Energy-loss probability in electron microscopy

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New general results on the self-energy of fast electrons interacting with metal surfaces are presented with emphasis on the energy-loss problem in electron microscopy. Some applications to both spherical and planar targets are considered. Our results are relevant to the understanding of inelastic electron scattering near small structures, at the nanometer scale.

In the past few years new developments and applications of the scanning transmission electron microscope (STEM) have stimulated renewed interest in the interaction of high-energy electron beams with surfaces and with small particles.[1–5] In a typical STEM configuration a well-focused 0.5-nm probe of 100-keV electrons provides a high-resolution transmission scanning image for samples with complex structure such as catalyst or semiconductor devices. It also yields, from selected local regions of the structure, x-ray-emission spectra and electron-energy-loss spectra. Usually the classical theory of energy loss has been employed to analyze the experimental energy-loss spectra, both for planar and spherical geometries. The free-electron model for spherical targets, originally used by Fujimoto and Komaki[6] in broad-beam geometry, has been applied to the focused-beam case by Schmeits[7] and Kohl[8] but only for the case of dipole or quadrupole excitations. Using a more general formalism Batson[3] has identified the resonance frequencies of small spheres and, very recently, Ferrell and Echenique[9] have presented a manageable formula, including all multipoles, for the case of a particle moving at fixed impact parameter outside a dielectric sphere.

In this paper we present a new general approach to the problem of the interaction of electrons with solid surfaces, of practical utility in electron microscopy but which can also be particularly useful in a variety of other problems involving electrons at surfaces, such as the definition of an optical potential in low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED),[10,11] or in the problem of surface states.[12–14] Our model is not restricted to the free-electron model for the medium response. Any local dielectric response function $\epsilon(\omega)$ can be used.

The mean energy Σ_0 of the incoming electron in a state ψ_0 of energy E_0 can be written as the average of an effective potential $V_{\text{eff}}(\mathbf{r})$

$$\Sigma_0 = \int d\mathbf{r}\, \psi_0^*(\mathbf{r}) V_{\text{eff}}(\mathbf{r}) \psi_0(\mathbf{r}) \ . \tag{1}$$

We use atomic units throughout. The real part of Σ_0 gives us the lowering of the energy of the particle due to virtual excitations of the medium, and the imaginary part is directly related to the probability of energy loss due to the interaction of the particle with real excitations. The effective potential is written in terms of the nonlocal self-energy $\Sigma(\mathbf{r},\mathbf{r}',E_0)$ as

$$V_{\text{eff}}(\mathbf{r})\psi_0(\mathbf{r}) = \int d\mathbf{r}' \sum(\mathbf{r},\mathbf{r}',E_0)\psi_0(\mathbf{r}') \ . \tag{2}$$

The self-energy can be written in the pair approximation[15] in terms of the Green's function $G(\mathbf{r},\mathbf{r}',\omega+E_0)$ and the causal screened interaction $W(\mathbf{r},\mathbf{r}',\omega)$. The Green's function is given as a sum over a complete set $\psi_f(\mathbf{r})$ of final states with energy E_f. After some algebra we get

$$\Sigma_0 = \frac{1}{\pi} \sum_f \int d\omega\, d\mathbf{r}\, d\mathbf{r}' \frac{\psi_f^*(\mathbf{r}')\psi_0(\mathbf{r}')\psi_f(\mathbf{r})\psi_0^*(\mathbf{r})}{\omega + \Delta E + i\delta} \times \text{Im}[W(\mathbf{r},\mathbf{r}',\omega)] \ , \tag{3}$$

where $\Delta E = E_0 - E_f$ and δ is an infinitesimal constant.

We are mainly interested in the energy-loss problem in electron microscopy. A great deal of information is contained in the probability of losing energy ω, P_ω, a quantity directly related to the energy-loss rate γ experienced by the particle

$$\frac{\gamma}{v} = \int d\omega\, P_\omega \ , \tag{4}$$

which, in turn, is given in terms of the imaginary part of the incident electron self-energy: $\gamma = -2\,\text{Im}\Sigma_0$. In equation (4) v is the electron velocity.

We now use Eq. (3) to calculate P_ω in a number of cases of practical interest in electron microscopy. We first consider an electron beam incident upon a metallic sphere, both for a broad beam and a well-focused beam geometry. Then we consider planar-geometry configurations. To illustrate our results we perform some numerical calculations for an electron beam incident on an Al sphere. A detailed study of the effects of electron energy, geometry, beam size, and material on energy-loss probability will be published elsewhere.

In the case of spherical geometry, we have an electron beam incident upon a metallic sphere of radius a, with dielectric response function $\epsilon(\omega)$, located in vacuum. The screened interaction is obtained from Poisson's equation as

$$W(\mathbf{r},\mathbf{r}',\omega)=\sum_{l,m}\frac{4\pi}{2l+1}\alpha_l(\omega)\frac{r^l(r')^l}{a^{2l+1}}Y^*_{lm}(\Omega')Y_{lm}(\Omega)\ ,\qquad r,r'\le a\ ,$$

$$W(\mathbf{r},\mathbf{r}',\omega)=\sum_{l,m}\frac{4\pi}{2l+1}\beta_l(\omega)\frac{r_<^l}{r_>^{l+1}}Y^*_{lm}(\Omega')Y_{lm}(\Omega)\ ,\qquad r_<\le a,\ \ r_>\ge a\ ,\tag{5}$$

$$W(\mathbf{r},\mathbf{r}',\omega)=\sum_{l,m}\frac{4\pi}{2l+1}\gamma_l(\omega)\frac{a^{2l+1}}{r^{l+1}(r')^{l+1}}Y^*_{lm}(\Omega')Y_{lm}(\Omega)\ ,\qquad r,r'\ge a\ ,$$

where $r_<$ ($r_>$) is the smallest (greatest) of r,r', and

$$\alpha_l(\omega)=\frac{(l+1)(\epsilon-1)}{\epsilon(l\epsilon+l+1)}\ ,$$
$$\beta_l(\omega)=\frac{2l+1}{l\epsilon+l+1}\ ,\tag{6}$$
$$\gamma_l(\omega)=\frac{l(1-\epsilon)}{l\epsilon+l+1}\ ,$$

and $Y_{lm}(\Omega)$ is the spherical harmonic function.

If we have a broad-beam geometry, i.e., when the width of the beam is much greater than the size of the sphere, we use plane waves to describe the incident electron states and we obtain

$$P_\omega=-\frac{4a^3}{\pi v}\sum_l\frac{1}{q^2}\{\mathrm{Im}[\alpha_l(\omega)]j^2_{l+1}(qa)+2\,\mathrm{Im}[\beta_l(\omega)]j_{l+1}(qa)j_{l-1}(qa)+\mathrm{Im}[\gamma_l(\omega)]j^2_{l-1}(qa)\}\ ,\tag{7}$$

where $j_l(x)$ is the spherical Bessel function of the first kind, $\mathbf{q}=(\mathbf{Q},q_z)$ is the momentum transfer, and ω and q satisfy

$$\omega-q_zv+\frac{q^2}{2}=0\ .\tag{8}$$

Equation (7) is new and it is a general expression, valid for any dielectric function $\epsilon(\omega)$. It cannot be derived from the formalisms already existing in the literature, which only apply to the free-electron gas model.[7,16] The terms β_l and γ_l contain the surface plasmon losses; α_l contains both surface losses and corrections to the bulk losses due to the presence of the surface.[17] In the free-electron gas model for $\epsilon(\omega)$ and if we neglect the recoil term $q^2/2$ in (8), Eq. (7) reproduces the results of Fujimoto and Komaki,[6] and including the recoil term but for forward scattering ($q=q_z$), it reproduces the results of Barberan and Bausells.[16]

In STEM experiments we are concerned with a well-focused beam incident upon a sphere of radius a. We look for the probability of energy loss at a given impact parameter b. A physical description of this situation can be obtained if we neglect beam size effects by taking, in Eq. (3), a δ function in the transverse direction and plane waves in the direction of motion to describe the electron. Thus we allow momentum transfer only in the direction of motion. After some algebra we get from Eqs. (3) and (5) for the probability of losing energy ω at impact parameter $b<a$

$$P_\omega(b)=\frac{-4}{\pi v^2}\sum_{l,m}\frac{(l-m)!}{(l+m)!}\left[\frac{(A^i_{lm})^2}{a^{2l+1}}\mathrm{Im}[\alpha_l(\omega)]+2A^0_{lm}A^i_{lm}\mathrm{Im}[\beta_l(\omega)]+(A^0_{lm})^2\mathrm{Im}[\gamma_l(\omega)]a^{2l+1}\right]\ ,\qquad b<a\ ,\tag{9}$$

where

$$A^i_{lm}=\int_0^{(a^2-b^2)^{1/2}}dz\,r^lP_{lm}\left[\frac{z}{r}\right]g\left[\frac{\omega z}{v}\right]\ ,\tag{10}$$

$$A^0_{lm}=\int_{(a^2-b^2)^{1/2}}^{\infty}dz\frac{P_{lm}(z/r)}{a^{2l+1}}g\left[\frac{\omega z}{v}\right]\ ,\tag{11}$$

where $r^2=b^2+z^2$; $g(x)=\cos(x)$ for $l+m$ even and $g(x)=\sin(x)$ for $l+m$ odd, and $P_{lm}(x)$ is the associated Lengendre function.

When the incident electron moves outside the sphere ($b>a$) only the term proportional to $\mathrm{Im}(\gamma_l)$ remains and Eq. (9) can be expressed in a compact manner.[9] Equation (9) solves, for the first time, the case of a STEM experiment with a trajectory penetrating a sphere for a general dielectric constant, and constitutes a very useful tool to calculate, as a function of impact parameter b, the probability of losing energy ω for any general dielectric function $\epsilon(\omega)$. In general, many (l,m) terms are necessary and the dipole ($l=1$) approximation is only valid when the electron is far away from the sphere, or for very small spheres ($\omega a/v\ll 1$), which is not the case in most experimental situations.

To illustrate the use of Eq. (9), we first consider a free-electron response $\epsilon(\omega)$ and calculate the energy-loss probability as a function of impact parameter for a 50-keV electron incident upon a sphere of radius 100 Å. We obtain two terms, one is due to surface plasmon losses and the other is the correction to the bulk losses due to the pres-

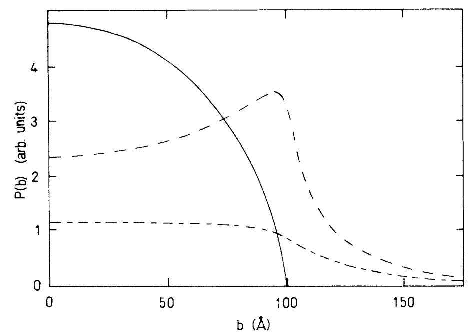

FIG. 1. Energy-loss probability as a function of impact parameter b for a 50-keV electron incident upon an aluminum sphere of radius 100 Å. Solid line: bulk mode; dashed line: total contribution of the first 20 surface modes ($\times 6$); dashed-dotted line: dipole ($l=1$) surface mode ($\times 6$).

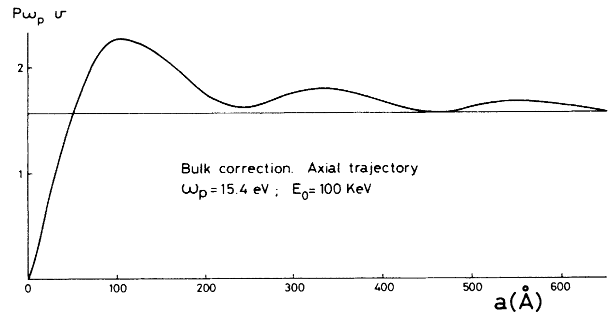

FIG. 2. Bulk correction to the plasmon excitation probability, as a function of the sphere radius for a 100 keV electron incident axially on an aluminum sphere. A free-electron $\epsilon(\omega)$ response function has been used in the calculation.

ence of the surface. In Fig. 1 we show the dipole mode contribution to the surface energy loss probability, the total contribution of the first 20 surface modes, and the full bulk-plasmon energy loss, which is obtained by adding to the bulk correction term the well-known bulk energy-loss probability for a classical particle[17]

$$P_{\omega}^{b}=2(a^2-b^2)^{1/2}\frac{\omega_p}{v^2}\ln\left[\frac{2v^2}{\omega_p}\right], \tag{12}$$

where ω_P is the plasma frequency. Both bulk and surface probabilities agree qualitatively with the experimental results.[18] The total contribution of the first 20 modes is not very different from the total surface mode excitation probability for the sphere radius we are considering.[9] The dipole contribution, however, does not show the probability enhancement near the surface, which can be seen in the experimental results.[18] Thus many modes are necessary to appropriately describe the experimental situation.

Now we consider an electron incident axially on an aluminum sphere. We concentrate on the dependence of the bulk correction term on the sphere radius a. We take a free-electron response function. The results are shown in Fig. 2. The calculation is greatly simplified by symmetry arguments (i.e., $m=0$) but for a big sphere radius we need to include a great number of modes to get good convergence. For small radius the bulk correction depends linearly on the sphere radius $P_{\omega_p}=\pi^2\omega_p a/(4v^2)$, but for a big radius, it tends, as it should, to the thick-slab result $P_{\omega_p}=\pi/(2v)$ first derived by Ritchie.[17] As can be seen in the figure, the bulk correction shows oscillations in the excitation probability as a function of the sphere radius. This is a new result which illustrates the usefulness of Eq. (9). A qualitatively similar behavior showing oscillations of the bulk plasmon scattering probability for small aluminum spheres as a function of the sphere diameter has been recently reported by Batson.[19] Further work, experimental and theoretical, is necessary to achieve a quantitative understanding of the oscillations in Baston's data, particularly the dependence of the oscillations on the probe size.

We shall now concern ourselves with planar-geometry configurations, in which we have an electron beam incident on a semi-infinite medium with dielectric response $\epsilon(\omega)$, bounded by the plane $z=0$, and located in the $z<0$ space region. The screened interaction is obtained, as in the spherical case, by solving Poisson's equation.

A well-focused incident beam can be described, as in the spherical geometry case, by a δ function in the transverse direction and a plane wave in the direction of motion. Then from Eq. (3) we reproduce, for a free-electron response, the energy-loss results of Núñez *et al.*,[20] although we obtain a more general result that can be used with any $\epsilon(\omega)$ response function.

For a general beam configuration, we can take plane waves in the direction parallel to the surface and a set of states $\Phi_n(z)$ in the direction normal to the surface. We obtain from (3)

$$\begin{aligned}\Sigma_0=\frac{1}{2\pi^2}\sum_n\int\frac{d^2Q}{Q}\int d\omega\frac{1}{\omega+\frac{Q^2}{2}+\Delta E_z-\mathbf{v}\cdot\mathbf{Q}-i\delta}&\Bigg[\operatorname{Im}\left[\frac{\epsilon-1}{\epsilon+1}\right]|\langle n\,|\,e^{-Qz}\Theta(z)\,|\,0\rangle|^2\\&+2\operatorname{Im}\left[\frac{2}{1+\epsilon}\right]\operatorname{Re}(\langle 0\,|\,e^{-Qz}\Theta(z)\,|\,n\rangle\langle n\,|\,e^{Qz}\Theta(-z)\,|\,0\rangle)\\&+\operatorname{Im}\left[\frac{1-\epsilon}{\epsilon(1+\epsilon)}\right]|\langle 0\,|\,e^{Qz}\Theta(-z)\,|\,n\rangle|^2\Bigg],\end{aligned} \tag{13}$$

where $|0\rangle$ and $|n\rangle$ are the initial and final states associated with motion normal to the surface with energies E_{0z} and E_{nz}, $\Theta(x)$ is the step function, and $\Delta E_z = E_{nz} - E_{0z}$. Equation (13) is a general expression which can be used to calculate several quantities of interest. The first term, which is the only nonzero term when the wave functions do not penetrate into the solid, reproduces the result of Manson and Ritchie[21] when their prescription is used to define a local z-dependent self-energy. Equation (13) can also be used to calculate the binding energy and effective-mass correction of an image state at a metal surface,[12–14] taking into account the penetration of the wave function into the crystal.[22] It also provides a valuable tool to evaluate the contribution to bulk losses due to the penetration of part of the incident electron packet into the crystal.[23]

If the electron is assumed to be always outside the solid, only the first term of Eq. (13) is nonzero. A further simplification might then be achieved by neglecting ΔE_z in the denominator of Eq. (13). This will give an upper-bound approximation to Σ_0. We can then use the closure relation to sum over intermediate states and obtain a local z-dependent self-energy using the prescription of Manson and Ritchie[21]

$$\Sigma_0(z) = \frac{1}{2\pi^2} \int \frac{d^2Q}{Q} \times \int d\omega \, \mathrm{Im} \left[\frac{\epsilon - 1}{\epsilon + 1} \right] \frac{e^{-2Qz}}{\omega + \frac{Q^2}{2} - \mathbf{v} \cdot \mathbf{Q} - i\delta} . \tag{14}$$

An important new feature of this result is that precisely at small distances from the surface, where greater surface sensitivity might be obtained, recoil effects avoid unphysical divergences at the origin, which are always present in the classical treatment.[5,23,24] Note as well a different ω dependence of the energy-loss function with respect to the classical solution which only depends on ω through the term $(1+\epsilon)^{-1}$.

In conclusion, a self-energy formalism has been used to describe the interaction between the incoming electron and the target. A very general formula has been derived for the complex electron self-energy of interest in electron microscopy, LEED, RHEED, and, in general, in any problem related to electrons interacting with surfaces. It also offers much possibility for insight into the problem of inelastic electron scattering near small structures at the nanometer scale. The real part of the self-energy defines the dynamical image potential, while the imaginary part is directly related to the probability of energy loss, a quantity directly measured in electron microscopy experiments. We present here, for the first time, new general formulas valid for any dielectric response function and thus not restricted to free-electron gas models, both for planar and spherical geometries and for different beam configurations. Earlier results, when existing, can be easily derived and the different approximations leading to them made clear as particular cases of our formulas.

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