From (4.96)–(4.98), we have

$$|\mathbf{r}_{ba}|^2 = \left(\frac{a_0}{Z}\right)^2 \frac{2^{15}}{3^{10}} [\delta_{m,1} + \delta_{m,-1} + \delta_{m,0}]$$

$$= \frac{1}{Z^2}\left(\frac{\hbar}{mc\alpha}\right)^2 \frac{2^{15}}{3^{10}} [\delta_{m,1} + \delta_{m,-1} + \delta_{m,0}] \qquad \textbf{(4.99)}$$

The transition rate from each magnetic substate is the same, and if each state is equally populated the full transition rate in the dipole approximation is, from (4.80b), (4.95) and (4.99),

$$W_{ab}^{\mathrm{s,D}} = \frac{1}{3}\sum_{m=-1}^{1} W_{1\mathrm{s},2\mathrm{p}m}^{\mathrm{s,D}}$$

$$= \left(\frac{2}{3}\right)^8 \frac{m\alpha^5 Z^4 c^2}{\hbar}$$

$$\simeq 6.27 \times 10^8 Z^4\ \mathrm{s}^{-1} \qquad \textbf{(4.100)}$$

4.4 The Einstein coefficients

We shall verify that (4.80) is the correct expression for the rate of spontaneous emission by using the treatment of emission and absorption of radiation given by Einstein in 1916. Consider an enclosure containing atoms (of a single kind) and radiation in equilibrium at absolute temperature T, and let a and b denote two non-degenerate atomic levels, with energy values E_a and E_b such that $E_b > E_a$. We assume that the radiation field is weak enough for a first-order perturbative treatment of absorption and stimulated emission to be valid, and denote by $\rho(\omega_{ba})$ the energy density of the radiation at the angular frequency $\omega_{ba} = (E_b - E_a)/\hbar$. The number of atoms making the transition from a to b per unit time by absorbing radiation, $\dot{N}_{ba}$, is proportional to the total number N_a of atoms in the state a and to the energy density $\rho(\omega_{ba})$. That is,

$$\dot{N}_{ba} = B_{ba} N_a \rho(\omega_{ba}) \qquad \textbf{(4.101)}$$

where B_{ba} is called the *Einstein coefficient for absorption*. Since $\rho = I/c$ (see (4.13)) and the transition rate for absorption (per atom) is W_{ba}, we have

$$B_{ba} = \frac{W_{ba}}{\rho} = \frac{4\pi^2}{3\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right)|\mathbf{D}_{ba}|^2 \qquad \textbf{(4.102)}$$

where in the last step we have used the dipole approximation (4.78) for W_{ba}.

On the other hand, the number of atoms making the transition $b \to a$ per unit time, $\dot{N}_{ab}$, is the sum of the number of spontaneous transitions per unit time, which is independent of ρ, and the number of stimulated transitions per unit time, which is proportional to ρ. Thus

$$\dot{N}_{ab} = A_{ab}N_b + B_{ab}N_b\rho(\omega_{ba}) \tag{4.103}$$

where N_b is the total number of atoms in the state b, A_{ab} is the *Einstein coefficient for spontaneous emission* and B_{ab} is the *Einstein coefficient for stimulated emission.* In our notation $A_{ab} \equiv W^{\mathrm{s}}_{ab}$. At equilibrium we have $\dot{N}_{ba} = \dot{N}_{ab}$, so that from (4.101) and (4.103) we deduce that

$$\frac{N_a}{N_b} = \frac{A_{ab} + B_{ab}\rho(\omega_{ba})}{B_{ba}\rho(\omega_{ba})} \tag{4.104}$$

We also know that at thermal equilibrium the ratio N_a/N_b is given by [8]

$$\frac{N_a}{N_b} = \exp[-(E_a - E_b)/(k_{\mathrm{B}}T)] = \exp[\hbar\omega_{ba}/(k_{\mathrm{B}}T)] \tag{4.105}$$

where k_{B} is Boltzmann's constant. From (4.104) and (4.105) we find for $\rho(\omega_{ba})$ the expression

$$\rho(\omega_{ba}) = \frac{A_{ab}}{B_{ba}\exp[\hbar\omega_{ba}/(k_{\mathrm{B}}T)] - B_{ab}} \tag{4.106}$$

Since the atoms are in equilibrium with the radiation at temperature T, the energy density $\rho(\omega)$ is given by the Planck distribution law discussed in Section 1.3. Using (1.31) together with the fact that $\rho(\omega)\,\mathrm{d}\omega = \rho(\nu)\,\mathrm{d}\nu$, with $\omega = 2\pi\nu$, the energy density at the particular angular frequency ω_{ba} is

$$\rho(\omega_{ba}) = \frac{\hbar\omega^3_{ba}}{\pi^2c^3}\,\frac{1}{\exp[\hbar\omega_{ba}/(k_{\mathrm{B}}T)] - 1} \tag{4.107}$$

In order for (4.106) and (1.107) to be identical, the three Einstein coefficients must be related by the two equations

$$B_{ba} = B_{ab} \tag{4.108a}$$

$$A_{ab} = \frac{\hbar\omega^3_{ba}}{\pi^2c^3}B_{ab} \tag{4.108b}$$

The relation (4.108a) expresses the principle of detailed balancing discussed previously. Using (4.102) and (4.108), we verify that W^{s}_{ab} ($\equiv A_{ab}$) is indeed given in the dipole approximation by the expression (4.80). It is a simple matter to generalise the above results to the case in which the energy levels E_a and (or) E_b are degenerate. Denoting by g_a and g_b the degeneracy of these levels, one finds (Problem 4.5) that (4.108a) becomes

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[8] See for instance the text by Kittel and Kroemer (1980).

$$g_a B_{ba} = g_b B_{ab} \tag{4.109}$$

while the relation (4.108b) remains unchanged.

4.5 Selection rules and the spectrum of one-electron atoms

In the last section, we obtained the probability of a radiative transition between two levels a and b, in the electric dipole approximation. For stimulated emission or absorption of linearly polarised radiation in the direction $\hat{\boldsymbol{\varepsilon}}$, the basic expression is given by (4.71) and for spontaneous emission by (4.79). In each case the transition rate depends on the key quantity $|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba}|^2$. In order to study this expression it is convenient to introduce the *spherical components* of the vectors $\hat{\boldsymbol{\varepsilon}}$ and $\mathbf{r}$. According to the definition (A4.48) of Appendix 4 the spherical components ε_q $(q = 0, \pm 1)$ of $\hat{\boldsymbol{\varepsilon}}$ are given in terms of its Cartesian components $(\hat{\varepsilon}_x, \hat{\varepsilon}_y, \hat{\varepsilon}_z)$ by

$$\varepsilon_1 = -\frac{1}{\sqrt{2}}(\hat{\varepsilon}_x + \mathrm{i}\hat{\varepsilon}_y), \qquad \varepsilon_0 = \hat{\varepsilon}_z, \qquad \varepsilon_{-1} = \frac{1}{\sqrt{2}}(\hat{\varepsilon}_x - \mathrm{i}\hat{\varepsilon}_y) \tag{4.110}$$

As we shall see later, if the direction of propagation of the radiation is along the Z axis $(\hat{\varepsilon}_z = 0)$, ε_1 and ε_{-1} describe states of circular polarisation.

Similarly, the spherical components r_q $(q = 0, \pm 1)$ of the vector $\mathbf{r}$ are given by

$$\begin{aligned}
r_1 &= -\frac{1}{\sqrt{2}}(x + \mathrm{i}y) = -\frac{1}{\sqrt{2}} r \sin\theta\, \mathrm{e}^{\mathrm{i}\phi} = r\left(\frac{4\pi}{3}\right)^{1/2} Y_{1,1}(\theta, \phi) \\
r_0 &= z = r\cos\theta = r\left(\frac{4\pi}{3}\right)^{1/2} Y_{1,0}(\theta, \phi) \\
r_{-1} &= \frac{1}{\sqrt{2}}(x - \mathrm{i}y) = \frac{1}{\sqrt{2}} r \sin\theta\, \mathrm{e}^{-\mathrm{i}\phi} = r\left(\frac{4\pi}{3}\right)^{1/2} Y_{1,-1}(\theta, \phi)
\end{aligned} \tag{4.111}$$

The scalar product $\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba}$ can be expressed in terms of spherical components as

$$\begin{aligned}
\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba} &= \sum_{q=0,\pm1} \varepsilon_q^*(\mathbf{r}_{ba})_q \\
&= \sum_{q=0,\pm1} \varepsilon_q^* I^q_{n'l'm',nlm}
\end{aligned} \tag{4.112}$$

where

$$\begin{aligned}
I^q_{n'l'm',nlm} = {} & \left(\frac{4\pi}{3}\right)^{1/2} \int_0^\infty \mathrm{d}r\, r^3 R_{n'l'}(r) R_{nl}(r) \\
& \times \int \mathrm{d}\Omega\, Y^*_{l'm'}(\theta, \phi) Y_{1,q}(\theta, \phi) Y_{lm}(\theta, \phi)
\end{aligned} \tag{4.113}$$

and where we have written the quantum numbers of the levels a and b of the hydrogenic atom as (nlm) and $(n'l'm')$, respectively. The radial integral in (4.113) is always non-zero, but the angular integrals are only non-zero for certain values of (l, m) and (l', m'), giving rise to *selection rules* which we shall now investigate.

Parity

Under the reflection $\mathbf{r} \to -\mathbf{r}$ we have shown in Section 3.3 that the hydrogenic wave functions behave like (see (3.69))

$$\begin{aligned} R_{nl}(r)Y_{lm}(\theta, \phi) &\to R_{nl}(r)Y_{lm}(\pi - \theta, \phi + \pi) \\ &= R_{nl}(r)(-1)^l Y_{lm}(\theta, \phi) \end{aligned} \tag{4.114}$$

and the parity of the wave function is even or odd according to whether l is even or odd. By making the coordinate transformation $\mathbf{r} \to -\mathbf{r}$ in (4.113) we see that

$$I^q_{n'l'm',nlm} = (-1)^{l+l'+1} I^q_{n'l'm',nlm} \tag{4.115}$$

Hence the quantity $I^q_{n'l'm',nlm}$ is only non-vanishing if $(l + l' + 1)$ is even. In other words, *the electric dipole operator only connects states of opposite parity.*

Magnetic quantum numbers

The integral over ϕ which must be performed in (4.113) is of the form

$$J(m, m', q) = \int_0^{2\pi} \exp[\mathrm{i}(m + q - m')\phi]\, \mathrm{d}\phi \tag{4.116}$$

We shall consider separately the two cases $q = 0$ and $q = \pm 1$, which correspond respectively to radiation polarised *parallel* to the Z axis and *perpendicular* to the Z axis, the Z direction being the quantisation direction to which the magnetic quantum number m refers.

1. **$q = 0$ (polarisation vector $\hat{\varepsilon}$ in the Z direction).**

In this case the integral (4.116) – and therefore the matrix element (4.113) – vanishes unless

$$m' = m, \quad \text{i.e.} \quad \Delta m = 0 \tag{4.117a}$$

2. **$q = \pm 1$ (propagation vector k in the Z direction).**

Here the ϕ integration in (4.116) yields for the matrix element (4.113) the selection rule

$$m' = m \pm 1, \quad \text{i.e.} \quad \Delta m = \pm 1 \tag{4.117b}$$

In a given transition, only one of the conditions $\Delta m = 0$ or $\Delta m = \pm 1$ can be satisfied, and hence only one of the matrix elements z_{ba} and $(x \pm \mathrm{i}y)_{ba}$ will be non-zero.

Orbital angular momentum

The integral over the angles in (4.113), which we call $\mathscr{A}(l, m; l', m'; q)$, can be evaluated by the methods of Appendix 4. The result, expressed in terms of Clebsch–Gordan coefficients, is (see (A4.40))

$$\begin{aligned}\mathscr{A}(l, m; l', m'; q) &= \int \mathrm{d}\Omega\, Y^*_{l'm'}(\theta, \phi) Y_{1,q}(\theta, \phi) Y_{lm}(\theta, \phi) \\ &= \left(\frac{3}{4\pi}\frac{2l+1}{2l'+1}\right)^{1/2} \langle l100|l'0\rangle\langle l1mq|l'm'\rangle \end{aligned} \tag{4.118}$$

From the properties of the Clebsch–Gordan coefficients we note that $\mathscr{A}(l, m; l', m'; q)$ vanishes unless $m' = m + q$, which is in agreement with the selection rules (4.117) we have just obtained for the magnetic quantum numbers. In addition, the properties of the Clebsch–Gordan coefficients also imply that $\mathscr{A}(l, m; l', m'; q)$ vanishes unless

$$l' = l \pm 1, \quad \text{i.e.} \quad \Delta l = \pm 1 \tag{4.119}$$

This is the orbital angular momentum selection rule for electric dipole transitions. This rule can also be deduced in a more elementary fashion by using the recurrence relations satisfied by the associated Legendre functions $P_l^m(\cos\theta)$. Indeed, using the expressions (2.181) for the spherical harmonics, together with the selection rules (4.117) for the magnetic quantum numbers, we see that the θ integration in (4.118) can be written, apart from numerical factors, as

$$\int_{-1}^{+1} \mathrm{d}(\cos\theta) P_l^m(\cos\theta) P_{l'}^m(\cos\theta)\cos\theta \quad \text{for} \quad q = 0 \tag{4.120a}$$

$$\int_{-1}^{+1} \mathrm{d}(\cos\theta) P_l^m(\cos\theta) P_{l'}^{m\pm 1}(\cos\theta)\sin\theta \quad \text{for} \quad q = \pm 1 \tag{4.120b}$$

where, in view of (2.181b), we need only deal with magnetic quantum numbers which are positive or zero. From the recurrence relations (2.176),

$$(2l+1)\cos\theta\, P_l^m(\cos\theta) = (l+1-m)P_{l+1}^m(\cos\theta) + (l+m)P_{l-1}^m(\cos\theta) \tag{4.121a}$$

and

$$(2l+1)\sin\theta\, P_l^{m-1}(\cos\theta) = P_{l+1}^m(\cos\theta) - P_{l-1}^m(\cos\theta) \tag{4.121b}$$

together with the orthogonality relation (2.177)

$$\int_{-1}^{+1} \mathrm{d}(\cos\theta) P_l^m(\cos\theta) P_{l'}^m(\cos\theta) = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!}\delta_{ll'} \tag{4.122}$$

we find that $l' = l \pm 1$, in accordance with (4.119). Using either of the above methods one can also obtain the explicit forms of the quantities $\mathscr{A}(l, m; l', m'; q)$, which is left as an exercise for the reader (Problem 4.6).

Electron spin

We note that the electric dipole operator does not act on the spin of the electron. It follows that the component of the electron spin in the direction of quantisation remains unaltered by the absorption or emission of dipole radiation.

The spin of the photon

The selection rules for electric dipole transitions have a simple interpretation in terms of the spin of the photon. To discuss this point, we must first explore in more detail the possible states of polarisation of an electromagnetic wave. In Section 4.1 we saw that a general state of polarisation for a plane wave propagating in the direction $\hat{\mathbf{k}}$ can be described by combining two independent *linearly polarised* plane waves (having in general different phases) with polarisation vectors $\hat{\varepsilon}_\lambda$ $(\lambda = 1, 2)$ orthogonal to $\hat{\mathbf{k}}$. The resulting polarisation vector $\hat{\varepsilon}$ lies in a plane perpendicular to $\hat{\mathbf{k}}$, so that a state of arbitrary polarisation can always be represented as

$$\hat{\varepsilon} = a_1\hat{\mathbf{e}}_1 + a_2\hat{\mathbf{e}}_2; \qquad a_1^2 + a_2^2 = 1 \tag{4.123}$$

where $\hat{\mathbf{e}}_i$ $(i = 1, 2)$ are fixed mutually orthogonal real unit vectors in a plane perpendicular to $\hat{\mathbf{k}}$. We shall take $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$ and $\hat{\mathbf{k}}$ to form a right-handed system, so that (see Fig. 4.1)

$$\hat{\mathbf{k}} = \hat{\mathbf{e}}_1 \times \hat{\mathbf{e}}_2; \qquad \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2 = 0 \tag{4.124}$$

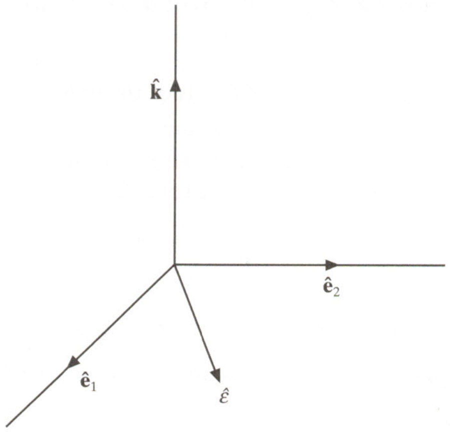


Figure 4.1 The vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$ and $\hat{\mathbf{k}}$, forming a right-handed set of mutually orthogonal unit vectors. Also shown is the polarisation vector $\hat{\varepsilon}$ which lies in the plane of $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$.

The foregoing discussion may of course be directly generalised to pulses of the form (4.14), for which the polarisation vector $\hat{\boldsymbol{\varepsilon}}$ is independent of ω.

An alternative description of a general state of polarisation of an electromagnetic wave may be given in terms of two *circularly polarised waves*. Let us first consider the particular case in which the direction of propagation is along the Z axis. In place of the vector potential (4.5), we consider the potentials $\mathbf{A}^{\mathrm{L}}(\mathbf{r}, t)$ and $\mathbf{A}^{\mathrm{R}}(\mathbf{r}, t)$ defined by

$$\begin{aligned} A_x^{\mathrm{L}} &= A_x^{\mathrm{R}} = (2)^{-1/2} A_0(\omega) \cos(kz - \omega t + \delta_\omega) \\ A_y^{\mathrm{L}} &= -A_y^{\mathrm{R}} = -(2)^{-1/2} A_0(\omega) \sin(kz - \omega t + \delta_\omega) \\ A_z^{\mathrm{L}} &= A_z^{\mathrm{R}} = 0 \end{aligned} \tag{4.125}$$

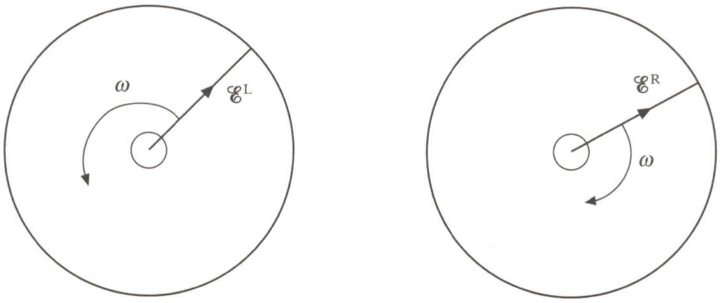
The corresponding electric field vectors $\mathcal{E}^{\mathrm{L}}$ and $\mathcal{E}^{\mathrm{R}}$ are such that

$$\begin{aligned} \mathcal{E}_x^{\mathrm{L}} &= \mathcal{E}_x^{\mathrm{R}} = -(2)^{-1/2} \omega A_0(\omega) \sin(kz - \omega t + \delta_\omega) \\ \mathcal{E}_y^{\mathrm{L}} &= -\mathcal{E}_y^{\mathrm{R}} = -(2)^{-1/2} \omega A_0(\omega) \cos(kz - \omega t + \delta_\omega) \\ \mathcal{E}_z^{\mathrm{L}} &= \mathcal{E}_z^{\mathrm{R}} = 0 \end{aligned} \tag{4.126}$$

On facing into the oncoming wave, the vector $\mathcal{E}^{\mathrm{L}}$ is seen to be of constant magnitude and to be rotating in an anticlockwise way in the (X, Y) plane at a frequency ω (see Fig. 4.2(a)), while the vector $\mathcal{E}^{\mathrm{R}}$ is of the same magnitude but rotates at a frequency ω in a clockwise way (see Fig. 4.2(b)). The radiation described by $\mathcal{E}^{\mathrm{L}}$ is said to be left-hand circularly polarised and that corresponding to $\mathcal{E}^{\mathrm{R}}$ is right-hand circularly polarised. By forming the combination

$$\mathcal{E} = a_{\mathrm{L}} \mathcal{E}^{\mathrm{L}} + a_{\mathrm{R}} \mathcal{E}^{\mathrm{R}} \tag{4.127}$$

where a_{L} and a_{R} are complex coefficients, radiation in any state of polarisation can be produced. For example, if $a_{\mathrm{L}} = a_{\mathrm{R}} = 1$, we obtain linearly polarised radiation, with the electric field vector oriented along the X axis.



(a) (b)

Figure 4.2 In circularly polarised radiation the electric field vectors $\mathcal{E}^{\mathrm{L}}$ and $\mathcal{E}^{\mathrm{R}}$ rotate in anticlockwise and clockwise directions when facing into the oncoming wave.

In terms of complex exponentials, $\mathbf{A}^{\mathrm{L}}$ and $\mathbf{A}^{\mathrm{R}}$ can be written as

$$\begin{aligned}\mathbf{A}^{\mathrm{L}} &= \frac{1}{2}A_0(\omega)[\hat{\mathbf{e}}^{\mathrm{L}}\,\mathrm{e}^{\mathrm{i}(kz-\omega t+\delta_\omega)} + \text{c.c.}]\\ \mathbf{A}^{\mathrm{R}} &= \frac{1}{2}A_0(\omega)[\hat{\mathbf{e}}^{\mathrm{R}}\,\mathrm{e}^{\mathrm{i}(kz-\omega t+\delta_\omega)} + \text{c.c.}]\end{aligned} \tag{4.128}$$

where c.c. denotes the complex conjugate. In (4.128), $\hat{\mathbf{e}}^{\mathrm{L}}$ and $\hat{\mathbf{e}}^{\mathrm{R}}$ are two complex orthogonal unit vectors such that

$$\hat{\mathbf{e}}^{\mathrm{L}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} + \mathrm{i}\hat{\mathbf{y}}), \qquad \hat{\mathbf{e}}^{\mathrm{R}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} - \mathrm{i}\hat{\mathbf{y}}) \tag{4.129}$$

describing respectively the states of left-hand and right-hand circularly polarised radiation. An arbitrary state of polarisation can be specified by a complex vector $\hat{\mathbf{n}}$ such that

$$\hat{\mathbf{n}} = a^{\mathrm{L}}\hat{\mathbf{e}}^{\mathrm{L}} + a^{\mathrm{R}}\hat{\mathbf{e}}^{\mathrm{R}}, \qquad |a^{\mathrm{L}}|^2 + |a^{\mathrm{R}}|^2 = 1 \tag{4.130}$$

and this description is as general as the one given by (4.123). We note that if the direction of propagation is not along the Z axis, then we can write more generally

$$\hat{\mathbf{e}}^{\mathrm{L}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{e}}_1 + \mathrm{i}\hat{\mathbf{e}}_2), \qquad \hat{\mathbf{e}}^{\mathrm{R}} = \frac{1}{\sqrt{2}}(\hat{\mathbf{e}}_1 - \mathrm{i}\hat{\mathbf{e}}_2) \tag{4.131}$$

where $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are the unit vectors introduced in (4.123).

We have already seen in Section 4.2 that the terms in $\mathbf{A}$ associated with $\exp[\mathrm{i}(\mathbf{k}\cdot\mathbf{r} - \omega t)]$ give rise to the absorption of photons (see (4.52)) and those with $\exp[-\mathrm{i}(\mathbf{k}\cdot\mathbf{r} - \omega t)]$ to the emission of photons (see (4.54)). From (4.56), (4.49), (4.71) and (4.79) we see that, in the electric dipole approximation, we should use the expressions $\hat{\mathbf{e}}^{\mathrm{L}}\cdot\mathbf{r}_{ba}$ or $\hat{\mathbf{e}}^{\mathrm{R}}\cdot\mathbf{r}_{ba}$ to describe the *absorption* of a left-hand or a right-hand circularly polarised photon, respectively, while the expressions $\hat{\mathbf{e}}^{\mathrm{L}*}\cdot\mathbf{r}^*_{ba}$ $(= \hat{\mathbf{e}}^{\mathrm{L}*}\cdot\mathbf{r}_{ab})$ or $\hat{\mathbf{e}}^{\mathrm{R}*}\cdot\mathbf{r}^*_{ba}$ $(= \hat{\mathbf{e}}^{\mathrm{R}*}\cdot\mathbf{r}_{ab})$ must be used to describe the *emission* of the corresponding circularly polarised photons. Thus, if a left-hand circularly polarised photon is emitted in the Z direction, the appropriate expression is

$$\begin{aligned}\hat{\mathbf{e}}^{\mathrm{L}*}\cdot\mathbf{r}_{ab} &= \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} - \mathrm{i}\hat{\mathbf{y}})\cdot\mathbf{r}_{ab}\\ &= \frac{1}{\sqrt{2}}(x_{ab} - \mathrm{i}y_{ab})\end{aligned} \tag{4.132}$$

If we denote by $m\hbar$ the Z component of the angular momentum for the initial (upper) state b, we see from (4.111) and (4.117) that the matrix element (4.132) vanishes unless the final (lower) state a of the atom has a component $(m-1)\hbar$ of angular momentum in the Z direction. A similar reasoning leads to the conclusion that the emission of a right-hand circularly polarised photon increases the component of the angular momentum of the atom along the Z axis by $\hbar$.

By conservation of angular momentum, each photon must have a component of angular momentum parallel to the Z axis (the direction of propagation) of $\pm\hbar$. Since photons travelling parallel to the Z axis cannot have a component of *orbital* angular momentum in the Z direction, the angular momentum carried by the photons in this case can only be due to their intrinsic spin. Further, for electric dipole radiation, the orbital angular momentum of the photon must be zero, since the wave function (the vector potential) is spherically symmetrical (we have replaced $\exp(i\mathbf{k}\cdot\mathbf{r})$ by 1). From these remarks, and from the selection rule $\Delta l = \pm 1$, we infer that the photon has spin of unit magnitude, that is $\mathbf{S}^2 = s(s+1)\hbar^2$ with $s = 1$. The components of the spin in the direction of propagation are $S_z = m_s\hbar$ with $m_s = \pm 1$. The component of the spin along the direction of motion is called the *helicity* of a particle. For the photon, only two helicity states are possible, because the electromagnetic wave is transverse and the case $m_s = 0$ is excluded. From the definition of helicity it is clear that a photon with helicity $+\hbar$ is always left-hand circularly polarised and one with helicity $-\hbar$ is always right-hand circularly polarised, and this is independent of any particular choice of axes.

Beth's experiment

If a beam of light, propagating parallel to the positive Z axis, is left circularly polarised, each photon in the beam will have a positive angular momentum $+\hbar$ along the Z axis. If the beam contains N photons per unit volume, the energy density of the beam, ρ, will be $\rho = N\hbar\omega$, where ω is the angular frequency of the radiation, and a unit volume will possess an angular momentum $L_z = N\hbar$. The ratio $\rho/\omega = N\hbar$ is independent of frequency and is equal in magnitude to the angular momentum L_z. Similarly, for a right-hand circularly polarised beam $\rho/\omega = -L_z$ (a plane polarised beam carries no angular momentum). These facts are consistent with the results of a remarkable experiment carried out in 1936 by R.A. Beth.

In Beth's experiment an anisotropic crystalline plate is prepared, which has the property that (at a certain wavelength) it converts left-hand circularly polarised light passing through it to right-hand circularly polarised light, acting as a half-wave plate. Because of this, the plate must be subjected to a couple of magnitude Γ_z per unit area, where

$$\Gamma_z = 2cL_z = 2\rho c/\omega \qquad \textbf{(4.133)}$$

The couple is measured by suspending the plate from a quartz fibre and measuring the angle through which the plate rotates. The effect can be doubled by reflecting the light which has passed through the plate, so it passes through the plate a second time. A fixed quarter-wave plate must be inserted, so that the polarisation of the light is in the correct sense to reinforce the couple (see Fig. 4.3). The angle of deflection is extremely small, but the constancy of the ratio ρ/ω can be observed, and a result of the expected order of magnitude obtained

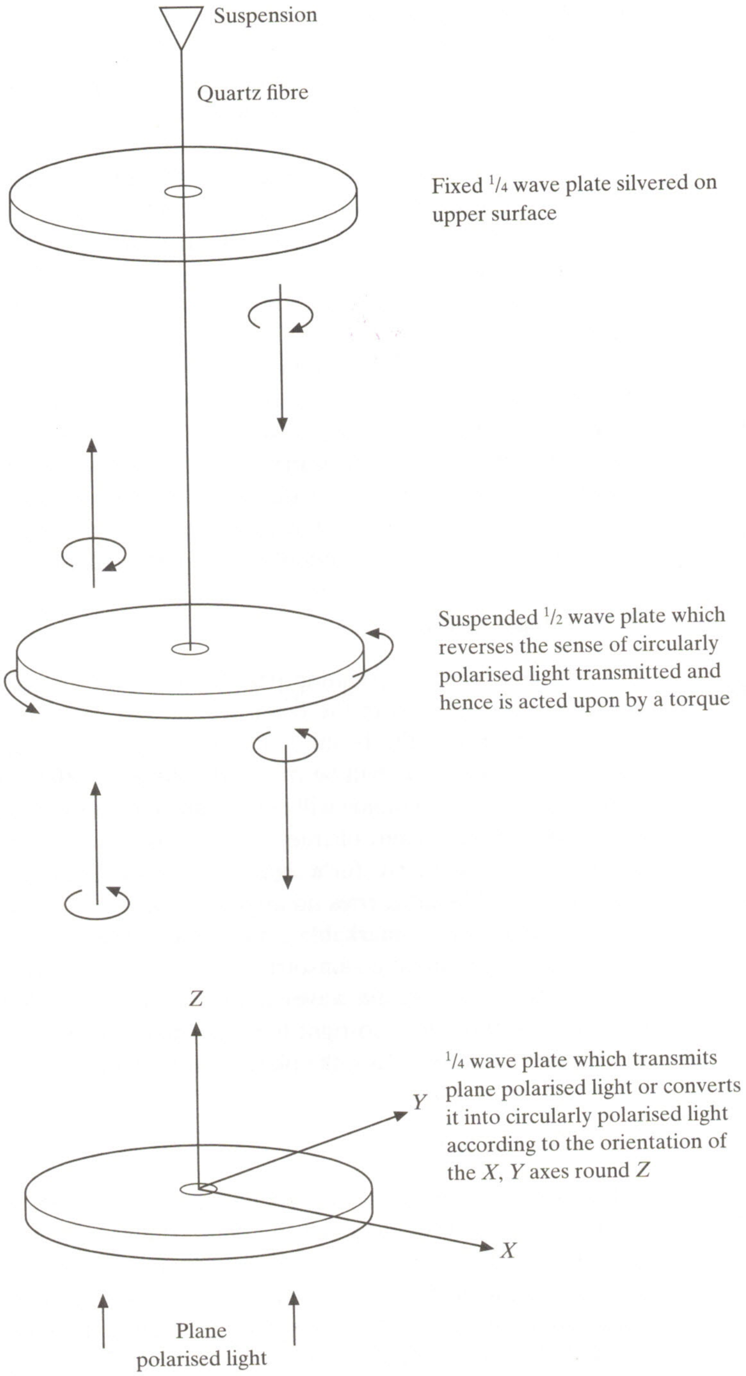


Figure 4.3 Schematic diagram of Beth's experiment.

provided the experiment is carried out with due precautions. For example, the whole apparatus must be in a vacuum to avoid the effect of currents in the air, and the power of the source of illumination must be known accurately.

Parity of the photon

Provided tiny effects due to the weak nuclear interactions are neglected, a system of electrons interacting with the electromagnetic field conserves parity [9]. From the behaviour of the vector potential **A** under reflections, it can be inferred that the photon has negative parity, which is consistent with the selection rule (4.115) showing that an electric dipole transition causes a change in parity of the atom.

The spectrum of one-electron atoms

In Chapter 3 it was shown that in the non-relativistic approximation, and neglecting spin–orbit coupling, the bound states of a one-electron atom were degenerate in the quantum numbers l and m and the energy of a level depended only on the principal quantum number n. That is (see (3.29) and (3.31)),

$$\begin{aligned} E_n &= -\frac{1}{2n^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\frac{\mu}{\hbar^2} \\ &= -\frac{Z^2}{2n^2}\left(\frac{\mu}{m}\right) \quad \text{in a.u.} \end{aligned} \tag{4.134}$$

where μ is the reduced mass, given in terms of the mass of the nucleus M and the mass of the electron m by $\mu = mM/(m+M)$ (see (3.3)). Since there is no selection rule limiting n, the hydrogenic spectrum contains all frequencies given by the expression (3.34) which we recall here, namely

$$\nu_{ab} = Z^2R(M)\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) \tag{4.135}$$

where $n_a = 1, 2, 3, \ldots, n_b = 2, 3, 4, \ldots$ with $n_b > n_a$ and $R(M)$ is given by (1.102). The gross structure of the spectra of one-electron atoms, described in Chapter 1 within the framework of the Bohr model, agrees with this formula. The foregoing discussion in this chapter has led to a consistent derivation of the result (4.135). However, it is important to note that the selection rules (4.117) and (4.119) limit the values of the quantum numbers m and l of the levels concerned. This is illustrated in Fig. 4.4 for the case of the orbital angular momentum quantum number l.

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[9] Very small parity-violating terms in the electromagnetic interaction, involving the so-called 'neutral currents', were discovered in 1978 in the deep inelastic scattering of polarised electrons by protons and deuterons. These neutral currents, which are a consequence of a unified description of electromagnetic and weak interactions, imply very small parity-violating effects in atomic transitions.

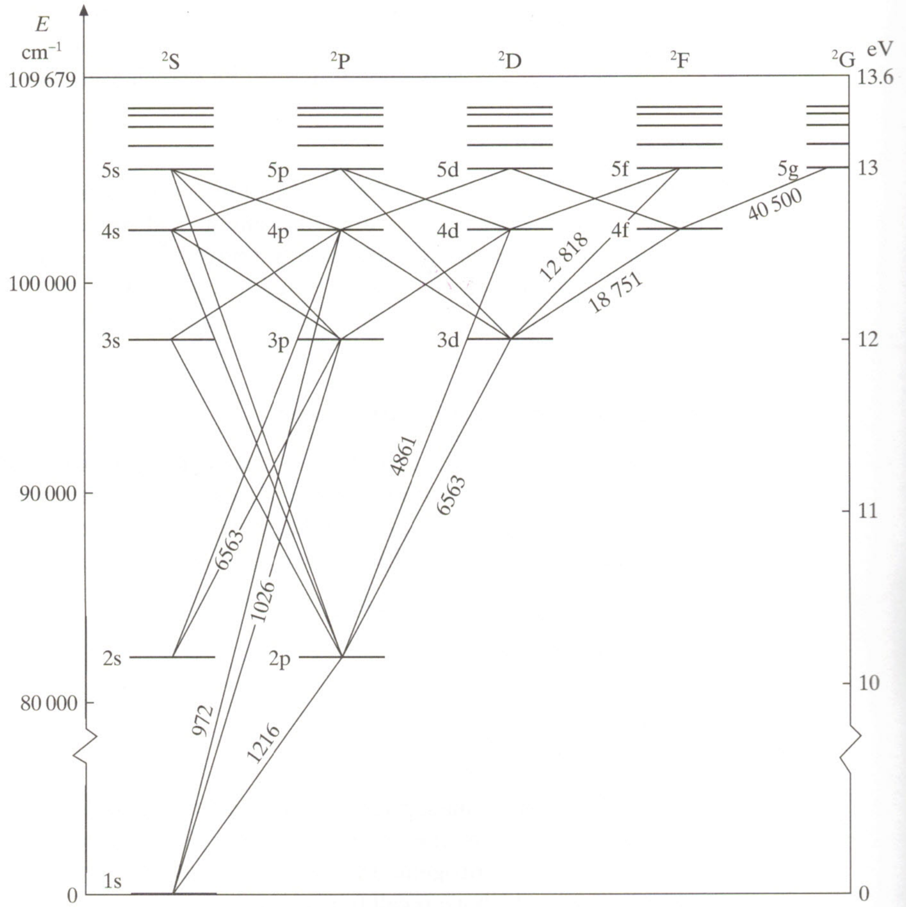

Figure 4.4 Term, or Grotrian, diagram for atomic hydrogen. The ordinate shows the energy above the 1s ground state in cm^{-1} (8065 cm^{-1} $\equiv$ 1 eV) on the left and in eV on the right and the energy levels are shown plotted against the orbital angular momentum. Transitions obeying the $\Delta l = \pm 1$ selection rule are indicated by solid lines. The numbers against the lines indicate the wavelength in ångström units (1 Å $\equiv 10^{-8}$ cm). For clarity, only transitions between the lower-lying levels are shown, and the wavelengths are shown only for a selection of lines. The splitting due to fine structure is too small to be shown on a diagram of this scale.

4.6 Line intensities and the lifetimes of excited states

As we have seen in Section 4.3, the intensity of a transition between a pair of states a and b is proportional, in the dipole approximation, to the quantity $|\mathbf{r}_{ba}|^2$. Thus the relative intensities of a series of transitions from a given initial state a to various final states k are determined by the quantities $|\mathbf{r}_{ka}|^2$.

Oscillator strengths and the Thomas–Reiche–Kuhn sum rule

In discussions of intensities it is customary to introduce a related dimensionless quantity f_{ka}, called the *oscillator strength*. It is defined as

$$f_{ka} = \frac{2m\omega_{ka}}{3\hbar} |\mathbf{r}_{ka}|^2 \tag{4.136}$$

with $\omega_{ka} = (E_k - E_a)/\hbar$. We note that this definition implies that $f_{ka} > 0$ for absorption, where $E_k > E_a$. On the other hand we have $f_{ka} < 0$ for emission processes.

The oscillator strengths (4.136) obey the sum rule, due to Thomas, Reiche and Kuhn,

$$\sum_k f_{ka} = 1 \tag{4.137}$$

where the sum is over all states, including the continuum. This sum rule can be proved as follows. Let f^x_{ka} be defined as

$$\begin{aligned} f^x_{ka} &= \frac{2m\omega_{ka}}{3\hbar} |x_{ka}|^2 \\ &= \frac{2m\omega_{ka}}{3\hbar} \langle a|x|k\rangle\langle k|x|a\rangle \end{aligned} \tag{4.138}$$

where we have used the simplified notation $\langle a|x|k\rangle \equiv \langle\psi_a|x|\psi_k\rangle$. From (4.67), we have

$$x_{ka} = \langle k|x|a\rangle = -\frac{\mathrm{i}}{m\omega_{ka}}\langle k|p_x|a\rangle \tag{4.139a}$$

$$x_{ak} = \langle a|x|k\rangle = \frac{\mathrm{i}}{m\omega_{ka}}\langle a|p_x|k\rangle \tag{4.139b}$$

and hence

$$f^x_{ka} = \frac{2\mathrm{i}}{3\hbar}\langle a|p_x|k\rangle\langle k|x|a\rangle \tag{4.140a}$$

$$= -\frac{2\mathrm{i}}{3\hbar}\langle a|x|k\rangle\langle k|p_x|a\rangle \tag{4.140b}$$

$$= \frac{\mathrm{i}}{3\hbar}\{\langle a|p_x|k\rangle\langle k|x|a\rangle - \langle a|x|k\rangle\langle k|p_x|a\rangle\} \tag{4.140c}$$

where the last line has been obtained by taking half the sum of the two expressions (4.140a) and (4.140b).

We can now use the closure property of the hydrogenic wave functions which form a complete set, namely $\sum_k |k\rangle\langle k| = I$ to find from (4.140c) that

$$\sum_k f^x_{ka} = \frac{\mathrm{i}}{3\hbar}\langle a|p_x x - x p_x|a\rangle \tag{4.141}$$

But since $[x, p_x] = i\hbar$, we have the sum rule

$$\sum_k f^x_{ka} = \frac{1}{3} \tag{4.142}$$

The same argument holds for f^y_{ka} and f^z_{ka}, which proves the sum rule (4.137).

The oscillator strengths and transition probabilities can be easily calculated for one-electron atoms and ions, because the hydrogenic wave functions are known exactly. The labels a and k in f_{ka} include all the quantum numbers of the initial and final states, and in particular f_{ka} depends on the magnetic quantum numbers. It is convenient to define an *average oscillator strength* for the transition $nl \to n'l'$, which is independent of the magnetic quantum numbers and hence of the polarisation of the radiation, by

$$\bar{f}_{n'l',nl} = \frac{1}{2l+1} \sum_{m'=-l'}^{l'} \sum_{m=-l}^{l} f_{n'l'm',nlm} \tag{4.143}$$

It can be shown (Problem 4.8) that the average oscillator strengths also obey the sum rule (4.137). Some calculated values of $\bar{f}_{n'l',nl}$ for hydrogenic atoms (or ions) are given in Table 4.1.

The transition rates for spontaneous emission in the dipole approximation are given in terms of oscillator strengths (see (4.80) and (4.136)) by

$$W^{\mathrm{s,D}}_{ka} = \frac{2\hbar\alpha}{mc^2} \omega^2_{ka} |f_{ka}| \tag{4.144}$$

For hydrogenic atoms the oscillator strengths and transition probabilities decrease as the principal quantum number n of the upper level increases, W^{s}_{ka} decreasing like n^{-3} for large n.

Atomic lifetimes

If $N(t)$ atoms are in an excited state b at a particular time t, the rate of change of $N(t)$ is

$$\dot{N}(t) = -N(t) \sum_k W^{\mathrm{s}}_{kb} \tag{4.145}$$

Table 4.1 Average oscillator strengths for some transitions in hydrogenic atoms and ions[†].

Initial level	*Final level*			*Discrete spectrum*		$\sum_{n=5}^{\infty}$	*Conrinuum spectrum*
		$n = 1$	$n = 2$	$n = 3$	$n = 4$		
1s	*np*	–	0.416	0.079	0.029	0.041	0.435
2s	*np*	–	–	0.435	0.103	0.111	0.351
2p	*ns*	−0.139	–	0.014	0.003	0.003	0.008
2p	*nd*	–	–	0.696	0.122	0.109	0.183

[†] More complete tabulations can be found in Bethe and Salpeter (1957).

Table 4.2 Lifetime of some levels of atomic hydrogen (in 10^{-8} s).

Level	2p	3s	3p	3d	4s	4p	4d	4f
Lifetime	0.16	16	0.54	1.56	23	1.24	3.65	7.3

where W_{kb}^{s} is the transition rate for spontaneous emission and the sum is over all states k, of lower energy, to which decay is allowed by the selection rules. On integration, $N(t)$ can be expressed in terms of $N(t=0)$ by

$$N(t) = N(t=0)\exp(-t/\tau_b) \tag{4.146}$$

where τ_b is called the *lifetime* or *half-life* of the level b, and

$$\tau_b^{-1} = \sum_k W_{kb}^{s} \tag{4.147}$$

For example, using the result (4.100), the lifetime of the 2p level of a hydrogenic atom is seen to be $\tau = (0.16 \times 10^{-8}/Z^4)$ s.

In the absence of external fields, the lifetime of an atomic level cannot depend on the orientation of the atom, and hence cannot depend on the magnetic quantum number m of the level b. This property can also be verified by evaluating (4.147) explicitly in the dipole approximation, and remembering that the sum over k includes all the magnetic substates of the final levels k to which the atom can decay. The lifetimes τ of some of the lower levels of atomic hydrogen, calculated in the dipole approximation, are shown in Table 4.2. The corresponding lifetimes of hydrogenic ions, with nuclear charge Z, are shorter and are given by the scaling law (Problem 4.9)

$$\tau(Z) = Z^{-4}\tau(Z=1) \tag{4.148}$$

In general the lifetime of a highly excited state is longer than that of a low-lying level. It is also interesting to note that the 2s level has an infinite lifetime in the dipole approximation. In fact the 2s level of atomic hydrogen has a lifetime of 1/7 s, the dominant decay process, 2s → 1s, occurring by the emission of two photons (that is, through higher order in the interaction between the atom and the electromagnetic field). The lifetime of 1/7 s is very long on the atomic time-scale, and the 2s level is said to be *metastable*.

4.7 Line shapes and widths

In the approximation used in Section 4.2 to calculate transition rates, we found that the angular frequency of the radiation emitted or absorbed between two atomic levels of energies E_a and E_b (with $E_b > E_a$) was exactly $\omega_{ba} = (E_b - E_a)/\hbar$, so that the spectral line was infinitely sharp. This cannot be completely accurate for the following reason. Every atomic level, except the ground state, decays with a finite lifetime τ. By the uncertainty principle, the energy of such a level cannot be precisely determined, but must be uncertain by an amount of order $\hbar/\tau$, which is called the *natural width* of the level. Therefore there is a finite probability that photons will be emitted with energies in an interval about $(E_b - E_a)$ of width $(\hbar/\tau_a + \hbar/\tau_b)$, where τ_a and τ_b are the lifetimes of the states a and b, respectively.

Let us consider for example the spontaneous decay of an excited state b of the atom to the state a which we choose to be the ground state. We return to the coupled equations (4.32) – with the perturbation H' given by (4.28) – and retain only those terms which contain the two atomic states a and b. The initial state of the system is characterised by an amplitude $c_b(t)$, while the final state consists of a photon of angular frequency ω, emitted in a direction (θ, ϕ) with a polarisation $\hat{\boldsymbol{\varepsilon}}_\lambda$, in addition to the ground state atom. The corresponding amplitude depends on ω, (θ, ϕ) and λ, but we will write it in shortened form as $c_a(\omega, t)$. When summing over the possible final states, we must make use of the density of states factor (4.59). Using (4.28), the expression (4.14) of $\mathbf{A}(\mathbf{r}, t)$ and remembering that M^λ_{ba} is given by (4.40), with $\hat{\boldsymbol{\varepsilon}}$ replaced by $\hat{\boldsymbol{\varepsilon}}_\lambda$, the equation (4.32) for $\dot{c}_b(t)$ can be written in explicit form as

$$\dot{c}_b(t) = -\frac{e}{m}\frac{V}{(2\pi)^3c^3}\sum_{\lambda=1}^{2}\int \mathrm{d}\omega\,\omega^2\int \mathrm{d}\Omega A_0(\omega)M^\lambda_{ba}(\omega)\exp[\mathrm{i}(\omega_{ba}-\omega)t+\mathrm{i}\delta_\omega]c_a(\omega, t) \tag{4.149}$$

where we have only retained the part of $\mathbf{A}(\mathbf{r}, t)$ that corresponds to the emission of a photon. Since a single photon is emitted $A_0(\omega)$ is found from (4.54) with $N(\omega) = 0$, namely

$$A_0(\omega) = \left(\frac{2\hbar}{V\varepsilon_0\omega}\right)^{1/2} \tag{4.150}$$

The equation for the time derivative of the amplitude $c_a(\omega, t)$ is again given by (4.32), with the same value of $A_0(\omega)$. We find that

$$\dot{c}_a(\omega, t) = -\frac{e}{m}A_0(\omega)\bar{M}^\lambda_{ab}(\omega)\exp[\mathrm{i}(\omega-\omega_{ba})t-\mathrm{i}\delta_\omega]\,c_b(t) \tag{4.151}$$

where (see (4.49))

$$\bar{M}^\lambda_{ab} = -M^{\lambda *}_{ba} \tag{4.152}$$

Since there is only a single amplitude $c_b(t)$, there is no sum over states on the right-hand side of (4.151).

In our previous treatment we solved the coupled equations by making the approximation $c_b(t) = 1$ on the right-hand side of (4.151), but we now allow for the decay of the upper level by writing

$$\begin{aligned} c_b(t) &= 1, & t &< 0 \\ c_b(t) &= \exp[-t/(2\tau_b)], & t &\geqslant 0 \end{aligned} \tag{4.153}$$

so that for $t \geqslant 0$ the component of the total wave function which describes the initial state b can be expressed as

$$\Psi_b(\mathbf{r}, t) = c_b(t)\psi_b(\mathbf{r}) \exp(-\mathrm{i}E_b t/\hbar) = \psi_b(\mathbf{r}) \exp\{-\mathrm{i}[E_b - \mathrm{i}\hbar/(2\tau_b)]t/\hbar\} \tag{4.154}$$

where ψ_b is a time-independent atomic wave function satisfying (4.30). For later convenience, since we are not interested in $\Psi_b(\mathbf{r}, t)$ for $t < 0$, we set $\Psi_b = 0$ for $t < 0$.

In the absence of any coupling to the radiation field, an excited atomic state b would be stable and the wave function would be $\Phi_b(\mathbf{r}, t) = \psi_b(\mathbf{r}) \exp(-\mathrm{i}E_b t/\hbar)$. This is a stationary state which is an eigenstate of the energy operator since

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Phi_b(\mathbf{r}, t) = E_b\Phi_b(\mathbf{r}, t) \tag{4.155}$$

and the system possesses a well-defined real energy E_b. In contrast, when the coupling to the radiation field is taken into account, the time variation of the initial wave function is given by (4.154) and

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi_b(\mathbf{r}, t) = \left(E_b - \mathrm{i}\frac{\hbar}{2\tau_b}\right)\Psi_b(\mathbf{r}, t) \tag{4.156}$$

showing that $\Psi_b(\mathbf{r}, t)$ does not describe a state with a well-defined *real* energy. This is a general result: a decaying state is never a state with a definite real energy.

Inserting $c_b(t)$ given by (4.153) into (4.151), and integrating over t, we find that

$$\begin{aligned} c_a(\omega, t) &= -\frac{e}{m}A_0(\omega)\bar{M}^{\lambda}_{ab}(\omega)\,\mathrm{e}^{-\mathrm{i}\delta_\omega}\int_0^t \exp[\mathrm{i}(\omega - \omega_{ba})t' - t'/(2\tau_b)]\,\mathrm{d}t' \\ &= -\frac{e}{m}A_0(\omega)\bar{M}^{\lambda}_{ab}(\omega)\,\mathrm{e}^{-\mathrm{i}\delta_\omega}\frac{\exp[\mathrm{i}(\omega - \omega_{ba})t - t/(2\tau_b)] - 1}{\mathrm{i}(\omega - \omega_{ba}) - 1/(2\tau_b)} \end{aligned} \tag{4.157}$$

At times $t \gg \tau_b$ the probability that a photon has been emitted is given by $|c_a(\omega, t)|^2$, which is proportional to

$$\left|\frac{1}{\mathrm{i}(\omega - \omega_{ba}) - 1/(2\tau_b)}\right|^2 = \frac{1}{(\omega - \omega_{ba})^2 + 1/(4\tau_b^2)} \tag{4.158}$$

The intensity of the emitted radiation therefore reaches a maximum when $\omega = \omega_{ba} = (E_b - E_a)/\hbar$, and decreases to one-half of the maximum value at

$$\begin{aligned} \omega &= \omega_{ba} \pm 1/(2\tau_b) \\ &= (E_b - E_a \pm \Gamma_b/2)/\hbar \end{aligned} \tag{4.159}$$

where

$$\Gamma_b = \frac{\hbar}{\tau_b} \tag{4.160}$$

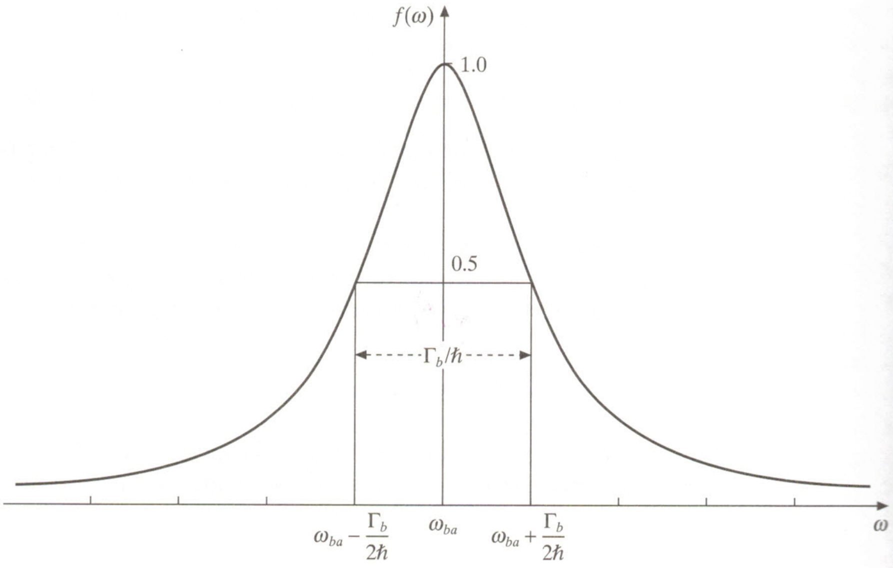

Figure 4.5 A plot of the Lorentzian intensity distribution.

is the *natural width* of the line. The intensity distribution given by (4.158) is said to be *Lorentzian* in shape. It is proportional to the function

$$f(\omega) = \frac{\Gamma_b^2/(4\hbar^2)}{(\omega - \omega_{ba})^2 + \Gamma_b^2/(4\hbar^2)} \qquad \textbf{(4.161)}$$

which is plotted in Fig. 4.5.

To calculate the lifetime τ_b, we insert the expression (4.157) for $c_a(\omega, t)$ into (4.149). Using (4.150) for $A_0(\omega)$ we find that

$$\dot{c}_b(t) = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{4\pi^2 m^2 c^3}$$
$$\times \sum_{\lambda=1}^{2} \int \mathrm{d}\Omega \int \mathrm{d}\omega\, \omega\, |M_{ba}^{\lambda}(\omega)|^2 \left\{\frac{\exp[-t/(2\tau_b)] - \exp[\mathrm{i}(\omega_{ba} - \omega)t]}{\mathrm{i}(\omega - \omega_{ba}) - 1/(2\tau_b)}\right\} \qquad \textbf{(4.162)}$$

The function in curly brackets is sharply peaked about $\omega = \omega_{ba}$. The term $\omega|M_{ba}^{\lambda}(\omega)|^2$ is slowly varying, and so can be evaluated at $\omega = \omega_{ba}$. The range of integration can then be taken from $\omega_{ba} - \eta$ to $\omega_{ba} + \eta$, with $\eta \rightarrow +\infty$. Using [10]

$$\lim_{\eta \to +\infty} \int_{-\eta}^{+\eta} \frac{1}{x - \alpha + \mathrm{i}\beta}\, \mathrm{d}x = -\mathrm{i}\pi \qquad \textbf{(4.163a)}$$

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[10] The second integral can be evaluated by using contour integration.

$$\int_{-\infty}^{+\infty} \frac{\exp(-\mathrm{i}xt)}{x-\alpha+\mathrm{i}\beta}\,\mathrm{d}x = -2\pi\mathrm{i}\exp[-\mathrm{i}(\alpha-\mathrm{i}\beta)t] \qquad \textbf{(4.163b)}$$

with $x = \omega$, $\alpha = \omega_{ba}$ and $\beta = 1/(2\tau_b)$, we find that

$$\dot{c}_b(t) = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{4\pi m^2c^3}\int \mathrm{d}\Omega \sum_{\lambda=1}^{2} \omega_{ba}|M^{\lambda}_{ba}(\omega_{ba})|^2 \exp[-t/(2\tau_b)] \qquad \textbf{(4.164)}$$

Now, from (4.153), we see that

$$\dot{c}_b(t) = -\frac{1}{2\tau_b}\exp[-t/(2\tau_b)], \quad t \geqslant 0 \qquad \textbf{(4.165)}$$

Comparing (4.164) with (4.165), and remembering that the transition rate is given by $W^{\mathrm{s}}_{ab} = \tau_b^{-1}$, we have

$$W^{\mathrm{s}}_{ab} = \frac{1}{\tau_b} = \frac{\hbar}{2\pi m^2c^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\int \mathrm{d}\Omega \sum_{\lambda=1}^{2} \omega_{ba}|M^{\lambda}_{ba}(\omega_{ba})|^2 \qquad \textbf{(4.166)}$$

which agrees with our previous result (4.61).

In the dipole approximation, after integration over the angles and summing over the two directions of polarisation, the expressions (4.80) for $W^{\mathrm{s,D}}_{ab}$ are regained. In particular, we have that

$$W^{\mathrm{s,D}}_{ab} = \frac{1}{\tau_b} = \frac{\Gamma_b}{\hbar} = \frac{4}{3\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega^3_{ba}|\mathbf{D}_{ba}|^2 \qquad \textbf{(4.167)}$$

For a one-electron atom in which the quantum numbers of the initial (decaying) and final states are (nlm) and $(n'l'm')$, respectively, the total transition rate from the level b to the level a is given by summing over the final and averaging over the initial magnetic substates. We have that

$$W^{\mathrm{s,D}}_{ab} = \frac{1}{\tau_b} = \frac{4}{3\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega^3_{ba}\frac{1}{g_b}\sum_{m'=-l'}^{l'}\sum_{m=-l}^{l}|\langle nlm|\mathbf{D}|n'l'm'\rangle|^2 \qquad \textbf{(4.168)}$$

where $g_b = (2l+1)$ is the degeneracy of the initial state b.

The distribution in angular frequency $a(\omega)$ of the spectral lines corresponding to absorption and stimulated emission can be shown, in the same way, to be proportional to the expression (4.161). To determine the constant of proportionality we note that for a line of zero width the distribution in ω is the delta function $\delta(\omega - \omega_{ba})$. Using the result

$$\lim_{\varepsilon\to 0^+} \frac{\varepsilon}{\pi(x^2+\varepsilon^2)} = \delta(x) \qquad \textbf{(4.169)}$$

we obtain, setting $\varepsilon = \Gamma_b/(2\hbar)$ and $x = \omega - \omega_{ba}$,

$$a(\omega) = \frac{1}{\pi}\frac{\Gamma_b/(2\hbar)}{(\omega-\omega_{ba})^2 + \Gamma_b^2/(4\hbar^2)} \qquad \textbf{(4.170)}$$

In the limit of zero line width, an absorption cross-section $\sigma_{ba}(\omega)$ can be defined as

$$\sigma_{ba}(\omega) = \frac{\hbar\omega_{ba}}{I(\omega_{ba})} W_{ba}\, \delta(\omega - \omega_{ba}) \tag{4.171}$$

where W_{ba} is the integrated transition rate for absorption. Using the expression (4.45) for W_{ba}, we find that, for linearly polarised radiation,

$$\sigma_{ba}(\omega) = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{ba}} |M_{ba}(\omega_{ba})|^2 \delta(\omega - \omega_{ba}) \tag{4.172}$$

To allow for the finite width of the line, we replace $\delta(\omega - \omega_{ba})$ in the above expression by the spectral distribution $a(\omega)$ given by (4.170), so that

$$\sigma_{ba}(\omega) = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{ba}} |M_{ba}(\omega_{ba})|^2 a(\omega) \tag{4.173}$$

Since the natural width Γ_b is extremely small compared to $(E_b - E_a)$, we have, to a high degree of accuracy,

$$\int_0^\infty a(\omega)\, \mathrm{d}\omega \simeq 1 \tag{4.174}$$

The integrated cross-section for absorption can be defined as

$$\sigma_{ba} = \int_0^\infty \sigma_{ba}(\omega)\, \mathrm{d}\omega \tag{4.175}$$

Using (4.173) and (4.174), we find that

$$\sigma_{ba} = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{ba}} |M_{ba}(\omega_{ba})|^2 \tag{4.176}$$

This result, which also follows by substituting the zero line width absorption cross-section (4.172) in (4.175), is in agreement with the expression (4.46) obtained in Section 4.2. It is worth noting that the absorption cross-section $\sigma_{ba}(\omega)$ has the dimensions of an area, whereas the integrated cross-section σ_{ba} has the dimensions of area divided by time, as we saw earlier.

In the dipole approximation, the absorption cross-section (4.173) for linearly polarised radiation becomes, using (4.74),

$$\sigma_{ba}^{\mathrm{D}}(\omega) = \frac{4\pi^2}{c\hbar}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega_{ba}\, |\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{D}_{ba}|^2 a(\omega) \tag{4.177}$$

For unpolarised radiation, we have (see (4.78))

$$\sigma_{ba}^{\mathrm{D}}(\omega) = \frac{4\pi^2}{3c\hbar}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega_{ba}|\mathbf{D}_{ba}|^2 a(\omega) \tag{4.178}$$

Comparing this result with (4.167), we see that $\sigma_{ba}^{\mathrm{D}}(\omega)$ can be written in the form

$$\sigma_{ba}^{\mathrm{D}}(\omega) = \left(\frac{c\pi}{\omega_{ba}}\right)^2 \frac{\Gamma_b}{\hbar} a(\omega) \tag{4.179}$$

If the ground state level E_a is non-degenerate, and the excited level E_b is degenerate, with degeneracy g_b, the generalisation of (4.179) is

$$\sigma_{ba}^{\mathrm{D}}(\omega) = g_b \left(\frac{c\pi}{\omega_{ba}}\right)^2 \frac{\Gamma_b}{\hbar} a(\omega) \tag{4.180}$$

The maximum of this cross-section occurs when $\omega = \omega_{ba}$, and from (4.170) is given by

$$\sigma_{ba}^{\mathrm{D,max}} = 2\pi g_b \left(\frac{c}{\omega_{ba}}\right)^2 \tag{4.181}$$

This interesting result which is independent of the value of the matrix element $\mathbf{D}_{ba}$ will be used in Section 4.9 to make a comparison with the magnitude of the cross-section for scattering of radiation.

As the uncertainty principle suggests, a more complete treatment demonstrates that the natural width of a line from one excited level b to another excited level a is given by

$$\Gamma = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right) \tag{4.182}$$

where τ_a and τ_b are the lifetimes of each of the levels, taking into account all the possible ways in which the levels can decay. The line intensity is proportional to the function $f(\omega)$ given by (4.161), with Γ_b replaced by Γ.

The natural width of atomic energy levels is very small. For example, the width of the 2p level of atomic hydrogen, which has an unperturbed energy of -3.40 eV and a lifetime of 0.16×10^{-8} s, is $\Gamma = 4.11 \times 10^{-7}$ eV. The profile of a spectral line can be measured, either by recording the spectrum on a photographic plate and subsequently measuring the density of the image as a function of wavelength, or by scanning the spectrum with a photoelectric detector. It is found, after allowing for the finite resolving power of the spectrograph employed, that observed spectral lines usually have much greater widths than the natural width. The reasons for this will now be examined.

Pressure broadening

In deriving the exponential law (4.146), we assumed that the transition rate between the atomic state b of a higher energy E_b and the states k of lower energy was entirely due to spontaneous emission. However, the population of the state b must also decrease if there are other mechanisms which lead to transitions out of b. Thus in (4.147) each of the spontaneous transition rates W_{kb}^{s} should be replaced by the sum of the transition rates for all processes depleting the level b. If W_{tot} is this sum, then the lifetime of the state b is now reduced to

$$\tilde{\tau}_b = \frac{1}{W_{\text{tot}}} \tag{4.183}$$

Similarly, if the level a is unstable, and there are other mechanisms than spontaneous emission leading out of a, the natural lifetime τ_a of this level is reduced to $\tilde{\tau}_a$.

The observed width $\tilde{\Gamma}$ of a spectral line from b to a is now given by

$$\tilde{\Gamma} = \hbar\left(\frac{1}{\tilde{\tau}_a} + \frac{1}{\tilde{\tau}_b}\right) \tag{4.184}$$

and the line intensity is proportional to the Lorentzian function $f(\omega)$ given by (4.161), with Γ_b replaced by $\tilde{\Gamma}$. The principal mechanism of this type, broadening lines of radiation from atoms in a gas, arises from *collisions* between the atoms. In each collision there is a certain probability that an atom initially in a state b will make a radiationless transition to some other state. The corresponding transition rate W_c is proportional to the number density of the atoms concerned, n, and to the relative velocity between pairs of atoms, v, so that

$$W_c = nv\sigma \tag{4.185}$$

where σ is a quantity with dimensions of area called the *collision cross-section*. This cross-section depends on the species of atom and on v. Since n depends on the pressure, the broadening of a spectral line due to this cause is called *pressure broadening* or, alternatively, *collisional broadening*. Both n and v also depend on the temperature, so that information about the temperature and the pressure of a gas can be obtained by measuring the profiles of spectral lines. This is a major source of knowledge about physical conditions in stellar atmospheres, which in turn provides most of our evidence about stellar structure.

When the observed width $\tilde{\Gamma}_b = \hbar/\tilde{\tau}_b$ of a spectral line between an excited state b and the ground state a is greater than the natural width Γ_b, the absorption cross-section $\sigma_{ba}(\omega)$ is still given by the expression (4.180), provided $a(\omega)$ represents the observed line profile. When the line profile is Lorentzian as in the case of pressure broadening, the maximum of the absorption cross-section (see (4.181)) becomes

$$\sigma_{ba}^{\text{D, max}} = 2\pi g_b\left(\frac{c}{\omega_{ba}}\right)^2 \frac{\Gamma_b}{\tilde{\Gamma}_b} \tag{4.186}$$

where the initial state a is again taken to be non-degenerate.

Doppler broadening

The wavelength of the light emitted by a moving source is shifted by the Doppler effect. If the emitting source is moving at a non-relativistic velocity, and v is the component of the velocity of the source along the line of sight, the wavelength λ of the emitted light is, to first order in v/c,

$$\lambda = \lambda_0 \left(1 \pm \frac{v}{c}\right) \tag{4.187}$$

where λ_0 is the wavelength emitted by a stationary source. The plus sign corresponds to a source receding from the observer, and the minus sign to an approaching source. To first order in v/c, the angular frequency $\omega = 2\pi c/\lambda$ of the light emitted by a moving source is therefore related to the angular frequency $\omega_0 = 2\pi c/\lambda_0$ emitted by a stationary source as

$$\omega = \omega_0 \left(1 \mp \frac{v}{c}\right) \tag{4.188}$$

The formulae (4.187) and (4.188) describe the *first-order* Doppler effect [11].

If the light is emitted from a gas at absolute temperature T, the number of atoms, $\mathrm{d}N$, with velocities between v and $v + \mathrm{d}v$ is given by Maxwell's distribution

$$\mathrm{d}N = N_0 \exp[-Mv^2/(2k_\mathrm{B}T)]\,\mathrm{d}v \tag{4.189}$$

where k_B is Boltzmann's constant, M is the atomic mass and N_0 is a constant. The intensity $\mathcal{I}(\omega)$ of light emitted in an angular frequency interval ω to $\omega + \mathrm{d}\omega$ is proportional to the number of atoms with velocities between v and $v + \mathrm{d}v$. Hence, using (4.188) and (4.189), we obtain the *Gaussian distribution*

$$\mathcal{I}(\omega) = \mathcal{I}(\omega_0) \exp\left[-\frac{Mc^2}{2k_\mathrm{B}T}\left(\frac{\omega - \omega_0}{\omega_0}\right)^2\right] \tag{4.190}$$

If ω_1 is the angular frequency at half-maximum, then

$$(\omega_1 - \omega_0)^2 = \frac{2k_\mathrm{B}T}{Mc^2}\,\omega_0^2 \log 2 \tag{4.191}$$

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[11] The formulae (4.187) and (4.188) are only accurate to first order in v/c. The *relativistic* Doppler formula replacing (4.188) is

$$\omega = \left(\frac{1 \mp v/c}{1 \pm v/c}\right)^{1/2} \omega_0$$

Expanding the square root as a power series in v/c, we find that

$$\omega - \omega_0 = \mp\frac{v}{c}\omega_0 + \frac{1}{2}\frac{v^2}{c^2}\omega_0 + \dots$$

The first term on the right, which involves v/c to the first power, yields the *linear Doppler effect*. The second term, involving $(v/c)^2$, yields a *second-order Doppler* shift which does not change if the sign of the velocity is changed, that is, whether the source and observer are approaching or receding from each other.

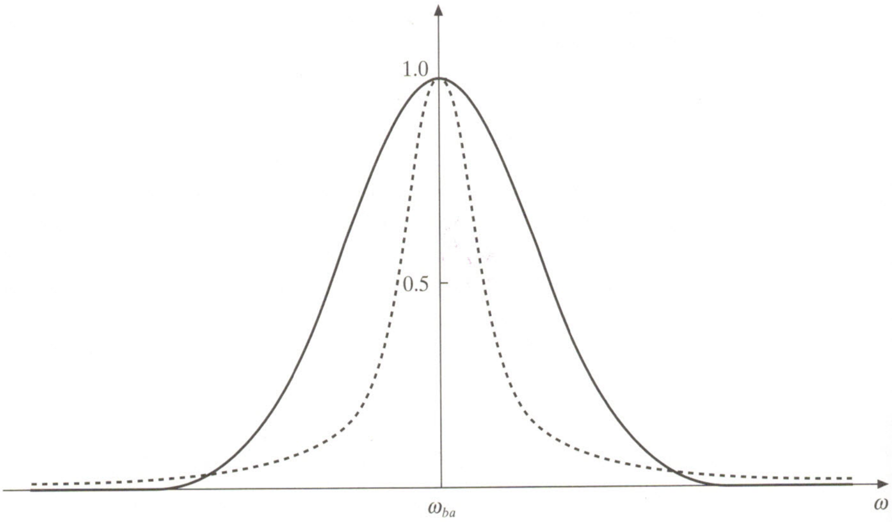

Figure 4.6 A comparison of a Gaussian distribution (solid line) of the form

$$F(\omega) = \exp[-\alpha(\omega - \omega_{ba})^2]$$

with a Lorentzian distribution (dashed line) of the form

$$f(\omega) = \frac{\Gamma^2/(4\hbar^2)}{(\omega - \omega_{ba})^2 + \Gamma^2/(4\hbar^2)}$$

The total Doppler width at half-maximum $\Delta\omega^{\mathrm{D}}$ is $2|\omega_1 - \omega_0|$ and hence

$$\Delta\omega^{\mathrm{D}} = \frac{2\omega_0}{c}\left[\frac{2k_{\mathrm{B}}T}{M}\log 2\right]^{1/2} \tag{4.192}$$

This width increases with temperature and with the frequency of the line, and decreases as the atomic mass increases. Several spectroscopic methods have been developed in which Doppler broadening is reduced or completely eliminated. One of these methods, *level crossing spectroscopy*, will be discussed in Chapter 9 where we consider the effect of external magnetic fields on atomic energy levels. Another method, *saturation spectroscopy*, will be described in Section 15.2, devoted to laser spectroscopy.

While pressure broadening increases the width of a spectral line, but preserves the Lorentzian profile, the Gaussian profile produced by Doppler broadening is quite different. The two shapes are compared in Fig. 4.6. In general, both pressure and Doppler broadening are present, and the observed profile, called a *Voigt profile*, is due to a combination of both effects. The decrease of the Gaussian distribution away from ω_0 (= ω_{ba}) is so rapid that the 'wings' of spectral lines are determined by the residual Lorentzian distribution. Thus, if both Doppler and pressure broadening are present, the characteristics of each effect can be distinguished provided sufficiently accurate experimental profiles can be obtained.

4.8 The photoelectric effect

If electromagnetic radiation of sufficiently high frequency is absorbed by an atomic system A the final state may lie in the continuum and one or several electrons will be ejected from A. This is known as *photoionisation* and is the process responsible for the photoelectric effect (see Section 1.4).

In this section we shall obtain the cross-section for a particular photoionisation process, in which the electron is ejected from a hydrogenic atom (ion). We assume that this atom (ion) is initially in the ground state (1s), described by the wave function $\psi_a(\mathbf{r}) \equiv \psi_{1s}(r)$ and having the energy E_{1s}. We denote by $E = h\nu = \hbar\omega$ the energy of the absorbed photon, and by $\mathbf{k}$ its wave vector. Let $\mathbf{k}_f$ be the wave vector of the electron in the final state and $\mathbf{p}_f = \hbar\mathbf{k}_f$ its momentum. Assuming that the ejected electron is non-relativistic, its kinetic energy in the final state is given by

$$E_f = \frac{\hbar^2 k_f^2}{2m} \tag{4.193}$$

with $E_f \ll mc^2$.

The final state $\psi_b(\mathbf{k}_f, \mathbf{r})$ represents a continuum state corresponding to an electron with a wave vector $\mathbf{k}_f$ and an energy E_f moving in the Coulomb field of a nucleus of charge Ze, which we assume to be infinitely heavy. Thus $\psi_b(\mathbf{k}_f, \mathbf{r})$ is a positive energy Coulomb wave function [12] satisfying the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r} - E_f\right)\psi_b(\mathbf{k}_f, \mathbf{r}) = 0 \tag{4.194}$$

For sufficiently high energies of the ejected electron (that is, when $E_f \gg |E_{1s}|$), and when the nuclear charge Ze is relatively small [13] ($Z\alpha \ll 1$), the interaction of the outgoing electron with the nucleus can be neglected in the first approximation [14] and $\psi_b(\mathbf{k}_f, \mathbf{r})$ can be represented by a plane wave

$$\psi_b(\mathbf{k}_f, \mathbf{r}) = (2\pi)^{-3/2} \exp(\mathrm{i}\mathbf{k}_f \cdot \mathbf{r}) \tag{4.195}$$

where we have chosen the Dirac delta function normalisation (2.35).

The photoelectric total cross-section can be obtained by using (4.172) and integrating over all final states of the ejected electron. That is,

$$\sigma_{\text{tot}} = \frac{4\pi^2 \alpha\hbar^2}{m^2} \int \mathrm{d}\mathbf{k}_f \, \frac{1}{\omega_{ba}} |M_{ba}(\omega_{ba})|^2 \, \delta(\omega - \omega_{ba}) \tag{4.196}$$

where $\omega_{ba} = (E_f - E_{1s})/\hbar$. The delta function in (4.196) ensures energy conservation:

$$E_f = \hbar\omega + E_{1s} \tag{4.197}$$

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[12] Positive energy Coulomb wave functions will be discussed in Section 12.5.

[13] If $Z\alpha \ll 1$, the bound state of the electron can be treated non-relativistically (see (1.103)).

[14] A more detailed treatment of the photoionisation of one-electron atoms, including the Coulomb interaction of the ejected electron with the nucleus, will be given in Section 13.5.