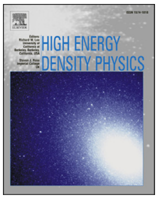
High Energy Density Physics 13 (2014) 55–83

Contents lists available at ScienceDirect

High Energy Density Physics

journal homepage: www.elsevier.com/locate/hedp



Quantum theory of Thomson scattering

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ARTICLE INFO

Article history:
Received 6 June 2014
Received in revised form
18 August 2014
Accepted 21 August 2014
Available online 3 September 2014

Keywords:
Thomson scattering
Scattering of electromagnetic radiation

ABSTRACT

The general theory of the scattering of electromagnetic radiation in atomic plasmas and metals, in the non-relativistic regime, in which account is taken of the Kramers–Heisenberg polarization terms in the Hamiltonian, is described from a quantum mechanical viewpoint. As well as deriving the general formula for the double differential Thomson scattering cross section in an isotropic finite temperature multi-component system, this work also considers closely related phenomena such as absorption, refraction, Raman scattering, resonant (Rayleigh) scattering and Bragg scattering, and derives many essential relationships between these quantities. In particular, the work introduces the concept of scattering strength and the strength-density field which replaces the normal particle density field in the standard treatment of scattering by a collection of similar particles and it is the decomposition of the strength-density correlation function into more familiar-looking components that leads to the final result. Comparisons are made with previous work, in particular that of Chihara [1].

1. Introduction

Thomson scattering is the scattering of electromagnetic radiation by electrons in matter, in the non-relativistic or near-relativistic regime. Two key features of Thomson scattering are that it is sensitive to correlations between electrons and that the polarization of the scattered radiation is entirely determined by the initial polarization and the scattering geometry. This is unlike Compton scattering, which is incoherent scattering by individual electrons and which contains a polarization-independent contribution. Nevertheless Compton and Thomson scattering are descriptions of the same phenomenon to the extent that incoherent Thomson scattering and Compton scattering are interchangeable descriptions of scattering by effectively free and uncorrelated non-relativistic electrons. In matter, electrons are correlated via their mutual interactions, collective motions, exchange and degeneracy, and interactions with other particles (ions). These correlations are directly probed by X-ray Thomson scattering (XRTS) measurements, making the technique an important emerging diagnostic tool for studying the equation-of-state properties of cold and warm dense matter [2–8]. Understanding these correlation effects allows quantities such as temperature and density to be deduced directly from measurements. A baseline description of Thomson scattering from ideal plasmas is provided by the Random Phase Approximation (RPA) which ignores short-range correlations between electrons, with only large-scale collective motion taken into account. For dense plasmas and plasmas in which bound electrons contribute to the scattering, a more general treatment is required both to provide more accurate modelling and to be able to extract meaningful information from scattering measurements.

Coherent X-ray Thomson back-scattering is also a potentially useful spectroscopic tool for carrying out material assays as the cross-sections depend strongly on atomic spectra as well as being amplified by an underlying proportionality of the cross-sections to the square of the number of bound electrons.

This report presents a quantum mechanical derivation of the general Thomson differential scattering cross-section for scattering of electromagnetic radiation in a fully or partially ionised plasma comprising one or more nuclear species. The work generalizes the work of Chihara [1] who applies a fundamentally classical approach to a two component system comprising electrons and ions. While the current method and the results yielded have clear parallels to the earlier work, they provide a different perspective while incorporating a proper quantal treatment of the electrons as well as a more consistent treatment of the polarization terms in the interaction. A second-quantized approach is used to treat the electrons thus including the effects of antisymmetry and the Pauli principle from the outset. However a classical approach is maintained for the nuclear ions, as is justified by their large masses and extremely

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http://dx.doi.org/10.1016/j.hedp.2014.08.002

short deBroglie wavelengths. The new work is generally important for extending existing detailed methodologies for treating Thomson scattering by warm dense matter, e.g. Ref. [9], to heavier elements.

This work also generalizes our previous work [10] which introduces, in the context of a simplified form of the Hamiltonian, the basic quantum mechanical approach employed here.

At a fundamental level, the scattering process is represented by the non-relativistic Hamiltonian

$$\mathbf{H} = \frac{1}{2m_\mathrm{e}}(\mathbf{p} - e\mathbf{A})^2 + \mathbf{H}_\mathrm{field} + \ldots = \mathbf{H}_0 + \mathbf{H}' + \mathbf{H}_\mathrm{field} \tag{1}$$

where m_e, e and $\mathbf{p}$ are respectively the mass, charge and canonical momentum of the electron, $\mathbf{A}$ is the electromagnetic vector potential of the incident (probe) radiation and $\mathbf{H}_\mathrm{field}$ is the Hamiltonian for the *in vacuo* electromagnetic field, which comprises the probe radiation and any ambient radiation field. The electron interacts with the field through the perturbation,

$$\mathbf{H}' = -\frac{e}{2m_\mathrm{e}}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2m_\mathrm{e}}\mathbf{A}^2 \tag{2}$$

which comprises two terms, the first of which is the Kramers–Heisenberg (KH) polarization, which represents absorption and emission of photons by the electron, while the second is the quiver energy. The quiver motion gives rise to point scattering in the first order (Born) approximation and tends to dominate the scattering of high energy photons in the non-relativistic regime, while the KH part gives rise to scattering only in second order via transition operators of the form $\mathbf{A}\cdot\mathbf{p}\,\mathbf{G}\,\mathbf{A}\cdot\mathbf{p}$ in which the propagator $\mathbf{G}$ represents an intermediate virtual state of the electron. Although the two scattering processes occur in different orders of perturbation theory, they are of the same order in the electromagnetic coupling constant and therefore must be considered together. It is noteworthy that the $\mathbf{A}^2$ term does not arise in the linearized Dirac Hamiltonian and so is not treated as a separate term in a fully relativistic QED theory of Compton scattering. The fully relativistic formulations of the theory are discussed elsewhere [10–12].

For transverse waves, $[\mathbf{p},\mathbf{A}]=\mathbf{p}\cdot\mathbf{A} - \mathbf{A}\cdot\mathbf{p} = 0$ and a second-quantized representation of the electromagnetic field experienced by an electron at position $\mathbf{r}$, in terms of photon (boson) creation and annihilation field operators, $\mathbf{b}_{\mathbf{k},\mathbf{e}}$, $\mathbf{b}^\dagger_{\mathbf{k},\mathbf{e}}$, is represented in terms of the Hermitian operator $\mathbf{A} = \tilde{\mathbf{A}} + \tilde{\mathbf{A}}^\dagger$ where [10]

$$\tilde{\mathbf{A}}(\mathbf{r}) = \sum_{\mathbf{k},\mathbf{e}} \frac{-\mathrm{i}}{\sqrt{2V\varepsilon_0\omega}}\mathbf{e}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\mathbf{b}_{\mathbf{k},\mathbf{e}},\quad \tilde{\mathbf{A}}^\dagger(\mathbf{r}) = \sum_{\mathbf{k},\mathbf{e}} \frac{\mathrm{i}}{\sqrt{2V\varepsilon_0\omega}}\mathbf{e}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\mathbf{b}^\dagger_{\mathbf{k},\mathbf{e}} \tag{3}$$

where $\mathbf{k}$ and $\mathbf{e}$ are respectively the wavenumber and direction of polarization ($\mathbf{e}\cdot\mathbf{e} = 1$, $\mathbf{e}\cdot\mathbf{k} = 0$) of the photon modes present, $\omega = k\,c$ is the frequency, V is the volume and ε_0 is the permittivity of free space. The operators $\tilde{\mathbf{A}}$ and $\tilde{\mathbf{A}}^\dagger$ therefore represent the absorption and emission of a photon respectively while the terms in the transition operator representing scattering are those involving the operator pairs $\tilde{\mathbf{A}}^\dagger, \tilde{\mathbf{A}}$, in either order.

2. Scattering by a single electron: the Kramers, Heisenberg, Waller formula

In lowest-order perturbation theory, without making any other approximations, the above yields the differential cross-section for the angular distribution of scattering of photons, from the channel $\mathbf{e},\mathbf{k}$ into the channel $\mathbf{e}',\mathbf{k}'$, by a single electron initially in the state β, according to the formula

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'} = r_\mathrm{e}^2 \sum_\alpha \left(\frac{\omega'}{\omega}\right)^2 \left|\langle\alpha|\mathbf{F}(\mathbf{e},\mathbf{k},z;\mathbf{e}',\mathbf{k}',z';E_\beta)|\beta\rangle\right|^2 (1 + n_{\mathbf{k}'} - \delta_{\mathbf{k}\mathbf{k}'}) \tag{4}$$

where $r_\mathrm{e} = e^2/4\pi\,\varepsilon_0 m_\mathrm{e} c^2$ is the *classical electron radius*,

$$\begin{aligned} z &= \omega + \mathrm{i}0^+ \\ z' &= \omega' + \mathrm{i}0^+ \\ E_\beta + \omega &= E_\alpha + \omega' \end{aligned} \tag{5}$$

$$\begin{aligned} \mathbf{F}(\mathbf{e},\mathbf{k};\mathbf{e}',\mathbf{k}',z,z';E) = -\frac{1}{m_\mathrm{e}}\Big(&\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}}\mathbf{e}'\cdot\mathbf{p}G(E+z)\mathbf{e}\cdot\mathbf{p}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \\ &+\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\mathbf{e}\cdot\mathbf{p}G(E-z')\mathbf{e}'\cdot\mathbf{p}\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}}\Big) \\ &-\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}}\mathbf{e}'\cdot\mathbf{e}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \end{aligned} \tag{6}$$

$$\mathbf{G}(E) = (E - \mathbf{H}_0)^{-1} \tag{7}$$

α denotes an electron state in the final channel, and the factor $(1 + n_{\mathbf{k}'} - \delta_{\mathbf{k}\mathbf{k}'})$ accounts for the effect of *stimulated scattering* in the presence of $n_{\mathbf{k}'} - \delta_{\mathbf{k}\mathbf{k}'}$ spectator photons in the exit channel. Eqs. (4)–(7) constitute the Kramers, Heisenberg, Waller formula [11].

3. Scattering from a many-electron system

3.1. Effective photon scattering operator

Our previous work [10] describes a general quantum-mechanical treatment of Thomson scattering, but considers only the $\mathbf{A}^2$ term in the Hamiltonian, which corresponds to the right-most term on the right-hand side of Eq. (6). In the present work, we generalize this to include the remaining polarization term in the case of a system of electrons that is initially isotropic and unpolarized. In order to simplify the ensuing formalism, it is convenient to carry out the average over the directions of the electron motions at this stage. The scattering depends on the average of an expression like $|a(\mathbf{e}'\cdot\mathbf{p})(\mathbf{e}\cdot\mathbf{p}) + b(\mathbf{e}'\cdot\mathbf{e})|^2$, where a and b are constant coefficients, over the direction of the vector $\mathbf{p}$. Expanding and applying the average yields

$$\begin{aligned} \overline{|a(\mathbf{e}'\cdot\mathbf{p})(\mathbf{e}\cdot\mathbf{p}) + b(\mathbf{e}'\cdot\mathbf{e})|^2} = {} & |a|^2\overline{(\mathbf{e}'\cdot\mathbf{p})^2(\mathbf{e}\cdot\mathbf{p})^2} \\ & + (a^*b + b^*a)(\mathbf{e}'\cdot\mathbf{e})\overline{(\mathbf{e}'\cdot\mathbf{p})(\mathbf{e}\cdot\mathbf{p})} \\ & + |b|^2(\mathbf{e}'\cdot\mathbf{e})^2 \end{aligned} \tag{8}$$

where the average is defined as $\overline{X(\mathbf{p})} = (4\pi)^{-1}\int X(\mathbf{p})\mathrm{d}\Omega_\mathbf{p}$.

and

$$\begin{aligned} \overline{(\mathbf{e}'\cdot\mathbf{p})(\mathbf{e}\cdot\mathbf{p})} &= \frac{1}{3}\mathbf{p}^2(\mathbf{e}'\cdot\mathbf{e}) \\ \overline{(\mathbf{e}'\cdot\mathbf{p})^2(\mathbf{e}\cdot\mathbf{p})^2} &= \frac{1}{9}\mathbf{p}^4(\mathbf{e}'\cdot\mathbf{e})^2 \end{aligned} \tag{9}$$

Hence

$$\begin{aligned} \overline{|a(\mathbf{e}'\cdot\mathbf{p})(\mathbf{e}\cdot\mathbf{p}) + b(\mathbf{e}'\cdot\mathbf{e})|^2} &= \left(\frac{1}{9}|a|^2\mathbf{p}^4 + \frac{1}{3}(a^*b + b^*a)\mathbf{p}^2 + |b|^2\right) \\ &\quad \times (\mathbf{e}'\cdot\mathbf{e})^2 \\ &= \left|\frac{1}{3}a\mathbf{p}^2 + b\right|^2(\mathbf{e}'\cdot\mathbf{e})^2 \\ &= |ap_\sigma p_\sigma + b|^2(\mathbf{e}'\cdot\mathbf{e})^2 \end{aligned} \tag{10}$$

where $\mathbf{p}^2 = \sum_\sigma p_\sigma p_\sigma$, $\sigma = x, y, z$. Now we seek an effective one-electron operator $\overline{\mathbf{F}}$ with the property that it preserves the electron-direction-averaged expectation value of the cross-section with respect to states of a free-electron in a system in which the electron motion is isotropic, i.e.,

$$\overline{\left|\langle \mathbf{p}|\overline{\mathbf{F}}|\mathbf{p}\rangle\right|^2} = \overline{\left|\langle \mathbf{p}|\mathbf{F}|\mathbf{p}\rangle\right|^2} \tag{11}$$

With the aid of Eq. (10), such an operator is found to be

$$\begin{aligned}\overline{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e}',\mathbf{k}',z,z';E) &= -\frac{\mathbf{e}\cdot\mathbf{e}'}{m_e}\left(\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}}p_n\mathbf{G}(E+z)p_n\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} + \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}p_n\mathbf{G}(E-z')p_n\mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\mathbf{r}} + e^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\right)\\ &= \mathbf{e}\cdot\mathbf{e}'\ \mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\ \mathbf{f}(\mathbf{k},\mathbf{k}';\omega,\omega';E)\end{aligned} \tag{12}$$

where p_n is the component of the momentum in some arbitrary fixed direction, which we are therefore free to *choose* to be in the direction normal to the scattering plane, i.e. perpendicular to both $\mathbf{k}$ and $\boldsymbol{k}'$, which both denote predefined fixed directions. This direction is henceforth denoted by the suffix n (see Fig. 1). The one-electron operator $\mathbf{f}$ defined by Eq. (12) is given by

$$\mathbf{f}(\mathbf{k},\mathbf{k}';\omega,\omega';E) = \frac{1}{2}\left(\mathbf{f}^+(\mathbf{k},\omega;E) + \mathbf{f}^-(-\mathbf{k}',-\omega';E)\right) \tag{13}$$

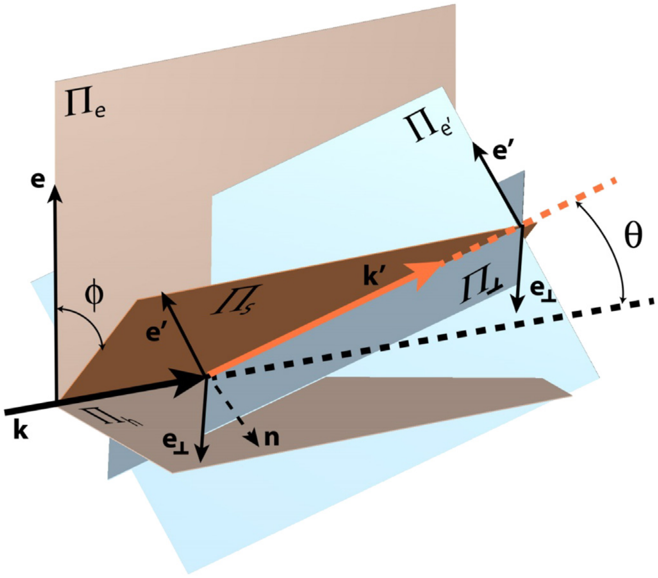

Fig. 1. Diagram illustrating the geometry of Thomson scattering of plane-polarized electromagnetic radiation from the channel ($\mathbf{k}$,$\mathbf{e}$) where the black arrow labelled $\mathbf{k}$ denotes the direction of the radiation. and $\mathbf{e}$ is the direction of the (electric) polarization ($\mathbf{e}\cdot\mathbf{k} = 0$), into the channel ($\mathbf{k}'$,$\mathbf{e}'$) where the red arrow labelled $\mathbf{k}'$ denotes the direction of the scattered radiation and $\mathbf{e}'\cdot\mathbf{k}' = 0$. $\Pi_\mathbf{e}$ denotes the initial polarization plane, which is a plane containing both $\mathbf{e}$ and $\mathbf{k}$, and $\Pi_{\mathbf{e}'}$ denotes the final polarization plane. The scattering plane Π_S is that containing both $\mathbf{k}$ and $\mathbf{k}'$. The scattering is defined by the polar and azimuthal angles, θ and ϕ, which are respectively the angles between $\mathbf{k}$ and $\mathbf{k}'$ and between $\Pi_\mathbf{e}$ and Π_S. The plane $\Pi_\perp$ is the plane containing $\mathbf{k}'$ that is orthogonal to $\Pi_\mathbf{e}$; and $\mathbf{e}_\perp$ is the vector in $\Pi_\perp$ that is orthogonal to $\mathbf{k}'$. The linear dynamics of the scattering process imposes the requirement that $\mathbf{e}'\cdot\mathbf{e}_\perp = 0$, so that $\Pi_{\mathbf{e}'}$ and $\Pi_\perp$ are mutually orthogonal. The diagram also features $\mathbf{n}$, which is the normal to Π_S in the direction of $\mathbf{k}\times\mathbf{k}'$ and $\Pi_\mathbf{h}$, which is the magnetic polarization plane of the incident radiation (the plane containing $\mathbf{k}$ that is normal to $\Pi_\mathbf{e}$ and which necessarily contains $\mathbf{e}_\perp$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\mathbf{f}^\pm(\mathbf{k},\omega;E) = -1 - \frac{2}{m_e}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}p_n\mathbf{G}^\pm(E+\omega)p_n\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \tag{14}$$

$$\mathbf{G}^\pm(E) = \left(E - \mathbf{H}_0 \pm \mathrm{i}0^+\right)^{-1} \tag{15}$$

The operator (6) acts on the Hilbert space of a single electron. We now transform this into an equivalent operator acting on the many electron Fock space, by means of the general formula,

$$\widehat{\mathbf{F}} = \sum_{\alpha,\beta}\mathbf{a}_\alpha^\dagger\mathbf{a}_\beta\langle\alpha|\mathbf{F}|\beta\rangle \tag{16}$$

where $\widehat{\mathbf{F}}$ is the Fock-space equivalent of a Hilbert space operator $\mathbf{F}$ and $\mathbf{a}_\alpha^\dagger$ and $\mathbf{a}_\alpha$ are the creation and annihilation operators for the embedded one-electron states $|\alpha\rangle$. (see Appendix A). Replacing the general operator $\mathbf{F}$ in Eq. (16) with $\overline{\mathbf{F}}$ given by Eq. (12) yields

$$\begin{aligned}\widehat{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e}',\mathbf{k}',\omega,\omega') &= \sum_{\alpha,\beta}\mathbf{a}_\alpha^\dagger\mathbf{a}_\beta\langle\alpha|\overline{\mathbf{F}}|\beta\rangle\\ &= \mathbf{e}\cdot\mathbf{e}'\sum_{\alpha,\beta}\mathbf{a}_\alpha^\dagger\mathbf{a}_\beta\langle\alpha|\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\mathbf{f}(\mathbf{k},\mathbf{k}';\omega,\omega';E_\beta)|\beta\rangle\end{aligned} \tag{17}$$

which is the effective scattering operator on the electron Fock space for scattering of electromagnetic radiation by unpolarized isotropically moving electrons.

Eq. (17) involves a sum over all possible transitions of the state of an electron induced by the operator $\overline{\mathbf{F}}$ and thereby embraces all types of photon scattering process, which are interactions between radiation and matter in which the number of photons is unchanged. These include Raman scattering, in which the scattering induces discrete changes in the (bound) state of an electron with commensurate changes in the frequency of the scattered photons; Compton scattering in which the state of a quasi-free electron is affected by recoil resulting from the change in the momentum of the electromagnetic field; scatterings that cause excitation or de-excitation of collective modes (Brillouin scattering); scattering from tightly bound electrons (Rayleigh scattering); scattering from bound electrons near resonance (Resonance scattering) and scatterings by non-relativistic electrons that leave the state of the electron virtually unchanged (Thomson scattering). In the following, we shall be primarily concerned with the latter, to which end further approximations to Eq. (17) are appropriate.

3.2. Selection rules and angular distribution

An important property of the Hamiltonian $\mathbf{H}'(\mathbf{A})$ defined by Eq. (2) is that, for any decomposition $\mathbf{A} = \mathbf{A}_1 + \mathbf{A}_2$ such that $\mathbf{A}_1\cdot\mathbf{A}_2 = 0$, $\mathbf{H}(\mathbf{A}_1+\mathbf{A}_2) = \mathbf{H}(\mathbf{A}_1) + \mathbf{H}(\mathbf{A}_2)$, which allows orthogonal components of the electromagnetic field to be treated independently, in the first-order (Born) approximation. In particular, for a defined entrance channel polarization $\widehat{\mathbf{e}} = \mathbf{e}$, we can define the exit channel polarization $\widehat{\mathbf{e}'} = \widehat{\mathbf{e}}'_\parallel \oplus \widehat{\mathbf{e}}'_\perp$ to be a superposition of an in-plane mode,

$\widehat{\mathbf{e}}'_{\parallel}$, lying in the plane containing the vectors $\widehat{\mathbf{e}}$ and $\widehat{\mathbf{k}}' = \mathbf{k}'/|\mathbf{k}'|$, and an orthogonal, out of plane mode, $\widehat{\mathbf{e}}'_{\perp}$. (In this section, the caret ˆ is used to denote a unit vector.) This is the canonical exit channel basis. So, rather than treating $\widehat{\mathbf{e}}'$ as a continuous variable, we need only consider scattering into the discrete channels $\mathbf{A}'_{\perp}$ and $\mathbf{A}'_{\parallel}$. The same is true for the second-order terms involving $\mathbf{A}\boldsymbol{\cdot}\mathbf{p}$, which, when averaged over the direction of $\mathbf{p}$, as described above, yield $\overline{\mathbf{A}\cdot\mathbf{p}\mathbf{G}\mathbf{A}\cdot\mathbf{p}} = \mathbf{A}^2 p_\sigma \mathbf{G} p_\sigma = (\mathbf{A}_1^2 + \mathbf{A}_2^2) p_\sigma \mathbf{G} p_\sigma$.

The scattering cross-section given by Eq. (17) vanishes if $\widehat{\mathbf{e}}' \cdot \widehat{\mathbf{e}} = 0$. Therefore, because $\widehat{\mathbf{e}}'_{\perp} \cdot \widehat{\mathbf{e}} \equiv 0$, there is no scattering into the $\perp$ mode, which implies that $\widehat{\mathbf{e}}' = \widehat{\mathbf{e}}'_{\parallel}$. The condition $\widehat{\mathbf{e}}' \cdot \widehat{\mathbf{e}} \neq 0$ is thus expressed by

$$\begin{aligned} &\widehat{\mathbf{k}}' \cdot (\widehat{\mathbf{e}}' \times \widehat{\mathbf{e}}) = 0 \\ &\widehat{\mathbf{e}} \times \widehat{\mathbf{k}}' \neq 0 \end{aligned} \tag{18}$$

which can be solved for $\widehat{\mathbf{e}}'$ subject to $\widehat{\mathbf{e}}' \cdot \widehat{\mathbf{e}}' = 1$, $\widehat{\mathbf{k}}' \cdot \widehat{\mathbf{e}}' = 0$ to yield

$$\widehat{\mathbf{e}}' = \frac{\widehat{\mathbf{k}}' \times \left(\widehat{\mathbf{e}} \times \widehat{\mathbf{k}}'\right)}{\left|\widehat{\mathbf{k}}' \times \left(\widehat{\mathbf{e}} \times \widehat{\mathbf{k}}'\right)\right|} = \frac{\widehat{\mathbf{e}} - \widehat{\mathbf{k}}'\left(\widehat{\mathbf{e}} \cdot \widehat{\mathbf{k}}'\right)}{\sqrt{1 - \left(\widehat{\mathbf{e}} \cdot \widehat{\mathbf{k}}'\right)^2}} \tag{19}$$

Defining θ, the scattering angle, to be the angle between $\widehat{\mathbf{k}}'$ and $\widehat{\mathbf{k}}$, and ϕ, the azimuthal angle, to be the angle between the scattering plane and the initial plane of polarization, then

$$\left(\widehat{\mathbf{k}}' \times \widehat{\mathbf{k}}\right) \cdot \left(\widehat{\mathbf{e}} \times \widehat{\mathbf{k}}\right) \equiv \widehat{\mathbf{e}} \cdot \widehat{\mathbf{k}}' = \cos(\phi)\sin(\theta) \tag{20}$$

which, in combination with Eq. (19), yields the scattering angular distribution according to

$$(\widehat{\mathbf{e}}' \cdot \widehat{\mathbf{e}})^2 = 1 - \left(\widehat{\mathbf{e}} \cdot \widehat{\mathbf{k}}'\right)^2 = 1 - \cos^2(\phi)\sin^2(\theta) \tag{21}$$

The full scattering geometry is illustrated in Fig. 1.

Looking at this from a quantum mechanical perspective, we see that the scattering operator is the direct product of two dipole operators respectively representing absorption by and polarization of the medium, and emission of the scattered radiation. This operator decomposes, according to the tensor rule $1 \otimes 1 = 0 \oplus 2$, into a scalar and second rank tensor part, which is an inherent property of Eq. (21).

In this model, there is no coupling to the electron spin, which is therefore unchanged by the scattering. Nevertheless spin still needs to be accounted for in a many-electron system, because of the Pauli principle.

3.3. *Dielectric function and the optical theorem*

For forward scattering, $\mathbf{k} = \mathbf{k}'$, $\omega = \omega'$, $\mathbf{e} = \mathbf{e}'$, when there is no change in the state of the scatterer, the diagonal matrix element of Eq. (17) with respect to an arbitrary Fock state Ψ is

$$\begin{aligned} \langle\Psi|\widehat{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e},\mathbf{k},\omega,\omega)|\Psi\rangle &= \sum_{\alpha,\beta}\langle\Psi|\mathbf{a}_\alpha^\dagger\mathbf{a}_\beta|\Psi\rangle\langle\alpha|\mathbf{f}(\mathbf{k},\mathbf{k};\omega,\omega;E_\beta)|\beta\rangle \\ &= \sum_\alpha\langle\Psi|\mathbf{a}_\alpha^\dagger\mathbf{a}_\alpha|\Psi\rangle\langle\alpha|\mathbf{f}(\mathbf{k},\omega;E_\alpha)|\alpha\rangle \\ &= \sum_\alpha n_\alpha f_\alpha(\mathbf{k};\omega) \end{aligned} \tag{22}$$

where $n_\beta = 0$ or 1 is the occupancy of the electron state β in the state Ψ, and where $\mathbf{f}$ is the one-electron polarization operator,

$$\mathbf{f}(\mathbf{k},\omega;E) \equiv \mathbf{f}(\mathbf{k},\mathbf{k};\omega,\omega;E) = \frac{1}{2}\left(\mathbf{f}^+(\mathbf{k},\omega;E) + \mathbf{f}^-(-\mathbf{k},-\omega;E)\right) \tag{23}$$

whose diagonal matrix elements are

$$f_\alpha(\mathbf{k},\omega) = \langle\alpha|\mathbf{f}(\mathbf{k},\omega;E_\alpha)|\alpha\rangle = \frac{1}{2}\left(f_\alpha^+(\mathbf{k},\omega) + f_\alpha^-(-\mathbf{k},-\omega)\right) \tag{24}$$

where the elementary amplitudes,

$$f_\alpha^\pm(\mathbf{k},\omega) = \langle\alpha|\mathbf{f}^\pm(\mathbf{k},\omega;E_\alpha)|\alpha\rangle \tag{25}$$

for forward scattering from the state α, are defined by

$$\begin{aligned} f_\alpha^+(\mathbf{k},\omega) &= -1 - \frac{2}{m_e}\langle\alpha|e^{-i\mathbf{k}\cdot\mathbf{r}}p_n\mathbf{G}^+(E_\alpha+\omega)p_n e^{i\mathbf{k}\cdot\mathbf{r}}|\alpha\rangle \\ &= -1 - \frac{2}{m_e}\sum_\beta\frac{\left|\langle\alpha|e^{-i\mathbf{k}\cdot\mathbf{r}}p_n|\beta\rangle\right|^2}{E_\alpha - E_\beta + \omega + i0^+} \\ &= -1 - \sum_\beta f_{\alpha\beta}(\mathbf{k},\omega) \end{aligned} \tag{26}$$

$$\begin{aligned} f_\alpha^-(-\mathbf{k},-\omega) &= -1 - \frac{2}{m_e}\langle\alpha|e^{i\mathbf{k}\cdot\mathbf{r}}p_n\mathbf{G}^-(E_\alpha-\omega)p_n e^{-i\mathbf{k}\cdot\mathbf{r}}|\alpha\rangle \\ &= -1 - \frac{2}{m_e}\sum_\beta\frac{\left|\langle\beta|p_n e^{-i\mathbf{k}\cdot\mathbf{r}}|\alpha\rangle\right|^2}{E_\alpha - E_\beta - \omega - i0^+} \\ &= -1 + \sum_\beta f_{\beta\alpha}(\mathbf{k},\omega) \end{aligned} \tag{27}$$

where, since p_n commutes with $e^{-i\mathbf{k}\cdot\mathbf{r}}$,

$$f_{\alpha\beta}(\mathbf{k},\omega) = \frac{2}{m_e}\frac{\left|\langle\alpha|e^{-i\mathbf{k}\cdot\mathbf{r}}p_n|\beta\rangle\right|^2}{E_\alpha - E_\beta + \omega + i0^+} \tag{28}$$

which possesses the property

$$f_{\beta\alpha}(\mathbf{k},\omega) = -f_{\alpha\beta}^*(-\mathbf{k},-\omega) \tag{29}$$

The forward scattering amplitude $f(\mathbf{k},\omega)$ is the average expectation value of the forward scattering operator, and follows directly from Eq. (22) as follows

$$\begin{aligned} f(\mathbf{k},\omega) &\equiv \langle\widehat{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e},\mathbf{k},\omega,\omega)\rangle \\ &\equiv \mathrm{trace}\left(\boldsymbol{\rho}\widehat{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e},\mathbf{k},\omega,\omega)\right) \\ &= \sum_\alpha\langle n_\alpha\rangle f_\alpha(\mathbf{k},\omega) \end{aligned} \tag{30}$$

where $\boldsymbol{\rho}$ is the statistical operator (Appendix A.2) and $\langle n_\alpha\rangle = \langle\mathbf{a}_\alpha^\dagger\mathbf{a}_\alpha\rangle$ is the average number of electrons in the state α. The effect of scattering on the propagation of a plane wave $\Psi = \Psi_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$ in a homogeneous medium is described by introducing a source term $4\pi\mathbf{F}_0\Psi$ into the governing wave equation, where $\mathbf{F}_0$ is the forward scattering operator, whose eigenvalues $F_0(\mathbf{k},\omega) = r_e f(\mathbf{k},\omega)/V$ correspond to the forward scattering amplitude per unit volume for the mode $(\mathbf{k},\omega)$. (See Appendix B) Since $F_0(\mathbf{k},\omega)$ is generally complex, this requires, for real ω, that $\mathbf{k}$ must also become complex, and we therefore make the replacement $\mathbf{k} \to (k + \frac{1}{2}i\kappa)\widehat{\mathbf{k}}$ where k and κ are both real. The modified wave equation $c^{-2}\partial_{tt}\Psi = \nabla^2\Psi + 4\pi\mathbf{F}_0\Psi$ then implies the dispersion relation,

$$\left(k + \frac{1}{2}i\kappa\right)^2 = \frac{\omega^2}{c^2} + 4\pi r_e\frac{f(\mathbf{k},\omega)}{V} \tag{31}$$

The quantity κ is the *attenuation coefficient*, which is equivalent to the total cross-section per unit volume,

$$\kappa \equiv N_e \sigma_e / V \tag{32}$$

where

$$N_e = \sum_\alpha \langle n_\alpha \rangle \tag{33}$$

is the total number of electrons and σ_e is the mean cross section per electron, which describes all processes whereby flux is removed from (or coherently added to by stimulated processes) the channel ($\mathbf{k}$,ω). In a non-magnetic medium, the dispersion relation can also be written in terms of the dielectric function $\varepsilon(\mathbf{k},\omega)$ as follows

$$\left(k + \frac{1}{2} i\kappa\right)^2 c^2 = \omega^2 \varepsilon(\mathbf{k}, \omega) \tag{34}$$

Combining Eqs. (31) and (34) then yields the fundamental relationship between the dielectric function and the forward scattering amplitude,

$$\varepsilon(\mathbf{k}, \omega) = 1 + \frac{4\pi}{V} \frac{c^2}{\omega^2} r_e f(\mathbf{k}, \omega) = 1 + \frac{e^2}{\omega^2 \varepsilon_0 m_e V} f(\mathbf{k}, \omega) \tag{35}$$

in which both $f(\mathbf{k},\omega)$ and $\varepsilon(\mathbf{k},\omega)$ are complex. Now, the imaginary part of the dielectric function directly gives the attenuation coefficient according to

$$k\kappa = \frac{\omega^2}{c^2} \mathrm{Im}\varepsilon(\mathbf{k}, \omega) \tag{36}$$

which, when combined with Eqs. (35) and (32), yields

$$N_e \sigma_e = \frac{4\pi}{k} r_e \mathrm{Im} f(\mathbf{k}, \omega) \tag{37}$$

which is a general statement of the *optical theorem* [13].

$$\mathbf{f}^{\pm}(\omega; E) = -1 - \frac{2}{3m_e} \sum_\sigma p_\sigma \mathbf{G}^{\pm}(E + \omega) p_\sigma \tag{39}$$

In these and subsequent equations, there is no longer a dependence on $\mathbf{k}$ and it is therefore no longer necessary to restrict p_n to being in the direction normal to the scattering plane, allowing it to be replaced by p_σ, which is the component of the momentum operator in an arbitrary fixed direction. Restoring the summation over σ means that usage of these operators is no longer restricted to the context of the expectation of the cross-section. The scattering operator for isotropically moving electrons (17) then becomes

$$\begin{aligned} \widehat{\mathbf{F}}(\mathbf{e}, \mathbf{k}; \mathbf{e}', \mathbf{k}', \omega, \omega') &\simeq \mathbf{e}\cdot\mathbf{e}' \sum_{\alpha,\beta} \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \langle \alpha | \mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \mathbf{f}(\omega, \omega'; E_\beta) | \beta \rangle \\ &= \mathbf{e}\cdot\mathbf{e}' \sum_{\alpha,\beta,\gamma} \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \langle \alpha | \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} | \gamma \rangle \langle \gamma | \mathbf{f}(\omega, \omega'; E_\beta) | \beta \rangle \end{aligned} \tag{40}$$

in which the summation over γ factorizes the operator terms into a diffraction part, $\langle \alpha | e^{i\mathbf{q}\cdot\mathbf{r}} | \gamma \rangle$, which depends upon the recoil momentum, $\mathbf{q} = \mathbf{k} - \boldsymbol{k}'$, transferred to the scattering system; and a part, $\langle \gamma | \mathbf{f}(\omega, \omega'; E_\beta) | \beta \rangle$ which, beyond the leading diagonal term, incorporates dipole-induced transitions between the electron states. The leading terms in Eq. (40), for which $\gamma = \beta$, represent Thomson scattering and higher-order terms, those for which $\gamma \neq \beta$, where the energy differences are resolvable (as in low-lying atomic states) are generally considered to represent strongly inelastic Raman scattering and treated separately. Bearing in mind that $\omega \gg |\omega - \omega'|$, the essential difference is that the diffraction part represents direct scattering where recoil gives rise to angle-dependent weak inelasticity (small energy changes) while the part $\langle \gamma | \mathbf{f} | \beta \rangle$ involves virtual excitation of the electron to a state of energy $E_\beta + \omega$ and thus readily allows strong discrete (angle independent) inelastic transitions to much higher energy states. In the case of Thomson scattering by electrons occupying quasi-free states or high-lying atomic states, the matrix $\langle \gamma | \mathbf{f}(\omega, \omega'; E_\beta) | \beta \rangle$ is considered to be quasi diagonal, although the matrix elements themselves are off the energy shell. This leads to the operator for Thomson scattering being given by

$$\begin{aligned} \widehat{\mathbf{F}}(\mathbf{e}, \mathbf{k}' + \mathbf{q}; \mathbf{e}', \mathbf{k}', \omega, \omega') \rightarrow \widehat{\mathbf{F}}_T(\mathbf{q}; \mathbf{e}\cdot\mathbf{e}'; \omega, \omega') &= \mathbf{e}\cdot\mathbf{e}' \sum_{\alpha,\beta} \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \langle \alpha | \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} | \beta \rangle \langle \beta | \mathbf{f}(\omega, \omega'; E_\beta) | \beta \rangle \\ &= \mathbf{e}\cdot\mathbf{e}' \sum_{\alpha,\beta} \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \langle \alpha | \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} | \beta \rangle f_\beta(\omega, \omega') \end{aligned} \tag{41}$$

3.4. Thomson dipole approximation

The main approximation to be made is the Thomson dipole approximation, which is appropriate if the wavelength ~1/k of the radiation is much larger than the electron Compton wavelength, $\bar{\lambda} = r_e \alpha_0^{-1}$, where $\alpha_0 = 1/137.036\ldots$ is the fine structure constant. This is equivalent to assuming $\omega << m_e c^2$, which implies $k\, r_e << \alpha_0 < 1$, and $k^2/2m_e << \omega$, in which case the Compton recoil energy of a single electron is very small *compared with the energy of the photon*, which essentially defines the Thomson scattering regime.

In the Thomson regime, $k\bar{\lambda} < < 1$, the operator $\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ effectively commutes with the electron propagator (since the commutator introduces only second order quantum terms, of order $k^2/2m_e$, via the kinetic energy term in the Hamiltonian) in which case the operators given by Eqs. (13) and (14) reduce to

$$\mathbf{f}(\mathbf{k}, \mathbf{k}'; \omega, \omega'; E) \rightarrow \mathbf{f}(\omega, \omega'; E) = \frac{1}{2}\left(\mathbf{f}^{+}(\omega; E) + \mathbf{f}^{-}(-\omega'; E)\right) \tag{38}$$

where

$$f_\alpha(\omega, \omega') = \frac{1}{2}\left(f_\alpha^{+}(\omega) + f_\alpha^{-}(-\omega')\right) \tag{42}$$

where $f_\alpha^{\pm}(\omega)$ are the dipole strengths, which correspond, in the dipole approximation, to Eqs. (26) and (27) according to

$$\begin{aligned} f_\alpha^{+}(\mathbf{k}, \omega) \rightarrow f_\alpha^{+}(\omega) &= -1 - \frac{2}{3m_e} \sum_\sigma \langle \alpha | p_\sigma \mathbf{G}^{+}(E_\alpha + \omega) p_\sigma | \alpha \rangle \\ &= -1 - \frac{2}{m_e} \sum_\beta \sum_\sigma \frac{\left|\langle \alpha | p_\sigma | \beta \rangle\right|^2}{E_\alpha - E_\beta + \omega + \mathrm{i}0^{+}} \\ &= -1 - \sum_\beta f_{\alpha\beta}(\omega) \end{aligned} \tag{43}$$

and

$$\begin{aligned} f_\alpha^-(-\mathbf{k},-\omega)\rightarrow f_\alpha^-(-\omega) &= -1-\frac{2}{3m_\mathrm{e}}\sum_\sigma\langle\alpha|p_\sigma\mathbf{G}^-(E_\alpha-\omega)p_\sigma|\alpha\rangle \\ &= -1-\frac{2}{3m_\mathrm{e}}\sum_\beta\sum_\sigma\frac{|\langle\beta|p_\sigma|\alpha\rangle|^2}{E_\alpha-E_\beta-\omega-\mathrm{i}0^+} \\ &= -1+\sum_\beta f_{\beta\alpha}(\omega) \end{aligned} \tag{44}$$

and where

$$f_{\alpha\beta}(\omega)=f_{\alpha\beta}(\mathbf{0},\omega)=\frac{2}{3m_\mathrm{e}}\sum_\sigma\frac{|\langle\alpha|p_\sigma|\beta\rangle|^2}{E_\alpha-E_\beta+\omega+\mathrm{i}0^+} \tag{45}$$

Expressing Eq. (40) in terms of the time-dependent *strength-density operator*, $\tilde{\rho}_\mathbf{q}(t)$ defined by

$$\tilde{\rho}_\mathbf{q}(t)\equiv\sum_{\alpha,\beta}\mathbf{a}_\alpha^\dagger\mathbf{a}_\beta\langle\alpha|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\mathbf{f}|\beta\rangle\mathrm{e}^{\mathrm{i}(E_\alpha-E_\beta)t} \tag{46}$$

$$\mathbf{f}|\beta\rangle=f_\beta(\omega,\omega')|\beta\rangle \tag{47}$$

where the amplitudes $f_\beta(\omega,\omega')$ are given by Eq. (42), yields

$$\widehat{\mathbf{F}}(\mathbf{e},\mathbf{k};\mathbf{e}',\mathbf{k}',\omega,\omega';t)=\mathbf{e}\cdot\mathbf{e}'\tilde{\rho}_{\mathbf{k}'-\mathbf{k}}(t) \tag{48}$$

Some transparency is gained by expressing the operators $\tilde{\rho}_\mathbf{q}$ and $\tilde{\rho}_\mathbf{q}^\dagger$ symbolically in terms of the standard density operator $\rho_\mathbf{q}$ (Appendix A, Eq. (218)) according to: $\tilde{\rho}_\mathbf{q}(t)\equiv\rho_\mathbf{q}(t)\tilde{\mathbf{f}}$, $\tilde{\rho}_\mathbf{q}^\dagger(t)\equiv\tilde{\mathbf{f}}^\dagger\rho_{-\mathbf{q}}(t)$ in which $\tilde{\mathbf{f}}$ and $\tilde{\mathbf{f}}^\dagger$ are *superoperators* acting on the density operator immediately to the. left and right respectively.

The scattering operator for Thomson scattering thus reduces to the elegant and simple forms.

$$\widehat{\mathbf{F}}_\mathrm{T}(\mathbf{q};\mathbf{e}\cdot\mathbf{e}';\omega,\omega';t)=\mathbf{e}\cdot\mathbf{e}'\tilde{\rho}_{-\mathbf{q}}(t)=\mathbf{e}\cdot\mathbf{e}'\rho_{-\mathbf{q}}(t)\tilde{\mathbf{f}} \tag{49}$$

3.5. Electrical conductivity, oscillator strengths and sum-rules

In the Thomson dipole approximation, the forward scattering amplitude (30) becomes

$$f(\omega)\equiv f(\mathbf{0},\omega)=\sum_\alpha\langle n_\alpha\rangle f_\alpha(\omega) \tag{50}$$

where

$$\begin{aligned} f_\alpha(\omega)=f_\alpha(\omega,\omega) &= \frac{1}{2}\left(f_\alpha^+(\omega)+f_\alpha^-(-\omega)\right) \\ &= -1-\frac{1}{2}\sum_\beta\left(f_{\alpha\beta}(\omega)-f_{\beta\alpha}(\omega)\right) \end{aligned} \tag{51}$$

Combining Eqs. (50) and (51) yields

$$\begin{aligned} f(\omega) &= -N_\mathrm{e}-\frac{1}{2}\sum_{\alpha,\beta}\langle n_\alpha\rangle\left(f_{\alpha\beta}(\omega)-f_{\beta\alpha}(\omega)\right) \\ &= -N_\mathrm{e}-\frac{1}{2}\sum_{\alpha,\beta}(\langle n_\alpha\rangle-\langle n_\beta\rangle)f_{\alpha\beta}(\omega) \end{aligned} \tag{52}$$

where $f_{\alpha\beta}(\omega)$ is given by Eq. (45), in terms of which the long-wavelength limit of the dielectric function (35) is

$$\varepsilon(\omega)=\varepsilon(\mathbf{0},\omega)=1+\frac{e^2}{\omega^2\varepsilon_0 m_\mathrm{e}V}f(\omega) \tag{53}$$

This yields the electrical conductivity $\varsigma(\omega)$ according to

$$\begin{aligned} \varsigma(\omega)=\omega\varepsilon_0\mathrm{Im}\varepsilon(\omega) &= -\frac{e^2}{3m_\mathrm{e}^2\omega V}\sum_{\alpha,\beta}\sum_\sigma(\langle n_\alpha\rangle-\langle n_\beta\rangle)|\langle\beta|p_\sigma|\alpha\rangle|^2\mathrm{Im}\frac{1}{E_\alpha-E_\beta+\omega+\mathrm{i}0^+} \\ &= \frac{\pi e^2}{3m_\mathrm{e}^2\omega V}\sum_{\alpha,\beta}\sum_\sigma(\langle n_\alpha\rangle-\langle n_\beta\rangle)|\langle\beta|p_\sigma|\alpha\rangle|^2\delta(E_\alpha-E_\beta+\omega) \\ &= \frac{\pi e^2}{2m_\mathrm{e}V}\sum_{\alpha,\beta}(\langle n_\alpha\rangle-\langle n_\beta\rangle)f_{\alpha\beta}^0\delta(E_\alpha-E_\beta+\omega) \end{aligned} \tag{54}$$

which is the Kubo–Greenwood formula [14,15]. The final expression on the right of Eq. (54) expresses the result in terms of the one-electron dipole oscillator strengths,

$$f_{\alpha\beta}^0=\frac{2}{3m_\mathrm{e}}\sum_\sigma\frac{|\langle\beta|p_\sigma|\alpha\rangle|^2}{(E_\beta-E_\alpha)} \tag{55}$$

which are related to the $f_{\alpha\beta}$ by the Cauchy identity

$$\mathrm{Im}f_{\alpha\beta}(\omega)=-\pi\omega\delta(E_\alpha-E_\beta+\omega)f_{\alpha\beta}^0 \tag{56}$$

and which satisfy the Thomas–Reiche–Kuhn sum rule in the velocity gauge,

$$\sum_\beta f_{\alpha\beta}^0=-\sum_\alpha f_{\alpha\beta}^0=1 \tag{57}$$

Integrating the Kubo-Greenwood formula, (54), with respect to ω, making use of Eqs. (55) and (57), yields

$$\begin{aligned}\frac{1}{\varepsilon_0}\int_{-\infty}^{+\infty}\varsigma(\omega)d\omega &= \int_{-\infty}^{+\infty}\omega\mathrm{Im}\varepsilon(\omega)\mathrm{d}\omega\\ &= \frac{\pi e^2}{2m_\mathrm{e}\varepsilon_0 V}\int_{-\infty}^{+\infty}\sum_{\alpha,\beta}(\langle n_\alpha\rangle-\langle n_\beta\rangle)f^0_{\alpha\beta}\delta(E_\alpha-E_\beta+\omega)d\omega\\ &= \frac{\pi e^2}{2m_\mathrm{e}\varepsilon_0 V}\sum_{\alpha,\beta}(\langle n_\alpha\rangle-\langle n_\beta\rangle)f^0_{\alpha\beta} = \frac{\pi e^2}{m_\mathrm{e}\varepsilon_0 V}\sum_\alpha\langle n_\alpha\rangle\\ &= \frac{\pi e^2}{m_\mathrm{e}\varepsilon_0}\frac{N_\mathrm{e}}{V}\equiv\pi\Omega_0^2\end{aligned} \tag{58}$$

which is the *conductivity sum rule*. Since $\mathrm{Im}\varepsilon(\omega)$ is an odd function of ω, this can also be written,

$$\frac{1}{\varepsilon_0}\int_0^\infty\varsigma(\omega)d\omega = \int_0^\infty\omega\mathrm{Im}\varepsilon(\omega)d\omega = \frac{\pi}{2}\Omega_0^2 \tag{59}$$

Combining Eqs. (52), (53) and (57) yields the sum rule in yet another form:

$$\begin{aligned}\frac{2}{\pi}\int_0^\infty\mathrm{Im}f(\omega)\frac{d\omega}{\omega} &= \frac{1}{2}\sum_{\alpha,\beta}(\langle n_\alpha\rangle-\langle n_\beta\rangle)f^0_{\alpha\beta}\\ &= \sum_\alpha\langle n_\alpha\rangle = N_\mathrm{e}\end{aligned} \tag{60}$$

Note that Eqs. (58)–(60) embrace all of the electrons in the system ($=N_\mathrm{e}$) including bound electrons. This is because the integral over frequency extends to infinity, so all possible transitions between electron states are encompassed.

If the electrons are in LTE at a temperature T, then $\langle n_\alpha\rangle=\mathfrak{p}(E_\alpha)$, where $\mathfrak{p}(E)$ is the Fermi–Dirac distribution.

$$\mathfrak{p}(E) = \frac{1}{1+\exp(E/T-\eta)} \tag{61}$$

and $\eta=\mu_\mathrm{e}/T$ is the degeneracy parameter, which is determined by the normalization to the particle number, (33). Hence

$$\begin{aligned}(\langle n_\alpha\rangle-\langle n_\beta\rangle)\delta(E_\alpha-E_\beta+\omega) &= \left(1-\mathrm{e}^{-\omega/T}\right)\mathfrak{p}(E_\alpha)\mathfrak{q}(E_\alpha+\omega)\\ &\quad\times\delta(E_\alpha-E_\beta+\omega)\end{aligned} \tag{62}$$

where $\mathfrak{q}(E)=1-\mathfrak{p}(E)$, by which (54) may be recast in the following form

$$\begin{aligned}\varsigma(\omega)=\omega\varepsilon_0\mathrm{Im}\varepsilon(\omega) &= \frac{\pi\mathrm{e}^2}{2m_\mathrm{e}V}\left(1-\mathrm{e}^{-\omega/T}\right)\sum_{\alpha,\beta}\mathfrak{p}(E_\alpha)\mathfrak{q}(E_\alpha+\omega)\delta(E_\alpha-E_\beta+\omega)f^0_{\alpha\beta}\\ &= -\frac{\mathrm{e}^2}{2m_\mathrm{e}V}\frac{\left(1-\mathrm{e}^{-\omega/T}\right)}{\omega}\sum_{\alpha,\beta}\mathfrak{p}(E_\alpha)\mathfrak{q}(E_\alpha+\omega)\mathrm{Im}f_{\alpha\beta}(\omega)\\ &= \frac{\mathrm{e}^2 n_\mathrm{e}}{2m_\mathrm{e}}\frac{\left(1-\mathrm{e}^{-\omega/T}\right)}{\omega}\sum_\alpha\mathfrak{p}(E_\alpha)\mathfrak{q}(E_\alpha+\omega)\mathrm{Im}f^+_\alpha(\omega)\Big/\sum_\alpha\mathfrak{p}(E_\alpha)\end{aligned} \tag{63}$$

use having been made of Eqs. (56) and (43) and in which the sum over α can be interpreted as a sum over probabilities of transitions whereby a photon of frequency ω is absorbed by an electron initially in state α with probability $\mathfrak{p}(E_\alpha)$ leading to a state whose probability of being initially unoccupied and therefore available is $\mathfrak{q}(E_\alpha+\omega)$. The factor $(1-\mathrm{e}^{-\omega/T})$ incorporates the effect of induced emissions, as required by detailed balance. Eq. (63) is a standard formula for the absorption coefficient, κ_abs, which is closely related to the opacity. Making reference to Eq. (36), noting that the approximations leading to Eqs. (54) and (63) retain only contributions of $\mathrm{O}(\alpha_0)$ while the scattering contribution to the attenuation coefficient is $\mathrm{O}(\alpha_0^2)$ and therefore not included, leads to

$$\kappa_\mathrm{abs}(\omega) = \frac{\zeta(\omega)}{\mathfrak{n}(\omega)\varepsilon_0 c} \tag{64}$$

where $\mathfrak{n}(\omega)=ck/\omega=\mathrm{Re}\sqrt{\varepsilon(\omega)}=\left(\frac{1}{2}\mathrm{Re}\varepsilon(\omega)+\frac{1}{2}|\varepsilon(\omega)|\right)^{1/2}$ is the *refractive index*, and hence the absorption contribution to the attenuation coefficient is

$$\kappa_\mathrm{abs}(\omega)=n_\mathrm{e}\frac{4\pi r_\mathrm{e}}{k}\left(1-\mathrm{e}^{-\omega/T}\right)\sum_\alpha\mathfrak{p}(E_\alpha)\mathfrak{q}(E_\alpha+\omega)\mathrm{Im}f^+_\alpha(\omega)\Big/\sum_\alpha\mathfrak{p}(E_\alpha) \tag{65}$$

A feature of Eqs. (64) and (65) is the presence of a factor of $1/\mathfrak{n}(\omega)$ compared with the versions of these formulae that apply *in vacuo*, as has been previously noted [16–18].

3.6. Strength functions

The function $f_\alpha(\omega)$ defined by Eq. (51) is the *strength function* (sometimes loosely referred to as a response function) or *scattering factor* [19] which is a function that describes the dynamical response, via virtual excitations, of an electron in the state α, to a photon of frequency ω, relative to that of an entirely free electron, for which $f(\omega)\equiv-1$, where the minus sign is a manifestation of Lenz's law. Basically, the strength function encodes how the electron's response to the radiation is modified by the interaction between the electron and its environment (e.g. through interaction with a potential or by collisions with other particles). In the case of electrons that are tightly bound in an atomic potential, when the photon energy is insufficient to cause real excitations, the strength function tends to zero. In general, the strength function is a complex function modulated by resonances, when the photon energy can excite the electron to a higher discrete level, or, most significantly, by photoionization when the photon energy is sufficient to cause ionization. It is evident from Eq. (39), for example, that the deviation of the strength function from -1 is entirely due to the polarization ($\mathbf{A}\cdot\mathbf{p}$) terms in the Hamiltonian.

Let

$$f_\alpha(\omega) = -(1+\chi_\alpha) \tag{66}$$

and let the *reduced absorption cross-section* associated with state α be defined by

$$\tilde{\sigma}_\alpha(\omega) = \frac{4\pi r_e c}{\omega}\mathrm{Im} f_\alpha(\omega) \tag{67}$$

in terms of which, referring to Eqs. (64), (54) and (50), the absorption coefficient is given by

$$\begin{aligned}\mathfrak{n}(\omega)\kappa_{\mathrm{abs}}(\omega) &= \frac{\omega}{c}\mathrm{Im}\varepsilon(\omega) = \frac{e^2}{\omega c\varepsilon_0 m_e V}\sum_\alpha \langle n_\alpha\rangle \mathrm{Im} f_\alpha(\omega)\\ &= \frac{1}{V}\sum_\alpha \langle n_\alpha\rangle \tilde{\sigma}_\alpha(\omega)\end{aligned} \tag{68}$$

The conductivity sum rule is then expressed by

$$\int_0^\infty \mathrm{Im}\chi_\alpha(\omega)\frac{d\omega}{\omega} = -\frac{\pi}{2} \tag{69}$$

and the Kramers–Krönig dispersion relation relating the real and imaginary parts of the dielectric function yields

$$\chi_\alpha(\omega) = \frac{-1}{4\pi r_e c}\left(\frac{2}{\pi}\wp\int_0^\infty \frac{\tilde{\sigma}_\alpha(\omega')}{\omega'^2-\omega^2}\omega'^2 d\omega' + \mathrm{i}\omega\tilde{\sigma}_\alpha(\omega)\right) \tag{70}$$

The functions $\tilde{\sigma}^a_\alpha(\omega)$ for a specified species a can be obtained from an opacity calculation, for example, and Eq. (70) then provides the means of determining $\chi^a_\alpha(\omega)$.

A useful analytic function in $\mathrm{Im}\omega > 0$ that fulfils these requirements precisely and corresponds to a bound-free edge characterised by the archetypal above-threshold absorption profile, $\propto \omega^{-3}$ [20,21], is

$$\chi_\alpha(\omega) = \frac{E_\alpha^2+2\Delta_\alpha^2}{\omega(\omega+\mathrm{i}\nu_\alpha)}\ln\left(1-\frac{\omega^2}{E_\alpha^2}-\frac{2\mathrm{i}\Delta_\alpha}{\sqrt{E_\alpha^2+2\Delta_\alpha^2}}\frac{\omega}{E_\alpha}\right) \tag{71}$$

in which $E_\alpha > 0$ is the binding energy, Δ_α is a measure of the spectral width of the level α and $\nu_\alpha = 2(\Delta_\alpha/E_\alpha)\sqrt{E_\alpha^2+2\Delta_\alpha^2}$. The real and imaginary parts of Eq. (71) are as follows;

$$\begin{aligned}\mathrm{Re}\chi_\alpha(\omega) &= \frac{E_\alpha^2+2\Delta_\alpha^2}{\omega^2+\nu_\alpha^2}\left(\frac{1}{2}\ln\left(1-\frac{2\omega^2}{E_\alpha^2+2\Delta_\alpha^2}+\frac{\omega^4}{E_\alpha^4}\right)-\frac{\nu_\alpha}{\omega}\tan^{-1}\left(\frac{2\Delta_\alpha E_\alpha}{\sqrt{E_\alpha^2+2\Delta_\alpha^2}}\frac{\omega}{E_\alpha^2-\omega^2}\right)\right)\\ \mathrm{Im}\chi_\alpha(\omega) &= -\frac{E_\alpha^2+2\Delta_\alpha^2}{\omega^2+\nu_\alpha^2}\left(\frac{\nu_\alpha}{2\omega}\ln\left(1-\frac{2\omega^2}{E_\alpha^2+2\Delta_\alpha^2}+\frac{\omega^4}{E_\alpha^4}\right)+\tan^{-1}\left(\frac{2\Delta_\alpha E_\alpha}{\sqrt{E_\alpha^2+2\Delta_\alpha^2}}\frac{\omega}{E_\alpha^2-\omega^2}\right)\right)\end{aligned} \tag{72}$$

where, for $\omega > 0$ the inverse tangent is defined in the range $(0,\pi)$. For small ω,

$$\begin{aligned}\mathrm{Re}\chi_\alpha(\omega) &= -1-\left(1-\frac{4}{3}\frac{\Delta_\alpha^2}{E_\alpha^2+2\Delta_\alpha^2}\right)\frac{\omega^2}{E_\alpha^2}+\mathrm{O}\left(\frac{\omega^4}{E_\alpha^4}\right)\\ \mathrm{Im}\chi_\alpha(\omega) &= -\frac{3E_\alpha^4+16\Delta_\alpha^2E_\alpha^2+12\Delta_\alpha^4}{12\Delta_\alpha\left(E_\alpha^2+2\Delta_\alpha^2\right)^{3/2}}\frac{\omega^3}{E_\alpha^3}+\mathrm{O}\left(\frac{\omega^5}{E_\alpha^5}\right)\end{aligned} \tag{73}$$

while for large $\omega \gg E_\alpha$

$$\begin{aligned}\mathrm{Re}\chi_\alpha(\omega) &\sim \frac{E_\alpha^2+2\Delta_\alpha^2}{\omega^2}\left(\ln\left(\frac{\omega^2}{E_\alpha^2}\right)-\frac{\nu_\alpha}{|\omega|}\pi\right)\\ \mathrm{Im}\chi_\alpha(\omega) &\sim -\frac{E_\alpha^2+2\Delta_\alpha^2}{\omega^2}\left(\frac{\nu_\alpha}{|\omega|}\ln\left(\frac{\omega^2}{E_\alpha^2}\right)+\pi\right)\end{aligned} \tag{74}$$

according to which the function $f_\alpha(\omega)$ defined by Eqs. (66) and (71) possesses the following limits

$$\begin{aligned}f_\alpha(\omega) &\underset{\omega\to 0}{\to}\left(1-\frac{4}{3}\frac{\Delta_\alpha^2}{E_\alpha^2+2\Delta_\alpha^2}\right)\frac{\omega^2}{E_\alpha^2}\\ f_\alpha(\omega) &\underset{\omega\to\infty}{\to} -1-\frac{E_\alpha^2+2\Delta_\alpha^2}{\omega^2}\left(\ln\left(\frac{\omega^2}{E_\alpha^2}\right)-\pi\mathrm{i}\right)\to -1\end{aligned} \tag{75}$$

At resonance, $\omega = E_\alpha$,

$$\chi_\alpha(E_\alpha) = -\frac{1}{2}\left(\frac{E_\alpha^2+2\Delta_\alpha^2}{E_\alpha(E_\alpha+\mathrm{i}\nu_\alpha)}\ln\left(\frac{1}{2}+\left(\frac{E_\alpha}{2\Delta_\alpha}\right)^2\right)+\pi\mathrm{i}\right) \tag{76}$$

so, for $\Delta_\alpha \ll E_\alpha$,

$$f_\alpha(E_\alpha) = -1-\chi_\alpha(E_\alpha) \simeq \ln\left(\frac{E_\alpha}{2\Delta_\alpha}\right)-1+\frac{1}{2}\pi\mathrm{i} \tag{77}$$

in which the real part is characterised by a logarithmic spike while the imaginary part passes through ½π. The full function $f_\alpha(\omega)$ for $\Delta_\alpha/E_\alpha = 0.01$ is illustrated in Fig. 2.

For sharp edges ($\Delta_\alpha \ll E_\alpha$) the width $2\Delta_\alpha$ is the full-width at half maximum (FWHM) of the broadening profile defined as

$$L_\alpha(\omega) = \frac{1}{E_\alpha}\frac{\partial}{\partial\omega}\left(\omega^2\,\mathrm{Im} f_\alpha(\omega)\right) \tag{78}$$

i.e.

$$2\Delta_\alpha = \mathrm{FWHM}(L_\alpha(\omega)) \tag{79}$$

which approximation is found to be valid when $\Delta/E \lesssim 0.1$.

Note that this model ignores the effect of higher lying vacant bound levels. In general, some of the strength that has been

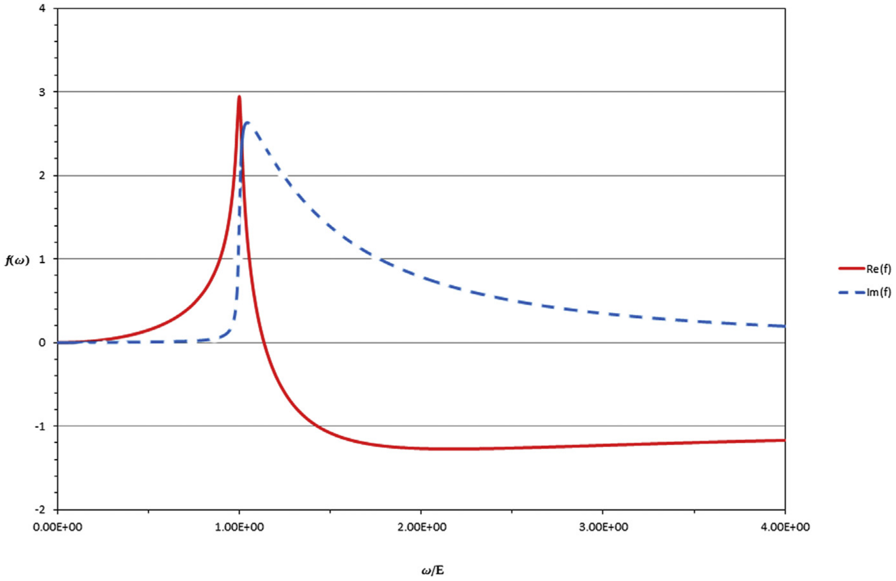

Fig. 2. Illustration of the analytic function $f(\omega)$ defined by Eqs. (66) and (71) for $\Delta/E = 0.01$. The red curve denotes the real part of the function, which is the polarizability, and the blue curve denotes the imaginary part, which gives the absorption coefficient through Equation (68). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assigned to the bound-free edge at $\omega = E_\alpha$ would become associated with the bound–bound lines corresponding to transitions $\alpha \rightarrow \beta$ in which a photon is absorbed. High lying bound levels merging with the continuum contribute to the effective width, while sparse deeply-bound levels may be considered to make a relatively small contribution to the total strength. In general, a Kramers–Krönig transform of the complete absorption spectrum $\alpha\rightarrow$, including the effect of stimulated emission, would be needed to determine the resonance profile accurately. In the special case of a highly degenerate electron system (cold metal or degenerate warm dense matter) all the bound levels are filled so there are only edges, and no lines, in the spectrum, and the model is directly applicable.

For the continuum electrons, we invoke the Drude free electron model,

$$\varepsilon(\omega) = 1 - \frac{\Omega_\mathrm{e}^2}{\omega(\omega + \mathrm{i}\nu)} \tag{80}$$

where

$$\Omega_\mathrm{e} = \sqrt{\frac{n_\mathrm{e} e^2}{\varepsilon_0 m_\mathbf{e}}} \tag{81}$$

is the free-electron plasma frequency and ν is a characteristic collision frequency. Eqs. (53) and (50) then yield

$$\sum_{\alpha>0} \langle n_\alpha \rangle f_\alpha(\omega) = -\frac{\omega}{\omega + \mathrm{i}\nu} \sum_{\alpha>0} \langle n_\alpha \rangle = -\frac{\omega}{\omega + \mathrm{i}\nu} n_\mathrm{e} V \tag{82}$$

where n_e is the average free electron density. Hence

$$\langle f_{\alpha>0}(\omega) \rangle = f_\mathrm{f}(\omega) = -\frac{\omega}{\omega + \mathrm{i}\nu} \tag{83}$$

Taking the imaginary part of Eq. (80) and making use of Eq. (54), taking account of only the free electrons, leads to a formula for ν as follows

$$\frac{\nu}{\omega^2 + \nu^2} = \frac{\pi}{2 n_\mathrm{e} V} \sum_{\alpha>0,\, \beta>0} \left(\langle n_\alpha \rangle - \langle n_\beta \rangle \right) f_{\alpha\beta}^0 \delta(E_\alpha - E_\beta + \omega) \tag{84}$$

which renders ν as a function of ω. Application of Eqs. (62) and (63) then leads to

$$\frac{\nu}{\omega^2 + \nu^2} = \frac{1 - \mathrm{e}^{-\omega/T}}{2 n_\mathrm{e} V \omega} \sum_{\alpha>0} \mathfrak{p}(E_\alpha) \mathfrak{q}(E_\alpha + \omega) \mathrm{Im} f_\alpha^+(\omega) \tag{85}$$

By means of the anzatz

$$\mathrm{Im} \frac{-1}{\omega + \mathrm{i}\nu_\alpha(\omega)} = \frac{3}{4E_\alpha} \mathrm{Im} f_\alpha^+(\omega) \tag{86}$$

for real $\omega \geq 0$, Eq. (85) can be recast in the following form

$$\frac{\nu}{\omega^2 + \nu^2} = \frac{2}{3} \frac{1 - \mathrm{e}^{-\omega/T}}{\omega} \left\langle E_\alpha \frac{\nu_\alpha}{\omega^2 + \nu_\alpha^2} \mathfrak{q}(E_\alpha + \omega) \right\rangle_{\alpha>0} \tag{87}$$

which provides a means of interpolating between the conductivity collision frequency

$$\frac{1}{\nu_\mathrm{c}} \equiv \frac{1}{\nu(0)} = \frac{2}{3T} \left\langle \frac{1}{\nu_\alpha(0)} E_\alpha \mathfrak{q}(E_\alpha) \right\rangle_{\alpha>0} \tag{88}$$

in terms of which the DC conductivity is given, in accordance with Eq. (63), by

$$\varsigma(0) = \frac{e^2 n_\mathrm{e}}{m_\mathrm{e} \nu_\mathrm{c}} \tag{89}$$

and the high-frequency bremsstrahlung collision frequency

$$\nu_\mathrm{br}(\omega) \equiv \frac{\omega}{T} \nu(\omega) \big|_{\omega>>T, \nu_\alpha} = \frac{2}{3T} \langle E_\alpha \nu_\alpha(\omega) \mathfrak{q}(E_\alpha + \omega) \rangle_{\alpha>0} \tag{90}$$

in terms of which the bremsstrahlung reduced absorption coefficient is

$$\tilde{\kappa}_\mathrm{br}(\omega) = 2 \frac{\Omega_\mathrm{e}^2 T}{\omega^3 c} \left(1 - \mathrm{e}^{-\omega/T} \right) \nu_\mathrm{br}(\omega) \tag{91}$$

In dense plasmas and metals, ν_c and ν_br are typically less than or of the order of a few eV in both regimes, so, at x-ray energies, and temperatures $T \ll \omega^2/\nu_{\mathrm{br}}$, the factor $\omega^2/(\omega^2+\nu^2)$ can reasonably be approximated by unity.

3.7. Differential cross-section

Following the general argument given in Ref. [10], the differential cross-section for the scattering of photons from the channel $\omega,\mathbf{k}$ into the element $d\omega' d\Omega'$ about the channel ω', $\mathbf{k}'$ is obtained as follows

$$\begin{aligned}\frac{\partial\sigma}{\partial\Omega'\partial\omega'} &= \frac{1}{2\pi} r_{\mathrm{e}}^2 \, \frac{\omega'}{\omega} \int\limits_{-\infty}^{+\infty} \langle \widehat{\mathbf{F}}^{\dagger}\left(\frac{1}{2}t\right)\widehat{\mathbf{F}}\left(-\frac{1}{2}t\right)\rangle \exp(\mathrm{i}(\omega-\omega')t)dt \\ &= \frac{1}{2\pi} r_e^2 (\mathbf{e}\cdot\mathbf{e}')^2 \, \frac{\omega'}{\omega} \int\limits_{-\infty}^{+\infty} \langle \tilde{\mathbf{f}}^{\dagger} \rho_{\mathbf{q}}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}}\rangle \exp(\mathrm{i}(\omega-\omega')t)dt\end{aligned} \tag{92}$$

electronic level energies. Since only the electron coordinates have been integrated over, the functions (95) depend upon the nuclear dynamics. The expectation average in Eq. (94) represents an average over both electronic and nuclear configurations. This is treated using the Born-Oppenheimer approximation [22,23] which depends upon the assertion that the ion motion is sufficiently slow for the electron dynamics to be determined independently of it. This allows the electronic states α, β,... to be effectively treated within a static nuclear configuration, with the nuclear motion subsequently introduced via an adiabatic approximation.

We evaluate (94), for a particular ion configuration denoted by the ion coordinates, $\mathbf{R}_i$, $i = 1 \ldots N_{\mathrm{i}}$, corresponding to some instant in time, using: (i) that the expectation value only contains contributions from terms when equal numbers of particles are created and annihilated in each state and (ii) the fermion commutation relations (Appendix A, Eq. (199)) together with the fermion rule $\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \rangle = \langle n_\alpha^2 \rangle = \langle n_\alpha \rangle = \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \rangle$ (where $n_\alpha = 0$ or 1 is the number of electrons in the state α). The quantities $\phi_{\alpha\beta}$ can then be treated as scalars. This procedure yields

$$\begin{aligned}\langle \tilde{\mathbf{f}}^{\dagger} \rho_{\mathbf{q}}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}}\rangle &= \sum_{\alpha,\beta,\gamma,\delta} \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \mathbf{a}_\gamma^\dagger \mathbf{a}_\delta \rangle f_\alpha^* f_\delta \phi_{\alpha\beta}\phi_{\delta\gamma}^* = \sum_{\alpha\neq\beta}\left(\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\beta^\dagger \mathbf{a}_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* + \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \mathbf{a}_\beta^\dagger \mathbf{a}_\alpha \rangle |f_\alpha|^2 \phi_{\alpha\beta}\phi_{\alpha\beta}^*\right) + \sum_\alpha \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \rangle |f_\alpha|^2 |\phi_{\alpha\alpha}|^2 \\ &= \sum_{\alpha\neq\beta}\left(\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\beta^\dagger \mathbf{a}_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* + \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\beta \mathbf{a}_\beta^\dagger \rangle |f_\alpha|^2 \phi_{\alpha\beta}\phi_{\alpha\beta}^*\right) + \sum_\alpha \langle n_\alpha \rangle |f_\alpha|^2 |\phi_{\alpha\alpha}|^2 \\ &= \sum_{\alpha\neq\beta}\left(\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\beta^\dagger \mathbf{a}_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* + \left(\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \rangle - \langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\alpha \mathbf{a}_\beta^\dagger \mathbf{a}_\beta \rangle\right) |f_\alpha|^2 \phi_{\alpha\beta}\phi_{\alpha\beta}^*\right) + \sum_\alpha n_\alpha |f_\alpha|^2 |\phi_{\alpha\alpha}|^2 \\ &= \sum_{\alpha,\beta}\left(\langle n_\alpha n_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* + \langle n_\alpha (1-n_\beta)\rangle |f_\alpha|^2 \phi_{\alpha\beta}\phi_{\alpha\beta}^*\right)\end{aligned} \tag{96}$$

where $\widehat{\mathbf{F}}$ is the operator given by Eq. (48) and $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, which is the generalization of Eqs. (18) and (21) in Ref. [10]. Note the fact that the factor ω'/ω is not squared. The integral on the right-hand side of Eq. (92) is the *strength-density dynamic structure factor* (which is the dynamic structure factor defined in terms of the strength density instead of the electron density.) In the forward direction ($\mathbf{q} = 0$), Eq. (92) reduces to

$$\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\Big|_{\mathbf{q}=0} = r_{\mathrm{e}}^2 \langle \Big| \sum_\alpha n_\alpha f_\alpha(\omega)\Big|^2 \rangle \delta(\omega-\omega') \tag{93}$$

Expanding the kernel using Eqs. (46) and (47) yields the intermediate strength-density correlation function,

$$\begin{aligned}\left\langle \tilde{\mathbf{f}}^{\dagger} \rho_{\mathbf{q}}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}}\right\rangle = \sum_{\alpha,\beta,\gamma,\delta} \left\langle \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta \phi_{\alpha\beta}\left(\mathbf{q},\frac{1}{2}t\right)\phi_{\gamma\delta}\left(-\mathbf{q},-\frac{1}{2}t\right)\mathbf{a}_\gamma^\dagger \mathbf{a}_\delta\right\rangle \\ \times f_\alpha^*(\omega,\omega') f_\delta(\omega,\omega')\end{aligned} \tag{94}$$

in which

$$\begin{aligned}\phi_{\alpha\beta}(\mathbf{q},t) &= \langle\alpha|\mathrm{e}^{\mathrm{i}Ht}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\mathrm{e}^{-\mathrm{i}Ht}|\beta\rangle = \langle\alpha|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\beta\rangle \mathrm{e}^{\mathrm{i}(E_\alpha - E_\beta)t} \\ &= \langle\alpha|e^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}(t)}|\beta\rangle\end{aligned} \tag{95}$$

are scalars on the Fock space of the electrons but operators on the Fock space of the atomic nuclei, and in which E_α, E_β are the

in which $f_\alpha = f_\alpha(\omega,\omega')$ and $\phi_{\alpha\beta}$ and $\phi_{\alpha\beta}^*$(without arguments) denote

$$\begin{aligned}\phi_{\alpha\beta} &= \phi_{\alpha\beta}\left(\mathbf{q},\frac{1}{2}t\right) = \langle\alpha\Big|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}\left(\frac{1}{2}t\right)}\Big|\beta\rangle \\ \phi_{\alpha\beta}^* &= \phi_{\beta\alpha}\left(-\mathbf{q},-\frac{1}{2}t\right) = \langle\beta\Big|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}\left(-\frac{1}{2}t\right)}\Big|\alpha\rangle\end{aligned} \tag{97}$$

The first term in the sum on the right-hand side of the final expression of Eq. (96) represents *coherent scattering*. The second term describes *incoherent inelastic scattering*, which is recoil-induced Raman scattering [24], also sometimes referred to as nonresonant inelastic X-ray scattering (NIXS) [25], as a sum over one-electron transitions $\alpha \rightarrow \beta$.

4. Scattering from atomic systems

4.1. Decomposition of the strength–density correlation function

We now proceed to make the customary decomposition of Eq. (96) into sums over bound (or core) and free states, where the bound states are defined to be one-electron states that are localised well within the dimensions of the wavelength of the radiation. For atomic states generally to satisfy this requirement, it is appropriate to make the *long-wavelength assumption*, which asserts that the wavelength is much greater than the atomic size as characterised by the Bohr radius. This requires $1/k >> r_{\mathrm{e}}\alpha_0^{-2}$, which is equivalent to

$\omega \ll \alpha_0 m_e c^2 \simeq 3.6$ keV, which is a weaker assumption than that required for the Thomson dipole approximation, as discussed in section 3.4. It is typically a very valid assumption in the optical regime, but becomes less true in the x-ray regime, where one needs to be careful about its applicability, and it may be appropriate to consider the approximations on a state-by-state basis. In hot plasma, for example, the core states in highly excited ions will be confined within much smaller distances than the Bohr radius, by factors ~$1/(Z-Z_b)^2$), thus extending the validity of the assumption, while highly excited electron states (e.g. Rydberg states) in atoms or ions, may be less confined. The long-wavelength assumption is generally necessary to make the *atomic dipole approximation* in the treatment of the absorption and emission of radiation by atomic systems, though the validity of this approximation in the X-ray regime is not without question [26].

The sum $\sum_{\alpha,\beta}$ on the right hand side of Eq. (96) can then be decomposed according to

$$\sum_{\alpha,\beta} = \sum_{\alpha<0,\beta} + \sum_{\alpha>0,\beta<0} + \sum_{\alpha>0,\beta>0} \tag{98}$$

where $\alpha < 0$, for example, denotes a bound state and $\beta > 0$ a free state. The third term, which comprises a double sum over free states only, is then restored to the original form,

$$\sum_{\substack{\alpha>0,\\ \beta>0}} \left(\langle n_\alpha n_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha} \phi_{\beta\beta}^* + \langle n_\alpha (1-n_\beta) \rangle |f_\alpha|^2 \phi_{\alpha\beta} \phi_{\alpha\beta}^* e^{i(E_\alpha - E_\beta)t} \right) = \langle \tilde{\mathbf{f}}^\dagger \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}} \rangle \tag{99}$$

where $\rho_{\mathbf{q}}^{f}\tilde{\mathbf{f}} = \tilde{\rho}_{\mathbf{q}}^{f}$ is the free-electron strength density operator.

The result, after some manipulation, is

$$\begin{aligned} \langle \tilde{\mathbf{f}}^\dagger \rho_{\mathbf{q}}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}} \rangle = {} & \langle \tilde{\mathbf{f}}^\dagger \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}} \rangle \\ & + \sum_{\alpha<0,\beta} \langle n_\alpha (1-n_\beta) \rangle |f_\alpha|^2 \phi_{\alpha\beta} \phi_{\alpha\beta}^* \\ & + \sum_{\alpha<0,\ \beta<0} \langle n_\alpha n_\beta \rangle f_\alpha^* f_\beta \phi_{\alpha\alpha} \phi_{\beta\beta}^* \\ & + \sum_{\alpha<0,\ \beta>0} \langle n_\alpha n_\beta \rangle \\ & \times \left(f_\alpha^* f_\beta \phi_{\alpha\alpha} \phi_{\beta\beta}^* + f_\alpha f_\beta^* \phi_{\alpha\alpha}^* \phi_{\beta\beta} \right) \end{aligned} \tag{100}$$

Eq. (100) decomposes the scattering cross-section into separate contributions represented by the four terms on the right hand side. The first term represents the principal contribution from free electrons; the second and third terms represent respectively incoherent and coherent scattering from bound electrons; and the fourth term represents interference between coherent scatterings from bound and from free electrons.

For very dilute free electron systems, the operator $\mathbf{f}$ tends to -1. More generally, the free electron term is taken to be represented by

$$\langle \tilde{\mathbf{f}}^\dagger \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}} \rangle = |f_f(\omega)|^2 \langle \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \rangle \tag{101}$$

where $f_f(\omega)$ is given by Eq. (83), which leads to the minimal approximation,

$$\langle \tilde{\mathbf{f}}^\dagger \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \tilde{\mathbf{f}} \rangle = \frac{\omega^2}{\omega^2 + \nu^2} \langle \rho_{\mathbf{q}}^{f}\left(\frac{1}{2}t\right) \rho_{-\mathbf{q}}^{f}\left(-\frac{1}{2}t\right) \rangle \tag{102}$$

where ν is the characteristic collision frequency in the Drude model.

The remaining three terms involve bound states. Assuming that there are no molecules present, each bound state can be associated with a single nucleus. We can then resolve the bound states $\alpha < 0$, according to $\alpha \to \alpha, i$, where α, i denotes the electronic bound state α in the field of the nucleus i. The coordinates of the electron are then written $\mathbf{r} \to \mathbf{r}_{ei} + \mathbf{R}_i$, where $\mathbf{r}_{ei}$ is the electron's position relative to the nucleus, i, and $\mathbf{R}_i$ is the nuclear coordinate, which is treated classically. This separation restricts the Fock space $\{|\alpha\rangle\}$ to that of the electrons only. When both or either of the states α, β denote a bound state, with respect to nuclei i, j, the functions defined by Eq. (97) then become

$$\left.\begin{aligned} \phi_{\alpha\beta} &\to \delta_{ij} \phi_{\alpha\beta}^{i}\left(\mathbf{q}, \frac{1}{2}t\right) \\ \phi_{\alpha\beta}^* &\to \delta_{ij} \phi_{\beta\alpha}^{i}\left(-\mathbf{q}, -\frac{1}{2}t\right) \end{aligned}\right\} \quad \alpha<0,\ \beta<0$$
$$\left.\begin{aligned} \phi_{\alpha\beta} &\to \phi_{\alpha\beta}^{i}\left(\mathbf{q}, \frac{1}{2}t\right) \\ \phi_{\alpha\beta}^* &\to \phi_{\beta\alpha}^{i}\left(-\mathbf{q}, -\frac{1}{2}t\right) \end{aligned}\right\} \quad \left\{\begin{array}{l} \alpha<0,\ \beta>0 \\ \text{or} \\ \alpha>0,\ \beta<0 \end{array}\right. \tag{103}$$

where

$$\begin{aligned} \phi_{\alpha\beta}^{i}(\mathbf{q}, t) &= \langle \alpha, i | e^{-i\mathbf{q}\cdot\mathbf{r}_{ei}(t)} | \beta, i \rangle e^{-i\mathbf{q}\cdot\mathbf{R}_i(t)} \\ &= e^{i(E_\alpha - E_\beta)t} \phi_{\alpha\beta}^{a}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_i(t)}, \quad i \in a \end{aligned} \tag{104}$$

and

$$\phi_{\alpha\alpha}^{a}(\mathbf{q}) = \langle \alpha, i | e^{-i\mathbf{q}\cdot\mathbf{r}_{ei}(0)} | \alpha, i \rangle |_{i\in a} = \int \left| \psi_{\alpha}^{a}(\mathbf{r}_{ei}) \right|^2 e^{-i\mathbf{q}\cdot\mathbf{r}_{ei}} d^3\mathbf{r}_{ei} \tag{105}$$

is the Fourier transform of the bound electron density and where a denotes a particular ion species defined by the nuclear species (Z,A) and charge state Z_a and where any overlap between bound states associated with different nuclei has been ignored. The sum over individual nuclei $\{i\}$ then transforms into a sum over atomic species $\{a\}$ according to

$$\sum_i = \sum_a \sum_{i\in a} \tag{106}$$

where the sum over $i \in a$ denotes a sum over all ions of the same species.

4.2. Incoherent scattering

Incoherent scattering is represented by the second term on the right-hand side of Eq. (100), which may now be recast as follows

$$\begin{aligned}\sum_{\alpha<0,\beta}\langle n_\alpha(1-n_\beta)\rangle\left|f_\alpha\right|^2\phi_{\alpha\beta}\phi_{\alpha\beta}^* &= \sum_i\sum_{\alpha<0,\beta}\langle n_\alpha^i\left(1-n_\beta^i\right)\rangle\left|f_\alpha^i\right|^2\phi_{\alpha\beta}^i\left(\mathbf{q},\frac{1}{2}t\right)\phi_{\beta\alpha}^i\left(-\mathbf{q},-\frac{1}{2}t\right)\\ &= \sum_a\sum_{i\in a}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\left(\mathbf{R}_i\left(\frac{1}{2}t\right)-\mathbf{R}_i\left(-\frac{1}{2}t\right)\right)}\sum_{\alpha<0,\beta}\langle n_\alpha(1-n_\beta)\rangle_a\left|f_\alpha^a\right|^2\mathrm{e}^{\mathrm{i}(E_\alpha-E_\beta)t}\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2\\ &= \sum_a\sum_{i\in a}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\left(\mathbf{R}_i\left(\frac{1}{2}t\right)-\mathbf{R}_i\left(-\frac{1}{2}t\right)\right)}\left(\sum_{\alpha<0}\langle n_\alpha\rangle_a\left|f_\alpha^a\right|^2\Sigma_\alpha^a(\mathbf{q},t)\right)\end{aligned}\tag{107}$$

where $\langle\rangle_a$ represents an average over the subset of ions of species a.

and where

$$\begin{aligned}\Sigma_\alpha^a(\mathbf{q},t) &= \sum_\beta\frac{\langle n_\alpha(1-n_\beta)\rangle_a}{\langle n_\alpha\rangle_a}\ \mathrm{e}^{\mathrm{i}(E_\alpha-E_\beta)t}\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2\\ &= \xi_\alpha^a(\mathbf{q},t)-\sum_{\beta(\neq\alpha)}\frac{\langle n_\alpha n_\beta\rangle_a}{\langle n_\alpha\rangle_a}\ \mathrm{e}^{\mathrm{i}(E_\alpha-E_\beta)t}\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2\end{aligned}\tag{108}$$

Optically inactive states are those bound states in which the electron is confined within dimensions very much smaller than the wavelength. Localised states for which the long-wavelength approximation does not hold are referred to as *optically active*. Such states may exist in the optical regime and the modification of the spectral properties of scattered radiation that they give rise to is perceived as *colour*. However these states are generally associated with continuum electrons, rather than core states.

$$\begin{aligned}\xi_\alpha^a(\mathbf{q},t) &= \sum_{\beta(\neq\alpha)}\mathrm{e}^{\mathrm{i}(E_\alpha-E_\beta)t}\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2 = \langle\mathrm{e}^{\mathrm{i}E_\alpha t}\sum_\beta\langle\alpha,i\left|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\right|\beta,i\rangle e^{-\mathrm{i}\varepsilon_\beta t}\langle\beta,i\left|\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}}\right|\alpha,i\rangle\rangle\big|_{i\in a}-\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2\\ &= \langle\langle\alpha,i\left|\mathrm{e}^{-\frac{1}{2}\mathrm{i}Ht}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\mathrm{e}^{-\mathrm{i}Ht}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}\mathrm{e}^{\frac{1}{2}\mathrm{i}Ht}\right|\alpha,i\rangle\rangle\big|_{i\in a}-\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2\\ &= \langle\langle\alpha\left|\exp\left(-i\mathbf{q}\cdot\mathbf{r}\left(\frac{1}{2}t\right)\right)\exp\left(i\mathbf{q}\cdot\mathbf{r}\left(-\frac{1}{2}t\right)\right)\right|\alpha\rangle-\left|\langle\alpha\right|\exp(-i\mathbf{q}\cdot\mathbf{r}(0))\left|\alpha\rangle\right|^2\rangle\end{aligned}\tag{109}$$

where it has been assumed that the one-electron states β associated with a particular ion comprise a complete set. The term (107) represents incoherent inelastic scattering in which the electrons undergo direct excitations (de-excitations) $\alpha\to\beta$, in which energy $E_\beta-E_\alpha$ is transferred from (to) the photon in the process. The transitions can occur only when there is an electron in the initial state and none in the final state, which accounts for the $\langle n_\alpha(1-n_\beta)\rangle$ factor. The function $\Sigma_\alpha^a(\mathbf{q},t)$ defined by (108) is the *particle-hole intermediate time autocorrelation function* for the bound state α, a; and $\xi_\alpha^a(\mathbf{q},t)$ defined by (109) is the corresponding *particle–particle intermediate time autocorrelation function*.

The corresponding dynamic structure factors are

$$\begin{aligned}\Sigma_\alpha^a(\mathbf{q},\omega) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\Sigma_\alpha^a(\mathbf{q},t)\mathrm{e}^{\mathrm{i}\omega t}dt = \xi_\alpha^a(\mathbf{q},\omega)-\sum_{\beta(\neq\alpha)}\frac{\langle n_\alpha n_\beta\rangle_a}{\langle n_\alpha\rangle_a}\delta(\omega+E_\alpha-E_\beta)\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2\\ \xi_\alpha^a(\mathbf{q},\omega) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\xi_\alpha^a(\mathbf{q},t)\mathrm{e}^{\mathrm{i}\omega t}dt = \sum_{\beta(\neq\alpha)}\delta(\omega+E_\alpha-E_\beta)\left|\phi_{\alpha\beta}^a(\mathbf{q})\right|^2\end{aligned}\tag{110}$$

For Thomson scattering in the optical regime, it is reasonable to treat the core states (occupied bound states) as being optically inactive. For such states, the long-wavelength approximation is equivalent to setting the matrix elements of the commutator $[\mathbf{H},\mathbf{q}\cdot\mathbf{r}]$ between such states to zero. Referring to (109), this yields $\xi_\alpha^a(\mathbf{q},t)+\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2\simeq 1$, which corresponds to the static (geometrical optics) limit. In effect, this means that the Compton recoil is insufficient to perturb the internal state of the ion and that the recoil is taken up by the ion as a whole or by the ions collectively. In the long-wavelength approximation, we then have,

$$\xi_\alpha^a(\mathbf{q},t)\simeq 1-\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2,\quad \alpha<0\tag{111}$$

$$\langle n_\alpha n_\beta\rangle_a\left|\phi^a_{\alpha\beta}\right|^2 = \delta_{\alpha\beta}\langle n_\alpha\rangle_a\left|\phi^a_{\alpha\alpha}\right|^2 + \langle n_\alpha n_\beta\rangle_a(1-\delta_{\alpha\beta})\left|\langle\alpha,a|\left(\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}-1\right)|\beta,a\rangle\right|^2$$
$$= \delta_{\alpha\beta}\langle n_\alpha\rangle_a\left|\phi^a_{\alpha\alpha}\right|^2 + (1-\delta_{\alpha\beta})\langle n_\alpha n_\beta\rangle_a\left|\mathbf{q}\cdot\mathbf{r}^a_{\alpha\beta}\right|^2\left(1+\mathcal{O}\left(\mathbf{q}\cdot\mathbf{r}^a_{\alpha\beta}\right)^2\right)\simeq\delta_{\alpha\beta}\langle n_\alpha\rangle_a\left|\phi^a_{\alpha\alpha}\right|^2 \quad \alpha,\beta<0 \tag{112}$$

where $\mathbf{q}\cdot\mathbf{r}^a_{\alpha\beta}=\langle\alpha,a|\mathbf{q}\cdot\mathbf{r}|\beta,a\rangle$, which is real. Note that completeness demands that there are some optically active states present, since

$$\sum_{\substack{\beta \\ (\beta\neq\alpha)}}\phi^a_{\alpha\beta}\phi^{a*}_{\alpha\beta}\equiv 1-\left|\phi^a_{\alpha\alpha}\right|^2\neq 0 \tag{113}$$

The approximation represented by (112) is applicable when the summation over β is weighted by the occupancy of the state and the optically active states are sparsely populated ($\langle n_\beta\rangle\ll 1$). For example, while Rydberg states in low-density plasmas are candidates to be optically active, such states, when they exist, are generally well above the level of the chemical potential and therefore weakly populated.

On the other hand, for free states (which can be treated as non-localised quasi-plane-wave states corresponding to points on the reciprocal lattice of a 3-torus) we can neglect any coupling between bound and free states induced by the operator $e^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}$ when the Compton recoil is insufficient to cause ionization of any *core state*, which is defined to be a bound state having non-negligible occupancy. This is tantamount to saying that, in the long wavelength approximation, at least, $e^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\alpha>|_{\alpha>0}$ comprises a superposition of free states that are orthogonal to any core bound state, i.e.,

$$\langle n_\alpha n_\beta\rangle_a\phi^a_{\alpha\beta}(\mathbf{q})\simeq 0,\quad \alpha>0,\ \beta<0\ \text{ or }\ \alpha<0,\ \beta>0 \tag{114}$$

Even in Thomson scattering, the recoil, although classically negligible, is still finite. If it is taken up by an individual electron, the state of that electron must change, however slightly, and the Pauli principle comes into effect. This can have a disproportionally large effect on the scattering if the final state is blocked, as is typically the case in degenerate plasma. If however the electron is bound and the recoil does not change the internal state, there is no Pauli blocking and the recoil is taken up by the ion, or ions collectively. This is described by the intermediate ion self-correlation function,

$$S^{\mathrm{s}}_{aa}(\mathbf{q},t)=\langle\exp\left(-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_i\left(\frac{1}{2}t\right)\right)\exp\left(\mathrm{i}\mathbf{q}\cdot\mathbf{R}_i\left(-\frac{1}{2}t\right)\right)\rangle|_{i\in a} \tag{115}$$

which when applied to Eq. (107), while applying the approximations (111)–(114), yields

$$\sum_{\alpha<0,\beta}\langle n_\alpha(1-n_\beta)\rangle|f_\alpha|^2\phi_{\alpha\beta}\phi^*_{\alpha\beta}\simeq\sum_a\langle N_a\rangle S^{\mathrm{s}}_{aa}(\mathbf{q},t)\sum_{\alpha<0}\langle n_\alpha\rangle_a\left|f^a_\alpha\right|^2 \times\left(1-\left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2\right) \tag{116}$$

Equation (116) describes incoherent scattering by electrons in optically-inactive bound states where the scattering is according to ordinary wave optics, while momentum and energy conservation are accommodated through recoil of the ions.

At the other extreme, when the recoil energy is large (so that $|\omega-\omega'|>>|E_\alpha|$) which is a situation which commonly arises in the treatment of the incoherent (NIXS) component of XRTS from weakly bound electrons, other approximations become applicable. One that seems to be particularly favoured is the *impulse approximation* (IA) [27], in which any motion, relative to the potential, of the active electron during the scattering is ignored, so that only the kinetic energy changes. The resulting dynamic structure factor resembles RPA in the sense of being an average of $\delta(\omega-\omega'-(\mathbf{p}\cdot\mathbf{q}/m)-(q^2/2m))$ over the distribution of initial electron momenta $\mathbf{p}$, while accounting for Pauli blocking in the final state. However, the momentum distribution, instead of being given by the plane-wave density of states as in the RPA, is given in terms of the momentum spectral distribution or the real-space Green functions [25], as may be determined from Hartree–Fock (HF) or density functional theory (DFT) calculations. Recent extensions of the IA [28] that take account of the electron binding energy in bound-free scattering, for example, have yielded good agreement with recent XRTS measurements in warm dense matter (WDM) [5,6].

In general, an atom may contain both optically active and inactive states, in which case the sum over states may be split accordingly and the appropriate approximations applied as required.

4.3. Ion correlations

The ion self-correlation function (115) is related to the intermediate ion correlation matrix defined by,

$$S_{ab}(\mathbf{q},t)=\frac{1}{\sqrt{N_aN_b}}\langle\sum_{i\in a,j\in b}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_i\left(\frac{1}{2}t\right)}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_j\left(-\frac{1}{2}t\right)}\rangle$$
$$=\frac{1}{\sqrt{N_aN_b}}\langle\sum_{i\in a,j\in b(i\neq j)}\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_i\left(\frac{1}{2}t\right)}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_j\left(-\frac{1}{2}t\right)}\rangle + \delta_{ab}S^{\mathrm{s}}_{aa}(\mathbf{q},t) \tag{117}$$

which represents the temporal and spatial correlations between ions of species *a* and *b*, and which reduces to the static structure factor, $S_{ab}(\mathbf{q},0)\equiv S_{ab}(\mathbf{q})$, when the nuclei are stationary. If the temporal fluctuations (velocities) are independent of the spatial correlations (positions), an assumption that may be considered appropriate for systems interacting via short range forces (e.g. small hard cores) then $S_{aa}(\mathbf{q},t)=S_{aa}(\mathbf{q})S^{\mathrm{s}}_{aa}(\mathbf{q},t)$. More generally, we may write

$$S_{aa}(\mathbf{q},t)=S_{aa}(\mathbf{q})S^{\mathrm{s}}_{aa}(\mathbf{q},t)+\Delta_{aa}(\mathbf{q},t) \tag{118}$$

where

$$S^{\mathrm{s}}_{aa}(\mathbf{q},t=0)=1$$
$$\Delta_{aa}(\mathbf{q},t=0)=0,\quad \Delta_{aa}(\mathbf{q},t\to\infty)=0,\quad \Delta_{aa}(\mathbf{q},-t)=\Delta_{aa}(\mathbf{q},t) \tag{119}$$

The Fourier transform of (117) with respect to time gives the ion–ion dynamic structure factor,

$$S_{ab}(\mathbf{q},\omega)=\frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}S_{ab}(\mathbf{q},t)e^{i\omega t}dt \tag{120}$$

and hence, from Eq. (118),

$$S_{aa}(\mathbf{q},\omega)=S_{aa}(\mathbf{q})S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)+\Delta_{aa}(\mathbf{q},\omega) \tag{121}$$

where $S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)$ and $\Delta_{aa}(\mathbf{q},\omega)$ are calculated from their corresponding intermediate functions in accordance with (120). A reasonable model of the self-correlation for weakly-coupled Coulomb systems is provided by

$$S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)=\left|\varepsilon_a(\mathbf{q},\omega)\right|^2S_{aa}(\mathbf{q},\omega) \tag{122}$$

where $\varepsilon_a(\mathbf{q},\omega)$ is the dielectric function of the ion species a defined so that the total dielectric function is $\varepsilon(\mathbf{q},\omega)=\varepsilon_{\mathrm{e}}(\mathbf{q},\omega)+\sum\limits_a(\varepsilon_a(\mathbf{q},\omega)-1)$. Equation (122) holds for classical (Boltzmann) particles in the RPA, for example, when $S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)$ would be the dynamic structure factor for non-interacting particles, which then comprises only the self part. Equation (122) is claimed to have more general validity, potentially applicable to non-equilibrium systems, through the deployment of a more accurate dielectric function [29]. For equilibrium systems, application of the Fluctuation-dissipation theorem [30–32], yields

$$S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)=\frac{q^2D_a^2}{T}\frac{1}{1-e^{-\omega/T}}\mathrm{Im}(\varepsilon_a(\mathbf{q},\omega)) \tag{123}$$

where D_a is the Debye length defined by $1/D_a^2=m_a\Omega_a^2/T=n_aZ_a^2e^2/\varepsilon_0T$. Integration of (123) over frequency yields, for non-degenerate systems,

$$\begin{aligned}\int\limits_{-\infty}^{\infty}S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)d\omega&=\frac{q^2D_a^2}{\pi T}\int\limits_{-\infty}^{\infty}\frac{1}{1-e^{-\omega/T}}\mathrm{Im}(\varepsilon_a(\mathbf{q},\omega))d\omega\\&=\frac{q^2D_a^2}{\pi T}\int\limits_{0}^{\infty}\coth\left(\frac{\omega}{2T}\right)\mathrm{Im}(\varepsilon_a(\mathbf{q},\omega))d\omega=1\end{aligned} \tag{124}$$

which complies with the first of Equation (119). Note that we have not made recourse to the usual classical assumption that $\omega<<T\Rightarrow1-\mathrm{e}^{-\omega/T}\simeq\omega/T$. Equation (124) is exact, in the context of RPA, but would require additional assumptions and approximations were the classical form to be used: Firstly, the classical integral is exhausted by the compressibility sum rule but, because the integral extends to infinity, beyond the classical regime, the correct result is yielded only if $\mathrm{Im}\varepsilon_a(\mathbf{q},\omega)$ vanishes or makes a negligible contribution in the regime $\omega>\sim T$. The classical assumption is not generally valid, even for ions: It is not difficult to envisage that $\omega,\ \Omega_a\gtrsim T$ in situations involving x-ray scattering in metals or warm dense matter, for example. For freely moving weakly interacting ions with a Maxwellian velocity distribution, a semiclassical calculation yields [33]

$$S^{\mathrm{s}}_{aa}(\mathbf{q},\omega)=\sqrt{\frac{m_a}{2\pi q^2T}}\exp\left(-\frac{m_a}{2q^2T}\left(\omega-\frac{q^2}{2m_a}\right)^2\right) \tag{125}$$

which describes the effect of both Doppler broadening and recoil on the scattering by such particles. For interacting particles in a plasma fluid, Eq. (125) is a reasonable description for frequencies ω much greater than the putative collision frequency.

In strongly coupled systems, the ion correlations depend upon the frequencies, $\Omega_{\mathbf{K}}=\Omega_{-\mathbf{K}}$, of the collective modes $\{\mathbf{K}\}$, each defined by its wavevector $\mathbf{K}$ and polarization $\mathbf{e}_{\mathbf{K}}$. In a monoatomic crystalline solid comprising a single species, the dynamic ion–ion structure factor takes the (approximate) form [34]

$$S_{aa}(\mathbf{q},\omega)=B(\mathbf{q})\Sigma_{aa}(\mathbf{q})\delta(\omega)+(1-B(\mathbf{q}))S^{\mathrm{inel}}_{aa}(\mathbf{q},\omega) \tag{126}$$

where $\Sigma_{aa}(\mathbf{q})$ is the 'zero excitation' lattice static structure factor defined as the static structure factor in the limit $\mathcal{N}_{\mathbf{K}}+1/2\rightarrow0$ when all collective modes, including zero-point modes, are suppressed. (Note that $\Sigma_{aa}(\mathbf{q})\neq S_{aa}(\mathbf{q})$.) Both $S_{aa}(\mathbf{q})=\int_{-\infty}^{\infty}S_{aa}(\mathbf{q},\omega)d\,\omega$ and $\Sigma_{aa}(\mathbf{q})$ are quantum mechanical objects and subject to a quantum uncertainty. Even in the zero excitation limit, incoherent quantum fluctuations persist and are characterised by the correlation length $L_{\mathrm{q}}=(m_ac_{\mathrm{s}}/n_a\hbar)^{1/2}$ where c_s is the sound velocity and n_a the particle density. (See Appendix C) This accounts for the decay in the pair correlation at large distances, something that does not occur in the equivalent classical structure factor in which all the particles would be placed at precisely fixed locations. For typical metals, this distance seems to be of the order of a nanometre. Particular implications of this include the limits, $S_{aa}(\mathbf{q})\underset{|\mathbf{q}|\rightarrow\infty}{\rightarrow}1\equiv\Sigma_{aa}(\mathbf{q})\underset{|\mathbf{q}|\rightarrow\infty}{\rightarrow}1$, yielding, in both instances, pair correlation functions that are square integrable over all space.

In Eq. (126), the function

$$\begin{aligned}B(\mathbf{q})&=\exp\left(-\sum_{\{\mathbf{K}\}}\frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{2M_a\Omega_{\mathbf{K}}}(2\mathcal{N}_{\mathbf{K}}+1)\right)\\&\simeq1-\sum_{\{\mathbf{K}\}}\frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{2M_a\Omega_{\mathbf{K}}}(2\mathcal{N}_{\mathbf{K}}+1)\end{aligned} \tag{127}$$

is the Debye–Waller factor, in which $M_a=\langle N_a\rangle m_a$, $\mathcal{N}_{\mathbf{K}}=1/(\exp(\Omega_{\mathbf{K}}/T)-1)$ is the Bose–Einstein occupancy of the mode $\mathbf{K}$, and

$$S^{\mathrm{inel}}_{aa}(\mathbf{q},\omega)=\frac{\sum\limits_{\{\mathbf{K}\}}\frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{\Omega_{\mathbf{K}}}((\mathcal{N}_{\mathbf{K}}+1)\delta(\omega-\Omega_{\mathbf{K}})\Sigma_{aa}(\mathbf{q}-\mathbf{K})+\mathcal{N}_{\mathbf{K}}\delta(\omega+\Omega_{\mathbf{K}})\Sigma_{aa}(\mathbf{q}+\mathbf{K}))}{\sum\limits_{\{\mathbf{K}\}}\frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{\Omega_{\mathbf{K}}}(2\mathcal{N}_{\mathbf{K}}+1)} \tag{128}$$

is the inelastic dynamic structure factor which describes the excitation and de-excitation of phonon modes $\mathbf{K}$ in the scattering system. The first term in Eq. (126) describes Laue and Bragg scattering, and the second describes Brillouin scattering by the collective modes (phonons). Subject to the approximation (127), the dynamic structure factor (126) satisfies the f-sum $\int_{-\infty}^{\infty} S_{aa}(\mathbf{q},\omega)\,\omega d\omega = q^2/2m_a$, by virtue of the lemma (see Appendix C),

$$\sum_{\{\mathbf{K}\}} (\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2 f(\mathbf{K}) \Sigma_{aa}(\mathbf{q}-\mathbf{K}) = q^2 f(\mathbf{q})\langle N_a\rangle \tag{129}$$

which holds for any finitely bounded function *f*(**q**) for which the sum $\sum_{\mathbf{q}} f(\mathbf{q})$ is absolutely convergent. The self-correlation is given by (126) with $\Sigma_{aa} = 1$, [34], which yields

$$S^S_{aa}(\mathbf{q},\omega) = B(\mathbf{q})\delta(\omega) + (1-B(\mathbf{q})) \times \frac{\sum_{\{\mathbf{K}\}} \frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{\Omega_{\mathbf{K}}}((\mathcal{N}_{\mathbf{K}}+1)\delta(\omega-\Omega_{\mathbf{K}}) + \mathcal{N}_{\mathbf{K}}\delta(\omega+\Omega_{\mathbf{K}}))}{\sum_{\{\mathbf{K}\}} \frac{(\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2}{\Omega_{\mathbf{K}}}(2\mathcal{N}_{\mathbf{K}}+1)} \tag{130}$$

which satisfies $\int_{-\infty}^{\infty} S^S_{aa}(\mathbf{q},\omega)d\omega = 1$ identically, and the f-sum $\int_{-\infty}^{\infty} S^S_{aa}(\mathbf{q},\omega)\,\omega d\omega = q^2/2m_a$ by virtue of $\sum_{\{\mathbf{K}\}} (\mathbf{q}\cdot\mathbf{e}_{\mathbf{K}})^2 = q^2\langle N_a\rangle$, which is a limiting case of (129), and the approximation (127).

4.4. Scattering by bound electrons

In order to take account of the coupling (mixing) between electron states within the same atom, *i*, it is appropriate to define the electron pair distribution for a pair of electron states, α, β, as follows, where **r** and **r′** denote the electron coordinate operators.

$$\begin{aligned}\Phi^{ii}_{\alpha\beta}(\mathbf{q},t) &= \langle\Sigma_a(\alpha,\beta),i|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}|\Sigma_a(\alpha,\beta),i\rangle \\ &= \Phi^a_{\alpha\beta}(\mathbf{q})\exp\left(-\mathrm{i}\mathbf{q}\cdot\left(\mathbf{R}_i\left(\frac{1}{2}t\right)-\mathbf{R}_i\left(-\frac{1}{2}t\right)\right)\right), \quad i\in a \\ \Phi^{ij}_{\alpha\beta}(\mathbf{q},t) &= \langle\alpha,i;\beta,j|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}|\alpha,i;\beta,j\rangle \\ &= \phi^a_{\alpha\alpha}(\mathbf{q})\phi^b_{\beta\beta}(-\mathbf{q})\exp\left(-\mathrm{i}\mathbf{q}\cdot\left(\mathbf{R}_i\left(\frac{1}{2}t\right)-\mathbf{R}_j\left(-\frac{1}{2}t\right)\right)\right), \\ & \qquad i\neq j,\ i\in a,\ j\in b\end{aligned} \tag{131}$$

which effectively replace $\phi^i_{\alpha\alpha}\phi^{i*}_{\beta\beta}$ and $\phi^i_{\alpha\alpha}\phi^{j*}_{\beta\beta}$ respectively, where $|\Sigma_a(\alpha,\beta),i\rangle$ denotes a two-electron state $\Sigma_a(\alpha,\beta)$ in the field of the nucleus *i* and where

$$\begin{aligned}\Phi^a_{\alpha\beta}(\mathbf{q}) &= \Phi^{ii}_{\alpha\beta}(\mathbf{q},0)\Big|_{i\in a} \\ \Phi^a_{\alpha\beta}(0) &= \Phi^{ii}_{\alpha\beta}(0,t)\Big|_{i\in a} = \langle\Sigma_a(\alpha,\beta),i|\Sigma_a(\alpha,\beta),i\rangle = 1 \\ \Phi^a_{\alpha\alpha}(\mathbf{q}) &= \left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2\end{aligned} \tag{132}$$

In Equation (131), $\Phi^a_{\alpha\beta}$ is the distribution function for a pair of electrons occupying the mixed state $\Sigma_a(\alpha,\beta)$ in the average field of the remaining electrons within the same ion species *a*, while $\phi^a_{\alpha\alpha}$ is the equivalent function for a single electron in the state α. For coupled identical particles, it is appropriate to use a symmetrised form of the joint density such that

$$\Phi^a_{\alpha\beta}(\mathbf{q}) = \Phi^a_{\beta\alpha}(\mathbf{q}) = \Phi^a_{\alpha\beta}(-\mathbf{q}) = \Phi^a_{\beta\alpha}(-\mathbf{q}) \tag{133}$$

and

$$\frac{1}{2}\left(\phi^a_{\alpha\alpha}(\mathbf{q}) + \phi^a_{\beta\beta}(\mathbf{q})\right) = \langle\Sigma_a(\alpha,\beta),i|\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\Sigma_a(\alpha,\beta),i\rangle\Big|_{i\in a} \tag{134}$$

Substituting into the third terms of (100) according to (103) and subsequently averaging over the ion configurations, yields

$$\begin{aligned}\sum_{\alpha<0,\beta<0}\langle n_\alpha n_\beta\rangle f^*_\alpha f_\beta \phi_{\alpha\alpha}\phi^*_{\beta\beta} &= \sum_{i,j}\sum_{\alpha<0,\beta<0}\langle n^i_\alpha n^j_\beta \Phi^{ij}_{\alpha\beta}(\mathbf{q},t)\rangle f^*_\alpha f_\beta \\ &= \sum_{a,b}\sum_{i\in a,j\in b}\sum_{\alpha<0,\beta<0}\langle n^i_\alpha n^j_\beta\rangle \Phi^{ij}_{\alpha\beta}(\mathbf{q},t) f^{a*}_\alpha f^b_\beta\end{aligned} \tag{135}$$

We now make the *independence assumption* that the electronic states in *different* atoms are uncorrelated with each other *and* with the positions of the atoms. Moreover, we take the one electron states to be of definite parity, as in the Hartree central field approximation, in which case the densities $\phi^a_{\alpha\alpha}(\mathbf{q})$ are real, so that $\phi^a_{\alpha\alpha}(\mathbf{q}) = \phi^{a*}_{\alpha\alpha}(\mathbf{q}) = \phi^a_{\alpha\alpha}(-\mathbf{q})$. Then, referring to Eq. (131) and making use of Eq. (115),

$$\begin{aligned}\langle\sum_{i\in a,j\in b} n^i_\alpha n^j_\beta \Phi^{ij}_{\alpha\beta}(\mathbf{q},t)\rangle &= \sum_{i\neq j}\langle n_\alpha\rangle_a\langle n_\beta\rangle_b\langle \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{R}_i\left(\frac{1}{2}t\right)}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{R}_j\left(-\frac{1}{2}t\right)}\rangle \phi^a_{\alpha\alpha}(\mathbf{q})\phi^b_{\beta\beta}(-\mathbf{q}) + \delta_{ab}\sum_{i\in a}\langle n_\alpha n_\beta\rangle_a \Phi^{ii}_{\alpha\beta}(\mathbf{q},t) \\ &= N_\mathrm{i}\left(\sum_{a,b}\sqrt{P_aP_b}S_{ab}(\mathbf{q},t)\langle n_\alpha\rangle_a\langle n_\beta\rangle_b \phi^a_{\alpha\alpha}(\mathbf{q})\phi^b_{\beta\beta}(\mathbf{q}) + \sum_a P_a S^\mathrm{s}_{aa}(\mathbf{q},t)\gamma^a_{\alpha\beta}(\mathbf{q})\right)\end{aligned} \tag{136}$$

where $P_a = \langle N_a\rangle/N_\mathrm{i}$ is the average fraction of atoms in the charge state *a*, $\langle n_\alpha\rangle_a = \langle n^i_\alpha | i\in a\rangle = 1/\langle N_a\rangle \sum_{i\in a}\langle n^i_\alpha\rangle$ denotes the average number of electrons in the state α associated with ions of species *a* and where

$$\begin{aligned}\gamma^a_{\alpha\beta}(\mathbf{q}) &= \langle n_\alpha n_\beta\rangle_a \Phi^a_{\alpha\beta}(\mathbf{q}) - \langle n_\alpha\rangle_a\langle n_\beta\rangle_a \phi^a_{\alpha\alpha}(\mathbf{q})\phi^a_{\beta\beta}(\mathbf{q}) \\ &= \langle n_\alpha n_\beta\rangle_a\left(\Phi^a_{\alpha\beta}(\mathbf{q}) - \phi^a_{\alpha\alpha}(\mathbf{q})\phi^a_{\beta\beta}(\mathbf{q})\right) + (\langle n_\alpha n_\beta\rangle_a \\ &\quad - \langle n_\alpha\rangle_a\langle n_\beta\rangle_a)\phi^a_{\alpha\alpha}(\mathbf{q})\phi^a_{\beta\beta}(\mathbf{q})\end{aligned} \tag{137}$$

is the internal bound-state covariance for electron states α, β in ions of species *a*, which, in the final expression on the rhs of Eq. (137), is divided up into two parts: the dynamical correlation due to configuration interactions, representing two-electron correlations beyond

Hartree–Fock, and the statistical correlation due to fluctuations in the electron populations. (Exchange correlations are dealt with via the commutation relations obeyed by the fermion creation and annihilation operators.) Substitution into Eq. (135), yields

$$\sum_{\alpha<0,\beta<0}\langle n_\alpha n_\beta\rangle f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* = N_\mathrm{i}\sum_{a,b}\sqrt{P_aP_b}\Big(S_{ab}(\mathbf{q},t)\tilde{\rho}_a^<(\mathbf{q})\tilde{\rho}_b^{<*}(\mathbf{q}) + \delta_{ab}S_{aa}^s(\mathbf{q},t)\gamma_{\alpha\beta}^a(\mathbf{q})\Big) \tag{138}$$

in which (suppressing the dependence on ω)

$$\tilde{\rho}_a^<(\mathbf{q}) = \tilde{\rho}_a^<(-\mathbf{q}) = \sum_{\alpha<0}\langle n_\alpha^a\rangle f_\alpha^* \phi_{\alpha\alpha}^a(\mathbf{q}) \tag{139}$$

Combining (138) with (116) yields the total bound electron strength correlation function,

$$\begin{aligned}\langle\tilde{\mathbf{f}}^\dagger \rho_\mathbf{q}^b\left(\tfrac{1}{2}t\right)\rho_{-\mathbf{q}}^b\left(-\tfrac{1}{2}t\right)\tilde{\mathbf{f}}\rangle &= \sum_{\alpha<0,\beta}\langle n_\alpha(1-n_\beta)\rangle|f_\alpha|^2\phi_{\alpha\beta}\phi_{\alpha\beta}^* \\ &\quad + \sum_{\alpha<0,\beta<0}\langle n_\alpha n_\beta\rangle f_\alpha^* f_\beta\phi_{\alpha\alpha}\phi_{\beta\beta}^* \\ &= N_\mathrm{i}\sum_{a,b}\sqrt{P_aP_b}\Bigg(S_{ab}(\mathbf{q},t)\tilde{\rho}_a^<(\mathbf{q})\tilde{\rho}_b^{<*}(\mathbf{q}) + \delta_{ab}S_{aa}^s(\mathbf{q},t) \\ &\quad\times\Bigg(\sum_{\substack{\alpha<0\\ \beta<0}} f_\alpha^* f_\beta\gamma_{\alpha\beta}^a(\mathbf{q}) + \sum_{\alpha<0}\langle n_\alpha^a\rangle|f_\alpha^a|^2\left(1-|\phi_{\alpha\alpha}^a(\mathbf{q})|^2\right)\Bigg)\Bigg)\end{aligned} \tag{140}$$

Finally, substituting (140) into (92) and carrying out the time integration, yields the bound electron contribution, in the static limit, to the Thomson scattering cross-section as follows.

$$\begin{aligned}\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\Big|_\mathrm{b} &= r_\mathrm{e}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}N_\mathrm{i}\sum_{a,b}\sqrt{P_aP_b}\Bigg(S_{ab}(\mathbf{q},\omega-\omega')\tilde{\rho}_a^<(\mathbf{q})\tilde{\rho}_b^{<*}(\mathbf{q}) \\ &\quad+\delta_{ab}S_{aa}^S(\mathbf{q},\omega-\omega')\Bigg(\Gamma_a + \sum_{\alpha<0}\langle n_\alpha^a\rangle\left|f_\alpha^a\right|^2 \\ &\quad\times\left(1-\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2\right)\Bigg)\Bigg)\end{aligned} \tag{141}$$

where, referring to (137),

$$\Gamma_a(\mathbf{q},\omega) = \sum_{\alpha<0,\beta<0} f_\alpha^{a*}(\omega)f_\beta^a(\omega)\gamma_{\alpha\beta}^a(\mathbf{q}) \tag{142}$$

which is the total strength variance $\langle\Delta\tilde{\rho}_a^2\rangle$ for the bound electrons. This term is difficult to calculate and is often ignored or overlooked in calculations. Equation (141) holds in the static (optical) limit by virtue of the interim approximation (116), which affects only the final term. The more general unapproximated form of this term is substituted later at Equation (176).

4.5. Scattering by free electrons

The free electron part of the cross-section is, making use of Eq. (101), given by.

$$\begin{aligned}\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\Big|_\mathrm{f} &= \frac{1}{2\pi}r_\mathrm{e}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}\int\limits_{-\infty}^{+\infty}\langle\tilde{\mathbf{f}}^\dagger\rho_\mathbf{q}^\mathrm{f}\left(\tfrac{1}{2}t\right)\rho_{-\mathbf{q}}^\mathrm{f}\left(-\tfrac{1}{2}t\right)\tilde{\mathbf{f}}\rangle \\ &\quad\times\exp(\mathrm{i}(\omega-\omega')t)dt \\ &= r_\mathrm{e}^2(\mathbf{e}\cdot\mathbf{e}')^2N_\mathrm{i}Z_\mathrm{f}\frac{\omega'}{\omega}\left|f_\mathrm{f}(\omega)\right|^2S_\mathrm{ee}^\mathrm{f}(\mathbf{q},\omega-\omega')\end{aligned} \tag{143}$$

where

$$S_\mathrm{ee}^\mathrm{f}(\mathbf{q},\omega) = \frac{1}{2\pi N_\mathrm{i}Z_\mathrm{f}}\int\limits_{-\infty}^{+\infty}\langle\rho_\mathbf{q}^\mathrm{f}\left(\tfrac{1}{2}t\right)\rho_{-\mathbf{q}}^\mathrm{f}\left(-\tfrac{1}{2}t\right)\rangle\exp(\mathrm{i}(\omega-\omega')t)dt \tag{144}$$

is the free-electron dynamic structure factor and $f_\mathrm{f}(\omega)$ is the free electron strength function, which is given, in the Drude model, by Eq. (83).

4.6. Free electron structure factor

The free electron correlations described by the structure factor (144) are affected by correlations with the ion fluctuations. In the Born–Oppenheimer approximation, the free electron density operator is given semi-classically by

$$\rho_\mathrm{e}(\mathbf{r},t) = \rho_\mathrm{e}^0(\mathbf{r},t) + n_\mathrm{e}\sum_a\int\hat{g}_{\mathrm{e}a}^\mathrm{f}(\mathbf{r}-\mathbf{r}')(\rho_a(\mathbf{r}',t)-n_a)d^3\mathbf{r}' \tag{145}$$

where $\hat{g}_{\mathrm{e}a}^\mathrm{f}(\mathbf{r})$ is the effective (atom-in-jellium) pair correlation function between free electrons and a single ion of species a, and $\rho_\mathrm{e}^0(\mathbf{r},t)$ is the free electron density in the presence of a homogeneous positively charged background, and $\rho_a(\mathbf{r},t)$ is the ion density.

$$\begin{aligned}\langle\rho_\mathrm{e}\rangle &= \frac{1}{V}\int\limits_V\rho_\mathrm{e}(\mathbf{r},t)d^3\mathbf{r} = \frac{1}{V}\int\limits_V\rho_\mathrm{e}^0(\mathbf{r},t)d^3\mathbf{r} = n_\mathrm{e} = \sum_a n_aZ_a \\ \langle\rho_a\rangle &= \frac{1}{V}\int\limits_V\rho_a(\mathbf{r},t)d^3\mathbf{r} = n_a = \frac{N_a}{V} = P_an_\mathrm{i}\end{aligned} \tag{146}$$

$$\sum_a\langle N_a\rangle\int\hat{g}_{\mathrm{e}a}^\mathrm{f}(\mathbf{r})d^3\mathbf{r} = V \tag{147}$$

In the first instance, the labels $\{a\}$ label individual nuclei, in which case, $\{a\} = \{i\}$, $N_i=1$, $\rho_i(\mathbf{r},t) = \delta(\mathbf{r}-\mathbf{r}_i(t))$. In Coulomb systems, the electron-ion correlation function can be regarded as being dominated by the monopole interaction, which depends only on the charge state of the ion, while being much less dependent on higher multipole terms, which would depend on the internal state of the ion. Accordingly, we take $\langle N_a\rangle$ to be the average number of ions of a particular nuclear species in the charge state Z_a. Formally, it is straightforward to generalize the definition of the ion species to include information about the ion's internal state.

The complete free-electron–ion correlation function implied by Eq. (145) is

$$g_{\mathrm{e}a}(\mathbf{r}) = \hat{g}_{\mathrm{e}a}^\mathrm{f}(\mathbf{r}) + \sum_b n_b\int\hat{g}_{\mathrm{e}b}^\mathrm{f}(\mathbf{r}-\mathbf{r}')g_{ba}(\mathbf{r}')d^3\mathbf{r}' \tag{148}$$

which confirms $\hat{g}_{\mathrm{e}a}^\mathrm{f}$ to be the electron-ion correlation function that one would obtain from using a single-centre atom-in-jellium approximation. Fourier transforming Eq. (148), taking the general definition of the Fourier transform of the pair correlation between particle species a, b to be

$$g_{ab}(\mathbf{q}) = \sqrt{n_a n_b}\int g_{ab}(\mathbf{r})\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{r} \tag{149}$$

yields

$$g_{\mathrm{e}a}(\mathbf{q}) = \sum_b \widehat{g}^{\mathrm{f}}_{\mathrm{e}b}(\mathbf{q})(\delta_{ab} + g_{ba}(\mathbf{q})) \tag{150}$$

Expressing (145) in terms of the density fluctuation operators, $\delta\rho = \rho - \langle\rho\rangle$, yields

$$\delta\rho_{\mathrm{e}}(\mathbf{r},t) = \delta\rho^0_{\mathrm{e}}(\mathbf{r},t) + n_{\mathrm{e}}\sum_a\int \widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{r}-\mathbf{r}')\delta\rho_a(\mathbf{r}',t)d^3\mathbf{r}' \tag{151}$$

the Fourier transform of which yields

$$\delta\rho^{\mathrm{f}}_{\mathbf{q}}(t) \equiv \delta\rho_{\mathrm{e}}(\mathbf{q},t) = \delta\rho^0_{\mathrm{e}}(\mathbf{q},t) + \sum_a\sqrt{\frac{Z_{\mathrm{f}}}{P_a}}\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\delta\rho_a(\mathbf{q},t) \tag{152}$$

in which

$$\rho(\mathbf{q},t) = \int \rho(\mathbf{r},t)\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{r} \tag{153}$$

$$Z_{\mathrm{f}} = \sum_a P_a Z_a \tag{154}$$

The electron–electron correlation function, which is the electron dynamic structure factor, is defined by

$$S_{\mathrm{ee}}(\mathbf{q},\omega) = \frac{1}{2\pi n_{\mathrm{e}}V}\int\limits_{-\infty}^{\infty}\langle\delta\rho_{\mathrm{e}}\left(\mathbf{q},\frac{1}{2}t\right)\delta\rho_{\mathrm{e}}\left(-\mathbf{q},-\frac{1}{2}t\right)\rangle\mathrm{e}^{\mathrm{i}\omega t}dt \tag{155}$$

This yields,

$$S^{\mathrm{f}}_{\mathrm{ee}}(\mathbf{q},\omega) = S^0_{\mathrm{ee}}(\mathbf{q},\omega) + \sum_{a,b}\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\widehat{g}^{\mathrm{f}}_{\mathrm{e}b}(\mathbf{q})S_{ab}(\mathbf{q},\omega) \tag{156}$$

where

$$S_{ab}(\mathbf{q},\omega) = \frac{1}{2\pi\sqrt{N_a N_b}}\int\limits_{-\infty}^{\infty}\langle\delta\rho_a(-\mathbf{q},t)\delta\rho_b(-\mathbf{q},0)\rangle\mathrm{e}^{\mathrm{i}\omega t}dt \tag{157}$$

is the ion–ion dynamic structure factor, which is equivalent to (120) for the classical ion density

$$\rho_{\mathrm{i}}(\mathbf{r},t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \tag{158}$$

and

$$S^0_{\mathrm{ee}}(\mathbf{q},\omega) = \frac{1}{2\pi n_{\mathrm{e}}V}\int\limits_{-\infty}^{\infty}\langle\delta\rho^0_{\mathrm{e}}\left(\mathbf{q},\frac{1}{2}t\right)\delta\rho^0_{\mathrm{e}}\left(-\mathbf{q},-\frac{1}{2}t\right)\rangle\mathrm{e}^{\mathrm{i}\omega t}dt \tag{159}$$

is the electron dynamic structure factor *in the absence of electron-ion correlations*, such as would exist if the ions were replaced by an equivalent uniform continuous positive charge distribution. When the electrons can be regarded as being weakly coupled $S^0_{\mathrm{ee}}(\mathbf{q},\omega)$ can be reasonably approximated by the RPA dynamic structure factor, while local field corrections, as proposed by Chihara [35] for example, can, in principle, extend the theory to regimes of strong electron coupling.

The static sum rule then yields,

$$S^{\mathrm{f}}_{\mathrm{ee}}(\mathbf{q}) = S^0_{\mathrm{ee}}(\mathbf{q}) + \sum_{a,b}S_{ab}(\mathbf{q})\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\widehat{g}^{\mathrm{f}}_{\mathrm{e}b}(\mathbf{q}) \tag{160}$$

from which one obtains, making reference to Eq. (150),

$$g_{\mathrm{ee}}(\mathbf{q}) = g^0_{\mathrm{ee}}(\mathbf{q}) + \sum_{a,b}(\delta_{ab} + S_{ab}(\mathbf{q}))\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\widehat{g}^{\mathrm{f}}_{\mathrm{e}b}(\mathbf{q}) \tag{161}$$

Similarly, the f-sum rule yields (Assuming $\int_{-\infty}^{\infty}\omega S_{ab}(\mathbf{q},\omega)d\omega = \delta_{ab}q^2/2m_a$),

$$\int\limits_{-\infty}^{\infty}\omega S^{\mathrm{f}}_{\mathrm{ee}}(\mathbf{q},\omega)d\omega = \frac{q^2}{2m^*} \tag{162}$$

$$\frac{1}{m^*} = \frac{1}{m_{\mathrm{e}}} + \sum_a\frac{\left|\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\right|^2}{m_a} \tag{163}$$

which defines an effective $\mathbf{q}$-dependent (reduced) mass m^* that depends on the electron-ion correlations. Since, $m_{\mathrm{i}} >> m_{\mathrm{e}}$, for all practical purposes $m^* = m_{\mathrm{e}}$.

Combining Eqs. (143) and (156) yields the free-electron part of the cross-section as follows

$$\left.\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\right|_{\mathrm{f}} = r^2_{\mathrm{e}}(\mathbf{e}\cdot\mathbf{e}')^2 N_{\mathrm{i}}Z_{\mathrm{f}}\frac{\omega'}{\omega}|f_{\mathrm{f}}(\omega)|^2\Big(S^0_{\mathrm{ee}}(\mathbf{q},\omega-\omega') + \sum_{a,b}\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q})\widehat{g}^{\mathrm{f}}_{\mathrm{e}b}(\mathbf{q})S_{ab}(\mathbf{q},\omega-\omega')\Big) \tag{164}$$

Equations (145)–(164) hold when the electron–electron and electron–ion correlations are sufficiently weak for the density fluctuations to be additive in first order, as per Eq. (145). In condensed matter, for example, it may be appropriate to seek alternative or modified approaches in order to capture the details of the electronic structure. Chihara [35] extends the above equations to the liquid metal regime through the incorporation of dynamical local field corrections into the definition of $S^0_{\mathrm{ee}}(\mathbf{q},\omega)$ within the context of formal linear response theory. In the low-temperature ($T = 0$) limit, when there is no final state blocking above the Fermi surface and electron–electron correlations are fully suppressed, the momentum density distribution is given in terms of the one-electron real space Green function (RSGF) [25], which can be linked to density functional theory calculations, thus potentially providing a detailed approach to treating scattering from conduction and valence bands in crystalline solids.

4.7. Bound-free interference

Interference between coherent scatterings from bound and free electrons is expressed by the fourth term on the right hand side of Eq. (100). In the same manner as given at Eqs. (135)–(140) where

$$\begin{aligned}\sum_{\alpha<0,\beta>0}\langle n_\alpha n_\beta\rangle\left(f_\alpha^* f_\beta \phi_{\alpha\alpha}\phi_{\beta\beta}^* + f_\alpha f_\beta^* \phi_{\alpha\alpha}^*\phi_{\beta\beta}\right) &= N_{\mathrm{i}}\sum_{\alpha<0,\beta>0}\langle n_\alpha n_\beta\rangle\left(S_{\alpha\beta}(\mathbf{q})f_\alpha^* f_\beta\phi_\alpha\phi_\beta^* + S_{\beta\alpha}(\mathbf{q})f_\beta^* f_\alpha\phi_\beta\phi_\alpha^*\right)\\ &= N_{\mathrm{i}}\sum_{a,b}\sqrt{P_aP_b}\left(S_{ab}(\mathbf{q},t)\left(\tilde{\rho}_a^{<}\tilde{\rho}_b^{>*} + \tilde{\rho}_a^{<*}\tilde{\rho}_b^{>}\right) + \delta_{ab}\sum_{\alpha<0,\beta>0}\left(\gamma_{\alpha\beta}^a + \gamma_{\beta\alpha}^a\right)\right)\end{aligned} \tag{165}$$

$$\tilde{\rho}_a^{>}(\mathbf{q}) = \sum_{\alpha>0}\langle n_\alpha^a\rangle f_\alpha^*\phi_{\alpha\alpha}^a(\mathbf{q}) = f_{\mathrm{f}}^*\sum_{\alpha>0}\langle n_\alpha^a\rangle\phi_{\alpha\alpha}^a(\mathbf{q}) \tag{166}$$

Hence, the bound-free interference contribution to the cross section becomes

$$\begin{aligned}\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\Big|_{\mathrm{bf}} = r_{\mathrm{e}}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}N_{\mathrm{i}}\Bigg(\sum_{a,b}\sqrt{P_aP_b}\Bigg(&S_{ab}(\mathbf{q},\omega-\omega')\\ &\times\left(\tilde{\rho}_a^{<}(\mathbf{q})\tilde{\rho}_b^{>*}(\mathbf{q}) + \tilde{\rho}_a^{<*}(\mathbf{q})\tilde{\rho}_b^{>}(\mathbf{q})\right)\\ &+\delta_{ab}S_{ab}^{\mathrm{S}}(\mathbf{q},\omega-\omega')\sum_{\alpha<0,\beta>0}\left(\gamma_{\alpha\beta}^a(\mathbf{q}) + \gamma_{\beta\alpha}^a(\mathbf{q})\right)\Bigg)\Bigg)\end{aligned} \tag{167}$$

The dynamical and statistical correlations involving free states can be expected to be much weaker than those between bound states. It is therefore reasonable to neglect those contributions by setting $\gamma_{\alpha\beta}^a(\mathbf{q}) = 0$ whenever either or both of the states α, β are not bound, whereupon (167) reduces to

$$\begin{aligned}\frac{\partial\sigma}{\partial\Omega'\partial\omega'}\Big|_{\mathrm{bf}} = r_{\mathrm{e}}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}N_{\mathrm{i}}\Big(&\sum_{a,b}\sqrt{P_aP_b}S_{ab}(\mathbf{q},\omega-\omega')\\ &\times\left(\tilde{\rho}_a^{<}(\mathbf{q})\tilde{\rho}_b^{>*}(\mathbf{q}) + \tilde{\rho}_a^{<*}(\mathbf{q})\tilde{\rho}_b^{>}(\mathbf{q})\right)\Big)\end{aligned} \tag{168}$$

4.8. *Total cross-section*

Finally, we add the bound and free electron contributions given by Eqs. (141) and (164) respectively, together with the interference contribution (168), to yield the total differential cross-section for photon scattering. By making the formal identification

$$\sqrt{P_a}\tilde{\rho}_a^{>}(\mathbf{q},\omega) = \sqrt{Z_{\mathrm{f}}}f_{\mathrm{f}}^*(\omega)\hat{g}_{\mathrm{e}a}^{\mathrm{f}}(\mathbf{q}) \tag{169}$$

where the dependence on ω has now been made explicit, the result (given here for optically-inactive bound states) is

$$\begin{aligned}\frac{\partial^2\sigma}{\partial\Omega'\partial\omega'} = r_{\mathrm{e}}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}N_{\mathrm{i}}\Bigg(&Z_{\mathrm{f}}\left|f_{\mathrm{f}}(\omega)\right|^2 S_{\mathrm{ee}}^0(\mathbf{q},\omega-\omega') + \sum_{a,b}\sqrt{P_aP_b}\\ &\times\Bigg(S_{ab}(\mathbf{q},\omega-\omega')\tilde{\rho}_a(\mathbf{q},\omega)\tilde{\rho}_b^*(\mathbf{q},\omega) + \delta_{ab}S_{ab}^{\mathrm{S}}(\mathbf{q},\omega-\omega')\\ &\times\left(\Gamma_a + \sum_{\alpha<0}\langle n_\alpha^a\rangle\left|f_\alpha^a\right|^2\left(1-\left|\phi_{\alpha\alpha}^a(\mathbf{q})\right|^2\right)\right)\Bigg)\Bigg)\end{aligned} \tag{170}$$

where, Γ_a is given by (142) and

$$\tilde{\rho}_a(\mathbf{q},\omega) = \tilde{\rho}_a^{>}(\mathbf{q},\omega) + \tilde{\rho}_a^{<}(\mathbf{q},\omega) \tag{171}$$

is the total strength-density density of the electrons associated with ion species a.

The general result for the total double-differential cross-section is

$$\begin{aligned}\frac{\partial^2\sigma}{\partial\Omega'\partial\omega'} = r_{\mathrm{e}}^2(\mathbf{e}\cdot\mathbf{e}')^2\ \frac{\omega'}{\omega}N_{\mathrm{i}}\Big\{&F_{\mathrm{f}}^0(\mathbf{q},\omega,\omega') + F^{\mathrm{coh}}(\mathbf{q},\omega,\omega')\\ &+F_{\mathbf{b}}^{\mathrm{incoh}}(\mathbf{q},\omega,\omega')\Big\}\end{aligned} \tag{172}$$

in which the quantity in {} is the complete dynamic structure factor for the scattering process. This comprises the following terms:

$$F_{\mathrm{f}}^0(\mathbf{q},\omega,\omega') = Z_{\mathrm{f}}\left|f_{\mathrm{f}}(\omega)\right|^2 S_{\mathrm{ee}}^0(\mathbf{q},\omega-\omega') \tag{173}$$

which is free electron contribution in the absence of electron-ion correlations. The dynamic structure factor $S_{\mathrm{ee}}^0(\mathbf{q},\omega)$ is the electron dynamic structure factor in the presence of a uniform positive charge distribution, and, in the weak coupling limit, which typically applies to electrons, is adequately given by RPA, while admitting the possibility of local field corrections to deal with regimes of stronger electron coupling [35]. Equation (173) is in the standard form apart from the factor $\left|f_{\mathrm{f}}(\omega)\right|^2$ where $f_{\mathrm{f}}(\omega)$ is free electron strength function, which can be taken to be given by (83). For X-rays, this factor is effectively unity.

The second term in Eq. (172) is the coherent scattering contribution

$$\begin{aligned}F^{\mathrm{coh}}(\mathbf{q},\omega,\omega') = \sum_{a,b}\sqrt{P_aP_b}\Big(&S_{ab}(\mathbf{q},\omega-\omega')\tilde{\rho}_a(\mathbf{q},\omega)\tilde{\rho}_b^*(\mathbf{q},\omega)\\ &+\delta_{ab}S_{aa}^{\mathrm{S}}(\mathbf{q},\omega-\omega')\Gamma_a\Big)\end{aligned} \tag{174}$$

which involves a double summation over all the different ion species, which are present in proportions given by P_{a}, P_{b},… where $\sum_a P_a = 1$. The quantity $S_{ab}(\mathbf{q},\omega-\omega')$ is the ion–ion dynamic structure factor representing the correlations between ions of species *a*,*b*, which, for crystalline solids, provides a description of *Bragg scattering* and *Laue scattering.* For a monoatonic lattice, the ion–ion dynamic structure factor $S_{aa}(\mathbf{q},\omega)$ and the self-correlation function $S_{aa}^{\mathrm{S}}(\mathbf{q},\omega)$ are expressed by Eqs. (126) and (130) in terms of the phonon modes $\{\mathbf{K}\}$ of the lattice. The quantity

$$\begin{aligned}\sqrt{P_a}\tilde{\rho}_a(\mathbf{q},\omega) &= \sqrt{P_a}\sum_\alpha\langle n_\alpha^a\rangle f_\alpha(\omega)\phi_{\alpha\alpha}^a(\mathbf{q})\\ &= \sqrt{P_a}\sum_{\alpha<0}\langle n_\alpha^a\rangle f_\alpha(\omega)\phi_{\alpha\alpha}^a(\mathbf{q}) + \sqrt{Z_{\mathrm{f}}}f_{\mathrm{f}}(\omega)\hat{g}_a^{\mathrm{f}}(\mathbf{q})\end{aligned} \tag{175}$$

is the strength cloud correlated with an ion of species *a* (cf Chihara's 'electron cloud' [1]) where $\phi_{\alpha\alpha}^a(\mathbf{q})$ is the Fourier transform of the normalised electron bound-state density associated with the one-electron bound state α in that ion species, normalised such that $\phi^a_{\alpha\alpha}(0) = 1$; $0 \leq \langle n^a_\alpha \rangle \leq 1$ is the average occupancy of the state; and $\widehat{g}^{\mathrm{f}}_a(\mathbf{q})$ is the Fourier-transformed electron-ion pair correlation function, as defined by Eq. (149) in terms of the effective (atom-in-jellium) pair correlation $\widehat{g}^{\mathrm{f}}_{ea}(\mathbf{r})$ between free electrons and a single ion of species a. The first term on the right-hand side of (174) represents coherent scattering from uncoupled bound states. The second term treats the correlations, both static and dynamic, between different electron states in the same ion and comprises the product of the ion self-correlation function and the strength variance, $\Gamma_a(\mathbf{q},\omega) = \langle \Delta\tilde{\rho}^2_a \rangle = \sum_{\alpha<0,\beta<0} f^{a*}_\alpha(\omega) f^a_\beta(\omega) \gamma^a_{\alpha\beta}(\mathbf{q})$, which accounts for correlations between bound electrons in the same ion, where the level-specific covariance $\gamma^a_{\alpha\beta}(\mathbf{q})$ is defined by (137). The quantity $\Gamma_a(0,\omega)$ is the variance $\overline{\Delta f^2_a}$ of the strength function of the particular atomic species, which reduces to the variance in the number of bound electrons in that species when $f_\alpha(\omega) = 1 \;\; \forall \alpha$. In general, the bound-state strength function $f_\alpha(\omega)$ can be determined by Kramers–Krönig transformation of the contribution of the state to the monochromatic absorption coefficient. Alternatively, a useful approximate analytic formula for the strength function for bound electrons is provided by Eqs. (66) and (71). The self-correlation $S^{\mathrm{s}}_{aa}(\mathbf{q},\omega-\omega')$ also accounts for the effect of the ion recoil on the scattered photon through the possibility of $\omega \neq \omega'$. Coherent scattering is typically the dominant contribution to Thomson scattering from complex atomic systems due to the quadratic dependence on the electron strengths.

The third term in Eq. (172) is the bound-state incoherent scattering contribution, which, referring to Eqs. (107) and (108), is given generally by

$$F^{\mathrm{incoh}}_{\mathbf{b}}(\mathbf{q},\omega,\omega') = \sum_a P_a \sum_{\alpha<0} \langle n^a_\alpha \rangle \left| f^a_\alpha(\omega) \right|^2 \int\limits_{-\infty}^{\infty} S^{\mathrm{s}}_{aa}(\mathbf{q},\omega-\omega'-\omega'') \times \Sigma^a_\alpha(\mathbf{q},\omega'') d\omega'' \tag{176}$$

where $\Sigma^a_\alpha(\mathbf{q},\omega)$ is the bound-state dynamic structure factor as defined by (110). This contribution vanishes in the forward direction and at long wavelengths ($\mathbf{q} = 0$) and morphs into Compton scattering at very short wavelengths (high photon energies), with a suitably modified structure factor. The convolution with the ion self–correlation function accounts for the effect of ion motion (Doppler and recoil) on the scattering. In the static limit of wave optics, $\Sigma^a_\alpha(\mathbf{q},\omega) = (1 - \left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2)\delta(\omega)$ and Eq. (176) reduces to the simplified form

$$F^{\mathrm{incoh}}_{\mathbf{b}}(\mathbf{q},\omega,\omega') = \sum_a P_a S^{\mathrm{s}}_{aa}(\mathbf{q},\omega-\omega') \sum_{\alpha<0} \langle n^a_\alpha \rangle \left| f^a_\alpha(\omega) \right|^2 \times \left(1 - \left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2 \right) \tag{177}$$

as already embodied in some previous formulae, notably Eqs. (140), (141) and (170).

5. Example applications

5.1. Low-frequency resonance scattering

Let us consider scattering, by a single atomic species a, of low energy photons whose energy is very much less than the ionization energy of an atom. In an un-ionised gas, the absorption coefficient is dominated by the coherent scattering term, which, in this case, is given by:

$$\begin{aligned} F^{\mathrm{coh}}(\mathbf{q},\omega,\omega') &= \left(S_{aa}(\mathbf{q},\omega-\omega') \left| \tilde{\rho}_a(\mathbf{q},\omega) \right|^2 + S^{\mathrm{s}}_{aa}(\mathbf{q},\omega-\omega') \Gamma_a \right) \\ &\simeq \delta(\omega-\omega') \sum_{\alpha<0,\beta<0} \Big(S_{aa}(\mathbf{q}) \langle n^a_\alpha \rangle \langle n^a_\beta \rangle \phi^a_{\alpha\alpha}(\mathbf{q}) \phi^{a*}_{\beta\beta}(\mathbf{q}) \\ &\quad + \gamma^a_{\alpha\beta}(\mathbf{q}) \Big) f_\alpha(\omega) f^*_\beta(\omega) \end{aligned} \tag{178}$$

Using the low-energy limit of the strength function given by Eq. (75), while assuming $\Delta_\alpha \ll E_\alpha$ (for general simplicity) this becomes

$$\begin{aligned} F^{\mathrm{coh}}(\mathbf{q},\omega,\omega') &\simeq \omega^4 \delta(\omega-\omega') \sum_{\alpha<0,\beta<0} \frac{1}{(E_\alpha E_\beta)^2} \\ &\quad \times \left(S_{aa}(\mathbf{q}) \langle n^a_\alpha \rangle \langle n^a_\beta \rangle \phi^a_{\alpha\alpha}(\mathbf{q}) \phi^{a*}_{\beta\beta}(\mathbf{q}) + \gamma^a_{\alpha\beta}(\mathbf{q}) \right) \end{aligned} \tag{179}$$

which exhibits the well-known ω^4 frequency-dependence characteristic of Rayleigh scattering. The incoherent scattering contribution is, by contrast, given as follows, where $\langle r^2 \rangle_\alpha$ is the mean square radius of the state density $\left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2$ so that, for small q, $\phi^a_{\alpha\alpha}(\mathbf{q}) \simeq 1 - \frac{1}{6} q^2 \langle r^2 \rangle_\alpha = 1 - \frac{1}{3}(1-\mu)(\omega/c)^2 \langle r^2 \rangle_\alpha$,

$$\begin{aligned} F^{\mathrm{incoh}}_{\mathbf{b}}(\mathbf{q},\omega,\omega') &= \delta(\omega-\omega') \sum_{\alpha<0} \langle n^a_\alpha \rangle \left| f^a_\alpha(\omega) \right|^2 \left(1 - \left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2 \right) \\ &= \omega^4 \delta(\omega-\omega') \sum_{\alpha<0} \frac{\langle n^a_\alpha \rangle}{E^4_\alpha} \left(1 - \left|\phi^a_{\alpha\alpha}(\mathbf{q})\right|^2 \right) \\ &\simeq \frac{\omega^6}{c^2} (1-\mu) \delta(\omega-\omega') \sum_{\alpha<0} \frac{2\langle n^a_\alpha \rangle}{3E^4_\alpha} \langle r^2 \rangle_\alpha \end{aligned} \tag{180}$$

(in which $\mu = \cos(\theta)$ is the cosine of the scattering angle) which is generally very much smaller than the coherent contribution (178).

5.2. Two component plasma – comparison with previously published formulae

In the case of a two component plasma comprising a mixture of electrons and a single ion species (a) the coherent scattering contribution (174) becomes (making use of Eq. (122))

$$F^{\mathrm{coh}}(\mathbf{q},\omega,\omega') = S_{aa}(\mathbf{q},\omega-\omega') \left(\left| \tilde{\rho}_a(\mathbf{q},\omega) \right|^2 + \Gamma_a(\mathbf{q},\omega) \left| \varepsilon_a(\mathbf{q},\omega-\omega') \right|^2 \right) \tag{181}$$

in which

$$\tilde{\rho}_a(\mathbf{q},\omega) = \sum_\alpha \langle n_\alpha \rangle f^*_\alpha(\omega) \phi_{\alpha\alpha}(\mathbf{q}) \tag{182}$$

Decomposing the sum on the right-hand side of Eq. (182) yields

$$\begin{aligned} \tilde{\rho}_a(\mathbf{q},\omega) &= \sum_\alpha \langle n_\alpha \rangle (1 + f^*_\alpha(\omega))(\phi_{\alpha\alpha}(\mathbf{q}) - 1) - \sum_\alpha \langle n_\alpha \rangle \phi_{\alpha\alpha}(\mathbf{q}) \\ &\quad + \sum_\alpha \langle n_\alpha \rangle f^*_\alpha(\omega) + \sum_\alpha \langle n_\alpha \rangle \\ &= \sum_\alpha \langle n_\alpha \rangle (1 + f^*_\alpha(\omega))(\phi_{\alpha\alpha}(\mathbf{q}) - 1) - \rho_{\mathrm{e}}(\mathbf{q}) + f^*(\omega) + Z \end{aligned} \tag{183}$$

where

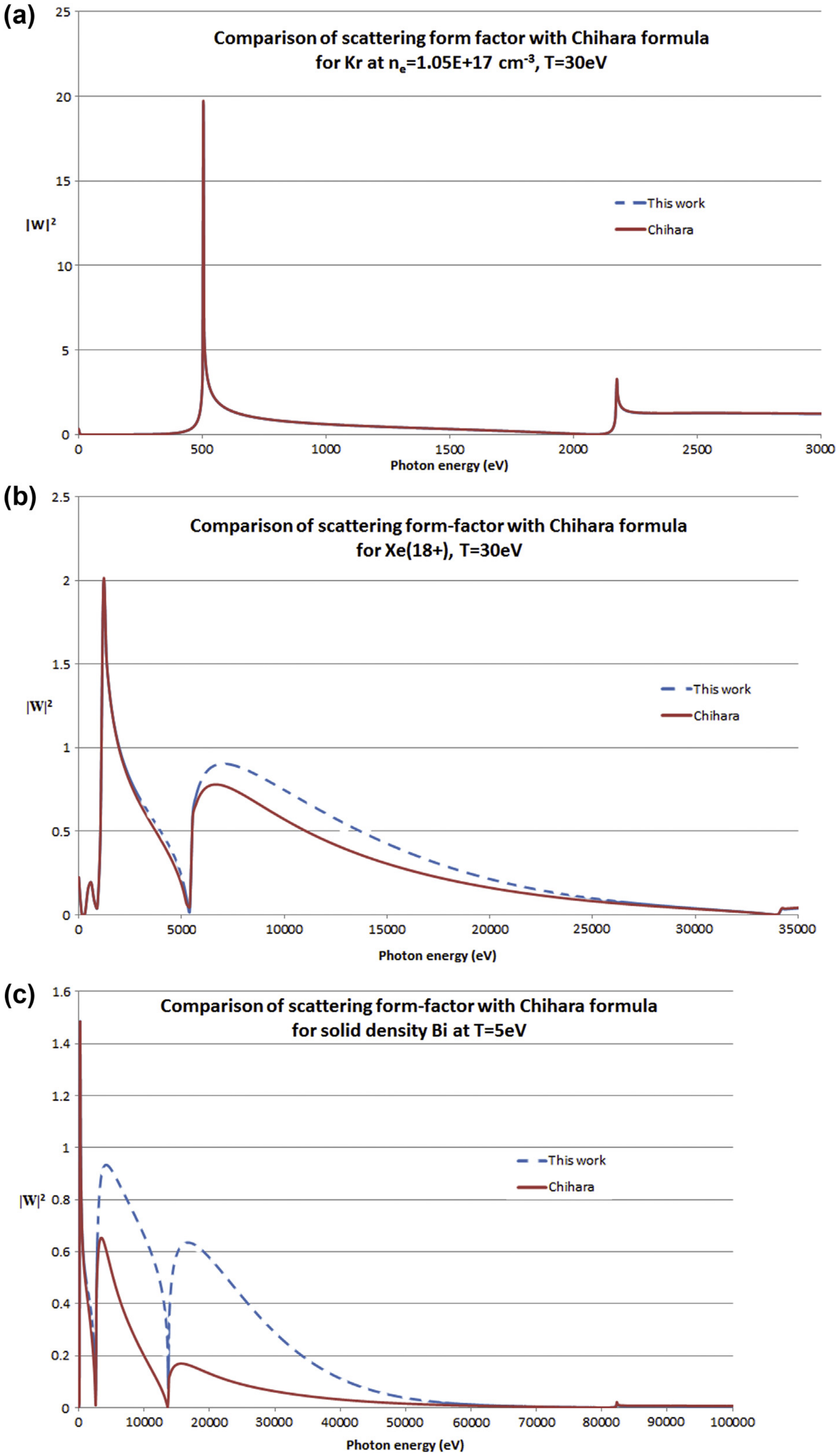

Fig. 3. Calculations of the form factor $|W(\omega)|^2$ defined by Eq. (187), for 90° scattering ($\mu = 0$) of X-rays by different chemical elements under a range of LTE conditions. Comparisons are made between calculations using the complete Formula (182) derived in this work (blue curves) and calculations, using identical atomic data, with the Chihara approximation (194) (red curves). The calculations illustrate (a) Kr ($Z = 36$) at $T = 30$ eV and $n_e = 1.05 \times 10^{-17}$ cm^{-3} for which the calculations are in very close agreement, with the maximum absolute discrepancy in the L-band being <0.02; (b) Xe ($Z = 54$) at the same temperature and electron density, for which there is noticeable disagreement in the L-band of $\lesssim 0.2$; and (c) Bi ($Z = 83$) at solid density (9.75 g/cm^3) and $T = 5$ eV for which there is very significant disagreement ($\lesssim 0.5$) in both the L and M bands. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\rho_{\mathrm{e}}(\mathbf{q}) = \sum_{\alpha} \langle n_\alpha \rangle \phi_{\alpha\alpha}(\mathbf{q}) = \sum_{\alpha<0} \langle n_\alpha \rangle \phi_{\alpha\alpha}(\mathbf{q}) + \sqrt{Z_{\mathrm{f}}}\,\widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q}) \tag{184}$$

is the unweighted electron density, which, for an intrinsically unpolarized system, is real and is a function of q^2;

$$\begin{aligned} f(\omega) &= \sum_{\alpha} \langle n_\alpha \rangle f_\alpha(\omega) = \sum_{\alpha<0} \langle n_\alpha \rangle f_\alpha(\omega) + (Z - Z_{\mathrm{b}}) f_{\mathrm{f}}(\omega) \\ &= f_{\mathrm{b}}(\omega) - (Z - Z_{\mathrm{b}}) \frac{\omega}{\omega + \mathrm{i}\nu} \end{aligned} \tag{185}$$

and $Z = \sum_{\alpha} \langle n_\alpha \rangle$ is the total number of electrons associated with each ion. Chihara [1] defines

$$\widehat{\alpha}^{\mathrm{ce}}(\omega) = \frac{c^2 r_{\mathrm{e}}}{\omega^2} f_{\mathrm{b}}(\omega) = \frac{e^2}{4\pi\varepsilon_0 m_{\mathrm{e}} \omega^2} f_{\mathrm{b}}(\omega) \tag{186}$$

while setting $f_{\mathrm{f}}(\omega) = -1 \;\Leftrightarrow\; \nu = 0$, and neglects the sum $\sum_{\alpha} \langle n_\alpha \rangle (1 + f^*_\alpha(\omega))(\phi_{\alpha\alpha}(\mathbf{q}) - 1)$ by virtue of the polarization contribution being calculated in the long wavelength ($\mathbf{q} = 0$) limit, as a result of which $|\tilde{\rho}(\mathbf{q},\omega)|^2 = |\rho_{\mathrm{e}}(\mathbf{q}) - Z_{\mathrm{b}} - (4\pi\varepsilon_0 m_{\mathrm{e}} \omega^2/e^2)\widehat{\alpha}^{\mathrm{ce}}(\omega)|^2$. This is essentially the formula for the coherent scattering form factor given in Ref. [1] where $\rho_{\mathrm{e}}(\mathbf{q})$ is the Fourier transform of the total electron density, which is here expressed in terms of its bound and free components according to Eqs. (171) and (169). However the neglect of the remaining terms in Eq. (183) appears inconsistent with the need to maintain the dependence on $\mathbf{q}$. This approximation can be avoided by using either of the formulae (182) or (183) instead.

To understand the significance of the approximation made by Chihara, we have performed calculations of the coherent scattering form factor, $W(\mathbf{q},\omega)$ defined, for $Z_{\mathrm{b}} \neq 0$, by

$$W(\mathbf{q},\omega) = \frac{1}{Z_{\mathrm{b}}} \tilde{\rho}_a(\mathbf{q},\omega) \tag{187}$$

in terms of which, the principal contribution to the coherent photon cross-section is given by

$$\frac{\partial^2\sigma}{\partial\Omega'\partial\omega'}\Big|_{\mathrm{coh}} = r_{\mathrm{e}}^2 (\mathbf{e}\cdot\mathbf{e}')^2 \frac{\omega'}{\omega} N_{\mathrm{i}} Z_{\mathrm{b}}^2 \, |W(\mathbf{q},\omega)|^2 S_{aa}(\mathbf{q}, \omega - \omega\prime) \tag{188}$$

(Note that normalising to the number of bound electrons is quite arbitrary – we could just have as easily used the total electron number Z instead. The reason for the choice is that the high frequency coherent scattering is dominated by bound electrons, due to the free electrons being relatively weakly correlated, so that, classically, we would then expect $W \simeq 1$. This allows meaningful direct comparisons between the (non-classical) values of this parameter for different elements.) The atomic model used for these calculations was a screened hydrogenic average-atom using the Slater rules [36] combined with a Debye–Hückel/Thomas–Fermi model for the free electrons. This model is not intended to provide an accurate representation of the real physical systems but rather to capture sufficient physics to allow a comparison of the different scattering models within an otherwise identical framework. In this atomic model, the broadening of an edge corresponding to a level α with ionization potential E_α, neglecting the effect of any ℓ-splitting and any variation of the density of states across the edge, is represented by a combination of Doppler and Fermi broadening according to

$$\Delta_\alpha = \sqrt{\left(\frac{\Delta_{\mathrm{F}}}{1 + \exp(-\mu_e/T)}\right)^2 + \Delta_{\mathrm{D}}^2} \tag{189}$$

in which μ_{e} denotes the electronic chemical potential and where, in accordance with (79),

$$\begin{aligned} 2\Delta_{\mathrm{F}} &= \mathrm{FWHM}(\mathrm{Fermi}) = \mathrm{FWHM}\left(\frac{\partial}{\partial E} \frac{1}{1 + \exp((E - \mu_{\mathrm{e}})/T)}\right) \\ &= 2T \ln\left(3 + 2\sqrt{2}\right) \simeq 3.5T \\ 2\Delta_{\mathrm{D}} &= \mathrm{FWHM}(\mathrm{Doppler}) = \sqrt{\frac{8T \ln 2}{m_a c^2}}\, E_\alpha \end{aligned} \tag{190}$$

in terms of which the strength functions are calculated according to Eqs. (66) and (71).

Suitable convergent functions $\phi_{\alpha\alpha}(\mathbf{q})$ are given, in the long-wavelength approximation, by $\phi_{\alpha\alpha}(\mathbf{q}) \simeq \exp(-\frac{1}{6} q^2 \langle r^2 \rangle_\alpha)$ where $\langle r^2 \rangle_\alpha = \int r^2 |\psi_\alpha(\mathbf{r})|^2 d^3\mathbf{r}$ is the mean square radius of the bound state α. For ℓ – degenerate hydrogenic states ($\alpha = n$)

$$\begin{aligned} \langle r^2 \rangle_n &= \frac{\sum_{\ell=0}^{n-1} (2\ell+1) \langle r^2 \rangle_{n\ell}}{\sum_{\ell=0}^{n-1} (2\ell+1)} \\ &= \frac{1}{4m_{\mathrm{e}}E_n} \frac{\sum_{\ell=0}^{n-1} (2\ell+1)\left(5n^2 + 1 - 3\ell(\ell+1)\right)}{\sum_{\ell=0}^{n-1} (2\ell+1)} = \frac{5 + 7n^2}{8m_{\mathrm{e}}E_n} \end{aligned} \tag{191}$$

in which $\langle r^2 \rangle_{n\ell} = (5n^2 + 1 - 3\ell(\ell+1))/(4m_{\mathrm{e}}E_n)$ is the mean square radius of the hydrogenic state with principal and orbital quantum numbers n and ℓ respectively [37], and

$$E_n = \frac{Z_n^2 e^2}{8\pi\varepsilon_0 a_0 n^2} = \frac{Z_n^2 m_{\mathrm{e}}}{2n^2} \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = \frac{m_{\mathrm{e}}c^2}{2n^2} (Z_n \alpha_0)^2, \quad n = 1,\, 2,\, 3\ldots \tag{192}$$

where $a_0 = 4\pi\,\varepsilon_0/m_{\mathrm{e}}e^2$ is the Bohr radius, $\alpha_0 = e^2/4\pi\varepsilon_0\hbar c$ is the Fine Structure Constant and Z_n ($Z_\alpha < Z_n \leq Z$) is the effective (screened) nuclear charge.

Using this model, we have performed rudimentary atomic calculations for various elements across the periodic table under a range of temperatures between room temperature and ~700 eV and densities between solid density down to 10^{17} electrons per cubic centimetre. Comparisons are made between the scattering form factor $|W(\mathbf{q},\omega)|^2$ obtained using the new formula.

$$\begin{aligned} W(\mathbf{q},\omega) &= \frac{1}{Z_{\mathrm{b}}} \sum_{\alpha} \langle n_\alpha \rangle f^*_\alpha(\omega) \phi_{\alpha\alpha}(\mathbf{q}) \\ &= \langle f^*_\alpha(\omega) \phi_{\alpha\alpha}(\mathbf{q}) \rangle_{\alpha<0} + \frac{\sqrt{Z_{\mathrm{f}}}}{Z_{\mathrm{b}}} f^*_{\mathrm{f}}(\omega) \widehat{g}^{\mathrm{f}}_{\mathrm{e}a}(\mathbf{q}) \end{aligned} \tag{193}$$

and the same quantity calculated according to Chihara's formula,

$$W(\mathbf{q},\omega) = 1 + \frac{1}{Z_{\mathrm{b}}} \left(f^*_{\mathrm{b}}(\omega) - \rho_{\mathrm{e}}(\mathbf{q})\right) = 1 + \langle f_\alpha(\omega) \rangle_{\alpha<0} - \frac{\rho_{\mathrm{e}}(\mathbf{q})}{Z_{\mathrm{b}}} \tag{194}$$

In this notation, the residual term in $\tilde{\rho}$ (183), that ignored by Chihara, is.

$$\Delta\tilde{\rho}(\mathbf{q},\omega) \equiv -\sum_{\alpha}\langle n_\alpha\rangle\left(1+f_\alpha^*(\omega)\right)(\phi_{\alpha\alpha}(\mathbf{q})-1) \simeq -\frac{1}{3}q^2\sum_n \mathfrak{p}_n n^2\chi_n(\omega)\langle r^2\rangle_n \tag{195}$$

where $\mathfrak{p}_n = \langle n_\alpha\rangle/2n^2$, $1 \geq \mathfrak{p}_n \geq 0$. Combining Eqs. (195), (191) and (192) while using that $q^2 = 2(\omega/c)^2(1-\mu)$, where $\mu = \cos(\theta)$, yields

$$\Delta\tilde{\rho} \simeq -\frac{1}{6}(1-\mu)\left(\frac{\omega}{\alpha_0 m_e c^2}\right)^2 \sum_n \frac{1}{Z_n^2}\mathfrak{p}_n n^4\left(5+7n^2\right)\chi_n(\omega) \tag{196}$$

For non-resonant situations (ω not close to an ionization threshold, E_n) making use of Eqs. (73) and (74), this can be very approximately estimated by

$$\begin{aligned}\Delta\tilde{\rho} &\simeq \frac{1}{6}(1-\mu)\left(\frac{\omega}{\alpha_0 m_e c^2}\right)^2\left\{\sum_{n|E_n<\omega}\frac{1}{Z_n^2}\mathfrak{p}_n n^4\left(5+7n^2\right)\frac{E_n^2}{\omega^2}\ln\left(\frac{\omega^2}{E_n^2}\right)+\sum_{n|E_n>\omega}\frac{1}{Z_n^2}\mathfrak{p}_n n^4\left(5+7n^2\right)\right\}\\ &\simeq \frac{1}{6}(1-\mu)\left\{\sum_{n\geq N}\mathfrak{p}_n(Z_n\alpha_0)^2\left(5+7n^2\right)\ln\left(\frac{Z_N n}{Z_n n_\omega}\right)+\frac{1}{4}\sum_{n<N}\mathfrak{p}_n(Z_n\alpha_0)^2\left(5+7n^2\right)\left(\frac{Z_N n}{Z_n n_\omega}\right)^4\right\}\\ &\simeq \frac{1}{6}(1-\mu)\sum_{n\geq N}\mathfrak{p}_n(Z_n\alpha_0)^2\left(5+7n^2\right)\ln\left(\frac{Z_N n}{Z_n n_\omega}\right)\end{aligned} \tag{197}$$

where

$$n_\omega^2 = \frac{m_e c^2}{2\omega}(Z_N\alpha_0)^2 \tag{198}$$

and N is the smallest value of n for which $E_n > \omega$, ie, $N > n_\omega > N - 1$. For filled or nearly-filled shells, the sum is mainly controlled by the factor, $(Z_n\alpha_0)^2(5 + 7n^2)$, which, by making the approximation, $Z_n \approx Z - 3n^2$, which holds very roughly for such levels in mid-to-high Z elements, is found to be a maximum for $n^2 \approx Z/9$. We argue, albeit quite crudely, that the correction becomes important when, for the dominant terms in the sum, $\frac{7}{6}n^2\left((Z-3n^2)\alpha_0\right)^2 \gtrsim 0.2 \Rightarrow \frac{7}{54}Z\left(\frac{2}{3}Z\alpha_0\right)^2 \gtrsim 0.2 \Rightarrow Z > 40$ implying that the correction is likely to be important only for heavy elements, those in the upper half of the periodic table, with the greatest deviation in the spectrum for frequencies corresponding to ionization from filled levels for which $n^2 \approx Z/9$. With the factor scaling approximately as Z^3, we would expect to see very close agreement between the formulae for light elements and significant disagreement for heavy elements. These rough predictions are borne out by the detailed calculations using the model described above and hold independently of temperature and density, subject only to the requisite electron shells being occupied. Fig. 3 illustrates comparisons of the form-factor $|W(\mathbf{q},\omega)|^2 = |\tilde{\rho}_a(\mathbf{q},\omega)|^2/Z_b^2$ for $\mu = \cos(\theta) = 0$ between calculations using the full formula with $W(\mathbf{q},\omega)$ calculated according to Eq. (193) or (182), and calculations using Chihara's more approximate formula, (194). The results show that the Chihara formula is accurate for light elements, but can be expected to underestimate the cross-section in certain heavy-element regimes (L- and M-bands) by as much as a factor of 4. The applicability of the Chihara formula to light elements is supported by experiment, in which it is found to give a good account of Thomson X-ray scattering in WDM [7,8].

A term corresponding to $\Gamma_a S_{aa}^s(\mathbf{q},\omega-\omega')$, which describes, via the atomic strength variance $\Gamma_a(\mathbf{q},\omega)$, given by Eq. (142), the static correlations between bound electrons in the same atomic ion, is also absent from Chihara's formula (as it is from our numerical calculations). These correlations are generally difficult to calculate in detail. This is especially true of the dynamical correlations arising from corrections to Hartree–Fock, though these can reasonably be ignored, where a Hartree-based central field model provides an adequate description of the atom. The remaining contribution of the statistical correlations to Eq. (181) is equivalent, at $\mathbf{q} = 0$, to the application of a factor $1 + \mathrm{O}\left(\overline{\Delta Z_b^2}/Z_b^2\right)$, where $\overline{\Delta Z_b^2}$ is the variance in the number of bound electrons. There are plasma regimes where this factor deviates significantly from unity, so any prevailing assumption that the Γ_a term can be ignored is not always justified.

These calculations have been carried out using a very simplified atomic model. More realistic results applicable to real systems would result from using, for example, average-atom modelling techniques such as those described in Ref. [9].

6. Conclusions

A quantum mechanically based derivation of the formula for the differential cross-section for Thomson scattering of photons by a many-atom system, in which electrons are either bound in localised core states associated with single nuclei or exist in delocalised states in which they are able to move throughout the whole system, has been presented. The model encompasses scattering of electromagnetic radiation spanning the optical and X-ray spectral regimes by atomic systems, which may include plasmas, metals, and monoatomic fluids and crystalline solids, though the main envisaged applications would be to metals and dense plasmas. A notable departure from previous work on this topic is the formulation of the cross-section directly in terms of the correlation between electron strength-density fields, which comprise the product of the particle density for each electron state and the strength function for that state, where the strength function is a complex function, equivalent to the forward scattering amplitude, that gives the scattering response of an electron in a particular quantum state to a photon of a particular energy. The strength functions are generally obtainable via Kramers–Krönig transformation of the absorption coefficients, and a useful analytical formula is given, in the case of bound states for which the above-threshold photoionization cross-section falls off inversely with the cube of the frequency, by Eqs. (71) and (72) in conjunction with Eq. (66). A key result of this work is the scattering cross-section (92), in which the strength-density correlation function (94) replaces the particle correlation function in the standard treatment. Another key result, provided by Eq. (96), is the reduction of this correlation function, for a many electron system, into its coherent and incoherent parts. Breaking this down further into its more recognisable components, while distinguishing between bound and free electrons, leads to the main result, expressed by Eqs. (172)–(177), which gives the scattering differential cross-section for an arbitrary mixture of ionic or atomic species. The general result comprises three parts: (i) a free-electron part that does not depend on the ion configuration; (ii) a coherent atomic scattering part that depends upon the ion–ion correlations as well as the internal correlation between electrons within individual atoms; and (iii) an incoherent atomic part that depends on the convolution of the ion self-correlation dynamic structure factor with the bound state dynamic structure factor, and which, in the high-energy (relativistic) limit, would carry over to Compton scattering. These formulae distinguish between the effects of electron dynamics (expressed by the strength functions) and correlations (expressed by structure factors). In atomic systems with large numbers of bound electrons, coherent scattering typically dominates the scattering of optical and x-ray photons, because of the proportionality of the cross-section to the square of the number of correlated electrons, and encompasses Rayleigh, Bragg and Laue scattering. For a two-component plasma or metal, comprising electrons and a single ionic species, the coherent scattering part bears a close resemblance to the formula given by Chihara [1], with which it is compared in section 5.2. The most notable differences between the formulae are due to the electron polarization, which Chihara treats the long-wavelength limit, and the quantum and statistical correlations between bound states in the same atom, as expressed by Eq. (137). Our analysis and numerical calculations show that Chihara's approximation for the polarization holds very well for light elements ($Z < 40$) consistently with experimental observation [7,8], but is increasingly deficient for heavier elements. This result is of particular significance for the monitoring and diagnosis of heavy elements by means of Thomson scattering.

Appendix A. Representations the Fock space operators

A.1. Creation and annihilation operators

We start with the elementary creation and annihilation operators $\mathbf{a}_\alpha^\dagger, \mathbf{a}_\alpha, \ldots$ acting on the many-electron Fock space satisfying the standard equal-time fermion anti-commutation relations

$$\begin{aligned} \mathbf{a}_\alpha \mathbf{a}_\beta^\dagger + \mathbf{a}_\beta^\dagger \mathbf{a}_\alpha &= \delta_{\alpha\beta} \\ \mathbf{a}_\alpha^\dagger \mathbf{a}_\beta^\dagger + \mathbf{a}_\beta^\dagger \mathbf{a}_\alpha^\dagger &= 0 \\ \mathbf{a}_\alpha \mathbf{a}_\beta + \mathbf{a}_\beta \mathbf{a}_\alpha &= 0 \end{aligned} \tag{199}$$

and whose time dependence is expressed, in the interaction picture, by

$$\mathbf{a}_\alpha(t) = \mathrm{e}^{-\mathrm{i}E_\alpha t}\mathbf{a}_\alpha(0) \tag{200}$$

where E_α is the energy of the one-electron state $|\alpha\rangle = \mathbf{a}_\alpha^\dagger|0\rangle$. In the first instance, the label α encompasses the spin state σ of the electron. The field operator that creates an electron with spin σ at position $\mathbf{r}$ within some volume V at time t is

$$\begin{aligned} \mathbf{a}_{\mathbf{r},\sigma}^\dagger(t) &= \sqrt{V}\sum_\alpha \langle\alpha|\mathbf{r},\sigma\rangle \mathbf{a}_\alpha^\dagger(t) \\ &= \sqrt{V}\sum_\alpha \mathrm{e}^{\mathrm{i}E_\alpha t}\langle\alpha|\mathbf{r},\sigma\rangle \mathbf{a}_\alpha^\dagger(0) \end{aligned} \tag{201}$$

Henceforth the time dependence will be suppressed, and, unless indicated otherwise, all operators are given at the same arbitrary time $t = 0$. Then Eq. (201) becomes

$$\mathbf{a}_{\mathbf{r},\sigma}^\dagger = \sqrt{V}\sum_\alpha \langle\alpha|\mathbf{r},\sigma\rangle \mathbf{a}_{\alpha,\sigma}^\dagger \tag{202}$$

in which $\langle\mathbf{r},\sigma|\alpha\rangle = \psi_\alpha(\mathbf{r},\sigma)$ where $\psi_\alpha(\mathbf{r},\sigma)$, the normalized wavefunctions, expressed in terms of spatial and spin coordinates, satisfy normalization and completeness conditions as follows

$$\begin{aligned} &\langle\alpha|\beta\rangle = \sum_\sigma \int_V \langle\alpha|\mathbf{r},\sigma\rangle\langle\mathbf{r},\sigma|\beta\rangle d^3\mathbf{r} = \sum_\sigma \int_V \psi_\alpha^*(\mathbf{r},\sigma)\psi_\beta(\mathbf{r},\sigma) d^3\mathbf{r} = \delta_{\alpha\beta} \\ &\langle\mathbf{r},\sigma|\mathbf{r}',\sigma'\rangle = \sum_\alpha \langle\mathbf{r},\sigma|\alpha\rangle\langle\alpha|\mathbf{r}',\sigma'\rangle = \sum_\alpha \psi_\alpha(\mathbf{r},\sigma)\psi_\alpha^*(\mathbf{r}',\sigma') = \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma\sigma'} \end{aligned} \tag{203}$$

so

$$\mathbf{a}_{\mathbf{r},\sigma}^\dagger|0\rangle = \sqrt{V}|\mathbf{r},\sigma\rangle \tag{204}$$

$$\begin{aligned} \mathbf{a}_{\mathbf{k},\sigma} &= \frac{1}{V}\int_V \mathbf{a}_{\mathbf{r},\sigma}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \frac{1}{\sqrt{V}}\sum_\alpha \mathbf{a}_\alpha \int_V \langle\mathbf{r},\sigma|\alpha\rangle \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r} \\ &= \sum_\alpha \langle\mathbf{k},\sigma|\alpha\rangle \mathbf{a}_\alpha \end{aligned} \tag{205}$$

$$\begin{aligned} &\mathbf{a}_{\mathbf{k},\sigma}^\dagger|0\rangle = |\mathbf{k},\sigma\rangle = \frac{1}{\sqrt{V}}\int_V |\mathbf{r},\sigma\rangle \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r} \\ &V\langle\mathbf{k},\sigma|\mathbf{k}',\sigma'\rangle = V\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'} \xrightarrow[V\to\infty]{} (2\pi)^3\delta(\mathbf{k}-\mathbf{k}')\delta_{\sigma\sigma'} \\ &\langle\mathbf{r},\sigma|\mathbf{k},\sigma\rangle = \frac{1}{\sqrt{V}}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \end{aligned} \tag{206}$$

$$\mathbf{a}_{\mathbf{r},\sigma} = \sum_\mathbf{k} \mathbf{a}_{\mathbf{k},\sigma}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \tag{207}$$

The commutation relations for the operators $\mathbf{a}_{\mathbf{r},\sigma}$, $\mathbf{a}_{\mathbf{k},\sigma}$,… are readily deduced from the definitions above and the archetypal relations (199)

$$\begin{aligned} \mathbf{a}_{\mathbf{r},\sigma}\mathbf{a}_{\mathbf{r}',\sigma'}^\dagger + \mathbf{a}_{\mathbf{r}',\sigma'}^\dagger \mathbf{a}_{\mathbf{r},\sigma} &= V\delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma\sigma'} \\ \mathbf{a}_{\mathbf{r},\sigma}^\dagger \mathbf{a}_{\mathbf{r}',\sigma'}^\dagger + \mathbf{a}_{\mathbf{r}',\sigma'}^\dagger \mathbf{a}_{\mathbf{r},\sigma}^\dagger &= 0 \\ \mathbf{a}_{\mathbf{r},\sigma}\mathbf{a}_{\mathbf{r}',\sigma'} + \mathbf{a}_{\mathbf{r}',\sigma'}\mathbf{a}_{\mathbf{r},\sigma} &= 0 \end{aligned} \tag{208}$$

$$\begin{aligned} \mathbf{a}_{\mathbf{k},\sigma}\mathbf{a}_{\mathbf{k}',\sigma'}^\dagger + \mathbf{a}_{\mathbf{k}',\sigma'}^\dagger \mathbf{a}_{\mathbf{k},\sigma} &= \delta(\mathbf{k},\mathbf{k}')\delta_{\sigma\sigma'} \\ \mathbf{a}_{\mathbf{k},\sigma}^\dagger \mathbf{a}_{\mathbf{k}',\sigma'}^\dagger + \mathbf{a}_{\mathbf{k}',\sigma'}^\dagger \mathbf{a}_{\mathbf{k},\sigma}^\dagger &= 0 \\ \mathbf{a}_{\mathbf{k},\sigma}\mathbf{a}_{\mathbf{k}',\sigma'} + \mathbf{a}_{\mathbf{k}',\sigma'}\mathbf{a}_{\mathbf{k},\sigma} &= 0 \end{aligned} \tag{209}$$

For most purposes, the spin coordinates can be suppressed through the replacement

$$\begin{aligned} \langle\mathbf{r},\sigma|\alpha\rangle &= \langle\mathbf{r}|\alpha\rangle\delta_{\sigma\sigma_\alpha} \\ \Psi_\alpha(\mathbf{r},\sigma) &= \Psi_\alpha(\mathbf{r})\delta_{\sigma\sigma_\alpha} \end{aligned} \tag{210}$$

where $\langle\mathbf{r}|\alpha\rangle = \Psi_\alpha(\mathbf{r})$ is the purely spatial part of the wavefunction where a convention is adopted whereby the spatial state is labelled solely by the spatial quantum numbers equivalent to making the replacement $\alpha \to \alpha, \sigma_\alpha$. When this is done, Eqs. (204)–(207) reduce to the standard forms for a spinless particle:

$$\mathbf{a}_r^{\dagger}|0\rangle = \sqrt{V}|\mathbf{r}\rangle \tag{211}$$

$$\begin{aligned}\mathbf{a}_{\mathbf{k}} &= \frac{1}{V}\int\limits_V \mathbf{a}_{\mathbf{r}}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{r} \\ &= \frac{1}{\sqrt{V}}\sum_\alpha \mathbf{a}_\alpha \int\limits_V \langle\mathbf{r}|\alpha\rangle e^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{r} \\ &= \sum_\alpha \langle\mathbf{k}|\alpha\rangle\mathbf{a}_\alpha\end{aligned} \tag{212}$$

$$\begin{aligned}&\mathbf{a}_k^{\dagger}|0\rangle = |\mathbf{k}\rangle = \frac{1}{\sqrt{V}}\int\limits_V |\mathbf{r}\rangle\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{r} \\ &V\langle\mathbf{k}|\mathbf{k}'\rangle = V\delta_{\mathbf{k}\mathbf{k}'} \xrightarrow[V\to\infty]{} (2\pi)^3\delta(\mathbf{k}-\mathbf{k}') \\ &\langle\mathbf{r}|\mathbf{k}\rangle = \frac{1}{\sqrt{V}}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\end{aligned} \tag{213}$$

$$\mathbf{a}_{\mathbf{r}} = \sum_{\mathbf{k}} \mathbf{a}_{\mathbf{k}}\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \tag{214}$$

Note that, in Eqs. (211)–(214), the spin coordinate, upon which the one-body expressions on both sides of each equation generally depends, has been merely suppressed. It has not been necessary to make the assumption of spin symmetry at this stage.

A.2. Density operator

The density operator $\rho(\mathbf{r})$ that gives the particle density at the point $\mathbf{r}$, is given, in the first instance, by

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{1}{V}\sum_\sigma \mathbf{a}_{\mathbf{r},\sigma}^{\dagger}\mathbf{a}_{\mathbf{r},\sigma} = \sum_{\alpha,\beta,\sigma}\langle\alpha|\mathbf{r},\sigma\rangle\langle\mathbf{r},\sigma|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta \\ &= \sum_{\alpha,\beta}\langle\alpha|\mathbf{r}\rangle\langle\mathbf{r}|\beta\rangle\delta_{\sigma_\alpha\sigma_\beta}\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta\end{aligned} \tag{215}$$

The expectation of this operator within a many body system that is represented by the statistical operator

$$\boldsymbol{\rho} = \sum_B |\Psi_B\rangle P_B\langle\Psi_B| \tag{216}$$

in which P_{B} is the probability of the system being in the state Ψ_{B}, is given by

$$\begin{aligned}\langle\rho(\mathbf{r})\rangle &= \mathrm{Tr}(\boldsymbol{\rho}\rho(\mathbf{r})) \\ &= \sum_{A,B}\langle\Psi_A|\Psi_B\rangle P_B\langle\Psi_B|\sum_{\alpha,\beta,\sigma}\langle\alpha|\mathbf{r},\sigma\rangle\langle\mathbf{r},\sigma|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta|\Psi_A\rangle \\ &= \sum_{A,\alpha,\beta,\sigma} P_A\langle\Psi_A|\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta|\Psi_A\rangle\langle\alpha|\mathbf{r},\sigma\rangle\langle\mathbf{r},\sigma|\beta\rangle \\ &= \sum_{A,\alpha,\sigma} P_A\langle\Psi_A|\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\alpha|\Psi_A\rangle\langle\alpha|\mathbf{r},\sigma\rangle\langle\mathbf{r},\sigma|\alpha\rangle \\ &= \sum_{A,\alpha,\sigma} P_A n_\alpha^{(A)}|\Psi_\alpha(\mathbf{r},\sigma)|^2 \\ &= \sum_\alpha\langle n_\alpha\rangle|\Psi_\alpha(\mathbf{r})|^2\end{aligned} \tag{217}$$

where $\langle n_\alpha\rangle = \sum_{A,\sigma} P_A n_\alpha^{(A)}$; and its Fourier transform is, making use of Eqs. (214) and (212),

$$\begin{aligned}\rho_{\mathbf{q}} &= \int\limits_V \rho(\mathbf{r})\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{r} = \sum_{\mathbf{k},\sigma}\mathbf{a}_{\mathbf{k},\sigma}^{\dagger}\mathbf{a}_{\mathbf{k}+\mathbf{q},\sigma} \\ &= \sum_{\alpha,\beta,\mathbf{k},\sigma}\langle\alpha|\mathbf{k},\sigma\rangle\langle\mathbf{k}+\mathbf{q},\sigma|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta \\ &= \sum_{\alpha,\beta}\langle\alpha|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\beta\rangle\delta_{\sigma_\alpha\sigma_\beta}\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta \\ &= \sum_{\alpha,\beta}\langle\alpha|\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta\end{aligned} \tag{218}$$

Note that, in Eqs. (215)–(218), as throughout the body of this paper, α, β,… label both the spin and spatial state coordinates of a single particle. For fermions, such states have an occupancy n_α of either 0 or 1. For spin-symmetric systems, one in which the electron's properties do not depend upon its spin state, the labels α, β,... may be used to refer only to the spatial state coordinates while the operators $\mathbf{a}_\alpha^{\dagger}, \mathbf{a}_\beta$ denote the creation and annihilation of particles having a definite, but arbitrary spin. This allows the spin labels in Eqs. (215)–(218) to be suppressed altogether, whereupon

$$\rho(\mathbf{r}) = \mathfrak{g}\sum_{\alpha,\beta}\langle\alpha|\mathbf{r}\rangle\langle\mathbf{r}|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta \tag{219}$$

$$\langle\rho(\mathbf{r})\rangle = \sum_\alpha\langle n_\alpha\rangle|\Psi_\alpha(\mathbf{r})|^2 \tag{220}$$

$$\rho_{\mathbf{q}} = \mathfrak{g}\sum_{\alpha,\beta}\langle\alpha|e^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}|\beta\rangle\mathbf{a}_\alpha^{\dagger}\mathbf{a}_\beta \tag{221}$$

provided that the spin degeneracy is accounted for through the factor, $\mathfrak{g}(=2)$, and where, in (220), $\langle n_\alpha\rangle$ represents the average number of electrons in the spatial state α. However the n_α s themselves no longer represent the single fermion occupancies. While Eqs. (217) and (220) appear formally identical, there are, for electrons, twice as many terms in the former. In general, it is not possible to disregard spin altogether.

Appendix B. Wave propagation in a homogeneous linear scattering medium

B.1. Treatment of localised scattering

We consider scattering of waves governed by the standard wave equation

$$\left(\nabla^2 - c^{-2}\partial_{tt}\right)\Psi_0(\mathbf{r},t) = 0 \tag{222}$$

which may be used to describe, for example, the propagation of the components of the electromagnetic field *in vacuo*. Let a monochromatic wave $\Psi_0(\mathbf{r},t) = \Psi_0(\mathbf{r})\mathrm{e}^{-\mathrm{i}\omega t} = \exp(\mathrm{i}\mathbf{k}_0\cdot\mathbf{r})\mathrm{e}^{-\mathrm{i}\omega t}$, which is a solution of Eq. (222) for frequency $\omega = k_0c$, be incident upon an element of linear scattering medium (one that does not give rise to a change in frequency) occupying a volume element $d^3\mathbf{r}'$ located at the point $\mathbf{r}'$. The resulting wavefunction, $\Psi(\mathbf{r},t) = \Psi(\mathbf{r})\mathrm{e}^{-\mathrm{i}\omega t}$ is then given by the Lippmann–Schwinger equation

$$\Psi(\mathbf{r}) = \Psi_0(\mathbf{r}) + 4\pi G_0^{+}(k_0;\mathbf{r},\mathbf{r}')F\left(\widehat{\mathbf{k}}',\mathbf{k}_0\right)\Psi_0(\mathbf{r}')d^3\mathbf{r}' \tag{223}$$

where

$$G_0^{+}(k_0;\mathbf{r},\mathbf{r}') = \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}\exp(\mathrm{i}k_0|\mathbf{r}-\mathbf{r}'|) \tag{224}$$

is the retarded Green function, which satisfies the inhomogeneous wave equation

$$\left(\nabla^2 + k_0^2 + \mathrm{i}0^+\right) G_0^+(k_0; \mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{225}$$

The external wave field beyond $d^3\mathbf{r}'$, in the direction defined by $\widehat{\mathbf{k}}' = (\mathbf{r} - \mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$, is

$$\Psi_0(\mathbf{r}) + \frac{1}{|\mathbf{r} - \mathbf{r}'|} F\left(\widehat{\mathbf{k}}', \mathbf{k}_0\right) \exp(\mathrm{i}k_0|\mathbf{r} - \mathbf{r}'|)\Psi_0(\mathbf{r}')d^3\mathbf{r}' \tag{226}$$

which identifies $F(\widehat{\mathbf{k}}', \mathbf{k}_0)$ as the elementary scattering amplitude per unit volume in the direction $\widehat{\mathbf{k}}'$. If the scattering occurs in an extended volume, then the external wave field (outside the scattering volume) is

$$\begin{aligned}\Psi(\mathbf{r}) &= \Psi_0(\mathbf{r}) + \int\limits_V \frac{1}{|\mathbf{r} - \mathbf{r}'|} F\left(\widehat{\mathbf{k}}', \mathbf{k}_0\right) \exp(\mathrm{i}k_0|\mathbf{r} - \mathbf{r}'|)\Psi_0(\mathbf{r}')d^3\mathbf{r}' \\ &= \Psi_0(\mathbf{r}) + \exp(\mathrm{i}\mathbf{k}_0\cdot\mathbf{r}) \int \int\limits_{\varepsilon}^{R} F\left(\widehat{\mathbf{k}}', \mathbf{k}_0\right) \\ &\quad \times \exp\left(\mathrm{i}k_0 R'\left(1 - \widehat{\mathbf{k}}_0\cdot\widehat{\mathbf{k}}'\right)\right) R' dR' d^2\widehat{\mathbf{k}}'\end{aligned} \tag{227}$$

in which, for sake of argument, the scattering volume is taken to be a spherical shell with internal radius ε and external radius R, centred at $\boldsymbol{r}' = \boldsymbol{r}$.

B.2. Wave propagation in a scattering medium

Now suppose that the scattering region fills all of local space, by which is meant the dimensions R of the scattering region are large such that $k_0 R >> 1$ together with $\varepsilon \to 0$. In this limit, the integral over R' in (227) vanishes unless $\widehat{\mathbf{k}}_0 \cdot \widehat{\mathbf{k}}' = 1$, which means that only forward scattering contributes, while scattering in other directions cancels by destructive interference. If the scattering component fills all space and there is no residual unscattered component, then the source of the scattering becomes the scattered wave itself. The source wave and the scattered wave are therefore identical, and Eqs. (223)–(227) become replaced by the homogeneous equation

$$\psi(\mathbf{r}) = 4\pi F_0(\mathbf{k}, \omega) \int G_0^+(k_0; \mathbf{r}, \mathbf{r}')\psi(\mathbf{r}')d^3\mathbf{r}' \tag{228}$$

where $\mathbf{k}$ denotes the modified wavevector associated with the plane wave solution, $\psi(\mathbf{r}, t) = e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$. Formally, (228) is expressed by

$$\Psi = 4\pi \mathbf{G}_0^+ \mathbf{F}_0 \Psi \tag{229}$$

where the operators $\mathbf{F}_0$ and $\mathbf{G}_0^+$ are defined by

$$\begin{aligned}\mathbf{F}_0 \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r} - \mathrm{i}\omega t} &= F_0(\mathbf{k}, \omega)\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r} - \mathrm{i}\omega t} \\ \mathbf{G}_0^+ &= \left(\nabla^2 - c^{-2}\partial_{tt} + \mathrm{i}0^+\right)^{-1}\end{aligned} \tag{230}$$

Eq. (229) is therefore equivalent to

$$\left(\nabla^2 - c^{-2}\partial_{tt} - 4\pi\mathbf{F}_0\right)\Psi = 0 \tag{231}$$

which is the form of the wave equation that is deemed to hold in the scattering medium.

The argument applies to vector fields in an unpolarized medium, in which case $F(\widehat{\mathbf{k}}', \mathbf{k}_0)$ generalizes to $F(\widehat{\mathbf{e}}', \widehat{\mathbf{k}}', \widehat{\mathbf{e}}_0, \mathbf{k}_0)$ which is now a tensor acting in the polarization space of the wave, e.g. according to the rules (19). However, in the forward direction this becomes unit diagonal, so the operator $\mathbf{F}_0$ remains scalar.

Appendix C. Lemmas

C.1. Introduction

Let $\mathbf{M}$ be a smooth manifold in $\mathbb{R}^3$ of volume $\mathfrak{V} = \mathbf{a}\cdot(\mathbf{b} \times \mathbf{c})$ having the topology of a 3-torus with fixed primitive lattice vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, such that for any function f on $\mathbf{M}$,

$$f(\mathbf{r} + \mathbf{a}) = f(\mathbf{r} + \mathbf{b}) = f(\mathbf{r} + \mathbf{c}) = f(\mathbf{r}) \tag{232}$$

A regular (Bravais) lattice may be represented on $\mathbf{M}$, in which case $\mathfrak{V}$ is the volume of the unit cell. More generally, $\mathbf{M}$ may be used to represent any homogeneous physical system, i.e. one whose properties are, on some scale ($\ll|\mathbf{a}|$, $|\mathbf{b}|$, $|\mathbf{c}|$), the same everywhere, including crystalline solids at finite temperature and even disordered systems, by means of the imposition of cyclic boundary conditions, in which case $\mathfrak{V}$ is the total volume of the system. In terms of the above, the reciprocal space is defined by the possible values of the vector

$$\mathbf{K} = \frac{2\pi}{\mathfrak{V}}(\ell\mathbf{a}^* + m\,\mathbf{b}^* + n\,\mathbf{c}^*), \quad \ell, m, n \in \mathbb{Z} \tag{233}$$

where $\mathbf{a}^* = \mathbf{b} \times \mathbf{c}$, $\mathbf{b}^* = \mathbf{c} \times \mathbf{a}$, $\mathbf{c}^* = \mathbf{a} \times \mathbf{b}$, in terms of which

$$f(\mathbf{r}) = \sum_{\mathbf{K}} \tilde{f}(\mathbf{K})\mathrm{e}^{-\mathrm{i}\mathbf{K}\cdot\mathbf{r}} \tag{234}$$

where

$$\tilde{f}(\mathbf{K}) = \frac{1}{\mathfrak{V}} \int\limits_{\mathfrak{V}} f(\mathbf{r})\mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{r}} d^3\mathbf{r} \tag{235}$$

Now let a spatial ‘lattice’ be defined by the set of points $\{\mathbf{r}_i\}$, $i = 1\ldots N$ denoting the positions of N similar particles (of mass m_p) in a physical system. The static structure factor of the lattice is defined, for any $\mathbf{q}$, to be

$$S(\mathbf{q}) = \frac{1}{\langle N\rangle}\left\langle \sum_i^N \sum_j^N \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\right\rangle \tag{236}$$

where the $\langle\rangle$ denotes an ensemble or time average and includes convolution with the incoherent quantum fluctuations, which ensure that, even in the zero excitation limit when all collective motion, including zero point motion, ceases, the correlations decay over distance characterized by a finite correlation length L_q. The Heisenberg uncertainty principle implies that the uncertainty in the position of each particle measured relative to its neighbour satisfies $\langle\Delta x^2\rangle \gtrsim \hbar\Delta t/m_\mathrm{p}$ where Δt is the corresponding time uncertainty. The propagation distance of any discernable disturbance is limited, by definition, to L_q which implies $\Delta t \gtrsim L_\mathrm{q}/c_\mathrm{s}$ where c_s is the longitudinal sound speed. The correlation length also corresponds to the distance beyond which the positions of neighbouring particles can no longer be resolved so that any correlations disappear. Since, for incoherent fluctuations, the uncertainties add in quadrature, this yields $L_\mathrm{q} \approx 1/n_\mathrm{p}\langle\Delta x^2\rangle$ where n_p is the particle density. Combining the preceding formulae yields the upper limit to the correlation length given by

$$L_{\mathrm{q}}^2 \approx \frac{m_{\mathrm{p}} c_{\mathrm{S}}}{n_{\mathrm{p}} \hbar} \tag{237}$$

This has particular implications for the *pair correlation function* (pcf) $\mathfrak{g}(\mathbf{r})$, which is related to the static structure factor by

$$1 + \mathfrak{g}(\mathbf{r}) = \frac{1}{\langle N \rangle} \sum_{\mathbf{K}} (S(\mathbf{K}) - 1) \mathrm{e}^{-\mathrm{i}\mathbf{K}\cdot\mathbf{r}} \tag{238}$$

namely that it is guaranteed to be square integrable over all space, even in the zero excitation limit, i.e., $\int_{\mathfrak{V}} |\mathfrak{g}(\mathbf{r})|^2 d^3\mathbf{r}$ exists and is finite in the limit of $\mathfrak{V} \rightarrow \infty$. The pcf has the following additional properties

$$\frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} \mathfrak{g}(\mathbf{r}) d^3\mathbf{r} = -1 \tag{239}$$

$$\frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} \mathfrak{g}(\mathbf{r}) \mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{r}} d^3\mathbf{r} = S(\mathbf{K}) - 1, \quad \mathbf{K} \neq 0 \tag{240}$$

We prove the following lemmas:

C.2. Lemma 1

For any function f on $\mathbf{M}$,

$$\frac{1}{\langle N \rangle} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} f(\mathbf{r}_i - \mathbf{r}_j) \rangle = f(0) + \frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} f(\mathbf{r})(1 + \mathfrak{g}(\mathbf{r})) d^3\mathbf{r} \tag{241}$$

[Proof: Using Eqs. (234) and (236) it is straightforward to show that

$$\frac{1}{\langle N \rangle} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} f(\mathbf{r}_i - \mathbf{r}_j) \rangle = \sum_{\mathbf{K}} \tilde{f}(\mathbf{K}) S(\mathbf{K}) \tag{242}$$

Rearranging terms on the right-hand side and substituting for $\tilde{f}(\mathbf{K})$ from Eq. (235) and then making use of Eqs. (234) and (238) yields

$$\begin{aligned} \frac{1}{\langle N \rangle} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} f(\mathbf{r}_i - \mathbf{r}_j) \rangle &= \sum_{\mathbf{K}} \tilde{f}(\mathbf{K})(S(\mathbf{K}) - 1) + \sum_{\mathbf{K}} \tilde{f}(\mathbf{K}) \\ &= \frac{1}{\mathfrak{V}} \sum_{\mathbf{K}} \int_{\mathfrak{V}} f(\mathbf{r}) \mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{r}} d^3\mathbf{r} (S(\mathbf{K}) - 1) + f(0) \\ &= \frac{1}{\mathfrak{V}} \int_{\mathfrak{V}} f(\mathbf{r}) \sum_{\mathbf{K}} \mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{r}} (S(\mathbf{K}) - 1) d^3\mathbf{r} + f(0) \\ &= \frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} f(\mathbf{r})(1 + \mathfrak{g}(\mathbf{r})) d^3\mathbf{r} + f(0) \end{aligned} \tag{243}$$

QED]

C.3. Lemma 2

If $\tilde{f}(\mathbf{K})$ is a given function that is everywhere finite or zero on the reciprocal space and for which the sum $\sum_{\mathbf{K}} \tilde{f}(\mathbf{K})$ is absolutely convergent so that the Fourier transform $f(\mathbf{r})$ defined by (234) exists for $\forall \mathbf{r}$, then, in the limit of very large $\langle N \rangle \gg 1$, and large $\mathfrak{V}$, such that $\langle N \rangle / \mathfrak{V} = n$,

$$\sum_{\mathbf{K}} S(\mathbf{K} - \mathbf{q}) \tilde{f}(\mathbf{K}) = \langle N \rangle \tilde{f}(\mathbf{q}) \tag{244}$$

[Proof: First use Eqs. (236) and (234) to write

$$\sum_{\mathbf{K}} S(\mathbf{K} - \mathbf{q}) \tilde{f}(\mathbf{K}) = \frac{1}{\langle N \rangle} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} f(\mathbf{r}_i - \mathbf{r}_j) \rangle \tag{245}$$

Application of the Lemma 1 (241) to the right-hand side then yields

$$\begin{aligned} \sum_{\mathbf{K}} S(\mathbf{K} - \mathbf{q}) \tilde{f}(\mathbf{K}) &= f(0) + \frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} f(\mathbf{r})(1 + \mathfrak{g}(\mathbf{r})) d^3\mathbf{r} \\ &= f(0) + \frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} f(\mathbf{r}) \mathfrak{g}(\mathbf{r}) d^3\mathbf{r} + \frac{\langle N \rangle}{\mathfrak{V}} \int_{\mathfrak{V}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} f(\mathbf{r}) d^3\mathbf{r} \\ &= \langle N \rangle \left(\tilde{f}(\mathbf{q}) + \frac{f(0)}{\langle N \rangle} + \frac{1}{\mathfrak{V}} \int_{\mathfrak{V}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} f(\mathbf{r}) \mathfrak{g}(\mathbf{r}) d^3\mathbf{r} \right) \end{aligned} \tag{246}$$

Application of the Schwarz inequality yields

$$\frac{1}{\mathfrak{V}} \left| \int_{\mathfrak{V}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} f(\mathbf{r}) \mathfrak{g}(\mathbf{r}) d^3\mathbf{r} \right| < a \left(\frac{1}{\mathfrak{V}} \int_{\mathfrak{V}} |\mathfrak{g}(\mathbf{r})|^2 d^3\mathbf{r} \right)^{1/2} \tag{247}$$

where a is the upper bound on $|f|$ in $\mathfrak{V}$. Since $\mathfrak{g}$ is square integrable, the third term in the parenthesis on the right hand side of Eq. (246) vanishes in the limit of $\mathfrak{V} \rightarrow \infty$ at least as fast as $\mathfrak{V}^{-1/2}$.

We now let $\langle N \rangle$ and $\mathfrak{V}$ become arbitrarily large, while remaining finite, and retain only the leading non-vanishing term in the parenthesis on the right hand side of Eq. (246), which then reduces the postulated result.

QED]

Appendix D. Free electron collision frequency model

For the purposes of the calculations described above, the free-electron collision frequency ν used in the Drude model, Eqs. (80)–(87), is estimated by the general form of the standard formula for the electron-ion collision frequency used in the conductivity,

$$\nu = \nu(0) = \nu_{\mathrm{c}} = \sum_a \frac{2\pi n_a m_{\mathrm{e}}}{\langle p^3 \rangle} \left(\frac{Z_a e^2}{4\pi\varepsilon_0} \right)^2 \ln \Lambda_a \tag{248}$$

(Eq. (88)) in which $\langle p^3 \rangle$ is the thermal average of the cube of the free electron wave-number (taken over a Fermi-Dirac distribution) and the Coulomb Logarithm is taken to be given by

$$\ln \Lambda_a = \frac{1}{2}\left(\ln(1+xy) - \frac{xy}{1+y}\right)$$
$$x = \frac{1}{1+4\eta_C^2}, \quad y = 4\eta_C^2\Lambda_0^2 = 4(\overline{p}D_e)^2 \tag{249}$$

where $\eta_C = Z_a e^2 m_e / 4\pi\varepsilon_0 \overline{p}$ and $\Lambda_0 = \overline{p}D_e/\eta_C = 8\pi\varepsilon_0 D_e \overline{E}/Z_a e^2$ are the effective Born–Sommerfeld parameter and the argument of the classical Coulomb logarithm respectively, where

$$\overline{E} = \frac{\hbar^2\overline{p}^2}{2m_e} = \frac{3}{2}E_B + \frac{2T^2}{E_B} \tag{250}$$

where

$$E_B = \frac{\int_0^\infty \mathfrak{p}(E)\mathfrak{q}(E)E^{3/2}dE}{\int_0^\infty \mathfrak{p}(E)\mathfrak{q}(E)E^{1/2}dE} = \frac{2}{\langle E^{-1}\rangle} \tag{251}$$

which is directly proportional to the electron bulk-modulus. The energy $\overline{E}$ corresponds to the saddle-point in the determination, by the Laplace method, of the integral $\int_0^\infty E^{5/2}\mathfrak{p}(E)\mathfrak{q}(E)E^{1/2}dE$, which arises in the calculation of the average (88), given that the leading (non-logarithmic) energy dependence of the collision frequency is $\nu_\alpha(0) \sim E_\alpha^{-3/2}$.

The Formula (249) is positive definite for $\forall x, y$ and interpolates between the classical Coulomb logarithm $\ln \Lambda_0$, for $\eta_C \gg 1$, and the Born Coulomb Logarithm for a screened-Coulomb potential, $\ln \Lambda_{Born} = 1/2(\ln(1+y) - y/(1+y))$, for $\eta_C \ll 1$.

Appendix E. List of symbols

E.1. List of symbols used for mathematical and physical quantities

Unit used throughout this paper are generally such that Planck's constant $\hbar$ and Boltzmann's constant k_B are both equal to unity, so that same symbols are used for energy and frequency as well as for wavenumber and momentum.

$\mathbf{A}$	operator corresponding to the electromagnetic vector potential
$\mathbf{a}_\alpha^\dagger, \mathbf{a}_\alpha$	creation and annihilation operators for electron in state α
$B(\mathbf{q})$	Debye–Waller factor
$\mathbf{b}_{\mathbf{k},\mathbf{e}}^\dagger, \mathbf{b}_{\mathbf{k},\mathbf{e}}$	creation and annihilation operators for photon in state $\mathbf{k},\mathbf{e}$
$a, b\ldots$	atomic/ionic species or state labels
a_0	Bohr radius, $= 4\pi\varepsilon_0\hbar^2/m_e e^2 = r_e\alpha_0^{-2}$
c	velocity of light
c_s	longitudinal sound speed in a solid
E	electron energy
E_α	energy of electron in level α, equivalent to ionization threshold energy in the case of a bound electron
E_n	ionization threshold energy for bound electron in hydrogenic level with principal quantum number n
e	charge on an electron
e	Euler's constant
$\mathbf{e} = \hat{\mathbf{e}}$	unit vector in direction of (electric) polarization
$\mathbf{e}_\mathbf{K}$	polarization of a collective (phonon) mode $\{\mathbf{K}\}$ of the scattering medium
$\mathbf{F}$	scattering operator in Hilbert space of an electron
$\mathbf{F}_0$	forward scattering operator (Appendix B)
$\overline{\mathbf{F}}$	scattering operator in electron Hilbert space averaged over the direction of the electron's motion
$\widehat{\mathbf{F}}$	scattering operator in Fock space
$\widehat{\mathbf{F}}_T$	Fock space scattering operator for Thomson scattering
F_0	forward scattering amplitude per unit volume (eigenvalue of $\mathbf{F}_0$)
F^{coh}	$F^{coh}(\mathbf{q}, \omega, \omega')$ coherent scattering form-factor defined as in Eq. (172) and given by Eq. (174)
F^{incoh}	$F^{incoh}(\mathbf{q}, \omega, \omega')$ incoherent scattering form-factor defined as in Eq. (172) and given by Eq. (176)
F_f^0	$F_f^0(\mathbf{q}, \omega, \omega')$ = form-factor for scattering by free electrons, in the absence of electron-ion correlations, defined as in Eq. (172) and given by Eq. (173)
$\mathbf{f}$	$\mathbf{f}(\mathbf{k},\boldsymbol{k}';\omega,\omega';E)$ = polarization part of the scattering operator $\overline{\mathbf{F}}$ as defined by Eq. (12)
$\mathbf{f}$	$\mathbf{f}(\mathbf{k},\omega;E) = ½(\mathbf{f}^+(\mathbf{k},\omega;E) + \mathbf{f}^-(-\mathbf{k},-\omega;E)) = \mathbf{f}(\mathbf{k},\mathbf{k};\omega,\omega;E)$ = polarization operator = forward scattering limit of $\mathbf{f}(\mathbf{k},\boldsymbol{k}';\omega,\omega';E)$
$\mathbf{f}$	$\mathbf{f}(\omega,\omega';E) = ½(\mathbf{f}^+(\omega;E) + \mathbf{f}^-(-\omega';E)) = \mathbf{f}(\mathbf{0},\mathbf{0};\omega,\omega';E)$ = polarization part of the scattering operator in dipole approximation
$\mathbf{f}^\pm$	$\mathbf{f}^\pm(\mathbf{k},\omega;E)$ = advanced and retarded polarization operators as defined by Eq. (14)
$\mathbf{f}^\pm$	$\mathbf{f}^\pm(\omega;E) = \mathbf{f}^\pm(\mathbf{0},\omega;E)$ = advanced and retarded polarization operators as defined by Eq. (39)
$\tilde{\mathbf{f}}, \tilde{\mathbf{f}}^\dagger$	strength superoperators defined by $\tilde{\rho}_\mathbf{q}(t) \equiv \rho_\mathbf{q}(t)\tilde{\mathbf{f}}$, $\tilde{\rho}_\mathbf{q}^\dagger(t) \equiv \tilde{\mathbf{f}}^\dagger \rho_{-\mathbf{q}}(t)$
f_α	$f_\alpha(\ldots) = \langle\alpha\|\mathbf{f}(\ldots;E_\alpha)\|\alpha\rangle$: $f_\alpha(\mathbf{k},\omega)$ is the forward scattering amplitude for photon scattering by an electron in state α; $f_\alpha(\omega)$ is the forward scattering amplitude (in dipole/long-wavelength approximation) for photon scattering by electron in (bound) state α, =strength function that gives the response of an electron in the (bound) state α to radiation of frequency ω
$f_\alpha^\pm$	$f_\alpha^\pm(\ldots) = \langle\alpha\|\mathbf{f}^\pm(\ldots;E_\alpha)\|\alpha\rangle$ = advanced and retarded amplitudes/strength functions
$f(\mathbf{k},\omega)$	average expectation value of the forward scattering amplitude as defined by Eq. (30), which is directly related to the dielectric function $\varepsilon(\mathbf{k}, \omega)$ by Eq. (35)
$f(\omega)$	$=f(\mathbf{0},\omega)$ = forward scattering amplitude in dipole/long-wavelength approximation
$f_f(\omega)$	free electron strength function = contribution to the forward scattering amplitude due to continuum (free) electrons
$f_b(\omega)$	$= f(\omega) - Z_f f_f(\omega) = \sum_{\alpha<0} \langle n_\alpha\rangle f_\alpha(\omega)$ bound electron part of $f(\omega)$
$f_{\alpha\beta}^0$	one-electron oscillator strengths for transition $\alpha\rightarrow\beta$, which are real
$\mathbf{G}$	electron propagator
$G^\pm(E)$	retarded and advanced propagators for electron with energy E
g_{ab}	$g_{ab}(\mathbf{r})$ = actual pair correlation function between particles of species a and b, which may represent electrons (e) or ions $(a, b, \ldots)$. $g_{ab}(\mathbf{q})$ is the Fourier transform defined in accordance with (149)
g_{ee}^0	$g_{ee}^0(\mathbf{r})$ = free electron pair correlation function given in the absence of electron-ion correlations. (cf S_{ee}^0) $g_{ee}^0(\mathbf{q})$ is the Fourier transform defined in accordance with (149)
$\tilde{g}_{ea}^f$	$\tilde{g}_{ea}^f(\mathbf{r})$ = effective (atom-in-jellium) pair correlation function between free electrons and single ion of species a. $\tilde{g}_{ea}^f(\mathbf{q})$ is the Fourier transform defined in accordance with (149)
$\mathbf{H}$	Hamiltonian operator

$\mathbf{H}_0$	unperturbed electron Hamiltonian operator
$\mathbf{H}_{\mathrm{field}}$	unperturbed electromagnetic field Hamiltonian operator
$\mathbf{H}'$	electron-field interaction part of Hamiltonian
i	$\sqrt{-1}$, or label denoting a general ion
i, j	labels designating individual ions or atomic nuclei
$\mathbf{K}$	wavevector of collective mode $\{\mathbf{K}\}$ of the medium
$\mathbf{k}$	incident photon wavevector
$\mathbf{k}'$	scattered photon wavevector
k	(real part of) photon wavenumber
k_{B}	Boltzmann's constant (where rendered explicit)
ℓ	orbital angular momentum quantum number (of hydrogenic electron bound state)
$L_\alpha(\omega)$	edge broadening profile for level α
L_{q}	correlation length due to incoherent quantum fluctuations
m_{e}	electron mass
m_a	mass of ion species a
m^*	effective reduced mass of electron as modified by electron-ion correlations
N_{e}	number of electrons in system
N_{i}	number of ions in system $= \sum_a N_a$
N_a	number of ions of species a
$\mathcal{N}_{\mathbf{K}}$	number of phonons in the mode $\mathbf{K}$, $= 1/(\exp(\Omega_{\mathbf{K}}/T) - 1)$
n	principal quantum number (of hydrogenic electron bound state)
n_0	principal quantum number of hydrogenic state that is in resonance with the incident photon energy
n_a	density of ions of species a, $= \langle \rho_a \rangle = N_a/V = P_a\, n_{\mathrm{i}}$
n_{e}	free electron density, $= \langle \rho_{\mathrm{e}} \rangle = \sum_a n_a Z_a = Z_{\mathrm{f}} n_{\mathrm{i}}$
n_{i}	total ion density $= \sum_a n_a = N_{\mathrm{i}}/V$
n_α	occupancy, $=$1 or 0, of electron state α
$\mathfrak{n}(\omega)$	refractive index
P_a	$= \langle N_a \rangle / N_{\mathrm{i}} =$ fraction of ions that are of species a
$\mathbf{p}$	electron momentum operator
p_x	Cartesian component of $\mathbf{p}$
p_{n}	component of electron's momentum normal to the scattering plane for a particular scattering geometry
$\mathfrak{p}(E)$	Fermi–Dirac distribution function defined by Eq. (61)
$\mathbf{q}$	scattering wavevector $= \mathbf{k}' - \mathbf{k}$
$\mathfrak{q}(E)$	$= 1 - \mathfrak{p}(E)$
$\mathbf{R}_i$	position of ith ion
r_{e}	$= e^2/4\pi\varepsilon_0 m_{\mathrm{e}} c^2 =$ classical electron radius
$\mathbf{r}$	electron position in general coordinate system
$\mathbf{r}_{\mathrm{ei}}$	$= \mathbf{r} - \mathbf{R}_i =$ electron position relative to ith ion
S_{ab}	$S_{ab}(\mathbf{q}, t) =$ intermediate ion–ion correlation function. $S_{ab}(\mathbf{q}, \omega) =$ ion–ion dynamic structure factor. $S_{ab}(\mathbf{q}) = S_{ab}(\mathbf{q}, t = 0) =$ ion–ion static structure factor
$S^{\mathrm{f}}_{\mathrm{ee}}$	$S^{\mathrm{f}}_{\mathrm{ee}}(\mathbf{q}, \omega) =$ free electron dynamic structure factor. $S^{\mathrm{f}}_{\mathrm{ee}}(\mathbf{q}) =$ corresponding static structure factor
S^0_{ee}	$S^0_{\mathrm{ee}}(\mathbf{q}, \omega) =$ free electron dynamic structure factor calculated in the absence of electron-ion correlations
T	temperature
t	time
V	volume
Z	mean atomic number $= N_{\mathrm{e}}/N_{\mathrm{i}}$
Z_a	charge state of ion species a
Z_{b}	average number of bound electrons per ion $= Z - Z_{\mathrm{f}}$
Z_{f}	mean ionization $= \sum_a P_a Z_a$
$\alpha, \beta, \ldots$	one electron state labels. The notation $\alpha < 0$ refers to a bound state for which $E_\alpha < 0$, and $\beta > 0$ to a continuum state for which $E_\beta > 0$
α_0	fine structure constant $= e^2/4\pi\varepsilon_0\hbar c \simeq 1/137.036$

$\widehat{\alpha}^{\mathrm{ce}}$	$\widehat{\alpha}^{\mathrm{ce}}(\omega)$ Chihara's core electron polarization function, as defined by Eq. (186)
Γ_α	$\Gamma_\alpha(\mathbf{q}, \omega) =$ bound state covariance correction to scattering cross-section, as defined by Eq. (142), representing effect of correlations between bound states in the same ion(s)
$\gamma^a_{\alpha\beta}$	$\gamma^a_{\alpha\beta}(\mathbf{q}) =$ bound–bound state covariance function defined by Eq. (137), which describes the static correlations between bound states in the same ion
Δ_α	spectral width of level α
ΔX	the deviation of a quantity X from its average
$\overline{\Delta X^2}$	$= \langle \Delta X^2 \rangle =$ the variance of X
$\delta(x)$	Dirac delta function
$\delta\rho_a$	$\delta\rho_a(\mathbf{r}, t) = \rho_a(\mathbf{r}, t) - \langle \rho_a \rangle$
ε_0	permittivity of free space
$\varepsilon(\mathbf{k}, \omega)$	dielectric function
$\varepsilon(\omega)$	$= \varepsilon(\mathbf{0}, \omega) =$ dielectric function in long wavelength limit
ε_a	$= \varepsilon_a(\mathbf{q}, \omega) =$ dielectric function of ion species a
$\varsigma(\omega)$	(complex) electrical conductivity
η	electron degeneracy parameter $= \mu_{\mathrm{e}}/T$
η_{C}	effective (electron-energy averaged) Born–Sommerfeld parameter for a Coulomb collision $= Z_a e^2 m_{\mathrm{e}}/4\pi\varepsilon_0\overline{p}$ (Appendix D).
θ	scattering angle
κ	attenuation coefficient $=$ total effective cross-section per unit volume
κ_{abs}	absorption coefficient, Eqs. (64) and (65)
$\tilde{\kappa}_{\mathrm{br}}$	Bremsstrahlung reduced absorption coefficient defined by Eq. (91)
Λ_0	argument of the classical Coulomb logarithm, ln Λ_0
$\lambdabar$	electron Compton wavelength
μ_{e}	electron chemical potential
μ	$\cos(\theta)$
ν	effective free-electron collision frequency
ν_{C}	conductivity collision frequency defined by Eq. (88)
ν_α	damping frequency relating to the broadening of a bound-free edge associated with bound state α
ξ^a_α	$\xi^a_\alpha(\mathbf{q}, t) =$ intermediate bound-state self-correlation function defined by Eq. (109), $\xi^a_\alpha(\mathbf{q}, \omega) =$ corresponding dynamic structure factor
χ_α	$= -(1 + f_\alpha) =$ strength modification due to binding for electron in state α
$\rho(\mathbf{r})$	density operator in coordinate ($\mathbf{r}$) space
$\rho_{\mathbf{q}}$	density operator in momentum ($\mathbf{q}$) space
ρ_a	$\rho_a(\mathbf{r}, t) =$ density of particle species a where a may represent electrons (e), ions (i) or particular ion species $(a, b, \ldots)$
ρ^0_{e}	$\rho^0_{\mathrm{e}}(\mathbf{r}, t) =$ free electron density calculated in the presence of a homogeneous positively charged background charge density, i.e., in the absence of electron–ion correlations
$\tilde{\rho}_{\mathbf{q}}$	$= \tilde{\rho}_{\mathbf{q}}(t) =$ strength density operator in momentum ($\mathbf{q}$) space, as defined by Eq. (46)
$\tilde{\rho}^<_a$	$\tilde{\rho}^<_a(\mathbf{q}, \omega) = \tilde{\rho}^<_a(\mathbf{q}) =$ Fourier transform of the strength density of the bound electrons associated with ion species a, as defined by Eq. (139)
$\tilde{\rho}^>_a$	$\tilde{\rho}^>_a(\mathbf{q}, \omega) = \tilde{\rho}^>_a(\mathbf{q}) =$ Fourier transform of the strength density of the free electrons associated with ion species a, as defined by Eq. (166), $= \sqrt{Z_{\mathrm{f}}/P_a} f^*_{\mathrm{f}}(\omega)\tilde{g}^{\mathrm{f}}_{\mathrm{ea}}(\mathbf{q})$
$\tilde{\rho}_a$	$\tilde{\rho}_a(\mathbf{q}, \omega) = \tilde{\rho}^>_a(\mathbf{q}, \omega) + \tilde{\rho}^<_a(\mathbf{q}, \omega) =$ total strength density of the electrons associated with ion species a, and given by Eq. (175)
$\mathrm{\rho}$	statistical operator (as defined by Eq. (216))
Σ_i	quantum state of atom or ion, i
Σ_a	quantum numbers corresponding to atomic or ionic state a

Σ^a_α	$\Sigma^a_\alpha(\mathbf{q},t)$ = intermediate bound-state weighted self-correlation function defined by Eq. (108)
$\Sigma^a_\alpha(\mathbf{q},\omega)$	corresponding dynamic structure factor
$\Sigma_{aa}(\mathbf{q})$	lattice structure factor for a solid, in which the atoms are fixed at their true (finite temperature) equilibrium positions, i.e., in the absence of any collective motions, including zero point motion
σ	label denoting one of the Cartesian coordinates, x, y, z, of a vector
σ	electron spin (Appendix A only)
σ_e	mean total photon cross-section per electron
σ_α	photon absorption cross-section due to electron in state α
$\tilde{\sigma}_\alpha$	photon reduced absorption cross-section due to electron in state α
$\Phi^{ij}_{\alpha\beta}$	$\Phi^{ij}_{\alpha\beta}(\mathbf{q},t)$ = Fourier transform of the pair distribution for two electrons in the correlated state $\lvert\Sigma(\alpha,\beta)\rangle$ generated from the Hartree state $\lvert\alpha\rangle\lvert\beta\rangle$
ϕ	Azimuthal scattering angle
$\phi_{\alpha\beta}$	$= \phi_{\alpha\beta}(\mathbf{q},t) = \langle\alpha\lvert\exp(-i\mathbf{q}\cdot\mathbf{r}(t))\rvert\beta\rangle$ for electron states α and β, Eq. (95)
$\phi^i_{\alpha\beta}$	$= \phi^i_{\alpha\beta}(\mathbf{q},t) = \langle\alpha,i\lvert\exp(-i\mathbf{q}\cdot\mathbf{r}_{\mathbf{e}i}(t))\rvert\beta,i\rangle$ for electron states α and β relative to ith ion
$\chi_\alpha(\omega)$	polarizability of electron state α, $= -(1+f_\beta(\omega))$
Ψ	Fock state representing system of many electrons
ψ^a_α	wavefunction of bound electron level α, in ion species a
Ω	scattering channel direction
Ω_e	free electron plasma frequency $= \sqrt{n_\mathrm{e}e^2/\varepsilon_0 m_\mathrm{e}} = \sqrt{Z_\mathrm{f}n_\mathrm{i}e^2/\varepsilon_0 m_\mathrm{e}}$
Ω_0	total electron plasma frequency $= \sqrt{Zn_\mathrm{i}e^2/\varepsilon_0 m_\mathrm{e}} = \sqrt{N_\mathrm{e}e^2/\varepsilon_0 m_\mathrm{e}V}$
Ω_a	plasma frequency of ion species a, $= \sqrt{Z_a^2 n_a e^2/\varepsilon_0 m_a} = \sqrt{N_\mathrm{i}P_a Z_a^2 e^2/\varepsilon_0 m_a V}$
$\Omega_\mathbf{K}$	frequency of phonon mode $\mathbf{K}$
ω	(initial) photon frequency
ω'	scattered photon frequency

Other symbols, particularly those used in the appendices, are defined locally in their respective contexts.

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