4 Interaction of one-electron atoms with electromagnetic radiation

In this chapter, we shall discuss the interaction of hydrogenic atoms with electromagnetic radiation. We shall first show how spectral lines arise, and at a later stage we shall study the photoelectric effect and the scattering of radiation by atomic systems. In considering the interaction of an atom with radiation, there are three basic processes to analyse. First, just as a classical oscillating charge will radiate spontaneously, an atom can make a spontaneous transition from an excited state to a state of lower energy, emitting a photon which is the quantum of the electromagnetic field. This process is called *spontaneous emission*. Secondly, an atom can *absorb* a photon from an external radiation field, making a transition from a state of lower to a state of higher energy. Finally, an atom can also emit a photon under the influence of an external radiation field. This process is called *stimulated emission*; it is distinct from spontaneous emission because it requires (like absorption) the presence of an external radiation field. Stimulated emission has important applications in the LASER (an acronym for Light Amplification by Stimulated Emission of Radiation) and the MASER (Microwave Amplification by Stimulated Emission of Radiation), which produce intense beams of coherent radiation, and which will be discussed in Chapter 15.

In a rigorous treatment, we would have to start by studying quantum electrodynamics, in which the electromagnetic field is expressed in terms of its quanta – the photons. Each photon corresponding to a field of frequency ν carries an amount of energy $h\nu$. Even in comparatively weak fields the photon density can be very high (see Problem 4.1). Under these circumstances the number of photons can be treated as a continuous variable and the field can be described classically by using Maxwell's equations. We shall proceed by using a *semi-classical* theory in which the radiation field is treated classically, but the atomic system is described by using quantum mechanics. The approximation will also be made that the influence of the atom on the external field can be neglected. Clearly these assumptions do not hold in the case of spontaneous emission, because only one photon is concerned – and one is not a large number! The proper treatment of spontaneous emission is well understood, but is beyond the scope of this book. Nevertheless, we shall be able to find the transition rate for spontaneous emission indirectly using a statistical argument due to Einstein.

4.1 The electromagnetic field and its interaction with charged particles

The classical electromagnetic field is described by electric and magnetic field vectors $\mathcal{E}$ and $\mathcal{B}$, which satisfy Maxwell's equations [1]. We shall express these and other electromagnetic quantities in rationalised MKS units, which form part of the standard SI system. The electric field $\mathcal{E}$ and magnetic field $\mathcal{B}$ can be generated from scalar and vector potentials ϕ and $\mathbf{A}$ by

$$\mathcal{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}, t) \tag{4.1}$$

and

$$\mathcal{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \tag{4.2}$$

The potentials are not completely defined by (4.1) and (4.2), since the fields, $\mathcal{E}$ and $\mathcal{B}$, are invariant under the (classical) *gauge transformation* $\mathbf{A} \to \mathbf{A} + \nabla\chi$, $\phi \to \phi - \partial\chi/\partial t$, where χ is any real, differentiable function of $\mathbf{r}$ and t. The freedom implied by this *gauge invariance* allows us to impose a further condition on the vector potential $\mathbf{A}$, which we shall choose to be

$$\nabla \cdot \mathbf{A} = 0 \tag{4.3}$$

When $\mathbf{A}$ satisfies this condition, we are said to be using the *Coulomb gauge*. This choice of gauge is convenient when no sources are present, which is the case considered here. One may then take $\phi = 0$, and $\mathbf{A}$ satisfies the wave equation

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = 0 \tag{4.4}$$

where c is the velocity of light *in vacuo*.

A monochromatic plane wave solution of (4.4) corresponding to the angular frequency ω (that is, to the frequency $\nu = \omega/(2\pi)$) is

$$\mathbf{A}(\mathbf{r}, t) = A_0(\omega)\hat{\boldsymbol{\varepsilon}} \cos(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega) \tag{4.5}$$

where $\mathbf{k}$ is the wave (or propagation) vector and δ_ω is a real constant phase. Substituting (4.5) in (4.4), it is found that the angular frequency ω and the wave number k (the magnitude of the wave vector $\mathbf{k}$) are related by

$$\omega = kc \tag{4.6}$$

The vector potential $\mathbf{A}$ has an amplitude $|A_0(\omega)|$ and is in the direction specified by the unit vector $\hat{\boldsymbol{\varepsilon}}$, called the *polarisation vector*. In addition, equation (4.3) is satisfied if

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[1] Useful texts on electromagnetism are those by Duffin (1968) and Jackson (1998).

$$\mathbf{k}\cdot\hat{\boldsymbol{\varepsilon}} = 0 \tag{4.7}$$

so that $\hat{\boldsymbol{\varepsilon}}$ is perpendicular to **k** and the wave is *transverse*.

Using the Coulomb gauge, with $\phi = 0$, the electric and magnetic fields are given from (4.1), (4.2) and (4.5) by

$$\mathscr{E}(\mathbf{r}, t) = \mathscr{E}_0(\omega)\hat{\boldsymbol{\varepsilon}} \sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega) \tag{4.8a}$$

and

$$\mathscr{B}(\mathbf{r}, t) = \mathscr{E}_0(\omega)\omega^{-1}(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}}) \sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega) \tag{4.8b}$$

where $\mathscr{E}_0(\omega) = -\omega A_0(\omega)$. The electric field vector $\mathscr{E}$ has an amplitude $|\mathscr{E}_0(\omega)|$ and is in the direction of the polarisation vector $\hat{\boldsymbol{\varepsilon}}$. From (4.6) and (4.8), we see that for a radiation field of a given frequency, $|\mathscr{B}|/|\mathscr{E}| = 1/c$. We also note that the vectors $\mathscr{E}$, $\mathscr{B}$ and **k** are mutually perpendicular. An electromagnetic plane wave such as (4.8), for which the electric field vector points in a fixed direction $\hat{\boldsymbol{\varepsilon}}$, is said to be *linearly polarised*. 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 with polarisation vectors $\hat{\boldsymbol{\varepsilon}}_\lambda$ ($\lambda = 1, 2$) perpendicular to $\hat{\mathbf{k}}$, where the phases of the two component waves are, in general, different. Any radiation field can be expressed as a superposition of monochromatic fields.

It is useful to relate the energy density of the field to the photon density, keeping in mind that each photon at a frequency ν carries a quantum of energy of magnitude $h\nu = \hbar\omega$. The energy density of the field is given by

$$\frac{1}{2}(\varepsilon_0|\mathscr{E}|^2 + |\mathscr{B}|^2/\mu_0) = \varepsilon_0\mathscr{E}_0^2(\omega)\sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega) \tag{4.9}$$

where ε_0 and μ_0 are the permittivity and permeability of free space, and $\varepsilon_0\mu_0 = c^{-2}$. The average of $\sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega)$ over a period $T = 2\pi/\omega$ is given by

$$\frac{1}{T}\int_0^T \sin^2(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega)\,\mathrm{d}t = \frac{1}{2} \tag{4.10}$$

Using this result the average energy density $\rho(\omega)$ is

$$\rho(\omega) = \frac{1}{2}\varepsilon_0\mathscr{E}_0^2(\omega) = \frac{1}{2}\varepsilon_0\omega^2 A_0^2(\omega) \tag{4.11}$$

If the number of photons of angular frequency ω within a volume V is $N(\omega)$, the energy density is $\hbar\omega N(\omega)/V$, and equating this with (4.11) the amplitude of the electric field is found to be

$$|\mathscr{E}_0(\omega)| = [2\rho(\omega)/\varepsilon_0]^{1/2} = [2\hbar\omega N(\omega)/(\varepsilon_0 V)]^{1/2} \tag{4.12}$$

The average rate of energy flow through a unit cross-sectional area, normal to the direction of propagation of the radiation, defines the intensity $I(\omega)$. Since the velocity of electromagnetic waves in free space is c, we have

$$I(\omega) = \rho(\omega)c = \frac{1}{2}\varepsilon_0 c \mathscr{E}_0^2(\omega) = \frac{1}{2}\varepsilon_0 c\omega^2 A_0^2(\omega) = \hbar\omega N(\omega)c/V \tag{4.13}$$

A general pulse of radiation can be described by representing the vector potential $\mathbf{A}(\mathbf{r}, t)$ as a superposition of plane waves of the form (4.5). Taking each plane wave component to have the same direction of propagation $\hat{\mathbf{k}}$ and to be linearly polarised in the direction $\hat{\boldsymbol{\varepsilon}}$, we have

$$\mathbf{A}(\mathbf{r}, t) = \hat{\boldsymbol{\varepsilon}} \int_0^\infty A_0(\omega)\cos(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega)\,\mathrm{d}\omega \tag{4.14}$$

When the radiation is nearly monochromatic, the amplitude $A_0(\omega)$ is sharply peaked about some value ω_0 of ω. The radiation from a hot gas or glowing filament arises from many atoms each emitting photons independently. As a result, within the integral over ω the phases δ_ω are distributed completely at random, and the radiation is said to be *incoherent*. This is characteristic of light from all sources with the exception of lasers. Because of the random phase distribution, when the average energy density is calculated from the squares of $\mathscr{E}$ and $\mathscr{B}$, the contribution to the energy density from each frequency can be added together, the cross terms averaging to zero [2]. The average energy density ρ and intensity I for radiation composed of a range of frequencies can then be expressed as

$$\rho = \int_0^\infty \rho(\omega)\,\mathrm{d}\omega, \qquad I = \int_0^\infty I(\omega)\,\mathrm{d}\omega \tag{4.15}$$

where $\rho(\omega)$ and $I(\omega)$ are the *energy density* and *intensity per unit angular frequency range*, given by (4.11) and (4.13), respectively.

In Chapter 15, the radiation from a single mode laser, which exhibits a high degree of coherence and is nearly monochromatic, is discussed. In this case, the phase δ_ω is constant in a small region of width $\Delta\omega$ centred about an angular frequency ω_0, so that δ_ω can be eliminated from (4.14) by changing the (arbitrary) zero of time. It follows that the expressions (4.15) remain valid for nearly monochromatic coherent radiation.

Charged particles in an electromagnetic field

The Hamiltonian of a spinless particle of charge q and mass m in an electromagnetic field is

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi \tag{4.16}$$

where $\mathbf{p}$ is the generalised momentum of the particle. The steps leading to (4.16) are given in Appendix 6. Ignoring for the present small spin-dependent terms, the

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[2] While this is intuitively clear, a detailed proof is too long to be given here. This point is discussed by Marion and Heals (1980).

Hamiltonian of an electron of mass m in an electromagnetic field is given by (4.16), with $q = -e$.

Since the Hamiltonian H must be Hermitian, we shall write (4.16) in the form

$$H = \frac{\mathbf{p}^2}{2m} - \frac{q}{2m}(\mathbf{A}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{A}) + \frac{q^2}{2m}\mathbf{A}^2 + q\phi \tag{4.17}$$

In the position representation, $\mathbf{p}$ is the operator $-\mathrm{i}\hbar\boldsymbol{\nabla}$ and the time-dependent Schrödinger equation is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{i}\hbar\frac{q}{2m}(\mathbf{A}\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\mathbf{A}) + \frac{q^2}{2m}\mathbf{A}^2 + q\phi\right]\Psi(\mathbf{r}, t) \tag{4.18}$$

An important property of equation (4.18) is that its form is unchanged under the *gauge transformation*

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}'(\mathbf{r}, t) + \boldsymbol{\nabla}\chi(\mathbf{r}, t) \tag{4.19a}$$

$$\phi(\mathbf{r}, t) = \phi'(\mathbf{r}, t) - \frac{\partial}{\partial t}\chi(\mathbf{r}, t) \tag{4.19b}$$

$$\Psi(\mathbf{r}, t) = \Psi'(\mathbf{r}, t)\exp[\mathrm{i}q\chi(\mathbf{r}, t)/\hbar] \tag{4.19c}$$

where χ is an arbitrary real, differentiable function of $\mathbf{r}$ and t. That is, the wave function $\Psi'(\mathbf{r}, t)$ satisfies the equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi'(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{i}\hbar\frac{q}{2m}(\mathbf{A}'\cdot\boldsymbol{\nabla} + \boldsymbol{\nabla}\cdot\mathbf{A}') + \frac{q^2}{2m}\mathbf{A}'^2 + q\phi'\right]\Psi'(\mathbf{r}, t) \tag{4.20}$$

Since, as seen from (4.19c), a gauge transformation is a particular case of a unitary transformation, measurable quantities (such as expectation values or transition probabilities) calculated in different gauges must be the same. The property of gauge invariance allows us to adopt the Coulomb gauge defined by (4.3) and to take $\phi = 0$, as we have seen above. The time-dependent Schrödinger equation (4.18) then reduces to

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + \mathrm{i}\hbar\frac{q}{m}\mathbf{A}\cdot\boldsymbol{\nabla} + \frac{q^2}{2m}\mathbf{A}^2\right]\Psi(\mathbf{r}, t) \tag{4.21}$$

where we have used the fact that in the Coulomb gauge

$$\begin{aligned}\boldsymbol{\nabla}\cdot(\mathbf{A}\Psi) &= \mathbf{A}\cdot(\boldsymbol{\nabla}\Psi) + (\boldsymbol{\nabla}\cdot\mathbf{A})\Psi \\ &= \mathbf{A}\cdot(\boldsymbol{\nabla}\Psi)\end{aligned} \tag{4.22}$$

Interaction of one-electron atoms with an electromagnetic field

Let us now consider the interaction of the electromagnetic field (4.8) with a one-electron atom (ion), containing a nucleus of charge Ze and mass M and an electron of charge $q = -e$ and mass m. We shall restrict ourselves here to 'ordinary' hydrogenic systems such as H, He^+, ... In that case the nuclear mass M is very large compared to the electronic mass m. In fact, we shall make the infinite nuclear mass approximation, thus neglecting recoil effects (see Problem 1.16) and reduced mass effects. The interaction between the radiation field and the nucleus can be ignored to a high degree of accuracy. However, we must include in the Hamiltonian the electrostatic Coulomb potential $-Ze^2/(4\pi\varepsilon_0 r)$ between the electron and the nucleus. It is convenient to regard this electrostatic interaction as an additional potential energy term, while the radiation field is described in terms of a vector potential alone satisfying the Coulomb gauge condition (4.3), as discussed above. The time-dependent Schrödinger equation for a one-electron atom in an electromagnetic field then reads

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = H(t)\Psi(\mathbf{r}, t) \tag{4.23}$$

where

$$H(t) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r} - \mathrm{i}\hbar\frac{e}{m}\mathbf{A}\cdot\boldsymbol{\nabla} + \frac{e^2}{2m}\mathbf{A}^2 \tag{4.24}$$

We can also write (4.23) in the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = [H_0 + H_{\mathrm{int}}(t)]\,\Psi(\mathbf{r}, t) \tag{4.25}$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{4.26}$$

is the time-independent Hamiltonian of the one-electron atom (ion) in the absence of the electromagnetic field, and

$$\begin{aligned} H_{\mathrm{int}}(t) &= \frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m}\mathbf{A}^2 \\ &= -\mathrm{i}\hbar\frac{e}{m}\mathbf{A}\cdot\boldsymbol{\nabla} + \frac{e^2}{2m}\mathbf{A}^2 \end{aligned} \tag{4.27}$$

is the Hamiltonian describing the interaction of the hydrogenic atom with the radiation field.

In this chapter, we shall treat only the weak field case [3] in which the term in $\mathbf{A}^2$ is negligible [4] compared with the term linear in $\mathbf{A}$. Accordingly, we shall write $H_{\mathrm{int}}(t) = H'(t)$, where

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[3] Atoms in intense electromagnetic fields will be discussed in Chapter 15.

[4] Although we are treating the case for which $\mathbf{A}^2$ is very small compared with $\mathbf{A}$, the photon density is assumed to be high enough for the radiation field to be treated classically. Both conditions are well satisfied in the emission and absorption processes we shall describe.

$$H'(t) = -\mathrm{i}\hbar\frac{e}{m}\mathbf{A}\cdot\nabla = \frac{e}{m}\mathbf{A}\cdot\mathbf{p} \qquad \textbf{(4.28)}$$

will be treated as a small perturbation.

4.2 Transition rates

Having neglected the term in $\mathbf{A}^2$, we see that the time-dependent Schrödinger equation (4.25) may be written as

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = [H_0 + H'(t)]\Psi(\mathbf{r}, t) \qquad \textbf{(4.29)}$$

where H_0 is given by (4.26) and $H'(t)$ by (4.28).

We shall study this problem by using the time-dependent perturbation theory given in Chapter 2. Referring to equation (2.297), and dropping the superscript (0) for notational simplicity, we denote by E_k the eigenvalues and by ψ_k the corresponding normalised eigenfunctions of the hydrogenic Hamiltonian (4.26), so that

$$H_0\psi_k = E_k\psi_k \qquad \textbf{(4.30)}$$

Because the set of functions ψ_k (including both the discrete set studied in Chapter 3 and the continuous set corresponding to unbound states) is complete, the general solution Ψ of the time-dependent Schrödinger equation (4.29), which we assume to be normalised to unity, can be expanded as

$$\Psi(\mathbf{r}, t) = \sum_k c_k(t)\psi_k(\mathbf{r})\exp(-\mathrm{i}E_k t/\hbar) \qquad \textbf{(4.31)}$$

where the sum is over both the discrete set and the continuous set of hydrogenic eigenfunctions ψ_k. The coefficients $c_k(t)$ satisfy the coupled equations (2.336) with $\lambda = 1$, namely

$$\dot{c}_b(t) = (\mathrm{i}\hbar)^{-1}\sum_k H'_{bk}(t)c_k(t)\exp(\mathrm{i}\omega_{bk}t) \qquad \textbf{(4.32)}$$

where

$$H'_{bk}(t) = \langle\psi_b|H'(t)|\psi_k\rangle \qquad \textbf{(4.33)}$$

and

$$\omega_{bk} = (E_b - E_k)/\hbar \qquad \textbf{(4.34)}$$

Let us suppose that the system is initially in a well-defined stationary bound state of energy E_a described by the wave function ψ_a and that the pulse of radiation is switched on at the time $t = 0$. Thus the initial conditions are given by

$$c_k(t \leqslant 0) = \delta_{ka} \qquad \textbf{(4.35)}$$

and, to first order in the perturbation H', we have (see (2.343b))

$$\begin{aligned} c_b^{(1)}(t) &= (\mathrm{i}\hbar)^{-1}\int_0^t H'_{ba}(t')\exp(\mathrm{i}\omega_{ba}t')\,\mathrm{d}t' \\ &= -\frac{e}{m}\int_0^t \langle\psi_b|\mathbf{A}\cdot\boldsymbol{\nabla}|\psi_a\rangle\exp(\mathrm{i}\omega_{ba}t')\,\mathrm{d}t' \end{aligned} \qquad \textbf{(4.36)}$$

where $\omega_{ba} = (E_b - E_a)/\hbar$ and

$$\langle\psi_b|\mathbf{A}\cdot\boldsymbol{\nabla}|\psi_a\rangle = \int \psi_b^*(\mathbf{r})\mathbf{A}\cdot\boldsymbol{\nabla}\psi_a(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad \textbf{(4.37)}$$

To proceed further, we use the vector potential $\mathbf{A}(\mathbf{r}, t)$ given by (4.14) to obtain

$$\begin{aligned} c_b^{(1)}(t) = -\frac{e}{2m}\int_0^\infty \mathrm{d}\omega A_0(\omega)\Bigg[&\exp(\mathrm{i}\delta_\omega)\langle\psi_b|\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{\nabla}|\psi_a\rangle\int_0^t \mathrm{d}t'\exp[\mathrm{i}(\omega_{ba}-\omega)t'] \\ &+ \exp(-\mathrm{i}\delta_\omega)\langle\psi_b|\exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{\nabla}|\psi_a\rangle\int_0^t \mathrm{d}t'\exp[\mathrm{i}(\omega_{ba}+\omega)t']\Bigg] \end{aligned} \qquad \textbf{(4.38)}$$

In general, the duration of the pulse is much larger than the periodic time $(2\pi/\omega_{ba})$ which is for example about 2×10^{-15} s for the yellow sodium D line at 5890 Å. It follows that the first integral over t' will be negligible unless $\omega_{ba} \simeq \omega$, that is unless $E_b \simeq E_a + \hbar\omega$. Thus we see that in this case the final state of the atom has greater energy than the initial state and one photon of energy $\hbar\omega$ is *absorbed* from the radiation field. On the other hand, the second integral over t' in (4.38) will be negligible unless $\omega_{ba} \simeq -\omega$, that is unless $E_b \simeq E_a - \hbar\omega$. In this case the initial state of the atom has greater energy than the final state and one photon of energy $\hbar\omega$ is *emitted*. Since only one of these conditions can be satisfied for a pair of states *a* and *b*, we can deal with the two terms separately.

We shall assume for the moment that both the initial and final atomic states are *discrete* ('bound–bound' transitions). The photoelectric effect, which corresponds to transitions from a discrete initial state to final states lying in the continuum ('bound–free' transitions) will be studied in Section 4.8.

Absorption

We start with the first term of (4.38), describing absorption. Using the fact that the radiation is incoherent – so that no interference terms occur – we find that the probability for the system to be in the state *b* at time *t* is

$$|c_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{m}\right)^2\int_0^\infty A_0^2(\omega)|M_{ba}(\omega)|^2 F(t, \omega - \omega_{ba})\,\mathrm{d}\omega \qquad \textbf{(4.39)}$$

where we have defined the matrix element M_{ba} as

$$M_{ba} = \langle\psi_b|\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{\nabla}|\psi_a\rangle = \int \psi_b^*(\mathbf{r})\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{\nabla}\psi_a(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad \textbf{(4.40)}$$

and we recall that $\omega = kc$. Upon setting $\bar{\omega} = \omega - \omega_{ba}$, the function $F(t, \bar{\omega})$ which appears in (4.39) is seen to be the same as the function $F(t, \omega)$ introduced in Chapter 2. That is (see (2.348)),

$$F(t, \bar{\omega}) = \frac{1 - \cos \bar{\omega} t}{\bar{\omega}^2}, \qquad \bar{\omega} = \omega - \omega_{ba} \tag{4.41}$$

The properties of $F(t, \omega)$ discussed in Section 2.8 may therefore be used directly here, provided that we make the substitution $\omega \to \bar{\omega}$. In particular, since for large t the function $F(t, \bar{\omega})$ has a sharp maximum at $\bar{\omega} = 0$, namely at $\omega = \omega_{ba}$, we can set $\omega = \omega_{ba}$ in the slowly varying quantities $A_0^2(\omega)$ and $|M_{ba}(\omega)|^2$, take these factors outside the integral in (4.39) and extend the limits of integration to ±∞. Hence we have

$$|c_b^{(1)}(t)|^2 = \frac{1}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 \int_{-\infty}^{+\infty} F(t, \bar{\omega})\, \mathrm{d}\omega \tag{4.42}$$

and using the result (2.349), we obtain

$$|c_b^{(1)}(t)|^2 = \frac{\pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 t \tag{4.43}$$

Thus the probability $|c_b^{(1)}(t)|^2$ increases linearly with time and a *transition rate for absorption* (integrated over ω) can be defined in first-order perturbation theory as

$$W_{ba} = \frac{\mathrm{d}}{\mathrm{d}t}|c_b^{(1)}(t)|^2 = \frac{\pi}{2}\left(\frac{e}{m}\right)^2 A_0^2(\omega_{ba})|M_{ba}(\omega_{ba})|^2 \tag{4.44}$$

In terms of the intensity per unit angular frequency range, $I(\omega)$, given by (4.13), the integrated transition rate for absorption is given by

$$W_{ba} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}|M_{ba}(\omega_{ba})|^2 \tag{4.45}$$

and is seen to be proportional to $I(\omega_{ba})$.

The rate of absorption of energy from the radiation field, per atom, is $(\hbar\omega_{ba})W_{ba}$. It is convenient to define an integrated *absorption cross-section* σ_{ba} which is the rate of absorption of energy (per atom) divided by $I(\omega_{ba})$. That is,

$$\sigma_{ba} = \frac{4\pi^2 \alpha \hbar^2}{m^2 \omega_{ba}}|M_{ba}(\omega_{ba})|^2 \tag{4.46}$$

where $\alpha = e^2/(4\pi\varepsilon_0 \hbar c) \simeq 1/137$ is the fine structure constant. Since the incident flux of photons of angular frequency ω_{ba} is given by $I(\omega_{ba})/(\hbar\omega_{ba})$, we see that the integrated cross section σ_{ba} may also be defined as the transition probability per unit time per atom (integrated over ω), W_{ba}, divided by the incident photon flux. It should be noted that the integrated absorption cross section σ_{ba} has the dimensions of area divided by time ($[\mathrm{L}]^2 [\mathrm{T}]^{-1}$).

Stimulated emission

To calculate the transition rate for stimulated emission, we return to (4.38) and in particular to the second term in the expression for $c_b^{(1)}(t)$, which corresponds to a downward transition ($E_b \simeq E_a - \hbar\omega$) in which a photon of energy $\hbar\omega$ is emitted. It is convenient to interchange the labels of the states a and b so that the state b is again the one with higher energy. The transition $b \to a$ corresponding to stimulated emission may then be viewed as the reverse transition of the absorption process $a \to b$ which we have just studied. Carrying out the same manipulations as we did for absorption, we find that the *transition rate* for stimulated emission (integrated over ω) is given by

$$\bar{W}_{ab} = \frac{4\pi^2}{m^2 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{I(\omega_{ba})}{\omega_{ba}^2}|\bar{M}_{ab}(\omega_{ba})|^2 \tag{4.47}$$

where

$$\begin{aligned}\bar{M}_{ab} &= \langle \psi_a | \exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\nabla|\psi_b\rangle \\ &= \int \psi_a^*(\mathbf{r})\exp(-\mathrm{i}\mathbf{k}\cdot\mathbf{r})\hat{\boldsymbol{\varepsilon}}\cdot\nabla\psi_b(\mathbf{r})\,\mathrm{d}\mathbf{r}\end{aligned} \tag{4.48}$$

Integrating by parts, and using the fact that $\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{k} = 0$, we have

$$\bar{M}_{ab} = -M_{ba}^* \tag{4.49}$$

and comparing (4.45) and (4.47), we find that

$$\bar{W}_{ab} = W_{ba} \tag{4.50}$$

Thus we see that under the same radiation field the number of transitions per second exciting the atom from the state a to the state b is the same as the number de-exciting the atom from the state b to the state a. This is consistent with the *principle of detailed balancing*, which says that in an enclosure containing atoms and radiation in equilibrium, the transition probability from a to b is the same as that from b to a, where a and b are any pair of states.

An integrated *stimulated emission cross-section* $\bar{\sigma}_{ab}$ can be defined in analogy with the absorption cross-section (4.46) by dividing the rate at which energy is radiated by the atom, $(\hbar\omega_{ba})\bar{W}_{ab}$, by the intensity $I(\omega_{ba})$. From (4.50) we have

$$\bar{\sigma}_{ab} = \sigma_{ba} \tag{4.51}$$

Despite the fact that the transition rates W_{ba} and $\bar{W}_{ab}$ are equal, stimulated emission is usually much less intense than absorption. Indeed, under equilibrium conditions the initial population of the upper level b is smaller than that of the lower level a because of the Boltzmann factor $\exp(-\hbar\omega_{ba}/(k_\mathrm{B}T))$. However, if a *population inversion* is achieved between the two levels a and b, then stimulated emission becomes the dominant process. This is the case in the *maser* and the *laser* where stimulated emission enables atomic or molecular systems to amplify incident radiation, as we shall see in Chapter 15.

Spontaneous emission

In quantum electrodynamics (QED), the part of the vector potential describing the *absorption* of a linearly polarised photon with wave vector **k** from an N-photon state has the form [5]

$$\mathbf{A}_1 = \hat{\varepsilon}\left[\frac{2N(\omega)\hbar}{V\varepsilon_0\omega}\right]^{1/2}\frac{1}{2}\exp[\mathrm{i}(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega)] \qquad \textbf{(4.52)}$$

and it can be shown that the QED transition rate for absorption is given in first-order perturbation theory by

$$W_{ba} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{N(\omega_{ba})\hbar}{V\omega_{ba}}|M_{ba}|^2\delta(\omega - \omega_{ba}) \qquad \textbf{(4.53)}$$

Using (4.13) and integrating over a range of angular frequencies about ω_{ba}, this result is seen to be identical to (4.45).

The corresponding part of the vector potential describing the *creation* of a photon, adding a single photon to an N-photon state, is

$$\mathbf{A}_2 = \hat{\varepsilon}\left[\frac{2[N(\omega)+1]\hbar}{V\varepsilon_0\omega}\right]^{1/2}\frac{1}{2}\exp[-\mathrm{i}(\mathbf{k}\cdot\mathbf{r} - \omega t + \delta_\omega)] \qquad \textbf{(4.54)}$$

and the first-order QED transition rate for emission is given by

$$\bar{W}_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{[N(\omega_{ba})+1]\hbar}{V\omega_{ba}}|M_{ba}|^2\delta(\omega - \omega_{ba}) \qquad \textbf{(4.55)}$$

After integrating over ω, this expression is seen to be identical to the semi-classical result (4.47), *provided* $N(\omega_{ba}) + 1$ *is replaced by* $N(\omega_{ba})$. The semi-classical approximation amounts to the neglect of 1 compared with $N(\omega_{ba})$, which is the same as neglecting the possibility of spontaneous emission. In the absence of an external field one has $N = 0$ and the *transition rate* for the spontaneous emission of a photon, W^{s}_{ab}, is given from (4.55) by

$$W^{\mathrm{s}}_{ab} = \frac{4\pi^2}{m^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{\hbar}{V\omega_{ba}}|M_{ba}|^2\delta(\omega - \omega_{ba}) \qquad \textbf{(4.56)}$$

What can be observed is the emission of a photon within an element of solid angle $\mathrm{d}\Omega$ about the direction $\hat{\mathbf{k}}$ specified by the polar angles (θ, ϕ). In order to obtain the physical transition rate, we must sum (4.56) over the number of allowed photon states in this interval. To do this, we need to calculate the density $\rho_a(\omega)$ of the final photon states, in accordance with the Golden Rule (2.362).

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[5] A detailed discussion can be found in Sakurai (1967).

Density of states

Let the volume V be a cube of side L. (In fact the shape does not matter provided V is large.) We can impose periodic boundary conditions [6] on the function $\exp(-i\mathbf{k}\cdot\mathbf{r})$ which is contained in the expression (4.54) representing the wave function of the emitted photon. That is,

$$k_x = \frac{2\pi}{L} n_x, \qquad k_y = \frac{2\pi}{L} n_y, \qquad k_z = \frac{2\pi}{L} n_z \tag{4.57}$$

where n_x, n_y, n_z are positive or negative integers, or zero. Since L is very large, we can treat n_x, n_y and n_z as continuous variables, and the number of states in the range $\mathrm{d}\mathbf{k} = \mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z$ is

$$\begin{aligned} \mathrm{d}n_x\,\mathrm{d}n_y\,\mathrm{d}n_z &= \left(\frac{L}{2\pi}\right)^3 \mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z \\ &= \left(\frac{L}{2\pi}\right)^3 k^2\,\mathrm{d}k\,\mathrm{d}\Omega \end{aligned} \tag{4.58}$$

Expressed in terms of $V = L^3$ and $\omega = kc$, the number of states in the angular frequency interval $\mathrm{d}\omega$ with directions of propagation within $\mathrm{d}\Omega$ is

$$\rho_a(\omega)\,\mathrm{d}\omega\,\mathrm{d}\Omega = \frac{V}{(2\pi)^3}\frac{\omega^2}{c^3}\,\mathrm{d}\omega\,\mathrm{d}\Omega \tag{4.59}$$

Using (4.56) and integrating over the angular frequency ω, the transition rate for the emission of a linearly polarised photon into the solid angle $\mathrm{d}\Omega$ in the direction (θ, ϕ) is then given by

$$W^{\mathrm{s}}_{ab}(\theta,\phi)\,\mathrm{d}\Omega = \frac{\hbar}{2\pi m^2 c^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\omega_{ba}|M_{ba}(\omega_{ba})|^2\,\mathrm{d}\Omega \tag{4.60}$$

The total transition rate is found by summing over each of the two independent polarisations of the photon, corresponding to polarisation vectors $\hat{\boldsymbol{\varepsilon}}_\lambda$ $(\lambda = 1, 2)$ and integrating over all angles of emission. That is,

$$W^{\mathrm{s}}_{ab} = \frac{\hbar}{2\pi m^2 c^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\int \mathrm{d}\Omega \sum_{\lambda=1}^{2} \omega_{ba}|M^{\lambda}_{ba}(\omega_{ba})|^2 \tag{4.61}$$

where M^{λ}_{ba} is given by (4.40), with $\hat{\boldsymbol{\varepsilon}}$ replaced by $\hat{\boldsymbol{\varepsilon}}_\lambda$.

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[6] The imposition of periodic boundary conditions amounts to assuming that all space can be divided into identical large cubes of volume L^3, each containing an identical physical system. The vector potential $\mathbf{A}$ must then be periodic with period L along each of the three Cartesian axes.

4.3 The dipole approximation

In many cases of practical interest the matrix element M_{ba} defined in (4.40) can be simplified by expanding the exponential $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ as

$$\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}) = 1 + (\mathrm{i}\mathbf{k}\cdot\mathbf{r}) + \frac{1}{2!}(\mathrm{i}\mathbf{k}\cdot\mathbf{r})^2 + \ldots \tag{4.62}$$

Consider for example the case of optical transitions. The atomic wave functions extend over distances of the order of the first Bohr radius of the atom, that is about 1 Å (= 10^{-8} cm). On the other hand, the wavelengths associated with optical transitions are of the order of several thousand ångströms, so that the corresponding wave number $k = 2\pi/\lambda$ is of the order of 10^5 cm^{-1}. Thus the quantity (kr) is small for $r < 1$ Å and we can replace $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ by unity in (4.40). More generally, if a is a distance characteristic of the linear dimensions of the atomic wave functions, and if $ka \ll 1$, we can replace $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$ by unity in (4.40). This is known as the *dipole approximation*. We note that since $\lambda \gg a$ this is a *long-wavelength approximation*, which amounts to *neglecting the spatial variation of the radiation field* (that is, neglecting *retardation effects*) across the atom.

As the wavelength of the radiation decreases (that is, as the frequency increases), the dipole approximation becomes less accurate. For example, it is a poor approximation for 'bound–bound' X-ray transitions. Retardation effects must also be taken into account for the continuous spectrum when photons of high frequency (whose wavelength λ does not satisfy the condition $\lambda \gg a$) are absorbed or emitted. This will be illustrated in Section 4.8, where we shall study the photoelectric effect.

It is important to note that in the dipole approximation both the vector potential $\mathbf{A}(t)$ and the electric field $\mathscr{E}(t)$ depend only on the time t, and it follows from (4.2) that the magnetic field $\mathscr{B}$ vanishes. In addition, the matrix element M_{ba} of equation (4.40) is replaced by M_{ba}^{D}, where

$$M_{ba}^{\mathrm{D}} = \hat{\boldsymbol{\varepsilon}}\cdot\langle\psi_b|\boldsymbol{\nabla}|\psi_a\rangle \tag{4.63}$$

In terms of the momentum operator $\mathbf{p} = -\mathrm{i}\hbar\boldsymbol{\nabla} = m\dot{\mathbf{r}}$, we can also write (4.63) in the form

$$M_{ba}^{\mathrm{D}} = \frac{\mathrm{i}}{\hbar}\hat{\boldsymbol{\varepsilon}}\cdot\langle\psi_b|\mathbf{p}|\psi_a\rangle = \frac{\mathrm{i}m}{\hbar}\hat{\boldsymbol{\varepsilon}}\cdot\langle\psi_b|\dot{\mathbf{r}}|\psi_a\rangle \tag{4.64}$$

Now, applying the Heisenberg equation of motion (2.113) to the operator $\mathbf{r}$, we have

$$\dot{\mathbf{r}} = (\mathrm{i}\hbar)^{-1}[\mathbf{r}, H_0] \tag{4.65}$$

where we have replaced H by H_0 since we are working in perturbation theory. Therefore

$$\begin{aligned}\langle\psi_b|\dot{\mathbf{r}}|\psi_a\rangle &= (\mathrm{i}\hbar)^{-1}\langle\psi_b|\mathbf{r}H_0 - H_0\mathbf{r}|\psi_a\rangle \\ &= (\mathrm{i}\hbar)^{-1}(E_a - E_b)\,\langle\psi_b|\mathbf{r}|\psi_a\rangle\end{aligned} \tag{4.66}$$

or, in a more compact notation,

$$\mathbf{p}_{ba} = \mathrm{i}m\omega_{ba}\mathbf{r}_{ba} \tag{4.67}$$

where

$$\mathbf{p}_{ba} = \langle\psi_b|\mathbf{p}|\psi_a\rangle = m\langle\psi_b|\dot{\mathbf{r}}|\psi_a\rangle \tag{4.68}$$

and

$$\mathbf{r}_{ba} = \langle\psi_b|\mathbf{r}|\psi_a\rangle \tag{4.69}$$

This allows us to express M_{ba}^{D} in the form

$$M_{ba}^{\mathrm{D}} = -\frac{m\omega_{ba}}{\hbar}\,\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba} \tag{4.70}$$

The transition rate for absorption in the electric dipole approximation may now be obtained by substituting M_{ba}^{D} for M_{ba} in (4.45). That is,

$$W_{ba}^{\mathrm{D}} = \frac{4\pi^2}{c\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)I(\omega_{ba})|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba}|^2 \tag{4.71}$$

It is convenient at this point to introduce the *electric dipole moment* operator

$$\mathbf{D} = -e\mathbf{r} \tag{4.72}$$

and its matrix element

$$\mathbf{D}_{ba} = -e\mathbf{r}_{ba} \tag{4.73}$$

so that

$$M_{ba}^{\mathrm{D}} = \frac{m\omega_{ba}}{\hbar e}\,\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{D}_{ba} \tag{4.74}$$

and the transition rate W_{ba}^{D} becomes

$$W_{ba}^{\mathrm{D}} = \frac{4\pi^2}{c\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right)I(\omega_{ba})|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{D}_{ba}|^2 \tag{4.75}$$

The quantity $\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{D}_{ba}$ is the matrix element of the component of the electric dipole moment in the direction of polarisation $\hat{\boldsymbol{\varepsilon}}$, between the states b and a. If $\mathbf{D}_{ba}$ is non-vanishing, the transition is said to be an *allowed* or *electric dipole* (E1) transition. If $\mathbf{D}_{ba}$ vanishes, the transition is said to be *forbidden*. When the transition is forbidden, higher terms in the series (4.62) may give rise to non-vanishing transition rates, but these are much smaller than for allowed transitions. These higher terms lead to transitions which are somewhat similar to the types of radiation arising from a multipole expansion in classical radiation theory [7]. For example, the second term ($\mathrm{i}\mathbf{k}\cdot\mathbf{r}$) in the expansion (4.62) gives rise to *magnetic dipole* (M1)

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[7] See for example Jackson (1998).

and *electric quadrupole* (E2) transitions. These transitions will be studied in Chapter 9 for a general atom.

If the matrix element M_{ba} in its unapproximated form (4.40) vanishes, the transition is said to be *strictly forbidden* (in first order of perturbation theory). In this case, higher orders of perturbation theory must be considered, and the transition may occur through the simultaneous absorption or emission of two or more photons. It should be noted that the quadratic term $e^2\mathbf{A}^2/(2m)$ of the interaction Hamiltonian (4.27) must then be included in addition to the linear term (e/m) $\mathbf{A}\cdot\mathbf{p}$ considered in the above treatment.

Let us now return to (4.71). Defining Θ as the angle between the vectors $\hat{\boldsymbol{\varepsilon}}$ and $\mathbf{r}_{ba}$, we may write

$$W^{\mathrm{D}}_{ba} = \frac{4\pi^2}{c\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right) I(\omega_{ba})\,|\mathbf{r}_{ba}|^2\cos^2\Theta \tag{4.76}$$

where

$$|\mathbf{r}_{ba}|^2 = |x_{ba}|^2 + |y_{ba}|^2 + |z_{ba}|^2 \tag{4.77}$$

For unpolarised radiation, the orientation of $\hat{\boldsymbol{\varepsilon}}$ is at random, and $\cos^2\Theta$ can be replaced by its average over all solid angles of 1/3 (Problem 4.2), giving

$$W^{\mathrm{D}}_{ba} = \frac{4\pi^2}{3c\hbar^2}\left(\frac{1}{4\pi\varepsilon_0}\right) I(\omega_{ba})\,|\mathbf{D}_{ba}|^2 \tag{4.78}$$

It is worth noting that because of (4.50) the expression (4.78) also represents the transition rate for *stimulated emission in the dipole approximation* corresponding to the transition $b \to a$, namely the dipole approximation to $\bar{W}_{ab}$. On the other hand, the transition rate for *spontaneous emission* of a photon into the solid angle $\mathrm{d}\Omega$ is given in the *dipole approximation* by substituting (4.74) into (4.60). That is,

$$\begin{aligned} W^{\mathrm{s,D}}_{ab}(\theta,\phi)\,\mathrm{d}\Omega &= \frac{1}{2\pi\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega^3_{ba}|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{D}_{ba}|^2\,\mathrm{d}\Omega \\ &= \frac{1}{2\pi\hbar c^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\omega^3_{ba}|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}_{ba}|^2\,\mathrm{d}\Omega \end{aligned} \tag{4.79}$$

By summing this expression with respect to the two polarisation directions of the photon and integrating over the angles one obtains the full transition rate for spontaneous emission of a photon in the dipole approximation, namely (Problem 4.2)

$$W^{\mathrm{s,D}}_{ab} = \frac{4}{3\hbar c^3}\left(\frac{1}{4\pi\varepsilon_0}\right)\omega^3_{ba}|\mathbf{D}_{ba}|^2 \tag{4.80a}$$

$$= \frac{4\alpha}{3c^2}\,\omega^3_{ba}|\mathbf{r}_{ba}|^2 \tag{4.80b}$$

where α is the fine structure constant.

The velocity and acceleration forms of the dipole matrix elements

The matrix elements $\mathbf{D}_{ba}$ of the electric dipole operator have been written in terms of what is often called the length matrix elements $\mathbf{r}_{ba}$ given by (4.69). They can also be expressed in terms of the momentum operator $\mathbf{p} = -\mathrm{i}\hbar\boldsymbol{\nabla}$ or the gradient of the potential energy

$$V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r} \tag{4.81}$$

in which case the matrix elements are said to be expressed in *velocity* or *acceleration* forms, respectively. To see this, we first remark that by using (4.69) and (4.30) we can write

$$\mathbf{r}_{ba} = \frac{1}{E_b - E_a}\langle\psi_b|H_0\mathbf{r} - \mathbf{r}H_0|\psi_a\rangle \tag{4.82}$$

Taking $H_0 = -(\hbar^2/2m)\nabla^2 + V$, and using the fact that V commutes with $\mathbf{r}$, we have

$$\mathbf{r}_{ba} = -\frac{\hbar^2}{2m}\frac{1}{E_b - E_a}\langle\psi_b|\nabla^2\mathbf{r} - \mathbf{r}\nabla^2|\psi_a\rangle \tag{4.83}$$

Noting that

$$\nabla^2[\mathbf{r}\psi_a(\mathbf{r})] = 2\boldsymbol{\nabla}\psi_a(\mathbf{r}) + \mathbf{r}\nabla^2\psi_a(\mathbf{r}) \tag{4.84}$$

and that $\mathbf{p} = -\mathrm{i}\hbar\boldsymbol{\nabla}$, we retrieve the result (4.67). That is,

$$\mathbf{r}_{ba} = -\frac{\mathrm{i}\hbar}{m}\frac{1}{E_b - E_a}\langle\psi_b|\mathbf{p}|\psi_a\rangle = -\frac{\mathrm{i}}{m\omega_{ba}}\mathbf{p}_{ba} \tag{4.85}$$

In a similar way, we can write the matrix element $\mathbf{p}_{ba}$ in the form

$$\begin{aligned}\mathbf{p}_{ba} &= -\frac{\mathrm{i}\hbar}{E_b - E_a}\langle\psi_b|H_0\boldsymbol{\nabla} - \boldsymbol{\nabla}H_0|\psi_a\rangle \\ &= -\frac{\mathrm{i}\hbar}{E_b - E_a}\langle\psi_b|V\boldsymbol{\nabla} - \boldsymbol{\nabla}V|\psi_a\rangle \\ &= \frac{\mathrm{i}\hbar}{E_b - E_a}\langle\psi_b|(\boldsymbol{\nabla}V)|\psi_a\rangle = \frac{\mathrm{i}}{\omega_{ba}}(\boldsymbol{\nabla}V)_{ba}\end{aligned} \tag{4.86}$$

Using these results the length, velocity and acceleration forms of $\mathbf{D}_{ba}$ are, respectively,

$$\mathbf{D}^{\mathrm{L}}_{ba} = -e\mathbf{r}_{ba} \tag{4.87a}$$

$$\mathbf{D}^{\mathrm{V}}_{ba} = \frac{\mathrm{i}e}{m\omega_{ba}}\mathbf{p}_{ba} \tag{4.87b}$$

and

$$\mathbf{D}^{\mathrm{A}}_{ba} = -\frac{e}{m\omega^2_{ba}}(\boldsymbol{\nabla}V)_{ba} \tag{4.87c}$$

Provided that the wave functions ψ_a and ψ_b are exact eigenfunctions of H_0, the three forms of $\mathbf{D}_{ba}$ give identical results. However, if approximate wave functions are employed, the three forms of $\mathbf{D}_{ba}$ will yield different numerical values.

The Schrödinger equation in the velocity and length gauges

Let us rewrite the time-dependent Schrödinger equation (4.25) in the form

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r}, t) = \left[H_0 + \frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m}\mathbf{A}^2\right]\Psi(\mathbf{r}, t) \tag{4.88}$$

where H_0 is given by (4.26) and we have used (4.27). It is interesting to note that *within the dipole approximation* (so that the vector potential $\mathbf{A}$ depends only on the time t), the term in $\mathbf{A}^2$ in (4.88) can be eliminated by performing the gauge transformation

$$\Psi(\mathbf{r}, t) = \exp\left[-\frac{\mathrm{i}}{\hbar}\frac{e^2}{2m}\int^t \mathbf{A}^2(t')\,\mathrm{d}t'\right]\Psi^{\mathrm{V}}(\mathbf{r}, t) \tag{4.89}$$

This gives for $\Psi^{\mathrm{V}}(\mathbf{r}, t)$ the new time-dependent Schrödinger equation (Problem 4.3)

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi^{\mathrm{V}}(\mathbf{r}, t) = \left[H_0 + \frac{e}{m}\mathbf{A}(t)\cdot\mathbf{p}\right]\Psi^{\mathrm{V}}(\mathbf{r}, t) \tag{4.90}$$

which is said to be in the *velocity gauge* since the interaction term

$$H^{\mathrm{V}}_{\mathrm{int}}(t) = \frac{e}{m}\mathbf{A}(t)\cdot\mathbf{p} = -\frac{\mathrm{i}\hbar e}{m}\mathbf{A}(t)\cdot\boldsymbol{\nabla} \tag{4.91}$$

couples the vector potential $\mathbf{A}(t)$ to the velocity operator $\mathbf{p}/m$.

Another form of the time-dependent Schrödinger equation in the dipole approximation can be obtained by returning to equation (4.88) and performing a gauge transformation specified by taking $\chi(\mathbf{r}, t) = \mathbf{A}(t)\cdot\mathbf{r}$. Using the fact that in the dipole approximation the electric field is given by $\mathcal{E}(t) = -\mathrm{d}\mathbf{A}(t)/\mathrm{d}t$, we see from equations (4.19) with $q = -e$ that

$$\mathbf{A}' = 0 \tag{4.92a}$$

$$\phi' = \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{A}(t)\cdot\mathbf{r} = -\mathcal{E}(t)\cdot\mathbf{r} \tag{4.92b}$$

$$\Psi'(\mathbf{r}, t) = \exp\left[\frac{\mathrm{i}e}{\hbar}\mathbf{A}(t)\cdot\mathbf{r}\right]\Psi(\mathbf{r}, t) \tag{4.92c}$$

The new time-dependent Schrödinger equation for $\Psi'(\mathbf{r}, t) \equiv \Psi^{\mathrm{L}}(\mathbf{r}, t)$ is (Problem 4.4)

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi^{\mathrm{L}}(\mathbf{r}, t) = [H_0 + e\mathcal{E}(t)\cdot\mathbf{r}]\Psi^{\mathrm{L}}(\mathbf{r}, t) \tag{4.93}$$

which is said to be in the *length gauge* because the interaction term

$$H^{\mathrm{L}}_{\mathrm{int}}(t) = e\mathcal{E}(t)\cdot\mathbf{r} \tag{4.94}$$

couples the electric field $\mathcal{E}(t)$ to the position operator $\mathbf{r}$. Since the electric dipole operator is given by $\mathbf{D} = -e\mathbf{r}$, we see that $H^{\mathrm{L}}_{\mathrm{int}} = -\mathcal{E}(t)\cdot\mathbf{D}$. This is the reason why the approximation in which the electromagnetic field is taken to be uniform over the atom is called the *dipole approximation*.

Spontaneous emission from the 2p level of hydrogenic atoms

As an example of the calculation of a transition rate for spontaneous emission in the dipole approximation, we shall consider the transition from the 2p level of a hydrogenic atom with nuclear charge Ze to the ground state, starting from (4.80b). In this equation, b represents the 2p state of the atom with magnetic quantum number m while a is the 1s ground state. The angular frequency ω_{ba} can be found from (4.34) and (3.30). It is

$$\begin{aligned}\omega_{ba} &= (E_b - E_a)/\hbar \\ &= \frac{3}{8}\frac{mc^2}{\hbar}(Z\alpha)^2\end{aligned} \tag{4.95}$$

From (4.69) and (3.53) the matrix element $\mathbf{r}_{ba}$ is seen to be

$$\mathbf{r}_{ba} = \int_0^\infty R_{21}(r)R_{10}(r)r^3\,\mathrm{d}r \int Y^*_{1m}(\theta,\phi)\,\hat{\mathbf{r}}\,Y_{00}(\theta,\phi)\,\mathrm{d}\Omega \tag{4.96}$$

where $\hat{\mathbf{r}}$ is a unit vector in the direction of $\mathbf{r}$. Using the expressions for $R_{21}(r)$ and $R_{10}(r)$ given in (3.59) the radial integral in (4.96) can be evaluated:

$$\begin{aligned}\int_0^\infty R_{21}(r)R_{10}(r)r^3\,\mathrm{d}r &= \left(\frac{Z}{a_0}\right)^4 \frac{1}{\sqrt{6}}\int_0^\infty r^4\exp[-3Zr/(2a_0)]\,\mathrm{d}r \\ &= \frac{a_0}{Z}\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5\end{aligned} \tag{4.97}$$

To perform the angular integration in (4.96), the x, y and z components of $\hat{\mathbf{r}}$ are expressed as

$$\begin{aligned}(\hat{\mathbf{r}})_x &= \sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}}\,[-Y_{1,1}(\theta,\phi) + Y_{1,-1}(\theta,\phi)] \\ (\hat{\mathbf{r}})_y &= \sin\theta\sin\phi = \sqrt{\frac{2\pi}{3}}\,\mathrm{i}\,[Y_{1,1}(\theta,\phi) + Y_{1,-1}(\theta,\phi)] \\ (\hat{\mathbf{r}})_z &= \cos\theta = \sqrt{\frac{4\pi}{3}}\,Y_{1,0}(\theta,\phi)\end{aligned} \tag{4.98}$$