Chapter 4
Radiation Scattering on Atoms, Plasmas, and Nanoparticles

Abstract Radiation scattering on free electrons, atoms, plasmas, and nanoparticles is considered using various approaches both quantum and classical ones. Scattering on atoms is described in dipole and non-dipole approximations while the high-frequency limit is applied for elastic (Rayleigh) and Compton scattering. The high-frequency limit is treated using the dynamical form factor (DFF), the Compton profile, and the impulse approximation. The DFF of the plasma component is also used for the description of the radiation scattering in plasmas, namely Compton scattering, transient scattering, and scattering with plasmon generation and absorption. Radiation scattering and absorption on nanoparticles placed in homogeneous media are presented within the framework of the Mie theory. Numerical examples are given for radiation scattering and absorption on silver nanospheres with different radii in glass in the vicinity of surface plasmon resonances.

4.1 Photon Scattering by a Free Electron

Scattering of a photon can be interpreted as virtual absorption of an incident photon and simultaneous emission of a scattered photon. At first, let us consider the simplest case, when a photon is scattered by a free electron. Strictly speaking, the model of a free (not interacting with the environment) electron is always approximate. Nevertheless, in a number of cases, this approximation is well satisfied. Moreover, as we will see further, even a bound electron under certain parameter conditions of scattering can be considered to be free.

Scattering of a photon with a frequency ω and a wave vector $\boldsymbol{k}$ by a free electron is accompanied by a change in frequency $\omega \to \omega'$ and in wave vector $\boldsymbol{k} \to \boldsymbol{k}'$. If the angle of photon scattering θ is introduced (Fig. 4.1), then due to the conservation of energy–momentum it is possible to obtain the following relation between the frequency change and the angle of photon scattering:

$$\frac{1}{\omega'} - \frac{1}{\omega} = \frac{\hbar}{m c^2}(1 - \cos\,\theta), \tag{4.1}$$

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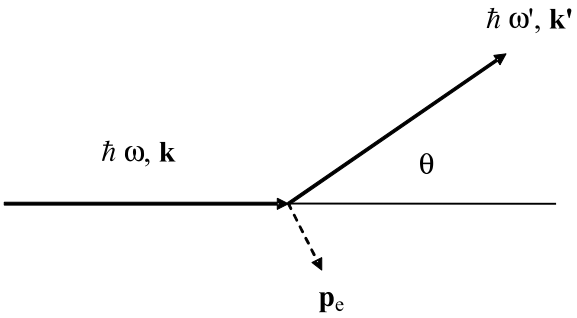

Fig. 4.1 Scattering of a photon by an electron at rest, $\boldsymbol{p}_e$ is the recoil momentum of the electron

where m is the electron mass and c is the velocity of light. The factor in front of the parentheses in the right-hand side of (4.1) can be rewritten as $\lambda_C/2\pi c$, where $\lambda_C = h/mc \cong 2.42 \times 10^{-10}$ cm is the Compton wavelength of an electron.

It is easily seen from the expression (4.1) that at zero-scattering angle $\theta = 0$ the change in photon frequency is equal to zero: $\omega = \omega'$. If $\theta \neq 0$, the frequency of a scattered photon is found to be less than its initial frequency $\omega' < \omega$ since part of the photon energy is transferred to a scattered electron (the "recoil" energy). A decrease in frequency corresponds to an increase in radiation wavelength, so photon scattering through a nonzero angle is accompanied by an increase in wavelength.

With the use of standard rules of quantum electrodynamics (Berestetskii et al. 1982), the following expression (the Klein-Nishina-Tamm formula) can be obtained for the cross section of photon scattering by a free electron in the laboratory frame of reference (connected with an electron):

$$d\sigma = \frac{r_e^2}{2}\left(\frac{\omega'}{\omega}\right)^2\left(\frac{\omega}{\omega'} + \frac{\omega'}{\omega} - \sin^2\theta\right)d\Omega', \tag{4.2}$$

where $r_e = e^2/mc^2 \cong 2.82 \times 10^{-13}$ cm is the so-called classical electron radius, $d\Omega'$ is an element of the solid angle in the direction of the wave vector of a scattered photon. If $\hbar\omega \ll mc^2$, the frequency change is small (see (4.1)) in comparison with the frequency itself: $|\Delta\omega| \ll \omega$, and in (4.2) it can be assumed $\omega \approx \omega'$. Then from the expression (4.2), the well-known nonrelativistic *Thomson formula* is obtained for the cross section of photon scattering by a free electron at rest that is differential with respect to the angle:

$$d\sigma^{Th} = \frac{1}{2}r_e^2\left(1 + \cos^2\theta\right)\left(\frac{\omega'}{\omega}\right)^2 d\Omega'. \tag{4.3}$$

It is seen that in this case the value of the cross section is defined by the squared of the classical electron radius, that is, a very small quantity.

The cross section integrated with respect to the angle of scattering in the case of an arbitrary photon energy can be obtained from (4.2):

$$\sigma(x) = 2\pi r_e^2 \frac{1}{x}\left\{\left(1 - \frac{4}{x} - \frac{8}{x^2}\right)\ln(1+x) + \frac{1}{2} + \frac{8}{x} - \frac{1}{2(1+x)^2}\right\}, \tag{4.4}$$

where $x = 2\hbar\omega/mc^2$. The scattering cross section (4.4) normalized to the squared classical electron radius is given in Fig. 4.2.

In the nonrelativistic limit of low photon energy, when $x \ll 1$, the first terms of the expansion of the right-hand side of the (4.4) give

$$\sigma = \sigma^{\mathrm{Th}}\left(1 - \frac{2\hbar\omega}{mc^2}\right), \quad \hbar\omega \ll mc^2, \tag{4.5}$$

here, the Thomson cross section $\sigma^{\mathrm{Th}} = 8\pi r_e^2/3$ of photon scattering by an electron integrated with respect to the angle is introduced. This fact is illustrated by Fig. 4.2, in which it is seen that the normalized scattering cross section in the limit of low photon energy is $8\pi/3 \cong 8.378$. The inflection point of the curve shown in Fig. 4.2 corresponds to the approximate equality of the photon energy and the electron rest energy, when $x = 1$.

In the ultrarelativistic case $x \gg 1$, when the photon energy is much higher than the electron rest energy $\hbar\omega \gg mc^2$, we obtain from (4.4):

$$\sigma = \pi r_e^2 \frac{mc^2}{\hbar\omega}\left(\ln\left(\frac{2\hbar\omega}{mc^2}\right) + \frac{1}{2}\right), \tag{4.6}$$

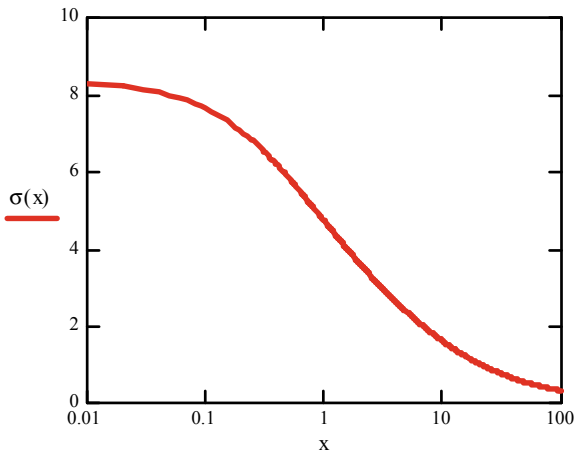

Fig. 4.2 The normalized cross section of photon scattering by a free electron in a wide range of photon energies, $x = 2\hbar\omega/mc^2$

that is, the scattering cross section decreases in inverse proportion to the photon energy.

It should be noted that in the ultrarelativistic limit the differential scattering cross section in the laboratory frame of reference has a sharp maximum in the direction of the initial propagation of the photon. On the other hand in the nonrelativistic limit, the distribution of scattered radiation is of dipole character [as can be seen from the formula (4.3)].

4.2 Radiation Scattering on Atoms

Within the classical framework, when electromagnetic radiation acts on an atom, bound electrons begin oscillation, which, according to known electrodynamic laws, results in the emission of a secondary or scattered electromagnetic wave. In quantum terms, this process represents a scattering of the photon by an atomic electron: the atomic electron is virtually excited to some intermediate atomic state and finally reaches the steady state. We note that by virtual excitation it is meant the transition of an electron to a state with another energy: this transition is then "instantly" followed by the reverse transition to a steady state with the initial or another energy. If this final steady state coincides with the initial state, we encounter the so-called *Rayleigh scattering*, and in the other case, there is *Raman scattering*.

Quite another situation is possible in X-ray scattering, namely when an atomic electron in the course of photon scattering is ionized. This process is referred to as *Compton scattering* of a photon by an atomic electron.

4.2.1 Classical Description

We will dwell first on Rayleigh scattering of radiation by an atom. In order not to resort to the quantum mechanical formalism, we employ the spectroscopic principle of correspondence for the description of this process. According to this principle, an atom behaves as a set of oscillators with frequencies equal to eigenfrequencies of atomic electrons when interacting with radiation. These oscillators are called transition oscillators since each of them corresponds to some transition between two steady states of an electron in an atom.

To calculate the Rayleigh scattering cross section, we proceed from the expression for the power of dipole radiation induced by the action of an electromagnetic wave on an atom (Landau and Lifschitz 1975):

$$Q(t) = \frac{2}{3c^3}\left|\ddot{\boldsymbol{d}}(t)\right|^2, \tag{4.7}$$

where c is the speed of light, two dots above the dipole moment vector denote differentiation with respect to time. The criterion of applicability of the dipole approximation (formula (4.7)) can be formulated by the following inequality:

$$\lambda \gg a, \tag{4.8}$$

where a is the size of the region of space responsible for radiation, λ is the radiation wavelength. In case of an atom, when $a \approx 10^{-8}$ cm, the condition (4.8) covers a wide range of wavelengths down to soft X-rays. We note that for modern X-ray Free Electron Laser installations, where photon energies up to about 20 keV are reached, the dipole condition (4.8) is not anymore valid.

The expression (4.7) describes the instantaneous power of radiation at a given instant of time t. In experiments, the power averaged over the period of oscillation of the field in an electromagnetic wave causing dipole moment oscillations $T = 2\pi/\omega$ is measured. In case of monochromatic radiation, the formula for the average radiation power follows from (4.7), i.e.,

$$\langle Q(t)\rangle_{\mathrm{T}} = \sum_{n=1}^{\infty} Q_{\mathrm{n}}, \tag{4.9}$$

$$Q_{\mathrm{n}} = \frac{4}{3c^3}\left|(\ddot{\boldsymbol{d}})_{\mathrm{n}}\right|^2, \tag{4.10}$$

where $(\ddot{\boldsymbol{d}})_{\mathrm{n}}$ is the nth Fourier harmonic of the second derivative of the dipole moment. Using the periodicity of dipole moment oscillations, with the use of the Fourier transform, it is possible to obtain the radiation power at a frequency of periodic motion of an electron $\omega(n = 1)$ as

$$Q \equiv Q_{n=1} = \frac{4\omega^4}{3c^3}|\boldsymbol{d}_\omega|^2. \tag{4.11}$$

Substituting (2.37) in (4.11) and using the formula for the intensity of monochromatic radiation in terms of the Fourier harmonic of the electric field strength, i.e.,

$$I = \frac{c}{2\pi}|\boldsymbol{E}_\omega|^2, \tag{4.12}$$

we obtain for the cross section of the Rayleigh scattering of radiation by an atom in an ith state

$$\sigma_{\mathrm{i}}^{(\mathrm{Rsc})}(\omega) = \frac{8\pi}{3}\left|\frac{\omega^2}{c^2}\beta_{\mathrm{i}}(\omega)\right|^2, \tag{4.13}$$

where $\beta_i(\omega)$ is the dynamic polarizability of an atom in an ith state. The detailed consideration of the dynamic polarizability was presented in Chap. 2.

Let us consider for comparison the classical Thomson formula for the cross section of radiation scattering by a free electron

$$\sigma_{sc}^{(Th)}(\omega) = \frac{8\pi}{3}\left(\frac{e^2}{mc^2}\right)^2. \tag{4.14}$$

In order to compare (4.13) and (4.14), we consider different limiting cases of the expression for the cross section of radiation scattering by an atom (4.13). The first case corresponds to the scattering of low-frequency radiation, when $\omega \ll \omega_{ni}$: the radiation frequency is much less than the frequencies of the transition of an atom from the initial state to excited states. In this limit, the scattering cross section is given by a formula similar to (4.13), in which the frequency-independent static polarizability of an atom $\beta_0 = \beta(\omega = 0)$ is dominating. Thus from the expression (4.13), it follows that in the low-frequency limit the scattering cross section increases as the fourth power of frequency, which, in particular, defines the blue color of the sky (solar radiation scattered in the air).

Resonant scattering of radiation by an atom occurs if the radiation frequency is close to one of the atomic eigenfrequencies. Then the previous formulas give

$$\sigma_i^{(ressc)}(\omega \approx \omega_{ni}) = \frac{2\pi}{3} f_{ni}^2 r_e^2 \frac{\omega_{ni}^2}{(\omega - \omega_{ni})^2 + (\delta_{ni}/2)^2}, \tag{4.15}$$

where $r_e \approx 2.8 \times 10^{-13}$ cm is the electron classical radius. In case of an exact resonance with natural broadening of a transition, when $(\delta_{ni})_{nat} = A_{ni}$ (A_{ni} is the Einstein coefficient for spontaneous radiation), it follows from (4.15) that

$$\sigma_i^{(ressc)}(\omega = \omega_{ni}) \approx \lambda_{ni}^2, \tag{4.16}$$

i.e., the resonant scattering cross section is proportional to the squared of the radiation wavelength, which in the optical range exceeds the geometrical size of an atom by several orders of magnitude.

Finally, in the high-frequency limit, when the eigenfrequencies of the atom can be neglected in comparison with the radiation frequency, we obtain

$$\sigma_i^{(Rsc)}(\omega \gg \omega_{ni}) = \frac{8\pi}{3} r_e^2 N_a^2, \tag{4.17}$$

where N_a is the number of atomic electrons. In derivation of (4.17), the sum rule for oscillator strengths, i.e.,

$$\sum_n f_{ni} = N_a \tag{4.18}$$

was used. The condition of the high-frequency approximation $\omega \gg \omega_{ni}$ can be rewritten as $\omega \gg I_P/\hbar$, where I_P is the ionization potential of the atomic shell that mostly contributes to the scattering cross section.

The Rayleigh scattering cross section in the high-frequency limit (4.17) obtained in the dipole approximation is proportional to the squared number of atomic electrons. This reflects the fact that if the dipole condition (4.8) is valid the electronic charge of an atom oscillates as a single entity under the action of an electromagnetic wave. As a result, secondary radiation leading to scattering is coherent with respect to the contributions of all atomic electrons. It is the presence of the factor N_a^2 in the cross section that manifests this coherence.

For atoms with only one electron, (4.17) coincides with the Thomson formula (4.14), i.e., with the cross section of radiation scattering by a free electron. This coincidence is not accidental since neglecting the binding energy of the atomic electron corresponds to the condition $\omega \gg \omega_{ni}$.

The above cross sections describe photon scattering in total solid angle. These are the so-called integrated cross sections. To obtain a differential cross section describing photon scattering by a spherically symmetric system into a specified solid angle $\Omega' + d\Omega'$, one has to multiply the integrated cross sections by the factor of the angular dependence of dipole radiation, $3(1 + \cos^2\theta)/16\pi$, where θ is the angle between the wave vector of incident radiation $\boldsymbol{k}$ and the wave vector of scattered radiation $\boldsymbol{k}'$. Then, instead of formula (4.17), we have

$$\frac{d\sigma_i^{(Rsc)}(\omega \gg \omega_{ni})}{d\Omega'} = \frac{1 + \cos^2\theta}{2} r_e^2 N_a^2. \tag{4.19}$$

Hence, it is seen that the cross section maximum corresponds to forward $(\theta = 0)$ and backward $(\theta = 180^\circ)$ scattering of photons.

The expression (4.19) is valid for spherically symmetric systems in the dipole approximation, when the change in the wave vector of radiation as a result of scattering $\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k}$ is small in comparison with the atomic momentum, i.e., $|\boldsymbol{r}_j||\Delta\boldsymbol{k}| \ll 1$. It can be generalized to the non-dipole case via the replacement $N_a \to n(\Delta\boldsymbol{k})$, where $n(\Delta\boldsymbol{k})$ is the spatial Fourier transform of the atomic electron density. The latter statement means that radiation scattering "tests" the distribution of the electron density inside an atom. Within the framework of the quantum mechanical formalism, the Fourier transform $n(\Delta\boldsymbol{k})$ is equal to the atomic form factor in a specified electronic state:

$$n(\Delta\boldsymbol{k}) \to n_{ii}(\Delta\boldsymbol{k}) \equiv F_i(\Delta\boldsymbol{k}) = \langle i| \sum_j \exp\left(i\,\Delta\boldsymbol{k}\,\boldsymbol{r}_j\right)|i\rangle, \tag{4.20}$$

where the sum is calculated over all electrons of an atom, and the symbol $\langle i|\ldots|i\rangle$ is the Dirac notation for the matrix element (the integral of an operator …. calculated with atomic wave functions $\psi_i(\boldsymbol{r}_j)$). It immediately follows from (4.20) that in the framework of the dipole approximation [see relation (4.8)] $F_i(\Delta\boldsymbol{k}) \cong N_a$ since in this case the exponents in the sum (4.20) are small.

In the exponential screening approximation, the electron density decreases with increasing distance to the nucleus on a characteristic scale length R_a (the average atomic radius). The atomic form factor and accordingly the Fourier transform of the electron density is given by

$$F_i(\Delta \boldsymbol{k}) = \frac{N_a}{1 + \Delta \boldsymbol{k}^2 R_a^2}. \tag{4.21}$$

The radius R_a for multielectron atoms can be assumed to be equal to the Thomas–Fermi radius $R_a \cong r_{TF} = b\hbar^2/\sqrt[3]{Z} m_e e^2$ ($b \cong 0.8853$, Z is the nuclear charge).

From the given expression and the formulas (4.17), (4.19), it follows that if a condition opposite to the dipole condition is fulfilled, i.e., $|\Delta \boldsymbol{k}| > R_a^{-1}$, the cross section of the Rayleigh scattering of radiation by an atom starts to decrease because of the loss of coherence between the contributions of different atomic electrons. Thus in the general case, (4.19) is replaced by the expression for the differential cross section of Rayleigh scattering in the high-frequency limit:

$$\frac{d\sigma_i^{(Rsc)}(\omega \gg \omega_{ni})}{d\Omega'} = \frac{1 + \cos^2\theta}{2} r_e^2 |n_{ii}(\boldsymbol{k}' - \boldsymbol{k})|^2. \tag{4.22}$$

As follows from (4.20)–(4.22), the dipole expression for the cross section (4.19) works reasonably well for small scattering angles even if the dipole condition (4.8) is violated.

Formula (4.22) is valid for radiation scattering by nonrelativistic electrons. It should be noted that in Rayleigh scattering the radiation frequency remains the same despite of the fact that a considerable momentum $\Delta \boldsymbol{p} = \hbar \Delta \boldsymbol{k}$ is transferred from the photon to the atom. This circumstance is connected with the fact that the momentum excess $\Delta \boldsymbol{p}$ is finally absorbed not by an atomic electron, but by the nucleus where the recoil energy is low (due to the heavy mass).

In the case of Raman scattering, when the state of an atom changes, the cross section can be expressed in terms of the scattering tensor, a quantity being the generalization of the dynamic polarizability. On the other hand, the radiation frequency changes by an amount equal to the change in energy of the atom.

4.2.2 *Quantum Description*

The quantum description of radiation scattering by an atom is based on the formula for the cross section of electromagnetic field scattering by a quantum system (Berestetskii et al. 1982):

$$\frac{\mathrm{d}\sigma_{\mathrm{fi}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = \frac{\omega(\omega')^3}{\hbar^2 c^4 g_{\mathrm{i}}} \left| \sum_{\mathrm{n}} \left[\frac{(\boldsymbol{e}'^* \boldsymbol{d}_{\mathrm{fn}})(\boldsymbol{e}\boldsymbol{d}_{\mathrm{ni}})}{\omega_{\mathrm{ni}} - \omega - i\gamma_{\mathrm{ni}}} + \frac{(\boldsymbol{e}\boldsymbol{d}_{\mathrm{fn}})(\boldsymbol{e}'^* \boldsymbol{d}_{\mathrm{ni}})}{\omega_{\mathrm{ni}} + \omega' - i\gamma_{\mathrm{ni}}} \right] \right|^2, \tag{4.23}$$

where $\omega' = \omega - \omega_{\mathrm{fi}}$, $\boldsymbol{e}$ and $\boldsymbol{e}'$ are unit polarization vectors of incident and scattered radiation, respectively. The formula (4.23) describes radiation scattering that can be accompanied by simultaneous excitation/de-excitation of a quantum system. Scattering in the case $\omega_{\mathrm{fi}} \neq 0$ is called *Raman scattering*, and if $\omega_{\mathrm{fi}} = 0$, there is *Rayleigh scattering*. It should be noted that the formula (4.23) was obtained by Kramers and Heisenberg before the advent of quantum mechanics. It is convenient to rewrite the expression (4.23) as

$$\frac{\mathrm{d}\sigma_{\mathrm{fi}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = \frac{\omega(\omega')^3}{c^4 g_{\mathrm{i}}} \left| e^l (e'^*)^s c_{\mathrm{fi}}^{\mathrm{ls}}(\omega', \omega) \right|^2, \tag{4.24}$$

where

$$c_{\mathrm{fi}}^{\mathrm{ls}}(\omega', \omega) = \frac{1}{\hbar} \sum_{\mathrm{n}} \left[\frac{(\boldsymbol{d}_{\mathrm{fn}})^l (\boldsymbol{d}_{\mathrm{ni}})^s}{\omega_{\mathrm{ni}} - \omega - i\gamma_{\mathrm{ni}}} + \frac{(\boldsymbol{d}_{\mathrm{fn}})^s (\boldsymbol{d}_{\mathrm{ni}})^l}{\omega_{\mathrm{ni}} + \omega' - i\gamma_{\mathrm{ni}}} \right] \tag{4.25}$$

is the *electromagnetic field scattering tensor* of the quantum system; l, s are the three-dimensional vector indices, over which summation in the formula (4.24) is assumed.

In the case of Rayleigh scattering (when $\omega_{\mathrm{fi}} = 0$), the scattering tensor changes to a *polarizability tensor*:

$$c_{\mathrm{fi}}^{\mathrm{ls}} \to \beta_{\mathrm{i}}^{\mathrm{ls}}(\omega) = \frac{1}{\hbar} \sum_{\mathrm{n}} \left[\frac{d_{\mathrm{in}}^l d_{\mathrm{ni}}^s}{\omega_{\mathrm{ni}} - \omega - i\gamma_{\mathrm{ni}}} + \frac{d_{\mathrm{in}}^s d_{\mathrm{ni}}^l}{\omega_{\mathrm{ni}} + \omega - i\gamma_{\mathrm{ni}}} \right]. \tag{4.26}$$

Note that the polarizability tensor relates the electric dipole moment vector to the strength of the electric field of frequency ω:

$$d_{\mathrm{i}}^l(\omega) = \beta_{\mathrm{i}}^{\mathrm{ls}}(\omega) E^s(\omega). \tag{4.27}$$

Here, summation over the index s is implied.

In the case of a spherically symmetric state of a quantum system, the polarizability tensor changes to a scalar: $\beta_{\mathrm{i}}^{\mathrm{ls}}(\omega) = \beta_{\mathrm{i}}(\omega)\delta^{\mathrm{ls}}$. Then it can be shown that the expression (4.26) coincides with (2.41) if the explicit form for the oscillator strength is used (2.18) and the relationship between the damping constants is taken into account ($\delta_{\mathrm{in}} = 2\gamma_{\mathrm{in}}$). The differential cross section of Rayleigh scattering by a quantum system in the spherically symmetric state is then given by

$$\frac{\mathrm{d}\sigma_{\mathrm{ii}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = \frac{\omega^4}{c^4}|\beta_{\mathrm{i}}(\omega)|^2|(\boldsymbol{e}'^{*}\boldsymbol{e})|^2. \tag{4.28}$$

We will sum this expression over the polarization directions of a scattered photon with the use of the formula

$$2\left\langle|(\boldsymbol{e}'^{*}\boldsymbol{e})|^2\right\rangle = \sin^2\theta. \tag{4.29}$$

In (4.29), averaging is carried out over all possible directions of the vector $\boldsymbol{e}'$ at a specified angle θ between the vectors $\boldsymbol{e}$ and $\boldsymbol{n}'$ ($\boldsymbol{n}'$ is the unit vector in the direction of the scattered photon). As a result, we have

$$\frac{\mathrm{d}\sigma_{\mathrm{ii}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = \frac{\omega^4}{c^4}|\beta_{\mathrm{i}}(\omega)|^2\left(1-(\boldsymbol{n}'\boldsymbol{e})^2\right). \tag{4.30}$$

For non-polarized incident radiation, formula (4.30) should be averaged over the direction of the vector $\boldsymbol{e}$, and we obtain

$$\frac{\mathrm{d}\sigma_{\mathrm{ii}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = \frac{\omega^4}{c^4}|\beta_{\mathrm{i}}(\omega)|^2\,\frac{1+(\boldsymbol{n}'\boldsymbol{n})^2}{2}, \tag{4.31}$$

where $\boldsymbol{n}$ is the unit vector in the direction of an incident photon. In derivation of (4.31), the averaging rule, i.e., $\left\langle e^l e^s\right\rangle = (\delta^{\mathrm{ls}} - n^l n^s)/2$ was used.

The expression (4.31) describes the cross section of Rayleigh scattering of radiation by a spherically symmetric system as a function of frequency ω and scattering angles $\theta = \arccos(\boldsymbol{n}'\boldsymbol{n})$. At high frequencies $\omega \gg \omega_{\mathrm{a}}$ (ω_{a} is the characteristic frequency of transitions in a discrete spectrum), we obtain with (2.43) and (4.31)

$$\frac{\mathrm{d}\sigma_{\mathrm{ii}}^{(\mathrm{scat})}}{\mathrm{d}\Omega'} = N_{\mathrm{e}}^2 r_{\mathrm{e}}^2\,\frac{1+\cos^2\theta}{2}, \tag{4.32}$$

where θ is the angle of scattering, N_{e} is the number of electrons in the quantum system, $r_{\mathrm{e}} = e^2/(m_{\mathrm{e}}c^2)$ is the electron classical radius ($r_{\mathrm{e}} = 2.8 \times 10^{-13}$ cm). It should be noted that the expression (4.32) was obtained on the basis of the quantum approach that is identical to the result of classical scattering in the high-frequency approximation (4.19).

For $N_{\mathrm{e}} = 1$, the expression (4.32) coincides with the Thomson formula for the cross section of radiation scattering by a free electron. This coincidence is not accidental since there are no bound states for a free electron, i.e., $\omega_{\mathrm{a}} = 0$, and the condition of the high-frequency approximation is fulfilled automatically. The squared number N_{e}^2 appearing in (4.32) corresponds to the coherence of photon scattering by all electrons of the quantum system. Coherence of scattering is a

consequence of the dipole approximation $\lambda \gg a$ used in derivation of all formulas of this chapter. In the opposite limit, i.e., $\lambda \ll a$, coherence is disturbed, and N_e^2 in (4.32) is replaced by N_e.

In the opposite limit (low frequencies), when the dynamic polarizability can be replaced by its static value, the Rayleigh scattering cross section increases with the fourth power of frequency as it follows from formulas (4.28)–(4.31).

Let the frequency of scattered radiation be close to one of the eigenfrequencies of a transition in the quantum system, where the following relation holds true:

$$|\omega - \omega_{ni}| \leq \gamma_{ni}. \tag{4.33}$$

In this case, the sum over the intermediate states in (4.23) can be replaced by one resonance summand:

$$\frac{d\sigma_{fi}^{(scat)}}{d\Omega'} = \frac{\omega(\omega')^3}{\hbar^2 c^4 g_i} \frac{\left|\sum_{M_n} (\boldsymbol{e}'^* \boldsymbol{d}_{fn})(\boldsymbol{e}\boldsymbol{d}_{ni})\right|^2}{(\omega - \omega_{ni})^2 + \gamma_{ni}^2}. \tag{4.34}$$

Here, only the summation over the degenerate states of the resonance level is left. The phenomenon described by the cross section (4.34) is called *resonance fluorescence*. Let us consider a Rayleigh case, when $\omega_{fi} = 0$ and accordingly the frequencies of incident and scattered photons coincide: $\omega = \omega'$. We will assume for simplicity that the initial state is non-degenerate: $g_i = 1$. Then (4.34) takes the following form

$$\frac{d\sigma_i^{(RF)}}{d\Omega'} = \frac{1}{16}\left(\frac{c}{\omega_{ni}}\right)^2 \frac{A_{ni}^2 |(\boldsymbol{e}'^* \boldsymbol{e})|^2}{(\omega - \omega_{ni})^2 + \gamma_{ni}^2}, \tag{4.35}$$

where A_{ni} is the Einstein coefficient of spontaneous radiation.

In the case of natural line broadening, when the half-width is defined by spontaneous radiation, i.e., $\gamma_{ni} = A_{ni}/2$ and of an exact resonance $\omega = \omega_{ni}$, we obtain from (4.35)

$$\frac{d\sigma_i^{(RF)}}{d\Omega'} \propto \lambda^2. \tag{4.36}$$

Hence it follows that the cross section of resonance fluorescence in the optical range in the case of natural line broadening exceeds by many orders of magnitude the scattering cross section far from the resonance. It should be noted that relation (4.36) has already be obtained (see (4.19)) on the basis of a classical consideration.

4.3 High-Frequency Radiation Scattering on Atoms

For scattering of electromagnetic radiation in the X-ray range $\lambda \leq 1$ Å ($k = 2\pi/\lambda \geq 10$ Å^{-1}), the dipole approximation (4.8) is violated, and instead (4.23) has to be used to take into account the wave vectors of incident and scattered photons. This is of particular interest for modern X-ray Free Electron Laser (i.e., LCLS in USA, EU-XFEL in Germany, SACLA in Japan) driven scattering experiments where photon energies larger than 10 keV can be generated.

4.3.1 Non-dipole Character of Scattering

The non-dipole scattering tensor defining the scattering cross section with the use of (4.24) is given by

$$c_{\mathrm{fi}}^{\mathrm{ls}}(\boldsymbol{k}',\boldsymbol{k}) = \frac{e^2}{m\omega'\omega}\left\{\frac{m}{\hbar}\sum_{\mathrm{n}}\left[\frac{j_{\mathrm{fn}}^{l}(\boldsymbol{k})j_{\mathrm{ni}}^{s}(\boldsymbol{k}')}{\omega_{\mathrm{fn}}+\omega-i0}+\frac{j_{\mathrm{fn}}^{s}(\boldsymbol{k}')j_{\mathrm{ni}}^{l}(\boldsymbol{k})}{\omega_{\mathrm{in}}-\omega-i0}\right]-\delta^{\mathrm{ls}}n_{\mathrm{fi}}(\boldsymbol{q})\right\}, \quad (4.37)$$

where $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$ is the change in the photon wave vector, δ^{lk} is the Kronecker symbol, $j^{l}(\boldsymbol{k}) = \frac{1}{2m}\sum_{j=1}^{N}\left\{\hat{p}_{\mathrm{j}}^{l}\exp\left(-i\boldsymbol{k}\boldsymbol{r}_{\mathrm{j}}\right)+\exp\left(-i\boldsymbol{k}\boldsymbol{r}_{\mathrm{j}}\right)\hat{p}_{\mathrm{j}}^{l}\right\}$ and $\hat{n}(\boldsymbol{q}) = \sum_{j=1}^{N}\exp\left(-i\boldsymbol{q}\boldsymbol{r}_{\mathrm{j}}\right)$ are the Fourier transforms of the atomic electron current density and electron density operators, $|i\rangle, |f\rangle$ are the initial and final atomic states.

It should be noted that in the high-frequency limit that can be determined by the inequality $\hbar\omega \gg I$ (I is the characteristic atomic ionization potential) the main contribution to the scattering tensor is made by the second summand in braces of (4.37). The sum in square brackets has an order of magnitude of $(I/\omega)^2$. In the high-frequency domain, the scattering tensor $c_{\mathrm{fi}}^{\mathrm{ls}}(\boldsymbol{k}',\boldsymbol{k})$ is found to be a scalar equal to

$$c_{\mathrm{fi}}^{\mathrm{hf}}(\boldsymbol{k}',\boldsymbol{k}) = -\frac{e^2}{m\omega'\omega}n_{\mathrm{fi}}(\boldsymbol{q}=\boldsymbol{k}'-\boldsymbol{k}). \quad (4.38)$$

It should be emphasized that the condition of the high-frequency limit $\hbar\omega \gg I$ is fulfilled for the majority of atomic electrons in the X-ray range of photon energies, i.e. when $\hbar\omega \geq 10$ keV. Exceptions are electrons of inner shells (in particular K- and L-shells) of heavy elements with a nuclear charge $Z \geq 60$.

Substituting the expression for the scattering tensor in the high-frequency limit (4.38) into the formula for the scattering cross section (4.24) and averaging over photon polarizations, we find

$$\mathrm{d}\sigma^{\mathrm{hf}} = \frac{1}{2}r_{\mathrm{e}}^2\left(1+\cos^2\vartheta\right)\left(\frac{\omega'}{\omega}\right)|n_{\mathrm{fi}}(\boldsymbol{q})|^2\mathrm{d}\Omega'. \quad (4.39)$$

The obtained expression differs from the classical Thomson formula (4.3) by the presence of an additional factor that is proportional to the squared absolute value of the matrix element of the Fourier transform of the atomic electron density operator calculated for the wave vector $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$.

4.3.2 Dynamic Form Factor of an Atom

The expression (4.39) should be supplemented with (4.24) expressing the law of conservation of energy in scattering. It is convenient to write this equation in terms of the delta function $\delta(\omega - \omega' + (E_\mathrm{i} - E_\mathrm{f})/\hbar)$. Using its integral representation $\delta(x) = (1/2\pi)\int \exp(ixt)dt$ and the Heisenberg operator $\hat{q}(t) = \exp(i\hat{H}t/\hbar)\hat{q}\exp(-i\hat{H}t/\hbar)$, it is possible to obtain the following frequency-angular cross section of photon scattering by an atom in the initial state $\langle i\rangle$ in the *high-frequency approximation*:

$$\frac{\mathrm{d}\sigma_\mathrm{i}}{\mathrm{d}\Omega' d(\Delta\omega)} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'}\right)^{\mathrm{Th}} \left(\frac{\omega}{\omega'}\right) S_\mathrm{i}(\Delta\omega, \boldsymbol{q}), \tag{4.40}$$

where $(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega'})^{\mathrm{Th}}$ is given by the formula (4.3). $S_\mathrm{i}(\Delta\omega, \boldsymbol{q})$ is the dynamic form factor (DFF) of an atom (Platzman and Wolf 1973), i.e.,

$$S_\mathrm{i}(\Delta\omega, \boldsymbol{q}) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \mathrm{d}t e^{-i\Delta\omega t}\langle i|\hat{n}(\boldsymbol{q}, t)\hat{n}(-\boldsymbol{q})|i\rangle. \tag{4.41}$$

As can be seen from (4.41), the DFF is a space-time Fourier transform of the density–density correlation function for atomic electrons. The dynamic form factor satisfies a number of sum rules. In the case of a hydrogen-like atom we have the simple relations

$$\int\limits_{-\infty}^{\infty} S(\omega, \boldsymbol{k})\mathrm{d}\omega = 1, \quad \int\limits_{-\infty}^{\infty} S(\omega, \boldsymbol{k})\omega\mathrm{d}\omega = \hbar\boldsymbol{k}^2/2m. \tag{4.42}$$

Thus the frequency-angular distribution of photons scattered by an atom in the high-frequency approximation $\hbar\omega \gg I$ is determined by the formula (4.40). If $\hbar\omega < I$, the expression (4.40) becomes, generally speaking, invalid. This is particularly the case, when the frequency of the scattered radiation approaches one of the atomic eigenfrequencies (then, so-called resonant scattering arises and the cross section has a pronounced maximum).

In case of Rayleigh scattering ($|i\rangle = |f\rangle$) by a ground state of a hydrogen-like atom, the diagonal matrix element $n_{\mathrm{ii}}(\boldsymbol{q})$ included in the expression for the cross section (4.39) is easily calculated analytically, and (4.39) is transformed to the form

$$\frac{d\sigma_{ii}}{d\Omega'} = \left(\frac{d\sigma}{d\Omega'}\right)^{Th} \frac{1}{\left[1 + a_H^2 \boldsymbol{q}^2/4\right]^4}, \tag{4.43}$$

where $a_H = \hbar^2/Z\,m\,e^2$ is the characteristic radius of a hydrogen-like ion. From the given expression, it follows that the Rayleigh scattering cross section sharply decreases ($\propto (1/a_H q)^8$) if $q > a_H^{-1}$.

Thus for high recoil momenta (in comparison with the characteristic atomic momentum) scattering proceeds with a change of the atomic state. In this case, if an atom is ionized, there is Compton scattering; if it is excited to the state of a discrete spectrum, scattering is combinational (Raman). It should be noted that the Raman scattering cross section increases at small q from zero, reaches its maximum at $q \approx 1/a$, and then decreases. The calculation for the ground state of a hydrogen-like atom shows that the value of this cross section is always less than the value of its Rayleigh analog. At maximum, it reaches a value about 20% of the Thomson cross section.

In the opposite case ($q < a_H^{-1}$), photon scattering proceeds with no changes in the atomic states. This can be ascertained with the use of the formulas (4.40)–(4.41). Really, in case of small changes in the wave vector of the scattered photon, the Fourier transform of the electron density operator is equal to the number of atomic electrons $\hat{n}(q < a_H^{-1}) \cong N$. Then from (4.41), it follows that the DFF of an atom looks like $S_i = N^2\delta(\omega - \omega')$, that is, $\omega = \omega'$ and accordingly $E_i = E_f$. Hence, in the case of small transfered momenta, the scattering is of coherent character with respect to the contribution of atomic electrons and the cross section is proportional to the squared number of electrons. On the contrary, in the case of high transferred momenta $q > 1/a$, scattering is incoherent, and its cross section is proportional to N. In view of these dependencies, the following approximate expression for the DFF of an atom can be proposed:

$$S(\Delta\omega, q) \approx \theta(1/a - q)N^2\delta(\Delta\omega) + \theta(q - 1/a)N\delta\left(\Delta\omega + \hbar q^2/2m\right). \tag{4.44}$$

The first summand in the right-hand side of this equation describes coherent processes occurring in the case of small recoil. The second summand in the right-hand side of (4.44) relates to incoherent phenomena, when an energy–momentum excess (that appears in the course of scattering) is carried away by an ionized electron.

4.3.3 *Impulse Approximation in the Theory of Compton Scattering*

It was indicated above that (leaving out the contribution of inner K-shells) for the description of the X-ray scattering by an atom, the high-frequency approximation

(4.40) can be used, where the dynamic properties of an atom are essential for photon scattering (defined by its dynamic form factor (4.41)). As a rule, the DFF of an atom can not be calculated in the general form. The qualitative formula for the DFF (4.44) does not take into account the details of the electronic structure of an atom and is not precise enough for comparison with experimental data. However, there exist an approximate method for the calculation of the cross section of X-ray scattering by an atom that was used at the very early days for the analysis of experimental data. This is the so-called impulse approximation (IA) assuming that atomic electrons in the course of X-ray scattering behave as free electrons to a greater extent than as bound electrons. The exact definition of the IA will be given below.

The impulse approximation for the description of the Compton scattering of X-rays by an atom, as was shown by Platzman and Wolf (1973), can be obtained from the first principles. For this purpose, it is necessary to use the expression for the DFF (4.41) and the explicit form of the spatial Fourier transform of the electron density operator $\hat{n}(\boldsymbol{q}) = \sum_{j=1}^{N} \exp(-i\,\boldsymbol{q}\boldsymbol{r}_j)$. In the expression for the Heisenberg operator $\hat{n}(\boldsymbol{q}, t) = \exp(i\hat{H}t/\hbar)\hat{n}(\boldsymbol{q})\,\exp(-i\hat{H}t/\hbar)$, the complete Hamiltonian of the system $\hat{H}$ is the sum of the operators of kinetic $\hat{T}$ and potential $\hat{V}$ energies: $\hat{H} = \hat{T} + \hat{V}$ (Note that the potential energy operator commutes with the electron density operator, whereas the kinetic energy operator does not commute). Then we will write down the known expansion of the operator exponent included in the determination of the DFF:

$$\exp\left(\frac{i\hat{H}t}{\hbar}\right) = \exp\left(\frac{i\hat{T}t}{\hbar}\right)\exp\left(\frac{i\hat{V}t}{\hbar}\right)\exp\left(\frac{-i\left[\hat{T},\hat{V}\right]}{\hbar^2}\frac{t^2}{2}\right)\ldots, \tag{4.45}$$

where $\left[\hat{A},\hat{B}\right]$ is the commutator of the operators $\hat{A}$ and $\hat{B}$, the dots at the end of (4.45) denote exponents with multiple commutators containing higher powers of the time parameter t. In fact, (4.45) is a power expansion of the time interval t. The value of this interval is given by the value $1/\Delta\omega$ as it follows from (4.41). Really, the contribution to the time integral in the determination of the DFF for large values of the variable t is small due to strong oscillations of the exponent. The IA condition is given by the equation

$$\exp\left(-i\left[\hat{T},\hat{V}\right]t^2/2\hbar^2\right) = 1, \tag{4.46}$$

according to which the non-commutativity of the operators $\hat{T}$ and $\hat{V}$ can be neglected *for times responsible for the process*. Physically, this means that during photon scattering, the potential in which an atomic electron moves practically does not change. If (4.46) is valid, the contribution of exponents with multiple commutators to the expansion (4.45) can be neglected and the expression for the DFF in the impulse approximation looks simply like

$$S_{\mathrm{i}}^{\mathrm{IA}}(\Delta\omega,\boldsymbol{q})=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}\mathrm{d}t e^{-i\Delta\omega t}\langle i|e^{i\hat{T}t/\hbar}\hat{n}(\boldsymbol{q})e^{-i\hat{T}t/\hbar}\hat{n}(-\boldsymbol{q})|i\rangle, \tag{4.47}$$

where $\boldsymbol{q}=\boldsymbol{k}'-\boldsymbol{k}$. From this equation, it follows that in the framework of the IA the potential $\hat{V}$ vanishes from the determination of the DFF. However, it should be emphasized that this does not mean to neglect the binding of atomic electrons to a nucleus. As was already noted, in the impulse approximation, the potential $\hat{V}$ is assumed to be constant, and therefore it cancels out in the expressions for the energy of initial and final atomic states. In other words, the energy of the initial and final states of an ionized electron within the framework of the IA is measured with respect to a constant instantaneous value of the potential $\hat{V}$. The expression (4.47) can be evaluated approximately replacing the sum over the complete set of wave functions by plane waves. Using the fact that a plane wave is an eigenfunction of the operator $\exp\left(-i\,\hat{T}\,t/\hbar\right)$ we then obtain for the DFF of a (nl)th electron subshell of an atom

$$S_{\mathrm{nl}}^{\mathrm{IA}}(\Delta\omega,\boldsymbol{q})=\int\frac{\mathrm{d}\boldsymbol{p}}{4\pi\hbar^3}\delta\left(\Delta\omega+\frac{(\boldsymbol{p}-\hbar\boldsymbol{q})^2}{2m\hbar}-\frac{\varepsilon_{\mathrm{nl}}}{\hbar}\right)|R_{\mathrm{nl}}(p)|^2, \tag{4.48}$$

$\varepsilon_{\mathrm{nl}}$ is the subshell binding energy, $R_{\mathrm{nl}}(p)$ is the radial wave function of the electron subshell in the momentum representation that is determined by the expression

$$R_{\mathrm{nl}}(p)=\sqrt{\frac{2}{\pi}}\int\limits_{0}^{\infty}R_{\mathrm{nl}}(r)j_{\mathrm{l}}(pr)r^2\mathrm{d}r, \tag{4.49}$$

here $j_{\mathrm{l}}(p\,r)$ is the spherical Bessel function of the first kind, $R_{\mathrm{nl}}(r)$ is the normalized radial wave function of the electron subshell. If the relation between a momentum and the energy of atomic electrons in the quasi-free approximation is used, i.e.,

$$p^2/2m=\varepsilon_{\mathrm{nl}}, \tag{4.50}$$

we have instead of (4.48)

$$S_{\mathrm{nl}}^{\mathrm{IA}}(\Delta\omega,\boldsymbol{q})=\int\frac{\mathrm{d}\boldsymbol{p}}{4\pi\hbar^3}\delta\left(\Delta\omega+\frac{\hbar q^2}{2m}-\frac{\boldsymbol{p}\boldsymbol{q}}{m}\right)|R_{\mathrm{nl}}(p)|^2. \tag{4.51}$$

As can be seen from this formula, the frequency shift in Compton scattering within the framework of the impulse approximation is related to the Doppler shift in photon scattering due to a moving atomic electron (the summand $\boldsymbol{p}\boldsymbol{q}$ under the sign of the delta function in (4.51)). In this case, the spectrum of scattered photons is defined by the distribution of atomic electrons by momenta given by the function $|R_{\mathrm{nl}}(p)|^2$.

The cross section of Compton scattering of X-rays by an atom is usually expressed in terms of the Compton profile (CP) of an electron subshell. The CP is determined by the formula

$$J_{\mathrm{nl}}(Q) = \frac{1}{2\hbar^3} \int\limits_{\mathrm{Q}}^{\infty} |R_{\mathrm{nl}}(p)|^2 p \mathrm{d}p. \tag{4.52}$$

In view of this determination, the dynamic form factor of an electron subshell within the framework of the impulse approximation (4.51) can be expressed in terms of the CP as follows:

$$S_{\mathrm{nl}}^{\mathrm{IA}}(q) = \frac{m}{|\boldsymbol{q}|} J_{\mathrm{nl}}\left(Q = \frac{m|\Delta\omega| - \hbar\boldsymbol{q}^2/2}{|\boldsymbol{q}|}\right). \tag{4.53}$$

It should be noted that the CP satisfies the normalizing condition:

$$2 \int\limits_{0}^{\infty} J_{\mathrm{nl}}(Q) \mathrm{d}Q = 1. \tag{4.54}$$

Since Compton scattering is an incoherent process, the atomic CP is equal to the sum of CPs of all electron subshells.

Using the relation (4.40) and the formula (4.53), we find for the cross section of Compton scattering of X-rays by an atom:

$$\frac{\mathrm{d}\sigma^{\mathrm{IA}}}{\mathrm{d}\Omega' d(\Delta\omega)} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)^{\mathrm{Th}} \left(\frac{\omega}{\omega'}\right) \frac{m}{q} J(Q), \tag{4.55}$$

where $Q = \dfrac{m|\Delta\omega| - \hbar\boldsymbol{q}^2/2}{|\boldsymbol{q}|}$. Thus the expression (4.55), together with the formula (4.3) for $\left(\mathrm{d}\sigma/\mathrm{d}\Omega'\right)^{\mathrm{Th}}$, gives the frequency-angular distribution of X-rays scattered by an atom within the framework of the high-frequency and impulse approximations. It is seen that the frequency distribution for a specified angle of scattering is defined by the Compton profile of an atom (4.52) that in turn depends on the wave functions $R_{\mathrm{nl}}(r)$ of the atomic electron. The corresponding frequency dependence is a bell-shaped curve. Its width is defined by the width of the distribution of the atomic momenta wave functions. Let us give the expression for the CP of the ground state of a hydrogen-like ion:

$$J_{1\mathrm{s}}^{H}(Q) = \frac{8p_{\mathrm{H}}^5}{3\pi\left(p_{\mathrm{H}}^2 + Q^2\right)^3}, \tag{4.56}$$

where $p_H = Z m e^2/\hbar$ is the characteristic momentum of a hydrogen-like ion. Substituting (4.56) in (4.55), we find the frequency function of the distribution of X-rays within the framework of the IA for a fixed angle of scattering by a hydrogen-like ion in the 1s-state:

$$\frac{d\sigma_{1s}^{H}}{d\Delta\omega} = \sigma_{1s}(q)\frac{q^6 p_H^6}{\left[q^2 p_H^2 + (m|\Delta\omega| - \hbar q^2/2)^2\right]^3}, \tag{4.57}$$

where $q = |\boldsymbol{k}' - \boldsymbol{k}|$ is the magnitude of the photon wave vector change in scattering. From this formula, it follows that the central frequency of scattered radiation is determined by the equation $m(\omega - \omega') = \hbar q^2/2$. This equation represents the law of conservation of energy–momentum for the process of radiation scattering by a free electron at rest. The width of the frequency distribution (4.57) is proportional to the parameter $q p_H/m$, which corresponds to a Doppler broadening of the spectrum of radiation scattered by an electron moving with the velocity $\upsilon_H = p_H/m = Z e^2/\hbar$.

Presented in Fig. 4.3 are the spectral cross sections of Compton scattering (in relative units) by a hydrogen-like ion in the 1s-state calculated in the high-frequency approximation with the use of the exact wave functions (curves 1, 3) and within the framework of the impulse approximation (curves 2, 4) according to formulas (4.55)–(4.56). Two values of ionic charges are considered: $Z = 1$ (curves 1, 2) and $Z = 2$ (curves 3, 4). The incident photon energy is $\hbar\omega = 17.4$ keV (639.7 a.u.) (which corresponds to the line K_{α_1} in a molybdenum atom), the angle of radiation scattering is $\vartheta = 133.75°$. As can be seen from Fig. 4.3, the

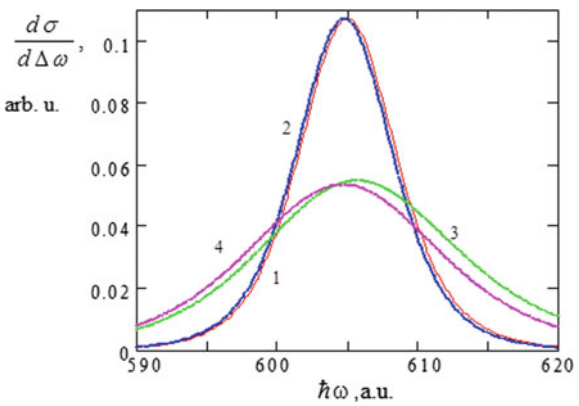

Fig. 4.3 The spectral cross section of Compton scattering of X-rays ($\hbar\omega = 17.4$ keV, the angle of scattering is $\vartheta = 133.75°$) by a ground state hydrogen-like ion calculated in the high-frequency approximation with the use of the exact functions (curves 1, 3) and within the framework of the impulse approximation (curves 2, 4) for different ionic charges: curves 1, 2—$Z = 1$, curves 3, 4—$Z = 2$

maximum of the spectral cross section corresponds to a scattered photon energy of $\hbar\omega = 605$ a.u. (16.456 keV) and a recoil energy of $E_R = \hbar|\Delta\omega| = 944$ eV.

It should be noted that the recoil energy in scattering by a free electron at rest for otherwise same parameters is 949 eV, being in good agreement with the above value E_R at the maximum of the spectral cross section. It should be emphasized that for the case of a free electron there is a univocal correspondence between the scattering angle and the frequency of the scattered photon and the spectral cross section represents a delta function of the frequency detuning $\omega - \omega' - E_R/\hbar$. Binding of an electron to a nucleus results in a finite spectral width $\delta\omega$ of the frequency distribution of the scattered photons at a specified angle of scattering θ. Naturally, the stronger the binding to a nucleus is, the higher the value of the parameter $\delta\omega$ is. This also follows from Fig. 4.3: for larger charge values, the frequency dependence is broader. Figure 4.3 also demonstrates that the accuracy of the IA decreases with increasing binding energy E_B ($E_B = Z^2 Ry$ for a hydrogen-like ions) at fixed recoil energy E_R. Thus the value of the ratio $\xi = E_B/E_R$ can serve as a criterion for the applicability of the IA; with decreasing parameter ξ the IA accuracy increases. Figure 4.3 shows also an asymmetry of the frequency distribution of the scattered photons when the exact wave functions are employed (curves 1, 3). In the high-frequency wing of the line, the intensity of the scattered radiation decreases more slowly than in the low-frequency wing. This asymmetry increases with the binding energy E_B. At the same time, the calculation within the framework of the IA gives a symmetric (for the present case "Lorentz") profile. It should be noted that the asymmetry could be to some extent taken into account within the framework of the impulse approximation if in the right-hand side of (4.45) succeeding expansion terms are taken into account.

4.4 Scattering on Plasmas

We now consider the scattering of electromagnetic radiation by electrons in plasmas. The cross section of radiation scattering by ions is negligible because of the heavy mass of an ion. In contrast to atomic electrons, plasma electrons execute an infinite motion, that is, they are delocalized throughout the plasma volume. Therefore, strictly speaking, the condition for the application of the dipole approximation (4.8) is not fulfilled for plasma electrons because the radius of the area of their localization is very large. Since plasma electrons are quasi-free, the potential of their ionization I_P is equal to zero, the condition of the high-frequency approximation is naturally fulfilled, and it is possible to use the expression for the scattering cross section according to formula (4.22).

The adjective "quasi-free" is used in reference to plasma electrons is not accidentally. The prefix "quasi" reflects the fact that plasma electrons interact with other particles and collective plasma excitations. This interaction manifests itself in the scattering of electromagnetic waves by plasma electrons in the vicinity of frequencies of collective plasma excitations. For example, a momentum excess

transferred from a photon in scattering can be absorbed by a plasma electron itself but can be as well transferred to another particle or a quasi-particle. Depending on these possibilities, the frequency of scattered radiation differs. Therefore, by recording the spectrum of the scattered photons, it is possible to obtain information on the plasma properties.

4.4.1 General Expression for the Cross Section of Radiation Scattering in Plasmas

Let us generalize the scattering cross section (4.22) taking into account a possible change in the state of a plasma electron in the course of scattering:

$$\frac{\mathrm{d}\sigma_{\mathrm{fi}}^{(\mathrm{plas})}(\boldsymbol{k},\boldsymbol{k}')}{\mathrm{d}\Omega'\mathrm{d}\omega'} = \frac{1+\cos^2\theta}{2}\delta(\Delta\omega+\omega_{\mathrm{fi}})r_{\mathrm{e}}^2|n_{\mathrm{fi}}(\boldsymbol{k}'-\boldsymbol{k})|^2\mathrm{d}V, \tag{4.58}$$

where $\Delta\omega = \omega' - \omega$ is the change in radiation frequency, $\mathrm{d}V$ is the element of the volume in which the scattering plasma electrons are located (the volume of interaction). The given expression describes radiation scattering with the transition of a plasma electron from the state $|i\rangle$ to the state $|f\rangle$ (here Dirac ket vectors are used to designate electronic states). Expression (4.58) gives the cross section of photon scattering in the frequency interval $\omega' + \mathrm{d}\omega'$ and is therefore differential not only with respect to the angle, but also with respect to the frequency of the scattered radiation. The delta function in the right-hand side of (4.58) expresses the conservation law of energy in the scattering process.

Since in the experiment the initial and final states of a plasma electron are not fixed, formula (4.58) should be summed over the final states and averaged over the initial ones. As a result, we obtain

$$\frac{\mathrm{d}\sigma_{\Sigma}^{(\mathrm{plas})}(\boldsymbol{k},\boldsymbol{k}')}{\mathrm{d}\Omega'\mathrm{d}\omega'} = \frac{1+\cos^2\theta}{2}r_{\mathrm{e}}^2 S(\Delta\boldsymbol{k},\Delta\omega))\mathrm{d}V, \tag{4.59}$$

where the function $S(\Delta\boldsymbol{k},\Delta\omega)$ is the so-called electron *dynamic form factor* (DFF) of the plasma or the spectral density function. The DFF reflects the influence of plasma characteristics on the radiation scattering cross section. In the general case, the determination of the DFF in terms of the Fourier component of the plasma density time-domain correlator looks like (Platzman and Wolf 1973).

$$S(\Delta\boldsymbol{k},\Delta\omega) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty}\mathrm{d}t\, e^{i\Delta\omega t}\langle\hat{n}(\Delta\boldsymbol{k},t)\hat{n}(-\Delta\boldsymbol{k})\rangle, \tag{4.60}$$

where $\hat{n}$ is the electron density operator, the angle brackets include quantum mechanical and statistical averaging. Equation (4.58) can be obtained from the formula

$$S(\Delta\boldsymbol{k}, \Delta\omega) = \sum_{f,i} w(i)\delta(\Delta\omega + \omega_{\mathrm{fi}})|n_{\mathrm{fi}}(\Delta\boldsymbol{k})|^2, \tag{4.61}$$

in which averaging over initial states and summation over final states of plasma electrons are carried out explicitly ($w(i)$ is the probability of a plasma electron being in the ith state).

Physically, the electron DFF defines the probability of absorption of a four-dimensional energy–momentum wave vector $\Delta k = (\Delta\boldsymbol{k}, \Delta\omega)$ by a plasma in terms of the action of external disturbance on an electronic component. It should be emphasized that in case of a homogeneous distribution of charges in plasmas this probability would be equal to zero since then the Fourier transform of the electron density is given by the delta function $n(\Delta\boldsymbol{k}) \to \delta(\Delta\boldsymbol{k})$, that is, $\Delta\boldsymbol{k} = 0$ and $\boldsymbol{k} = \boldsymbol{k}'$. Radiation scattering is therefore a result of plasma density fluctuations. These fluctuations can be due to various reasons. A typical cause of electronic charge fluctuations is Debye screening of ions by plasma electrons, when the electron density is increased in the vicinity of a positive ion. Another type of fluctuations is connected with collective excitations in plasmas, for example, plasmons. Then, electronic charge fluctuations are of nonstationary character: they oscillate at a plasma frequency $\omega_{\mathrm{pe}} = \sqrt{4\pi e^2 n_{\mathrm{e}}/m_{\mathrm{e}}}$ (n_{e} is the density of the plasma electrons). Scattering by nonstationary fluctuations changes the radiation spectrum. Thus, from the observed scattered radiation spectrum the fluctuation spectrum of the electron density in a plasma that is given by the DFF (4.60)–(4.61) can be deduced.

To calculate the DFF, it is possible to use the formula relating the DFF of a plasma component to the function of plasma response to external electromagnetic disturbance (a fictitious external potential). This relation is known as the fluctuation–dissipative theorem (Platzman and Wolf 1973):

$$S(\Delta\boldsymbol{k}, \Delta\omega) = \frac{Im\{F_{\mathrm{ee}}(\Delta\boldsymbol{k}, \Delta\omega)\}}{\pi e^2[\exp(-\hbar\Delta\omega/T) - 1]}, \tag{4.62}$$

where $F_{\mathrm{ee}}(\Delta\boldsymbol{k}, \Delta\omega)$ is a linear function of the response of the electronic component to a fictitious external potential that acts on plasma electrons, T is the plasma temperature (in energy units). The imaginary part of the response function appearing in (4.62) describes energy dissipation in plasmas. For this reason, the theorem is called the fluctuation–dissipation theorem. The response function is expressed in terms of the dielectric permittivity of the plasma and describes the propagation of various electromagnetic disturbances. After a number of mathematical transformations, the following result can be obtained from (4.62) for the dynamic form factor of an electronic component in a plasma:

$$S(\Delta k) = \left|\frac{\varepsilon^{l(i)}}{\varepsilon^{l}}\right|^2 |\delta n_{\mathrm{e}}|^2 + Z_{\mathrm{i}}\left|\frac{1 - \varepsilon^{l(e)}}{\varepsilon^{l}}\right|^2 |\delta n_{\mathrm{i}}|^2, \tag{4.63}$$

where

$$\left|\delta n_{\mathrm{e,i}}\right|^2 = \frac{n_{\mathrm{e,i}}}{\sqrt{2\pi}\upsilon_{\mathrm{Te}}|\Delta\boldsymbol{k}|}\exp\left(-\frac{\Delta\omega^2}{2\Delta\boldsymbol{k}^2\upsilon_{\mathrm{T,ie}}^2}\right) \tag{4.64}$$

are the Fourier transforms of the squared thermal fluctuations of the electronic and ionic components of the plasma, $\varepsilon^l = \varepsilon^l(\Delta k)$ is the longitudinal part of the plasma dielectric permittivity that describes the propagation of longitudinal plasma waves (corresponding to the density fluctuations), υ_{T} is the thermal velocity of the plasma particles. The indices (i) and (e) designate for the dielectric permittivity and the thermal velocity that these quantities belong to an ionic or electronic plasma component.

Hereafter, the expressions for the longitudinal part of the electronic and ionic dielectric plasma permittivities appearing in the right-hand side of the (4.63) are needed. Their explicit form depends on the relationship between the spatial and time components of the four-vector $\Delta k = (\Delta\boldsymbol{k}, \Delta\omega)$, that is, between the spatial and time characteristics of the electronic and ionic components of the plasma. Thus, the electronic part of the function $\varepsilon^{l(e)}$, for which the relation $|\Delta\omega| < \upsilon_{\mathrm{Te}}|\Delta\boldsymbol{k}|$ holds true, describes the effect of charge screening in a plasma. The corresponding expression looks like

$$\varepsilon^{l(e)}(\Delta\boldsymbol{k}) \cong 1 + \frac{1}{d_{\mathrm{e}}^2|\Delta\boldsymbol{k}|^2}, \tag{4.65}$$

where d_{e} is the Debye screening radius of the electronic component. On the contrary, the reverse inequality $|\Delta\omega| > \upsilon_{\mathrm{Ti}}|\Delta\boldsymbol{k}|$ is characteristic for the ionic component of the longitudinal dielectric permittivity (because of the low velocity of ions). This results in the frequency-dependent relation

$$\varepsilon^{l(i)}(\Delta\omega) \cong 1 - \frac{\omega_{\mathrm{pi}}^2}{\Delta\omega^2}, \tag{4.66}$$

where $\omega_{\mathrm{pi}} = \sqrt{4\pi e^2 n_{\mathrm{i}}/m_{\mathrm{i}}}$ is the ion plasma frequency.

4.4.2 Radiation Scattering by Plasma Electrons

Substituting the DFF of (4.63)–(4.64) into the expression for the cross section of radiation scattering in a plasma (4.59), it is possible to obtain a cross section being a sum of two terms. The first of them is related to the first summand in braces of (4.63). It looks like

$$\frac{\mathrm{d}\sigma_{\mathrm{e}}^{(\mathrm{plas})}(\boldsymbol{k},\boldsymbol{k}')}{\mathrm{d}\Omega'\mathrm{d}\omega'} \cong \frac{\exp\left(-\dfrac{\Delta\omega^2}{2\Delta\boldsymbol{k}^2\upsilon_{\mathrm{Te}}^2}\right)}{\sqrt{2\pi}\upsilon_{\mathrm{Te}}|\Delta\boldsymbol{k}|}\left[\frac{\Delta\boldsymbol{k}^2 d_{\mathrm{e}}^2}{1+\Delta\boldsymbol{k}^2 d_{\mathrm{e}}^2}\right]^2 \frac{1+\cos^2\theta}{2} r_{\mathrm{e}}^2 n_{\mathrm{e}}\mathrm{d}V. \qquad (4.67)$$

The above cross section is connected with radiation scattering by an electronic charge that screens the electron density fluctuation. The electron density fluctuation is described by the factor in the first row of (4.67) containing the thermal velocity of plasma electrons. The factor in square brackets is responsible for screening. It is small in the case of small transferred wave vectors $|\Delta\boldsymbol{k}| < d_{\mathrm{e}}^{-1}$ and tends to one in the opposite limit. Thus scattering by electron density fluctuations is suppressed for small angles of scattering $\theta < 2\arcsin(\lambda/4\pi d_{\mathrm{e}})$ (this inequality is valid for sufficiently short wavelengths $\lambda < 4\pi d_{\mathrm{e}}$).

As can be seen from the frequency dependence in the formula (4.67), the width of the radiation spectrum (scattered by the electron density fluctuations) is defined by the thermal velocity of plasma electrons that in turn is a measure of plasma temperature. The higher the temperature, the wider is the spectrum of scattered photons. The value of the cross section is proportional to the concentration of plasma electrons. Therefore, measuring the intensity and the spectrum of scattered radiation, it is possible to judge such important characteristics of plasma as the temperature and the electron concentration.

The process described by the cross section (4.67) is similar to Compton scattering since a momentum excess is transferred to a plasma electron that carries away considerable recoil energy as in case of the Compton effect with an atom. If the change in wave vector is larger than the reciprocal of the Debye radius, a photon is scattered by each plasma electron "separately", and collective plasma effects can be neglected. Compton scattering of radiation in a plasma is shown in Fig. 4.4, in which the recoil momentum of a plasma electron $\boldsymbol{p}_{\mathrm{e}} = \hbar \cdot \Delta\boldsymbol{k}$ is presented.

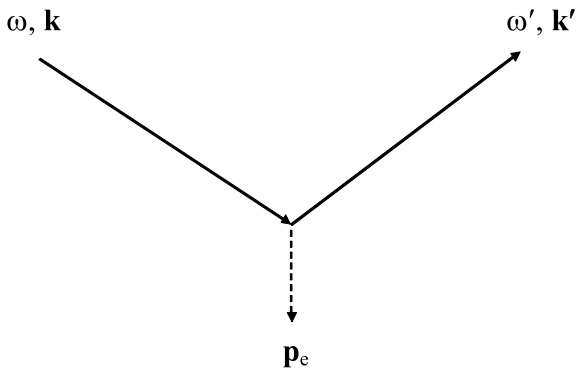

Fig. 4.4 Radiation scattering by a plasma electron

The value of the radiation scattering cross section for one electron is proportional to the squared electron classical radius $r_e^2 \cong 7.84 \times 10^{-25}$ cm^2, i.e. a very small quantity. Note that an atomic unit of cross section that defines, for example, the cross section of electron scattering by atoms is equal to 2.8×10^{-17} cm^2 . Therefore, the possibility to study plasma characteristics with the use of radiation scattering appeared only after the development of laser radiation sources of high spectral radiance (Kunze 1968; Sheffield 1975).

4.4.3 Transient Scattering of Radiation in Plasmas

The cross section of radiation scattering by an electronic charge screening ion density fluctuations looks like

$$\frac{\mathrm{d}\sigma_{\mathrm{i}}^{(\mathrm{plas})}(\boldsymbol{k},\boldsymbol{k}')}{\mathrm{d}\Omega'\mathrm{d}\omega'} \cong \frac{\exp\left(-\dfrac{\Delta\omega^2}{2\Delta\boldsymbol{k}^2 v_{\mathrm{Ti}}^2}\right)}{\sqrt{2\pi}v_{\mathrm{Ti}}|\Delta\boldsymbol{k}|}\left[\frac{Z_{\mathrm{i}}}{1+\Delta\boldsymbol{k}^2 d_{\mathrm{e}}^2}\right]^2 \frac{1+\cos^2\theta}{2} r_{\mathrm{e}}^2 n_{\mathrm{i}}\mathrm{d}V, \qquad (4.68)$$

Z_{i} is the charge of a plasma ion, $n_{\mathrm{i}} = n_{\mathrm{e}}/Z_{\mathrm{i}}$ is the concentration of ions in an electrically neutral plasma. Here the first factor describes ion fluctuations, and the expression in square brackets represents the electronic charge of a Debye sphere that scatters radiation with a specified value $\Delta\boldsymbol{k}$. In the case $|\Delta\boldsymbol{k}| < d_{\mathrm{e}}^{-1}$, the scattering cross section is proportional to the squared charge of an ion, in which the coherent character of the process with respect to the contribution of electrons inside the Debye sphere manifests itself. In case of fulfillment of the reverse inequality, coherence is disturbed, and the scattering cross section decreases as $\Delta\boldsymbol{k}^{-4} d_{\mathrm{e}}^{-4}$. For sufficiently long wavelengths of scattered radiation $\lambda > d_{\mathrm{e}}$, coherence takes place for all angles of scattering. In the opposite limit of short-wavelength radiation, the scattering cross section is maximum in the range $\theta < 2\arcsin(\lambda/4\pi d_{\mathrm{e}})$ and sharply decreases with increasing angle of scattering.

Radiation scattering by a Debye sphere (4.68) is called *transient scattering* (Ginzburg and Tsytovich 1990). This process is represented schematically in Fig. 4.5, in which the recoil momentum of an ion $\boldsymbol{p}_{\mathrm{i}} = \hbar|\Delta\boldsymbol{k}|$ arises in the course of scattering.

Transient scattering is accompanied by the transfer of a momentum excess to a heavy ion, so the change in photon energy is insignificant. The last fact can be demonstrated with the use of the limiting transition

$$\frac{\exp\left(-\dfrac{\Delta\omega^2}{2\Delta\boldsymbol{k}^2 v_{\mathrm{Ti}}^2}\right)}{\sqrt{2\pi}v_{\mathrm{Ti}}|\Delta\boldsymbol{k}|} \to \delta(\Delta\omega) \qquad (4.69)$$

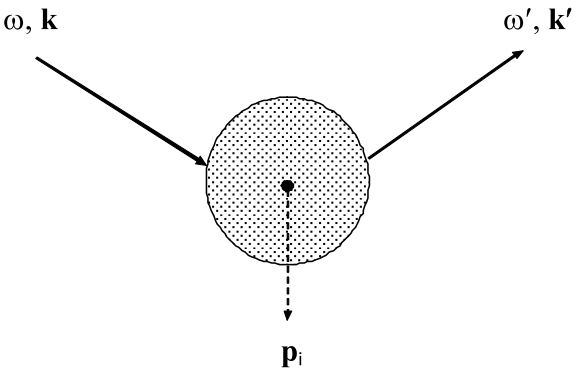

Fig. 4.5 Transient scattering of radiation by a Debye sphere in plasma

that is valid if $|\Delta\omega| \gg \upsilon_{\mathrm{Ti}}|\Delta \boldsymbol{k}|$. From the relation (4.69), it follows that in this case scattering proceeds practically with no change in radiation frequency: $\omega' \cong \omega$. Thus radiation scattering by a Debye sphere is an analog of Rayleigh scattering of radiation by an atom, when the radiation frequency does not change.

4.4.4 Radiation Scattering by a Plasmon

So far, we have considered a photon momentum excess $\Delta \boldsymbol{p}_{\mathrm{ph}} = \hbar\, \Delta \boldsymbol{k}$ that was transferred to individual plasma excitations: electrons and ions. A process involving collective plasma excitation is also possible, when a momentum excess is transferred to a *plasmon* representing a coupled oscillation of an electronic charge and a longitudinal electric field. This process is represented schematically in Fig. 4.6.

A plasmon is characterized by a corresponding dispersion law. It will be remembered that the dispersion law describes the relation between a frequency and a wave vector. For collective excitations (quasi-particles) in plasmas, the dispersion can be obtained from the condition that the dielectric permittivity of a medium is zero, that is, from the condition of the plasma wave propagation. In the case of longitudinal electric field oscillations (a plasmon), the dispersion law is determined by the equation

$$\varepsilon^{(l)}(\boldsymbol{k}, \omega) = 0, \tag{4.70}$$

where $\varepsilon^{(l)}(\boldsymbol{k}, \omega)$ is the longitudinal part of the dielectric permittivity of the medium. In view of the explicit form of the dielectric permittivity of a plasma for $|\boldsymbol{k}| < d_{\mathrm{e}}^{-1}$ according (4.65), we obtain from (4.70):

$$\omega_{\mathrm{pl}}(\boldsymbol{k}) \cong \omega_{\mathrm{pe}} \sqrt{1 + 3\,\boldsymbol{k}^2 d_{\mathrm{e}}^2} \approx \omega_{\mathrm{pe}}. \tag{4.71}$$

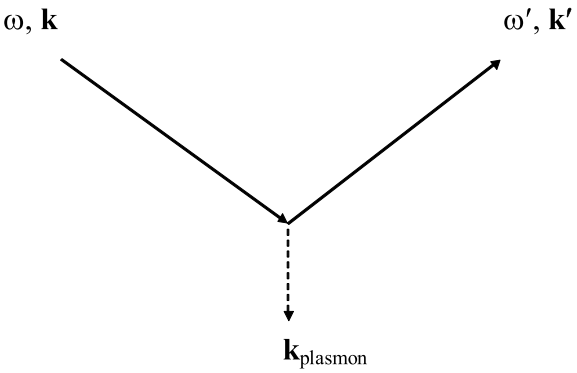

Fig. 4.6 Radiation scattering by a plasmon

Equation (4.71) represents the dispersion law for a plasmon. It corresponds to the propagation of plasmons at the plasma frequency ω_{pe}. For sufficiently large wave vectors $|\boldsymbol{k}| > d_{\mathrm{e}}^{-1}$, a plasmon is a not well-defined excitation since it disappears during times of the order of the plasmon oscillation period.

In case of fulfillment of the plasmon resonance condition (4.70), a singularity appears in the expression for the electron DFF (4.63) that corresponds to emission/absorption of a plasmon. This singularity is caused by the presence of the function $\varepsilon^{(l)}(\Delta\boldsymbol{k}, \Delta\omega)$ in the denominator of the formula (4.63). Due to the presence of the imaginary part in the dielectric permittivity, it approaches a delta function of the form $\delta\big(\Delta\omega \pm \omega_{\mathrm{pl}}(\Delta\boldsymbol{k})\big)$ describing the energy conservation law (the plus sign corresponds to emission of a plasmon, the minus sign corresponds to absorption). Omitting mathematical details, we will write down the expression for the electron DFF with the transfer of an energy–momentum to an emitted plasmon:

$$S_{\mathrm{pl}}(\Delta\boldsymbol{k}, \Delta\omega) = \big(N_{\mathrm{pl}}(\Delta\boldsymbol{k}) + 1\big)\frac{\hbar\omega_{\mathrm{pl}}(\Delta\boldsymbol{k})\Delta\boldsymbol{k}^2}{8\pi e^2}\delta\big(\Delta\omega + \omega_{\mathrm{pl}}(\Delta\boldsymbol{k})\big)\Theta(1 - |\Delta\boldsymbol{k}|d_{\mathrm{e}}), \tag{4.72}$$

where $\Theta(x)$ is the Heaviside step theta function and

$$N_{\mathrm{pl}}(\Delta\boldsymbol{k}) = \frac{1}{\exp\big(\omega_{\mathrm{pl}}(\Delta\boldsymbol{k})/T\big) - 1} \tag{4.73}$$

is the number of plasmons at a specified temperature in thermodynamic equilibrium. Substituting (4.72) into the formula (4.59), after integration with respect to the scattered photon frequency, we obtain the cross section of radiation scattering with generation of a plasmon:

$$\frac{\mathrm{d}\sigma_{\mathrm{pl}}^{(\mathrm{plas})}}{\mathrm{d}\Omega'} = \frac{1+\cos^2\theta}{2} r_{\mathrm{e}}^2 \Theta(1-|\Delta k| d_{\mathrm{e}}) \left(N_{\mathrm{pl}}(\Delta k)+1\right) \frac{\hbar\omega_{\mathrm{pl}}(\Delta k)\Delta k^2}{8\pi e^2} \mathrm{d}V. \quad (4.74)$$

The frequency of the scattered radiation is $\omega' = \omega - \omega_{\mathrm{pl}}(\Delta \boldsymbol{k})$.

For the scattering cross section with plasmon absorption, the expression is similar to (4.74) and the replacement $N_{\mathrm{pl}}(\Delta \boldsymbol{k}) + 1 \to N_{\mathrm{pl}}(\Delta \boldsymbol{k})$ and $\omega' = \omega + \omega_{\mathrm{pl}}(\Delta \boldsymbol{k})$ is quite accurate. From the calculations it follows that by recording the dependence of the scattered photon frequency on the angle of scattering it is possible to determine experimentally the dispersion law for plasmons.

Similar expressions are valid for cross sections of radiation scattering at collective plasma excitations of other types, such as ion-sound waves.

By recording the radiation spectrum (scattered by the plasma), it is possible to study various quasi-particles in plasma. The width of the radiation spectrum scattered by some collective excitation defines the damping constant and accordingly the lifetime of the quasi-particle. Scattering by collective excitations in plasmas accompanied by a change in radiation frequency is an analog of Raman scattering of radiation by atoms and molecules.

Scattering in the X-ray spectral range became an important diagnostic tool for high-energy density science (Glenzer and Redmer 2009; Sheffield et al. 2010) and attracted in particular attention to study the so-called Warm Dense Matter regime (Lee et al. 2003) produced by various means (Kozyreva et al. 2003; Soho et al. 2008; Tauschwitz et al. 2007; Sheffield et al. 2010). The small scattering cross section, however, makes it rather difficult to obtain good signal-to-noise ratios for spectrally resolved analysis unless X-ray scattering sources are not driven by multikilojoule lasers (Glenzer and Redmer 2009; Gamboa et al. 2012).

The advent of the X-ray Free Electron Lasers installations, however, has entirely changed the experimental landscape: dense plasmas are produced with powerful optical lasers (that are built near the experimental XFEL facilities itself) and are then diagnosed with the XFEL (Fletcher et al. 2013; MacDonald et al. 2016). The first experiment where a dense plasma was created with an optical laser and then probed by XFEL has been carried out in 2011 at LCLS (Seely et al. 2011): here, X-ray pumping of inner-shell transitions in dense aluminum plasma has been demonstrated for various charge states (Rosmej et al. 2016).

It should be noted, however, that the high intensity of the XFEL beam perturbs considerably the material to be studied itself, in particular, via strong heating that proceeds from inner-shell ionization followed by subsequent equilibration of photoelectrons (kinetic energy being equal to the access energy of the ionization potential) and Auger electrons in the valence band (so-called Auger electron heating) (Galtier et al. 2011; Rosmej et al. 2012). Therefore, high-resolution X-ray spectroscopy remains a primary diagnostic tool (Renner and Rosmej 2019) although many important parameters can be accessed with scattering diagnostics (e.g., temperature, density, average charge number, collective plasma effects). The access to atomic structure in dense plasmas via X-ray scattering diagnostics is only indirect (via the dynamic form factor) and also therefore high-resolution X-ray spectroscopy appears to be an important complementary diagnostic.

4.5 Scattering on Nanoparticles

The color of the strongest colorants (organic dyes) is defined, as a rule, by absorption of radiation by dye molecules. In interaction of radiation with metal nanoparticles, we encounter a different situation. For small nanosphere radii $r_s < 15 \div 35$ nm absorption dominates, for large radii radiation scattering begins to play a decisive role. The combined effect of absorption and scattering on the passage of a light beam through a substance is described by the extinction cross section $\sigma_{ext} = \sigma_{scat} + \sigma_{abs}$. The quantity $\sigma_{ext} I_0$ represents the power removed from a light beam of intensity I_0 due to absorption and scattering. The ratio of the scattering cross section to the extinction cross section is called *quantum efficiency* $\eta = \sigma_{scat}/\sigma_{ext}$. The quantum efficiency characterizes the relative value of power removed from a light beam that goes into radiation scattering, that is, can be recorded by a photodetector. From the aforesaid, it follows that the quantum efficiency increases with nanoparticle size, but, as it will be seen from further consideration, another important characteristic come into play, namely the quality factor of resonant scattering that decreases with increasing radius.

An important specific feature of photoprocesses with metal nanoparticles is the absence of luminescence under the action of radiation (characteristic of targets with strong optical transitions in the discrete spectrum). As a result, radiation of metal nanoparticles is completely driven by the scattering of the electromagnetic waves. This results, in particular, in a narrow radiation spectrum, when a metal nanosphere is excited by a laser in narrow spectral range.

Spherical nanoparticles of noble metals (gold and silver) find wide application in various fields of research and technologies. In particular, gold nanospheres are used as active nanomarkers in medicine and biology. Besides, the use of metal nanoparticles in various sensors shows promising results.

From the fundamental point of view, the advantage of the spherical form of a nanoparticle consists first of all in the fact that there is no dependence of its optical properties (absorption and scattering cross sections) on the form, i.e. the optical properties depend essentially only on size. This makes it possible to control the characteristics of the electromagnetic response of a nanosphere by changing its radius. Besides, cross sections of radiation scattering and absorption by metal spheres can be described within the framework of a relatively simple analytical approach.

4.5.1 Mie Theory of Radiation Scattering and Absorption

The Mie theory of radiation scattering by a metal sphere in a homogeneous medium is based on the expansion of an electromagnetic field in terms of cylindrical harmonics (due to the cylindrical symmetry of the problem) and "joining" of tangential components of the strength of electric and magnetic fields at the boundary of the

sphere (Jackson 2007). To satisfy these boundary conditions, it is necessary to take into account the field irradiating the sphere. A field inside the sphere and a secondary wave field representing the scattered wave. The derivation of corresponding formulas is rather cumbersome, but they are available in classical monographs on optics (Van de Hulst 1981; Born and Wolf 1999), and we will give here only the final result. The cross section of radiation scattering by a metal sphere according to the Mie theory is

$$\sigma_{\text{scat}}^{(\text{Mie})} = \frac{2\pi c^2}{\varepsilon_{\text{m}}\omega^2}\sum_{n=1}^{\infty}(2n+1)\left\{|a_{\text{n}}(x,mx,m)|^2 + |b_{\text{n}}(x,mx,m)|^2\right\}, \tag{4.75}$$

where a_{n}, b_{n} are the Mie coefficients that are given by the formulas (2.78)–(2.81), the parameters x and m are given by:

$$x = kr_{\text{s}} = \sqrt{\varepsilon_{\text{m}}}\frac{\omega}{c}r_{\text{s}}. \tag{4.76}$$

The variable x from (4.76) is the product of the wave vector of radiation in the matrix with the nanosphere radius and

$$m = \sqrt{\varepsilon_{\text{s}}(\omega)/\varepsilon_{\text{m}}} \tag{4.77}$$

is the ratio of the refractive indices of the nanosphere and the matrix material.

Equation (4.75), in contrast to (4.74), takes into account not only the dipole summand $(n = 1)$, but also the terms corresponding to the contribution of higher order multipoles $(n > 1)$. This is essential for short wavelengths, when the condition of the dipole approximation $(\lambda \gg r_{\text{s}})$ is not fulfilled.

The results of calculation of the cross section of radiation scattering by silver spheres of different sizes within the framework of the Mie theory are presented in Fig. 4.7 in the spectral range close to the plasmon resonance.

From Fig. 4.7, it follows that with increasing size of the metal nanosphere the position of the scattering cross section maximum is shifted to the long-wavelength region, and the width of the spectral maximum increases. For radii of 30 and 40 nm, a second peak appears due to a quadrupole resonance in excitation of a surface plasmon. The quadrupole term corresponds to $n = 2$ in the sum (4.75).

A decrease in frequency and an increase in the spectral width of the plasmon resonance with increasing nanosphere size result in a decrease of the quality factor Q of plasmon excitation that by definition is $Q = \omega_{\text{res}}/\Delta\omega$. For a gold nanosphere, the value of the quality factor decreases from 8 to 2.5 as the radius changes from 30 to 80 nm. In this case, the resonance energy decreases from 2.2 to 1.7 eV. In case of a similar change in the radius of a silver nanosphere, the quality factor of a surface plasmon decreases from 11 to 4, and the resonance energy decreases from 2.7 to 2.5 eV.

The quality factor of a plasmon resonance is very important since it is equal to the coefficient of amplification of a local field, i.e., it defines the value of the

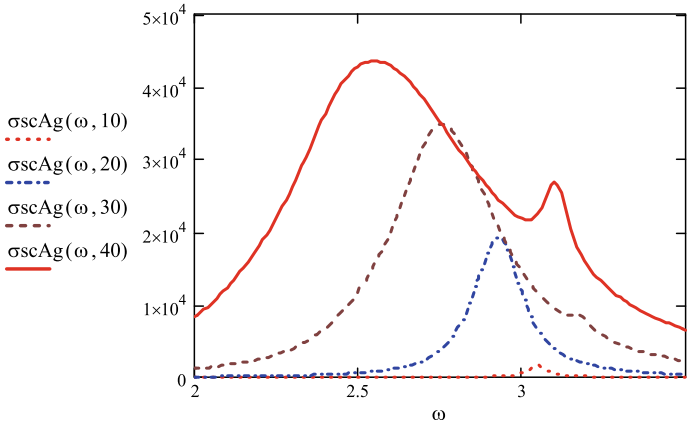

Fig. 4.7 Cross sections of radiation scattering by silver nanospheres of different radii (10, 20, 30, 40 nm) in a medium with $\varepsilon_m = 2.25$ and in the vicinity of a plasmon resonance; the abscissa is the photon energy in eV, the ordinate is the cross section in nm^2

strength of an electric field connected with a surface plasmon (this field is acting on particles in the vicinity of the surface). As a result of this amplification, it is possible to observe a whole class of nonlinear optical phenomena, such as Raman scattering that are otherwise practically not observable (or would require otherwise super-strong electromagnetic fields for their recording).

For the cross section of radiation extinction by a metal sphere, the Mie theory gives (Van de Hulst 1981)

$$\sigma_{\text{ext}}^{(\text{Mie})} = \frac{2\pi c^2}{\varepsilon_m \omega^2} \sum_{n=1}^{\infty} (2n+1) Re\{a_n(x, mx, m) + b_n(x, mx, m)\}. \tag{4.78}$$

The expressions for the expansion coefficients a_n, b_n are given in Chap. 2 [formulas (2.78)–(2.81)], the parameters x and m are given by (4.76)–(4.77). The extinction describes the radiation intensity as a result of absorption and scattering by the substance particles.

As was already mentioned, the cross section of radiation absorption is equal to the difference of the cross sections of extinction and scattering $\sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{scat}}$. With the use of this relation and the expressions (4.75), (4.78), it is possible to calculate the cross section of photoabsorption by a metal sphere. The calculations for silver spheres in a medium with $\varepsilon_m = 2.25$ (glass) of different radii are presented in Fig. 4.8. It is seen that in contrast to the scattering cross section the absorption cross section has a considerably more strong quadrupole resonance that even dominates over the dipole resonance even at a sphere radius of 30 nm.

The numerical analysis within the framework of the Mie theory shows that in the case of silver nanospheres the cross sections maxima of absorption and scattering of radiation at a plasmon become equal for a radius of 15 nm; for larger radii, scattering dominates over absorption. In the case of gold nanospheres, scattering

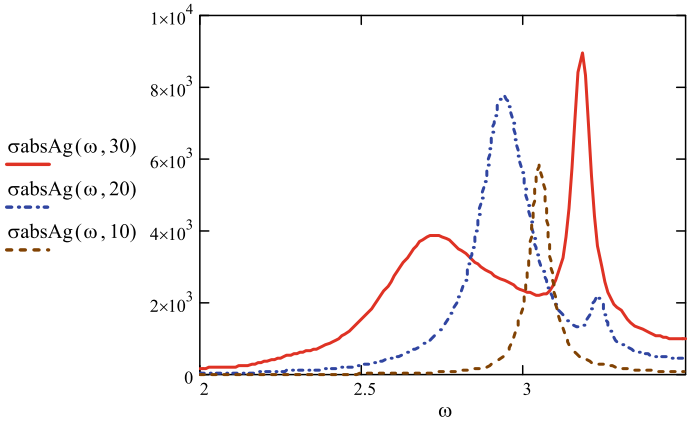

Fig. 4.8 The cross section of radiation absorption by silver spheres of different radii (10, 20, 30 nm) calculated within the framework of the Mie theory in the region of a plasmon resonance. The abscissa is the photon energy in eV, the ordinate is the cross section in nm^2

becomes equal to absorption for a radius of 37 nm and the maximum of the spectral cross section of scattering is shifted (with respect to the absorption maximum) to the region of lower photon energies by about 0.1 eV. The ratio of scattering and absorption cross sections is related to the quantum efficiency of scattered radiation that is an important parameter for the practical application of nanoparticles.

It should be emphasized that the strong dependence of spectra of radiation scattering and absorption in the vicinity of a plasmon resonance on the sphere radius results in inhomogeneous broadening for an ensemble of nanoparticles with an appreciable spread of radii. This should be taken into account in the analysis of corresponding experimental data.

Naturally, the Mie theory has a certain range of applicability. This is connected first of all with the phenomenological description of a nanoparticle material by the use of the dielectric permittivity. Such an approach is valid for sufficiently large nanoparticles and radiation wavelengths, when the substance can be considered as a continuum. In the case of small-sized nanoparticles, local effects become important that are not taken into account when using the bulk dielectric permittivity of a metal. Finally, the Mie theory assumes the presence of a sharp boundary of a metal sphere, which is also an approximation.

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