Interaction of charges with surface polaritons

M. S. Tomaš* and M. Šunjić*
International Centre for Theoretical Physics, Trieste, Italy
(Received 30 January 1975)

A quantum-mechanical Hamiltonian of a nonrelativistic charge interacting with long-wavelength nonradiative surface polaritons in a semi-infinite solid is constructed. The theory is applied to determine the velocity and retardation corrections to the image potential, and the problem is solved exactly in the no-recoil (semiclassical) approximation, which is justified for particles of large momenta. The influence of retardation in inelastic energy spectra of electrons in low-energy-electron diffraction and reflected-high-energy-electron diffraction is considered in detail, and it is shown to be negligible for grazing-incidence electrons, though it generally changes the spectrum of outgoing electrons.

I. INTRODUCTION

Surface collective oscillations are a common feature of all finite bodies. They play a very important role in the building up of various macroscopic properties of solids, such as the image potential,[1–3] adhesion,[4] surface energy of metals,[5] etc. Charged-particle spectroscopy is a particularly useful tool for investigating the properties of these oscillations. A large amount of theoretical work has been concerned with energy-loss spectra of particles transmitted or reflected from variously shaped solids. The early theories were developed in the framework of classical electrodynamics. Ritchie[6] used Maxwell's equations in the quasistatic limit to compute the theoretical loss function of fast electrons transmitted through a metallic slab. Later, Hattori and Yamada[7] and Fujiwara and Ohtaka[8] computed the same quantity for a dielectric slab. Kröger,[9] Lucas and Kartheuser,[10] and Chase and Kliewer[11] used a complete set of Maxwell's equations, thus including retardation effects. Chase and Kliewer[11] showed that retardation corrections to the outgoing-electron-energy spectrum can be neglected for electrons transmitted through a thin dielectric slab. The same conclusion may not be true for thicker slabs.[11] When retardation effects are taken into account, there is a possibility of radiative losses through Cherenkov radiation[9,10] and transition radiation,[12] which contribute to the overall electron-energy loss.

The first quantum-mechanical theory of energy-loss spectra was developed by Lucas, Kartheuser, and Badro.[13] They used optical polarization eigenmodes for a dielectric slab, calculated in the quasistatic approximation by Fuchs and Kliewer,[14] and quantized the polarization field in the slab. The probe, a fast electron, was treated classically, and the problem was then solved exactly in first and second order. Probabilities of multiple-phonon (both bulk and surface) excitation were computed. The same approach was used by Šunjić and Lucas[15] for a metallic slab. They considered energy losses of electrons transmitted through the slab and reflected from the surface of a metal and, later, they studied energy losses in other experimental situations[16] (field-ion emission, ion scattering, etc.). In all these theories retardation effects were neglected. As a by-product of these calculations the conclusions emerged that the classical image potential for the charge outside a metal surface has its origin in the virtual excitation of surface plasmons, in agreement with the results of similar independent studies.[1–3] Following this approach the velocity corrections to the image potential and also recoil corrections coming from the quantum nature of the external charge were found.[17] Ritchie used the same approach to calculate retardation corrections in the case of a static external charge.[18] These are due to the excitations in the $k < k_p = \omega_p/c$ region of the wave vector and become important at larger distances $z > k_p^{-1}$. Ritchie also showed that at such distances the potential felt by a charge goes as $1/z^2$ rather than $1/z$, the latter corresponding to the result of classical electrodynamics.

It must be added that this kind of approach limits the validity of the results obtained to distances which are not too close to the surface where other quantum corrections become important; in other words, the long-wavelength or continuum approximation breaks down at small distances. A lot of work has recently been done on the problem of screening of the charge near the surface. There exist a number of papers in which approaches different from this were used. For further literature we refer the reader to the papers by Harris and Jones,[19] Mahan,[20] and Heinrichs.[21]

In this work we investigate the quantum-mechanical formulation of the interaction of charged particles with surface excitations, taking into account retardation effects. This formulation enables one to treat quantum mechanically various effects involving long-wavelength surface polaritons in dielectrics and metals. We confine ourselves to the case where the particle remains outside the solid and therefore couples only to surface excitations. In Sec. II we quantize the long-wavelength surface-polariton field in a semi-infinite dielectric solid using the point-ion model. The corresponding results for the metallic case are easily obtained by taking the limit when the TO frequency goes to zero and the LO phonon frequency becomes the plasma frequency of metallic electrons ($\omega_{\text{TO}} \to 0$, $\omega_{\text{LO}} \to \omega_p$). In Sec. III the interaction with external charged particles is derived. In Sec. IV the problem is solved in principle, using the nonperturbational approach in a general case, and applied to find an approximate solution for the case of a fast particle. The dynamical version of the image charge potential together with retardation corrections is derived in Sec. V. Finally, in Sec. VI we use our theory to compute energy losses of a particle reflected specularly from the solid, corresponding to the LEED (low-energy-electron diffraction) or RHEED (reflected-high-energy-electron diffraction) type of experiments. A detailed comparison with similar quasistatic theories[22] is also made.

II. SURFACE-POLARITON HAMILTONIAN

In order to introduce the notation, we shall briefly review the derivation of surface-polariton eigenmodes of an ionic crystal in the retarded case, following the procedure of Kliewer and Fuchs.[23] We consider an ionic solid with an ideal flat surface, occupying the $z<0$ half-space. Because of the translational invariance in the (x, y) plane we may look for the solutions of every physical quantity $\vec{F}(\vec{r}, t)$ in the form

$$\vec{F}(\vec{r}, t) = \vec{F}(\vec{k}, z)\, e^{i\vec{k}\cdot\vec{\rho} - i\omega t} , \tag{1}$$

where $\vec{r} = (\vec{\rho}, z)$ and $\vec{k}$ is a two-dimensional wave vector parallel to the surface. It is also convenient to introduce the coordinate system defined by the unit vectors

$$\hat{k} = \vec{k}/k, \quad \hat{z}, \quad \hat{n} = \hat{z}\times\hat{k} , \tag{2}$$

so that every vector field $\vec{F}(\vec{k}, z)$ can be written in the form

$$\vec{F}(\vec{k}, z) = F(\vec{k}, z)\hat{k} + F^{z}(\vec{k}, z)\hat{z} + F^{n}(\vec{k}, z)\hat{n} . \tag{3}$$

The first two components represent the P-polarized field, while the third component represents the S-polarized field. Maxwell's equations are now written in the Coulomb gauge, $-\nabla\vec{P}$ and $\partial\vec{P}/\partial t$ being the charge and current density, respectively. In the point-ion model, the polarization vector satisfies the equation of motion:

$$\frac{\partial^2\vec{P}}{\partial t^2} + \omega_T^2\vec{P} = \frac{\omega_p^2}{4\pi}\left(-\nabla\phi - \frac{1}{c}\dot{\vec{A}}\right) , \tag{4}$$

where ϕ and $\vec{A}$ are the scalar and vector potential, respectively, ω_T is the TO-phonon frequency, and ω_p is the ionic plasma frequency. Maxwell's equations solved with the usual boundary conditions for the electric and displacement fields at the surface, together with (1) and (4), give an integral equation for $\vec{P}$

$$\overleftrightarrow{\Lambda}\vec{P}(\vec{k}, z) = \int_{-\infty}^{0} dz'\, \overleftrightarrow{M}(z - z')\vec{P}(\vec{k}, z') , \tag{5}$$

where the tensor $\overleftrightarrow{\Lambda}$ is

$$\overleftrightarrow{\Lambda} = \frac{4\pi}{\omega_p^2}\begin{pmatrix} \omega_T^2 - \omega^2 & 0 & 0 \\ 0 & \omega_L^2 - \omega^2 & 0 \\ 0 & 0 & \omega_T^2 - \omega^2 \end{pmatrix} . \tag{6}$$

Here $\omega_L = (\omega_T^2 + \omega_p^2)^{1/2}$ is the LO-phonon frequency and ω is the polariton eigenfrequency to be determined. The kernel $\overleftrightarrow{M}(z - z')$ is Hermitian, and it can be written in the form

$$\overleftrightarrow{M}(\vec{k}, \omega;\, z - z') = 2\pi\alpha_0\, e^{-\alpha_0|z - z'|}\begin{pmatrix} \dfrac{k^2}{\alpha_0^2}\vec{\chi}' \otimes \vec{\chi}' & 0 \\ 0 & \dfrac{\omega^2}{\alpha_0^2 c^2} \end{pmatrix} , \tag{7}$$

where $\vec{\chi}' \otimes \vec{\chi}'$ is the tensor product of vectors

$$\vec{\chi}' = i(\alpha_0/k)\hat{k} - \operatorname{sgn}(z - z')\hat{z} \tag{8}$$

and α_0 is defined as

$$\alpha_0 = (k^2 - \omega^2/c^2)^{1/2} . \tag{9}$$

We shall restrict our considerations to the nonradiative region $\omega < kc$ (Fig. 1), where α_0 can be regarded as a real quantity, and the fields are exponentially damped outside the solid. The eigenvalue problem (5) splits naturally into two, one eigenvalue equation for each type of polarization. We are looking for the solutions inside the solid which are exponentially damped, and with eigenfrequencies which differ from ω_T and ω_L, there-

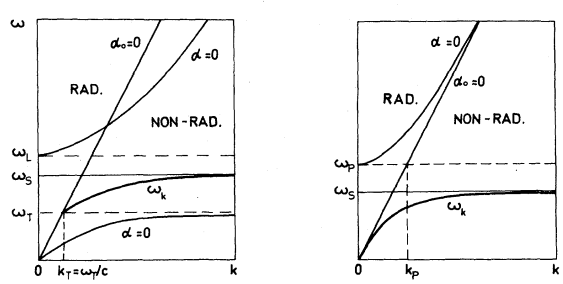

FIG. 1. Different regions of the polariton frequency spectrum for the case of a semi-infinite polar crystal (a) and a metal (b). Radiative and nonradiative regions are separated by the $\alpha_0 = 0$ ($\omega = kc$) line. We shall be interested in the nonradiative surface-polariton branch ω_k.

fore corresponding to surface waves. By differentiating Eq. (5) twice it is easy to show that the polarization vector $\vec{P}(k, z)$ for $z<0$ varies as $e^{\alpha z}$, where

$$\alpha = [k^2 - \epsilon(\omega)\omega^2/c^2]^{1/2} , \tag{10}$$

ϵ being the dielectric function. In our point-ion model (4) we have

$$\epsilon(\omega) = (\omega^2 - \omega_L^2)/(\omega^2 - \omega_T^2) . \tag{11}$$

Inserting the solution for $\vec{P}(\vec{k}, z)$ back into (5), one obtains the dispersion relations determined by the conditions for $\vec{P}$ to be a true solution. For S-polarized waves we find

$$1 = -\alpha/\alpha_0 , \tag{12}$$

which obviously cannot be satisfied, and we can only have a trivial solution $P^n(\vec{k}, z) = 0$.

For P-polarized modes we obtain the dispersion relation

$$k^2 = \alpha\alpha_0$$

or, in a more familiar form[24]

$$\epsilon(\omega) = -\alpha/\alpha_0 , \tag{13}$$

which determines the surface-polariton eigenfrequency $\omega = \omega_k$. The polarization eigenvector has the form

$$\vec{P}(\vec{k}, z) = N_k(i(\alpha/k)\hat{k} + \hat{z})\, e^{\alpha z} , \tag{14}$$

where N_k is some constant. We choose the normalization condition

$$\int_{-\infty}^{0} dz\, \vec{P}^*(\vec{k}, z)\cdot\vec{P}(\vec{k}, z) = 1 ,$$

which gives

$$N_k = k[2/(\alpha+\alpha_0)]^{1/2} . \tag{15}$$

Knowing the polarization eigenvector, we can compute the corresponding scalar potential

$$\phi(\vec{k}, z) = -2\pi\int_{-\infty}^{0} dz'\, e^{-k|z-z'|}\,\vec{\chi}\cdot\vec{P}(\vec{k}, z') \tag{16}$$

and the vector potential

$$\vec{A}(\vec{k}, z) = \frac{ic}{\omega_k}\, 2\pi k\int_{-\infty}^{0} dz'\Big(e^{-k|z-z'|}\,\vec{\chi}\vec{\chi}\cdot\vec{P}(\vec{k}, z) - \frac{k}{\alpha_0}e^{-\alpha_0|z-z'|}\,\vec{\chi}'\vec{\chi}'\cdot\vec{P}(\vec{k}, z')\Big) , \tag{17}$$

where

$$\vec{\chi} = i\hat{k} - \mathrm{sgn}(z-z')\hat{z} .$$

Performing the integration in (16) and (17), we obtain

$$\phi(\vec{k}, z) = N_k(2\pi/k)\, e^{-k|z|} , \tag{18}$$

$$\vec{A}(\vec{k}, z) = N_k 2\pi i\,\frac{c}{\omega_k}\left[\frac{2k}{\alpha+\alpha_0}\Big(i\hat{k} - \mathrm{sgn}\, z\cdot\frac{k}{\bar{\alpha}}\hat{z}\Big)e^{-\bar{\alpha}|z|} - (i\hat{k} - \mathrm{sgn}\, z\cdot\hat{z})\, e^{-k|z|}\right] , \tag{19}$$

where

$$\bar{\alpha} = \begin{cases}\alpha_0 & \text{for } z>0\\ \alpha & \text{for } z<0 .\end{cases} \tag{20}$$

Now we can perform the quantization. The total energy of the system is

$$H_0 = \int d^3r\left[\frac{1}{8\pi}\Big(\frac{1}{c^2}\dot{\vec{A}}^2 + (\nabla\times\vec{A})^2 - (\nabla\phi)^2\Big) + \frac{2\pi}{\omega_p^2}(\dot{\vec{P}}^2 + \omega_T^2\vec{P}^2) + \vec{P}\cdot\nabla\phi\right] . \tag{21}$$

Because of the symmetry properties

$$\phi(\vec{k}, z) = \phi^*(-\vec{k}, z),\quad \vec{P}(\vec{k}, z) = \vec{P}^*(-\vec{k}, z),$$
$$\vec{A}(\vec{k}, z) = -\vec{A}^*(-\vec{k}, z) \tag{22}$$

and the reality conditions for the fields, we expand them in the following way:

$$\phi(\vec{r}, t) = \sum_{\vec{k}}\phi(\vec{k}, z)\, e^{i\vec{k}\cdot\vec{\rho}}D_k(a_{\vec{k}} + a^\dagger_{-\vec{k}}) ,$$
$$\vec{P}(\vec{r}, t) = \sum_{\vec{k}}\vec{P}(\vec{k}, z)\, e^{i\vec{k}\cdot\vec{\rho}}D_k(a_{\vec{k}} + a^\dagger_{-\vec{k}}) , \tag{23}$$

$$\vec{A}(\vec{r}, t) = \sum_{\vec{k}}\vec{A}(\vec{k}, z)\, e^{i\vec{k}\cdot\vec{\rho}}D_k(a_{\vec{k}} - a^\dagger_{-\vec{k}}) . \tag{24}$$

Here a and $a^\dagger$ are the usual annihilation and creation operators for surface-polariton modes, respectively, obeying boson commutation relations. The constants D must be determined in such a way that the Hamiltonian (21), after inserting the quantized form of the fields (23, 24), takes the standard form

$$H_p = \sum_{\vec{k}}\hbar\omega_k(a^\dagger_{\vec{k}}a_{\vec{k}} + \tfrac{1}{2}) . \tag{25}$$

This is achieved if we take

$$D_k = \left(\frac{\hbar\omega_p^2}{8\pi A\,\omega_k}\right)^{1/2}\left(1 + \frac{\omega_p^2}{\omega_k^2}\,\frac{\alpha(\alpha-\alpha_0)}{(\alpha+\alpha_0)^2}\right)^{-1/2} \equiv \left(\frac{\hbar\omega_k}{8\pi A}\right)^{1/2} d_k , \tag{26}$$

where A is the unit area of the solid surface. In all these expressions we have assumed that the quantities α_0, α, and ω_k are single-valued functions of k, given by (9), (10) and (13), respectively.

The main results of this section, Eqs. (23)–(26), are in agreement with the recent result of Nkoma, Loudon, and Tilley,[25] which has been obtained by using the correspondence principle.

A. Extension to a metallic surface

Although this derivation of surface-polariton eigenmodes and the Hamiltonian (25) was performed for a simple model of a semi-infinite ionic crystal, the procedure is valid in a more general case, because it is obvious that the results depend only on the dielectric constant $\epsilon(\omega)$ of the semi-infinite medium. Therefore, by making a specific choice of $\epsilon(\omega)$ we can describe other types of long-wavelength surface oscillations, e.g., surface polaritons at a metallic surface corresponding to coupled plasmon-photon modes.

The metallic case can be obtained from the preceding considerations if we realize that the frequency of shear modes in the electron plasma vanishes, and formally substitute in all expressions

$$\omega_T \to 0, \quad \omega_L \to \omega_p ,$$

where ω_p is now the plasma frequency of metallic electrons. This gives the corresponding dielectric function

$$\epsilon_M(\omega) = 1 - \omega_p^2/\omega^2 . \tag{27}$$

The dispersion relation (13) for surface polaritons now takes the explicit form[26]

$$\omega_k = \frac{\omega_p}{\sqrt{2}} \left\{ 1 + 2\left(\frac{k}{k_p}\right)^2 - \left[1 + 4\left(\frac{k}{k_p}\right)^4\right]^{1/2} \right\}^{1/2} , \tag{28}$$

where $k_p = \omega_p/c$. Also, from (9), (10), and (28) we obtain

$$\alpha_0 = \frac{k_p}{\sqrt{2}} \left\{ \left[1 + 4\left(\frac{k}{k_p}\right)^4\right]^{1/2} - 1 \right\}^{1/2} ,$$
$$\alpha = \frac{k_p}{\sqrt{2}} \left\{ \left[1 + 4\left(\frac{k}{k_p}\right)^4\right]^{1/2} + 1 \right\}^{1/2} . \tag{29}$$

III. INTERACTION OF CHARGED PARTICLES WITH SURFACE POLARITONS

The Hamiltonian of a nonrelativistic particle with mass m and charge e in an external field V_{solid}, interacting with the field of surface polaritons, is

$$(1/2m)[\vec{p} - (e/c)\vec{A}(\vec{r}, t)]^2 + e\phi(\vec{r}, t) + V_{\text{solid}}(\vec{r}) , \tag{30}$$

where ϕ and $\vec{A}$ are given by (18) and (19), $\vec{r} = (\vec{\rho}, z)$ and $\vec{p} = (\vec{p}_\parallel, p_\perp)$ are the position and momentum operators of the charge, respectively. If we neglect the quadratic term in $\vec{A}$, which gives rise to the polariton-polariton interaction, the Hamiltonian (30) becomes

$$p^2/2m - (e/mc)\vec{p} \cdot \vec{A}(\vec{r}, t) + e\phi(\vec{r}, t) + V_{\text{solid}}(\vec{r}) . \tag{31}$$

Now we insert the quantized expressions (23) and (24) for the fields of surface polaritons and obtain the total Hamiltonian of the system

$$H = H_c + H_p + H_{\text{int}} ,$$
$$H_c = p^2/2m + V_{\text{solid}} , \tag{32}$$
$$H_{\text{int}} = \sum_{\vec{k}} [a_{\vec{k}} \Gamma(\vec{k}, \vec{p}, z) e^{i\vec{k}\cdot\vec{\rho}} + a_{\vec{k}}^\dagger \Gamma^*(\vec{k}, \vec{p}, z) e^{-i\vec{k}\cdot\vec{\rho}}] ,$$

and the coupling functions Γ's are given by

$$\Gamma(\vec{k}, \vec{p}, z) = eD_k[\phi(\vec{k}, z) - (1/mc)\vec{p} \cdot \vec{A}(\vec{k}, z)] . \tag{33}$$

Using (18), (19) and (26), we can find the explicit form of the coupling functions

$$\Gamma(\vec{k}, \vec{p}, z) = C_k \left[e^{-k|z|} + \frac{\vec{k} \cdot \vec{p}_\parallel}{m\omega_k} \left(\frac{2k}{\alpha + \alpha_0} e^{-\bar{\alpha}|z|} - e^{-k|z|} \right) + i \,\text{sgn}\, z \frac{kp_\perp}{m\omega_k} \left(\frac{2k^2}{\bar{\alpha}(\alpha + \alpha_0)} e^{-\bar{\alpha}|z|} - e^{-k|z|} \right) \right] , \tag{34}$$

where

$$C_k = (2\pi e/k) N_k D_k . \tag{35}$$

It is easy to verify that for $c \to \infty$ the Hamiltonian (32) reduces to the standard Hamiltonian in the nonretarded case.

IV. NONPERTURBATIVE SOLUTION OF THE PARTICLE-FIELD PROBLEM

The Hamiltonian (32) is applicable to a number of problems where charged particles interact with the surface-polariton field. It cannot be solved generally, and appropriate approximate methods should be sought.

We start from the Hamiltonian (32). In the interaction representation the wave function of the system develops in time according to

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle ,$$

where

$$i \frac{\partial}{\partial t} U(t, t_0) = V(t) U(t, t_0)$$

and

$$V(t) = e^{i(H_c + H_p)t} H_{\text{int}} e^{-i(H_c + H_p)t} . \tag{36}$$

From the knowledge of $U(t, t_0)$ we can find the spectrum of surface polaritons excited by an external charge between times t_0 and t,

$$S(\omega; t, t_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} S(\tau) , \tag{37}$$

$$S(\tau) = \langle \psi(t_0) | W^\dagger(\tau) W(0) | \psi(t_0) \rangle , \tag{38}$$

$$W(\tau) = e^{iH_p\tau} U(t, t_0) e^{-iH_p\tau} . \tag{39}$$

The usual Dyson solution for the evolution operator $U(t, t_0)$ in terms of a power series in V is not convenient in our case, since we want to obtain a nonperturbative result, and analyze solutions which reduce to the results of models[15] which are exactly soluble. However, in many cases, e.g., in the scattering of fast electrons[15] or heavy ions,[1] on in core-hole relaxation processes,[27] we can make the so-called semiclassical approximation, neglecting the quantum-mechanical character of charged particles. In this way it is possible to find an exact solution for U and W, and the solution for the correlation function (38) in the form[15]

$$S(\tau)=\exp\left(\sum_{\vec{k}}(e^{-i\omega_k\tau}-1)\,|I_{\vec{k}}(t,t_0)|^2\right), \tag{40}$$

where

$$I_{\vec{k}}(t,t_0)=-\frac{i}{\hbar}\int_{t_0}^{t}\Gamma^*(\vec{k},z_e(\tau))\,e^{i\omega_k\tau-i\vec{k}\cdot\vec{\rho}_e(\tau)}\ . \tag{41}$$

At the same time the wave function describing the surface polariton system becomes

$$|\psi(t)\rangle=\prod_{\vec{k}}|\psi_{\vec{k}}(t)\rangle\ . \tag{42}$$

Here each $|\psi_{\vec{k}}(t)\rangle$ represents a coherent state of the k-polariton field, with the amplitude $I_{\vec{k}}(t,t_0)$

$$|\psi_{\vec{k}}(t)\rangle=e^{-|I_{\vec{k}}|^2/2}\sum_{n_{\vec{k}}}\frac{|I_{\vec{k}}(t,t_0)|^2}{(n_{\vec{k}}!)^{1/2}}\,|n_{\vec{k}}\rangle\ , \tag{43}$$

where $|n_{\vec{k}}\rangle$ contains $n_{\vec{k}}$ excited surface polaritons.

V. RETARDATION CORRECTIONS TO THE DYNAMICAL IMAGE POTENTIAL

Let us now apply the results of the preceding sections to obtain the effective potential acting on a charged particle in the vicinity of a metallic surface. This potential is due to the interaction of the charge with surface polaritons. We consider a particle moving from infinity ($z_e=\infty$ at $t=-\infty$) perpendicularly towards the surface, with the normal velocity $v_\perp=-v$. At time t (taking the origin of time when the particle reaches the surface) the polariton field will be coherently displaced from its ground state, which leads to an energy shift corresponding to the image potential of classical electrodynamics

$$W(t)=\langle\psi(t)|H|\psi(t)\rangle\ . \tag{44}$$

From (32) and (43) we find

$$W(t)=\sum_{\vec{k}}\{\hbar\omega_k|I_{\vec{k}}(t,-\infty)|^2 + 2\mathrm{Re}[\Gamma(\vec{k},z_e(t)I_{\vec{k}}(t,-\infty)\,e^{-i\omega_k t}]\}\ . \tag{45}$$

Inserting (34) and (42), we find the effective potential for the particle at a distance $z_e=-vt>0$ from the surface

$$W(z_e)=\frac{e^2}{2}\int_0^{k_c}\frac{k\,dk}{\alpha+\alpha_0}\,d_k^2\left[\frac{7x^2-1}{1-x^2}\,e^{-2kz_e} + \left(\frac{2k^2}{\alpha_0(\alpha+\alpha_0)}\right)^2\frac{3x^2}{1+y^2}\,e^{-2\alpha_0 z_e} - \frac{4k^2x^2}{\alpha_0(\alpha+\alpha_0)}\,\frac{5+x^2+2y^2+2xy}{(1+x^2)(1+y^2)}\,e^{-(k+\alpha_0)z_e}\right], \tag{46}$$

where $x=kv/\omega_k$, $y=\alpha_0 v/\omega_k$, and d_k is defined in (26).

This result represents a generalization of the dynamical image potential which includes retardation corrections. It is instructive to evaluate (46) in two limiting cases.

(i) $k_c^{-1}<z_e\ll k_p^{-1}$: Here the main contribution to the integral in (46) comes from the large values of k, where retardation effects are unimportant, and $\omega_k\simeq\omega_s$

$$W(z_e)\simeq-\frac{e^2}{2}\int_0^{k_c}dk\,\frac{e^{-2kz}}{1+(kv/\omega_s)^2}\ . \tag{47}$$

This is the quasistatic result obtained previously.[17,28,29]

(ii) $z_e\gg k_p^{-1}$: Here the main contribution comes from the small-k region. The evaluation of the leading terms in (46), letting $k_c\gg(z_e^{-1},k_p)$, gives

$$W(z_e)\simeq\frac{e^2}{2}\,k_p\left[\frac{3\beta^2}{k_p z_e}-\frac{1}{(k_p z_e)^2}\left(\frac{1}{4}+\frac{18\beta^2+4\beta^4}{1+\beta^2}\right)+\cdots\right], \tag{48}$$

where $\beta=v/c$. For $\beta\approx 0$ we obtain Ritchie's result[18] for the static charge, which shows the characteristic z_e^{-2} deviation from the classical result. The other terms in (48) represent dynamical corrections to his theory because of the finite particle velocity, and for most cases they are small and can be neglected. Fig. 2 shows numerical plots

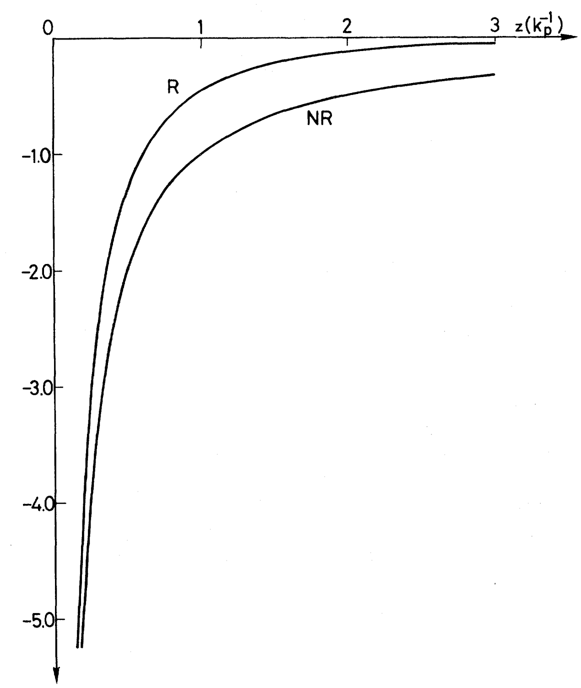

FIG. 2. Retarded (R) and nonretarded (NR) image potential (in units of $\frac{1}{4}e^2k_p$) for the case of a static charge.

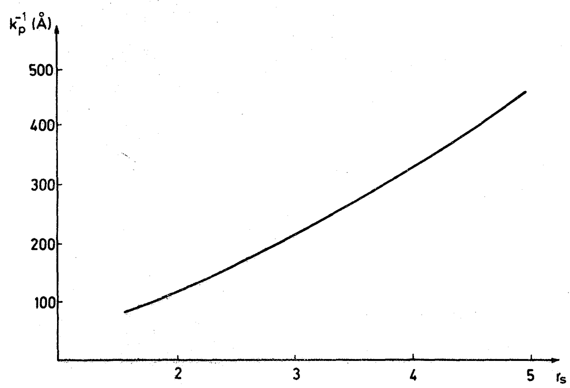

FIG. 3. Dependence of $k_p^{-1} = c/\omega_p$ on the dimensionless electron-density parameter r_s in the region of metallic densities, calculated in the free-electron model.

of (46) for the retarded and nonretarded case, respectively. The two curves start to split appreciably at rather small distances $z_e \simeq \frac{1}{10} k_p^{-1}$, which are several tens of angstroms for most metals, as can be seen from Fig. 3. At such distances other (quantum) effects, which have not been taken into account in our theory (exchange, particle-hole excitations), are still negligible, although they gradually become important as we further approach the surface ($z \lesssim k_c^{-1}$). Velocity corrections were also computed, but they were found to be small for electron energies up to 1 keV, and they could hardly be distinguished from the static curve on the same scale.

VI. SURFACE-POLARITON EXCITATION IN RHEED AND LEED

The approximate treatment of the particle-solid interaction, described in Sec. IV, has been employed in several theories of energy losses of fast particles transmitted or reflected from the crystal.[13,15,16] On the other hand, as pointed out by Economou and Ngai,[30] there have been no attempts, except a few purely classical approaches,[9–11] to investigate what kind of modifications retardation effects might introduce in the inelastic spectra observed. These effects can be naturally taken into account in the framework of the quantum-mechanical approach developed in this paper.

As an example we shall compute the energy loss of charged particles specularly reflected from the surface of the metal. This theory is applicable to the analysis of RHEED and high-energy LEED experiments, where our assumption that the impinging particle is so energetic that its recoil in the polariton-emission process can be neglected is very well satisfied.

The appropriate electron path for the case of specular reflection is

$$\vec{\rho}_e(t) = \vec{v}_\parallel t, \quad z_e(t) = v_\perp |t| , \tag{49}$$

where the origin of time was taken at the moment of reflection.

From the general results (Sec. III) we can easily find the probability $P(\omega)$ that the particle loses an amount of energy $\hbar\omega$ in the scattering process. It is given by the probability that the particle excites the solid, which is initially in its ground state with energy E_0, into a state $|\psi(t)\rangle$ which at $t \to \infty$ contains any number of excited surface polaritons with the total energy $\hbar\omega$ above E_0

$$P(\omega) = \lim_{t\to\infty} \sum_f |\langle\psi(t)|f\rangle|^2 \delta((E_f - E_0)/\hbar - \omega) .$$

Obviously, this must be equal to the Fourier transform of the correlation function $S(t)$ and is of the form (37)

$$P(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} e^{[Q(t)-Q(0)]} ,$$
$$Q(t) = \sum_{\vec{k}} |I_{\vec{k}}(+\infty, -\infty)|^2 e^{-i\omega_k t} . \tag{50}$$

$P_0 = e^{-Q(0)}$ is the normalization factor such that $\int P(\omega)\, d\omega = 1$, and it gives the strength of the no-loss line in the spectrum. Inserting (34) and (49) into (41), we find

$$Q(t) = \frac{8}{\pi}\frac{e^2}{\hbar}\int_0^{k_c} dk \frac{e^{-i\omega_k t}}{\omega_k}\frac{k^3}{(\alpha+\alpha_0)^3} d_k^2 F(k, v_\perp, v_\parallel) ,$$
$$F(k, v_\perp, v_\parallel) = \int_0^{\pi} d\phi \left(\frac{x[y - \gamma^2(y - \cos\phi)]}{x^2 + (y - \cos\phi)^2}\right)^2 , \tag{51}$$

where

$$x = \alpha_0 v_\perp / k v_\parallel, \quad y = \omega_k / k v_\parallel, \quad \gamma^2 = 1 - k^2/\alpha_0^2 ,$$

and γ vanishes in the quasistatic limit. The quantity $F(k, v_\perp, v_\parallel)$ depends strongly on the geometry of the scattering experiment, and in fact, it determines the whole spectrum. Performing the integration, we obtain

$$F(k, v_\perp, v_\parallel) = \frac{\pi}{2x}\,\mathrm{Re}\left[\frac{(y - i\gamma x)^2}{(1 - y^2 + x^2 + 2ixy)^{3/2}} \times \left(x(x+iy) + (1 - y^2 + x^2 + 2ixy)\,\frac{y + i\gamma x}{y - i\gamma x}\right)\right] . \tag{52}$$

A. Grazing incidence

In RHEED experiments electrons are incident onto the surface at a grazing angle, so that $v_\perp \ll v_\parallel$. In this limit we obtain for the leading term

$$F(k, v_\perp, v_\parallel) \simeq \tfrac{1}{2}\pi (y^2/x)(1 - y^2)^{-1/2} , \tag{53}$$

where

$$y = \omega_k / k v_\parallel < 1 \tag{54}$$

must be satisfied. From (54) we see that electrons incident at grazing angles will predominantly excite surface polaritons whenever their (parallel) velocity is larger than the polariton phase velocity, $v_{\parallel} > \omega_k/k$. In the region $v_{\parallel} < \omega_k/k$ we find

$$F(k, v_{\perp}, v_{\parallel}) \sim x^2 ,$$

and its contribution can be completely neglected in comparison with (53). In the case of metals we see from (28) that the condition $y<1$ can be satisfied for $k \geq k_0$, where

$$k_0 = k_p[(1-\beta_{\parallel}^2)/(2\beta_{\parallel}^2 - \beta_{\parallel}^4)]^{1/2} .$$

k_0 is clearly smaller than the cut-off wave vector $k_c \sim \omega_p/v_F$ whenever $v_{\parallel}$ exceeds the Fermi velocity v_F. However, in the region $k \geq k_0$, ω_k is very close to its nonretarded value ω_s, namely,

$$\omega_k \simeq \omega_s(1 - \tfrac{1}{4}\beta_{\parallel}^2) .$$

Therefore, one can conclude that for grazing-incidence electrons, as in RHEED, the main contribution to $Q(t)$ will come from the region in the k space where retardation effects become unimportant. Then one can use the quasistatic approximation, which gives

$$Q(t) = \frac{e^2}{\hbar v_{\perp}} \tan^{-1}\left[\left(\frac{k_c v_{\parallel}}{\omega_s}\right)^2 - 1\right]^{1/2} e^{-i\omega_s t} . \quad (55)$$

In the case $k_c v_{\parallel} \gg \omega_s$ we recover the result obtained by Lucas and Šunjić[22]

$$Q(t) \simeq X e^{-i\omega_s t}, \quad X = (\pi e^2/4\hbar v_{\perp})(\omega_p^2/\omega_s^2) . \quad (56)$$

The spectrum given by (50) and (56) consists of a series of δ-like peaks at energies which are the multiples of $\hbar\omega_s$, with the strength J_n of the nth peak given by the preexponential factor in (56)

$$J_n = e^{-X}(X^n/n!) .$$

One could easily take into account the surface-polariton damping phenomenologically, introducing a small imaginary part in the frequency ω_s in (56), and this would yield more realistic Lorentzian loss peaks in $P(\omega)$.

The conclusion of this short analysis is, therefore, that retardation effects can, to a very good approximation, be neglected in the theory of energy loss of grazing-incidence reflected electrons, so that the nonretarded theory of Lucas and Šunjić[22] remains quantitatively valid.

B. Normal incidence

The other limiting case—electrons at nearly normal incidence (which is applicable to LEED experiments)—shows a slightly different picture. Taking the limit $v_{\perp}/v_{\parallel} \gg 1$ in (52) (keeping $x/y = \alpha_0 v_{\perp}/\omega_k$ constant), we find

$$F(k, v_{\perp}, v_{\parallel}) \simeq \pi(1-\gamma^2)(x/y)^2[1+(x/y)^2]^{-2} , \quad (57)$$

which does not depend on $v_{\parallel}$ and therefore the cut-off condition (54) is not effective here. Inserting (57) into (51), we obtain

$$Q(t) = 8\,\frac{e^2}{\hbar}\int_0^{k_c} dk\,\frac{e^{-i\omega_k t}}{\omega_k}\,\frac{k^3}{(\alpha+\alpha_0)^3} \times d_k^2\left(\frac{k}{\alpha 0}\right)^4\left(\frac{\alpha_0 v_{\perp}/\omega_k}{1+(\alpha_0 v_{\perp}/\omega_k)^2}\right)^2 . \quad (58)$$

Converting (58) into an integral over ω and using (50), we obtain

$$Q(t) - Q(0) = 8\frac{e^2}{\hbar c}\beta_{\perp}^2\int_0^{\omega_c} d\omega'\,(e^{-i\omega' t} - 1)\,\frac{(-1-\epsilon)^{-1/2}}{\omega'} \times \frac{-\epsilon^2}{(1-\epsilon)(1+\epsilon-\beta_{\perp}^2)^2}\left[\frac{\epsilon(\epsilon+1)+\frac{1}{2}\omega'(d\epsilon/d\omega')}{\epsilon(\epsilon+1)+\omega'^2(1-\epsilon)^2/\omega_p^2}\right] , \quad (59)$$

where $\beta_{\perp} = v_{\perp}/c$ and $\omega_c = \omega_{k_c}$.

If we use the dielectric function (11) (i.e., point-ion model) or (27), the expression in the square brackets becomes equal to 1.

The spectrum given by (50) and (59) generally consists of the δ line at zero frequency and the positive-frequency side band. Its actual shape is determined by the behavior of the second factor in the integrand in (59) for small frequencies $\omega' \to 0$.[31] In our case, (e.g., for metals) this function approaches a constant value when ω' goes to zero. Therefore, the no-loss line has the finite strength, while the side band starts from a nonzero value for ω approaching zero.[31] This is quite different from the result in the quasistatic limit,[22] where we have δ peaks spaced at multiples of surface plasmon frequency ω_s. Obviously, the difference comes from the retardation which causes the dispersion of the surface plasmon frequency and, therefore, all frequencies starting from zero to ω_c contribute in the spectrum.

The strength of the no-loss line is given by $e^{-Q(0)}$, where

$$Q(0) \simeq \tfrac{1}{2}\pi(e^2/\hbar v_{\perp})[1 + 3\beta_{\perp}^2 + O(\beta_{\perp}^3)] . \quad (60)$$

The first term represents the quasistatic result and others are corrections due to retardation.

Separate contributions of different-order processes are obtained by expanding the exponential in (50)

$$P(\omega)/P_0 = \delta(\omega) + P_1(\omega) + P_2(\omega) + \cdots ,$$

where P_n gives the probability of emission of n surface polaritons. For the first-order process we obtain

$$P_1(\omega) = 8\,\frac{e^2}{\hbar c}\beta_{\perp}^2\frac{1}{\omega}(-1-\epsilon)^{-1/2}\,\frac{-\epsilon^3}{(1-\epsilon)(1+\epsilon-\beta_{\perp}^2)^2} \quad \text{for } \omega \leq \omega_c , \quad (61)$$

while the contributions of higher-order processes are expressed as convolutions of $P_1(\omega)$. We can easily see that

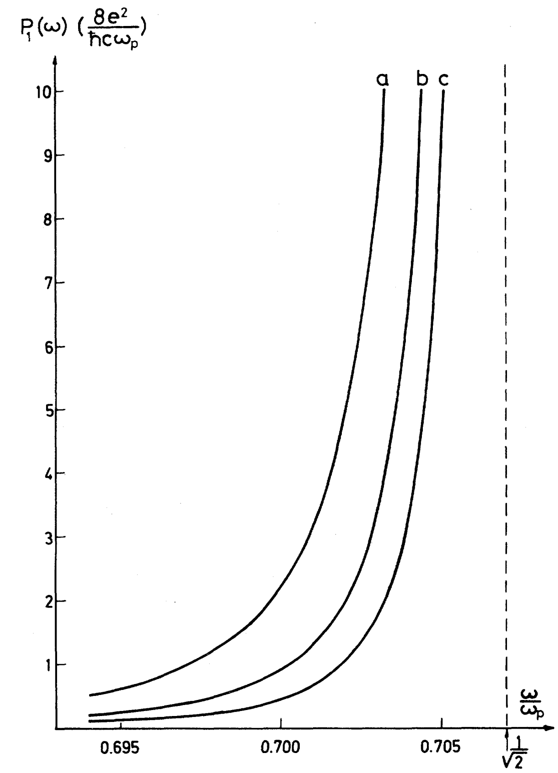

FIG. 4. Theoretical loss spectrum of specularly reflected electrons at normal incidence, as predicted by Eq. (61). The electron velocity v is (a) $\sqrt{10}\times 10^{-2}c$, (b) $2\times 10^{-2}c$, and (c) $\sqrt{2}\times 10^{-2}c$, corresponding to energies of approximately 250, 100, and 50 eV.

$$P_1(0) = 8(e^2/\hbar c)(\beta_\perp^2/\omega_p) .$$

However, in a typical LEED experiment, to which this theory applies, the electron energy is of the order of, say, 100 eV. For this energy, $\beta_\perp \simeq 2\times 10^{-2}$ and the spectrum given by (61) becomes very sharply peaked around the limiting surface-polariton frequency ω_s (Fig. 4). Indeed, for such low velocities we can use

$$\frac{1}{(-1-\epsilon)^{1/2}}\,\frac{\beta_\perp^2}{(1+\epsilon-\beta_\perp^2)^2} \simeq \frac{\pi}{\beta_\perp}\,\frac{\delta(\omega-\omega_s)}{|d\epsilon/d\omega|\,\omega_s} . \qquad (62)$$

After inserting (62) into (59), one exactly obtains the quasistatic result of Lucas and Šunjić[22] for $k_c = \infty$.

As we see, in both cases, i.e., in RHEED and nearly normal LEED experiments, retardation corrections to the spectrum of the outgoing electron are so small that they can, to a very good approximation, be neglected. For general incidence one should use (52) to compute the spectrum. However, partly because of the cutoff condition (54) and partly because retardation corrections go as $(v/c)^2$, one can hardly expect any appreciable change of the quasistatic result.

VII. CONCLUSIONS

In this paper we have derived the Hamiltonian formulation of the surface-polariton field and its coupling to the electromagnetic field of the moving charged particle. The method can easily be extended to the description of the surface-polariton field in other geometries, e.g., thin film, which makes possible the quantum-mechanical approach to the theory of energy losses of electrons transmitted through thin films.[32] To our knowledge, only classical theories have been developed in this field.

We have also presented a nonperturbative approach to the problem of particle-field interaction, thus avoiding the use of many-body perturbation theory, which is particularly inconvenient in translationally noninvariant problems involving surfaces. This theory was then applied to analyze the influence of retardation on the dynamical screening of charges at surfaces where it appreciably reduces the screening, even at distances which are physically interesting, e.g., in physisorption or tunneling problems. The calculation of energy losses in reflection experiments has shown that retardation corrections are of the order $(v/c)^2$ and can usually be neglected. However, it is not clear whether the same conclusion applies to other situations, e.g., transmission experiments, which would require further studies.[32]

While we expect the neglect of spatial dispersion, i.e., the use of the local dielectric constant, to be a very good approximation in the long-wavelength region where retardation corrections are important, we may still speculate about the effect of nonlocality and their inclusion in the framework of our model. We must stress that an exact analytical solution of the eigenvalue problem is impossible in this case and we should either resort to the complicated numerical methods, where the main advantage of our theoretical model is lost, or try some approximate methods. However, these extensions are outside of the scope of the present work, especially as we are concerned exclusively with charged particle surface-polariton scattering in experimental situations such as LEED or RHEED.

ACKNOWLEDGMENTS

We are grateful to Professor Abdus Salam, the IAEA, and UNESCO for kind hospitality extended to us during our stay at the International Center for Theoretical Physics, Trieste.

*Permanent address: Institute "Rudjer Bošković," Zagreb, Croatia, Yugoslavia.

[1]A. A. Lucas, Phys. Rev. B 4, 2939 (1971).
[2]P. J. Feibelman, Surf. Sci. 27, 438 (1971).
[3]J. C. Inkson, Surf. Sci. 28, 69 (1971).
[4]N. G. van Kampen, B. R. A. Nijboer, and K. Schram, Phys. Lett. A 26, 307 (1968).
[5]J. Schmit and A. A. Lucas, Solid State Commun. 11, 415 (1972).
[6]R. H. Ritchie, Phys. Rev. 106, 874 (1957).
[7]M. Hattori and K. Yamada, J. Phys. Soc. Jpn. 18, 200 (1963).
[8]T. Fujiwara and K. Ohtaka, J. Phys. Soc. Jpn. 24, 1326 (1968).
[9]E. Kröger, Z. Phys. 216, 115 (1968).
[10]A. A. Lucas and E. Kartheuser, Phys. Rev. B 1, 3588 (1970).
[11]J. B. Chase and K. L. Kliewer, Phys. Rev. B 2, 4389 (1970).
[12]I. M. Frank and V. I. Ginzburg, J. Phys. (USSR) 9, 353 (1945).
[13]A. A. Lucas, E. Kartheuser, and R. G. Badro, Phys. Rev. B 2, 2488 (1970).
[14]R. Fuchs and K. L. Kliewer, Phys. Rev. 140, 2076 (1965).
[15]M. Šunjić and A. A. Lucas, Phys. Rev. B 3, 719 (1971).
[16]M. Šunjić and A. A. Lucas, in *Electrons in Crystalline Solids* (IAEA, Vienna, 1973), p. 733.
[17]M. Šunjić, G. Toulouse, and A. A. Lucas, Solid State Commun. 11, 1629 (1972).
[18]R. H. Ritchie, Phys. Lett. A 38, 189 (1972).
[19]J. Harris and R. O. Jones, J. Phys. C 6, 3585 (1973).
[20]G. D. Mahan, in *Collective Properties of Physical Systems*, edited by B. and S. Lundqvist (Academic, New York, 1973), p. 164.
[21]J. Heinrichs, in *Elementary Excitations in Solids, Molecules and Atoms*, NATO Advanced Study Institutes Series B (1974) (unpublished).
[22]A. A. Lucas and M. Šunjić, Prog. Surf. Sci. 2, 75 (1972).
[23]K. L. Kliewer and R. Fuchs, Phys. Rev. 144, 495 (1966).
[24]R. H. Ritchie and H. B. Eldridge, Phys. Rev. 126, 1935 (1962).
[25]J. Nkoma, R. Loudon, and D. R. Tilley, J. Phys. C 7, 3547 (1974).
[26]See, e.g., R. A. Ferrell, Phys. Rev. 111, 1214 (1958).
[27]See, e.g., D. C. Langreth, Phys. Rev. B 1, 471 (1970).
[28]R. Ray and G. D. Mahan, Phys. Lett. A 42, 301 (1972).
[29]J. Heinrichs, Phys. Rev. B 8, 1346 (1973).
[30]E. N. Economou and K. L. Ngai, Adv. Chem. Phys. 27, 256 (1974).
[31]E. Müller-Hartmann, T. V. Ramakrishnan, and G. Toulouse, Phys. Rev. B 3, 1102 (1971).
[32]M. S. Tomaš, M. Šunjić, and Z. Lenac (unpublished).