

Appendix A

The First Born Approximation and the Rutherford Cross-Section

The Rutherford formula represents the differential elastic scattering cross-section obtained solving the Schrödinger equation in the first Born approximation [1].

A.1 The Elastic Scattering Cross-Section

The solid angle $d\Omega$ depends on the scattering angles $[\theta, \theta + d\theta]$ and the azimuthal angles $[\phi, \phi + d\phi]$. The differential elastic scattering cross-section $d\sigma/d\Omega$ is defined as the ratio between the flux of particles per unit of time emerging in the solid angle $d\Omega$ (divided by $d\Omega$) and the incident flux.

The flux of particles per unit time emerging after the collision in the solid angle $d\Omega$ depends on the component j_r of the current density in the outgoing direction from the centre of the atomic nucleus. The number of electrons emerging in the solid angle $d\Omega$ per unit time is given by $j_r r^2 d\Omega$ (note that $r^2 d\Omega$ is the cross-sectional area normal to the radius).

Let us consider a beam of incident electrons in the direction z normalised to one particle per unit of volume. Let $K = mv/\hbar$ be the electron momentum in the z direction, where v is the electron velocity, m the electron mass and \hbar the Planck constant divided by 2π . This beam can be represented by the plane wave $\exp(iKz)$.

Since the incident beam has been normalised to one particle per unit of volume, then the electron velocity v is the incident flux. As a consequence,

$$\frac{d\sigma}{d\Omega} = \frac{j_r r^2 d\Omega}{v d\Omega} = \frac{j_r r^2}{v}. \quad (\text{A.1})$$

At a large distance from the atomic nucleus, the potential $V(r)$ is negligible and the scattered particles can be described by a spherical wave, i.e. a function which is proportional to $\exp(iKr)/r$. If $f(\theta, \phi)$ is the constant of proportionality (scattering amplitude), then the wave function $\Psi(\mathbf{r})$ of the whole scattering process (i.e. of the

incident and the scattered electrons) satisfies the boundary conditions

$$\Psi(r) \underset{r \rightarrow \infty}{\sim} \exp(iKz) + f(\theta, \phi) \frac{\exp(iKr)}{r}. \quad (\text{A.2})$$

The electron position probability density P is given by $|\Psi|^2 = \Psi^* \Psi$, and the current density $\mathbf{j}(\mathbf{r}, t)$ is

$$\mathbf{j}(\mathbf{r}, t) = \frac{i\hbar}{2m} [(\nabla\Psi^*)\Psi - \Psi^*(\nabla\Psi)]. \quad (\text{A.3})$$

Let us now calculate the radial component of the current density \mathbf{j} , j_r :

$$\begin{aligned} j_r &= \frac{i\hbar}{2m} \left\{ f(\theta, \phi) \frac{\exp(iKr)}{r} \frac{\partial}{\partial r} \left[f^*(\theta, \phi) \frac{\exp(-iKr)}{r} \right] \right. \\ &\quad \left. - f^*(\theta, \phi) \frac{\exp(-iKr)}{r} \frac{\partial}{\partial r} \left[f(\theta, \phi) \frac{\exp(iKr)}{r} \right] \right\} \\ &= \frac{v|f(\theta, \phi)|^2}{r^2}. \end{aligned} \quad (\text{A.4})$$

Comparing this equation with (A.1), we can see that the differential elastic scattering cross-section is the square of the modulus of $f(\theta, \phi)$:

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2. \quad (\text{A.5})$$

A.2 The First Born Approximation

The first Born approximation is a high-energy approximation. If E is the incident electron energy, e the electron charge, a_0 the Bohr radius and Z the target atomic number, the main criterion of validity of the first Born approximation, for the case of electron-atom elastic scattering, is that [2]

$$E \gg \frac{e^2}{2a_0} Z^2. \quad (\text{A.6})$$

A.3 Integral-Equation Approach

Let us now introduce the Green function and the integral-equation approach. Starting from the Schrödinger equation,

$$(\nabla^2 + \mathbf{K}^2)\Psi(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r})\Psi(\mathbf{r}), \quad (\text{A.7})$$

with the boundary condition expressed by (A.2), it is possible to show that this is a problem equivalent to the following integral equation:

$$\Psi(\mathbf{r}) = \exp(iKz) + \frac{2m}{\hbar^2} \int d^3r' g(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}'), \quad (\text{A.8})$$

in which

$$g(\mathbf{r}, \mathbf{r}') = -\frac{\exp(iK|\mathbf{r} - \mathbf{r}'|)}{4\pi|\mathbf{r} - \mathbf{r}'|} \quad (\text{A.9})$$

is the Green function of the operator $\nabla^2 + \mathbf{K}^2$. As is known, this operator satisfies the equation

$$(\nabla^2 + \mathbf{K}^2)g(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (\text{A.10})$$

where $\delta(\mathbf{r} - \mathbf{r}')$ is the Dirac delta function.

Let us apply the operator $\nabla^2 + \mathbf{K}^2$ to the function $\Psi(\mathbf{r})$ defined by the integral equation (A.8):

$$\begin{aligned} (\nabla^2 + \mathbf{K}^2)\Psi(\mathbf{r}) &= (\nabla^2 + \mathbf{K}^2) \exp(iKz) \\ &+ \frac{2m}{\hbar^2} \int d^3r' (\nabla^2 + \mathbf{K}^2)g(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}'). \end{aligned} \quad (\text{A.11})$$

The application of the operator ∇^2 to the plane wave $\exp(iKz)$ gives

$$\nabla^2 \exp(iKz) = \frac{\partial^2}{\partial z^2} \exp(iKz) = -K^2 \exp(iKz) \quad (\text{A.12})$$

and, as a consequence, we can write

$$(\nabla^2 + \mathbf{K}^2) \exp(iKz) = 0. \quad (\text{A.13})$$

Therefore,

$$\begin{aligned} (\nabla^2 + \mathbf{K}^2)\Psi(\mathbf{r}) &= \frac{2m}{\hbar^2} \int d^3r' (\nabla^2 + \mathbf{K}^2)g(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}') \\ &= \frac{2m}{\hbar^2} \int d^3r' \delta(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \Psi(\mathbf{r}') \\ &= \frac{2m}{\hbar^2} V(\mathbf{r}) \Psi(\mathbf{r}). \end{aligned} \quad (\text{A.14})$$

For the boundary conditions, we have

$$\begin{aligned}
|\mathbf{r} - \mathbf{r}'| &= \sqrt{r^2 - 2\mathbf{r} \cdot \mathbf{r}' + r'^2} \\
&= r \sqrt{1 - \frac{2\hat{\mathbf{r}} \cdot \mathbf{r}'}{r} + \frac{r'^2}{r^2}} \\
&\sim r \left(1 - \frac{\hat{\mathbf{r}} \cdot \mathbf{r}'}{r} + O\left(\frac{1}{r^2}\right) \right). \tag{A.15}
\end{aligned}$$

Note that in the last equation,

$$\hat{\mathbf{r}} = \frac{\mathbf{r}}{r}. \tag{A.16}$$

Let us introduce \mathcal{K} , the wave number in the direction of the outgoing unit vector $\hat{\mathbf{r}}$,

$$\mathcal{K} \equiv K \hat{\mathbf{r}}. \tag{A.17}$$

So the Green function for the operator $\nabla^2 + \mathbf{K}^2$, expressed by (A.9), has the following asymptotic behaviour:

$$g(\mathbf{r}, \mathbf{r}') \underset{r \rightarrow \infty}{\sim} - \frac{\exp(iKr - i\mathcal{K} \cdot \mathbf{r}')}{4\pi r}. \tag{A.18}$$

Let us now introduce the asymptotic behaviour of the Green function (A.18) into the integral equation (A.8):

$$\Psi(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} \exp(iKz) - \frac{2m}{\hbar^2} \int d^3r' \frac{\exp(iKr - i\mathcal{K} \cdot \mathbf{r}')}{4\pi r} V(\mathbf{r}') \Psi(\mathbf{r}'). \tag{A.19}$$

From the equation

$$\begin{aligned}
&\int d^3r' \frac{\exp(iKr - i\mathcal{K} \cdot \mathbf{r}')}{4\pi r} V(\mathbf{r}') \Psi(\mathbf{r}') \\
&= \frac{\exp(iKr)}{r} \int d^3r' \frac{\exp(-i\mathcal{K} \cdot \mathbf{r}')}{4\pi} V(\mathbf{r}') \Psi(\mathbf{r}'), \tag{A.20}
\end{aligned}$$

we can conclude that, if the scattering amplitude is given by

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2} \int d^3r \exp(-i\mathcal{K} \cdot \mathbf{r}) V(\mathbf{r}) \Psi(\mathbf{r}), \tag{A.21}$$

then the boundary conditions are satisfied. In (A.21), \mathcal{K} is the wave number of the scattered particles, and $\Psi(\mathbf{r})$ is the scattering wave function.

Let us suppose that the ratio between the electron kinetic energy and the atomic potential energy is high enough to make the scattering weak and $\Psi(\mathbf{r})$ not very different from the incident plane wave $\exp(iKz)$. This is the assumption which is the basis of the first Born approximation, i.e.

$$\Psi(\mathbf{r}) = \exp(iKz) = \exp(i\mathbf{K} \cdot \mathbf{r}) . \quad (\text{A.22})$$

Utilising the first Born approximation, expressed by (A.22), the previous (A.21) becomes

$$f(\theta, \phi) = -\frac{m}{2\pi\hbar^2} \int d^3r \exp(-i\mathbf{K} \cdot \mathbf{r}) V(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) . \quad (\text{A.23})$$

If we use $\hbar\mathbf{q}$ to indicate the momentum lost by the incident electron,

$$\hbar\mathbf{q} = \hbar(\mathbf{K} - \mathbf{K}') , \quad (\text{A.24})$$

for fast particles we can write that

$$f(\mathbf{q}) = f(\theta, \phi) = -\frac{m}{2\pi\hbar^2} \int d^3r \exp(i\mathbf{q} \cdot \mathbf{r}) V(\mathbf{r}) . \quad (\text{A.25})$$

As we are interested in a central potential energy, then

$$V(\mathbf{r}) = V(r) , \quad (\text{A.26})$$

and, as a result,

$$\begin{aligned} f(\theta, \phi) &= f(\theta) \\ &= -\frac{m}{2\pi\hbar^2} \int_0^{2\pi} d\varphi \int_0^\pi \sin\vartheta d\vartheta \int_0^\infty r^2 dr \exp(iqr \cos\vartheta) V(r) . \end{aligned} \quad (\text{A.27})$$

We carry out the integrations over φ and over ϑ and obtain

$$f(\theta) = -\frac{2m}{\hbar^2 q} \int_0^\infty \sin(qr) V(r) r dr . \quad (\text{A.28})$$

A.4 The Rutherford Formula

Let us calculate the differential elastic scattering cross-sections in the first Born approximation for a screened Coulomb potential, such as a Wentzel-like potential [3],

$$V(r) = -\frac{Ze^2}{r} \exp\left(-\frac{r}{a}\right) . \quad (\text{A.29})$$

The exponential factor here represents a rough approximation of the screening of the nucleus by the orbital electrons, while the a parameter is

$$a = \frac{a_0}{Z^{1/3}}, \quad (\text{A.30})$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius.

Let us calculate the scattering amplitude:

$$f(\theta) = \frac{2m}{\hbar^2} \frac{Ze^2}{q} \int_0^\infty \sin(qr) \exp\left(-\frac{r}{a}\right) dr. \quad (\text{A.31})$$

As the equation

$$\int_0^\infty \sin(qr) \exp\left(-\frac{r}{a}\right) dr = \frac{q}{q^2 + (1/a)^2} \quad (\text{A.32})$$

holds, we can conclude that

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{4m^2}{\hbar^4} \frac{Z^2 e^4}{[q^2 + (1/a)^2]^2}. \quad (\text{A.33})$$

On the other hand, $|\mathbf{K}| = |\mathcal{K}|$ and $\mathbf{q} = \mathbf{K} - \mathcal{K}$, and, as a consequence

$$\begin{aligned} q^2 &= (\mathbf{K} - \mathcal{K}) \cdot (\mathbf{K} - \mathcal{K}) \\ &= \mathbf{K}^2 + \mathcal{K}^2 - 2K\mathcal{K} \cos \theta \\ &= 2K^2(1 - \cos \theta), \end{aligned} \quad (\text{A.34})$$

where θ is the scattering angle.

The electron kinetic energy is given by

$$E = \frac{\hbar^2 \mathbf{K}^2}{2m}, \quad (\text{A.35})$$

so that the differential elastic scattering cross-section for the collision of an electron beam with a Wentzel-like atomic potential is given in the first Born approximation by

$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{4E^2} \frac{1}{(1 - \cos \theta + \alpha)^2}. \quad (\text{A.36})$$

In the last equation, α is the *screening parameter*, given by

$$\alpha = \frac{1}{2K^2 a^2} = \frac{me^4 \pi^2}{\hbar^2} \frac{Z^{2/3}}{E}. \quad (\text{A.37})$$

The well-known classical Rutherford formula,

$$\frac{d\sigma}{d\Omega} = \frac{Z^2 e^4}{4E^2} \frac{1}{(1 - \cos \theta)^2}, \quad (\text{A.38})$$

can be obtained by imposing $\alpha = 0$ in (A.36).

The total elastic scattering cross-section can be obtained from

$$\sigma_{\text{el}} = \int \frac{d\sigma}{d\Omega} d\Omega . \quad (\text{A.39})$$

For a Wentzel-like potential, the total elastic scattering cross-section can be easily calculated as follows:

$$\begin{aligned} \sigma_{\text{el}} &= \frac{Z^2 e^4}{4E^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \vartheta d\vartheta \frac{1}{(1 - \cos \vartheta + \alpha)^2} \\ &= \frac{\pi Z^2 e^4}{E^2} \frac{1}{\alpha(2 + \alpha)} . \end{aligned} \quad (\text{A.40})$$

If $\alpha \rightarrow 0$ and, as a consequence, the differential elastic scattering cross-section is given by the classical Rutherford formula, the total elastic scattering cross-section diverges, reflecting the long-range nature of the pure Coulomb potential.

The elastic mean free path is the reciprocal of the total elastic scattering cross-section divided by the number N of atoms per unit of volume in the target:

$$\lambda_{\text{el}} = \frac{1}{N\sigma_{\text{el}}} = \frac{\alpha(2 + \alpha)E^2}{N\pi e^4 Z^2} . \quad (\text{A.41})$$

A.5 Summary

In this chapter we have deduced the Rutherford formula by solving the Schrödinger equation in a central field in the first Born approximation.

References

1. J.E.G. Farina, *The International Encyclopedia of Physical Chemistry and Chemical Physics*, vol. 4 (Pergamon, Oxford, 1973)
2. D. Bohm, *Quantum Theory* (Dover, New York, 1989)
3. G. Wentzel, *Z. Phys.* **40**, 590 (1927)

Appendix B

The Mott Theory

The original version of the Mott theory (also known as the relativistic partial wave expansion method, RPWEM) can be found in [1]. See, for details and several applications [2–5].

According to Mott, the elastic scattering process can be described by calculating the so-called phase shifts. If we indicate with r the radial coordinate, since the large- r asymptotic behavior of the radial wave function is known, the phase shifts can be computed by solving the Dirac equation for a central electrostatic field up to a large radius where the atomic potential can be neglected.

B.1 The Dirac Equation in a Central Potential

In order to appropriately treat the quantum-relativistic scattering theory, we need to know the form assumed by the Dirac equation for an electron in the presence of a central electrostatic field described by a central potential energy $e\varphi(r) = V(r)$. The natural units $\hbar = c = 1$ are used here and in the following section, as they are particularly convenient for the quantum-relativistic equations.

Let us first remind that the Dirac hamiltonian describing a spin-1/2 particle in the presence of an electromagnetic field described by the four-potential (φ, \mathbf{A}) is

$$H = e\varphi + \boldsymbol{\alpha} \cdot (\mathbf{p} - e\mathbf{A}) + \beta m, \tag{B.1}$$

where the 4×4 matrices $\boldsymbol{\alpha}$ and β are given by

$$\alpha^j = \begin{pmatrix} 0 & \sigma^j \\ \sigma^j & 0 \end{pmatrix}, \tag{B.2}$$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \tag{B.3}$$

Note that $(\sigma_x, \sigma_y, \sigma_z) = (\sigma^1, \sigma^2, \sigma^3)$ are the 2×2 Pauli matrices and I the 2×2 identity matrix.

Let us now introduce the operator \mathcal{K} defined by

$$\mathcal{K} \equiv \beta(1 + \boldsymbol{\sigma} \cdot \mathbf{L}) , \quad (\text{B.4})$$

where \mathbf{L} is the electron orbital angular momentum.

For an electron in a central electrostatic field, it is possible to show that

$$2 \frac{d\mathbf{L}}{dt} = - \frac{d\boldsymbol{\sigma}}{dt} . \quad (\text{B.5})$$

As a consequence, the total angular momentum, defined as $\mathbf{J} = \mathbf{L} + (1/2)\boldsymbol{\sigma}$, is a constant of the motion. On the other hand,

$$\mathbf{J}^2 - \mathbf{L}^2 = \boldsymbol{\sigma} \cdot \mathbf{L} + \frac{3}{4} , \quad (\text{B.6})$$

so we can conclude that

$$\mathcal{K} = \beta(\mathbf{J}^2 - \mathbf{L}^2 + 1/4) . \quad (\text{B.7})$$

\mathcal{K} commutes with H and is, as a consequence, a constant of the motion.

Let us now define the radial-momentum operator p_r , where

$$p_r \equiv -i \frac{1}{r} \frac{\partial}{\partial r} r = \frac{\mathbf{r} \cdot \mathbf{p} - i}{r} , \quad (\text{B.8})$$

and introduce the radial component α_r of the $\boldsymbol{\alpha}$ operator, where

$$\alpha_r = \frac{\boldsymbol{\alpha} \cdot \mathbf{r}}{r} ; \quad (\text{B.9})$$

this obeys the relation

$$\alpha_r^2 = 1 . \quad (\text{B.10})$$

For any pair of vectors \mathbf{a} and \mathbf{b} , the following equations hold:

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i \boldsymbol{\sigma} \cdot \mathbf{a} \times \mathbf{b} \quad (\text{B.11})$$

and

$$(\boldsymbol{\alpha} \cdot \mathbf{a})(\boldsymbol{\alpha} \cdot \mathbf{b}) = (\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) . \quad (\text{B.12})$$

As a consequence,

$$(\boldsymbol{\alpha} \cdot \mathbf{r})(\boldsymbol{\alpha} \cdot \mathbf{p}) = r p_r + i \beta \mathcal{K} . \quad (\text{B.13})$$

This last equation is equivalent to

$$(\boldsymbol{\alpha} \cdot \mathbf{p}) = \alpha_r \left(p_r + \frac{i\beta\mathcal{K}}{r} \right). \quad (\text{B.14})$$

As a result, the Dirac equation with the Hamiltonian

$$H = \alpha_r \left(p_r + \frac{i\beta\mathcal{K}}{r} \right) + \beta m + V(r) \quad (\text{B.15})$$

can be rewritten as the following:

$$\left[\alpha_r \left(p_r + \frac{i\beta\mathcal{K}}{r} \right) + \beta m + V(r) \right] \phi = E \phi. \quad (\text{B.16})$$

The operators β , \mathcal{K} , L^2 and J_z are mutually commutative. In the following, \mathcal{X} indicates an eigenvector common to those operators, so that

$$\beta \mathcal{X} = \mathcal{X}, \quad (\text{B.17})$$

$$\mathcal{K} \mathcal{X} = -k \mathcal{X}, \quad (\text{B.18})$$

$$L^2 \mathcal{X} = l(l+1) \mathcal{X}, \quad (\text{B.19})$$

$$J_z \mathcal{X} = m_j \mathcal{X}. \quad (\text{B.20})$$

Introducing the function \mathcal{Y} , where

$$\mathcal{Y} = -\alpha_r \mathcal{X}, \quad (\text{B.21})$$

we can observe that it has the following properties:

$$\mathcal{X} = -\alpha_r \mathcal{Y}, \quad (\text{B.22})$$

$$\mathcal{K} \mathcal{Y} = -k \mathcal{Y}, \quad (\text{B.23})$$

$$\beta \mathcal{Y} = \alpha_r \beta \mathcal{X} = -\mathcal{Y}. \quad (\text{B.24})$$

Let us now consider the following linear combination of \mathcal{X} and \mathcal{Y} :

$$\phi = F(r) \mathcal{Y} + iG(r) \mathcal{X}, \quad (\text{B.25})$$

which is an eigenvector common to H , \mathcal{K} and J_z and thus the spinor we are looking for.

Our objective is to determine the functions $F(r)$ and $G(r)$. The eigenvalues of L^2 are $(j \pm 1/2)(j \pm 1/2 + 1)$. As $\mathcal{K} = \beta(\mathbf{J}^2 - L^2 + 1/4)$, we have, for the case $j = l + 1/2$ (spin up),

$$k = -\left(j + \frac{1}{2}\right) = -(l + 1) . \quad (\text{B.26})$$

In the other case, where $j = l - 1/2$ (spin down),

$$k = \left(j + \frac{1}{2}\right) = l . \quad (\text{B.27})$$

We are now able to find the equations corresponding to the radial behaviour of the functions F and G . In order to do this, let us consider the Dirac equation (B.16) and observe the following:

$$\alpha_r p_r F(r) \mathcal{Y} = i \left[\frac{dF(r)}{dr} + \frac{F(r)}{r} \right] \mathcal{X} , \quad (\text{B.28})$$

$$i \alpha_r p_r G(r) \mathcal{X} = - \left[\frac{dG(r)}{dr} + \frac{G(r)}{r} \right] \mathcal{Y} , \quad (\text{B.29})$$

$$\frac{i \alpha_r \beta \mathcal{K}}{r} F(r) \mathcal{Y} = -\frac{i}{r} F(r) k \mathcal{X} , \quad (\text{B.30})$$

$$\frac{i \alpha_r \beta \mathcal{K}}{r} i G(r) \mathcal{X} = -\frac{1}{r} G(r) k \mathcal{Y} , \quad (\text{B.31})$$

$$\beta m F(r) \mathcal{Y} = -m F(r) \mathcal{Y} , \quad (\text{B.32})$$

$$\beta m i G(r) \mathcal{X} = i m G(r) \mathcal{X} . \quad (\text{B.33})$$

Hence, since \mathcal{X} and \mathcal{Y} belong to different eigenvalues of β and are, consequently, linearly independent, the fundamental equations of the theory of the elastic scattering of electrons (and positrons) by atoms are

$$[E + m - V(r)]F(r) + \frac{dG(r)}{dr} + \frac{1+k}{r}G(r) = 0 , \quad (\text{B.34})$$

$$- [E - m - V(r)]G(r) + \frac{dF(r)}{dr} + \frac{1-k}{r}F(r) = 0 . \quad (\text{B.35})$$

B.2 Relativistic Partial Wave Expansion Method

The fundamental equation of relativistic quantum mechanics is the Dirac equation. The wave function, as is well known, is a four-component spinor, and the asymptotic forms of the four components of the scattered wave are

$$\Psi_i \underset{r \rightarrow \infty}{\sim} a_i \exp(iKz) + b_i(\theta, \phi) \frac{\exp(iKr)}{r}, \quad (\text{B.36})$$

where $K = mv/\hbar$ is the electron momentum in the z direction.

The differential elastic scattering cross-section is given by

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{|b_1|^2 + |b_2|^2 + |b_3|^2 + |b_4|^2}{|a_1|^2 + |a_2|^2 + |a_3|^2 + |a_4|^2} \\ &= \frac{|b_1|^2 + |b_2|^2 + c|b_1|^2 + c|b_2|^2}{|a_1|^2 + |a_2|^2 + c|a_1|^2 + c|a_2|^2} \\ &= \frac{|b_1|^2 + |b_2|^2}{|a_1|^2 + |a_2|^2}, \end{aligned} \quad (\text{B.37})$$

where c is a constant of proportionality which takes into account the fact that the a_i and the b_i coefficients are not all independent. Indeed, asymptotically the scattered wave is made up of plane waves proceeding, from the centre, in various directions; the coefficients of the solutions for a plane wave are not all independent.

If the spin is parallel to the direction of incidence (spin up), $a_1 = 1$, $a_2 = 0$, $b_1 = f^+(\theta, \phi)$, $b_2 = g^+(\theta, \phi)$, where f^+ and g^+ are two scattering amplitudes.

The asymptotic behaviour is described by the following equations:

$$\Psi_1 \underset{r \rightarrow \infty}{\sim} \exp(iKz) + f^+(\theta, \phi) \frac{\exp(iKr)}{r}, \quad (\text{B.38})$$

$$\Psi_2 \underset{r \rightarrow \infty}{\sim} g^+(\theta, \phi) \frac{\exp(iKr)}{r}. \quad (\text{B.39})$$

The case of spin antiparallel to the direction of incidence (spin down) corresponds to $a_1 = 0$, $a_2 = 1$, $b_1 = g^-(\theta, \phi)$, $b_2 = f^-(\theta, \phi)$. The asymptotic behaviour is now given by

$$\Psi_1 \underset{r \rightarrow \infty}{\sim} g^-(\theta, \phi) \frac{\exp(iKr)}{r}, \quad (\text{B.40})$$

$$\Psi_2 \underset{r \rightarrow \infty}{\sim} \exp(iKz) + f^-(\theta, \phi) \frac{\exp(iKr)}{r}. \quad (\text{B.41})$$

The Dirac equations for an electron in a central field are given by the following (see previous section):

$$[E + m - V(r)]F_l^\pm(r) + \frac{dG_l^\pm(r)}{dr} + \frac{1+k}{r}G_l^\pm(r) = 0, \quad (\text{B.42})$$

$$- [E - m - V(r)]G_l^\pm(r) + \frac{dF_l^\pm(r)}{dr} + \frac{1-k}{r}F_l^\pm(r) = 0. \quad (\text{B.43})$$

The superscript “+” refers to the electrons with spin up ($k = -(l + 1)$) while “-” refers to electrons with spin down ($k = l$). Once the new variables

$$\mu(r) \equiv E + m - V(r), \quad (\text{B.44})$$

$$\nu(r) \equiv E - m - V(r), \quad (\text{B.45})$$

$$\mu' = \frac{d\mu}{dr} \quad (\text{B.46})$$

have been introduced, the Dirac equations become

$$F_l^\pm(r) = -\frac{1}{\mu} \left(\frac{dG_l^\pm}{dr} + \frac{1+k}{r}G_l^\pm \right) \quad (\text{B.47})$$

and

$$\begin{aligned} \frac{dF_l^\pm}{dr} &= \frac{\mu'}{\mu^2} \left(\frac{dG_l^\pm}{dr} + \frac{1+k}{r}G_l^\pm \right) \\ &- \frac{1}{\mu} \left(\frac{d^2G_l^\pm}{dr^2} + \frac{1+k}{r} \frac{dG_l^\pm}{dr} - \frac{1+k}{r^2}G_l^\pm \right). \end{aligned} \quad (\text{B.48})$$

Therefore, after simple algebraic manipulations, we obtain the following:

$$\frac{d^2G_l^\pm}{dr^2} + \left(\frac{2}{r} - \frac{\mu'}{\mu} \right) \frac{dG_l^\pm}{dr} + \left(\mu\nu - \frac{k(k+1)}{r^2} - \frac{1+k}{r} \frac{\mu'}{\mu} \right) G_l^\pm = 0. \quad (\text{B.49})$$

Let us now introduce the function \mathcal{G}_l^\pm , where

$$\mathcal{G}_l^\pm \equiv \frac{r}{\mu^{1/2}} G_l^\pm. \quad (\text{B.50})$$

Upon observing that

$$K^2 = E^2 - m^2, \quad (\text{B.51})$$

it is possible to see that

$$\mu\nu = K^2 - 2EV + V^2. \quad (\text{B.52})$$

We conclude that, once the function $U_l^\pm(r)$ has been defined, i.e.

$$-U_l^\pm(r) = -2EV + V^2 - \frac{k}{r} \frac{\mu'}{\mu} + \frac{1}{2} \frac{\mu''}{\mu} - \frac{3}{4} \frac{\mu'^2}{\mu^2}, \quad (\text{B.53})$$

the following equation holds:

$$\left[\frac{d^2}{dr^2} - \frac{k(k+1)}{r^2} + K^2 - U_l^\pm(r) \right] \mathcal{G}_l^\pm = 0. \quad (\text{B.54})$$

For large values of r , \mathcal{G}_l^\pm is essentially sinusoidal. Indeed, when r is large enough, $V(r)$ and U_l^\pm are negligible and the solution of the equation is therefore a linear combination of the regular and irregular spherical Bessel functions multiplied by Kr . Taking account of the fact that $\mathcal{G}_l^\pm = (r/\mu^{1/2}) G_l^\pm$, we can therefore conclude that

$$G_l^\pm \underset{r \rightarrow \infty}{\sim} j_l(Kr) \cos \eta_l^\pm - n_l(Kr) \sin \eta_l^\pm. \quad (\text{B.55})$$

Here η_l^\pm are constants to be determined. Taking into account the asymptotic behaviour of the Bessel functions,

$$j_l(Kr) \underset{r \rightarrow \infty}{\sim} \frac{1}{Kr} \sin \left(Kr - \frac{l\pi}{2} \right), \quad (\text{B.56})$$

$$n_l(Kr) \underset{r \rightarrow \infty}{\sim} -\frac{1}{Kr} \cos \left(Kr - \frac{l\pi}{2} \right), \quad (\text{B.57})$$

we can conclude that

$$G_l^\pm \underset{r \rightarrow \infty}{\sim} \frac{1}{Kr} \sin \left(Kr - \frac{l\pi}{2} \right) \cos \eta_l^\pm + \frac{1}{Kr} \cos \left(Kr - \frac{l\pi}{2} \right) \sin \eta_l^\pm. \quad (\text{B.58})$$

Therefore,

$$G_l^+ \underset{r \rightarrow \infty}{\sim} \frac{1}{Kr} \sin \left(Kr - \frac{l\pi}{2} + \eta_l^+ \right), \quad (\text{B.59})$$

and

$$G_l^- \underset{r \rightarrow \infty}{\sim} \frac{1}{Kr} \sin \left(Kr - \frac{l\pi}{2} + \eta_l^- \right). \quad (\text{B.60})$$

The phase shifts η_l^\pm represent the effect of the potential $V(r)$ on the phases of the scattered waves.

Before proceeding, we need to demonstrate the following equation:

$$\exp(iKr \cos \theta) = \sum_{l=0}^{\infty} (2l+1) i^l j_l(Kr) P_l(\cos \theta), \quad (\text{B.61})$$

where $P_l(\cos \theta)$ are the Legendre polynomials and $j_l(Kr)$ the spherical Bessel functions. In order to demonstrate this, let us first observe that a plane wave describing a free particle with the z axis in the direction of \mathbf{K} may be expressed as an expansion in a series of Legendre polynomials $P_l(\cos \theta)$:

$$\exp(iKz) = \exp(iKr \cos \theta) = \sum_{l=0}^{\infty} c_l j_l(Kr) P_l(\cos \theta) . \quad (\text{B.62})$$

Let us define the two new variables $s \equiv Kr$ and $t \equiv \cos \theta$, to have

$$\exp(ist) = \sum_l c_l j_l(s) P_l(t) . \quad (\text{B.63})$$

Differentiating with respect to s ,

$$it \exp(ist) = \sum_l it c_l j_l(s) P_l(t) = \sum_l c_l \frac{dj_l(s)}{ds} P_l(t) . \quad (\text{B.64})$$

Recalling the properties of the Legendre polynomials, we have:

$$P_l(t) = \frac{(l+1)P_{l+1}(t) + lP_{l-1}(t)}{t(2l+1)} . \quad (\text{B.65})$$

Therefore,

$$\begin{aligned} it \exp(ist) &= \sum_l it c_l j_l(s) \frac{(l+1)P_{l+1}(t) + lP_{l-1}(t)}{t(2l+1)} \\ &= \sum_l i P_l(t) \left[\frac{l}{2l-1} c_{l-1} j_{l-1}(s) + \frac{l+1}{2l+3} c_{l+1} j_{l+1}(s) \right] . \end{aligned} \quad (\text{B.66})$$

On the other hand, it is well known that

$$\frac{dj_l(s)}{ds} = \frac{l}{2l+1} j_{l-1}(s) - \frac{l+1}{2l+1} j_{l+1}(s) , \quad (\text{B.67})$$

and as a consequence,

$$it \exp(ist) = \sum_l c_l P_l(t) \left[\frac{l}{2l+1} j_{l-1}(s) - \frac{l+1}{2l+1} j_{l+1}(s) \right] . \quad (\text{B.68})$$

Consequently, from (B.66) and (B.68), the following is obtained:

$$\sum_l P_l(t) \left[j_{l-1}(s) l \left(\frac{c_l}{2l+1} - \frac{ic_{l-1}}{2l-1} \right) - j_{l+1}(s) (l+1) \left(\frac{c_l}{2l+1} + \frac{ic_{l+1}}{2l+3} \right) \right] = 0. \quad (\text{B.69})$$

The Legendre polynomials $P_l(t)$ are linearly independent (orthonormal), and therefore

$$\begin{aligned} & j_{l-1}(s) l \left(\frac{c_l}{2l+1} - \frac{ic_{l-1}}{2l-1} \right) \\ &= j_{l+1}(s) (l+1) \left(\frac{c_l}{2l+1} + \frac{ic_{l+1}}{2l+3} \right). \end{aligned} \quad (\text{B.70})$$

Every value of s satisfies the last equation if and only if

$$\frac{1}{2l+1} c_l = \frac{i}{2l-1} c_{l-1}. \quad (\text{B.71})$$

In order to obtain an explicit expression for c_l we need to know the value of the first coefficient of the set, i.e. c_0 . Imposing $r = 0$ in (B.62), we obtain

$$\exp(0) = 1 = \sum_l c_l j_l(0) P_l(\cos \theta). \quad (\text{B.72})$$

Since $j_l(0) = 0$ for any $l \neq 0$, while $j_0(0) = 1$ and $P_0(\cos \theta) = 1$, we may conclude that $c_0 = 1$. The recursive repetition of the relation (B.71) allows us to obtain the values of the coefficients,

$$c_l = (2l+1)i^l, \quad (\text{B.73})$$

and the expansion of the plane wave in Legendre polynomials,

$$\exp(iKr \cos \theta) = \exp(iKz) = \sum_{l=0}^{\infty} (2l+1)i^l j_l(Kr) P_l(\cos \theta). \quad (\text{B.74})$$

Let us remind the reader that we are looking for functions Ψ_1 and Ψ_2 which satisfy the asymptotic conditions. So, we must begin by expanding them in spherical harmonics:

$$\Psi_1 = \sum_{l=0}^{\infty} [A_l G_l^+ + B_l G_l^-] P_l(\cos \theta), \quad (\text{B.75})$$

$$\Psi_2 = \sum_{l=1}^{\infty} [C_l G_l^+ + D_l G_l^-] P_l^1(\cos \theta) \exp(i\phi), \quad (\text{B.76})$$

where $P_l^1(\cos \theta)$ are the associated Legendre polynomials

$$P_l^1(x) = (1 - x^2)^{1/2} \frac{dP_l(x)}{dx}. \quad (\text{B.77})$$

The coefficients A_l , B_l , C_l and D_l can be determined by considering the asymptotic behaviours of the functions involved. Let us begin with the function Ψ_1 and observe that

$$\Psi_1 - \exp(iKz) = \sum_{l=0}^{\infty} [A_l G_l^+ + B_l G_l^- - (2l+1)i^l j_l(Kr)] P_l(\cos \theta). \quad (\text{B.78})$$

As

$$\Psi_1 - \exp(iKz) \underset{r \rightarrow \infty}{\sim} \frac{\exp(iKr)}{r} f^+(\theta, \phi), \quad (\text{B.79})$$

the following occurs:

$$\begin{aligned} & \frac{1}{Kr} \sum_{l=0}^{\infty} \left[A_l \sin \left(Kr - \frac{l\pi}{2} + \eta_l^+ \right) + B_l \sin \left(Kr - \frac{l\pi}{2} + \eta_l^- \right) \right. \\ & \left. - (2l+1)i^l \sin \left(Kr - \frac{l\pi}{2} \right) \right] P_l(\cos \theta) \\ & = \frac{\exp(iKr)}{r} f^+(\theta, \phi). \end{aligned} \quad (\text{B.80})$$

As a consequence,

$$\begin{aligned} & \frac{\exp(iKr)}{2iKr} \sum_{l=0}^{\infty} \exp \left(-i \frac{l\pi}{2} \right) \\ & \times [A_l \exp(i\eta_l^+) + B_l \exp(i\eta_l^-) - (2l+1)i^l] P_l(\cos \theta) \\ & - \frac{\exp(-iKr)}{2iKr} \sum_{l=0}^{\infty} \exp \left(i \frac{l\pi}{2} \right) \\ & \times [A_l \exp(-i\eta_l^+) + B_l \exp(-i\eta_l^-) - (2l+1)i^l] P_l(\cos \theta) \\ & = \frac{\exp(iKr)}{r} f^+(\theta, \phi). \end{aligned} \quad (\text{B.81})$$

The asymptotic conditions are satisfied if

$$A_l \exp(-i\eta_l^+) + B_l \exp(-i\eta_l^-) = (2l+1)i^l. \quad (\text{B.82})$$

With the choices

$$A_l = (l+1)i^l \exp(i\eta_l^+), \quad (\text{B.83})$$

$$B_l = li^l \exp(i\eta_l^-), \quad (\text{B.84})$$

(B.82) is satisfied.

Proceeding in a similar way for the Ψ_2 function, we obtain

$$C_l \exp(-i\eta_l^+) + D_l \exp(-i\eta_l^-) = 0, \quad (\text{B.85})$$

so that we can choose

$$C_l = -i^l \exp(i\eta_l^+), \quad (\text{B.86})$$

$$D_l = i^l \exp(i\eta_l^-), \quad (\text{B.87})$$

In conclusion, for electrons with spins parallel to the direction of incidence, we have

$$\Psi_1 = \sum_{l=0}^{\infty} [(l+1) \exp(i\eta_l^+) G_l^+ + l \exp(i\eta_l^-) G_l^-] i^l P_l(\cos \theta), \quad (\text{B.88})$$

$$\Psi_2 = \sum_{l=1}^{\infty} [\exp(i\eta_l^-) G_l^- - \exp(i\eta_l^+) G_l^+] i^l P_l^1(\cos \theta) \exp(i\phi), \quad (\text{B.89})$$

and, by using (B.81),

$$\begin{aligned} f^+(\theta, \phi) &= f^+(\theta) \\ &= \frac{1}{2iK} \sum_{l=0}^{\infty} \{(l+1)[\exp(2i\eta_l^+) - 1] \\ &\quad + l[\exp(2i\eta_l^-) - 1]\} P_l(\cos \theta), \end{aligned} \quad (\text{B.90})$$

$$g^+(\theta, \phi) = \frac{1}{2iK} \sum_{l=1}^{\infty} [\exp(2i\eta_l^-) - \exp(2i\eta_l^+)] P_l^1(\cos \theta) \exp(i\phi). \quad (\text{B.91})$$

For electrons with spins antiparallel to the direction of incidence (spin down), where we indicate the scattering amplitudes by f^- and g^- , we can see that

$$f^-(\theta, \phi) = f^+(\theta, \phi) \quad (\text{B.92})$$

and

$$g^-(\theta, \phi) = -g^+(\theta, \phi) \exp(-2i\phi). \quad (\text{B.93})$$

It is therefore convenient to define the functions

$$f(\theta) = \sum_{l=0}^{\infty} \mathcal{A}_l P_l(\cos \theta), \quad (\text{B.94})$$

$$g(\theta) = \sum_{l=0}^{\infty} \mathcal{B}_l P_l^1(\cos \theta) , \quad (\text{B.95})$$

where

$$\mathcal{A}_l = \frac{1}{2iK} \{ (l+1) [\exp(2i\eta_l^+) - 1] + l [\exp(2i\eta_l^-) - 1] \} , \quad (\text{B.96})$$

$$\mathcal{B}_l = \frac{1}{2iK} \{ \exp(2i\eta_l^-) - \exp(2i\eta_l^+) \} . \quad (\text{B.97})$$

With this notation, we have

$$f^+ = f^- = f , \quad (\text{B.98})$$

$$g^+ = g \exp(i\phi) \quad (\text{B.99})$$

and

$$g^- = -g \exp(-i\phi) . \quad (\text{B.100})$$

For an arbitrary spin direction, the electron incident plane wave will be given by $\Psi_1 = A \exp(iKz)$ and $\Psi_2 = B \exp(iKz)$, and as a consequence $a_1 = A$, $a_2 = B$. Furthermore,

$$b_1 = Af^+ + Bg^- = Af - Bg \exp(-i\phi) , \quad (\text{B.101})$$

$$b_2 = Ag^+ + Bf^- = Bf + Ag \exp(i\phi) . \quad (\text{B.102})$$

Consequently,

$$\begin{aligned} & \frac{d\sigma}{d\Omega} \\ &= (|f|^2 + |g|^2) \left\{ 1 + iS(\theta) \left[\frac{AB^* \exp(i\phi) - A^*B \exp(-i\phi)}{|A|^2 + |B|^2} \right] \right\} , \end{aligned} \quad (\text{B.103})$$

where $S(\theta)$ is the Sherman function, defined by

$$S(\theta) = i \frac{fg^* - f^*g}{|f|^2 + |g|^2} . \quad (\text{B.104})$$

Note that

$$i \frac{AB^* \exp(i\phi) - A^*B \exp(-i\phi)}{|A|^2 + |B|^2} = \xi^\dagger (\sigma_y \cos \phi - \sigma_x \sin \phi) \xi , \quad (\text{B.105})$$

where σ_x , σ_y and σ_z are the Pauli matrices and ξ is the two-component spinor

$$\xi = \begin{pmatrix} A/\sqrt{|A|^2 + |B|^2} \\ B/\sqrt{|A|^2 + |B|^2} \end{pmatrix}, \quad (\text{B.106})$$

$$\xi^\dagger = \begin{pmatrix} \frac{A^*}{\sqrt{|A|^2 + |B|^2}} & \frac{B^*}{\sqrt{|A|^2 + |B|^2}} \end{pmatrix}. \quad (\text{B.107})$$

As the z axis has been chosen along the incidence direction, the unit vector perpendicular to the plane of scattering is given by

$$\hat{\mathbf{n}} = (-\sin \phi, \cos \phi, 0), \quad (\text{B.108})$$

so we can write

$$\xi^\dagger (\sigma_y \cos \phi - \sigma_x \sin \phi) \xi = \mathbf{P} \cdot \hat{\mathbf{n}}, \quad (\text{B.109})$$

where \mathbf{P} is the initial polarization vector of the electron beam. The differential elastic scattering cross-section can then be recast as follows:

$$\frac{d\sigma}{d\Omega} = (|f|^2 + |g|^2)[1 + S(\theta)\mathbf{P} \cdot \hat{\mathbf{n}}]. \quad (\text{B.110})$$

Note that, if the beam is completely unpolarised, then $\mathbf{P} = 0$ and

$$\frac{d\sigma}{d\Omega} = |f|^2 + |g|^2. \quad (\text{B.111})$$

The total elastic scattering cross-section (σ_{el}) and the transport cross-section (σ_{tr}) are defined by

$$\sigma_{\text{el}} = 2\pi \int_0^\pi \frac{d\sigma}{d\Omega} \sin \theta \, d\theta, \quad (\text{B.112})$$

$$\sigma_{\text{tr}} = 2\pi \int_0^\pi (1 - \cos \theta) \frac{d\sigma}{d\Omega} \sin \theta \, d\theta, \quad (\text{B.113})$$

which can be easily calculated by numerical integration.

Note that by assigning

$$\eta_l^- = \eta_l^+ = \eta_l \quad (\text{B.114})$$

in the previous equations, we can obtain the non-relativistic results. Indeed,

$$\begin{aligned} \mathcal{A}_l &= \frac{1}{2iK} \{ (l+1)[\exp(2i\eta_l) - 1] + l[\exp(2i\eta_l) - 1] \} \\ &= \frac{1}{2iK} (2l+1)[\exp(2i\eta_l) - 1], \end{aligned} \quad (\text{B.115})$$

$$\mathcal{B}_l = 0, \quad (\text{B.116})$$

so that

$$\begin{aligned} f(\theta) &= \frac{1}{2iK} \sum_{l=0}^{\infty} (2l+1) [\exp(2i\eta_l) - 1] P_l(\cos \theta) \\ &= \frac{1}{K} \sum_{l=0}^{\infty} (2l+1) \exp(i\eta_l) \sin \eta_l P_l(\cos \theta) , \end{aligned} \quad (\text{B.117})$$

$$g(\theta) = 0 \quad (\text{B.118})$$

and

$$\frac{d\sigma}{d\Omega} = |f|^2 . \quad (\text{B.119})$$

B.3 Phase Shift Calculations

In order to proceed, it is useful to perform the following transformation [6]:

$$F_l^\pm(r) = a_l^\pm(r) \frac{\sin \phi_l^\pm(r)}{r} , \quad (\text{B.120})$$

$$G_l^\pm(r) = a_l^\pm(r) \frac{\cos \phi_l^\pm(r)}{r} . \quad (\text{B.121})$$

After simple algebraic manipulations, (B.42) and (B.43) become

$$\begin{aligned} [E + m - V(r)] \tan \phi_l^\pm(r) + \frac{1}{a_l^\pm(r)} \frac{da_l^\pm(r)}{dr} \\ - \tan \phi_l^\pm(r) \frac{d\phi_l^\pm(r)}{dr} + \frac{k}{r} = 0 , \end{aligned} \quad (\text{B.122})$$

$$\begin{aligned} -[E - m - V(r)] \cot \phi_l^\pm(r) + \frac{1}{a_l^\pm(r)} \frac{da_l^\pm(r)}{dr} \\ + \cot \phi_l^\pm(r) \frac{d\phi_l^\pm(r)}{dr} - \frac{k}{r} = 0 , \end{aligned} \quad (\text{B.123})$$

and therefore

$$\frac{d\phi_l^\pm(r)}{dr} = \frac{k}{r} \sin 2\phi_l^\pm(r) - m \cos 2\phi_l^\pm(r) + E - V(r) , \quad (\text{B.124})$$

$$\frac{1}{a_l^\pm(r)} \frac{da_l^\pm(r)}{dr} = -\frac{k}{r} \cos 2\phi_l^\pm(r) - m \sin 2\phi_l^\pm(r) . \quad (\text{B.125})$$

For $0 < r < \hbar/mc$, the spherical symmetric electrostatic potential experienced by a point charge at distance r from the nucleus, $V(r)$, may be approximated by the following:

$$V(r) \underset{r \rightarrow 0}{\sim} -\frac{Z_0 + Z_1 r + Z_2 r^2 + Z_3 r^3}{r} . \quad (\text{B.126})$$

Expressing the electrostatic potential as the product of the potential of a bare nucleus multiplied by a screening function $\psi(r)$ having the analytical form

$$\psi(r) = \sum_{i=1}^p A_i \exp(-\alpha_i r) , \quad (\text{B.127})$$

$$\sum_{i=1}^p A_i = 1 , \quad (\text{B.128})$$

we can easily evaluate Z_0 , Z_1 , Z_2 and Z_3 :

$$Z_0 = Ze^2 \sum_{i=1}^p A_i = Ze^2 , \quad (\text{B.129})$$

$$Z_1 = -Z_0 \sum_{i=1}^p \alpha_i A_i , \quad (\text{B.130})$$

$$Z_2 = \frac{Z_0}{2} \sum_{i=1}^p \alpha_i^2 A_i , \quad (\text{B.131})$$

$$Z_3 = -\frac{Z_0}{6} \sum_{i=1}^p \alpha_i^3 A_i . \quad (\text{B.132})$$

Let us expand ϕ_l^\pm as a power series

$$\phi_l^\pm(r) = \phi_{l0}^\pm + \phi_{l1}^\pm r + \phi_{l2}^\pm r^2 + \phi_{l3}^\pm r^3 + \dots . \quad (\text{B.133})$$

As we can see, after simple algebraic manipulations, the relationships between the coefficients of this expansion and Z_0 , Z_1 , Z_2 and Z_3 are the following [7]:

$$\sin 2\phi_{l0}^\pm = -\frac{Z_0}{k} , \quad (\text{B.134})$$

$$\phi_{l1}^{\pm} = \frac{E + Z_1 - m \cos 2\phi_{l0}^{\pm}}{1 - 2k \cos 2\phi_{l0}^{\pm}}, \quad (\text{B.135})$$

$$\phi_{l2}^{\pm} = \frac{2\phi_{l1}^{\pm} \sin 2\phi_{l0}^{\pm}(m - k\phi_{l1}^{\pm}) + Z_2}{2 - 2k \cos 2\phi_{l0}^{\pm}}, \quad (\text{B.136})$$

$$\phi_{l3}^{\pm} = \frac{2\phi_{l2}^{\pm} \sin 2\phi_{l0}^{\pm}(m - 2k\phi_{l1}^{\pm}) + 2\phi_{l1}^{\pm 2} \cos 2\phi_{l0}^{\pm}[m - (2/3)k\phi_{l1}^{\pm}] + Z_3}{3 - 2k \cos 2\phi_{l0}^{\pm}}, \quad (\text{B.137})$$

with the extra conditions

$$0 \leq 2\phi_{l0}^{\pm} \leq \frac{1}{2}\pi \quad (\text{B.138})$$

if $k < 0$, and

$$\pi \leq 2\phi_{l0}^{\pm} \leq \frac{3}{2}\pi \quad (\text{B.139})$$

if $k > 0$.

Let us now calculate the phase shifts, examining (B.121):

$$G_l^{\pm} = \frac{a_l^{\pm} \cos \phi_l^{\pm}(r)}{r} - \frac{a_l^{\pm}}{r} \sin \phi_l^{\pm}(r) \phi_l^{\pm}(r) - \frac{a_l^{\pm} \cos \phi_l^{\pm}(r)}{r^2}, \quad (\text{B.140})$$

so that

$$\frac{G_l^{\pm}}{G_l^{\pm}} = \frac{a_l^{\pm}}{a_l^{\pm}} - \phi_l^{\pm}(r) \tan \phi_l^{\pm}(r) - \frac{1}{r}, \quad (\text{B.141})$$

or

$$\frac{G_l^{\pm}}{G_l^{\pm}} = -(E + m - V) \tan \phi_l^{\pm}(r) - \frac{1 + k}{r}. \quad (\text{B.142})$$

Let us observe that the asymptotic form of the solution in the regions corresponding to large values of r for which $V(r) \approx 0$ is (see (B.55))

$$G_l^{\pm} = j_l(Kr) \cos \eta_l^{\pm} - n_l(Kr) \sin \eta_l^{\pm}, \quad (\text{B.143})$$

where $K^2 = E^2 - m^2$, η_l^{\pm} are the l th phase shifts, and j_l and n_l are respectively the regular and irregular spherical Bessel functions. Therefore,

$$\frac{G_l^{\pm}}{G_l^{\pm}} = \frac{K j_l'(Kr) \cos \eta_l^{\pm} - K n_l'(Kr) \sin \eta_l^{\pm}}{j_l(Kr) \cos \eta_l^{\pm} - n_l(Kr) \sin \eta_l^{\pm}}. \quad (\text{B.144})$$

Taking into account the properties of the Bessel functions

$$j'_l(x) = \frac{l}{x} j_l(x) - j_{l+1}(x) , \quad (\text{B.145})$$

$$n'_l(x) = \frac{l}{x} n_l(x) - n_{l+1}(x) , \quad (\text{B.146})$$

we can conclude that

$$\tan \eta_l^\pm = \frac{(l/r)j_l(Kr) - Kj_{l+1}(Kr) - j_l(Kr)(G_l^\pm/G_l^\pm)}{(l/r)n_l(Kr) - Kn_{l+1}(Kr) - n_l(Kr)(G_l^\pm/G_l^\pm)} . \quad (\text{B.147})$$

Let us define

$$\tilde{\phi}_l^\pm = \lim_{r \rightarrow \infty} \phi_l^\pm(r) . \quad (\text{B.148})$$

For large values of r , (B.142) becomes

$$\frac{G_l^\pm}{G_l^\pm} = -(E + m) \tan \tilde{\phi}_l^\pm - \frac{1 + k}{r} , \quad (\text{B.149})$$

and therefore

$$\tan \eta_l^\pm = \frac{Kj_{l+1}(Kr) - j_l(Kr)[(E + m) \tan \tilde{\phi}_l^\pm + (1 + l + k)/r]}{Kn_{l+1}(Kr) - n_l(Kr)[(E + m) \tan \tilde{\phi}_l^\pm + (1 + l + k)/r]} . \quad (\text{B.150})$$

Using this last equation, we can calculate the phase shifts of the scattered wave and, therefore, the functions $f(\theta)$, $g(\theta)$ and the differential elastic scattering cross-section.

B.4 Analytic Approximation of the Mott Cross-Section

Taking advantage of the simple closed form of the equations deduced starting by the Rutherford cross-section, it is sometimes possible to look for an approximation where similar equations are used for the Mott cross-section [8, 9]. For low atomic number elements, the Mott differential elastic scattering cross-section can be roughly approximated by the following equation:

$$\frac{d\sigma_{el}}{d\Omega} = \frac{\Phi}{(1 - \cos \theta + \Psi)^2} , \quad (\text{B.151})$$

where the unknown parameters Φ and Ψ are calculated with the aim to get the best fit of the total and the first transport elastic scattering cross-section previously calculated using the relativistic partial wave expansion method. With

$$\Phi = \frac{Z^2 e^2}{4E^2} \quad (\text{B.152})$$

and

$$\Psi = \frac{m e^4 \pi^2 Z^{2/3}}{h^2 E} \quad (\text{B.153})$$

Equation (B.151) becomes the screened Rutherford formula.

Once we know the total elastic scattering cross-section and of the transport elastic scattering cross-section previously calculated using the Mott theory, we can now calculate Φ and Ψ in order to approximate the Mott theory [8]. From (B.112), it follows that:

$$\sigma_{\text{el}} = \frac{4\pi\Phi}{\Psi(\Psi + 2)}. \quad (\text{B.154})$$

As a consequence the differential elastic scattering cross-section can be rewritten as:

$$\frac{d\sigma_{\text{el}}}{d\Omega} = \frac{\sigma_{\text{el}}}{4\pi} \frac{\Psi(\Psi + 2)}{(1 - \cos\theta + \Psi)^2} \quad (\text{B.155})$$

Using (B.113) and (B.155) it is possible to obtain the ratio \mathcal{E} between the transport and the total elastic scattering cross-sections:

$$\mathcal{E} \equiv \frac{\sigma_{\text{tr}}}{\sigma_{\text{el}}} = \Psi \left[\frac{\Psi + 2}{2} \ln \left(\frac{\Psi + 2}{\Psi} \right) - 1 \right]. \quad (\text{B.156})$$

Once the values of the total and transport elastic scattering cross-sections have been numerically calculated using the relativistic partial wave expansion method, the ratio \mathcal{E} is determined as a function of electron kinetic energy E . In such a way it is possible to get the screening parameter Ψ as a function of E (using a bisection algorithm).

B.5 The Atomic Potential

The atomic potential can be approximated as a superimposition of Yukawa potentials which depend on a number of parameters. Such parameters have been determined by analytical fitting of self-consistent fields. Cox and Bonham [10] proposed an analytical approximation of the Hartree–Fock wavefunctions calculated by Clementi [11] for $Z = 1 - 54$, while Salvat et al. [12], gave an analytical approximation of their numerical calculation of the Dirac–Hartree–Fock–Slater atomic potential for $Z = 1 - 92$.

The atomic screening function $\psi(r)$ is defined as the ratio between the electrostatic potential experienced by a point charge at a distance r from the nucleus and the electrostatic potential of the bare nucleus (assuming spherical symmetry). The screening functions of Cox and Bonham and of Salvat et al. are given by (B.127) and

(B.128): $\psi(r) = \sum_{i=1}^p A_i \exp(-\alpha_i r)$, $\sum_{i=1}^p A_i = 1$, where p , A_i and α_i depend on the element and on the author. Note that such equations have the analytical form originally proposed by Molière in order to approximate the Thomas–Fermi screening function [13].

B.5.1 Electron Exchange

As electrons are identical particles, exchange effects have to be taken into account, since it can occur that the incident electron is captured by an atom and a new electron is emitted. Exchange effects are well described by adding, to the atomic potential described above, the Furness and McCarthy exchange potential [14]:

$$V_{\text{ex}} = \frac{1}{2}(E - V) - \frac{1}{2}[(E - V)^2 + 4\pi\rho e^2\hbar^2/m]^{1/2}. \quad (\text{B.157})$$

In this equation, E is the electron energy, V the electrostatic potential, ρ the atomic electron density (obtained by Poisson's equation), and e the electron charge.

B.5.2 Charge Cloud Polarization Effects

The polarization potential can be described, when the incident electron is relatively far from the target atom, by the so-called Buckingham potential [16]

$$V_{\text{pol}} = -\frac{1}{2} \frac{\alpha_d e^2}{(r^2 + d^2)^2}. \quad (\text{B.158})$$

Here α_d is the dipole polarizability of the atom. The cut-off parameter d is given by, according to Mittleman and Watson [17],

$$d^4 = 0.5\alpha_d a_0 Z^{-1/3} b_{\text{pol}}^2, \quad (\text{B.159})$$

where a_0 is the Bohr radius and [16]

$$b_{\text{pol}}^2 = \max[(E - 50)/16, 1], \quad (\text{B.160})$$

with E expressed in eV. According to Salvat et al. [16], in order to obtain a more accurate description of the charge cloud polarization effects, the long-range Buckingham potential has to be combined with the correlation potential. Such a potential can be calculated using the so-called local density approximation (LDA) [18]. According to the LDA, the correlation energy of the electron is calculated assuming that the

projectile were in a free-electron gas whose density is given by the local atomic electron density.

B.5.3 Solid-State Effects

For atoms bound in solids, the outer orbitals are modified, so that solid-state effects should be introduced. In the so-called *muffin-tin* model, the potential of every atom in the solid is changed by the nearest-neighbor atoms. If we assume that the nearest-neighbor atoms are located at distances equal to $2r_{\text{ws}}$, where r_{ws} is the radius of the Wigner–Seitz sphere [15], then the potential can be calculated, for $r \leq r_{\text{ws}}$, as follows

$$V_{\text{solid}}(r \leq r_{\text{ws}}) = V(r) + V(2r_{\text{ws}} - r) - 2V(r_{\text{ws}}). \quad (\text{B.161})$$

It is equal to zero outside the Wigner–Seitz sphere, i.e.,

$$V_{\text{solid}}(r \geq r_{\text{ws}}) = 0. \quad (\text{B.162})$$

The term $2V(r_{\text{ws}})$ was introduced in (B.161) to shift the energy scale so that $V_{\text{solid}}(r = r_{\text{ws}}) = 0$. According to Salvat and Mayol, it also has to be subtracted from the kinetic energy of the incident electrons [19].

B.6 Positron Differential Elastic Scattering Cross-Section

The electron differential elastic scattering cross-section shows diffraction-like structures. It is a typical quantum-mechanical phenomenon due to the interaction of the incident electron with the atomic electron cloud. On the contrary, the positron elastic scattering cross-section is a decreasing and monotonic Rutherford-like function [20, 21]. This is due to the different sign of the electric charges of electrons and positrons. Positrons are rejected by the atomic nucleus: as a consequence, they do not penetrate the atomic electron cloud as deeply as electrons do. Since electrons penetrate deeper into the core of atomic electrons, they draw closer to the nucleus than positron does. Thus, electrons can loop around the nucleus once or more times and electron outgoing wave—a superposition of the incoming and of the scattered wave—exhibits interference effects. This is just a semi-classical description that qualitatively explains the reason why the atomic electron cloud influences electrons more than positrons.

B.7 Summary

The Mott theory [1] (also known as the relativistic partial wave expansion method) was described in this chapter. It allows to calculate the electron elastic scattering cross-section. Atomic potential was described. Electron exchange, charge cloud polarization effects and solid state effects were also introduced. Differences among elastic scattering cross-sections of electrons and positrons were discussed.

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Appendix C

The Fröhlich Theory

The original version of the Fröhlich theory can be found in [1]. Also see [2] for further details. In his theory of the electron-phonon interaction, Fröhlich [1] considered, in particular, the interaction of free electrons with the longitudinal optical mode lattice vibrations. The interaction was described considering both phonon creation and phonon annihilation, corresponding to electron energy loss and to electrons energy gain, respectively. As the phonon generation probability is much higher than the phonon absorption probability, the latter is often neglected in Monte Carlo simulations. Furthermore, since, according to Ganachaud and Mokrani [3], the dispersion relation of the longitudinal phonons can be neglected in the optical branch, one can use a single phonon frequency. As a matter of fact, the Fröhlich theory adopts a single value of the frequency for all momenta, corresponding to a flat longitudinal optical branch. This approximation is quite reasonable and experimentally confirmed (see, for example, Fujii et al. [4] for the ionic crystal AgBr). In semiconductors the longitudinal optical branch is flat as well, as demonstrated both experimentally (see, for example, Nilsson and Neil for Ge [5] and Si [6]) and theoretically (see, for example, Gianozzi et al. for Si, Ge, GaAs, AlAs, GaSb, and AlSb [7]).

C.1 Electrons in Lattice Fields. Interaction Hamiltonian

According to Fröhlich [1], an electron traveling in a dielectric material polarizes the medium and the polarization reacts on the charged particle. Let us indicate with $\mathcal{P}(\mathbf{r})$ the electric polarization. The only source of the displacement vector, $\mathcal{D}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) + 4\pi\mathcal{P}(\mathbf{r})$, are the free charges. If \mathbf{r}_{el} represents the position of a single free electron, then

$$\nabla \cdot \mathcal{D} = -4\pi e \delta(\mathbf{r} - \mathbf{r}_{el}), \quad (\text{C.1})$$

where e is the electron charge. The electric polarization can be written as

$$\mathcal{P}(\mathbf{r}) = \mathcal{P}_{uv}(\mathbf{r}) + \mathcal{P}_{ir}(\mathbf{r}), \quad (\text{C.2})$$

where $\mathcal{P}_{\text{uv}}(\mathbf{r})$ and $\mathcal{P}_{\text{ir}}(\mathbf{r})$ are the polarizations corresponding, respectively, to the ultraviolet (atomic polarizability) and the infrared (displacement polarizability) optical absorptions [8]. They satisfy the harmonic oscillator equations

$$\frac{d^2\mathcal{P}_{\text{uv}}(\mathbf{r})}{dt^2} + \omega_{\text{uv}}^2\mathcal{P}_{\text{uv}}(\mathbf{r}) = \frac{\mathcal{D}(\mathbf{r}, \mathbf{r}_{\text{el}})}{\delta}, \quad (\text{C.3})$$

$$\frac{d^2\mathcal{P}_{\text{ir}}(\mathbf{r})}{dt^2} + \omega^2\mathcal{P}_{\text{ir}}(\mathbf{r}) = \frac{\mathcal{D}(\mathbf{r}, \mathbf{r}_{\text{el}})}{\gamma}. \quad (\text{C.4})$$

In these equations, ω_{uv} (atomic deformation) and ω (atomic displacement) are the angular frequencies for ultraviolet and infrared optical absorption, respectively, and δ and γ are constants that are related to the dielectric function.

To determine these constants, let us firstly consider the static case and indicate with ε_0 the static dielectric constant. Since

$$\mathcal{D}(\mathbf{r}) = \varepsilon_0 \mathcal{E}(\mathbf{r}), \quad (\text{C.5})$$

then

$$4\pi\mathcal{P}(\mathbf{r}) = \left[1 - \frac{1}{\varepsilon_0}\right]\mathcal{D}(\mathbf{r}). \quad (\text{C.6})$$

Furthermore, let us assume that the high frequency dielectric constant ε_∞ is determined in the hypothesis that the angular frequency ω_∞ of the external field is low compared with the atomic excitation frequencies ω_{uv} and high compared with the lattice vibrational frequencies ω [8]. Then $\mathcal{P}_{\text{ir}} \approx 0$, $d^2\mathcal{P}_{\text{uv}}/dt^2 \ll \omega_{\text{uv}}^2\mathcal{P}_{\text{uv}}(\mathbf{r})$, and $\mathcal{D}(\mathbf{r}) = \varepsilon_\infty \mathcal{E}(\mathbf{r})$, where ε_∞ is the high frequency dielectric constant ($\varepsilon_\infty^{1/2}$ is the refraction index). As a consequence, $\mathcal{P}_{\text{uv}}(\mathbf{r})$ can be approximated assuming that it has the value corresponding to a static field of the same strength [1]

$$4\pi\mathcal{P}_{\text{uv}}(\mathbf{r}) = \left[1 - \frac{1}{\varepsilon_\infty}\right]\mathcal{D}(\mathbf{r}) \quad (\text{C.7})$$

so that

$$4\pi\mathcal{P}_{\text{ir}}(\mathbf{r}) = \left[\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right]\mathcal{D}(\mathbf{r}) \quad (\text{C.8})$$

Since, in the static case, $d^2\mathcal{P}_{\text{uv}}/dt^2 = 0$ and $d^2\mathcal{P}_{\text{ir}}/dt^2 = 0$,

$$\mathcal{P}_{\text{uv}}(\mathbf{r}) = \frac{\mathcal{D}(\mathbf{r})}{\delta\omega_{\text{uv}}^2}, \quad (\text{C.9})$$

$$\mathcal{P}_{\text{ir}}(\mathbf{r}) = \frac{\mathcal{D}(\mathbf{r})}{\gamma\omega^2}, \quad (\text{C.10})$$

and hence we obtain

$$\frac{1}{\delta} = \frac{\omega_{uv}^2}{4\pi} \left(1 - \frac{1}{\varepsilon_\infty} \right), \quad (\text{C.11})$$

$$\frac{1}{\gamma} = \frac{\omega^2}{4\pi} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right). \quad (\text{C.12})$$

In order to describe a slow electron interacting with an ionic lattice field, Fröhlich considered the infrared contribution to the polarization and introduced the complex field $\mathcal{B}(\mathbf{r})$ such that

$$\mathcal{B}(\mathbf{r}) = \sqrt{\frac{\gamma\omega}{2\hbar}} \left(\mathcal{P}_{\text{ir}}(\mathbf{r}) + \frac{i}{\omega} \frac{d\mathcal{P}_{\text{ir}}(\mathbf{r})}{dt} \right). \quad (\text{C.13})$$

The phonon annihilation operators $a_{\mathbf{q}}$ are defined by the equation

$$\mathcal{B}(\mathbf{r}) = \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} a_{\mathbf{q}} \frac{\exp(i\mathbf{q} \cdot \mathbf{r})}{\sqrt{V}}, \quad (\text{C.14})$$

where $\mathcal{B}(\mathbf{r})$ is subject to a boundary condition over a cube of volume V . As a consequence

$$\left(\mathcal{P}_{\text{ir}}(\mathbf{r}) + \frac{i}{\omega} \frac{d\mathcal{P}_{\text{ir}}(\mathbf{r})}{dt} \right) = \sqrt{\frac{2\hbar}{\gamma\omega V}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} a_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (\text{C.15})$$

Taking the Hermitian adjoint we obtain

$$\left(\mathcal{P}_{\text{ir}}(\mathbf{r}) - \frac{i}{\omega} \frac{d\mathcal{P}_{\text{ir}}(\mathbf{r})}{dt} \right) = \sqrt{\frac{2\hbar}{\gamma\omega V}} \sum_{\mathbf{q}} \frac{\mathbf{q}}{q} a_{\mathbf{q}}^\dagger \exp(-i\mathbf{q} \cdot \mathbf{r}), \quad (\text{C.16})$$

so that

$$\mathcal{P}_{\text{ir}}(\mathbf{r}) = \sqrt{\frac{\hbar}{2\gamma\omega V}} \sum_{\mathbf{q}} \hat{\mathbf{q}} [a_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}) + a_{\mathbf{q}}^\dagger \exp(-i\mathbf{q} \cdot \mathbf{r})], \quad (\text{C.17})$$

where

$$\hat{\mathbf{q}} = \frac{\mathbf{q}}{q} \quad (\text{C.18})$$

and

$$q_i = \frac{2\pi}{L} n_i, \quad (\text{C.19})$$

with $n_i = 0, \pm 1, \pm 2, \dots$ and $L = V^{1/3}$. The quantities a_q^\dagger represent the phonon creation operators.

In order to write the interaction Hamiltonian, $\mathcal{H}_{\text{inter}}$, let's observe that the displacement vector \mathcal{D} is the external field that determines the crystal polarization. Since $\mathcal{D} = 0$ in the absence of free charges, the potential ϕ_{ir} is given by

$$-4\pi \mathcal{P}_{\text{ir}} = \mathcal{E} = -\nabla \phi_{\text{ir}}, \quad (\text{C.20})$$

so that

$$\begin{aligned} \mathcal{H}_{\text{inter}} &= e \phi_{\text{ir}} = \\ &4\pi i \sqrt{\frac{\hbar e^2}{2\gamma\omega V}} \sum_q \frac{1}{q} [a_q^\dagger \exp(-i\mathbf{q} \cdot \mathbf{r}) - a_q \exp(i\mathbf{q} \cdot \mathbf{r})], \end{aligned} \quad (\text{C.21})$$

with $\mathbf{q} \neq 0$.

C.2 Electron-Phonon Scattering Cross-Section

If we indicate with ω the angular frequency of the longitudinal optical vibrations of the lattice, then the average number of phonons at temperature T is given by the occupation function

$$n(T) = \frac{1}{\exp(\hbar\omega/k_B T) - 1}, \quad (\text{C.22})$$

where k_B is the Boltzmann constant. Fröhlich theory [1] uses the perturbation approach, assuming that the electron-lattice coupling is weak. If the electron energy, measured with respect to the bottom of the conduction band, is given by

$$E_k = \frac{\hbar^2 k^2}{2m^*}, \quad (\text{C.23})$$

where m^* is the electron effective mass and \mathbf{k} the electron wavenumber, then the unperturbed electron wavefunction can be written as

$$|\mathbf{k}\rangle = \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{V^{1/2}}, \quad (\text{C.24})$$

where, as above, we have indicated with V a cubic volume containing the electron. We know that, according to Fröhlich [1], the interaction Hamiltonian is given by (C.21)

$$\mathcal{H}_{\text{inter}} = 4\pi i \sqrt{\frac{e^2 \hbar}{2\gamma\omega V}} \sum_q \frac{1}{q} [a_q^\dagger \exp(-i\mathbf{q} \cdot \mathbf{r}) - a_q \exp(i\mathbf{q} \cdot \mathbf{r})],$$

where $\mathbf{q} \neq 0$ is the phonon wavenumber, $a_{\mathbf{q}}^{\dagger}$ and $a_{\mathbf{q}}$ are, respectively, the operators of creation and annihilation of phonons, and γ is related to the static dielectric constant ε_0 and to the high frequency dielectric constant ε_{∞} by the (C.12)

$$\frac{1}{\gamma} = \frac{\omega^2}{4\pi} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right).$$

In order to calculate the transition rate $W_{kk'}$ from the state $|\mathbf{k}\rangle$ to the state $|\mathbf{k}'\rangle$, Llacer and Garwin [2] used the standard results of the perturbation theory. In the case of phonon annihilation, corresponding to an electron energy gain, once should consider the frequency

$$\beta = \frac{E_{k'} - E_k - \hbar\omega}{2\hbar}, \quad (\text{C.25})$$

while, for phonon creation (electron energy loss), the frequency to be considered is the following

$$\beta = \frac{E_{k'} - E_k + \hbar\omega}{2\hbar}. \quad (\text{C.26})$$

With these definitions the rate is given by

$$W_{kk'} = \frac{|M'_{kk}|^2}{\hbar^2} \frac{\partial}{\partial t} \left(\frac{\sin^2 \beta t}{\beta^2} \right) \quad (\text{C.27})$$

where M'_{kk} is the matrix element for the transition from the state \mathbf{k} to the state \mathbf{k}' . They can be calculated by using the interaction Hamiltonian, (C.21), taking into account the properties of the creation and annihilation operators,

$$a_{\mathbf{q}} |n\rangle = \sqrt{n} |n-1\rangle, \quad (\text{C.28})$$

$$a_{\mathbf{q}}^{\dagger} |n\rangle = \sqrt{n+1} |n+1\rangle, \quad (\text{C.29})$$

and utilizing the conditions of orthonormality satisfied by the set of vectors $|n(T)\rangle$,

$$\langle n|n\rangle = 1, \quad (\text{C.30})$$

$$\langle n|n+m\rangle = 0. \quad (\text{C.31})$$

where m is any integer $\neq 0$.

For the case of annihilation of a phonon of wavenumber \mathbf{q} (electron energy gain), $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ and

$$M_{kk'} = 4\pi i \sqrt{\frac{e^2 \hbar}{2\gamma\omega V}} \frac{\sqrt{n(T)}}{q}, \quad (\text{C.32})$$

while, in the case of the creation of a phonon of wavenumber \mathbf{q} (electron energy loss), $\mathbf{k}' = \mathbf{k} - \mathbf{q}$ and

$$M_{kk'} = -4\pi i \sqrt{\frac{e^2 \hbar}{2\gamma\omega V}} \frac{\sqrt{n(T)+1}}{q}. \quad (\text{C.33})$$

The total scattering rate from a state \mathbf{k} to all the available states \mathbf{k}' can be obtained by integrating over \mathbf{q} . Let us first perform the integration for the case of phonon annihilation:

$$W_k^- = \int_{q_{\min}}^{q_{\max}} dq \int_0^{2\pi} d\phi \int_0^\pi \frac{16\pi^2 e^2}{2\hbar\gamma\omega V} \frac{n(T)}{q^2} \frac{\partial}{\partial t} \frac{\sin^2 \beta t}{\beta^2} \frac{V}{8\pi^3} q^2 \sin \alpha d\alpha. \quad (\text{C.34})$$

Note that α represents in this context the angle between the direction of \mathbf{k} and that of \mathbf{q} , while we will use the symbol ϑ to indicate the angle between \mathbf{k} and \mathbf{k}' . As

$$k'^2 = k^2 + q^2 - 2kq \cos \alpha, \quad (\text{C.35})$$

some simple algebraic manipulations allow us to see that

$$\beta = \frac{\hbar}{4m^*} q^2 - \frac{\hbar}{2m^*} kq \cos \alpha - \frac{\omega}{2}, \quad (\text{C.36})$$

so that

$$\sin \alpha d\alpha = \frac{2m^*}{\hbar} \frac{1}{kq} d\beta. \quad (\text{C.37})$$

As a consequence

$$W_k^- = \int_{q_{\min}}^{q_{\max}} dq \int_{\beta_{\min}}^{\beta_{\max}} \frac{4m^* e^2 n(T)}{\hbar^2 \gamma \omega} \frac{1}{kq} \frac{\partial}{\partial t} \frac{\sin^2 \beta t}{\beta^2} d\beta, \quad (\text{C.38})$$

where

$$\beta_{\min} = \frac{\hbar}{4m^*} q^2 - \frac{\hbar}{2m^*} kq - \frac{\omega}{2}, \quad (\text{C.39})$$

and

$$\beta_{\max} = \frac{\hbar}{4m^*} q^2 + \frac{\hbar}{2m^*} kq - \frac{\omega}{2}, \quad (\text{C.40})$$

Now

$$\begin{aligned}
& \int_{\beta_{\min}}^{\beta_{\max}} \frac{\partial \sin^2 \beta t}{\partial t} \frac{1}{\beta^2} d\beta = \int_{\beta_{\min}}^{\beta_{\max}} \frac{\sin 2\beta t}{\beta} d\beta = \\
& = \int_{\beta_{\min}}^{\beta_{\max}} \frac{\sin(2\beta t)}{(2\beta t)} 2t d\beta = \int_{2\beta_{\min} t}^{2\beta_{\max} t} \frac{\sin x}{x} dx = \\
& = \int_0^{2\beta_{\max} t} \frac{\sin x}{x} dx - \int_0^{2\beta_{\min} t} \frac{\sin x}{x} dx.
\end{aligned}$$

In order to carry out the calculation, we need to know the limits of integration, q_{\min} and q_{\max} . They can be obtained by using the law of conservation of energy, $E_{k'} = E_k + \hbar\omega$, which corresponds to $\beta = 0$.

Since $\cos \alpha$ can take all the values between -1 and $+1$, the limits of integration satisfy the following equations

$$q^2 + 2kq - \frac{k^2 \hbar\omega}{E_k} = 0, \quad (\text{C.41})$$

$$q^2 - 2kq - \frac{k^2 \hbar\omega}{E_k} = 0, \quad (\text{C.42})$$

so that, as q is positive,

$$q_{\min} = k \left(\sqrt{1 + \frac{\hbar\omega}{E_k}} - 1 \right), \quad (\text{C.43})$$

$$q_{\max} = k \left(\sqrt{1 + \frac{\hbar\omega}{E_k}} + 1 \right). \quad (\text{C.44})$$

Inserting these limits of integration in the definition of β_{\min} and β_{\max} , we see that $\beta_{\min} \leq 0$ and $\beta_{\max} \geq 0$. Therefore,

$$\begin{aligned}
& \lim_{t \rightarrow \infty} \int_{\beta_{\min}}^{\beta_{\max}} \frac{\partial \sin^2 \beta t}{\partial t} \frac{1}{\beta^2} d\beta = \\
& = \lim_{t \rightarrow \infty} \left(\int_0^{2\beta_{\max} t} \frac{\sin x}{x} dx - \int_0^{2\beta_{\min} t} \frac{\sin x}{x} dx \right) = \\
& = \int_0^{+\infty} \frac{\sin x}{x} dx - \int_0^{-\infty} \frac{\sin x}{x} dx = \\
& = \text{si}(+\infty) - \text{si}(-\infty) = \frac{\pi}{2} - \left(-\frac{\pi}{2} \right) = \pi,
\end{aligned}$$

so that

$$W_k^- = \int_{q_{\min}}^{q_{\max}} \frac{4\pi m^* e^2 n(T)}{\hbar^2 \gamma \omega} \frac{1}{kq} dq. \quad (\text{C.45})$$

As a consequence, we conclude that the total scattering rate for the phonon annihilation (electron energy gain) is given by

$$W_k^- = \frac{4\pi e^2 m^* n(T)}{\hbar^2 \gamma \omega k} \ln \left(\frac{\sqrt{1 + \hbar\omega/E_k} + 1}{\sqrt{1 + \hbar\omega/E_k} - 1} \right). \quad (\text{C.46})$$

The case of phonon creation (electron energy loss) is similar. Remember that, in this case, we have to use $\sqrt{n(T) + 1}$ instead of $\sqrt{n(T)}$ in the matrix element of the transition of the electron from the state \mathbf{k} to the state \mathbf{k}' . Furthermore, in this case,

$$\beta = \frac{1}{2\hbar} [E_{k'} - (E_k + \hbar\omega)] = \frac{\hbar}{4m^*} q^2 - \frac{\hbar}{2m^*} k q \cos \alpha + \frac{\omega}{2}, \quad (\text{C.47})$$

so that

$$q_{\min} = k \left(1 - \sqrt{1 - \frac{\hbar\omega}{E_k}} \right), \quad (\text{C.48})$$

$$q_{\max} = k \left(1 + \sqrt{1 - \frac{\hbar\omega}{E_k}} \right). \quad (\text{C.49})$$

Therefore,

$$W_k^+ = \frac{4\pi e^2 m^* [n(T) + 1]}{\hbar^2 \gamma \omega k} \ln \left(\frac{1 + \sqrt{1 - \hbar\omega/E_k}}{1 - \sqrt{1 - \hbar\omega/E_k}} \right). \quad (\text{C.50})$$

Concerning the angular distribution of the scattering, let us consider the angle ϑ between \mathbf{k} and \mathbf{k}' , so that

$$q^2 = k^2 + k'^2 - 2kk' \cos \vartheta \quad (\text{C.51})$$

and, hence,

$$q \, dq = k k' \sin \vartheta \, d\vartheta. \quad (\text{C.52})$$

The probability of scattering between ϑ and $\vartheta + d\vartheta$ can be calculated by considering the integrand of (C.45):

$$\begin{aligned} A \frac{dq}{kq} &= A \frac{q \, dq}{k q^2} = A \frac{k k' \sin \vartheta \, d\vartheta}{k (k^2 + k'^2 - 2kk' \cos \vartheta)} = \\ &= A \frac{k' \sin \vartheta \, d\vartheta}{k^2 + k'^2 - 2kk' \cos \vartheta}, \end{aligned}$$

where, for phonon annihilation,

$$A = \frac{4 \pi e^2 m^* n(T)}{\hbar^2 \gamma \omega}. \quad (\text{C.53})$$

Similar considerations hold for phonon creation, so that we conclude that the angular distribution is proportional, in both cases, to

$$d\eta = \frac{E_{k'}^{1/2} \sin \vartheta d\vartheta}{E_k + E_{k'} - 2(E_k E_{k'})^{1/2} \cos \vartheta} \quad (\text{C.54})$$

After an electron-phonon collision, the new angle ϑ' is obtained inverting this distribution. Indicating with μ the cumulative probability, we have

$$\begin{aligned} \mu &= \frac{\int_0^{\vartheta'} d\eta}{\int_0^\pi d\eta} = \\ &= \int_0^{\vartheta'} \frac{E_{k'}^{1/2} \sin \vartheta d\vartheta}{E_k + E_{k'} - 2(E_k E_{k'})^{1/2} \cos \vartheta} / \\ &/ \int_0^\pi \frac{E_{k'}^{1/2} \sin \vartheta d\vartheta}{E_k + E_{k'} - 2(E_k E_{k'})^{1/2} \cos \vartheta}, \end{aligned} \quad (\text{C.55})$$

and, as a consequence,

$$\cos \vartheta' = \frac{E_k + E_{k'}}{2 \sqrt{E_k E_{k'}}} (1 - B^\mu) + B^\mu, \quad (\text{C.56})$$

$$B = \frac{E_k + E_{k'} + 2 \sqrt{E_k E_{k'}}}{E_k + E_{k'} - 2 \sqrt{E_k E_{k'}}}. \quad (\text{C.57})$$

The relationship between the mean free path λ_{phonon} and the total scattering rate from a state \mathbf{k} to all the other available states \mathbf{k}' is

$$\lambda_{\text{phonon}} = \left(\frac{1}{v} \frac{dP}{dt} \right)^{-1}, \quad (\text{C.58})$$

where v is the electron velocity before the electron-phonon collision

$$v = \frac{\hbar k}{m^*} \quad (\text{C.59})$$

and

$$\frac{dP}{dt} = W_k^- + W_k^+. \quad (\text{C.60})$$

The electron-phonon mean free path can then be written as

$$\lambda_{\text{phonon}} = \frac{\hbar k/m^*}{W_k^- + W_k^+} = \frac{\sqrt{2} E_k/m^*}{W_k^- + W_k^+}, \quad (\text{C.61})$$

and, as a consequence,

$$\begin{aligned} \lambda_{\text{phonon}}^{-1} &= \frac{1}{a_0} \left[\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 \varepsilon_\infty} \right] \frac{\hbar \omega}{E_k} \frac{1}{2} \times \\ &\times \left\{ [n(T) + 1] \ln \left[\frac{1 + \sqrt{1 - \hbar \omega/E_k}}{1 - \sqrt{1 - \hbar \omega/E_k}} \right] + \right. \\ &\left. + n(T) \ln \left[\frac{\sqrt{1 + \hbar \omega/E_k} + 1}{\sqrt{1 + \hbar \omega/E_k} - 1} \right] \right\}, \end{aligned} \quad (\text{C.62})$$

where we have assumed that the electron effective mass m^* is equal to that of a free electron, $m^* = m$.

The probability of phonon creation is much higher than that of phonon annihilation [2, 3, 9], so that one can safely ignore the electron energy gain due to the phonon annihilation. As a consequence we can write

$$\lambda_{\text{phonon}} = \frac{\hbar k/m^*}{W_k^+}, \quad (\text{C.63})$$

so that, indicating with $E = E_k$ the energy of the incident electron and with $W_{\text{ph}} = \hbar \omega$ the energy of the created phonon (and assuming that $m^* = m$) we conclude that the inverse inelastic mean free path for electron energy loss due to phonon creation can be written as [2]

$$\begin{aligned} \lambda_{\text{phonon}}^{-1} &= \\ &= \frac{1}{a_0} \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 \varepsilon_\infty} \frac{W_{\text{ph}}}{E} \frac{n(T) + 1}{2} \ln \left[\frac{1 + \sqrt{1 - W_{\text{ph}}/E}}{1 - \sqrt{1 - W_{\text{ph}}/E}} \right]. \end{aligned} \quad (\text{C.64})$$

This equation was used in the Monte Carlo simulations of secondary electron emission from insulating materials presented in this book [3, 9, 10].

C.3 Summary

The Fröhlich theory [1, 2] concerning the interaction of free electrons with the longitudinal optical mode lattice vibrations was described in this chapter. Both phonon creation and phonon annihilation, corresponding to electron energy loss and to electrons energy gain, respectively, are described by the theory.

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Appendix D

The Ritchie Theory

The Ritchie theory describes the relationship between the dielectric function and the electron energy loss in a solid. It allows to calculate the differential inverse inelastic mean free path, the inelastic mean free path, and the stopping power. The original version of the Ritchie theory can be found in [1]. Also see [2–6] for further details.

D.1 Energy Loss and Dielectric Function

The response of the ensemble of conduction electrons to the electromagnetic disturbance due to electrons passing through a solid and losing energy in it, is described by a complex dielectric function $\varepsilon(\mathbf{k}, \omega)$, where \mathbf{k} is the wave vector and ω is the frequency of the electromagnetic field. If, at time t , the electron position is \mathbf{r} and its speed is \mathbf{v} , then, indicating with e the electron charge, the electron that passes through the solid can be represented by a charge distribution given by

$$\rho(\mathbf{r}, t) = -e \delta(\mathbf{r} - \mathbf{v}t). \tag{D.1}$$

The electric potential φ generated in the medium can be calculated as¹

$$\varepsilon(\mathbf{k}, \omega) \nabla^2 \varphi(\mathbf{r}, t) = -4\pi \rho(\mathbf{r}, t). \tag{D.2}$$

In the Fourier space we have

$$\varphi(\mathbf{k}, \omega) = -\frac{8\pi^2 e}{\varepsilon(\mathbf{k}, \omega)} \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2}. \tag{D.3}$$

¹The vector potential is zero due to the chosen gauge.

In fact, on the one hand,

$$\varphi(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d^3k \int_{-\infty}^{+\infty} d\omega \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \varphi(\mathbf{k}, \omega), \quad (\text{D.4})$$

so that

$$\nabla^2 \varphi(\mathbf{r}, t) = -\frac{1}{(2\pi)^4} \int d^3k \int_{-\infty}^{+\infty} d\omega \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] k^2 \varphi(\mathbf{k}, \omega), \quad (\text{D.5})$$

and, on the other hand,

$$\begin{aligned} \rho(\mathbf{k}, \omega) &= \int d^3r \int_{-\infty}^{+\infty} dt \exp[-i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \rho(\mathbf{r}, t) = \\ &= \int d^3r \int_{-\infty}^{+\infty} dt \exp[-i(\mathbf{k} \cdot \mathbf{r} + \omega t)] [-e \delta(\mathbf{r} - \mathbf{v}t)] = \\ &= -2\pi e \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp[-i(\mathbf{k} \cdot \mathbf{v} + \omega)t] = \\ &= -2\pi e \delta(\mathbf{k} \cdot \mathbf{v} + \omega), \end{aligned} \quad (\text{D.6})$$

so that

$$\rho(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int d^3k \int_{-\infty}^{+\infty} d\omega \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] [-2\pi e \delta(\mathbf{k} \cdot \mathbf{v} + \omega)]. \quad (\text{D.7})$$

Then, using (D.2), (D.5), and (D.7), we obtain

$$\varepsilon(\mathbf{k}, \omega) k^2 \varphi(\mathbf{k}, \omega) = -8\pi^2 e \delta(\mathbf{k} \cdot \mathbf{v} + \omega), \quad (\text{D.8})$$

which is equivalent to (D.3).

We are interested in calculating the energy loss $-dE$ of an electron due to its interaction with the electric field \mathcal{E} generated by the electrons passing through the solid. Let us indicate with \mathcal{F}_z the z component of the electric force, so that

$$-dE = \mathcal{F} \cdot d\mathbf{r} = \mathcal{F}_z dz. \quad (\text{D.9})$$

It should be noted that here and in the following equations, the electric force (and the electric field $\mathcal{E} = \mathcal{F}/e$) are considered at $\mathbf{r} = \mathbf{v}t$. Since

$$\mathcal{E}_z dz = \frac{dz}{dt} dt \mathcal{E}_z = \frac{d\mathbf{r}}{dt} \cdot \mathcal{E} dt = \frac{\mathbf{v} \cdot \mathcal{E}}{v} dz \quad (\text{D.10})$$

the energy loss $-dE$ per unit path length dz , $-dE/dz$, is given by

$$-\frac{dE}{dz} = \frac{e}{v} \mathbf{v} \cdot \boldsymbol{\mathcal{E}}. \quad (\text{D.11})$$

Since

$$\boldsymbol{\mathcal{E}} = -\nabla \varphi(\mathbf{r}, t) \quad (\text{D.12})$$

and $\varphi(\mathbf{k}, \omega)$ is the Fourier transform of $\varphi(\mathbf{r}, t)$ [see (D.4)], then

$$\begin{aligned} \boldsymbol{\mathcal{E}} &= \\ &= -\nabla \left\{ \frac{1}{(2\pi)^4} \int d^3k \int_{-\infty}^{+\infty} d\omega \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \varphi(\mathbf{k}, \omega) \right\}. \end{aligned} \quad (\text{D.13})$$

As a consequence

$$\begin{aligned} -\frac{dE}{dz} &= \\ &= \text{Re} \left\{ -\frac{8\pi^2 e^2}{(2\pi)^4 v} \times \right. \\ &\quad \times \left. \int d^3k \int_{-\infty}^{+\infty} d\omega (-\nabla) \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \cdot \mathbf{v} \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \Big|_{\mathbf{r}=\mathbf{v}t} \right\} = \\ &= \text{Re} \left\{ -\frac{8\pi^2 e^2}{(2\pi)^4 v} \times \right. \\ &\quad \times \left. \int d^3k \int_{-\infty}^{+\infty} d\omega (-i\mathbf{k}) \cdot \mathbf{v} \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \Big|_{\mathbf{r}=\mathbf{v}t} \right\} = \\ &= \text{Re} \left\{ \frac{i8\pi^2 e^2}{16\pi^4 v} \times \right. \\ &\quad \times \left. \int d^3k \int_{-\infty}^{+\infty} d\omega (\mathbf{k} \cdot \mathbf{v}) \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \Big|_{\mathbf{r}=\mathbf{v}t} \right\}. \end{aligned} \quad (\text{D.14})$$

Taking into account (i) that the electric field has to be calculated at $\mathbf{r} = \mathbf{v}t$ and (ii) of the presence in the integrand of the $\delta(\mathbf{k} \cdot \mathbf{v} + \omega)$ distribution, we have

$$\begin{aligned} -\frac{dE}{dz} &= \\ &= \text{Re} \left\{ \frac{i e^2}{2\pi^2 v} \times \right. \\ &\quad \times \left. \int d^3k \int_{-\infty}^{+\infty} d\omega \mathbf{k} \cdot \mathbf{v} \exp[i(\mathbf{k} \cdot \mathbf{v}t + \omega t)] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \right\} = \\ &= \text{Re} \left\{ \frac{i e^2}{2\pi^2 v} \times \right. \end{aligned}$$

$$\begin{aligned}
& \times \int d^3k \int_{-\infty}^{+\infty} d\omega \mathbf{k} \cdot \mathbf{v} \exp[i(-\omega t + \omega t)] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \Big\} = \\
& = \operatorname{Re} \left\{ \frac{i e^2}{2 \pi^2 v} \times \right. \\
& \times \int d^3k \int_{-\infty}^{+\infty} d\omega (-\omega) \exp[i(-\omega t + \omega t)] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \Big\} = \\
& = \operatorname{Re} \left\{ \frac{-i e^2}{2 \pi^2 v} \int d^3k \int_{-\infty}^{+\infty} d\omega \omega \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2 \varepsilon(\mathbf{k}, \omega)} \right\}. \tag{D.15}
\end{aligned}$$

Since

$$\begin{aligned}
& \operatorname{Re} \left\{ i \int d^3k \int_{-\infty}^{+\infty} d\omega \omega \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{\varepsilon(\mathbf{k}, \omega)} \right\} = \\
& = 2 \operatorname{Re} \left\{ i \int d^3k \int_0^{+\infty} d\omega \omega \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{\varepsilon(\mathbf{k}, \omega)} \right\},
\end{aligned}$$

we conclude that²

$$-\frac{dE}{dz} = \frac{e^2}{\pi^2 v} \int d^3k \int_0^{\infty} d\omega \omega \operatorname{Im} \left[\frac{1}{\varepsilon(\mathbf{k}, \omega)} \right] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2}, \tag{D.16}$$

or

$$-\frac{dE}{dz} = \int_0^{\infty} d\omega \omega \tau(\mathbf{v}, \omega), \tag{D.17}$$

where

$$\tau(\mathbf{v}, \omega) = \frac{e^2}{\pi^2 v} \int d^3k \operatorname{Im} \left[\frac{1}{\varepsilon(\mathbf{k}, \omega)} \right] \frac{\delta(\mathbf{k} \cdot \mathbf{v} + \omega)}{k^2} \tag{D.18}$$

is the probability of an energy loss ω per unit distance traveled by a non-relativistic electron of velocity \mathbf{v} [1].

D.2 Homogeneous and Isotropic Solids

Let us assume now that the solid is homogeneous and isotropic, and ε is a scalar depending only on the magnitude of \mathbf{k} and not on its direction

$$\varepsilon(\mathbf{k}, \omega) = \varepsilon(k, \omega) \tag{D.19}$$

so that

²Note that, for any complex number w , $\operatorname{Re}(i w) = -\operatorname{Im}(w)$.

$$\begin{aligned}
\tau(v, \omega) &= \\
&= \frac{e^2}{\pi^2 v} \int_0^{2\pi} d\phi \int_0^\pi d\vartheta \int_{k_-}^{k_+} dk k^2 \sin \vartheta \times \\
&\times \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right] \frac{\delta(kv \cos \vartheta + \omega)}{k^2} = \\
&= \frac{2e^2}{\pi v} \int_0^\pi d\vartheta \int_{k_-}^{k_+} dk \sin \vartheta \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right] \delta(kv \cos \vartheta + \omega) \quad (\text{D.20})
\end{aligned}$$

where

$$\hbar k_{\pm} = \sqrt{2mE} \pm \sqrt{2m(E - \hbar\omega)}. \quad (\text{D.21})$$

and $E = mv^2/2$. These limits of integration come from conservation of momentum (see Sect. 6.2.5).

Let us introduce the new variable ω' defined as

$$\omega' = -kv \cos \vartheta, \quad (\text{D.22})$$

so that

$$d\omega' = kv \sin \vartheta d\vartheta \quad (\text{D.23})$$

and, hence,

$$\begin{aligned}
\tau(v, \omega) &= \frac{2e^2}{\pi v} \int_{-kv}^{kv} d\omega' \int_{k_-}^{k_+} \frac{dk}{kv} \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right] \delta(-\omega' + \omega) \quad (\text{D.24}) \\
&= \frac{2me^2}{\pi m v^2} \int_{k_-}^{k_+} \frac{dk}{k} \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right].
\end{aligned}$$

We thus can write that

$$\tau(E, \omega) = \frac{m e^2}{\pi E} \int_{k_-}^{k_+} \frac{dk}{k} \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right], \quad (\text{D.25})$$

Indicating with $W = \hbar\omega$ the energy loss and with W_{\max} the maximum energy loss, the inverse electron inelastic mean free path, $\lambda_{\text{inel}}^{-1}$, can be calculated as

$$\begin{aligned}
\lambda_{\text{inel}}^{-1} &= \\
&= \frac{m e^2}{\pi \hbar^2 E} \int_0^{W_{\max}} d\hbar\omega \int_{k_-}^{k_+} \frac{dk}{k} \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right] = \\
&= \frac{1}{\pi a_0 E} \int_0^{W_{\max}} d\hbar\omega \int_{k_-}^{k_+} \frac{dk}{k} \operatorname{Im} \left[\frac{1}{\varepsilon(k, \omega)} \right]. \quad (\text{D.26})
\end{aligned}$$

D.3 Summary

The Ritchie theory [1] was described. It allows to establish the relationship between electron energy loss and dielectric function, and to calculate the differential inverse inelastic mean free path, the inelastic mean free path, and the stopping power.

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Appendix E

The Chen and Kwei and the Li et al. Theory

The original version of the Chen and Kwei theory can be found in [1] for outgoing projectiles. It was generalized by Li et al. [2] for incoming projectiles. Below, the Chen and Kwei and the Li et al. formulas are rewritten in terms of angular variables, according to [3].

E.1 Outgoing and Incoming Electrons

Let us consider the component q_x and q_y of the momentum transfer parallel to the surface. For outgoing electrons,

$$q_x = \frac{mv}{\hbar} (\vartheta \cos \phi \cos \alpha + \vartheta_E \sin \alpha), \quad (\text{E.1})$$

while, for incoming electrons,

$$q_x = \frac{mv}{\hbar} (\vartheta \cos \phi \cos \alpha - \vartheta_E \sin \alpha). \quad (\text{E.2})$$

For both outgoing and incoming electrons we have

$$q_y = \frac{mv}{\hbar} \vartheta \sin \phi. \quad (\text{E.3})$$

In these equations, α is the angle of the electron trajectory with respect to the normal to the target surface, ϑ and ϕ indicate the polar and azimuth angles, and

$$\vartheta_E = \frac{\hbar \omega}{2E}, \quad (\text{E.4})$$

where E is the electron energy and $\hbar \omega$ the energy loss.

E.2 Probability of Inelastic Scattering

If z is the coordinate along the normal to the surface target, the probability for inelastic scattering (the differential inverse inelastic mean free path, DIIMFP) is given by:

$$P_{\text{outside}}(z, \alpha) = \frac{1}{2\pi^2 a_0 E} \int_0^{\vartheta_{\text{cutoff}}} \frac{\vartheta \, d\vartheta}{\vartheta^2 + \vartheta_E^2} \int_0^{2\pi} d\phi f(z, \vartheta, \phi, \alpha) \quad (\text{E.5})$$

in the vacuum, and

$$P_{\text{inside}}(z, \alpha) = \frac{1}{2\pi^2 a_0 E} \int_0^{\vartheta_{\text{cutoff}}} \frac{\vartheta \, d\vartheta}{\vartheta^2 + \vartheta_E^2} \int_0^{2\pi} d\phi g(z, \vartheta, \phi, \alpha) \quad (\text{E.6})$$

inside the material. The cutoff angle is taken to be the Bethe ridge angle [4]

$$\vartheta_{\text{cutoff}} = \sqrt{\frac{\hbar\omega}{E}}. \quad (\text{E.7})$$

It should be noted that in the Chen and Kwei approach, [1] there is no proper limit for the high-momentum cutoff, while there exists a maximum angle, known as the Bethe ridge angle, only up to which electron excitation is allowed [5].

For outgoing electrons, functions $f(z, \vartheta, \phi, \alpha)$ and $g(z, \vartheta, \phi, \alpha)$ can be written as:

$$f(z, \vartheta, \phi, \alpha) = \text{Im} \left(\frac{2}{\varepsilon + 1} \right) h(z, \vartheta, \phi, \alpha) [p(z, \vartheta, \phi, \alpha) - h(z, \vartheta, \phi, \alpha)], \quad (\text{E.8})$$

$$g(z, \vartheta, \phi, \alpha) = \text{Im} \left(\frac{2}{\varepsilon + 1} \right) h^2(z, \vartheta, \phi, \alpha) + \text{Im} \left(\frac{1}{\varepsilon} \right) [1 - h^2(z, \vartheta, \phi, \alpha)]. \quad (\text{E.9})$$

For incoming electrons, the same functions $f(z, \vartheta, \phi, \alpha)$ and $g(z, \vartheta, \phi, \alpha)$ are given by:

$$f(z, \vartheta, \phi, \alpha) = \text{Im} \left(\frac{2}{\varepsilon + 1} \right) h^2(z, \vartheta, \phi, \alpha), \quad (\text{E.10})$$

$$g(z, \vartheta, \phi, \alpha) = \text{Im} \left(\frac{2}{\varepsilon + 1} \right) h(z, \vartheta, \phi, \alpha) [p(z, \vartheta, \phi, \alpha) - h(z, \vartheta, \phi, \alpha)] + \text{Im} \left(\frac{1}{\varepsilon} \right) [1 - h(z, \vartheta, \phi, \alpha)p(z, \vartheta, \phi, \alpha) + h^2(z, \vartheta, \phi, \alpha)]. \quad (\text{E.11})$$

Functions $h(z, \vartheta, \phi, \alpha)$ and $p(z, \vartheta, \phi, \alpha)$ are, in turn, given by:

$$h(z, \vartheta, \phi, \alpha) = \exp \left[\left(-|z| \frac{mv}{\hbar} \right) \sqrt{(\vartheta \cos \phi \cos \alpha + \vartheta_E \sin \alpha)^2 + \vartheta^2 \sin^2 \phi} \right], \quad (\text{E.12})$$

$$p(z, \vartheta, \phi, \alpha) = 2 \cos \left[\left(|z| \frac{mv}{\hbar} \right) (\vartheta_E \cos \alpha - \vartheta \cos \phi \sin \alpha) \right], \quad (\text{E.13})$$

for outgoing electrons and by:

$$h(z, \vartheta, \phi, \alpha) = \exp \left[\left(-|z| \frac{mv}{\hbar} \right) \sqrt{(\vartheta \cos \phi \cos \alpha - \vartheta_E \sin \alpha)^2 + \vartheta^2 \sin^2 \phi} \right], \quad (\text{E.14})$$

$$p(z, \vartheta, \phi, \alpha) = 2 \cos \left[\left(|z| \frac{mv}{\hbar} \right) (\vartheta_E \cos \alpha + \vartheta \cos \phi \sin \alpha) \right], \quad (\text{E.15})$$

for incoming electrons. Finally, $\varepsilon(\omega)$ is the dielectric function. The examples presented in this books about the use of the Chen and Kwey theory use, for the case of aluminium, the complex dielectric function

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\Gamma\omega}, \quad (\text{E.16})$$

while, for the case of silicon,

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \omega_g^2 - i\Gamma\omega}, \quad (\text{E.17})$$

where $\hbar\omega$ is the electron energy loss, $\hbar\omega_g$ is the average excitation energy for valence electrons in silicon, $\hbar\Gamma$ is the damping constant, and $\hbar\omega_p$ is the plasmon energy.

E.3 Summary

The Chen and Kwei theory for outgoing electrons [1], and its generalization proposed by Li et al. [2] for incoming projectiles, were described and rewritten in terms of angular variables, according to [3].

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Appendix F

The Mermin Theory and the Generalized Oscillator Strength Method

Dielectric formalism is the most used method for investigating the interaction of swift electrons with solid targets. In this chapter the Mermin energy loss function-generalized oscillator strength method (MELF-GOS method) is briefly described within the framework of dielectric formalism [1–4].

F.1 The Mermin Theory

The Mermin dielectric function [1] is given by:

$$\varepsilon_M(\mathbf{q}, \omega) = 1 + \frac{(1 + i/\omega\tau)[\varepsilon^0(\mathbf{q}, \omega + i/\tau) - 1]}{1 + (i/\omega\tau)[\varepsilon^0(\mathbf{q}, \omega + i/\tau) - 1]/[\varepsilon^0(\mathbf{q}, 0) - 1]}, \quad (\text{F.1})$$

where \mathbf{q} is the momentum, ω the frequency, τ the relaxation time, and $\varepsilon^0(\mathbf{q}, \omega)$ the Lindhard dielectric constant [5]

$$\varepsilon^0(\mathbf{q}, \omega) = 1 + \frac{4\pi^2 q^2}{e^2} B(\mathbf{q}, \omega), \quad (\text{F.2})$$

$$B(\mathbf{q}, \omega) = \int \frac{d\mathbf{p}}{4\pi^3} \frac{f_{\mathbf{p}+\mathbf{q}/2} - f_{\mathbf{p}-\mathbf{q}/2}}{\omega - (\varepsilon_{\mathbf{p}+\mathbf{q}/2} - \varepsilon_{\mathbf{p}-\mathbf{q}/2})/\hbar}. \quad (\text{F.3})$$

In these equations e is the electron charge, $f_{\mathbf{p}}$ is the Fermi–Dirac distribution, and $\varepsilon_{\mathbf{p}}$ the free electron energy.

Note that the Lindhard dielectric function [5] can be numerically calculated by using (F.2) and (F.3). The integration can also be carried out in closed form. The result of the integration is the following [2, 3, 6]:

$$\varepsilon^0(q, \omega) = 1 + \frac{\chi^2}{z^2} [f_1(u, z) + i f_2(u, z)], \quad (\text{F.4})$$

where $u = \omega/(qv_F)$, $z = q/(2q_F)$, and $\chi^2 = e^2/(\pi \hbar v_F)$ is a measure of the electron density [6]. In this equation, v_F is the Fermi velocity of the valence electrons of the target and $q_F = mv_F/\hbar$. The functions $f_1(u, z)$ and $f_2(u, z)$ are given by

$$f_1(u, z) = \frac{1}{2} + \frac{1}{8z} [g(z-u) + g(z+u)], \quad (\text{F.5})$$

$$f_2(u, z) = \begin{cases} \frac{\pi}{2}u, & z+u < 1 \\ \frac{\pi}{8z}[1 - (z-u)^2], & |z-u| < 1 < z+u \\ 0, & |z-u| > 1, \end{cases} \quad (\text{F.6})$$

where

$$g(x) = (1-x^2) \ln \left| \frac{1+x}{1-x} \right|. \quad (\text{F.7})$$

F.2 The Mermin Energy Loss Function-Generalized Oscillator Strength Method (MELF-GOS)

Let us now consider a superposition of free and bound oscillators. For any oscillator:

$$\text{Im} \left[\frac{1}{\varepsilon_M(\omega_i, \gamma_i; q, \omega)} \right] = \frac{-\varepsilon_{M_2}}{\varepsilon_{M_1}^2 + \varepsilon_{M_2}^2}, \quad (\text{F.8})$$

where

$$\varepsilon_M = \varepsilon_{M_1} + i\varepsilon_{M_2} \quad (\text{F.9})$$

and ω_i and γ_i are, respectively, the frequency and the damping constant associated to each specific oscillator. A linear combination of Mermin-type energy loss functions, one per oscillator, allows to calculate the energy loss function (ELF) for $q = 0$, for any specific material [2–4]:

$$\text{Im} \left[\frac{1}{\varepsilon(q=0, \omega)} \right] = \sum_i A_i \text{Im} \left[\frac{1}{\varepsilon_M(\omega_i, \gamma_i; q=0, \omega)} \right]. \quad (\text{F.10})$$

In this equation, A_i , ω_i , and γ_i are determined by looking for the best fit of the available experimental optical ELF. Actually, as both Mermin and Drude–Lorentz oscillators converge on the same values in the optical limit (i.e. for $q = 0$) [7]

$$\text{Im} \left[\frac{1}{\varepsilon(q=0, \omega)} \right] = \sum_i A_i \text{Im} \left[\frac{1}{\varepsilon_M(\omega_i, \gamma_i; q=0, \omega)} \right] = \sum_i A_i \text{Im} \left[\frac{1}{\varepsilon_D(\omega_i, \gamma_i; q=0, \omega)} \right], \quad (\text{F.11})$$

where the Drude–Lorentz functions $\text{Im} \left[\frac{1}{\varepsilon_D(\omega_i, \gamma_i; \mathbf{q}=0, \omega)} \right]$ are given by [8]

$$\text{Im} \left[\frac{1}{\varepsilon_D(\omega_i, \gamma_i; \mathbf{q}=0, \omega)} \right] = \frac{\gamma_i \omega}{(\omega_i^2 - \omega^2)^2 + (\gamma_i \omega)^2}, \quad (\text{F.12})$$

the best fit can also be obtained using a linear combination of Drude–Lorentz functions, instead of Mermin functions. Once the values of the best fit parameters have been established (see, for example [4, 9, 10]), the extension beyond the optical domain ($\mathbf{q} \neq 0$) can be obtained by [2–4]

$$\text{Im} \left[\frac{1}{\varepsilon(\mathbf{q}, \omega)} \right] = \sum_i A_i \text{Im} \left[\frac{1}{\varepsilon_M(\omega_i, \gamma_i; \mathbf{q}, \omega)} \right]. \quad (\text{F.13})$$

Planes et al. [2], Abril et al. [3], and de Vera et al. [4] construct the ELF in the optical limit including the contribution of the electrons from the outermost atomic inner shells as follows:

$$\text{Im} \left[\frac{1}{\varepsilon(q=0, \omega)} \right] = \begin{cases} \sum_i A_i \text{Im} \left[\frac{1}{\varepsilon_M(\omega_i, \gamma_i; q=0, \omega)} \right] & \omega < \omega_{i,\text{edge}} \\ \sum_{i,\text{sh}} A_{i,\text{sh}} \text{Im} \left[\frac{1}{\varepsilon_M(\omega_{i,\text{sh}}, \gamma_{i,\text{sh}}; q=0, \omega)} \right] & \omega \geq \omega_{i,\text{edge}} \end{cases} \quad (\text{F.14})$$

where the first term represents the contribution of the outer electrons while the second one includes the electrons of the outermost atomic inner shells.

F.3 Summary

In this chapter, after a brief discussion about the Mermin theory [1], the Mermin energy loss function–generalized oscillator strength method (MELF-GOS method), in the framework of the dielectric formalism, was shortly described [2–4].

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Appendix G

The Kramers–Kronig Relations and the Sum Rules

In this chapter we discuss the response of a material to applied electromagnetic radiations. The complex dielectric function is the response function of the medium corresponding to the electric polarization induced by an applied electric field. Similarly, the complex conductivity describes the electric current induced in response to an applied electric field. In general, the system response to a given stimulus is ruled by complex analysis and, in particular, by the so-called Kramers–Kronig relations. A consequence of the Kramers–Kronig analysis is constituted by the sum rules which must be satisfied by several optical parameters.

G.1 Linear Response to External Perturbations

Polarization $\mathbf{P}(t)$ of a material at time t depends on the electric field $\mathbf{E}(t)$ applied to the material from $t' = -\infty$ to $t' = t$, according to the following equation:

$$\mathbf{P}(t) = \int_{-\infty}^t G(t - t') \mathbf{E}(t') dt', \quad (\text{G.1})$$

where $G(t)$ is a real Green function of real variable [1]. Assuming that

$$\mathbf{E}(t) = \mathbf{E}_0 \exp[-i\omega t], \quad (\text{G.2})$$

it is thus easy to see that

$$\mathbf{P}(t) = \mathbf{E} \int_0^{\infty} G(\tau) \exp[i\omega\tau] d\tau. \quad (\text{G.3})$$

As a consequence, the electric susceptibility $\chi(\omega)$ can be written as

$$\chi(\omega) = \int_0^{\infty} G(\tau) \exp[i\omega\tau] d\tau. \quad (\text{G.4})$$

Since

$$\varepsilon \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P} = \mathbf{E} + 4\pi \chi \mathbf{E} = (1 + 4\pi \chi) \mathbf{E}, \quad (\text{G.5})$$

we conclude that the dielectric function $\varepsilon(\omega)$ is given by

$$\varepsilon(\omega) = 1 + 4\pi \chi(\omega) = 1 + 4\pi \int_0^{\infty} G(\tau) \exp[i\omega\tau] d\tau. \quad (\text{G.6})$$

Thus,

$$\begin{aligned} \varepsilon^*(\omega) &= 1 + 4\pi \int_0^{\infty} G(\tau) \exp[-i\omega\tau] d\tau = \\ &= \varepsilon(-\omega) = \varepsilon_1(-\omega) + i\varepsilon_2(-\omega). \end{aligned} \quad (\text{G.7})$$

Since

$$\varepsilon^*(\omega) = [\varepsilon_1(\omega) + i\varepsilon_2(\omega)]^* = \varepsilon_1(\omega) - i\varepsilon_2(\omega), \quad (\text{G.8})$$

we have demonstrated that the real part of the dielectric function is an even function in frequency

$$\varepsilon_1(\omega) = \varepsilon_1(-\omega), \quad (\text{G.9})$$

while its imaginary part is an odd function in frequency

$$\varepsilon_2(\omega) = -\varepsilon_2(-\omega). \quad (\text{G.10})$$

G.2 The Kramers–Kronig Relations

Using the Cauchy's residue theorem we obtain

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega)}{\omega - \omega_T} = i\pi \chi(\omega_T), \quad (\text{G.11})$$

and, as a consequence, keeping in mind that

$$\chi(\omega) = \frac{\varepsilon(\omega) - 1}{4\pi}, \quad (\text{G.12})$$

$$\varepsilon(\omega) = 1 + \frac{1}{i\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\varepsilon(\omega') - 1}{\omega' - \omega} d\omega'. \quad (\text{G.13})$$

Therefore, the real and the imaginary parts of the dielectric function can be expressed as follows

$$\varepsilon_1(\omega) = 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\varepsilon_2(\omega')}{\omega' - \omega} d\omega', \quad (\text{G.14})$$

$$\varepsilon_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\varepsilon_1(\omega') - 1}{\omega' - \omega} d\omega'. \quad (\text{G.15})$$

In order to eliminate the negative frequencies, let us rewrite the last equations through straightforward algebraic manipulations (since the real part of the dielectric function is an even function in frequency and the imaginary part of the dielectric function is an odd function in frequency) as follows

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (\text{G.16})$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_0^{\infty} \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'. \quad (\text{G.17})$$

These are the Kramers–Kronig relations relating the real and imaginary parts of the dielectric function. When the fields are longitudinal, the loss function is the response to the longitudinal displacement. As a consequence, also the components of the loss function obey the Kramers–Kronig relations that, in this case, assume the form:

$$\text{Re} \left[\frac{1}{\varepsilon(\omega)} \right] = 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \text{Im} \left[\frac{1}{\varepsilon(\omega')} \right] \frac{d\omega'}{\omega' - \omega}, \quad (\text{G.18})$$

$$\text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \left\{ \text{Re} \left[\frac{1}{\varepsilon(\omega')} \right] - 1 \right\} \frac{d\omega'}{\omega' - \omega}. \quad (\text{G.19})$$

G.3 Sum Rules

Physical arguments can be used to establish some sum rules that, taking into account the Kramers–Kronig relations, must be satisfied [2]. Let us consider, for example, the simple case of high frequency electric field interacting with a metal.

On the one hand, indicating as usual the plasma frequency with ω_p , according to the Drude model on optical properties of metals we can write

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \quad (\text{G.20})$$

On the other hand, according to the Kramers–Kronig theory and taking into account the high frequency hypothesis as well, we obtain

$$\varepsilon_1(\omega) = 1 - \frac{2}{\pi\omega^2} \mathcal{P} \int_0^\infty \omega' \varepsilon_2(\omega') d\omega'. \quad (\text{G.21})$$

Combining these two equations, we obtain the following sum rule that the imaginary part of the dielectric function must satisfy:

$$\int_0^\infty \omega \varepsilon_2(\omega) d\omega = \frac{\pi}{2} \omega_p^2. \quad (\text{G.22})$$

It is well known from the electromagnetic theory that the following relationship exists between complex dielectric function ε and conductivity σ of a metal:

$$\varepsilon = 1 + i \frac{4\pi}{\omega} \sigma. \quad (\text{G.23})$$

Simple algebraic manipulations allows us to express the real and imaginary parts of the complex conductivity, σ_1 and σ_2 , respectively, as follows

$$\sigma_1 = \frac{\omega}{4\pi} \varepsilon_2, \quad (\text{G.24})$$

$$\sigma_2 = \frac{\omega}{4\pi} (1 - \varepsilon_1). \quad (\text{G.25})$$

Thus, the real part of the complex conductivity must satisfy the sum rule

$$\int_0^\infty \sigma_1 d\omega = \frac{\omega_p^2}{8}. \quad (\text{G.26})$$

Two other very important sum rules are the so called f-sum rule and perfect-screening sum rule (ps-sum rule). In order to illustrate these two sum rules, let us consider the case of a metal with the following complex dielectric function

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\Gamma\omega}. \quad (\text{G.27})$$

From this equation it is possible to obtain $\text{Re} [1/\varepsilon(\omega)]$ and $\text{Im} [1/\varepsilon(\omega)]$:

$$\text{Re} \left[\frac{1}{\varepsilon(\omega)} \right] = 1 + \frac{(\omega^2 - \omega_p^2)\omega_p^2}{(\omega^2 - \omega_p^2)^2 + \Gamma^2\omega^2} \quad (\text{G.28})$$

$$\text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] = \frac{\Gamma\omega\omega_p^2}{(\omega^2 - \omega_p^2)^2 + \Gamma^2\omega^2}. \quad (\text{G.29})$$

Since $\text{Re} [1/\varepsilon(\omega)]$ is an even function in ω ($\text{Re} [1/\varepsilon(-\omega)] = \text{Re} [1/\varepsilon(\omega)]$) and $\text{Im} [1/\varepsilon(\omega)]$ is an odd function in ω ($\text{Im} [1/\varepsilon(-\omega)] = -\text{Im} [1/\varepsilon(\omega)]$), the Kramers–Kronig relations, (G.18) and (G.19), can be rewritten, in order to eliminate the negative frequencies, as follows

$$\text{Re} \left[\frac{1}{\varepsilon(\omega)} \right] = 1 + \frac{2}{\pi} \mathcal{P} \int_0^\infty \text{Im} \left[\frac{1}{\varepsilon(\omega')} \right] \frac{\omega'}{\omega'^2 - \omega^2} d\omega', \quad (\text{G.30})$$

$$\text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] = -\frac{2\omega}{\pi} \mathcal{P} \int_0^\infty \left\{ \text{Re} \left[\frac{1}{\varepsilon(\omega')} \right] - 1 \right\} \frac{1}{\omega'^2 - \omega^2} d\omega'. \quad (\text{G.31})$$

From (G.28) and (G.30) it follows that

$$\frac{(\omega^2 - \omega_p^2)\omega_p^2}{(\omega^2 - \omega_p^2)^2 + \Gamma^2\omega^2} = \frac{2}{\pi} \mathcal{P} \int_0^\infty \text{Im} \left[\frac{1}{\varepsilon(\omega')} \right] \frac{\omega'}{\omega'^2 - \omega^2} d\omega'. \quad (\text{G.32})$$

In the high frequency hypothesis, (G.32) becomes

$$\frac{\omega_p^2}{\omega^2} \approx -\frac{2}{\pi\omega^2} \int_0^\infty \text{Im} \left[\frac{1}{\varepsilon(\omega')} \right] \omega' d\omega', \quad (\text{G.33})$$

and we obtain the f-sum rule

$$\int_0^\infty \omega \text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] d\omega = -\frac{\pi}{2} \omega_p^2. \quad (\text{G.34})$$

Equation (G.34) can be also deduced by the use of an exact quantum mechanical approach [3].

Let us now consider the low frequency limit, $\omega \rightarrow 0$. In this case, from (G.32) we obtain

$$\frac{-\omega_p^4}{\omega_p^4} \approx \frac{2}{\pi} \int_0^\infty \text{Im} \left[\frac{1}{\varepsilon(\omega')} \right] \frac{1}{\omega'} d\omega'. \quad (\text{G.35})$$

From this equation the ps-sum rule follows:

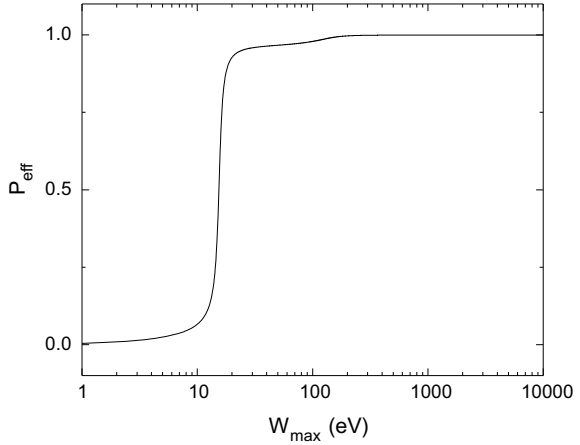
$$\int_0^\infty \frac{1}{\omega} \text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] d\omega = -\frac{\pi}{2}. \quad (\text{G.36})$$

The ps-sum rule can also be written in the form [4, 5]

$$-\frac{2}{\pi} \int_0^{\omega_{\max}} \frac{1}{\omega} \text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] d\omega = P_{\text{eff}}. \quad (\text{G.37})$$

where $P_{\text{eff}} \rightarrow 1$ when $\omega_{\max} \rightarrow \infty$. The trend of P_{eff} as a function of $\hbar\omega_{\max}$ for Al is shown in Fig. G.1.

Fig. G.1 Plot of P_{eff} versus $W_{\text{max}} = \hbar\omega_{\text{max}}$ for Al



In order to discuss in more details the f-sum rule, let us consider the plasma frequency expression

$$\omega_p = \left(\frac{4\pi n e^2}{m} \right)^{1/2}. \quad (\text{G.38})$$

In the original Drude theory we are interested in the optical response only due to the outer-shell electrons, so n represents the number of outer-shell electrons per unit volume. If N is the total number of atoms per unit volume, then $n = zN$ where z is the number of outer-shell electrons per atom. On the other hand, when the frequency becomes high enough, core electrons become involved in the excitation as well and the f-sum rule is still valid after including bound electrons in the dielectric function. Let us then introduce the quantity

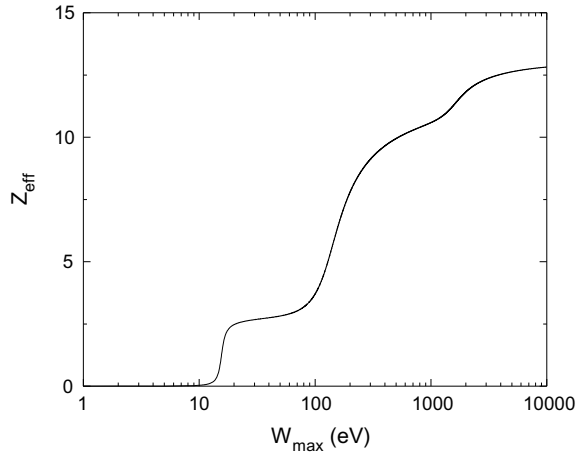
$$\Omega_p = \left(\frac{4\pi N e^2}{m} \right)^{1/2}, \quad (\text{G.39})$$

and rewrite the f-sum rule as follow [4, 5]:

$$-\frac{2}{\pi\Omega_p^2} \int_0^{\omega_{\text{max}}} \omega \text{Im} \left[\frac{1}{\varepsilon(\omega)} \right] d\omega = Z_{\text{eff}} \quad (\text{G.40})$$

where Z_{eff} is the effective number of electrons per atom involved in the excitation. With this notation, when $\omega_{\text{max}} \rightarrow \infty$, $Z_{\text{eff}} \rightarrow Z$, where Z is the atomic number of the target. The trend of Z_{eff} as a function of $\hbar\omega_{\text{max}}$ for Al is shown in Fig. G.2.

Fig. G.2 Plot of Z_{eff} versus $W_{\text{max}} = \hbar\omega_{\text{max}}$ for Al



G.4 Summary

In this chapter, we discussed the system response to a given stimulus. In particular we deduced the Kramers–Kronig relations. We also described the sum rules which must be satisfied by the imaginary part of the complex dielectric function and by the real part of the complex conductivity of a given metal. Furthermore we studied the so-called f-sum rule and ps-sum rule associated with the energy loss of electrons moving in a medium.

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Appendix H

From the Electron Energy Loss Spectrum to the Dielectric Function

The ELF in the optical limit can be obtained by means of a transformation of the experimental transmitted electron energy loss spectrum (EELS). Such a transformation can be applied to the EELS after erasing the elastic peak and multiple scattering in order to deal with the single-scattering spectrum $S(W)$.

H.1 From the Single-Scattering Spectrum to the Energy Loss Function

The relationship between the single-scattering spectrum $S(W)$ and the ELF, $\text{Im}\left[\frac{1}{\varepsilon(q=0, W)}\right]$, is given by [1, 2, 3]

$$S(W) = \frac{I_0 t}{\pi a_0 m v^2} \text{Im}\left[\frac{1}{\varepsilon(q=0, W)}\right] \ln\left[1 + \left(\frac{\beta}{\vartheta_W}\right)^2\right] \quad (\text{H.1})$$

where I_0 is the zero-loss density, t is the sample thickness, a_0 is the Bohr radius, m is the electron mass, v is the incident electron velocity, β is the collection semi-angle, $\vartheta_W = \frac{W^2}{\gamma m v^2}$ is a characteristic scattering angle for energy loss W , and γ is the relativistic factor.

After collecting the transmitted electron energy loss spectrum and applying to it the so called Fourier-Log transformation –for erasing the elastic peak and multiple scattering [1]–, the transformation described by (H.1) allows to obtain the ELF.

H.2 Summary

We described a method for calculating the ELF in the optical limit using the experimental transmitted electron energy loss spectrum.

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