ConF-8808159--2

THE COUPLING OF CONDENSED MATTER EXCITATIONS TO ELECTRON PROBES

R. H. Ritchie

Health and Safety Research Division
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, Tennessee 37831-6123

CONF-8808159--2

DE89 002340

(1) INTRODUCTION

In my first lecture some of the properties of electronic elementary excitations of interest in surface spectroscopy were sketched. Professor Howie has discussed many interesting aspects of Scanning Transmission Electron Microscopy in which several different elementary excitations play a part.

Today I will describe some of the basic physics of the coupling of swift electrons to interesting quanta of these modes. First I will present a brief, simple derivation of the energy loss by a charged particle to electronic excitations in matter and then a generalized dielectric theory of losses to condensed media.

(1.1) The Energy Loss from a Semiclassical Model

Consider an electron at rest and bound to a center of force located at distance b from the track of a particle with charge Z_1e and velocity $\underset{\sim}{v}$. The geometry of the collision is sketched in Fig. 1a. The force on the electron has two components but only that perpendicular to v is important for nonrelativistic particles. Neglecting the screening effect of other electrons in the vicinity, that force has a bell-shaped distribution in time with a maximum value equal to $F_{\perp}^{max} = Z_1e^2/b^2$. This is attained when the particle is just abreast of the electron. The force is symmetrical about the time of closest approach and has a width of $\tau_{coll} = 2b/v$ as sketched in Fig. 1b.

In some collisions electron binding may be neglected. In that regime and if the particle is traveling so fast that the electron does not move appreciably during the collision then the momentum transferred to it would be

$$\Delta p = \int_{-\infty}^{\infty} F_{\perp}^{max} \cdot \tau_{coll} = 2Z_1e^2/bv \quad . \tag{1.1}$$

The energy δE that it absorbs in the collision is

$$\delta E = (\Delta p)^2/2m = 2Z_1^2e^4/mv^2b^2 \quad . \tag{1.2}$$

Suppose that electrons are distributed uniformly through space with density n_o. Then the energy dE lost by the charged particle to the electrons in a cylindrical shell with length dx, radius b and thickness centered about the track will be $dE = \delta E \cdot dx \cdot 2\pi b db \cdot n_o$. Integrating over all impact parameters would result in divergent contributions from both limits. Instead one must employ maximum and minimum values, b_{max} and b_{min}, respectively. The electronic stopping power of the medium is

$$- dE/dx = \frac{4\pi Z_1^2 e^4 n_o}{mv^2} \int_{b_{min}}^{b_{max}} \frac{db}{b}$$

$$= \frac{4\pi Z_1^2 e^4 n_o}{mv^2} \ln\left[\frac{b_{max}}{b_{min}}\right] \quad . \tag{1.3}$$

This may be written also as integral over frequencies if we recognize[1] that the fundamental frequency, ω_b, of the disturbance seen by an electron at impact parameter b is $\omega_b \approx v/b$. Thus one sees that the distribution of frequencies presented to the electron by a passing ion is nearly "white" (uniform). The stopping power may be written

$$-dE/dx = \frac{4\pi Z_1^2 e^4 n_o}{mv^2} \int_{\omega_{min}}^{\omega_{max}} \frac{d\omega_b}{\omega_b}$$

$$= \frac{4\pi Z_1^2 e^4 n_o}{mv^2} \ln\left[\frac{\omega_{max}}{\omega_{min}}\right] \tag{1.4}$$

in the terms of the maximum and minimum values ω_{max} and ω_{min}, respectively.

The maximum impact parameter is easily found. When b becomes so large that the associated frequency v/b is appreciably smaller than the resonant frequency, ω_r of the electron, now considered as bound, energy transfer to it becomes negligible. Taking $b_{max} = v/\omega_r$, the "Bohr adiabatic impact parameter,"[1] gives a result that agrees with a rigorous calculation of the energy transfer to a bound electron. The corresponding minimum frequency $\omega_{min} = \omega_r$. A simple choice of b_{min} is made from the indeterminancy principle: One sets $b_{min} = \hbar/2mv$, which is proportional to the DeBroglie wavelength of the struck electron in the rest frame of the ion. This choice gives

$$-\frac{dE}{dx} = \frac{4\pi Z^2 e^4 n_o}{mv^2} \ln\left[\frac{2mv^2}{\hbar\omega_r}\right] . \tag{1.5}$$

which agrees with the form of the Bethe[2] stopping power relation in the limit in which $mv^2 \gg \hbar\omega_r$. In the general quantal approach of Bethe, ω_r is replaced by a mean excitation energy, averaged over all dipole-type transitions in the medium.

An approximate expression for Λ^{1}, the inverse mean free path for excitation of transitions in the medium, may be found by simply dividing Eq. 1.4 by the transition energy $\hbar\omega_r$. A more accurate formula is obtained by replacing b_{min} by k_c^{-1}, where k_c is a cutoff wave number for excitations in the medium. Thus

$$\Lambda^{-1} \approx \frac{1}{\hbar\omega_r}\left[-\frac{dE}{dx}\right]$$

$$= \frac{4\pi Z^2 e^4 n_o}{\hbar\omega_r m v^2} \ln\left[\frac{vk_c}{\omega_4}\right] \quad . \qquad (1.6)$$

In the case where excitation of plasmons with resonant frequency $\omega_r = \omega_p = (4\pi n_o e^2/m)^{1/2}$,

$$\Lambda^{-1} = \frac{Z^2 e^2 \omega_p}{v^2} \ln\left[\frac{vk_c}{\omega_p}\right] \qquad (1.7)$$

and $k_c \sim \omega_p/v_F$ where v_F is the Fermi velocity in the system.

(1.2) The Coupling of Bulk Excitations with Charged Particles by Dielectric Theory

Fermi[2] early realized that the response of an electronic system to the passage of a charged particle could, for many purposes, be couched in terms of its response to a spectrum of equivalent electromagnetic radiation. This idea was later developed by Williams[3] and Weizsäcker[4] and has been used to treat many different problems in the interaction of radiation with matter. Meanwhile Fermi[5] analyzed the Cherenkov radiation phenomenon by invoking the frequency-dependent dielectric response function of the medium in an electrodynamic approach. Subsequently the dielectric function was generalized to become an operator depending on space, or equivalently, to be a function of both wave vector and frequency.

Poisson's equation for the scalar electric potential $\varphi(\underset{\sim}{r},t)$ at r and at time t generated by an applied charge density p(r,t) in a medium characterized by the dielectric constant ϵ reads

$$\epsilon\nabla^2\phi = - 4\pi\rho(\underset{\sim}{r},t) \quad . \tag{1.8}$$

Expressing all quantities as Fourier integrals of the form

$$f(\underset{\sim}{r},t) = \int \frac{d^3k}{(2\pi)^3} \int \frac{d\omega}{2\pi} e^{i(\underset{\sim}{k}\cdot\underset{\sim}{r}-vt)} f_{k,\omega}$$

and considering $\epsilon = \epsilon_{k,\omega}$ Equation (1) leads to

$$\phi_{k,\omega} = \frac{4\pi\rho_{k,\omega}}{k^2\epsilon_{k,\omega}} \quad . \tag{1.9}$$

A bare particle with charge Z_1e may be considered to give rise to a density $\rho(\underset{\sim}{r},t) = Z_1e\delta^3(\underset{\sim}{r} - \underset{\sim}{v}t)$ if it moves with constant velocity $\underset{\sim}{v}$. Then $\rho_{k,\omega} = 2\pi Z_1e\delta(\omega - \underset{\sim}{k}\cdot\underset{\sim}{v})$ and the induced scalar electric potential, ϕ_{ind}, may be written

$$\phi_{ind}(r,t) = \frac{Z_1e}{2\pi^2} \int \frac{d^3k\exp[i\underset{\sim}{k}\cdot(\underset{\sim}{r}-\underset{\sim}{v}t)]}{k^2} (\epsilon^{-1}_{k,k\cdot v}-1) \quad . \tag{1.10}$$

The energy lost by the particle per unit path in the medium may be computed either from the energy deposited in the medium, or, more easily, by calculating the retarding force with which the medium acts on the particle. The latter is given by the electric field opposing the motion times the charge, evaluated at the position of the charge, viz., $F = Z_1 e\mathbf{v}\cdot\nabla\phi_{ind}(vt,t)/v$. In detail, one finds

$$-\frac{dE}{dx} = \frac{2(Z_1 e)^2}{\pi v^2}\int_0^{\infty}\frac{dk}{k}\int_0^{vk}\omega\, d\omega\ \mathrm{Im}\left[\frac{-1}{\epsilon_{k,\omega}}\right] \tag{1.11}$$

By using the RPA dielectric function, one may evaluate Eq. 5 numerically. The asymptotic form may be obtained by using the classical frequency-dependent dielectric function $\epsilon_{k,\omega} = 1 - \omega_p^2/\omega^2$, where $\omega_p = (4\pi n_e e^2/m^*)^{1/2}$ is the classical plasma frequency of a free electron gas with number density n_o and effective electron mass m^*. With this substitution in Eq. 1.11 one cuts off the integration over k at the value corresponding to the maximum momentum deliverable to a free electron and finds

$$-\frac{dE}{dx} = \frac{4\pi Z_1^2 e^4 n_o}{mv^2}\ \ln\left[\frac{2mv^2}{\hbar\omega_p}\right] \tag{1.12}$$

If the probe is an electron, $Z_1 = 1$ and the range of integrations must be altered to take into account the momentum-energy relation of the probe. One finds

$$-\frac{dE}{dx} = \frac{2e^2}{\pi v^2}\int_0^{mv^2/2}\omega d\omega\int_{k-}^{k+}\frac{dk}{k}\ \mathrm{Im}\left[-1/\epsilon_{k,\omega}\right] \tag{1.13}$$

where $k_{\pm} = \frac{m}{\hbar}(v \pm [v^2 - 2\hbar m/\omega]^{1/2})$. In the asymptotic limit $mv^2/2 \gg \hbar\omega_p$ (Eq. 13) still reduces to Eq. 12. One may obtain values for Λ^{-1} from Eq. 13 by dividing by $\hbar\omega$ under the integral sign.

An important sum rule that is of great value in theory and in numerical work involving the interactions under consideration is

$$\int_0^\infty \omega \, \mathrm{Im}[-1/\epsilon_{k,\omega}] \, d\omega = \frac{\pi}{2} \omega_p^{\,2} \tag{1.14}$$

and is valid for all values of k.

Extensive numerical work has been carried out by many workers in predictions of the distribution of energy losses in condensed matter by charged particles. Much use of different representations of the dielectric response of the medium has been made. Figure 2 shows the results of such a calculation[6] for swift electrons in electron gases of various densities. Here is displayed the differential inverse mean free path for creation of a secondary electron with energy ϵ. The quantities involved are explained in the caption. Figure 3 shows the differential inverse mean free path for creation of a plasmon as it depends on the energy imparted to the plasmon in an electron gas at the Al metal electron density. The calculations leading to these results were made using the Mermin form of $\epsilon_{k,\omega}$ for a particle-conserving damping process.[6] The results are shown for different values of the damping constant and for a primary energy of 1000 E_F. The distribution function indicated by the full width at half maximum of ~1.5 eV corresponds to the experimentally observed damping rate. The width of the distribution is determined in part by the intrinsic plasmon dispersion.

(2.0) COUPLING TO SURFACE EXCITATIONS

The coupling of swift particles with surface excitations may be approached at several different levels of complexity. Here we consider only the simpler ones.

(2.1) Dielectric Theory

A dielectric theory may be employed here and is most straightforward if a local dielectric function ($\epsilon_{k,\omega} \rightarrow \epsilon(\omega)$) is applicable. A simple result that has relevance to STEM work is found for the configuration consisting of a classical point electron traveling parallel with a plane boundary between two dielectrics.

Again solving Poisson's equation for the retarding force at a charge in uniform rectilinear motion, one finds for the differential inverse mean free path $d\Lambda^{-1}/d\omega$ the expression

$$d\lambda^{-1}/d\omega = \frac{2e^2}{\pi\hbar v^2} \ \mathrm{Im}\left\{ \frac{-2}{1+\epsilon} K_o \left[\frac{2\omega z}{v} \right] \right\} \qquad z > o \qquad (2.1a)$$

$$= \frac{2e^2}{\pi\hbar v^2} \left\{ \mathrm{Im}\left[\frac{-1}{\epsilon} \left[\ln \frac{vkc}{\omega} \right] - \kappa_o \left[\frac{2\omega z}{v} \right] \right] \right]$$

$$+ \mathrm{Im} \left[\frac{-2}{1+\epsilon} K_o \left[\frac{2\omega}{v} |z| \right] \right] \right\} \qquad z > 0 \qquad (2.1b)$$

where the medium in the region $z > o$ is assumed to have unit dielectric constant and z specifies the position of the electron relative to the dielectric with $\epsilon = \epsilon(\omega)$.

This is an interesting relation. For $z > o$ one finds a formula equivalent to that first given by Echenique and Pendry[8] for the special case of an electron gas. When $z < o$ there may be volume excitations corresponding to peaks in the response function Im $[-1/\epsilon(\omega)]$. There is a boundary correction[9] (the second term in Eq. 2.1b) to the expression for a constant rate of energy transfer to the medium at regions far from the surface. Equation 2.1a and the last term in Eq. 2.1b corresponds to the excitation of surface modes. Relations similar to Eq. 2.1 have been used by Echenique and coworkers[10] to analyze energy loss distributions in STEM experiments with MgO cubes.

(2.2) Electron-Surface Coupling in the Specular Reflection Model

A more comprehensive treatment of coupling to surface excitations may be given using the specular reflection model[11] described in Lecture I. Collective as well as single-particle excitations are described thereby. The differential inverse mean free path for a classical electron proceeding in vacuum parallel to an electron gas and at a distance z from it is given by

$$d\Lambda^{-1}/d\omega = \frac{2e^2}{\pi v^2} \int_0^\infty \frac{d\kappa_y}{\kappa} e^{-2z\kappa} \, \mathrm{Im}\left[\frac{1 - \tilde{\epsilon}_{\kappa,\omega}}{1 + \tilde{\epsilon}_{\kappa,\omega}} \right] \qquad (2.2)$$

where $\kappa^2 = k_y^2 + \omega^2/v^2$ and the surface dielectric function $\tilde{\epsilon}_{\kappa,\omega}$ $(\kappa/\pi) \int_{-\infty}^{\infty} dk_z/\epsilon_{\kappa,\omega}(\kappa^2 + k_z^2)$. Although a complete evaluation of $\tilde{\epsilon}_{\kappa,\omega}$ has not been made to date, Echenique et al.[12] have suggested a very useful approximate expression that contains collective effects, linear dispersion of the surface plasmon, single-particle effects and gives a dispersion relation that joins the single-particle continuum at the correct point. Nunez, Echenique and Ritchie[13] have employed the specular reflection model to treat a wide range of problems, while Gras-Marti et al.[14] have studied excitations by slow ions incident normally on the surface. More detailed work along these lines is indicated.

(2.3) Coupling with Excitations in a Spherical System

A local dielectric representation of the response function of a homogeneous spherical system, together with a classical representation of the effect of an electron moving on a rectilinear trajectory has been used by Ferrell and Echenique[15] to compute the probability of excitation of the system as a function of impact parameter and of the excitation frequency. Although it is necessary to include multipolar excitations of high order to describe the probability at small impact parameter, numerical computations have been carried out for a number of different dielectric media. These results are very useful in the interpretation of STEM experiments of the kind described by Professor Howie in this Summer School.

(3.0) A SELF-ENERGY APPROACH TO THE COUPLING OF PROBES TO ELEMENTARY EXCITATIONS

Treatments such as those discussed above approximate electron-matter coupling by considering the electron to be a classical point charge. As long as the electron has energy much greater than the excitation energies of interest, such treatments should be accurate. When this condition is not satisfied, the quantal character of the probe may be important.

It has been realized for some time[16] that a quantal self-energy formalism is of much value in representing the interaction between a probe and a polarizable system. Applications of the self-energy formalism have been numerous.[16]

The problem of obtaining a spatial representation of the self-energy is not trivial here. The probe, represented by a wave function, polarizes a target which then reacts back on the probe to change its state function. A spatially-dependent probe self-energy will in general be complex: the imaginary part represents the damping of, or energy loss by, the probe due to excitations in the target, while the real part corresponds to an image-type potential acting upon the probe.

Manson and Ritchie[17] have introduced a new method of obtaining a spatial representation of the self-energy from ordinary perturbation theory. An unfolding procedure, very simply effected in the second-order approximation to the energy shift due to interaction between the probe and the target, yields this self-energy in spatial representation. Most of the applications of this new technique[18] have been to systems in which the response function of the target may be expressed in terms of Boson creation and annihilation operators, but a more general representation is possible. A self-energy formulation of value in inelastic STEM theory has been given by Echenique, Bausells, and Rivacoba.[19]

(3) Summary

Aspects of coupling of a classical electron with bulk and surface excitations in condensed matter have been sketched. Some considerations of a self-energy approach to the complete quantal treatment of this coupling have been given.

(4) Acknowledgements

Research sponsored jointly by NATO Collaborative Research Grants Programme under grant number 0142/87, the U.S.-Spain Joint Committee for Scientific and Technological Cooperation under agreement number L-10106, and the Office of Health and Environmental Research, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

1. N. Bohr, *Kgl. Danske Selsk. Mat.-Fys. Medd.* 24, No. 19 (1948).
2. E. Fermi, *Z. Physik* 29, 315 (1927).
3. See, e.g. E. J. Williams, *Rev. Mod. Phys.* 17, 217 (1945) for a thorough review of this approach.
4. C. F. v Weizsacker, *Z. Phys.* 88, 612 (1934).
5. E. Fermi, *Phys. Rev.* 57, 485 (1940).
6. C. J. Tung and R. H. Ritchie, *Phys. Rev.* B16, 4302 (1977).
7. R. H. Ritchie, quoted in L. D. Marks, *Solid State Comm.* 43, 727 (1982).
8. P. M. Echenique and J. B. Pendry, *J. Phys.* C8, 2936 (1975).
9. R. H. Ritchie, *Phys. Rev.* 106, 874 (1957).
10. A. Howie and R. H. Milne, *J. Microsc.* 136, 279 (1985); *Ultramicroscopy* 18, 427 (1985). See also P. M. Echenique, A. Howie, and D. J. Wheatley, *Phil. Mag.* B56, 335 (1987).
11. R. H. Ritchie and A. L. Marusak, *Surf. Sci.* 4, 234 (1966).
12. P. M. Echenique, R. H. Ritchie, N. Barberan, and J. C. Inkson, *Phys. Rev.* B23, 6486 (1981).
13. R. Nuñez, P. M. Echenique, and R. H. Ritchie, *J. Phys.* C13, 4229 (1980).
14. A. Gras-Marti, P. M. Echenique, and R. H. Ritchie, *Surf. Sci.* 170, 310 (1986).
15. T. L. Ferrell and P. M. Echenique, *Phys. Rev. Lett.* 55, 1526 (1985); T. L. Ferrell, R. J. Warmack, V. E. Anderson, and P. M. Echenique, *Phys. Rev.* B35, 7365 (1987).

16. See, e.g. L. Hedin and S. Lundqvist, *Solid State Physics* 23, 1 (1969); J. C. Inkson, *Surf. Sci.* 28, 69 (1971); F. Flores and F. Garcia-Moliner, *J. Phys.* C12, 907 (1979); P. J. Feibelman, C. B. Duke, and A. Bagchi, *Phys. Rev.* B5, 2436 (1972).

17. J. R. Manson and R. H. Ritchie, *Phys. Rev.* B24, 4867 (1981).

18. A brief review of several of the applications that have been made of this method are given in R. H. Ritchie and J. R. Manson, *Int. J. Quant. Chem.: Quant. Chem. Symp.* 21, 363 (1987).

19. P. M. Echenique, J. Bausells, and A. Rivacoba, *Phys. Rev.* B35, 1521 (1987).

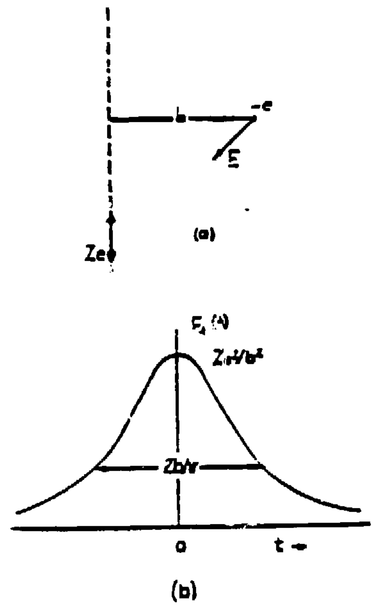

Fig. 1. The geometry of a collision between a swift, charged particle and a bound electron (a), and a sketch of the force perpendicular to the charged particle track experienced by a stationary electron (b).

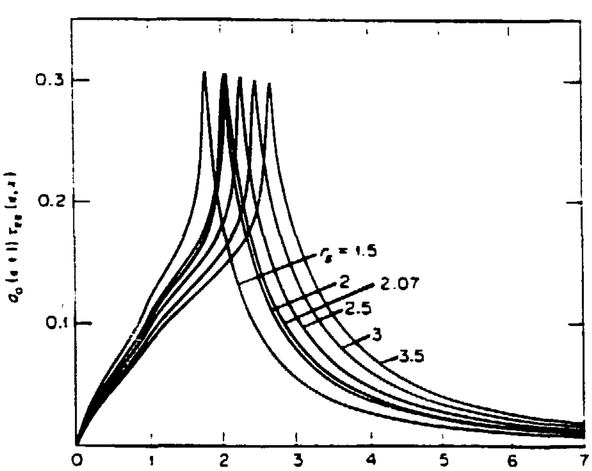

FIG. 2. Plot of $a_0(\epsilon+1)\tau_{ee}(\epsilon,x)$ vs x in electron gases of various densities. Here $\tau_{ee}(\epsilon,x)$ is the differential inverse mean free path for energy loss xE_F to electron-hole pair excitation in an electron gas by a primary electron of energy ϵE_F.

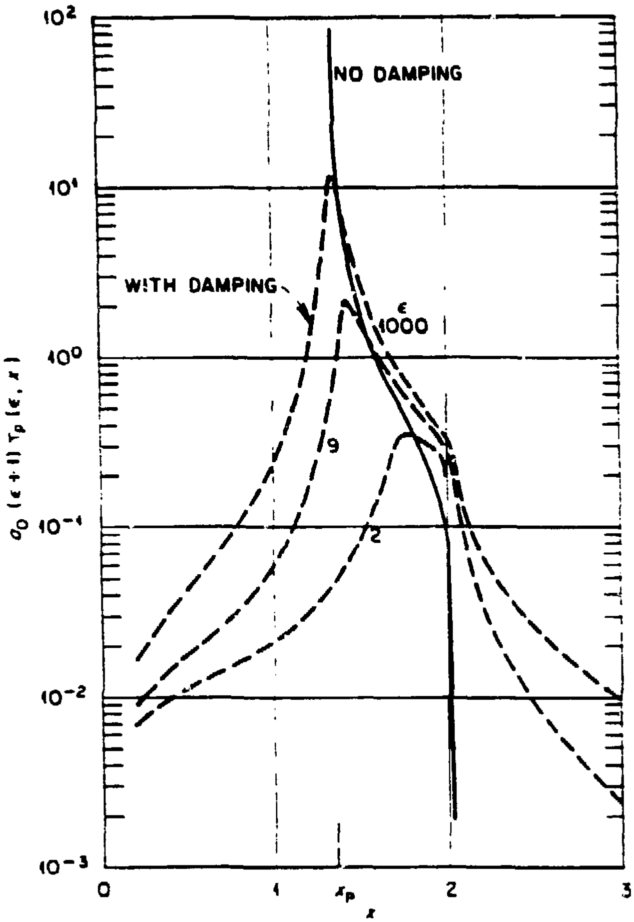

Figure 3. A plot of $a_0(\epsilon+1)\tau_p(\epsilon,x)$ versus x in an electron gas (r_s = 2.07) for various values of ϵ. The primary energy is ϵE_F, the energy loss is xE_F and $\tau(\epsilon,x)$ is the inverse mean free path, differential in x. The solid curve is obtained using the RPA dielectric function with no damping. The dashed curves were found using the Drude dielectric function with damping taken from experiment.