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Theory of inelastic x-ray scattering from condensed matter

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Abstract

We review the basic formation for the inelastic scattering of x-rays by matter. The differential cross sections are related to the scattering function $S(\mathbf{q}, \omega)$, which in turn can be expressed in terms of various correlation functions and response functions of the electron system. We show how the scattering by electronic excitations may be related to the dielectric function of the electron gas at high energy transfers, while at low energy transfers we derive the cross section for scattering by phonon excitations.

1. Introduction

In this paper, we shall develop the formal theory of the inelastic scattering of x-rays by condensed matter, starting from a quantum mechanical approach. We shall then proceed to make the connection with linear response functions and show how the inelastic scattering of x-rays at high energy transfers can be related to the dielectric function of the electron gas. Finally, we shall discuss the specific cases of scattering by phonons. Most of this development may be found (in slightly differing notation in some cases) in several monographs and review articles [1–4].

The Hamiltonian for a system of non-relativistic electrons interacting with an electromagnetic field is given by

$$H = \frac{1}{2m} \sum_i \left(\mathbf{P}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) \right) \cdot \left(\mathbf{P}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) \right) + \sum_i V(\mathbf{r}_i) + V_{\text{int}}^{e-e} \quad (1)$$

where \mathbf{P}_i and \mathbf{r}_i represent the momentum and position operators for the i th electron, e , m and c are respectively the electron charge, mass and the velocity of light, $\mathbf{A}(\mathbf{r})$ is the vector potential at the point \mathbf{r} in space, $V(\mathbf{r}_i)$ is the potential field for the i th electron, V_{int}^{e-e} is the electron–electron interaction and the sum is over all electrons. We have in equation (1) neglected electron spin-dependent contributions to H , which are in general much smaller.

Equation (1) may be expanded to yield

$$H = H_{el} + H_{\text{int}}^{(1)} + H_{\text{int}}^{(2)}$$

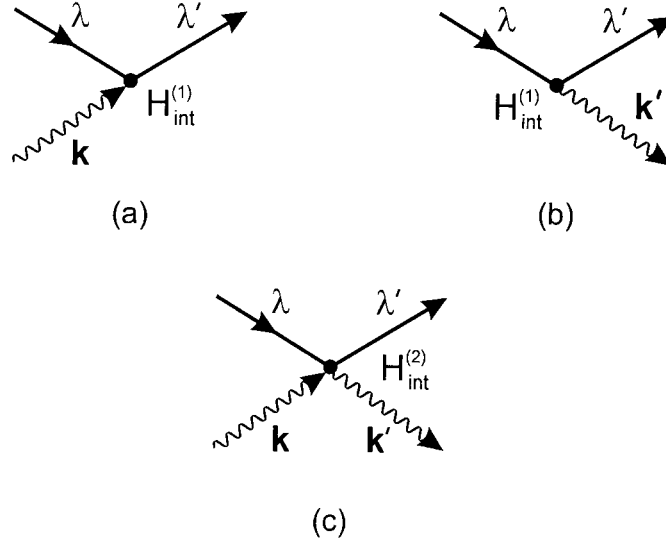


Figure 1. Schematic diagrams of one-photon (absorption) processes (a) and (b) and two-photon (scattering process (c) induced by H_{int} . k and k' represent the incoming and outgoing photon wavevectors respectively and λ and λ' the initial and final system states.

where

$$H_{el} = \sum_i \left\{ \frac{P_i^2}{2m} + V(r_i) \right\} \quad (2a)$$

$$H_{\text{int}}^{(1)} = -\frac{e}{2mc} \sum_i \{ \mathbf{P}_i \cdot \mathbf{A}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) + \mathbf{A}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) \cdot \mathbf{P}_i \} \quad (2b)$$

$$H_{\text{int}}^{(2)} = \frac{e^2}{2mc^2} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{A}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}). \quad (2c)$$

The vector potential may be written in terms of the photon creation and annihilation operators

$$\mathbf{A}(\mathbf{r}) = L^{-3/2} \sum_{\mathbf{k}\alpha} \left(\frac{\hbar}{\omega_{\mathbf{k}}} \right)^{1/2} c \{ \varepsilon_{\alpha} \mathbf{a}_{\mathbf{k}\alpha}^+ e^{i\mathbf{k}\cdot\mathbf{r}} + \varepsilon_{\alpha} \mathbf{a}_{\mathbf{k}\alpha}^- e^{-i\mathbf{k}\cdot\mathbf{r}} \} \quad (3)$$

where \mathbf{k} and α denote the photon wavevector and polarization state respectively, L^3 is a normalization box volume, $\omega_{\mathbf{k}}$ is the photon angular frequency and $\mathbf{a}_{\mathbf{k}\alpha}^+$ and $\mathbf{a}_{\mathbf{k}\alpha}^-$ are the photon creation and annihilation operators for the photon (\mathbf{k}, α) .

The first order perturbation diagrams for $H_{\text{int}}^{(1)}$ and $H_{\text{int}}^{(2)}$ are shown in figures 1(a) and 1(b) respectively. In first order, $H_{\text{int}}^{(1)}$ gives rise to one-photon absorption or emission, and only in the second order to scattering, whereas $H_{\text{int}}^{(2)}$ gives rise in the first order to scattering. Thus proceeding with the first order theory, we need only consider $H_{\text{int}}^{(2)}$. As we shall see later, scattering from $H_{\text{int}}^{(1)}$ can become of importance for incident photon energies near an x-ray resonance.

Let us consider photon states quantized in a box of side L with periodic boundary conditions, so that the only allowed \mathbf{k} values are given by $(2\pi/L)(n_x, n_y, n_z)$ where n_x , n_y and n_z are integers. The density of \mathbf{k} -points per unit volume of reciprocal space is thus

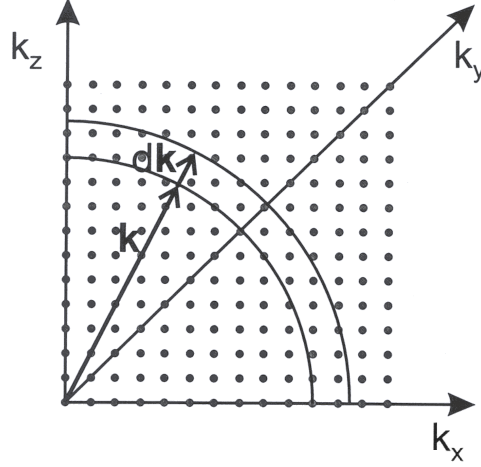


Figure 2. Schematic diagram of mesh of allowed k -vectors for photons in reciprocal space with spheres of photon energies E and $E + dE$ indicated.

$L^3/(2\pi)^3$. Consider allowed states for photons with energies between E' and $E' + dE'$ (figure 2). This corresponds to a shell in reciprocal space between radii k' and $k' + dk'$. Since $E' = \hbar ck'$ and $dE' = \hbar c dk'$, the number of k -points inside this shell (per polarization state) is $4\pi(k')^2 dkL^3/(2\pi)^3$. Let the number of points for k -vectors going into an element of solid angle $d\Omega$ for polarization state α with energies between E' and $E' + dE'$ be given by $\nu_{k\alpha} dE'$.

Then

$$\nu_{k\alpha} dE' = (k')^2 L^3 / (2\pi)^3 d\Omega dk' = (k')^2 \frac{L^3}{(2\pi)^3} \frac{d\Omega}{\hbar c} dE'$$

so that

$$\nu_{k\alpha} = (k')^2 d\Omega \frac{L^3}{(2\pi)^3} \frac{1}{\hbar c}. \quad (4)$$

The incident photon flux (photons/unit area/unit time) on the other hand is given (for this normalization) by

$$\phi = c/L^3. \quad (5)$$

Now consider a scattering process from a photon state (\mathbf{k}, α) to a state (\mathbf{k}, β) and let the initial sample state be written as $|\lambda\rangle$ and the final state by $|\lambda'\rangle$. The differential cross section for this process into solid angle $d\Omega$ is defined by

$$\left(\frac{d\sigma}{d\Omega} \right)_{k\alpha\lambda \rightarrow k'\beta\lambda'} = \frac{1}{\Phi} \frac{1}{d\Omega} \sum_{k'} W_{k\alpha\lambda \rightarrow k'\beta\lambda'} \quad (6)$$

where $W_{k\alpha\lambda \rightarrow k'\beta\lambda'}$ is the number of transitions made per unit time. By Fermi's golden rule [5] this is given by

$$\sum_{k'} W_{k\alpha\lambda \rightarrow k'\beta\lambda'} = \frac{2\pi}{\hbar} \nu_{k'\beta} |\langle \mathbf{k}'\beta\lambda' | H_{\text{int}}^{(2)} | \mathbf{k}\alpha\lambda \rangle|^2 \quad (7)$$

when $\nu_{k'\beta}$ is defined by equation (4), and $|\mathbf{k}\alpha\lambda\rangle$ is the combined (system + photon) state. From equations (4)–(7), we obtain

$$\left(\frac{d\sigma}{d\Omega} \right)_{k\alpha\lambda \rightarrow k'\beta\lambda'} = \frac{L^6}{\hbar^2 c^2 (2\pi)^2} (k')^2 |\langle \mathbf{k}'\beta\lambda' | H_{\text{int}}^{(2)} | \mathbf{k}\alpha\lambda \rangle|^2 \quad (8)$$

and substituting from equation (2c) for $H_{\text{int}}^{(2)}$, we obtain

$$\langle \mathbf{k}' \beta \lambda' | H_{\text{int}}^{(2)} | \mathbf{k} \alpha \lambda \rangle = \frac{1}{L^3} \left(\frac{e^2}{mc^2} \right) \frac{\hbar c}{(\omega_k \omega_{k'})^{1/2}} (\boldsymbol{\varepsilon}_\alpha^* \cdot \boldsymbol{\varepsilon}_\beta) \left\langle \lambda' \left| \sum_i e^{-i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}_i} \right| \lambda \right\rangle \quad (9)$$

where the matrix element is now an integral involving only the sample wavefunctions.

Using $\omega = ck$ etc, and finally putting in the energy conservation condition for the scattering process, we obtain the partial differential cross section

$$\left(\frac{d^2 \sigma}{d\Omega dE'} \right)_{\mathbf{k}\alpha\lambda \rightarrow \mathbf{k}'\beta\lambda'} = \left(\frac{e^2}{mc^2} \right)^2 |\boldsymbol{\varepsilon}_\alpha^* \cdot \boldsymbol{\varepsilon}_\beta|^2 (k'/k) \left\langle \lambda \left| \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \right| \lambda' \right\rangle \left\langle \lambda' \left| \sum_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \right| \lambda \right\rangle \times \delta(E_\lambda - E_{\lambda'} + \hbar\omega). \quad (10)$$

(The partial differential cross section is the differential cross section per unit scattered energy.)

In equation (10), we have defined the wave-vector and energy transfers as

$$\mathbf{q} = \mathbf{k} - \mathbf{k}' \quad (11)$$

and

$$\hbar\omega = E_k - E_{k'}. \quad (12)$$

If we sum now over all the possible final states λ' of the sample and thermally average over all initial states λ , we finally obtain

$$\left(\frac{d^2 \sigma}{d\Omega dE'} \right)_{\mathbf{k}\alpha \rightarrow \mathbf{k}'\beta} = (k'/k) \left(\frac{e^2}{mc^2} \right)^2 |\boldsymbol{\varepsilon}_\alpha^* \cdot \boldsymbol{\varepsilon}_\beta| S(\mathbf{q}, \omega) \quad (13)$$

where

$$S(\mathbf{q}, \omega) = \sum_{\lambda\lambda'} \sum_{ij} p_\lambda \langle \lambda | e^{-i\mathbf{q} \cdot \mathbf{r}_i} | \lambda' \rangle \langle \lambda' | e^{i\mathbf{q} \cdot \mathbf{r}_j} | \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega). \quad (14)$$

p_λ is the probability of initial state λ , given in the usual manner by $Z^{-1} \exp(-E_\lambda/kT)$, Z being the partition function.

2. Heisenberg time-dependent operators

In order to reduce equation (14) for $S(\mathbf{q}, \omega)$ to a more compact form, let us define the time-dependent Heisenberg operators in the following way. If A is any operator (in the so-called Schrödinger representation), and H is the system Hamiltonian, then

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar} \quad (15)$$

is the corresponding operator in the time-dependent Heisenberg representation.

Obviously

$$A(0) = A$$

Let us write the δ -function in equation (14) in integral representation

$$\delta(E_\lambda - E_{\lambda'} + \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{i(E_{\lambda'} - E_\lambda)t/\hbar}. \quad (16)$$

Then if A and B are any operators,

$$\begin{aligned} & \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle e^{i(E_{\lambda'} - E_\lambda)t/\hbar}. \end{aligned} \quad (17)$$

However, we may write $e^{-iE_\lambda t/\hbar}|\lambda\rangle$ as $e^{-iHt/\hbar}|\lambda\rangle$, so that equation (17) may be written

$$\begin{aligned} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B | \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\lambda'} \langle \lambda | A | \lambda' \rangle \langle \lambda' | B(t) | \lambda \rangle \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \lambda | A(0) B(t) | \lambda \rangle \end{aligned} \quad (18)$$

where we have used the completeness property to sum over λ' . We define the time-dependent correlation function of two operators A and B by

$$\sum_{\lambda} p_{\lambda} \langle \lambda | A(0) B(t) | \lambda \rangle \equiv \langle A(0) B(t) \rangle. \quad (19)$$

Using equation (18), we may write equation (14) as

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho(\mathbf{q}, 0) \rho^+(\mathbf{q}, t) \rangle \quad (20)$$

where we define the electron density fluctuation operator by

$$\rho(\mathbf{q}) = \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \quad (21)$$

where the sum is over all electrons i . It is trivial to see that $\rho(\mathbf{q})$ is the spatial Fourier transform of the electron density operator

$$\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (22)$$

We may also write $\langle \rho(\mathbf{q}, 0) \rho^+(\mathbf{q}, t) \rangle$ as the spatial Fourier transform of the function $G(\mathbf{r}, t)$,

$$\langle \rho(\mathbf{q}, 0) \rho^+(\mathbf{q}, t) \rangle = \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} G(\mathbf{r}, t) \quad (23)$$

where

$$G(\mathbf{r}, t) = \sum_{i,j} \int d\mathbf{r}' \langle \delta(\mathbf{r} - \mathbf{r}' - \mathbf{r}_i(0)) \delta(\mathbf{r}' + \mathbf{r}_j(t)) \rangle. \quad (24)$$

$G(\mathbf{r}, t)$ is known as the Van Hove space-time correlation function for the electrons [6]. From equations (20) and (23),

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} G(\mathbf{r}, t). \quad (25)$$

Integrating equation (13) over scattered energy E' (equivalent to integrating over ω for fixed incident energy), we obtain for the differential cross section

$$\left(\frac{d\sigma}{d\Omega} \right) = \left(\frac{e^2}{mc^2} \right)^2 |\boldsymbol{\varepsilon}_\alpha^* \cdot \boldsymbol{\varepsilon}_\beta|^2 S(\mathbf{q}) \quad (26)$$

where

$$S(\mathbf{q}) = \hbar \int_{-\infty}^{\infty} d\omega S(\mathbf{q}, \omega). \quad (27)$$

(We have assumed that the relevant energy transfers are small enough compared with the x-ray photon energies that (k'/k) can be replaced by unity.)

From equation (20), we have

$$S(\mathbf{q}) = \langle \rho(\mathbf{q}, 0) \rho^+(\mathbf{q}, 0) \rangle \equiv \langle \rho(\mathbf{q}) \rho^+(\mathbf{q}) \rangle \quad (28)$$

where the absence of an explicit time dependence in a correlation function implies an equal-time correlation function.

3. Response functions

Consider a weak external time-dependent perturbation which couples linearly to some operator B of the system, so that

$$H = H_0 + H_1 \quad (29)$$

and

$$H_1 = -Bh(t'). \quad (30)$$

If we consider only the linear response in the expectation value of some other operator A of the system at some different time t , we may write

$$\delta\langle A \rangle(t) = \int_{-\infty}^t dt' \phi_{AB}(t-t')h(t'). \quad (31)$$

$\phi_{AB}(t)$ is called the linear response function. Let us write

$$h(t) = 2h \cos \omega t e^{\varepsilon t} \quad (\varepsilon \rightarrow 0+) \quad (32)$$

implying that the perturbation is switched on adiabatically from time $(-\infty)$. Then

$$\begin{aligned} \delta\langle A \rangle(t) &= 2 \operatorname{Lt}_{\varepsilon \rightarrow 0+} h \int_{-\infty}^t dt' \phi_{AB}(t-t') \cos(\omega t') e^{\varepsilon t'} \\ &= 2h \operatorname{Re} \operatorname{Lt}_{\varepsilon \rightarrow 0+} \int_{-\infty}^t dt' \phi_{AB}(t-t') e^{i(\omega+\varepsilon)t'}. \end{aligned} \quad (33)$$

Changing to a new variable of integration $t'' = t - t'$ in equation (33) we may write

$$\delta\langle A \rangle(t) = 2h \operatorname{Re}[e^{i\omega t} \chi_{AB}(\omega)] \quad (34)$$

where

$$\chi_{AB}(\omega) = \operatorname{Lt}_{\varepsilon \rightarrow 0+} \int_0^{\infty} dt \phi_{AB}(t) e^{-(i\omega+\varepsilon)t} \quad (35)$$

is the frequency-dependent response function. This function has the following properties.

Define

$$\chi_{AB}(\omega) = \chi'_{AB}(\omega) + i\chi''_{AB}(\omega) \quad (36)$$

then

$$\chi'(-\omega) = \chi'(\omega) \quad \chi''(-\omega) = -\chi''(\omega) \quad (37)$$

$$\chi'(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\chi''(\omega')}{\omega - \omega'} \quad (38a)$$

$$\chi''(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\chi'(\omega')}{\omega - \omega'} \quad (38b)$$

where P stands for the 'principal part' of the integral.

Equations 38(a) and (b) are the well known Kramers–Kronig dispersion relations which hold between the real and the imaginary parts of any causal response function [3].

An explicit calculation of the response function can be obtained by using first order time-dependent perturbation theory. Let us write the system eigenfunctions as the set ψ_n at time t after the perturbation. The system wavefunction $\psi(t)$ can be written as

$$\psi(t) = \sum_n a_n(t) e^{-iE_n t/\hbar} \psi_n \quad (39)$$

since the ψ_n form a complete set. The coefficients obey the relations

$$\left. \begin{aligned} a_n(t) &= 1 \\ a_{n'} &= 0 (n' \neq n) \end{aligned} \right\} t \leq 0 \quad (40)$$

if the system was in a particular eigenstate ψ_n before the perturbation. Then

$$\begin{aligned} A(t) &= \langle \psi(t) | A | \psi(t) \rangle \\ &= \langle n | A | n \rangle + \sum_{n' \neq n} a_{n'}(t) e^{i(E_n - E_{n'})t/\hbar} \langle n | A | n' \rangle + \text{c.c.} \end{aligned} \quad (41)$$

where c.c. denotes the complex conjugate of the term before it.

By first order perturbation theory,

$$a_{n'}(t) = -h \langle n' | B | n \rangle \frac{e^{-i(E_n - E_{n'} + \hbar(\omega + i\varepsilon))t/\hbar}}{E_n - E_{n'} + \hbar(\omega + i\varepsilon)} - h \langle n' | B | n \rangle \frac{e^{-i(E_n - E_{n'} - \hbar(\omega - i\varepsilon))t/\hbar}}{E_n - E_{n'} - \hbar(\omega - i\varepsilon)}. \quad (42)$$

Substituting in equation (41) we obtain

$$\begin{aligned} \delta \langle A \rangle(t) &= -2h \operatorname{Re} \left\{ e^{i\omega t} \left[\sum_n p_n \sum_{n' \neq n} \frac{\langle n | A | n' \rangle \langle n' | B | n \rangle}{E_n - E_{n'} - \hbar(\omega - i\varepsilon)} \right. \right. \\ &\quad \left. \left. + \sum_{n \neq n'} \frac{\langle n | B | n' \rangle \langle n' | A | n \rangle}{E_n - E_{n'} + \hbar(\omega + i\varepsilon)} \right] \right\} \end{aligned} \quad (43)$$

the limit as $\varepsilon \rightarrow 0+$ being understood. (The thermodynamic average over initial states n has been taken above.)

Comparing this with equation (34), we thus finally obtain

$$\chi_{AB}(\omega) = - \operatorname{Lt}_{\varepsilon \rightarrow 0+} \sum'_{n, n'} p_n \left\{ \frac{\langle n | A | n' \rangle \langle n' | B | n \rangle}{E_n - E_{n'} - \hbar(\omega - i\varepsilon)} + \frac{\langle n | B | n' \rangle \langle n' | A | n \rangle}{E_n - E_{n'} + \hbar(\omega + i\varepsilon)} \right\} \quad (44)$$

where the prime over the summation means the term with $n' = n$ must be excluded.

Now

$$\operatorname{Lt}_{\varepsilon \rightarrow 0+} \frac{1}{x \pm i\varepsilon} = P \left(\frac{1}{x} \right) \mp i\pi \delta(x) \quad (45)$$

so we may write for the imaginary part of $\chi_{AB}(\omega)$

$$\begin{aligned} \chi''_{AB}(\omega) &= \pi \sum'_{n, n'} p_n [\langle n | B | n' \rangle \langle n' | A | n \rangle \delta(E_n - E_{n'} + \hbar\omega) \\ &\quad + \langle n | A | n' \rangle \langle n' | B | n \rangle \delta(E_n - E_{n'} - \hbar\omega)] \end{aligned} \quad (46)$$

since $p_n = Z^{-1} e^{-E_n/kT}$, by switching the n, n' terms in the second term in the summation on the right-hand side of equation (46), it may be verified that we have the result that

$$\frac{1}{\pi} \frac{1}{1 - e^{-\beta\omega}} \chi''_{AB}(\omega) = \sum'_{n, n'} p_n \langle n | B | n' \rangle \langle n' | A | n \rangle \delta(E_n - E_{n'} + \hbar\omega) \quad (47)$$

where $\beta = \hbar/kT$.

By equation (18), this implies that

$$\frac{1}{\pi} \frac{1}{1 - e^{-\beta\omega}} \chi''_{AB} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle B(O)A(t) \rangle. \quad (48)$$

The above result is very general and holds for the time-dependent correlation function of any two operators and relates it to the corresponding response function. In particular, if we choose A as $\rho^+(\mathbf{q})$ and B as $\rho(\mathbf{q})$, we obtain the famous fluctuation dissipation theorem,

$$S(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{1}{1 - e^{-\beta\omega}} \chi''_{\rho^+(\mathbf{q})\rho(\mathbf{q})}(\omega) \quad (49)$$

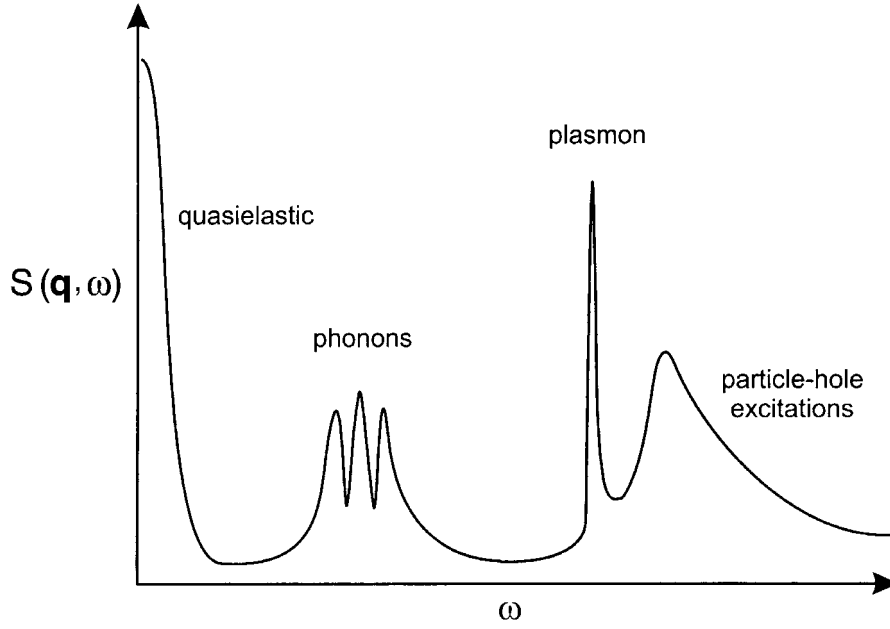


Figure 3. Schematic diagram of $S(\mathbf{q}, \omega)$ illustrating poles or quasi-poles of $\chi(\mathbf{q}, \omega)$ for various elementary excitations.

which relates the scattering function to the imaginary part of the electron density response function, which we may refer to henceforth as $\chi_{\rho\rho}(\mathbf{q}, \omega)$.

We thus see that the x-ray scattering will have peaks wherever the electron density response function $\chi_{\rho\rho}(\mathbf{q}, \omega)$ has poles. These will occur wherever there is a collective response of the electron gas (plasmons), or a response to the lattice vibrations (phonons), or a single particle response (particle–hole excitations, excitons etc).

For a given \mathbf{q} , we sketch in figure 3 a schematic diagram of what $\chi''_{\rho\rho}(\mathbf{q}, \omega)$ might look like for a typical solid as a function of ω .

There are methods to calculate the electron density response function in various approximations. A commonly used approximation is the so-called random phase approximation [3] (RPA), which is basically a self-consistent field approximation. Consider for the moment a frozen lattice and an external (weak) time-dependent potential acting on the electron system in the solid. This corresponds to a perturbation

$$H_1 = -e\rho(\mathbf{r})[e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}V_{\text{int}}(\mathbf{q}, \omega) + \text{c.c.}]. \quad (50)$$

If we switch off the electron–electron interactions, and write the electron states as independent free-electron states

$$|k\rangle = L^{-3/2} e^{ik\cdot\mathbf{r}}. \quad (51)$$

Equation (44) can be shown to yield for this so-called ‘non-interacting’ density–density response function

$$\chi_0(\mathbf{q}, \omega) = \sum_{k,k'} \frac{n(k) - n(k')}{E_{k'} - E_k - \hbar\omega} \langle k|e^{-i\mathbf{q}\cdot\mathbf{r}}|k'\rangle \langle k'|e^{i\mathbf{q}\cdot\mathbf{r}}|k\rangle \quad (52)$$

where $n(k)$ is the occupation number of electron state k (including spin).

For real crystals, even the non-interacting electron states are actually Bloch states of the form

$$\sum_{\mathbf{G}} \alpha_{\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

\mathbf{G} being a vector of the reciprocal lattice. This leads to an electron density response with Fourier component $\mathbf{q} + \mathbf{G}$, when the external potential has a Fourier component \mathbf{q} (or $\mathbf{q} + \mathbf{G}'$ generally), which may be different but related by a reciprocal lattice vector. Thus for such systems we have in general an electron density response *matrix*.

$$\chi_0(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) = \sum_{k,k'} \frac{n(k) - n(k')}{E_{k'} - E_k - \hbar\omega} \langle k | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | k' \rangle \langle k' | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | k \rangle. \quad (53)$$

For free-electron gas systems, this matrix is diagonal in \mathbf{G} , \mathbf{G}' , and we get simply the scalar function $\chi_0(\mathbf{q}, \omega)$ in equation (52). Staying in this limit, let us now switch on the interaction between the electrons, which is $v(\mathbf{r})$. (This is usually the Coulomb interaction (e^2/r) but may be modified to include exchange and correlation effects [8]). Then

$$\rho(\mathbf{q}, \omega) = -\chi_0(\mathbf{q}, \omega) V_{sc}(\mathbf{q}, \omega). \quad (54)$$

Now

$$V_{sc}(\mathbf{q}, \omega) = V_{ext}(\mathbf{q}, \omega) + v(\mathbf{q})\rho(\mathbf{q}, \omega) \quad (55)$$

where $v(\mathbf{q})$ is the Fourier transform of $v(\mathbf{r})$.

Thus, by equations (54) and (55), we have self-consistently.

$$V_{sc}(\mathbf{q}, \omega) = V_{int}(\mathbf{q}, \omega)/\varepsilon(\mathbf{q}, \omega) \quad (56)$$

where

$$\varepsilon(\mathbf{q}, \omega) = 1 + v(\mathbf{q})\chi_0(\mathbf{q}, \omega) \quad (57)$$

and is called the wave-vector and frequency-dependent dielectric function of the electron gas. More generally, for Bloch states.

$$V_{sc}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \varepsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) V_{ext}(\mathbf{q} + \mathbf{G}', \omega) \quad (58)$$

where ε^{-1} is the inverse of the matrix

$$\varepsilon = 1 + v(\mathbf{q})\chi_0 \quad (59)$$

χ_0 being the matrix defined in equation (53).

While $\chi_0(\mathbf{q}, \omega)$ was defined as the non-interacting density response function, the full density response function $\chi(\mathbf{q}, \omega)$ is defined by relating $\rho(\mathbf{q}, \omega)$ to the *external* potential $V_{ext}(\mathbf{q}, \omega)$:

$$\rho(\mathbf{q}, \omega) = -\chi(\mathbf{q}, \omega) V_{ext}(\mathbf{q}, \omega). \quad (60)$$

Using equations (55) and (56), we may write

$$\chi(\mathbf{q}, \omega) = \frac{1}{v(\mathbf{q})} \left(\frac{1}{\varepsilon(\mathbf{q}, \omega)} - 1 \right). \quad (61)$$

Thus, by equation (49), the scattering function can be written in terms of the inverse of the dielectric function of the electrons as

$$S(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{1}{v(\mathbf{q})} \text{Im} \left[\frac{1}{\varepsilon(\mathbf{q}, \omega)} \right]. \quad (62)$$

In the more general case of Bloch electrons $1/\varepsilon(\mathbf{q}, \omega)$ in equation (62) must be replaced by $\varepsilon^{-1}(\mathbf{q}, \mathbf{q}, \omega)$, involving the *inverse* of the dielectric *matrix*.

In the appendix we summarize the various forms in which the scattering cross section may be written and the relationships between them.

For completeness, we here discuss the case of resonant x-ray scattering. As stated in the introduction, the interaction term $H_{\text{int}}^{(1)}$ in the interaction between the electrons and the x-ray photon field can only give rise to scattering in second order in perturbation theory. The partial differential cross section (neglecting spin-dependent terms) may be written as

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{k\alpha \rightarrow k'\beta} = (k'/k) \left(\frac{e^2}{mc^2}\right)^2 \sum_{\lambda\lambda'} p_{\lambda} |\langle \lambda | M | \lambda' \rangle|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega) \quad (63)$$

where the matrix element is defined by

$$\langle \lambda | M | \lambda' \rangle = \sum_{\lambda''} \sum_{\nu, \nu'} \left\{ \frac{\langle \lambda | \sum_i P_{\nu}(i) e^{-iq \cdot r_i} | \lambda'' \rangle \langle \lambda'' | \sum_j P_{\nu'}(j) e^{iq \cdot r_j} | \lambda' \rangle}{E_{\lambda} - E_{\lambda''} + \hbar\omega_0 - i\Gamma/2} + \frac{\langle \lambda | \sum_j P_{\nu'}(j) e^{iq \cdot r_j} | \lambda'' \rangle \langle \lambda'' | \sum_i P_{\nu}(i) e^{-iq \cdot r_i} | \lambda' \rangle}{E_{\lambda} - E_{\lambda''} + \hbar\omega_0} \right\} \varepsilon_{\alpha\nu}^* \varepsilon_{\beta\nu'} \quad (64)$$

where λ'' denotes an intermediate (virtual) state, the sums over ij are over all electrons in the system and Γ is introduced to take into account core-hole lifetime effects for the intermediate states. ν, ν' denote Cartesian components (e.g. $\varepsilon_{\alpha,\nu}$ is the ν -component of the photon polarization vector in polarization state α , etc). ω_0 is the incident photon energy.

It may be seen that if the real part of the energy denominator becomes zero, this matrix element can become very large (e.g. when the incident photon energy is in the vicinity of an x-ray absorption edge of the atom in question), leading to a significant amount of scattering. This has been exploited to study magnetism in crystals [7–9] for the *elastic* scattering case. The case of resonant *inelastic* scattering has also been discussed in several recent papers [10, 11].

4. Scattering from lattice vibrations

The discussion above assumed scattering of x-rays at energy transfers much greater than lattice vibrational energies, so that the lattice could be regarded as frozen. At low energy transfers, we must take into account the atomic vibrations in calculating the electron density–density correlation functions. For simplicity, let us group the electrons into sets belonging to each of the atoms in the crystal, and assume that as the atoms vibrate, the electron cloud associated with that atom moves rigidly with it. (This is not quite true for the outer or valence electrons but the deviations are quite subtle and will be ignored in what follows.) We may write

$$\rho(\mathbf{q}) = \sum_i e^{-iq \cdot r_i} = \sum_{\ell} e^{-iq \cdot \mathbf{R}_{\ell}} \left[\sum_{i(\ell)} e^{-iq \cdot (r_i - \mathbf{R}_{\ell})} \right] \quad (65)$$

where ℓ runs over all atoms in the crystal and $i(\ell)$ in the second sum runs over all electrons on the ℓ th atom, \mathbf{R}_{ℓ} being the position of the ℓ th atom. The factor in the bracket on the right-hand side of equation (65) (which may be replaced by an integral) is actually the Fourier transform of the electron density on atom ℓ , $Zf(\mathbf{q})$, where $f(\mathbf{q})$ is the atomic form factor (normalized to unity for $q = 0$). Z is the atomic number and we have assumed for simplicity a Bravais lattice (i.e. one atom per unit cell and all atoms identical).

From equation (65) we have for the corresponding time-dependent operator

$$\rho(\mathbf{q}, t) = Zf(\mathbf{q}) \sum_{\ell} e^{-iq \cdot \mathbf{R}_{\ell}(t)} = Zf(\mathbf{q}) \sum_{\ell} e^{-iq \cdot (\ell + \mathbf{u}_{\ell}(t))} \quad (66)$$

where ℓ represents the equilibrium position of the ℓ th atom and \mathbf{u}_{ℓ} represents the displacement due to lattice vibrations.

Then using equation (20), we have

$$\begin{aligned} S(\mathbf{q}, \omega) &= \frac{Z^2}{2\pi\hbar} f^2(\mathbf{q}) \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\ell\ell'} \langle e^{-i\mathbf{q}\cdot\mathbf{R}_\ell(0)} e^{-i\mathbf{q}\cdot\mathbf{R}_\ell(t)} \rangle \\ &= \frac{Z^2}{2\pi\hbar} f^2(\mathbf{q}) \sum_{\ell\ell'} e^{i\mathbf{q}\cdot(\ell-\ell')} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{-i\mathbf{q}\cdot\mathbf{u}_\ell(0)} e^{i\mathbf{q}\cdot\mathbf{u}'_\ell(t)} \rangle. \end{aligned} \quad (67)$$

Now we can expand the phonon displacement $\mathbf{u}_\ell(t)$ in terms of the corresponding time-dependent phonon creation and annihilation operators, to obtain

$$\mathbf{u}_\ell(t) = \sum_{\mathbf{q}_0, j} e(\mathbf{q}_0, j) \left(\frac{\hbar}{2NM\omega_{\mathbf{q}_0, j}} \right)^{1/2} (\alpha_{\mathbf{q}_0, j} e^{-i\omega_{\mathbf{q}_0, j}t} + \alpha_{\mathbf{q}_0, j}^+ e^{i\omega_{\mathbf{q}_0, j}t}) \quad (68)$$

where $\alpha_{\mathbf{q}_0, j}^+ e^{i\omega_{\mathbf{q}_0, j}t}$ is the explicit representation of the phonon creation operator $\alpha_{\mathbf{q}_0, j}^+(t)$ and similarly for $\alpha_{\mathbf{q}_0, j}(t)$, the corresponding annihilation operator; \mathbf{q}_0, j are the phonon wavevector and polarization branch respectively, $\omega_{\mathbf{q}_0, j}$ the corresponding phonon angular frequency and $e(\mathbf{q}_0, j)$ is the phonon eigenvector. N is the total number of atoms in the crystal.

In order to evaluate the thermal average in equation (65), we use the Baker–Hausdorff theorem [1] which states that for two operators A, B , which both commute with their commutator $[A, B]$,

$$e^A e^B = e^{A+B+\frac{1}{2}[A, B]}. \quad (69)$$

Thus

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_\ell(0)} e^{i\mathbf{q}\cdot\mathbf{u}'_\ell(t)} \rangle = \langle e^{-i\mathbf{q}\cdot(\mathbf{u}_\ell(0)-\mathbf{u}'_\ell(t))+\frac{1}{2}[(\mathbf{q}\cdot\mathbf{u}_\ell(0)), (\mathbf{q}\cdot\mathbf{u}'_\ell(t))]} \rangle. \quad (70)$$

Since the commutator in the exponent of the right hand side of equation (70) is not an operator (because commutators of α, α^+ are simply scalars), we can take it as a simple factor and obtain

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_\ell(0)} e^{i\mathbf{q}\cdot\mathbf{u}'_\ell(t)} \rangle = \langle e^{\frac{1}{2}[(\mathbf{q}\cdot\mathbf{u}_\ell(0)), (\mathbf{q}\cdot\mathbf{u}'_\ell(t))]} \rangle \langle [e^{-i\mathbf{q}\cdot(\mathbf{u}_\ell(0)-\mathbf{u}'_\ell(t))}] \rangle. \quad (71)$$

For the second factor we may use the theorem which states that if A is an operator which is a linear combination of harmonic oscillator creation and annihilation operators, then

$$\langle e^A \rangle = e^{\frac{1}{2}\langle A^2 \rangle}. \quad (72)$$

Thus

$$\begin{aligned} \langle e^{-i\mathbf{q}\cdot(\mathbf{u}_\ell(0)-\mathbf{u}'_\ell(t))} \rangle &= e^{-\frac{1}{2}[(\mathbf{q}\cdot(\mathbf{u}_\ell(0)-\mathbf{u}'_\ell(t)))]^2} \\ &= e^{-\frac{1}{2}[(\mathbf{q}\cdot\mathbf{u}_\ell(0))]^2} e^{-\frac{1}{2}[\mathbf{q}\cdot\mathbf{u}_\ell(t)]^2} e^{\langle \mathbf{q}\cdot\mathbf{u}_\ell(0) \rangle \langle \mathbf{q}\cdot\mathbf{u}'_\ell(t) \rangle + \langle \mathbf{q}\cdot\mathbf{u}'_\ell(t) \rangle \langle \mathbf{q}\cdot\mathbf{u}_\ell(0) \rangle}. \end{aligned} \quad (73)$$

Thus from equation (71)

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_\ell(0)} e^{i\mathbf{q}\cdot\mathbf{u}'_\ell(t)} \rangle = e^{-2W} e^{\langle \mathbf{q}\cdot\mathbf{u}'_\ell(t) \rangle \langle \mathbf{q}\cdot\mathbf{u}_\ell(0) \rangle} \quad (74)$$

where we have written the Debye–Waller factor e^{-2W} as the square of

$$e^{-W} \equiv e^{-\frac{1}{2}\langle (\mathbf{q}\cdot\mathbf{u}_\ell(0))^2 \rangle} = e^{-\frac{1}{2}\langle (\mathbf{q}\cdot\mathbf{u}_\ell(t))^2 \rangle} \quad (75)$$

(by the properties of quantum simple harmonic oscillators, the two expectation values in equation (75) can be shown to be equal). Since in general the phonon displacements are small, we may expand the exponential in the right-hand side of equation (74) and obtain

$$e^{\langle \mathbf{q}\cdot\mathbf{u}_\ell(0) \rangle \langle \mathbf{q}\cdot\mathbf{u}_\ell(t) \rangle} = 1 + \langle (\mathbf{q}\cdot\mathbf{u}_\ell(0)) (\mathbf{q}\cdot\mathbf{u}_\ell(t)) \rangle + \dots = 1 + \sum_{\alpha\beta} q_\alpha q_\beta \langle u_{\ell\alpha}(0) u_{\ell\beta}(t) \rangle + \dots \quad (76)$$

when α, β denote Cartesian components. The higher order terms involve the so-called multi-phonon terms and we will neglect them here. Equations (74) and (76) enable us to write $S(\mathbf{q}, \omega)$ from equation (67) as

$$S(\mathbf{q}, \omega) = \frac{Z^2}{2\pi\hbar} f^2(\mathbf{q}) \sum_{\ell\ell'} e^{i\mathbf{q}\cdot(\ell-\ell')} \int_{-\infty}^{\infty} dt e^{i\omega t} \left[1 + \sum_{\alpha\beta} q_\alpha q_\beta \langle u_{\ell\alpha}(0) u_{\ell'\beta}(t) \rangle \right]. \quad (77)$$

The displacement–displacement correlation function may be evaluated from equation (68) as

$$\begin{aligned} \langle u_{\ell\alpha}(0) u_{\ell'\beta}(t) \rangle &= \sum_{\mathbf{q}_0 j} \left(\frac{\hbar}{2NM\omega_{\mathbf{q}_0 j}} \right) e_\alpha(\mathbf{q}_0 j) e_\beta(\mathbf{q}_0 j) [\langle n_{\mathbf{q}_0 j} \rangle e^{-i\omega_{\mathbf{q}_0 j} t} e^{i\mathbf{q}_0 \cdot (\ell-\ell')} \\ &+ \langle n_{\mathbf{q}_0 j} + 1 \rangle e^{i\omega_{\mathbf{q}_0 j} t} e^{-i\mathbf{q}_0 \cdot (\ell-\ell')}] \end{aligned} \quad (78)$$

where

$$\langle n_{\mathbf{q}_0 j} \rangle = \frac{1}{e^{\beta\omega_{\mathbf{q}_0 j}} - 1} \quad (79)$$

and represents the Bose–Einstein occupation factor for phonon $(\mathbf{q}_0 j)$.

Substituting in equation (77), carrying out the time integration, and using the standard results that

$$\sum_{\ell} e^{i\mathbf{k}\cdot\ell} = \frac{L^3}{(2\pi)^3} \sum_{\mathbf{G}} \delta(\mathbf{K} - \mathbf{G}) \quad (80)$$

where \mathbf{G} is a vector of the reciprocal lattice, we finally obtain

$$\begin{aligned} S(\mathbf{q}, \omega) &= \frac{Z}{\hbar} f^2(\mathbf{q}) e^{-2W} \frac{L^3}{(2\pi)^3} \left[\sum_{\mathbf{G}} \delta(\mathbf{q} - \mathbf{G}) \right] \delta(\omega) + Z^2 f^2(\mathbf{q}) e^{-2W} \left(\frac{v_0}{(2\pi)^3} \right) \\ &\times \sum_{\mathbf{q}_0 j} \left(\frac{1}{2M\omega_{\mathbf{q}_0 j}} \right) |\mathbf{q} \cdot \mathbf{e}(\mathbf{q}_0 j)|^2 \{ \langle n_{\mathbf{q}_0 j} \rangle \delta(\omega + \omega_{\mathbf{q}_0 j}) + \langle n_{\mathbf{q}_0 j} + 1 \rangle \delta(\omega - \omega_{\mathbf{q}_0 j}) \} \\ &\times \sum_{\mathbf{G}} \delta(\mathbf{q} \pm \mathbf{q}_0 - \mathbf{G}). \end{aligned} \quad (81)$$

The first term represents (elastic) Bragg scattering, while the second term represents one-phonon inelastic scattering, with both energy gain (phonon annihilation) and energy loss (phonon creation) processes represented. (v_0 is the unit cell volume.) As stated above, the higher order terms in the expansion contribute to multiphonon inelastic processes, and these are generally small except at very high sample temperatures, and usually do not show sharp peaks in the inelastic scattering function $S(\mathbf{q}, \omega)$.

Typically, experiments to measure *phonon dispersion* relations or $\omega_{\mathbf{q}_0 j}$ as a function of \mathbf{q}_0 require relatively high energy resolution (of the order of 1 meV–10 MeV). To obtain this with incident photon energies of 10 keV–30 keV requires special monochromator and analyser crystals, usually set in *backscattering* geometry, and count rates in the one-phonon peaks tend to be rather low notwithstanding the high brilliance of the synchrotron x-ray beams. Experimental details regarding these kinds of experiments have been reviewed by Burkel [12, 13]. There is another type of inelastic x-ray scattering experiment which utilizes the nuclear resonant scattering from ‘Mössbauer’ nuclei in the sample itself. Since this resonance is extremely sharp in energy (\sim neV) the effective energy resolution for these experiments is only limited by the energy resolution of the incident beam (\sim meV). The nuclear resonant process is *incoherent* and so what is effectively measured is the *phonon density of states* weighted with the contribution only of the resonant nuclei [14].

Appendix

We summarize below some of the relations derived in this chapter between the x-ray scattering cross section and various correlation functions and response functions. There are

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{k\alpha \rightarrow k'\beta} = \frac{k'}{k} \left(\frac{e^2}{mc^2} \right)^2 |\varepsilon_\alpha^* \cdot \varepsilon_\beta|^2 S(\mathbf{q}, \omega) \quad (\text{A1})$$

where \mathbf{k} , \mathbf{k}' , α , β are the initial and final wavevectors and polarization states of the photon respectively, and ε_α , ε_β the corresponding polarization vectors.

$$\left(\frac{d\sigma}{d\Omega} \right)_{k\alpha \rightarrow k'\beta} = \int d\omega S(\mathbf{q}, \omega) = \left(\frac{e^2}{mc^2} \right)^2 |\varepsilon_\alpha^* \cdot \varepsilon_\beta|^2 S(\mathbf{q}) \quad (\text{A2})$$

$$S(\mathbf{q}, \omega) = \sum_{\lambda\lambda'} p_\lambda \langle \lambda | \rho(\mathbf{q}) | \lambda' \rangle \langle \lambda' | \rho^+(\mathbf{q}) | \lambda \rangle \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \quad (\text{A3})$$

where

$$\begin{aligned} \rho(\mathbf{q}) &= \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \quad (i \text{ sums over electrons}) \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho(\mathbf{q}, 0) \rho^+(\mathbf{q}, t) \rangle \end{aligned} \quad (\text{A4})$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} G(\mathbf{r}, t) \quad (\text{A5})$$

$$= \frac{1}{\pi} \left[\frac{1}{1 - e^{-\beta\omega}} \right] \chi''_{\rho\rho}(\mathbf{q}, \omega) \quad (\text{A6})$$

$$= \frac{1}{\pi} \left[\frac{1}{1 - e^{-\beta\omega}} \right] \frac{1}{v(\mathbf{q})} \text{Im} \varepsilon^{-1}(\mathbf{q}, \mathbf{q}, \omega) \quad (\text{A7})$$

where the quantities have been defined in the text.

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