'dman, in: XVI Vsesoyuznaya konferentsiya po emissionnoi elektronike, Kratkie sodержaniya dokladov (Sixteenth All-union conference on emission electronics. Brief summaries of reports). Makhachkala, Dagestan Branch, Acad. Sci. USSR, 1976, Vol. 1, p. 125. É. F. Chaikovskii and A. A. Taran, cited in book of Ref. 104, p. 143.
- ¹⁶⁷A. I. Gubanov, Fiz. Tverd. Tela **17**, 1089 (1975) [Sov. Phys. Solid State **17**, 692 (1975)]; Fiz. Met. Metalloved. **41**, 457 (1976).
- ¹⁶⁸A. I. Gubanov, Fiz. Met. Metalloved. **43**, 15 (1977).
- ¹⁶⁹I. D. Moore, J. Phys. Ser. F **6**, L71 (1976).
- ¹⁷⁰W. A. Tiller, S. Ciraci, and J. P. Batra, Surf. Sci. **65**, 173 (1977); R. I. Mints, M. B. Partenskii and V. E. Kuzema, in: Tezisy dokladov II Vsesoyuznogo simpoziuma poaktivnoi poverkhnosti (Abstracts of reports at the Second All-Union Symposium on Active Surfaces), Tartu, 1977, p. 26.
- ¹⁷¹E. Zaremba and W. Kohn, Phys. Rev. Ser. B **13**, 2270 (1976); **15**, 1769 (1977).
- ¹⁷²A. I. Gubanov and S. M. Dunaevskii, Fiz. Tverd. Tela **19**, 1369 (1977) [Sov. Phys. Solid State **19**, 795 (1977)].
- ¹⁷³R. Evans, J. Phys. C **7**, 2808 (1974); R. M. Kobleva, B. R. Gel'chinskii, and V. F. Ukhov, Fiz. Met. Metalloved. **45**, 25 (1978).
- ¹⁷⁴C. H. Hodges and M. J. Stott, Phys. Rev. Ser. B **7**, 73 (1973).
- ¹⁷⁵R. L. Kantz and B. B. Schwartz, *ibid.* **14**, 2017 (1976).
- ¹⁷⁶N. Manninen, R. Nieminen, P. Hantojärvi, and J. Arponen, *ibid.* **12**, 4012 (1975); G. Mori, J. Phys. Ser. F **7**, L7 (1977).
- ¹⁷⁷J. Gyemant and G. Solt, Phys. Stat. Sol. Ser. B **82**, 651 (1977).
- ¹⁷⁸H. L. Lemberg, Phys. Rev. Ser. B **10**, 4079 (1974); P. Feibelman, *ibid.* **19**, 5077 (1977).
- ¹⁷⁹D. E. Inglesfield and E. Wikborn, J. Phys. Ser. F **5**, 1706 (1975).
- ¹⁸⁰S. G. Louie and M. L. Cohen, Phys. Rev. Ser. B **3**, 2461 (1976).
- ¹⁸¹G. A. Baraff, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. **38**, 237 (1977); S. G. Louie and M. L. Cohen, Phys. Rev. Ser. B **13**, 2461 (1976).
- ¹⁸²J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, *ibid.* Ser. B **14**, 588 (1976); **15**, 2408 (1977). G. P. Kerker, S. G. Louie, and M. L. Cohen, *ibid.* **17**, 706 (1978).
- ¹⁸³N. D. Mermin, *ibid.* **137**, 1441 (1965).
- ¹⁸⁴T. L. Gilbert, *ibid.* **12**, 2111 (1975).
- ¹⁸⁵J. R. Smith and J. G. Gay, *ibid.* p. 4238.
- ¹⁸⁶O. Yukio, J. Phys. Soc. Japan **39**, 574 (1975).
- ¹⁸⁷G. I. Bigun, Quoted on p. 44 of the collection of articles of Ref. 104.
- ¹⁸⁸V. E. Kuzema and M. B. Partenskii, in the book "Exoelectron emission and its application: Abstracts of papers presented at the First All-Union Scientific Conference," Sverdlovsk, 1979, p. 118.

Translated by W. H. Furry