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Electron-Scattering Cross Sections Pertinent to Electron Microscopy^{*}

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1. Introduction

Since the early work by Marton and Schiff [1], by Lenz [2], and by others, it has been recognized that analytical microscopy requires quantitative and trustworthy data on electron scattering cross sections. Much progress has been made in the physics of electronic collisions both experimentally and theoretically. The purpose of the present article is to discuss some elements of the physics that determine cross sections and to indicate various sources of data that should be useful for analytical microscopy. The discussion will concern atoms, molecules, and, to some extent, solids.

2. Inelastic Scattering

The energy loss of electrons in matter, at kinetic energies between tens of keV and several MeV, is largely attributable to atomic electrons, rather than to nuclei or to radiative processes such as bremsstrahlung. Let us first consider the simplest case in which the target is a single free electron at rest. The cross section is then given by the Rutherford formula

$$d\sigma = (2\pi e^4 / mv^2) Q^{-2} dQ, \quad (1)$$

where Q is the recoil energy and v is the incident electron speed. (For brevity, one ignores here the relativity and the indistinguishability of electrons; a more rigorous treatment would use the formulas of Mott and Møller.) The quantity Q is expressed in terms of momentum transfer $\hbar K$ as

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$$Q = (\hbar K)^2 / 2m , \quad (2)$$

and is connected, in classical mechanics, to the impact parameter b by

$$Q = 2e^4 / mv^2 b^2 . \quad (3)$$

Next let us consider an isolated atom or molecule. The binding of atomic electrons changes the cross section as follows. Although Q of Eq. (2), or the momentum transfer, remains to be a key variable, the energy loss E is not in general equal to Q ; E takes values corresponding to excitation energies of the target atom (both discrete and continuum). Furthermore, Eq. (1) is replaced by

$$d\sigma_E = (2\pi e^4 / mv^2) \phi(E, Q, v) Q^{-1} dQ , \quad (4)$$

where $\phi(E, Q, v)$ is a dynamical factor that depends on atomic structure. Provided that v greatly exceeds the orbital speed of atomic electrons so that the first Born approximation is justified, ϕ does not explicitly depend on v , as Bethe [3] first showed. Then, ϕ is expressed as

$$\phi(E, Q) = Q^{-1} \left| \langle E | \sum_j \exp(i\vec{K} \cdot \vec{r}_j) | 0 \rangle \right|^2 , \quad (5)$$

where $\langle E | \quad | 0 \rangle$ denotes an atomic matrix element between the state with excitation energy E and the ground state, and $\vec{r}_j$ is the position of the j th atomic electron. Bethe [3-5] gave many general consequences of Eq. (5), full exploitation of which even now continues to be a subject of serious study [6,7].

Among many results, the close connection to photoabsorption warrants the first mention. The quantity $E\phi(E, Q)$ is called the density of the generalized oscillator strength, $df(E, Q)/dE$. The limit of this quantity as $Q \rightarrow 0$ is the optical (dipole) oscillator-strength density $df(E)/dE$, which is equal to the cross section for absorption of a photon of energy E . Kinematics show that, for electron scattering into the forward direction, Q takes the minimum value

$$Q_{\min} \cong E^2/2mv^2, \quad (6)$$

which is quite small for the majority of atomic excitations. This is the basis for correlating electron energy-loss spectra with photoabsorption spectra—a theme pursued by many investigators.

When Q is much greater than atomic-electron binding energies, then the situation should resemble the scattering by a free electron. This means that $\phi(E, Q)$ should approach Z/Q only when $Q \approx E$ and should almost vanish otherwise, where Z is the number of pertinent atomic electrons. (Actually, because of the large disparity of binding energies of different shells, one observes the approach to the free-electron limit for each shell successively as one goes to higher and higher Q .)

All of these observations are best illustrated by a three-dimensional plot of $df(E, Q)/dE$ as a function of Q and E , called the Bethe surface [6].

When one integrates Eq. (4) over all possible values of Q for given excitation energy E , one obtains a compact expression called the Bethe cross section. (The following is actually the result incorporating relativistic effects.)

$$\sigma_E = 8\pi a_0^2 (R/mv^2) \{ M_E^2 [\ln(\beta^2/1 - \beta^2) - \beta^2] + C_E \} \quad (7)$$

where $a_0 = \hbar^2/me^2 = 0.52917 \text{ \AA}$ is the Bohr radius, and $R = me^4/2\hbar^2 = 13.606 \text{ eV}$ is the Rydberg energy. The dependence on incident speed $v = \beta c$ is given analytically and generally. The two parameters M_E^2 and C_E are atomic properties derived from the generalized oscillator strength. In particular, M_E^2 is the density of the dipole matrix element and is given by

$$M_E^2 = (R/E) df(E)/dE. \quad (8)$$

Any sum of σ_E over different E values has the same analytic dependence on v and is characterized by two parameters. In particular, the total inelastic-scattering cross section, i.e., the sum of σ_E over

all E (discrete and continuum), may be written as

$$\sigma_{\text{tot.inel.}} = 8\pi a_0^2 (R/mv^2) \{M_{\text{tot}} [\ln(\beta^2/1 - \beta^2) - \beta^2] + C_{\text{tot}}\} \quad (9)$$

and the parameters M_{tot}^2 and C_{tot} are often calculable from known information by use of certain sum rules [8].

Data on $\sigma_{\text{tot.inel.}}$ are important to the analytical microscopy, as discussed recently by Isaacson [9] and others. Figures 1 and 2 show values of M_{tot}^2 and $C_{\text{tot}} - 14.2268 M_{\text{tot}}^2$ for all atoms up to Kr, evaluated from current atomic models [10]. Several points are to be noted. First, the behavior of $\sigma_{\text{tot.inel.}}$ for any fixed v as a function of atomic number is largely governed by M_{tot}^2 . This is an obvious consequence of the dominance of dipole (glancing) interactions. Second, the Z dependence of M_{tot}^2 , and hence of $\sigma_{\text{tot.inel.}}$ is not monotonic (unlike results from the Thomas-Fermi model often quoted in the microscopy literature [1,2,9], but shows a pronounced manifestation of the shell structure. Analysis shows [11] that most of the periodicity arises from excitations from valence (outermost) shells. Third, one sees in Fig. 1 a general increase in M_{tot}^2 with Z as a background below the periodic variation; this trend is attributable to inner shells and is indeed in agreement with the Thomas-Fermi prediction.

It may be noted that $\sigma_{\text{tot.inel.}}$ discussed above may not be directly applicable to certain electron-microscopic situations. Sometimes the signal used for microscopy concerns the cross section $\sigma_{\text{inel}}(\hat{\theta})$ for inelastic scattering into a cone defined by an aperture angle $\hat{\theta}$, i.e.,

$$\sigma_{\text{inel}}(\hat{\theta}) = \int dE \int_0^{\hat{Q}} dQ (d\sigma_E/dQ), \quad (10)$$

where $\hat{Q}$ is the recoil-variable value corresponding to $\hat{\theta}$. The calculation of $\sigma_{\text{inel}}(\hat{\theta})$ for arbitrary $\hat{\theta}$ requires full knowledge of the Bethe surface, and is moreover complicated because $\hat{Q}$ depends on E .

However, it is possible to estimate $\sigma_{\text{inel}}^{\wedge}(\hat{\theta})$ for sufficiently large $\hat{\theta}$, say $\hat{\theta} > 10$ mrad. Instead of direct calculation, one may evaluate

$$\sigma_{\text{inel}}^{\text{out}}(\hat{\theta}) = \int dE \int_{\hat{Q}}^{\hat{Q}_{\text{max}}} dQ (d\sigma_E/dQ) , \quad (11)$$

where $\hat{Q}_{\text{max}}$ may be taken as $2mv^2$. Under the condition $E/mv^2 \ll \theta \ll 1$, one may set $Q \cong \frac{1}{2}mv^2\theta^2$ independent of E , where E is the excitation energy. Then it is possible to perform the E integration first, and the result is expressible in terms of the incoherent-scattering function [12]. Fortunately, in electron microscopy with light-atom targets, $E/mv^2 \cong 10^{-3}$ for the majority of atomic excitations. Tabulation [13] of the incoherent-scattering function from current sources enables one to estimate $\sigma_{\text{inel}}^{\text{out}}(\hat{\theta})$ and thence

$$\sigma_{\text{inel}}^{\wedge}(\hat{\theta}) = \sigma_{\text{tot. inel}} - \sigma_{\text{inel}}^{\text{out}}(\hat{\theta}) . \quad (12)$$

Preliminary calculations on carbon indicate that $\sigma_{\text{inel}}^{\text{out}}(\hat{\theta})$ would be several percent of $\sigma_{\text{tot. inel.}}$ for $\hat{\theta} = 10$ mrad, about 2% for $\hat{\theta} = 50$ mrad, and negligible for $\hat{\theta} = 100$ mrad, at 50 keV incident electron energy.

Finally, the applicability of the first Born approximation to inelastic scattering must be discussed briefly. The criterion that the incident electron be much faster than the orbital electrons is indeed well satisfied for valence and outer shells for any atom for electrons of microscopy interest. Indeed, significant departures from the first Born approximation are usually found for incident electrons with energies of 1 keV or less or for extremely large scattering angles. For inner-shell electrons, the velocity criterion does not hold well, especially when one recalls that the relativity forbids electron speed to increase indefinitely. Yet, as the current data show [14,15], the inner-shell ionization cross section can be fitted quite well to the Bethe formula for electron energies only four times the relevant binding energy and larger. This, together with other evidence, indicates that the range of validity of the first Born

approximation for inner-shell ionization is much more extensive than given by the velocity criterion.

3. Elastic Scattering

The cross section for elastic scattering in the energy range of our interest requires a different treatment. The first Born approximation is limited to lighter atoms and higher incident energies, as recognized by electron microscopists [9]. Detailed examination of the domain of validity of the first Born approximation is seen in a variety of literature [16,17]. It is now almost a routine matter to calculate phase shifts for a potential due to the atom and thence elastic-scattering cross sections [17,18].

A major issue here is the choice of atomic potential, which includes several contributions. First, the charge distribution of atomic electrons and nuclei gives rise to its electrostatic potential; this is the dominant part of the entire potential and behaves roughly as a Yukawa potential for any neutral atom at large distances. Current atomic-structure calculations, based on the Hartree-Fock method or on more advanced treatments including relativity and correlation effects, provide a trustworthy charge distribution and thence a trustworthy static potential for all atoms. (When the target is a molecule, the static potential is anisotropic and may include a long-range part. In this case, the calculation of phase shifts, especially at lower incident electron energies ($\lesssim 10$ keV), presents a major challenge. The recent work, e.g., by Dill and Dehmer [19] and co-workers, appears to be highly promising in meeting this challenge.

Second, the electron-exchange effects may be incorporated approximately by means of a local potential. But the precise method of obtaining this potential is a matter of current study. However, the exchange interactions are in general of short range, and their effects are important mainly for large scattering angles. Therefore, the relevance to electron

microscopy is limited to heavier atoms and to the largest of the scattering angles used in practice.

Finally, there is a so-called charge-polarization effect. An incident electron at a large distance from the target tends to push away atomic electrons, and thus induces a transient polarization of the electron distribution. This results in a net attractive potential of long range, which behaves roughly as $-\alpha e^2/2r^4$ where α is the dipole polarizability. This potential generally contributes to enhance elastic scattering into small angles that are relevant to electron microscopy [17]. The foregoing summary of this topic follows the standard discussion in atomic-collision physics, but there is an alternative, perhaps better, picture for the same effect, i.e., the idea of shadow scattering due to Bethe [20,21]. According to this idea, the enhancement of the elastic scattering in the forward direction over the first Born approximation is an inescapable consequence of the strong inelastic scattering.

4. Concluding Remarks: On Solid-State Effects

In condensed phases, excitation of electrons by fast charged particles may be discussed in the same framework as the Bethe theory according to Eq. (4). However, the factor ϕ in principle must be considered as a property of the entire macroscopic material because the excitation of two or more electrons may be correlated. Then, ϕ should be taken as $\text{Im} [-1/\epsilon(\omega, K)]$, apart from a proportionality constant, where ϵ is the dielectric response function at frequency $\omega = E/\hbar$ and wave number K ; alternatively, ϵ is in essence the Fourier component of the correlation function of the electron position [22-24]. For inner-shell excitations, the condensed phase effects are usually small. For valence-shell excitations in contrast the spectrum (i.e., the probability distribution of different E) may differ from that of isolated atoms or molecules, especially at small values of the momentum transfer $\hbar K$. To put the difference in the spectra precisely, one should compare $\text{Im} [-1/\epsilon(\omega, 0)]$ with

$$Z E^{-1} df(E)/dE.$$

Fano [25] gave a general criterion for observing an appreciable difference. Let df/dE be the spectrum for an isolated atom or molecule. For an aggregate of the same molecular species, one considers

$$u_f = (\hbar\omega_p)^2 df/dE^2 = \frac{1}{2} (\hbar\omega_p)^2 E^{-1} df/dE, \quad (13)$$

where

$$\omega_p = (4\pi e^2 \delta_e / m)^{\frac{1}{2}}, \quad (14)$$

is the plasma frequency corresponding to the electron density in the condensed medium. If $u_f \gtrsim 1$ the spectrum $\text{Im} [-1/\epsilon(\omega, 0)]$ will appreciably differ from the single-molecule spectrum if $u_f \gtrsim 1$. Generally the condensed-phase spectrum has intensities shifted to higher E values. If $u_f \gg 1$, then $\text{Im} [-1/\epsilon(\omega, 0)]$ will be virtually the same as the single-molecule spectrum. The quantity u_f means the spatial and spectral density of the oscillator strength, and obviously depends on E .

For inorganic crystals, there is indeed a domain of E where $u_f > 1$. The best known example is the Bohm-Pines plasmon [25,26], now well-known in the electron energy-loss spectra of virtually all metals and semi-conductors. Another example is the exciton of various types.

For molecular substances including water, liquid or solid organic materials, and biomolecules, our current understanding is inconclusive. The Fano parameter u_f has been examined in several instances [26], a typical example of which is seen in Fig. 5 of ref. 26. At the peak of isolated e_2H_5OH molecule (which curiously occurs around 20 eV for virtually all molecules in this class, u_f takes a maximum value of 0.2-0.3. This value is too large to let us say that the condensed-phase effect on the spectrum is negligible, but it is too small to let us say that such an effect is decidedly negligible.

The direct measurement of the $\text{Im} [1/\epsilon(\omega, 0)]$ spectra for many organic materials leaves us with the same inconclusive idea. For

example, Bickhoff and co-workers [27] studied $\epsilon(\omega, 0)$ of many organic substances. The $\text{Im} [-1/\epsilon(\omega, 0)]$ spectra of all these substances shows a prominent peak around 20 eV; yet, $\text{Re} [\epsilon(\omega, 0)]$ fails to show a zero—a condition for the Bohm-Pines plasmon. The results of electron-impact studies [28] also leave us with the same general impression.

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FIG. 1.--The total dipole matrix element M_{tot}^2 as a function of atomic number Z . The points connected with heavy lines show the Hartree-Slater values obtained in the work of ref. 10; those connected by broken lines show the Hartree-Fock values taken from the literature; and the circles show accurate theoretical values also taken from the literature. The triangles represent values computed from experimental oscillator-strength distributions.

FIG. 2.--The quantities $M_{\text{tot}}^2 \ln C_{\text{tot}}$ (solid line) and $\ln C_{\text{tot}}$ (broken line) as functions of atomic number Z . These quantities are related with C_{tot} of the text by $C_{\text{tot}} = M_{\text{tot}}^2 (\ln C_{\text{tot}} + 11.2268)$. The points connected with heavy lines represent results from a combined use of Hartree-Slater data, and the open circles represent results including more accurate theoretical data.