Let us write

$$\mathrm{d}\mathbf{k}_f = k_f^2\,\mathrm{d}k_f\,\mathrm{d}\Omega \tag{4.198}$$

where $\mathrm{d}\Omega \equiv \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ and (θ, ϕ) are the polar angles of $\mathbf{k}_f$. Using (4.193), we also have

$$\mathrm{d}\mathbf{k}_f = \frac{k_f m}{\hbar^2}\,\mathrm{d}E_f\,\mathrm{d}\Omega \tag{4.199}$$

so that we may rewrite (4.196) in the form

$$\sigma_{\mathrm{tot}} = \frac{4\pi^2\alpha}{m}\int_0^\infty \mathrm{d}E_f \int \mathrm{d}\Omega\,\frac{k_f}{\omega_{ba}}|M_{ba}(\omega_{ba})|^2\,\delta\left(\omega - \frac{E_f - E_{1s}}{\hbar}\right) \tag{4.200}$$

Performing the integration over E_f with the help of the delta function, we find that

$$\sigma_{\mathrm{tot}} = \frac{4\pi^2\alpha\hbar}{m}\left(\frac{k_f}{\omega}\right)\int |M_{ba}(\omega)|^2\,\mathrm{d}\Omega \tag{4.201}$$

The differential cross-section for an electron to be ejected within the solid angle $\mathrm{d}\Omega$ in the direction (θ, ϕ) is therefore

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{4\pi^2\alpha\hbar}{m}\left(\frac{k_f}{m}\right)|M_{ba}(\omega)|^2 \tag{4.202}$$

From (4.40) and (4.195) the matrix element M_{ba} is given by

$$M_{ba} = (2\pi)^{-3/2}\int \exp(-\mathrm{i}\mathbf{k}_f\cdot\mathbf{r})\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\,\hat{\boldsymbol{\varepsilon}}\cdot\nabla\psi_{1s}(r)\,\mathrm{d}\mathbf{r} \tag{4.203}$$

Upon integration by parts, we find that

$$M_{ba} = (2\pi)^{-3/2}[-\mathrm{i}\hat{\boldsymbol{\varepsilon}}\cdot(\mathbf{k}-\mathbf{k}_f)]\int \exp[\mathrm{i}(\mathbf{k}-\mathbf{k}_f)\cdot\mathbf{r}]\psi_{1s}(r)\,\mathrm{d}\mathbf{r} \tag{4.204}$$

Since $\mathbf{k}\cdot\hat{\boldsymbol{\varepsilon}} = 0$, we have

$$\hat{\boldsymbol{\varepsilon}}\cdot(\mathbf{k}-\mathbf{k}_f) = -k_f\cos\gamma \tag{4.205}$$

where γ is the angle between the direction of ejection and the direction of polarisation (see Fig. 4.7). The integral appearing in (4.204) is proportional to the Fourier transform of the ground state wave function $\psi_{1s}(r)$, namely

$$\int \exp(\mathrm{i}\mathbf{K}\cdot\mathbf{r})\,\psi_{1s}(r)\,\mathrm{d}\mathbf{r} = 8\pi\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}\frac{Z/a_0}{[(Z/a_0)^2 + K^2]^2} \tag{4.206}$$

where we have introduced the vector

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_f \tag{4.207}$$

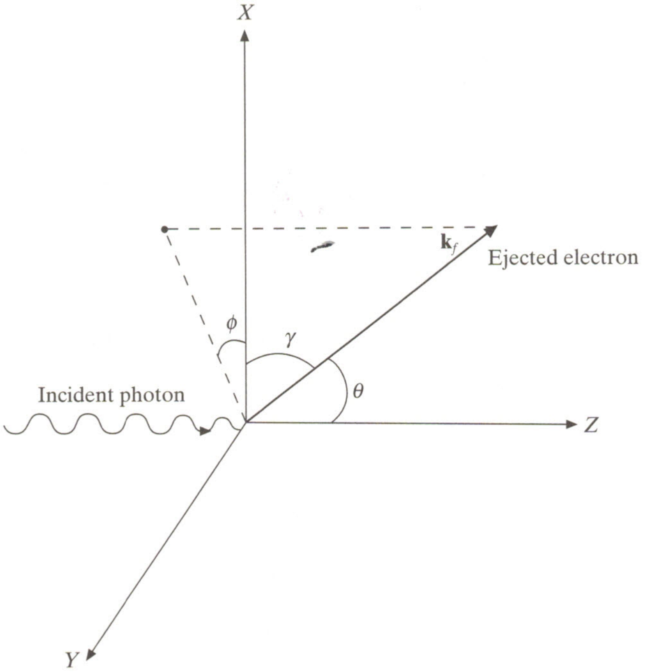

Figure 4.7 The angles employed in the discussion of the photoelectric effect. The incident radiation is in the Z direction, with polarisation vector in the X direction. The momentum of the ejected electron is $\hbar\mathbf{k}_f$.

From (4.202) and (4.204)–(4.207), the differential cross-section is seen to be given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = 32\alpha\left(\frac{\hbar}{m}\right)\left(\frac{k_f^3}{\omega}\right)\frac{Z^5 a_0^3 \cos^2\gamma}{[Z^2 + K^2 a_0^2]^4} \tag{4.208}$$

Without loss of generality we can take the direction of propagation $\hat{\mathbf{k}}$ of the radiation to be along the Z axis and the direction of the polarisation vector $\hat{\boldsymbol{\varepsilon}}$ to be the X direction. Then, as $\mathbf{k}_f$ is in the direction $\Omega \equiv (\theta, \phi)$, we have (see Fig. 4.7)

$$\cos\gamma = \sin\theta\cos\phi \tag{4.209}$$

and

$$K^2 = k^2 + k_f^2 - 2k\, k_f \cos\theta \tag{4.210}$$

At incident photon energies well in excess of the ionisation threshold ($\simeq$13.6 eV for atomic hydrogen), when $\hbar\omega \gg |E_{1s}|$, we have from (4.193) and (4.197)

$$\hbar\omega \simeq \frac{\hbar^2 k_f^2}{2m} \tag{4.211}$$

and since $\omega = kc$ it follows that

$$\frac{k}{k_f} \simeq \frac{\hbar k_f}{2mc} = \frac{v_f}{2c} \tag{4.212}$$

where v_f is the velocity of the ejected electron. In the non-relativistic regime, for which $v_f/c \ll 1$, we can use this result to write

$$K^2 \simeq k_f^2\left(1 - \frac{v_f}{c}\cos\theta\right) \tag{4.213}$$

Moreover, since $\hbar\omega \simeq \hbar^2 k_f^2/(2m) \gg |E_{1s}|$ and $E_{1s} = -Z^2[e^2/(4\pi\varepsilon_0)]/(2a_0)$, we have

$$k_f^2 a_0^2 \gg \frac{2m}{\hbar^2}|E_{1s}|a_0^2 = Z^2 \tag{4.214}$$

so that

$$Z^2 + K^2 a_0^2 \simeq k_f^2 a_0^2\left(1 - \frac{v_f}{c}\cos\theta\right) \tag{4.215}$$

and the differential cross-section (4.208) becomes

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = 32\alpha\left(\frac{\hbar}{m}\right)\frac{Z^5}{\omega(k_f a_0)^5}\frac{\sin^2\theta\cos^2\phi}{\left(1 - \frac{v_f}{c}\cos\theta\right)^4} \tag{4.216}$$

We note that the ejected electrons have a cosine-squared distribution with respect to the polarisation vector $\hat{\boldsymbol{\varepsilon}}$ of the incident radiation. For an *unpolarised* photon beam an average must be made over the polarisations of the photon, so that we have in that case

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = 16\alpha\left(\frac{\hbar}{m}\right)\frac{Z^5}{\omega(k_f a_0)^5}\frac{\sin^2\theta}{\left(1 - \frac{v_f}{c}\cos\theta\right)^4} \tag{4.217}$$

We remark that both cross-sections (4.216) and (4.217) exhibit a sine-squared distribution in the angle θ, which favours the ejection of the electrons at right angles to the incident photon beam. The quantity $(1 - v_f\cos\theta/c)^{-4}$ also affects the angular distribution by enhancing the ejection of electrons at small angles, but since $v_f/c \ll 1$ it only yields a small correction to the $\sin^2\theta$ distribution. In fact, because

$$\left(1 - \frac{v_f}{c}\cos\theta\right)^{-4} = 1 + 4\frac{v_f}{c}\cos\theta + \dots \tag{4.218}$$

we see that if we drop terms of order $(v_f/c)^2$ we may write the differential cross-section (4.217) as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = 16\alpha\left(\frac{\hbar}{m}\right)\frac{Z^5}{\omega(k_f a_0)^5}\sin^2\theta\left(1 + 4\frac{v_f}{c}\cos\theta\right) \tag{4.219}$$

Upon integration over the angles (θ, ϕ) of the ejected electron, the total cross-section (for an unpolarised incident photon beam) is given by

$$\sigma_{\text{tot}} = \frac{128\pi}{3}\alpha\left(\frac{\hbar}{m}\right)\frac{Z^5}{\omega(k_f a_0)^5} \tag{4.220a}$$

Using (4.211) and the fact that $E_{1s} = -Z^2[e^2/(4\pi\varepsilon_0)]/(2a_0) = -(1/2)mc^2(Z\alpha)^2$, we may also write (4.220a) as

$$\sigma_{\text{tot}} = \frac{256\pi}{3}\alpha Z^{-2}\left(\frac{|E_{1s}|}{\hbar\omega}\right)^{7/2} a_0^2 \tag{4.220b}$$

or

$$\sigma_{\text{tot}} = \frac{16\sqrt{2}\pi}{3}\alpha^8 Z^5\left(\frac{mc^2}{\hbar\omega}\right)^{7/2} a_0^2 \tag{4.220c}$$

We note from (4.220) that the photoelectric total cross-section decreases like $(\hbar\omega)^{-7/2}$ with increasing photon energy and increases like Z^5 with increasing nuclear charge. We also remark that the *dipole approximation* (obtained by setting $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}) = 1$ in the matrix element (4.203)) yields the leading term in the differential cross-section (4.219), such that retardation effects of order v_f/c are neglected. As seen from (4.212), these retardation effects become more important if the wave number k (and hence the frequency ν) of the photon increases, as expected from our discussion of the dipole approximation in Section 4.3.

Let us call $\mathrm{d}\sigma^{(0)}/\mathrm{d}\Omega$ the leading (dipole) term in (4.219). We then have

$$\frac{\mathrm{d}\sigma^{(0)}}{\mathrm{d}\Omega} = 16\alpha\left(\frac{\hbar}{m}\right)\frac{Z^5}{\omega(k_f a_0)^5}\sin^2\theta \tag{4.221a}$$

or

$$\frac{\mathrm{d}\sigma^{(0)}}{\mathrm{d}\Omega} = 32\alpha Z^{-2}\left(\frac{|E_{1s}|}{\hbar\omega}\right)^{7/2}\sin^2\theta\, a_0^2 \tag{4.221b}$$

It is also worth noting that the dipole approximation yields the *complete* result (4.220) for the total cross-section σ_{tot}.

Finally, we recall that the above formulae are applicable for sufficiently high, but non-relativistic energies E_f of the ejected electron, such that $|E_{1s}| \ll E_f \ll mc^2$ and for small enough values of Z. These formulae can be applied not only to photoionisation from the ground state of hydrogenic atoms and ions, but also approximately to the photoionisation of electrons from the K shell of complex atoms.

4.9 The scattering of radiation by atomic systems

So far in this chapter, the processes considered for obtaining information about the properties of atoms are the emission or absorption of radiation in the case that the electromagnetic field is weak enough for first-order perturbation theory to apply. Additional information can be obtained by using strong fields, and this will be considered in Chapter 15. Here we shall discuss briefly the *scattering* of radiation by atomic systems again in the weak field case.

The scattering of radiation by an atom or molecule must be at least a second-order process. In step 1, a photon of energy $\hbar\omega$ and wave vector $\mathbf{k}$ is absorbed exciting the atomic system from a state a to a state n. In step 2 the atomic system emits a photon of energy $\hbar\omega'$ and wave vector $\mathbf{k}'$, and is de-excited from the state n to a final state b. Alternatively, the two steps can occur in reverse order, the photon of energy $\hbar\omega'$ being emitted first and the photon of energy $\hbar\omega$ being absorbed subsequently. In what follows, it will be assumed that a represents a non-degenerate ground state.

If the final state b of the system is the same as the initial state a, then, neglecting very small recoil effects (see Problem 1.16), the emitted radiation has the same frequency as the incident radiation ($\omega' = \omega$). This elastic scattering process is called *Rayleigh scattering*; it was first discussed by Lord Rayleigh in connection with the scattering of light by molecules in the atmosphere. If the final state of the atom is different from the initial state, the scattering is inelastic, and by conservation of energy the angular frequency ω' of the emitted radiation is given by

$$\begin{aligned}\omega' &= \omega + (E_a - E_b)/\hbar \\ &= \omega - \omega_{ba}\end{aligned} \qquad \textbf{(4.222)}$$

This inelastic scattering process is called *Raman scattering* (or the Raman effect) after C.V. Raman who discovered this effect experimentally in 1927. The theory of both Rayleigh and Raman scattering may be developed in a straightforward way by solving the coupled equations (4.32) to second order. If the dipole approximation is made, the differential cross-section for the emission of a photon in the direction (θ, ϕ) when the incident photon direction is along the Z axis is found to be

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\theta, \phi) = r_0^2 \omega\omega'^3 \frac{m^2}{\hbar^2 e^4} \left| \sum_n \left[\frac{(\hat{\varepsilon}' \cdot \mathbf{D}_{bn})(\hat{\varepsilon} \cdot \mathbf{D}_{na})}{\omega_{na} - \omega} + \frac{(\hat{\varepsilon} \cdot \mathbf{D}_{bn})(\hat{\varepsilon}' \cdot \mathbf{D}_{na})}{\omega_{na} + \omega'} \right] \right|^2 \qquad \textbf{(4.223)}$$

where

$$r_0 = \frac{e^2}{(4\pi\varepsilon_0)mc^2} = 2.82 \times 10^{-15}\ \mathrm{m} \qquad \textbf{(4.224)}$$

is the *classical radius of the electron*. In (4.223), $\mathbf{D}_{ij}$ denotes the matrix element of the electric dipole moment operator of the atom between the states i and j, while $\hat{\varepsilon}$ and $\hat{\varepsilon}'$ are the polarisation vectors of the photons in the initial and final states, respectively. The sum over n is over all possible intermediate states.

By the usual electric dipole selection rules the intermediate state n must be of opposite parity to each of the states a and b. Thus, in second order, scattering does not change the parity of the atomic system, and the selection rules are, for a one-electron atom [15],

$$\Delta l = 0, \pm 2 \tag{4.225}$$

If the angular frequency of the incident radiation is such that $\omega = \omega_{na}$, where $\omega_{na} = (E_n - E_a)/\hbar$ and E_n is the energy of one of the intermediate states, then the first term in the cross-section formula (4.223) becomes infinite. This is due to the fact that in deriving the result (4.223) the width of the atomic energy levels has been neglected. Taking the state a to be a stable ground state of zero width and replacing E_n by $E_n - \mathrm{i}\Gamma_n/2$ where Γ_n is the width of the level n, the correct behaviour of the cross-section in the *resonance region*, in which ω is close to ω_{na}, is found to be

$$\frac{\mathrm{d}\sigma_{ba}}{\mathrm{d}\Omega}(\theta, \phi) = r_0^2 \omega \omega'^3 \frac{m^2}{\hbar^2 e^4} \left| \frac{(\hat{\varepsilon}' \cdot \mathbf{D}_{bn})(\hat{\varepsilon} \cdot \mathbf{D}_{na})}{\omega_{na} - \mathrm{i}\Gamma_n/(2\hbar) - \omega} \right|^2 \tag{4.226}$$

The corresponding total cross-section $\sigma_{ba}(\omega)$ is of Lorentzian form, being given by

$$\sigma_{ba}(\omega) = r_0^2 \omega \omega'^3 \frac{m^2}{\hbar e^4} \frac{1}{(\omega - \omega_{na})^2 + \Gamma_n^2/(4\hbar^2)} \int |(\hat{\varepsilon}' \cdot \mathbf{D}_{bn})\,(\hat{\varepsilon} \cdot \mathbf{D}_{na})|^2 \,\mathrm{d}\Omega \tag{4.227}$$

In the elastic case, with $\omega = \omega'$ and $E_a = E_b$, the scattered light is known as *resonance radiation*, while in the inelastic case (resonant Raman scattering), with $\omega \neq \omega'$ and $E_a \neq E_b$, the scattered radiation is called *resonance fluorescence*. As we have taken a to be the ground state, E_n is necessarily greater than E_a, so that $\omega' < \omega$ and the fluorescence is of longer wavelength than the incident radiation. Resonance radiation and resonance fluorescence are easily observed, for example by shining a collimated beam from a sodium vapour lamp on sodium vapour confined in a glass vessel.

Let us define τ_{an} as the lifetime of the state n for decay into the state a and τ_{bn} as the corresponding lifetime for decay from the state n to the state b. *Partial widths* Γ_{an} and Γ_{bn} can then be defined as $\Gamma_{an} = \hbar/\tau_{an}$ and $\Gamma_{bn} = \hbar/\tau_{bn}$. If decay to the states a and b are the only decay modes of the state n, then the full natural width Γ_n is given by the sum of the partial widths:

$$\Gamma_n = \Gamma_{an} + \Gamma_{bn} \tag{4.228}$$

In general, the state n will decay in additional ways, for example by collisions, and the observed width $\tilde{\Gamma}_n$ will be larger than $(\Gamma_{an} + \Gamma_{bn})$.

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[15] For a general atom the selection rules for second-order scattering are $\Delta J = 0, \pm 2$, where J is the total angular momentum quantum number, and the parity does not change.

Making use of (4.170) and (4.180), the total cross-section in the resonance region $\sigma_{ba}(\omega)$ can be written in the form

$$\sigma_{ba}(\omega) = \frac{1}{2} g_n \frac{\pi c^2}{\hbar^2 \omega^2} \frac{\Gamma_{bn}\Gamma_{an}}{(\omega - \omega_{na})^2 + \Gamma_n^2/(4\hbar^2)} \tag{4.229}$$

where g_n is the degeneracy of the intermediate state n. The maximum of the cross-section occurs at exact resonance ($\omega = \omega_{na}$). For Rayleigh (elastic) scattering ($\omega' = \omega$), it has the value

$$\sigma_{\text{el}}^{\max} = 2\pi g_n \left(\frac{c}{\omega_{na}}\right)^2 \left(\frac{\Gamma_{an}}{\Gamma_n}\right)^2 \tag{4.230}$$

while for resonant Raman scattering ($\omega' \neq \omega$), it is given by

$$\sigma_{ba}^{\max} = 2\pi g_n \left(\frac{c}{\omega_{na}}\right)^2 \frac{\Gamma_{bn}\Gamma_{an}}{\Gamma_n^2} \tag{4.231}$$

By setting $b = n$ in (4.181), and assuming that Γ_{an} and Γ_{bn} are similar in magnitude, it is found that the absorption cross-section from the state a to the state n is of the same order of magnitude as the resonant scattering cross-sections (4.230) and (4.231). The cross-section for non-resonant Rayleigh scattering is smaller than that for resonant Rayleigh scattering by a factor of up to 10^{10} while that for non-resonant Raman scattering is even smaller by a further factor of about 10^3. Nevertheless, Raman scattering is very important in the theory of rotational molecular spectra; this will be discussed in Chapter 11.

Non-resonant elastic scattering in the low- and high-frequency limits

The cross-section for non-resonant Rayleigh (elastic) scattering given by (4.223) can be written as

$$\frac{d\sigma}{d\Omega}(\theta, \phi) = r_0^2 \omega^4 \frac{m^2}{\hbar^2} \left| \sum_n (\hat{\boldsymbol{\varepsilon}}' \cdot \mathbf{r}_{an})(\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r}_{na}) \frac{2\omega_{na}}{\omega_{na}^2 - \omega^2} \right|^2 \tag{4.232}$$

where, for a one-electron atom, $\mathbf{D}$ has been set equal to $-e\mathbf{r}$ (see (4.72)).

We shall start by looking at the low-frequency limit of the cross-section for scattering by the ground state of the atom, where the initial state a is an s state with $l_a = 0$. By the dipole selection rules all the intermediate states n must be p states ($l_n = 1$) with magnetic quantum numbers $m_n = 0, \pm 1$. It is convenient to take the Z axis parallel to the unit vector $\hat{\boldsymbol{\varepsilon}}$, which is in the direction of polarisation of the incident radiation, so that

$$\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{r}_{na} = z_{na} \tag{4.233}$$

From (4.117a) it is seen that z_{na} vanishes unless $m_n = 0$. It follows that the only non-vanishing component of $\mathbf{r}_{an}$ is z_{an} so that $\hat{\boldsymbol{\varepsilon}}' \cdot \mathbf{r}_{an} = \hat{\varepsilon}'_z z_{an}$. Since $\hat{\boldsymbol{\varepsilon}}$ is a unit vector parallel to the Z axis, $\hat{\varepsilon}'_z = \hat{\boldsymbol{\varepsilon}}' \cdot \hat{\boldsymbol{\varepsilon}}$ and the cross-section (4.232) reduces to

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\theta, \phi) = r_0^2 \omega^4 \frac{m^2}{\hbar^2} (\hat{\varepsilon}' \cdot \hat{\varepsilon})^2 \left| \sum_n |z_{an}|^2 \frac{2\omega_{na}}{\omega_{na}^2 - \omega^2} \right|^2 \tag{4.234}$$

where the sum is over all p states of the atom, including both discrete and continuum states.

In the low-frequency limit ($\omega \ll \omega_{\bar{n}a}^2$) where $\bar{n}$ is the p state of lowest energy, the sum over n reduces to

$$\sum_n \frac{2}{\omega_{na}} |z_{an}|^2 = \frac{\hbar}{e^2} \bar{\alpha} \tag{4.235}$$

where

$$\bar{\alpha} = 2e^2 \sum_{n \neq a} \frac{|z_{an}|^2}{E_n - E_a} \tag{4.236}$$

is a quantity known as the *static dipole polarisability* of the atom in the ground state a.

From (4.234) and (4.235) the total cross-section for low-frequency scattering of radiation by the ground state of a one-electron atom is

$$\sigma_{\mathrm{tot}} = \left(\frac{r_0 m \bar{\alpha}}{e^2} \right)^2 \omega^4 \int (\hat{\varepsilon}' \cdot \hat{\varepsilon}) \, \mathrm{d}\Omega \tag{4.237}$$

To evaluate (4.237) it is easiest to take the polar axis parallel to $\hat{\boldsymbol{\varepsilon}}$. Two cases need to be considered, corresponding to the two independent possible polarisation directions of the scattered radiation: either $\hat{\boldsymbol{\varepsilon}}' = \hat{\boldsymbol{\varepsilon}}'(1)$ where $\hat{\boldsymbol{\varepsilon}}'(1)$ is in the plane containing $\hat{\boldsymbol{\varepsilon}}$ and $\mathbf{k}'$, or $\hat{\boldsymbol{\varepsilon}}' = \hat{\boldsymbol{\varepsilon}}'(2)$ where $\hat{\boldsymbol{\varepsilon}}'(2)$ is normal to the $(\hat{\boldsymbol{\varepsilon}}, \mathbf{k}')$ plane. In the second case the cross-section vanishes since $\hat{\boldsymbol{\varepsilon}} \cdot \hat{\boldsymbol{\varepsilon}}'(2) = 0$. In the first case, since $\mathbf{k}'$ and $\hat{\boldsymbol{\varepsilon}}'(1)$ must be at right angles to each other, we have

$$\hat{\boldsymbol{\varepsilon}}'(1) \cdot \hat{\boldsymbol{\varepsilon}} = \cos \alpha = \sin \theta \tag{4.238}$$

where α is the angle between the vectors $\hat{\boldsymbol{\varepsilon}}'(1)$ and $\hat{\boldsymbol{\varepsilon}}$ and θ, the angle of scattering, is the angle between $\mathbf{k}$ and $\mathbf{k}'$. From (4.237) and (4.238), we have

$$\begin{aligned} \sigma_{\mathrm{tot}} &= \left(\frac{r_0 m \bar{\alpha}}{e^2} \right)^2 \omega^4 \int \sin^2\theta \, \mathrm{d}\Omega \\ &= \frac{8\pi}{3} \left(\frac{r_0 m \bar{\alpha}}{e^2} \right)^2 \omega^4 \end{aligned} \tag{4.239}$$

The rapid increase of the scattering cross-section with ω at angular frequencies $\omega < \omega_{\bar{n}a}$, where $\bar{n}$ is the first excited p state, is a general feature, although the formula (4.239) is specific to hydrogenic atoms. As a consequence, the scattering of sunlight by atmospheric atoms increases towards the high-frequency end of the visible spectrum and is responsible for the blue appearance of the sky.

The second special case of the cross-section formula (4.232) is when ω is large compared with ω_{na} for all important intermediate states n. In this limit

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\theta, \phi) = 4r_0^2\left(\frac{m}{\hbar}\right)^2\left|\sum_n(\hat{\boldsymbol{\varepsilon}}'\cdot\mathbf{r}_{an})(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{na})\,\omega_{na}\right|^2 \tag{4.240}$$

Let us introduce axes so that $\hat{\boldsymbol{\varepsilon}}$ is parallel to the Z axis, with $\hat{\boldsymbol{\varepsilon}}'$ lying in the XZ plane. The sum over n is then given by

$$\sum_n(\hat{\boldsymbol{\varepsilon}}'\cdot\mathbf{r}_{an})(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{na})\,\omega_{na} = \hat{\varepsilon}'_x\sum_n x_{an}z_{na}\omega_{na} + \hat{\varepsilon}'_z\sum_n|z_{na}|^2\omega_{na} \tag{4.241}$$

Now z_{na} vanishes unless $m_n = m_a$, where m_n and m_a are the magnetic quantum numbers of the states n and a respectively. Similarly x_{an} vanishes unless $m_n = m_a \pm 1$. It follows that the sum $\Sigma_n\, x_{an}z_{na}\omega_{na}$ vanishes. The second sum in (4.241) can be seen from (4.138) and (4.142) to be given by $\Sigma_n|z_{na}|^2\omega_{na} = \hbar/(2m)$. From (4.240) the total scattering cross-section becomes

$$\sigma_{\text{tot}} = r_0^2\int\hat{\varepsilon}_z'^2\,\mathrm{d}\Omega = r_0^2\int(\hat{\boldsymbol{\varepsilon}}'\cdot\hat{\boldsymbol{\varepsilon}})^2\,\mathrm{d}\Omega \tag{4.242}$$

The integration over the angles in (4.242) is the same as in the previous case of low-frequency scattering, so that

$$\sigma_{\text{tot}} = \frac{8\pi}{3}r_0^2 \tag{4.243}$$

This result is independent of the initial state a, and hence can be applied to the scattering of radiation by a free electron. This is called *Thomson scattering*. The derivation which has been given here is non-relativistic and the cross-section formula (4.243) ceases to be accurate when the energy of the incident photon $\hbar\omega$ becomes comparable with the rest energy of the target electron mc^2. Both the low-frequency limit of Rayleigh scattering and the high-frequency Thomson scattering do not depend on Planck's constant h; these cross-sections were originally derived using classical electromagnetic theory (see Jackson, 1998).

Problems

4.1 Calculate how many photons per second are radiated from a monochromatic source, 1 watt in power, for the following wavelengths: (a) 10 m (radio wave) (b) 10 cm (microwave) (c) 5890 Å (yellow sodium light) (d) 1 Å (soft X-ray). At a distance of 10 m from the source, calculate the number of photons passing through unit area, normal to the direction of propagation, per unit time and the density of photons, in each case.

4.2 (a) Establish the result (4.78) starting from equation (4.76).

(b) The full transition rate for spontaneous emission of a photon from an atom is obtained in the dipole approximation from (4.79), by integrating over all angles of emission and summing over two independent polarisation directions $\hat{\boldsymbol{\varepsilon}}_1, \hat{\boldsymbol{\varepsilon}}_2$:

$$W_{ab}^{s,D} = \frac{1}{2\pi\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega_{ba}^3 \int d\Omega\{|\hat{\boldsymbol{\varepsilon}}_1\cdot\mathbf{D}_{ba}|^2 + |\hat{\boldsymbol{\varepsilon}}_2\cdot\mathbf{D}_{ba}|^2\}$$

Starting from this expression obtain the result (4.80).

4.3 Show that by performing the gauge transformation (4.89), one obtains for the new wave function $\Psi^V(\mathbf{r}, t)$ the Schrödinger equation in the velocity gauge (4.90).

4.4 Show that by performing the gauge transformation (4.92), one obtains for the new wave function $\Psi^L(\mathbf{r}, t)$ the Schrödinger equation in the length gauge (4.93).

4.5 Generalise the results of Section 4.4 to the case in which the level E_a is g_a times degenerate and the level E_b is g_b times degenerate, and show that the Einstein coefficients satisfy the relations

$$g_a B_{ba} = g_b B_{ab}; \qquad A_{ab} = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} B_{ab}$$

4.6 Obtain the explicit forms of the coefficients $\mathscr{A}(l, m; l', m'; q)$, either by using a table of Clebsch–Gordan coefficients, or by using the recurrence relations (4.121).

4.7 Show that

$$\sum_{m'} |\mathscr{A}(l, m; l', m'; m' - m)|^2 = \frac{3}{4\pi}\frac{l+1}{2l+1}$$

if $l' = l + 1$ and

$$\sum_{m'} |\mathscr{A}(l, m; l', m'; m' - m)|^2 = \frac{3}{4\pi}\left(\frac{l}{2l+1}\right)$$

if $l' = l - 1$. Find the transition rate for absorption of unpolarised isotropic radiation by a hydrogenic atom from a level (nl) to the $(2l' + 1)$ degenerate levels $(n'l')$ and show that it is independent of the magnetic quantum number of the initial sublevel.

4.8 Prove that the average oscillator strengths defined by (4.143) obey the Thomas–Reiche–Kuhn sum rule (4.137).

4.9 Prove the scaling law (4.148) for the lifetimes of the hydrogenic ions in the dipole approximation.

4.10 For a given initial level a of a hydrogen atom, show that

$$\sum_b \sigma_{ba} - \sum_b{}' \bar{\sigma}_{ba} = 2\pi^2 r_0 c$$

where σ_{ba} is the integrated absorption cross-section, in the electric dipole approximation, the sum Σ_b being over all states (including continuum states) with $E_b > E_a$, and $\bar{\sigma}_{ba}$ is the corresponding cross-section for stimulated emission, the sum Σ_b' being over all states with $E_b < E_a$. The quantity r_0 is the classical electron radius, which is given by $r_0 = e^2/(4\pi\varepsilon_0 mc^2)$.