Interaction of charges with the surface of a metal

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(Submitted 20 March 1986)
Zh. Eksp. Teor. Fiz. **92**, 137–151 (January 1987)

The long-wavelength approximation is used to analyze the way charges interact with the surface of a metal. The results obtained make it possible to identify the various reasons for changes in the image forces. It is shown that in discussing moving charges it is not sufficient to allow for the interaction with just longitudinal or transverse modes. A proof is given that surface Rydberg states are (like polarons) localized in all directions.

1. INTRODUCTION

The interaction of charged particles with the surface of a metal is of interest because it determines the characteristics of many important processes, particularly the laws governing electron emission from a metal, electron diffraction,[1] and statistical and dynamic behavior of ions near the surface.[2] In recent years there has been considerable interest in observations by the technique of inverse photoemission, and also two-photon photoemission from universal vacant surface Rydberg electron states on silver, nickel, copper, and some semiconductors, which are assumed to be confined by forces of the Coulomb type.[3–5] For a long time the microscopic descriptions of the behavior of charges near a metal have been limited to the introduction of the image forces cut off in one way or another at atomic distances from the metal.[1] The need for such a cutoff which follows from general considerations, is confirmed also by an analysis of direct experiments.[6] Recent investigations have required a fuller allowance for the way the properties of a metal affect the interaction with its surface than is possible with the use of classical image forces. A considerable stimulus for the development of a theory has been provided by a series of studies carried out on the assumption that the interaction of charges and dipoles with a metal reduces to the interaction with surface plasmons. Work of this kind carried out up to 1983 is reviewed by Schmeits and Lucas.[7] However, it is suggested in Ref. 8 that an analysis of the interactions only with surface plasmons without allowance for the bulk modes is incorrect. The important role played by bulk longitudinal modes is supported in Ref. 8 by the use in the calculations, on the one hand, of the general relativistic scheme for the quantization of an electromagnetic field with an indefinite metric and, on the other, of a very specific model of a metal. It would be desirable to check the conclusions reached in Ref. 8 by considering a more general case and to extend them to the case of moving charges.

The influence of the quantum nature of the motion of electrons near the surface requires special analysis because of contradictions in the published literature.[9,10] This problem has become more urgent because of the need to describe the surface Rydberg states mentioned above.[4,5]

It is necessary to make clear the relationship between the contributions made by longitudinal and transverse modes, to the interaction between charges and a metal particularly in the case of moving charges. This problem is related to objections against the use by some of the authors of the limit $c \to \infty$ right from the beginning of the calculations. In some of the investigations (where retardation[11] is allowed for) the results predict, contrary to the conclusions reached in Ref. 12, departures from the usual expressions for the image forces, even in the case when a charge is at rest at large distances from the surface. It is not clear why only the interaction with longitudinal modes is allowed for in some investigations, whereas others allow only for the interaction with transverse modes, as is done for example in a recent paper.[13]

The influence of the spatial dispersion has not yet been determined, although according to some authors,[9,14] it can influence the interactions even when the charges are relatively far from the metal.

It would be desirable to consider further the limitation on the long-wavelength approximation, which excludes the influence of short-wavelength modes or, more precisely, models it by means of a finite number of parameters. The corrections to the long-wavelength approximation used to describe the interaction of electrons with a metal at short distances, which are needed to allow for the exchange and correlation effects, have been considered frequently in the literature within the framework of the jellium model after the first studies (Ref. 15). In all such calculations (the more recent literature is cited in Ref. 16) only the influence of longitudinal modes (Coulomb interactions) has been allowed for, even when considering a moving electron. The proof that this restriction is unjustified within the framework of simple long-wavelength formalism, which allows analytic solution, means that corrections must be made to the calculations mentioned above.

It follows from this discussion that it would be desirable to reconsider the interaction of charges with the surface of a metal. In the present case we consider a dynamic system with complex kinematics in the presence of spatial and temporal dispersion, and it seems to us that it is best to use the Lagrangian formulation based on the introduction of the action, but with integration with respect to the frequency ω and not with respect to time. This action can be introduced either at $T = 0$ or under thermodynamic equilibrium conditions by going over to the Euclidean time (which varies from 0 to T^{-1}). We can then obtain an expression for the casual (at $T = 0$) and thermal Green's functions,[17] which can be rewritten in terms of functional integrals. The most important quantities representing the response and distribution functions can be expressed in terms of these Green's functions. We shall consider only those problems which can be solved by means of functional integrals using simple shifts of the variables followed by calculation of Gaussian integrals.

 0038-5646/87/010077-08$04.00

There is no need then for the tedious writing down of the formulas with functional integrals: it is sufficient to consider only the action. The structure of the functional integrals is used only in the rules for choosing the contours of integration with respect to ω and for interpretation of the results.

The main expression for the action is given in Sec. 2. An important feature of this expression is that it is given in terms of scalar dynamic variables that change over distances of the order of ω/c, but are approximately constant over atomic distances. The expression for the action is used in Sec. 3 to consider various aspects of the interaction of charges with the surface of a metal and to analyze the reasons for the deviation in the image forces. In the last section (Conclusions) we shall summarize the physical consequences of the formulas derived and consider by way of example the properties of surface Rydberg states.

2. EXPRESSION FOR THE ACTION

We assume that a metal occupies the left half-space $x_3<0$, whereas the right half-space contains a homogeneous structure-free insulator (vacuum) located at $x_3>l$. At the distance l which is of the order of atomic dimensions there is a continuous transition from metal to an insulator. We shall assume that $l_F \lesssim l \ll c/\omega_p$, where l_F and ω_p are, respectively, the electron mean free path (coherence loss length) and the plasma frequency in the metal. We shall use the following expressions for the components of the action S_A and S_{int} corresponding respectively to a long-wavelength electromagnetic field and its interaction with external charges:

$$S_A=\frac{1}{8\pi}\int\limits_{-\infty-i\delta}^{\infty+i\delta} d\omega\int d^3x\Big\{\frac{\omega^2}{c^2}A_i^*(\omega,\mathbf{x})\,(\varepsilon_{ij}A_j)\,(\omega,\mathbf{x}) - \operatorname{curl}\mathbf{A}^*(\omega,\mathbf{x})\operatorname{curl}\mathbf{A}(\omega,\mathbf{x})\Big\}, \tag{1}$$

$$S_{int}=\frac{e}{c}\int\limits_{-\infty-i\delta}^{\infty+i\delta} d\omega\int d^3x A_i^*(\omega,\mathbf{x})j_i(\omega,\mathbf{x}),\qquad \delta\to 0,$$

where the identical indices $i, j = 1, 2, 3$ are understood to imply summation and the gauge is selected so that only the vector potential A_i differs from zero. The choice of the contour of integration with respect to ω below the real axis for $\omega<0$ and above the axis for $\omega>0$ corresponds to the condition of the derivation of causal Green functions from the action. The spatial dispersion is usually allowed for in the literature by considering a longitudinal field. We shall therefore represent ε_{ij} in the form

$$\varepsilon_{ij}=\varepsilon[\delta_{ij}\varepsilon^{-1}-k_iK_{(1)}^{-1}k_j]\varepsilon+\varepsilon k_i[K_{(1)}+K_{(1)}\beta K_{(1)}]^{-1}k_j\varepsilon,$$
$$K_{(1)}=k_i\varepsilon k_i, \tag{2}$$

where $k_i=i\partial/\partial x_i$, $\varepsilon=\varepsilon(\omega,x_3)$ and the operator $\beta=\beta(\omega,x_3,\mathbf{k})$ are continuous functions of x_3, which assumes that the following are constant: $\varepsilon_1(\omega),\beta_1(\omega,\mathbf{k})$ when $x_3>l$ and $\varepsilon_2(\omega),\beta_2(\omega,\mathbf{k})$ when $x_3<0$. For simplicity, we shall consider only the case of cubic symmetry with the normal to the surface coinciding with the symmetry axis. The averaging is carried out in the $\mathbf{x}_\parallel=\{x_1,x_2\}$ plane, which is usually justified for values of c/ω_p much larger than the atomic dimensions. In writing down Eq. (2), which includes a generalization of the expression for the longitudinal permittivity of the type $\varepsilon_L^{-1}=(\varepsilon^{-1}+\beta k_i^2)^{-1}$ described in a homogeneous medium, we have included only the plasma components in ε_{ij}. In a dynamic description of the behavior of additional charged fields (particles), which correspond to the components of the current j_i, the expressions for S should include the action representing these particles. Similarly, additional inelastic processes may be allowed for.[1)] We can represent $\mathbf{A}(\omega,\mathbf{x})$ as follows:

$$\mathbf{A}(\omega,\mathbf{x})=\varepsilon^{-1}(\omega,x_3)\operatorname{curl}\operatorname{curl}\mathbf{n}a_p(\omega,\mathbf{x}) + \operatorname{curl}\mathbf{n}a_s(\omega,\mathbf{x})+\operatorname{grad}a_l(\omega,\mathbf{x}), \tag{3}$$

where $\mathbf{n}$ is the normal to the surface; the scalars $a_{p,s,l}$ describe, respectively, the p- and s-polarized and longitudinal waves.[2)] In the case of a p-polarized wave we can use also the representation

$$\varepsilon^{-1}\operatorname{curl}\operatorname{curl}\mathbf{n}a_p=-\mathbf{n}\left(\frac{\partial}{\partial x_3}\frac{1}{\varepsilon(\omega,x_3)}\frac{\partial}{\partial x_3}+\frac{1}{\varepsilon(\omega,x_3)}\frac{\partial^2}{\partial\mathbf{x}_\parallel^2}\right)a_p+\operatorname{grad}\frac{1}{\varepsilon(\omega,x_3)}\frac{\partial a_p}{\partial x_3}. \tag{4}$$

Substituting Eqs. (2) and (3) in Eq. (1), and Fourier-expanding in terms of $\exp(i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel)$, we obtain

$$S_A=-\frac{1}{8\pi}\int\limits_{-\infty-i\delta}^{\infty+i\delta}d\omega\int d^2k_\parallel\,dx_3\Big\{k_\parallel^2[a_p^*(\omega,\mathbf{k}_\parallel,x_3)\times K_{(2)}K_{(3)}a_p(\omega,\mathbf{k}_\parallel,x_3)] + k_\parallel^2[a_s^*(\omega,\mathbf{k}_\parallel,x_3)K_{(4)}a_s(\omega,\mathbf{k}_\parallel,x_3)] - \Big[a_l^*(\omega,\mathbf{k}_\parallel,x_3)\Big(K_{(1)}\frac{\omega^2/c^2}{K_{(1)}+K_{(1)}\beta K_{(1)}}K_{(1)}a_l\Big)(\omega,\mathbf{k}_\parallel,x_3)\Big]\Big\}, \tag{5}$$

$$S_{int}=\frac{e}{c}\int\limits_{-\infty-i\delta}^{\infty+i\delta}d\omega\int d^2k_\parallel\,dx_3\Big\{\mathbf{j}\mathbf{n}K_{(2)}a_p^*+i\Big(\mathbf{j}[\mathbf{k}_\parallel,\mathbf{n}]a_s^* + \omega\rho\Big(\frac{1}{\varepsilon}\frac{\partial a_p^*}{\partial x_3}+a_l^*\Big)\Big)\Big\},$$

$$K_{(2)}=k_i\varepsilon^{-1}(\omega,x_3)k_i,\quad K_{(3)}=k_i\varepsilon^{-1}(\omega,x_3)k_i-\frac{\omega^2}{c^2},$$

$$K_{(4)}=k_i^2-\varepsilon(\omega,x_3)\omega^2/c^2.$$

Equation (5) is obtained using integration by parts and the conservation equation $\operatorname{div}\mathbf{j}=-i\omega\rho$.

In the action (5) the fields $a_{p,s,l}$ are separable. When the boundaries of the metal are not planar and the specified symmetry and/or homogeneity of ε_{ij} are not observed in a plane $\mathbf{x}_\parallel$ in the region when $x_3<l$, this separation is no longer possible and the waves $a_{p,s,l}$ are coupled. This coupling can be included in our treatment employing perturbation theory in accordance with the scheme used in Ref. 18. Allowance for the dispersion in a longitudinal wave makes it possible to avoid the following complication. Without such an allowance the quantity $\omega c^{-1}a$ is not canonically conjugate and we are faced with the problem of a dynamic description of longitudinal waves which requires special measures. As pointed out earlier, this problem is solved in Ref. 8 by a relativistic formalism. In the nonrelativistic problem considered here it is more natural to avoid this difficulty by introducing in a suitable manner the dispersion, which can be given a relativistic meaning, or (in the case of vacuum) to go to the limit of zero dispersion at the end of calculations.

An important feature of the representation (3) and of the action described by Eq. (5) is that they are not affected by the simultaneous substitution

$$a_p(\omega, \mathbf{k}_\parallel, x_3) \to a_p(\omega, \mathbf{k}_\parallel, x_3) + \Lambda, \qquad a_l \to a_l - \frac{1}{\varepsilon}\frac{\partial \Lambda}{\partial x_3},$$

if $\Lambda = \Lambda(\omega, \mathbf{k}_\parallel, x_3)$ obeys the following equations which follow from one another:

$$K_{(2)}\Lambda = 0, \qquad K_{(1)}\frac{1}{\varepsilon}\frac{\partial \Lambda}{\partial x_3} = 0. \tag{6}$$

We shall avoid this indeterminacy assuming that when a_p is expanded in terms of normal modes, there are no modes that would obey Eq. (6) and that the operator $K_{(2)}$ has a reciprocal in the space of functions under consideration.

It is important to note that in Eq. (5) the interaction with the current j_i is described only by a combination of fields $K_{(2)}a_p$, $\varepsilon^{-1}\partial a_p/\partial x_3$, a_s, and a_l and in the frequency range $\omega \lesssim \omega_p$ of importance in the further treatment these fields change, on the basis of classical equations of motion, over distances which are large compared with the atomic distances even when ε_{ij} has a discontinuity at $x_3 = 0$. This is one of the reasons why we can limit ourselves to the long-wavelength approximation.

3. EXPRESSIONS FOR THE INTERACTION OF CHARGES WITH A SURFACE

We shall carry out the following canonical transformation (shift) of Eq. (5):

$$\begin{aligned} a_p &\to a_p + \frac{4\pi e}{c}\frac{1}{k_\parallel^2}K_{(2)}^{-1}K_{(3)}^{-1}\left[K_{(2)}(\mathbf{jn}) - i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\rho\right], \\ a_s &\to a_s + \frac{4\pi e}{c}\frac{1}{k_\parallel^2}K_{(4)}^{-1}i[\mathbf{k}_\parallel, \mathbf{n}]\mathbf{j}, \\ a_l &\to a_l - 4e\pi\frac{c}{i\omega}(K_{(1)}^{-1} + \beta)\rho, \end{aligned} \tag{7}$$

where the reciprocals of the operators represent the corresponding Green's functions. This transformation does not alter S_A, whereas S_{int} changes to

$$\begin{aligned} S_{\text{int}}^{\text{eff}} = \frac{2e^2\pi}{c^2}\int_{-\infty-i\delta}^{\infty+i\delta} d\omega \int d^2k_\parallel\, dx_3 \Big\{ &\left[K_{(2)}(\mathbf{jn}) - i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\rho\right]^* \\ &\times k_\parallel^{-2}\left(K_{(2)}^{-1}K_{(3)}^{-1}\right. \\ &\times\left.\left[K_{(2)}(\mathbf{jn}) - i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon(\omega, x_3)}\rho\right]\right)(\omega, \mathbf{k}_\parallel, x_3) \\ &+ ([\mathbf{k}_\parallel, \mathbf{n}]\mathbf{j})^* k_\parallel^{-2}(K_{(4)}^{-1}[\mathbf{k}_\parallel, \mathbf{n}]\mathbf{j})(\omega, \mathbf{k}_\parallel, x_3) \\ &- c^2\rho^*(\omega, \mathbf{k}_\parallel, x_3)([K_{(1)}^{-1} + \beta]\rho)(\omega, \mathbf{k}_\parallel, x_3)\Big\}. \end{aligned} \tag{8}$$

The integral operators in Eq. (8) can be represented as follows using the familiar expressions for the one-dimensional Green's functions:

$$\begin{aligned} (K_{(n)}^{-1}f)(\omega, \mathbf{k}_\parallel, x_3) = \frac{1}{2}\int dx_3' \{&[\chi_{(n)}^{(+)}(x_3)\chi_{(n)}^{(-)}(x_3')\theta(x_3 - x_3') \\ &+ \chi_{(n)}^{(+)}(x_3')\chi_{(n)}^{(-)}(x_3)\theta(x_3' - x_3)]f(\omega, \mathbf{k}_\parallel, x_3')\}, \qquad n = 1, 2, 3, 4, \end{aligned} \tag{9}$$

$$K_{(2)}^{-1}K_{(3)}^{-1} = \frac{c^2}{\omega^2}(K_{(3)}^{-1} - K_{(2)}^{-1}),$$

where $\chi_{(n)}^{(\pm)}$ are the solutions of the equations $\mathbf{K}_{(n)}\chi_{(n)}^{(\pm)} = 0$ $(n = 1, 2, 3, 4)$ which have the following form for $x_3 > l$:

$$\begin{aligned} &\chi_{(1)}^{(+)} = (\varepsilon_1 k_\parallel)^{-1/2}\exp(-k_\parallel x_3), \qquad \chi_{(1)}^{(-)} = (\varepsilon_1 k_\parallel)^{-1/2}(\exp k_\parallel x_3 \\ &- \alpha_{(1)}(\omega)\exp(-k_\parallel x_3)), \qquad \chi_{(2)}^{(+)} = \left(\frac{\varepsilon_1}{k_\parallel}\right)^{1/2}\exp(-k_\parallel x_3), \\ &\chi_{(2)}^{(-)} = \left(\frac{\varepsilon_1}{k_\parallel}\right)^{1/2}(\exp k_\parallel x_3 - \alpha_{(2)}(\omega)\exp(-k_\parallel x_3)), \\ &\chi_{(3)}^{(+)} = i\left(-\frac{\omega^2}{c^2}\varepsilon_1 + k_\parallel^2\right)^{-1/4}(\varepsilon_1)^{1/2}\exp\left\{i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}, \\ &\chi_{(3)}^{(-)} = i\left(-\frac{\omega^2}{c^2} + k_\parallel^2\right)^{-1/4}(\varepsilon_1)^{1/2}\left(\exp\left\{-i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}\right. \\ &\left.- \alpha_{(3)}(\omega)\exp\left\{i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}\right), \\ &\chi_{(4)}^{(+)} = i\left(-\frac{\omega^2}{c^2} + k_\parallel^2\right)^{-1/4}\exp\left\{i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}, \\ &\chi_{(4)}^{(-)} = i\left(-\frac{\omega^2}{c^2}\varepsilon_1 + k_\parallel^2\right)^{-1/4}\left(\exp\left\{-i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}\right. \\ &\left.- \alpha_{(4)}(\omega)\exp\left\{i\left(\frac{\omega^2}{c^2}\varepsilon_1 - k_\parallel^2\right)^{1/2}x_3\right\}\right). \end{aligned} \tag{10}$$

In the region $x_3 > l$ all the properties of the metal occur in Eq. (9) only via the coefficients[3] $\alpha_{(1)} = -\alpha_{(2)}, \alpha_{(3)}$, and $\alpha_{(4)}$ introduced in the system (10) and representing response functions with analytic properties governed by the positions of the energy levels and thresholds, together with the condition $\alpha_{(n)} \propto \omega^{-2}$ when $|\omega|^2 \gg \omega_p^2$. Therefore, the behavior of charges outside a metal can in principle be described using not the permittivity directly, but the characteristics of bulk and surface excitations. Then, the positions, residues, and widths of pole singularities are the parameters that represent the influence of a surface layer. This result is very general and is independent of the assumed model representations.

In the simplest case of a sharp boundary it follows from the conditions for matching of the solutions of the relevant equations at this boundary that

$$\begin{aligned} \alpha_{(1)} &= -\alpha_{(2)} = \frac{\varepsilon_2(\omega) - \varepsilon_1(\omega)}{\varepsilon_2(\omega) + \varepsilon_1(\omega)}, \\ \alpha_{(3)} &= \frac{\varepsilon_1(\omega)(\omega^2c^{-2}\varepsilon_2(\omega) - k_\parallel^2)^{1/2} - \varepsilon_2(\omega)(\omega^2c^{-2}\varepsilon_1(\omega) - k_\parallel^2)^{1/2}}{\varepsilon_1(\omega)(\omega^2c^{-2}\varepsilon_2(\omega) - k_\parallel^2)^{1/2} + \varepsilon_2(\omega)(\omega^2c^{-2}\varepsilon_1(\omega) - k_\parallel^2)^{1/2}}, \\ \alpha_{(4)} &= \frac{(\omega^2c^{-2}\varepsilon_2(\omega) - k_\parallel^2)^{1/2} - (\omega^2c^{-2}\varepsilon_1(\omega) - k_\parallel^2)^{1/2}}{(\omega^2c^{-2}\varepsilon_2(\omega) - k_\parallel^2)^{1/2} + (\omega^2c^{-2}\varepsilon_1(\omega) - k_\parallel^2)^{1/2}}. \end{aligned} \tag{11}$$

In the case of the charges and currents located in the region $x_3 > l$, substitution of Eqs. (9) and (10) into Eq. (8) gives

$$\begin{aligned} S_{\text{int}}^{\text{eff}} = &-i\frac{e^2\pi}{c^2} \\ &\times\int_{x_3>l} d\omega\, d^2k_\parallel\, dx_3\, dx_3' \frac{\exp\{i(\omega^2c^{-2}\varepsilon_1 - k_\parallel^2)^{1/2}(x_3 + x_3')\}}{i(\omega^2c^{-2}\varepsilon_1 - k_\parallel^2)^{1/2}} \\ &\times\left\{\left[K_{(2)}(\mathbf{jn}) - i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon_1}\rho\right]^*(\omega, \mathbf{k}_\parallel, x_3)\frac{\alpha_{(3)}\varepsilon_1c^2}{k_\parallel^2\omega^2}\left[K_{(2)}(\mathbf{jn})\right.\right. \end{aligned}$$

$$-i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon_1}\rho\Big](\omega,\mathbf{k}_\parallel,x_3')+([\mathbf{k}_\parallel,\mathbf{n}]\mathbf{j}(\omega,\mathbf{k}_\parallel,x_3))\cdot$$
$$\times\frac{\alpha_{(1)}(\omega)}{k_\parallel^2}([\mathbf{k}_\parallel,\mathbf{n}]\mathbf{j}(\omega,\mathbf{k}_\parallel,x_3'))\Big\}. \qquad (12)$$

In writing down Eq. (12) we have omitted from the integral the terms proportional to $\exp(x_3-x_3')$ or those including only the local operators acting on $\mathbf{j}$ and ρ (for example, the operator K_2) and corresponding to the expression for the self-interaction in an unbounded insulator. The main feature of Eq. (12) is that it does not contain dispersion if β is a local (or quasilocal) operator. The term with dispersion is retained only if we consider the region $x_3 \lesssim l$. However, in this region the retention only of the electromagnetic interactions with external microscopic charges ceases to be realistic and we have to allow for the dynamic quantum interaction of such charges with electrons in a metal.[15,16,19] An interesting property of Eq. (12) is that a term which appears because of the coupling with a longitudinal wave exactly cancels with a part of the term proportional to $K_{(2)}^{-1}$, which appears because of the coupling with a p wave. This result can be interpreted, ignoring the terms in Eq. (12) containing the current j, as the effective expression of the interaction of the charge density ρ at the surface with a scalar field a, which does not obey the Poisson equation $-K_{(1)}a=4\pi\rho$, but an equation with a term proportional to ω^2/c^2. Therefore, the use of the Poisson equation can give a correct result only in the static or quasistatic case [when $\rho(\mathbf{x},t)$ varies slowly with time]. In this case when the attenuation in a metal is sufficiently strong, it follows from Eq. (12) that if $\rho(\mathbf{x},t)=\rho(\mathbf{x})$ and if we employ $\delta^2(\omega)=\delta(\omega)\int dt/2\pi$, we obtain the usual expression for the potential V^{eff} of the image forces [$\rho(\mathbf{x})=0$ for $x_3<l$]:

$$S_{int}^{eff}=\int L_{int}^{eff}dt=\frac{e^2}{2}\int dt\,dx^3\,d^3x'\left\{\frac{1}{\varepsilon_1(0)}\frac{\varepsilon_2(0)-\varepsilon_1(0)}{\varepsilon_2(0)+\varepsilon_1(0)}\right.$$
$$\left.\times[(x_3+x_3')^2+(\mathbf{x}_\parallel-\mathbf{x}_\parallel')^2]^{-1/2}\rho(\mathbf{x})\rho(\mathbf{x}')\right\},\quad V^{eff}=-L^{eff}. \qquad (13)$$

We can describe the influence of particle motion on the interaction with a metal by considering the case of a point particle moving at an approximately constant velocity $\mathbf{v}$ when the attenuation is weak. We then can substitute in Eq. (12)

$$\rho(t,\mathbf{x})=\delta^2[\mathbf{x}-\mathbf{x}(t)],\ \mathbf{x}(t)=\mathbf{v}t \text{ for } t>0,$$
$$\varepsilon_1=1,\ \varepsilon_2=1-\omega_p^2/\omega^2. \qquad (14)$$

Retaining only the terms proportional to the square of the density and omitting in the subsequent expressions the terms proportional to $(v/c)^2$, we obtain

$$S_{int}^{eff}=-\frac{e^2\pi}{(2\pi)^3}\int d\omega\,d^2k_\parallel\,dx_3\,dx_3'\,dt\,dt'\left\{\exp[i\omega(t-t')]\right.$$
$$\times\exp[i\mathbf{k}_\parallel(\mathbf{x}_\parallel-\mathbf{x}_\parallel')]\delta^3(\mathbf{x}-\mathbf{x}(t))\delta^3(\mathbf{x}'-\mathbf{x}(t'))\frac{i(\omega^2/c^2-k_\parallel^2)^{1/2}}{k_\parallel^2}$$
$$\times\exp\{i(\omega^2/c^2-k_\parallel^2)^{1/2}(x_3+x_3')\}$$
$$\left.\times\frac{(\omega^2-\omega_p^2)[\omega^2/c^2-k_\parallel^2]^{1/2}-\omega^2[(\omega^2-\omega_p^2)/c^2-k_\parallel^2]^{1/2}}{(\omega^2-\omega_p^2)[\omega^2/c^2-k_\parallel^2]^{1/2}+\omega^2[(\omega^2-\omega_p^2)/c^2-k_\parallel^2]}\right\}$$
$$=-\frac{e^2\pi}{(2\pi)^3}\int dt\,dt'\,d\omega\,d^2k_\parallel\left\{\exp i\omega t'\exp i\mathbf{k}_\parallel\mathbf{v}_\parallel t'\right.$$
$$\times\frac{i[\omega^2/c^2-k_\parallel^2]^{1/2}}{k_\parallel^2}\exp\{2i(\omega^2/c^2-k_\parallel^2)^{1/2}x_3(t)\}$$
$$\left.\times\frac{(\omega^2-\omega_p^2)[\omega^2/c^2-k_\parallel^2]^{1/2}-\omega^2[(\omega^2-\omega_p^2)/c^2-k_\parallel^2]^{1/2}}{(\omega^2-\omega_p^2)[\omega^2/c^2-k_\parallel^2]^{1/2}+\omega^2[(\omega^2-\omega_p^2)/c^2-k_\parallel^2]^{1/2}}\right\}$$
$$=\frac{e^2}{2\pi}\int dt\,d\omega\frac{d^2k_\parallel}{k_\parallel}\delta(\mathbf{k}_\parallel\mathbf{v}_\parallel-\omega)\exp[-2k_\parallel x_3(t)]$$
$$\times\frac{(\omega^2-\omega_p^2)k_\parallel-\omega^2[\omega_p^2/c^2+k_\parallel^2]^{1/2}}{(\omega^2-\omega_p^2)k_\parallel+\omega^2[\omega_p^2/c^2+k_\parallel^2]^{1/2}}=\frac{e^2}{\pi}\int_0^\infty dt\int_0^\infty dk_\parallel\int_0^1\frac{du}{(1-u^2)^{1/2}}$$
$$\times\exp[-2k_\parallel x_3(t)]\frac{u^2k_\parallel v_\parallel^2(k_\parallel-[k_\parallel^2+\omega_p^2/c^2]^{1/2})-\omega_p^2}{u^2k_\parallel v_\parallel^2(k_\parallel+[k_\parallel^2+\omega_p^2/c^2]^{1/2})-\omega_p^2+i\delta}, \qquad (15)$$

where the imaginary correction $i\delta$ appears explicitly in the denominator. It follows from Eq. (15) that the effective interaction potential V^{eff} has an imaginary component equal to (terms of the order of v^2/c^2 are omitted)

$$\operatorname{Im}V^{eff}=-\operatorname{Im}L_{int}^{eff}=e^2\int_0^\infty dk_\parallel\int_0^1\frac{du}{(1-u^2)^{1/2}}$$
$$\times\left\{\exp\{-2k_\parallel x_3(t)\}\left[u^2k_\parallel v_\parallel^2\left[k_\parallel-\left(k_\parallel^2+\frac{\omega_p^2}{c^2}\right)^{1/2}\right]\right.\right.$$
$$\left.\left.-\omega_p^2\right]\delta\left(u^2k_\parallel v_\parallel^2\left[k_\parallel+\left(k_\parallel^2+\frac{\omega_p^2}{c^2}\right)^{1/2}\right]-\omega_p^2\right)\right\}$$
$$=-\frac{2^{1/2}e^2\omega_p}{4}\int_0^1\frac{du}{u|v_\parallel|(1-u^2)^{1/2}}\exp\left\{-\frac{2^{1/2}\omega_p x_3}{u|v_\parallel|}\right\}$$
$$=-\frac{2^{1/2}e^2\omega_p}{4|v_\parallel|}K_0\left(\frac{2^{1/2}\omega_p x_3}{|v_\parallel|}\right)$$
$$\to-\frac{e^2\pi^{1/2}}{4}\left(\frac{\omega_p}{x_3|v_\parallel|}\right)^{1/2}\exp\left\{-\frac{2^{1/2}\omega_p x_3}{|v_\parallel|}\right\}\quad\text{if}\quad x_3\gg|v_\parallel|/\omega_p. \qquad (15')$$

The real components obtained due to the conditions $x_3\gg c/\omega_p$ and $x_3\ll c/\omega_p$, respectively, are described, for $k_\parallel\sim\frac{1}{x_3}\ll\frac{\omega_p}{c}$ by

$$\operatorname{Re}V^{eff}=-\frac{e^2}{4x_3(t)}\left[1+O\left(\frac{v_\parallel^2}{c^2}\right)\right],$$

and for $k_\parallel\sim\frac{1}{x_3}\gg\frac{\omega_p}{c}$ by

$$\operatorname{Re}V^{eff}=\frac{e^2}{\pi}P\int_0^1\frac{du}{(1-u^2)^{1/2}}\int_0^\infty\frac{\omega_p^2\exp\{-2k_\parallel x_3(t)\}}{2u^2k_\parallel^2v_\parallel^2-\omega_p^2}dk_\parallel$$
$$=-\operatorname{Re}\frac{e^2}{\pi}\int_0^1\frac{du}{(1-u^2)^{1/2}}\int_0^{i\infty+\delta}dk_\parallel\exp\{-2k_\parallel x_3\}\frac{\omega_p^2}{\omega_p^2-2u^2k_\parallel^2v_\parallel}$$
$$=-\frac{e^2}{2}\operatorname{Re}\int_0^{i\infty+\delta}\exp\{-2k_\parallel x_3\}\frac{dk_\parallel}{[1-2k_\parallel^2v_\parallel^2/\omega_p^2]^{1/2}}$$
$$=-\frac{e^2\pi}{2^{3/2}}\frac{\omega_p}{|v_\parallel|}\operatorname{Re}i\left[\mathbf{H}_0\left(i\frac{2^{1/2}\omega_p x_3}{|v_\parallel|}\right)-Y_0\left(i\frac{2^{1/2}\omega_p x_3}{|v_\parallel|}\right)\right]$$
$$\to\begin{cases}-\dfrac{e^2}{4x_3(t)} & \text{if}\quad x_3\gg\dfrac{|v_\parallel|}{\omega_p}\\[2ex] \dfrac{e^2\pi\omega_p}{2^{3/2}|v_\parallel|}\left(-1+\dfrac{\omega_p x_3}{2^{1/2}|v_\parallel|}\right) & \text{if}\quad x_3<\dfrac{|v_\parallel|\sqrt{2}}{\omega_p}\end{cases}. \qquad (15'')$$

In Eq. (15″) the notation used for the special functions, their integral representations and asymptotes, and the expression for the last integral are taken from Ref. 12 and use is made of the formula $(x+i\delta)^{-1}=P(1/x)-i\pi\delta(x)$, where P represents the principal value. A rotation toward the imaginary axis is carried out in the last of the expressions in Eq. (15″) in the integral with respect to $dk_\parallel$. The imaginary component of Eq. (15) corresponds to generation of surface plasmons by a moving charge. This follows from the fact that the appearance of Eq. (15′) is due to the presence of a pole in the reflection coefficient. It follows from these expressions that in the nonrelativistic case when $l<x_3<c/\omega_p$ we can regard generation of surface plasmons as the main inelastic process predominating over the emission of bulk modes, proportional to (v/c^2), known as transition radiation in a spatially inhomogeneous medium.[21] One should point out also that it follows from Eq. (15′) that attraction at large values of x_3 changes to a repulsion at small values $x_3<|v_\parallel|/\omega_p$.

To continue the analysis of the consequences of Eq. (12), we can consider the case of a charge which is delocalized in space (assuming, specifically, that the distribution of the charge over $x_\parallel$ is Gaussian) and varies slowly with time so that

$$\rho(\omega,\mathbf{k}_\parallel,x_3)=\frac{\delta(\omega)}{(2\pi)^{1/2}}\rho(x_3)\frac{a^{-2}}{\pi}\int d^2x\exp\left(-\frac{x_\parallel^2}{a^2}\right)\times\exp i\mathbf{k}_\parallel\mathbf{x}_\parallel=\frac{1}{\sqrt{2\pi}}\rho(x_3)\exp\left(-\frac{k_\parallel^2a^2}{4}\right)\delta(\omega). \quad (16)$$

Substitution of Eq. (16) into Eq. (12) in the case when $|\varepsilon_2(0)|\gg\varepsilon_1(0)$ gives

$$S_{int}^{eff}=\frac{e^2}{4\pi}\int dt\int\frac{d^2k_\parallel\,dx_3\,dx_3'}{k_\parallel\varepsilon_1(0)}\times\exp\left[-\frac{k_\parallel^2a^2}{2}\right]\exp[-k_\parallel(x_3+x_3')]\rho(x_3)\rho(x_3')$$

$$=\frac{(2\pi)^{1/2}e^2}{4a}\int dt\,dx_3\,dx_3'\exp\left[\frac{(x_3+x_3')^2}{2a^2}\right]\times\operatorname{erfc}\left(\frac{x_3+x_3'}{\sqrt{2}a}\right)\rho(x_3)\rho(x_3'), \quad (17)$$

where erfc is the probability integral[20] with the following asymptotes

$$\exp\left[\frac{(x_3+x_3')^2}{2a^2}\right]\operatorname{erfc}\left(\frac{x_3+x_3'}{2^{1/2}a}\right)=\begin{cases}\dfrac{2^{1/2}a}{\pi^{1/2}(x_3+x_3')} & \text{if } (x_3+x_3')\gg 2^{1/2}a\\ \pi^{1/2} & \text{if } \dfrac{x_3+x_3'}{2^{1/2}a}\ll 1\end{cases}. \quad (18)$$

It follows from Eqs. (17) and (18) that a classical image force is established only at a distance x_3 from the surface and that this distance is much larger than the longitudinal delocalization size a.

Particularly in connection with the problem of allowing for the quantum nature of the motion of electrons outside the metal, the case when $\rho(\omega,\mathbf{k}_\parallel,x_3)$ contains for finite ω mainly small values of $\mathbf{k}_\parallel$ or even is proportional to $\delta^2(\mathbf{k}_\parallel)$ is worth noting. Such a situation occurs when the charge density is independent or almost independent of $\mathbf{x}_\parallel$. In this case the charge density is distributed along the surface over large distances and, in the main region of integration with respect to $\omega_\parallel$ and $k_\parallel$ in Eq. (12), the inequality $\varepsilon_1\omega^2/c^2>k_\parallel^2$ is obeyed, so that we cannot ignore the current components in Eq. (12) and retardation effects. It should be noted that if in this case we retain only the term proportional to $\rho\rho^*$ in Eq. (12), we find that the integral of $k_\parallel$ diverges at $k_\parallel=0$. Consequently, we shall transform the combination

$$K_{(2)}(\mathbf{jn})-i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\rho$$

occurring in Eq. (12) with the aid of the current conservation equation

$$K_{(2)}(\mathbf{jn})-i\omega\frac{\partial}{\partial x_3}\frac{1}{\varepsilon}\rho=\frac{\partial}{\partial x_3}\frac{i\mathbf{k}_\parallel\mathbf{j}_\parallel}{\varepsilon}+\frac{k_\parallel^2}{\varepsilon}(\mathbf{jn}). \quad (19)$$

Substitution of Eq. (19) into Eq. (12) demonstrates that the terms proportional to $k_\parallel^{-2}$ cancel out in the integrand.

In particular, retaining in the integrand of Eq. (12) only the terms of lowest order in $c^2k_\parallel^2/\omega^2$, we find from Eqs. (11) and (19) that

$$S_{int}=-\frac{e^2\pi}{c}\int d\omega\,dx_3\,dx_3'\,d^2k_\parallel\left\{\frac{\varepsilon_2^{1/2}(\omega)-\varepsilon_1^{1/2}(\omega)}{\varepsilon_2^{1/2}(\omega)+\varepsilon_1^{1/2}(\omega)}\times\frac{\exp[i(\omega^2\varepsilon_1/c^2)^{1/2}(x_3+x_3')]}{i[\omega^2\varepsilon_1/c^2]^{1/2}}\mathbf{j}_\parallel^*(\omega,\mathbf{k}_\parallel,x_3)\times\mathbf{j}_\parallel(\omega,\mathbf{k}_\parallel,x_3')\left[1+O\left(\frac{c^2k_\parallel^2}{\omega^2}\right)\right]\right\}. \quad (20)$$

Therefore, when the charge distribution is extended over the surface (over distances greater than c/ω_p), we must allow for retardation effects. Then, retaining the terms containing ρ or only $\mathbf{j}_\parallel$, we obtain paradoxical results at limiting values of $c^2k_\parallel^2/\omega^2$ because of the apparent divegences of the corresponding integrals. Some of the misunderstandings mentioned in the Introduction are associated with this circumstance.

We shall now consider a situation when a local dynamic exciton mode with a polarizability

$$P_i(\omega,\mathbf{k}_\parallel,x_3)\sim\delta(x_3)P_i(\omega,\mathbf{k}_\parallel)$$

and a dispersion law $\omega_i^2(\mathbf{k}_\parallel)$ appears, for example, because of adsorption on the surface of a metal or because of the presence of surface electron levels. In this case the action should be supplemented by a term of the type

$$S_p=\frac{1}{c}\int d\omega\,d^2k_\parallel\left\{\left[\gamma_\parallel(\omega,\mathbf{k}_\parallel)i\mathbf{k}_\parallel\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)+\gamma_3P_3(\omega,\mathbf{k}_\parallel)\right]^*\left[i\omega a_l(\omega,\mathbf{k}_\parallel,0)-\frac{1}{\varepsilon(\omega,0)}\frac{\partial a_p(\omega,\mathbf{k}_\parallel,x_3)}{\partial x_3}\Big|_{x_3=0}\right]+\mathbf{P}_\parallel^*(\omega,\mathbf{k}_\parallel)(\omega^2-\omega_\parallel^2(\mathbf{k}_\parallel))\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)+P_3^*(\omega,\mathbf{k}_\parallel)(\omega^2-\omega_3^2(\mathbf{k}_\parallel))P_3(\omega,\mathbf{k}_\parallel)\right\}, \quad (21)$$

where the constants $\gamma_i(\omega,\mathbf{k}_\parallel)$ are proportional to the amplitude of the corresponding mode. After substitution of Eq. (7) subject to Eqs. (9) and (10), we find that the component of the action (21) for the charges located at $x_3>l$ becomes

$$S_p=2\pi e\int d\omega\, d^2k_\parallel\, dx_3\,\frac{1}{k_\parallel}\Big\{\frac{\varepsilon_2(\omega)\,e^{-k_\parallel x_3}\rho(\omega,\mathbf{k}_\parallel,x_3)}{\varepsilon_1(\omega)\,(\varepsilon_2(\omega)+\varepsilon_1(\omega))}$$
$$\times(\gamma_\parallel(\omega,\mathbf{k}_\parallel)\,ik_\parallel\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)+\gamma_3(\omega,\mathbf{k}_\parallel)P_3)^*$$
$$+\mathbf{P}_\parallel^*(\omega,\mathbf{k}_\parallel)\,(\omega^2-\omega_\parallel^2(\mathbf{k}_\parallel))\,\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)$$
$$+P_3^*(\omega,\mathbf{k}_\parallel)\,(\omega^2-\omega_3^2(\mathbf{k}_\parallel)P_3(\omega,\mathbf{k}_\parallel)\Big\}. \qquad (22)$$

The expression (22) is obtained in the nonrelativistic approximation and the interaction of an electromagnetic field with the polarization is included in the modified quantities ω_i^2 and γ_i.

If Eq. (22) is modified by the shift

$$\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)\to\mathbf{P}_\parallel(\omega,\mathbf{k}_\parallel)-\frac{ie\pi\mathbf{k}_\parallel}{(\omega^2-\omega_\parallel^2(\mathbf{k}_\parallel))\,k_\parallel}\int dx_3$$
$$\times\frac{\varepsilon_2(\omega)\gamma_\parallel(\omega,\mathbf{k}_\parallel)\exp(-k_\parallel x_3)\rho(\omega,\mathbf{k}_\parallel,x_3)}{\varepsilon_1(\omega)\,(\varepsilon_2(\omega)+\varepsilon_1(\omega))},$$
$$\mathbf{P}_3(\omega,\mathbf{k}_\parallel)\to\mathbf{P}_3(\omega,\mathbf{k}_\parallel)-\frac{e\pi}{(\omega^2-\omega_3^2(\mathbf{k}_\parallel))\,k_\parallel}\int dx_3 \qquad (23)$$
$$\times\frac{\varepsilon_2(\omega)\gamma_3(\omega,\mathbf{k}_\parallel)\exp(-k_\parallel x_3)\rho(\omega,\mathbf{k}_\parallel,x_3)}{\varepsilon_1(\omega)\,(\varepsilon_2(\omega)+\varepsilon_1(\omega))},$$

we obtain

$$S_p^{eff}=-e^2\pi^2\int d\omega\, d^2k_\parallel\, dx_3\, dx_3'\Big\{\frac{\exp[-k_\parallel(x_3+x_3')]}{k_\parallel^2}$$
$$\times\Big(\frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)\,(\varepsilon_2(\omega)+\varepsilon_1(\omega))}\Big)^2\Big[\frac{k_\parallel^2\gamma_\parallel^2(\omega,\mathbf{k}_\parallel)}{\omega^2-\omega_\parallel^2(\mathbf{k}_\parallel)}$$
$$+\frac{\gamma_3^2(\omega,\mathbf{k}_\parallel)}{\omega^2-\omega_3^2(\mathbf{k}_\parallel)}\Big]\rho^*(\omega,\mathbf{k}_\parallel,x_3)\rho(\omega,\mathbf{k}_\parallel,x_3)\Big\}. \qquad (24)$$

For a fixed point charge $\rho(\omega,\mathbf{k}_\parallel,x_3)=(2\pi)^{-3/2}\delta(\omega)\delta(x_3-x_{30})$, we find from Eq. (24) that

$$\Delta S_{int}^{eff}=S_p^{eff}=\frac{e^2}{4}\int dt\, dk_\parallel^2\Big(\frac{\varepsilon_2(0)}{\varepsilon_1(0)\,(\varepsilon_2(0)+\varepsilon_1(0))}\Big)^2$$
$$\times\frac{\exp[-2k_\parallel x_{30}]}{k_\parallel^2}\Big[\frac{k_\parallel^2\gamma_\parallel^2(0,\mathbf{k}_\parallel)}{\omega_\parallel^2(\mathbf{k}_\parallel)}+\frac{\gamma_3^2(0,\mathbf{k}_\parallel)}{\omega_3^2(\mathbf{k}_\parallel)}\Big]. \qquad (25)$$

If the only important terms in the integrand are those sufficiently small to obey the inequality $k_\parallel\lesssim 1/2x_3$, we can assume that

$$\omega_\parallel^2(\mathbf{k}_\parallel)=\omega_\parallel^2+\sigma_\parallel^2\mathbf{k}_\parallel^2,\ \omega_3^2(\mathbf{k}_\parallel)$$
$$=\omega_3^2+\sigma_3^2k_\parallel^2,\ \gamma_\parallel(0,\mathbf{k}_\parallel)=\gamma_\parallel,\ \gamma_3(0,\mathbf{k}_\parallel)=\gamma_3,$$

where the quantities γ_i, σ_i, and ω_i on the right are constant. In this case we find that substitution of $k_\parallel\to k_\parallel x_{30}^{-1}$ in the integral of Eq. (25) yields

$$\Delta S_{int}^{eff}=\frac{e^2\pi}{2}\int dt\int_0^\infty dk_\parallel\Big\{\Big(\frac{\varepsilon_2(0)}{\varepsilon_1(0)\,(\varepsilon_2(0)+\varepsilon_1(0))}\Big)^2\frac{e^{-2k_\parallel}}{k_\parallel}\Big[\frac{k_\parallel^2\gamma_\parallel^2}{\omega_\parallel^2x_{30}^2+\gamma_\parallel^2k_\parallel^2}+\frac{\gamma_3^2x_{30}^2}{\omega_3^2x_{30}^2+\sigma_3^2k_\parallel^2}\Big]\Big\},$$
$$\Delta V^{eff}=\begin{cases}\text{const}+\dfrac{e^2\pi\gamma_3^2\sigma_3^2\varepsilon_2^2(0)}{8\varepsilon_1^2(0)\,(\varepsilon_1(0)+\varepsilon_2(0))^2}\dfrac{1}{\omega_3^2x_{30}^2}+\dots & \text{if}\quad x_{30}>\dfrac{\sigma_i}{\omega_i}\\ \text{const}+\dfrac{e^2\pi}{2}\dfrac{\varepsilon_2^2(0)}{\varepsilon_1^2(0)\,(\varepsilon_2(0)+\varepsilon_1(0))^2}\dfrac{\gamma_\parallel^2}{\sigma_\parallel^2}\ln\dfrac{x_{30}\omega_\parallel}{\gamma_\parallel}+\dots & \text{if}\quad x_{30}<\dfrac{\sigma_i}{\omega_i}\end{cases}. \qquad (26)$$

Therefore, in the case under discussion when the γ_i are sufficiently large, we find that the attraction corresponding to the image forces may change (for certain finite values of x_{30}) to repulsion; this is true even of localized charges.

4. CONCLUSIONS

It follows from the foregoing calculations that, above all, the interaction of charges with the surface of a metal includes contributions from longitudinal and transverse electromagnetic modes. Allowing only for the longitudinal modes (more precisely, those obeying the Poisson equation) or only for the transverse modes gives incorrect results, at least in the case of moving charges; this is particularly true in the case when the interaction with surface plasmons is considered. However, the most effective mechanism of energy losses in the case of nonrelativistic motion of charged particles near the surface of a metal is clearly the emission of surface plasmons. It should be noted that the relatively high probability of emission of surface plasmons is a consequence of the pole structure of the integrand in Eq. (15). This pole structure is the reason for the essentially nonmodel nature of the asymptotic form represented by Eq. (15″), which is identical with that obtained in Ref. 10 employing perturbation theory. When many poles are present in an asymptotic expression, it is necessary to retain only the contribution of the nearest pole. It follows from Eq. (15) that if $|v_\parallel|\sim 10^{-7}$–$10^{-8}$ cm/sec, then the imaginary part of the interaction with a metal is comparable with the real part up to distances on the order of tens of angstroms. The consequences of Eqs. (17) and (20) deserve special attention. An analysis of these equations confirms that in discussing the dynamics of electrons near the surface of a metal we must allow for many factors, including the ratio of the size of wave packets to their distance from the surface. The problem is nonlinear and the image forces are established only at a distance from the surface which is greater than the packet size. It follows from Eq. (26) that the interactions with the metal become greatly modified at short distances also because of the appearance of surface modes.

These effects are particularly important when we are considering electron levels of the Rydberg type mentioned in the Introduction. In theoretical treatments of these levels their energy $E=E(\mathbf{k}_\parallel,n)$ has been usually described by the following obvious formula[4,5]:

$$E(\mathbf{k}_\parallel,n)=\frac{\hbar^2k_\parallel^2}{2m}-\frac{\alpha^2m}{2(n+a)^2\hbar^2},\qquad \alpha=\frac{e^2}{4}, \qquad (27)$$

where $\mathbf{k}_\parallel$ is the momentum associated with free motion of an electron along the surface; a is the index of a defect the value

of which is assumed to lie between $-1/2$ and $-1/3$; n is the principal quantum number. Neglect of the exchange and correlation effects in Eq. (27) is justified by the fact that the bulk of the electron density lies at a distance exceeding 2 Å from the surface, even for $n = 1$, and at this distance the effects under discussion are considered unimportant in Ref. 16. Equation (27) describes satisfactorily the experimental results on inverse photoemission if we attribute to m a value which is 1.5–2 times greater than the electron mass. In spite of considerable effort,[5] no explanation has yet been found for this increase in the mass. According to the conclusions reached in the present study, when we consider the energy of electrons outside a metal under steady-state conditions, we can use the formulas

$$E=T+V_{int},$$
$$V_{int}=-\frac{e^2}{2}\int\frac{\varepsilon(0)-1}{\varepsilon(0)+1}\frac{\rho(\mathbf{x})\rho(\mathbf{x}')}{((\mathbf{x}_\parallel-\mathbf{x}_\parallel')^2+(x_3+x_3')^2)^{1/2}}d^3x\,d^3x', \tag{28}$$
$$\rho(\mathbf{x})=|\psi(\mathbf{x})|^2.$$

Within the energy gap we may assume, as is done in Refs. 4 and 5, that $\psi(\mathbf{x})$ satisfies a zero boundary condition at $x_3 = 0$. The expression (28) has much in common with the expression for the energy of a Fröhlich polaron after exclusion of phonon variables. In particular, exactly as in the case of a polaron,[22,23] we can prove the virial theorem and the formation of states which are localized in all directions.[4)] In the course of such proof, we replace (by hypothesis) a localized normalized wave eigenfunction $\psi(\mathbf{x})$ in Eq. (28) with $C^{3/2}\psi(C\mathbf{x})$ and after transforming the variables in the integrals we obtain

$$E(C)=C^2T+V_{int}C. \tag{29}$$

Since in the ground state $\partial E/\partial C$ should vanish for $C = 1$, it follows from Eq. (29) that $T = -\frac{1}{2}V_{\text{int}}$ and $E = \frac{1}{2}V_{\text{int}} < 0$. Therefore, in conflict with the hypothesis in Refs. 4 and 5, an electron in the ground state is localized in all directions on the basis of Eq. (17). This is due to the fact that spreading of the electron density along the surface reduces the absolute value of the negative energy of the interaction with the image forces (self-interaction) which exceeds (beginning from a certain value) the gain due to reduction in the kinetic energy. We shall now consider the case when the center of gravity of a surface Rydberg state moves along the surface at a constant nonrelativistic velocity $\mathbf{v}_\parallel$. In this case the interaction with a metal is characterized, in accordance with the above results, by the following component of the action:

$$S_{int}=\frac{e^2}{2}\int\frac{\varepsilon(\omega)-1}{\varepsilon(\omega)+1}\frac{\rho^*(\omega,\mathbf{x})\rho(\omega,\mathbf{x})\theta(x_3)\theta(x_3')}{[(\mathbf{x}_\parallel-\mathbf{x}_\parallel')^2+(x_3+x_3')^2]^{1/2}}d^3x\,d^3x'\,d\omega, \tag{30}$$

where $\rho(\omega,\mathbf{x})$ is the Fourier component of $\rho(t,\mathbf{x}) = \rho(\mathbf{x} - \mathbf{v}_\parallel t)$. Substituting $\varepsilon(\omega) = 1 - \omega_p^2/\omega^2$ in Eq. (30) and retaining only the terms which are quadratic in $v_\parallel^2$, we find that

$$L_{int}=\frac{e^2}{2}\frac{1}{2\pi}\int_{x_3,x_3'>0}\left(1+\frac{2\omega^2}{\omega_p^2}+\ldots\right)e^{i\omega t}$$
$$\times\frac{\rho(\mathbf{x})\rho(\mathbf{x}')\,d\omega\,dt\,d^3x\,d^3x'}{[(\mathbf{x}_\parallel-\mathbf{x}_\parallel'-\mathbf{v}_\parallel t)^2+(x_3+x_3')^2]^{1/2}}\approx\frac{e^2}{2}\int_{x_3,x_3'>0}d^3x\,d^3x'\,\rho(\mathbf{x})$$
$$\times\rho(\mathbf{x}')\left\{\left(1-\frac{v_\parallel^2}{\omega_p^2}\frac{\partial^2}{\partial\mathbf{x}_\parallel^2}\right)\left(\frac{1}{[(\mathbf{x}_\parallel-\mathbf{x}_\parallel')^2+(x_3+x_3')^2]^{1/2}}\right)\right\}. \tag{31}$$

The coefficient in front of $\frac{1}{2}v_\parallel^2$ in Eq. (31) can be interpreted as the effective mass. This mass is governed by an additional (besides those occurring in the Coulomb problem) parameter ω_p^2, and it should not be equal to m, which enables us to explain the results obtained in the course of inverse photoemission.

It also follows from the above discussion that the usual threshold laws describing external electron emission[1] cannot be derived without including corrections describing, for example, deviations from translational invariance along the surface. The condition on the finite dimensions of packets necessary to satisfy the threshold laws is usually obeyed by a large margin. However, it may be disobeyed in the case of emission from ultrapure crystals in systems exhibiting the anomalous skin effect. We are of the opinion that the results obtained also explain why the maximum photoemission current flowing into an electrolyte (when the emitted electrons are stopped at distances of the order of tens of angstroms) corresponds to the short-range potential and not to the interaction in a final state of the Coulomb type, which gives rise to the Fowler law for the photoemission in vacuum.[1] At the same time it follows from Eq. (17) that we are justified in neglecting the image forces when calculating the properties of metal surfaces governed by electron functions belonging to the continuous spectrum. We must bear in mind that these properties are dominated by the electrons which "climb out" furthest from the metal and have energies close to the Fermi energy as well as a near-zero longitudinal momentum (with the maximum delocalization in the directions along the metal).

Note that the results obtained confirm that the long-wavelength approximation is reasonable even when applied to microscopic problems, provided only that the characteristic distances to the surface are greater than the atomic dimensions. The influence of spatial dispersion is important only at shorter distances, when a purely electrodynamic analysis generally ceases to be valid. It should be noted that retention of only the long-wavelength interactions may be justified also when the metal is close and even when considering the charges inside the metal, provided the formulation of the problem is altered. This change in formulation involves consideration not of the characteristics of the ground state, which in the classical limit are governed by variation of the action, but of fluctuation corrections due to a change in temperature or pressure, because then the range of validity of the above approach can be wider. An important feature is the possibility of writing down the interactions only with (spatially) slowly varying fields even when a metal has a sharp boundary. A quantitative explanation can be provided in a similar manner of the considerable fluctuation component in the limiting threshold behavior of photoemission.[23]

The author is grateful to M. I. Urbakh for valuable comments.

[1)] Care is necessary to avoid double allowance for the effects already included in the plasma value of ε_{ij}, which differs from δ_{ij} primarily because of the interactions with electrons in a medium.

[2)] This representation is clearly the reason for the selection of the projec-

tion operators in Eq. (2). We can easily show that $k_i\varepsilon(A_i - \mathrm{grad}_i a) = 0$ and, in particular, that $\mathrm{grad}\,\varepsilon(\omega,x_3)\mathrm{curl}\,\mathbf{n}a_s = \mathrm{grad}\,\mathrm{curl}\varepsilon\mathbf{n}a_s = 0$.

[3)] The relationship $\alpha_{(1)}(\omega) = -\alpha_{(2)}(\omega)$ follows from the equation $K_{(1)}\varepsilon^{-1}\partial f/\partial x_3 = 0$ if $K_{(2)}f = 0$. Moreover, the equality $\alpha_{(3)} = -\alpha_{(4)}$ corresponding to $\mathbf{k}_\parallel = 0$ is also generally valid.

[4)] Calculations of such states by a variational procedure, using the interaction only with surface plasmons, are reported in Ref. 24 where the ideas put forward earlier[25] are developed.

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Translated by A. Tybulewicz