Final-state interactions in photoemission: Energy loss by the exiting electron

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(Received 23 May 2000)

In photoemission, the excited electron may lose energy when it is in the vacuum, on its outgoing trajectory. It may couple to excitations in the substrate (surface plasmons, for example) via the long-ranged Coulomb interaction, as is well known from electron energy-loss spectroscopy. Joynt has argued that such losses can be severe for poor conductors, with the consequence that their inclusion is essential for the interpretation of their photoemission spectra. We show that the losses considered by Joynt have their origin simply in the work done by the image force experienced by the outgoing electron. This then just shifts the kinetic energy of all photoemitted electrons downward by roughly the same amount, save for a correction with origin in the velocity dependence of the effective image force.

I. INTRODUCTION

It is widely recognized that photoemission spectroscopy is a most powerful means of probing the occupied electronic states of diverse materials. To interpret the data, it is commonly assumed that the photoemitted electron is a simple free electron, diffracted as it passes through the crystal surface, and whose kinetic energy at the detector differs from that within the crystal by a shift with origin in the inner potential.

When the kinetic energy of the photoemitted electron is not large, as in ultraviolet photoemission, the simple picture just described may require correction from interactions the photoelectron experiences when it is in the final state. These may range from band-structure effects, to self-energy corrections of many-body origin.

In a recent paper,[1] Joynt argued there are final-state effects as well, when the photoelectron is in the vacuum above the crystal, on its way to the detector. It may lose energy on this portion of its trajectory by creating excitations in the substrate via long-ranged Coulomb interactions. Indeed, we have known for many years from electron energy-loss spectroscopy [2](EELS) that electrons in the energy range of interest to Joynt can couple quite strongly to excitations in the substrate (surface plasmons, particle-hole pairs, surface optical phonons, etc.) while in the vacuum above the crystal, on the incoming and outgoing leg.

Joynt argues that in the particular case of poor conductors, this coupling can be very strong, with the consequence that the shape of the photoemission spectrum bears little resemblance to that expected in the absence of these losses. He suggests that the feature identified as the pseudogap in the photoemission spectra of the manganites is in fact an artifact produced as a consequence of the strong coupling of the photoelectron to substrate excitations on its outgoing trajectory. We note that in EELS, it is well established that the particle-hole contribution to the loss spectra is proportional to the dc resistivity of the substrate for small energy losses[3,4] and is thus very intense for poor conductors.

We have been motivated to explore this issue further by several considerations. First, while Joynt applies his expressions for the loss probability to examples where the coupling to the substrate excitations is so strong the elastic intensity which remains at large distances is very small, in fact his basic equations apply only in the weak-coupling regime. We see this from his Eq. (5), which through comparison with earlier discussions,[5] one sees applies only for weak coupling. At sufficiently low-electron energy, this statement leads to the unphysical result $P_0 < 0$ for example. Similarly, in Joynt's Eq. (6), in the strong-coupling limit, one must take due account of the depletion of the supply of electrons whose energy is $\hbar\omega'$ in his notation, as they progress along their outgoing trajectory. A consequence of these limitations is that quantitative conclusions are open to question, when expressions such as these are applied to circumstances when the coupling is not weak.

In the course of developing an appropriate transport equation that describes the ensemble of electrons that leave the crystal surface, we were led to inquire into the physical interpretation of the losses explored by Joynt. The answer is this.

As discussed some years ago,[6] in a very closely related context, an electron that leaves a crystal surface, to propagate off to infinity, feels a force that may be viewed to have two contributions. The first is the image force of classical dielectric theory, modified in form near the crystal surface by the finite velocity of the electron. This is supplemented by a contribution with origin in electric fields generated by excitations in the substrate that have been created earlier by the electron; this oscillates with a distance from the surface, and as we show below, does zero work on the electron, when integrated over its trajectory, in the present case.

Quite clearly, the image force, which decreases in strength monotonically as the electron recedes from the surface, does work on the electron, with the consequence that the electron loses a certain fraction of its kinetic energy before it strikes the detector. We show below that the energy losses discussed by Joynt are just those associated with the deceleration of the electron provided by the image force.

All electrons photoemitted from the surface are retarded by the image force, and thus its effect is simply to produce a downward shift in kinetic energy of the entire photoelectron energy spectrum. The effective image force is energy dependent by virtue of the finite velocity of the electron, as discussed earlier,[6] so there will be some distortion in the spectrum as well. However, of interest to Joynt are electrons whose kinetic energy is in the 20 eV range, and he focuses his attention on the shape of the spectrum within 500 meV of the Fermi cutoff. Over such a modest range of kinetic energies, the distortion in the spectrum produced by the energy variation of the effective image force will be very modest, so there will be very little influence of these losses on the study of a phenomenon such as the pseudogap.

We begin by discussing the nature of the electric field in the vacuum above the substrate itself, in response to a classical electron created at time $t=0$, which moves off to infinity with velocity v, directed normal to the surface. We then obtain the probability the electron suffers energy loss between $\hbar\omega$ and $\hbar(\omega+d\omega)$ by an argument patterned after Joynt's treatment, to find a result similar to his save for the numerical prefactor. We then present an argument that demonstrates that these losses are simply those associated with the work done by the effective image force, which attracts the electron back to the surface.

II. THE ANALYSIS

Following an earlier discussion,[6] and also Joynt's approach, we shall suppose the photoemitted electron may be viewed as a classical particle of charge $-e$, created at the crystal surface at time $t=0$, which moves away from the surface with velocity v along the z axis, taken perpendicular to the surface. The substrate lies in the lower half-plane $z<0$, and is characterized by the isotropic, frequency-dependent dielectric constant $\epsilon(\omega)$.

A. The electric field above and below the surface

The charge density associated with the electron is $\rho(\mathbf{r},t)=-e\,\delta(x)\,\delta(y)\,\delta(z-vt)\,\theta(t)$, where $\theta(t)=+1$ when $t\geqslant 0$ and $\theta(t)=0$ when $t<0$. We Fourier transform the charge density, and other quantities with respect to time:

$$\rho(\mathbf{r},t)=\int \rho(\mathbf{r},\omega)e^{i\omega t}\frac{d\omega}{2\pi}. \tag{2.1}$$

After a short calculation, we have

$$\rho(\mathbf{r},\omega)=-\frac{e}{v}\,\delta(x)\,\delta(y)\,\theta(z)e^{+i(\omega z/v)}. \tag{2.2}$$

We ignore retardation effects, so the electric field is written

$$\mathbf{E}(\mathbf{r},t)=-\boldsymbol{\nabla}\varphi(\mathbf{r},t), \tag{2.3}$$

where we solve Poisson's equation for $\varphi(\mathbf{r},\omega)$:

$$\nabla^2\varphi(\mathbf{r},\omega)=\frac{4\pi e}{v}\,\delta(x)\,\delta(y)\,\theta(z)e^{i(\omega z/v)} \tag{2.4}$$

subject to the boundary condition that $\varphi(\mathbf{r},\omega)$ is continuous at $z=0$, along with $\epsilon(\omega)E_z(\mathbf{r},\omega)$.

All quantities are Fourier transformed with respect to x and y, by writing

$$\varphi(\mathbf{r},\omega)=\int \varphi(z;\mathbf{k}_\parallel,\omega)e^{\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel}\frac{d^2k_\parallel}{(2\pi)^2}. \tag{2.5}$$

We shall append the superscripts $>$ and $<$ to various quantities, to indicate that they apply to the regimes $z>0$, and $z<0$, respectively. We then write the solution in the form

$$\varphi^>(z;\mathbf{k}_\parallel\omega)=\varphi_0^>(z;\mathbf{k}_\parallel\omega)+\Delta\varphi^>(z;\mathbf{k}_\parallel\omega), \tag{2.6}$$

and similarly for $\varphi^<(z;\mathbf{k}_\parallel\omega)$. One finds

$$\varphi_0^>(z;\mathbf{k}_\parallel\omega)=\frac{2\pi e}{k_\parallel}\left[\frac{e^{-k_\parallel z}}{vk_\parallel+i\omega}-\frac{2vk_\parallel e^{i\omega(z/v)}}{v^2k_\parallel^2+\omega^2}\right], \tag{2.7a}$$

$$\varphi_0^<(z;\mathbf{k}_\parallel\omega)=-\frac{2\pi e}{k_\parallel}\,\frac{e^{+k_\parallel z}}{vk_\parallel-i\omega}, \tag{2.7b}$$

and

$$\Delta\varphi^{>,<}(z;\mathbf{k}_\parallel,\omega)=\frac{2\pi e}{k_\parallel}\,\frac{e^{-k_\parallel|z|}}{vk_\parallel-i\omega}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right). \tag{2.7c}$$

The contributions with subscript zero appended simply generate the electrostatic potential of the electron in free space:

$$\varphi_0(\mathbf{r},t)=-\frac{e\,\theta(t)}{[r_\parallel^2+(z-vt)^2]^{1/2}}. \tag{2.8}$$

Our interest thus centers on the electric fields with origin in $\Delta\varphi^{>,<}(z;\mathbf{k}_\parallel,\omega)$. In what follows, we may set the subscripts $>$ and $<$ aside, to write the electrostatic potential produced by the disturbance in the substrate in the form

$$\Delta\varphi(\mathbf{r},t)=\frac{e}{4\pi^2}\int\frac{d^2k_\parallel\,d\omega}{k_\parallel}e^{i[\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel-\omega t]}\frac{e^{-k_\parallel|z|}}{vk_\parallel-i\omega}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right), \tag{2.9}$$

which may also be written as

$$\Delta\varphi(\mathbf{r},t)=\frac{e}{2\pi}\int_0^\infty dk_\parallel\int_{-\infty}^{+\infty}d\omega \times e^{-i\omega t}\frac{e^{-k_\parallel|z|}J_0(k_\parallel r_\parallel)}{vk_\parallel-i\omega}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right). \tag{2.10}$$

We pause to make contact with Joynt's analysis. In his Eq. (1), he displays an expression for the Fourier transform with respect to time of the total electric field in the substrate, which is the sum of that obtained from Eq. (2.8), and that obtained from Eq. (2.9). Upon combining Eq. (2.7b) with Eq. (2.7c) and taking the Fourier transform, for $z<0$ we write the total electrostatic potential in the form

$$\varphi^<(\mathbf{r},\omega)=-\frac{2e}{v}\,\frac{1}{\epsilon(\omega)+1}\int_0^\infty\frac{dk_\parallel\,J_0(k_\parallel r_\parallel)e^{-k_\parallel|z|}}{k_\parallel-i(\omega/v)}. \tag{2.11}$$

If we introduce the identity

$$\frac{1}{k_\parallel-i(\omega/v)}=\int_0^\infty dz'\,e^{-[k_\parallel-i(\omega/v)]z'} \tag{2.12}$$

and recall that

$$\int_0^\infty dz\, J_0(\alpha x)e^{-\beta x}=\frac{1}{(\alpha^2+\beta^2)^{1/2}} \tag{2.13}$$

then we rewrite Eq. (2.11) to read

$$\varphi^<(\mathbf{r},\omega)=-\frac{2e}{v}\frac{1}{1+\epsilon(\omega)}\int_0^\infty dz\,\frac{e^{i(\omega/v)z'}}{[r_\parallel^2+(z'+|z|)^2]^{1/2}}. \tag{2.14}$$

This yields an electric field in the substrate virtually identical to that in Joynt's Eq. (1), though he appears to employ a different Fourier transform convention than found in the present paper, to judge from the prefactor in his expression.

B. An expression for the energy lost by the electron

In a dielectric, the energy/unit time dissipated by time-dependent electric fields is written[7]

$$\frac{dW}{dt}=\frac{1}{4\pi}\int d^3r\,\mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t} \tag{2.15a}$$

$$=\frac{1}{8\pi}\frac{\partial}{\partial t}\int d^3r\,E^2+\int d^3\mathbf{r}\,\mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t}. \tag{2.15b}$$

Of interest, following Joynt, is the total-energy loss of the electron found by integrating this form over time, from $-\infty$ to $+\infty$. The energy lost by the electron as it travels from the crystal surface to the detector clearly equals the total energy dissipated in the substrate. Upon integrating over time, the first term in Eq. (2.15b) gives zero, and the total energy dissipated is

$$W=\int_{-\infty}^{+\infty}dt\int_{z<0}d^3r\,\mathbf{E}(\mathbf{r},t)\cdot\frac{\partial}{\partial t}\mathbf{P}(\mathbf{r},t) \tag{2.16}$$

or

$$W=\frac{1}{8\pi^2 i}\int_{z<0}d^3r\int_{-\infty}^{+\infty}d\omega[\epsilon(\omega)-1]\omega|\mathbf{E}(\mathbf{r},\omega)|^2, \tag{2.17}$$

where $\mathbf{E}(\mathbf{r},-\omega)=\mathbf{E}^*(\mathbf{r},\omega)$. Upon noting $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, where general considerations show $\epsilon_1(\omega)[\epsilon_2(\omega)]$ is an even (odd) function of frequency,

$$W=\frac{1}{8\pi^2}\int_{-\infty}^{+\infty}d\omega\,\omega\epsilon_2(\omega)\int_{z<0}d^3r|\mathbf{E}(\mathbf{r},\omega)|^2 \tag{2.18}$$

or

$$W=\frac{1}{32\pi^4}\int_{-\infty}^{+\infty}d\omega\,\omega\epsilon_2(\omega)\int_{-\infty}^{0}dz\int d^2k_\parallel \times\mathbf{E}(z;\mathbf{k}_\parallel\omega)\cdot\mathbf{E}^*(z;\mathbf{k}_\parallel\omega), \tag{2.19}$$

where one has, upon deriving the electric field in the region $z<0$ from Eq. (2.7b) and Eq. (2.7c),

$$W=\frac{e^2}{\pi^2v^2}\int_{-\infty}^{+\infty}\frac{d\omega\,\omega\epsilon_2(\omega)}{|1+\epsilon(\omega)|^2}\int_{-\infty}^{0}dz\int d^2k_\parallel\frac{e^{2k_\parallel z}}{k_\parallel^2+\omega^2/v^2}. \tag{2.20}$$

The integrals in Eq. (2.20) are performed readily, and the result can be arranged to read simply

$$W=\frac{e^2}{v}\int_0^\infty d\omega\,\mathrm{Im}\left\{\frac{-1}{1+\epsilon(\omega)}\right\}. \tag{2.21}$$

We wish to deduce an expression for $P(\omega)$, where $P(\omega)d\omega$ is the probability the electron loses energy in the interval between $\hbar\omega$ and $\hbar(\omega+d\omega)$. We deduce a form for $P(\omega)$, again following Joynt, by identifying Eq. (2.21) with

$$W=\int_0^\infty d\omega\,\hbar\omega P(\omega), \tag{2.22}$$

so we have

$$P(\omega)=\frac{e^2}{v}\frac{1}{\hbar\omega}\mathrm{Im}\left\{\frac{-1}{1+\epsilon(\omega)}\right\}. \tag{2.23}$$

Joynt arrives at an expression identical in form to Eq. (2.23), but with a different numerical prefactor. Upon comparing the result in Eq. (2.23) with Joynt's Eq. (4), we find that he has a prefactor he writes as $C/2\pi^2$, where he states that $C\cong 2.57$. We do not appreciate the origin of this difference; no details of the derivation have been provided in Ref. 1. We remark that we assume Joynt has obtained his result by calculating the total energy dissipated utilizing the electric field generated from the potential in Eq. (2.14). We have attempted to proceed in this manner, but in the end we find the prefactor expressed in terms of integrals difficult to evaluate, with subtle issues of convergence that must be addressed.

The dielectric response of conducting substrates can often be described by the Drude model, for which

$$\epsilon(\omega)=\epsilon_\infty-\frac{\omega_p^2}{\omega(\omega+i/\tau)}, \tag{2.24}$$

where ϵ_∞ has its origin in interband transitions; we assume ϵ_∞ is frequency independent here. For this model, the integrated strength of the loss probability is readily calculated:

$$\int_0^\infty P(\omega)d\omega=\frac{\pi}{2}\frac{e^2}{\hbar v}\frac{1}{(1+\epsilon_\infty)}. \tag{2.25}$$

It is interesting to compare this result with that appropriate to the dipole losses experienced by an electron in an EELS experiment. In EELS, the integrated strength of the loss probability is larger than that in Eq. (2.25) by a factor of 2.[8]

C. The physical origin of the losses experienced by the photoelectron

In this section, we inquire into the physical origin of the losses described in Sec. II B. We do this by examining the work done on the electron, by the electric field with origin in the polarization induced in the substrate by the photoelectron.

For this we require the electric field generated by the potential whose Fourier transform is in Eq. (2.7c). From this we

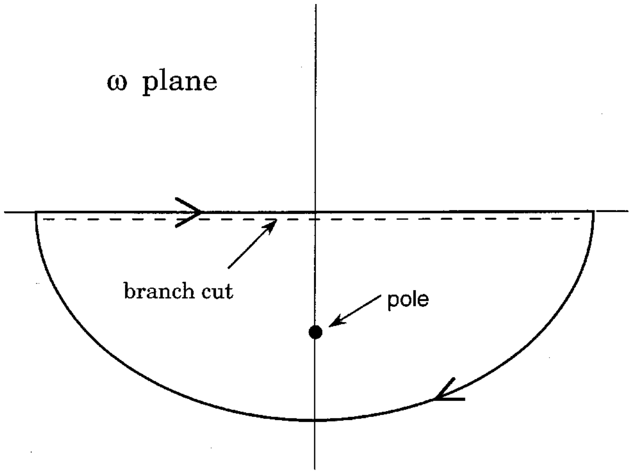

FIG. 1. The contour employed to obtain the results in Eq. (2.27). The figure illustrates the branch cut in $\epsilon(\omega)$, while the pole indicated is that at $\omega=-ivk_\parallel$.

calculate the z component of electric field at the site of the photoelectron $z=vt$. When this is done, the force on the photoelectron, when it is distance z above the surface, may be written

$$F_z=-\frac{e^2}{2\pi v}\int_0^\infty dk_\parallel\, k_\parallel e^{-k_\parallel z}\times\int_{-\infty}^{+\infty}\frac{d\omega}{k_\parallel-i(\omega/v)}\left(\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right)e^{-i\omega(z/v)},\quad(2.26)$$

an expression closely related to that found earlier.[6,9]

The dielectric function $\epsilon(\omega)$ in Eq. (2.26), considered as a function of complex frequency, is analytic in the upper-half ω plane, as a consequence of causality. From the many-body representations of this function, one sees it has a branch cut just below the real axis, along the line $z=\omega-i\eta$, where $\eta>0$. One has $\lim_{\eta\to 0}\epsilon(\omega+i\eta)=\epsilon_1(\omega)+i\epsilon_2(\omega)$, while $\lim_{\eta\to 0}\epsilon(\omega-i\eta)=\epsilon_1(\omega)-i\epsilon_2(\omega)$.

It is then possible, for $z>0$, to rearrange the integral on ω through use of the contour illustrated in Fig. 1. This allows us to separate F_z into the components

$$F_z(a)=F_z^{(1)}(z)+F_z^{(2)}(z),\quad(2.27a)$$

where

$$F_z^{(1)}(z)=-\frac{e^2}{v^2}\int_0^\infty dx\, xe^{-2x(z/v)}\left(\frac{\epsilon(ix)-1}{\epsilon(ix)+1}\right)\quad(2.27b)$$

and

$$F_z^2(z)=\frac{2e^2}{\pi}\int_0^\infty dk_\parallel\, k_\parallel e^{-k_\parallel z}\int_{-\infty}^{+\infty}\frac{d\omega\, e^{-i(\omega/v)z}}{\omega+ivk_\parallel}\times\mathrm{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right).\quad(2.27c)$$

Note that $\epsilon(ix)$ is real, and is an even function of x.

From the discussion in Ref. 6, we see that $F_z^{(1)}(z)$ is simply the classical image force on the electron.[10] Its form is modified from the elementary expression by the finite velocity of the electron, in combination with the frequency-dependent dielectric constant of the substrate. The image force is modified by the time delay in the response of the substrate to the instantaneous position of the electron. Notice that when $(z/v)\gg 1$ a limit applicable to either a slowly moving electron, or an electron far from the surface, we may replace $[\epsilon(ix)-1]/[\epsilon(ix)+1]$ by $[\epsilon(0)-1]/[\epsilon(0)+1]$ and remove it from the integral, to give

$$F_z^{(1)}(z)\simeq-\frac{e^2}{4z^2}\left(\frac{\epsilon(0)-1}{\epsilon(0)+1}\right),\quad(2.28)$$

the form of the image force that emerges from elementary dielectric theory. The quantity $\epsilon(0)$ is the static dielectric constant, denoted by ϵ_s in Ref. 6.

The contribution $F_z^{(2)}(z)$ to the force felt by the electron has its origin in electric fields, oscillatory in time, produced by excitations in the substrate created by the electron as it moves on its outgoing trajectory.

Consider, for example, a very good simple metal within which a long-lived plasmon exists in the bulk. Such a metal is described by the dielectric function in Eq. (2.24), where $\omega\tau\gg 1$ in the plasmon regime. Then to very good approximation we have

$$\mathrm{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right)=\frac{\pi}{2}\frac{\omega_{\mathrm{sp}}}{(1+\epsilon_\infty)}[\delta(\omega-\omega_{\mathrm{sp}})-\delta(\omega+\omega_{\mathrm{sp}})],\quad(2.29)$$

where $\omega_{\mathrm{sp}}=\omega_p/(1+\epsilon_\infty)^{1/2}$ is the surface plasmon frequency. One finds

$$F_z^{(2)}(z)=\frac{2e^2\omega_{\mathrm{sp}}}{1+\epsilon_\infty}\left[\omega_p^2\cos\left(\frac{\omega_{\mathrm{sp}}z}{v}\right)\int_0^\infty\frac{dk_\parallel\, e^{-k_\parallel z}}{\omega_{\mathrm{sp}}^2+v^2k_\parallel^2}-v\sin\left(\frac{\omega_{\mathrm{sp}}z}{v}\right)\int_0^\infty\frac{dk_\parallel\, k_\parallel e^{-k_\parallel z}}{\omega_{\mathrm{sp}}^2+v^2k_\parallel^2}\right].\quad(2.30)$$

Outside such a surface, the electron excites only surface plasmons, and these produce electric fields with the time dependence $\exp[\pm i\omega_{\mathrm{sp}}t]$. When the electron is at position z, we evaluate these at $t=z/v$. Hence, when the electron is at position z, the electron feels a force that is a linear combination of $\cos(\omega_{\mathrm{sp}}z/v)$ and $\sin(\omega_{\mathrm{sp}}z/v)$.

We approach the question of the physical origin of the losses described by Eqs. (2.21) and (2.23) by calculating the work done on the electron by the two forces just discussed. In the Appendix, we show that

$$W^{(2)}=\int_0^\infty F_z^{(2)}(z)dz\equiv 0.\quad(2.31)$$

Now

$$W^{(1)}=\int_0^\infty F_z^{(1)}(z)dz=-\frac{e^2}{2v}\int_0^\infty dx\left(\frac{\epsilon(ix)-1}{\epsilon(ix)+1}\right). \tag{2.32}$$

Now consider the function

$$G(w)=\frac{\epsilon(w)-1}{\epsilon(w)+1} \tag{2.33}$$

as a function of the complex variable w. Since $\epsilon(w)$ is analytic everywhere, save for a branch cut just below the real w axis, so is $G(w)$, which also has the same branch cut. This analytic structure ensures us that we may write

$$G(w)=\frac{1}{2\pi i}\int_{-\infty}^{+\infty}\frac{1}{\omega-w}[G(\omega+i\eta)-G(\omega-i\eta)]d\omega. \tag{2.34}$$

From Eq. (2.33), we see $G(\omega+i\eta)-G(\omega-i\eta)=2i\,\mathrm{Im}[G(\omega+i\eta)]=4i\,\mathrm{Im}\{-1/[1+\epsilon(\omega)]\}$, where in the last statement, $\epsilon(\omega)$ is evaluated on the real axis, just above the branch cut. Since $\mathrm{Im}\{-1/[1+\epsilon(\omega)]\}$ is an odd function of frequency, one has

$$\frac{\epsilon(ix)-1}{\epsilon(ix)+1}=\frac{4}{\pi}\int_0^\infty\frac{d\omega\,\omega}{\omega^2+x^2}\mathrm{Im}\left[\frac{-1}{1+\epsilon(\omega)}\right]. \tag{2.35}$$

Then we have

$$W^{(1)}=-\frac{2e^2}{\pi v}\int_0^\infty d\omega\,\omega\,\mathrm{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right)\int_0^\infty\frac{dx}{\omega^2+x^2}$$

or

$$W^{(1)}=-\frac{e^2}{v}\int_0^\infty d\omega\,\mathrm{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right). \tag{2.36}$$

Our primary conclusion follows upon comparing Eq. (2.36) with Eq. (2.21). We see that the losses calculated by Joynt, when integrated over all frequencies, precisely equal the work performed by the attractive image force felt by the electron as it makes its transit from the crystal surface to the detector.

In elementary dielectric theory, the work done by the image force is infinite, since the image force diverges as $1/z^2$ as $z\to\infty$. However, as discussed earlier, and as we see again, the finite velocity of the electron, in combination with the frequency-dependent response of the substrate, rounds off the singularity to leave the work done finite. For example, if we have a good metal whose plasmons are underdamped, we may use Eq. (2.29) to evaluate the work W. We find

$$W=\frac{\pi e^2\omega_{\mathrm{sp}}}{2(1+\epsilon_\infty)v}. \tag{2.37}$$

More generally, with the full dielectric function in Eq. (2.24) we have

$$W=\frac{\pi e^2\omega_{\mathrm{sp}}}{2(1+\epsilon_\infty)v}f\left(\frac{1}{\omega_{\mathrm{sp}}\tau}\right), \tag{2.38}$$

where

$$f(\eta)=\frac{\eta}{\pi}\int_0^\infty\frac{dx}{(x-1)^2+x\eta^2} \tag{2.39}$$

and $f(0)=1$. Note that $f(\eta)$ monotonically decreases with η. Thus, for poor metals, the energy lost is less than for good metals. When $\eta\gg1$, we can show that $f(\eta)\cong(4/\pi\eta)\ln(\eta/4)$.

III. CONCLUDING REMARKS

As a photoelectron propagates from a crystal surface to a detector, while it is in the vacuum above the crystal, it creates excitations in the substrate via the long-ranged Coulomb interaction. In the case of a metallic substrate, as we have seen, the coupling is to surface plasmons, which may be broad spectral features if the material is a poor conductor. A consequence is that the electron loses energy through this mechanism while it is in the vacuum above the crystal. We have shown here that the change in kinetic energy of the electron from this source equals the work done on it by the attractive image force, as it leaves the crystal. This work is finite, by virtue of the rounding off of the image force near the crystal surface, a consequence of the finite velocity of the electron in combination with the frequency dependence of the dielectric response of the substrate.

All electrons in the photoelectron spectrum suffer this same energy shift, whose effect is to simply displace the entire energy spectrum found at the detector, relative to that just outside the crystal surface. There is some distortion of the spectrum as well, since as we see from Eq. (2.21) this energy shift is inversely proportional to the electron's velocity at the crystal surface, within the present classical treatment of the problem. This distortion will be quite a small effect if, following Joynt, our interest centers on a portion of the spectrum width ΔE, where $\Delta E\ll E$, the mean kinetic energy in the portion of the spectrum of interest. We find the energy shift roughly equal to $e^2\omega_{\mathrm{sp}}/v$. For a 20 eV electron receding from the surface of a poor conductor with a surface-plasmon energy in the range of 1 eV, the energy shift from this source is in the range of 1 eV.

Our conclusion thus differs substantially from that in Joynt's paper. In our view, one may set the influence of these losses aside, unless one's interest lies in the overall shape of the photoemission spectrum, over a wide range of energies. If this is the issue, then one should employ a proper quantum theoretic description of the image force induced shift, rather than the simple classical picture employed here. This remains a challenge for theorists, if one wishes to address real materials, since standard local density approximation discussions of the electron/surface interaction fail to generate the image potential.

While the final expressions for the loss probability has features similar to that found in the description of near specular dipole losses in EELS, in fact the physical origin of the losses in EELS is very different than in the present case.

In EELS, the work done by the image force on the incoming leg of the electron trajectory precisely cancels that done on the outgoing leg, since the image force is the same on the two legs. One may verify this explicitly by casting the classical analysis of near dipole losses in EELS into the language utilized here. This is easily done for the case of normal incidence. One then sees the electron on both its incoming and outgoing trajectory experiences precisely the force in Eq. (2.27b), so the net work done by this contribution is zero, as expected for the image force. We note that an early treatment of EELS by Schaich[11] is most useful to consult.

ACKNOWLEDGMENTS

The author wishes to thank Professor G. Sawatzky for calling the issue addressed here to my attention. Also, subsequent interactions with Professor Sawatzky and Karina Schulte have been most valuable. This research has been supported by the U.S. Department of Energy, through Grant No. DE-FG03-84ER 45083.

APPENDIX: EVALUATION OF THE WORK DONE BY $F_z^{(2)}(z)$

If we calculate the work directly from Eq. (2.27c), we are left with an integral on frequency ω that vanishes, by virtue of the fact that $\text{Im}\{-1/[1+\epsilon(\omega)]\}$ is an odd function of frequency. However, for a fixed value of ω, the integral on $k_\parallel$ the expression contains diverges. One requires a more convincing procedure.

One may proceed by arranging Eq. (2.27c) to read

$$F_z^{(2)}(z) = \frac{2e^2}{i\pi v}\int_0^\infty dk_\parallel\, k_\parallel e^{-k_\parallel z}\int_{-\infty}^{+\infty} d\omega\, e^{-i(\omega/v)z} \times \text{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right) - \frac{2e^2}{i\pi v}\int_0^\infty dk_\parallel \int_{-\infty}^{+\infty}\frac{d\omega\,\omega}{[\omega+ivk_\parallel]}e^{-i[\omega/v-ik_\parallel]z} \times \text{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right) \tag{A1}$$

or

$$F_z^{(2)}(z) = -\frac{2e^2}{\pi v}\int_{-\infty}^{+\infty}\frac{d\omega\,\sin[(\omega/v)z]}{z}\text{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right) - \frac{2e^2}{i\pi v}\int_0^\infty dk_\parallel\int_{-\infty}^{+\infty}\frac{d\omega\,\omega}{[\omega+ivk_\parallel]}e^{-i[\omega/v-ik_\parallel]z} \times \text{Im}\left(\frac{-1}{1+\epsilon(\omega)}\right). \tag{A2}$$

One may now integrate each term in Eq. (A2) over z, with both terms well behaved. The first term cancels the second when this is done, so $W^{(2)}=0$.

[1] R. Joynt, Science **284**, 777 (1999).
[2] See the discussion in *Electron Energy Loss Spectroscopy and Surface Vibrations*, edited by H. Ibach and D. L. Mills (Academic, San Francisco, 1982), Chap. 3.
[3] D. L. Mills, R. B. Phelps, and L. L. Kesmodel, Phys. Rev. B **50**, 6394 (1994).
[4] R. Franchy, B. Decker, J. Masuch, and H. Ibach, Surf. Sci. **55**, 303 (1994).
[5] See Sec. 3.3.5 of Ref. 2, and the references cited therein for the discussion of the strong coupling regime in EELS. The analog of the second term in Joynt's Eq. (5) is Γ, and the statement $P_0 = 1-\Gamma$ applies only when $\Gamma \ll 1$. This is true in the context of photoemission as well.
[6] D. L. Mills, Phys. Rev. B **15**, 763 (1977).
[7] See *Classical Electrodynamics*, 2nd, edited by J. D. Jackson (Wiley, New York, 1975), p. 236.
[8] The result in Eq. (2.25) can be compared with Eq. (3.4) of Ref. 2. For this comparison, the static dielectric constant $\epsilon(0)$ in Eq. (3.40) should be taken to be infinitely large.
[9] In Ref. 6, an expression is given for the force on a charge moving away from a dielectric, along the normal to the surface with velocity v. The trajectory of this charge is given by $z=vt$, $-\infty \leq t \leq +\infty$. That is, the charge was not created at $t=0$, but in the interval $-\infty < t < 0$ it was propagating through the material itself.
[10] See Eq. (2.42) of Ref. 6, and the associated discussion. There is a typographical error in Eq. (2.42). The prefactor should be q^2/v^2 rather than q^2v^2.
[11] W. L. Schaich, Phys. Rev. B **24**, 686 (1981).