Chapter 3

Radiative transitions

In this chapter we shall look at the classical and quantum theories of radiative emission and absorption. This will enable us to derive certain selection rules which determine whether a particular transition is allowed or not. We shall also investigate the physical mechanisms that affect the shape of the spectral lines that are observed in atomic spectra.

3.1 Classical theories of radiating dipoles

The classical theories of radiation by atoms were developed at the end of the 19th century before the discoveries of the electron and the nucleus. With the benefit of hindsight, we can understand more clearly how the classical theory works. We model the atom as a heavy nucleus with electrons attached to it by springs with different spring constants, as shown in Fig. 3.1(a). The spring represents the binding force between the nucleus and the electrons, and the values of the spring constants determine the resonant frequencies of each of the electrons in the atom. Every atom therefore has several different natural frequencies.

The nucleus is heavy, and so it does not move very easily. However, the electrons can readily vibrate about their mean position, as illustrated in Fig. 3.1(b). The vibrations of the electron create a fluctuating **electric dipole**. In general, electric dipoles consist of two opposite charges of $\pm q$ separated by a distance d. The dipole moment $\boldsymbol{p}$ is defined by:

$$\boldsymbol{p} = q\boldsymbol{d} \, , \tag{3.1}$$

where $\boldsymbol{d}$ is a vector of length d pointing from $-q$ to $+q$. In the case of atomic dipoles, the positive charged is fixed, and so the time dependence of $\boldsymbol{p}$ is just determined by the movement of the electron:

$$p(t) = -ex(t) \, , \tag{3.2}$$

where $x(t)$ is the time dependence of the electron displacement.

It is well known that oscillating electric dipoles emit electromagnetic radiation at the oscillation frequency. This is how aerials work. Thus we expect an atom that has been excited into vibration to emit light waves at one of its natural resonant frequencies. This is the classical explanation of why atoms emit characteristic colours when excited electrically in a discharge tube. Furthermore, it is easy to see that an incoming light wave of frequency ω_0 can drive the natural vibrations of the atom through the oscillating force exerted on the electron by the electric field of the wave. This transfers energy from the light wave to the atom, which causes absorption at the resonant frequency. Hence the atom is also expected to absorb strongly at its natural frequency.

The classical theories actually have to assume that each electron has several natural frequencies of varying strengths in order to explain the observed spectra. If you do not do this, you end up predicting, for example, that hydrogen only has one emission frequency. There was no classical explanation of the origin of the atomic dipoles. It is therefore not surprising that we run into contradictions such as this when we try to patch up the model by applying our knowledge of electrons and nuclei gained by hindsight.

3.2 Quantum theory of radiative transitions

We have just seen that the classical model can explain why atoms emit and absorb light, but it does not offer any explanation for the frequency or the strength of the radiation. These can only be calculated

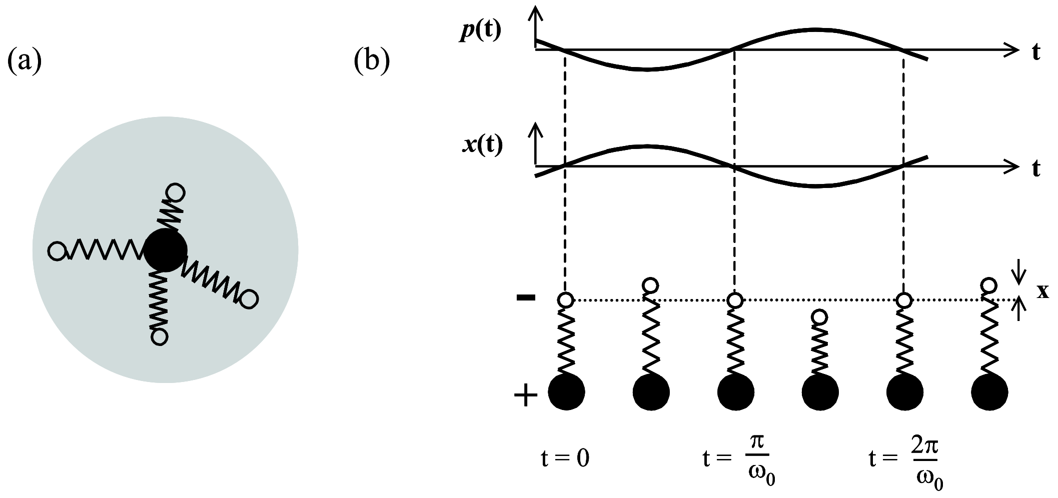

Figure 3.1: (a) Classical atoms consist of electrons bound to a heavy nucleus by springs with characteristic force constants. (b) The vibrations of an electron in an atom at its natural resonant frequency ω_0 creates an oscillating electric dipole. This acts like an aerial and emits electromagnetic waves at frequency ω_0. Alternatively, an incoming electromagnetic wave at frequency ω_0 can drive the oscillations at their resonant frequency. This transfers energy from the wave to the atom, which is equivalent to absorption.

by using quantum theory. Quantum theory tells us that atoms absorb or emit photons when they jump between quantized states, as shown in figure 3.2(a). The absorption or emission processes are called **radiative transitions**. The energy of the photon is equal to the difference in energy of the two levels:

$$h\nu = E_2 - E_1 \,. \tag{3.3}$$

Our task here is to calculate the *rate* at which these transitions occur.

The **transition rate** W_{12} can be calculated from the initial and final wave functions of the states involved by using **Fermi's golden rule**:

$$W_{12} = \frac{2\pi}{\hbar}|M_{12}|^2 g(h\nu)\,, \tag{3.4}$$

where M_{12} is the **matrix element** for the transition and $g(h\nu)$ is the **density of states**. The matrix element is equal to the overlap integral[1]:

$$M_{12} = \int \psi_2^*(\boldsymbol{r}) H'(\boldsymbol{r}) \psi_1(\boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r}\,. \tag{3.5}$$

where H' is the **perturbation** that causes the transition. This represents the interaction between the atom and the light wave. There are a number of physical mechanisms that cause atoms to absorb or emit light. The strongest process is the electric dipole (E1) interaction. We therefore discuss E1 transitions first, leaving the discussion of higher order effects to Section 3.5.

The density of states factor is defined so that $g(h\nu)\mathrm{d}E$ is the number of *final* states per unit volume that fall within the energy range E to $E+\mathrm{d}E$, where $E = h\nu$. In the standard case of transitions between quantized levels in an atom, the initial and final electron states are *discrete*. In this case, the density of states factor that enters the golden rule is the density of *photon* states.[2] In free space, the photons can have any frequency and there is a continuum of states available, as illustrated in Fig. 3.2(b). The atom can therefore always emit a photon and it is the matrix element that determines the probability for this to occur. Hence we concentrate on the matrix element from now on.

3.3 Electric dipole (E1) transitions

Electric dipole transitions are the quantum mechanical equivalent of the classical dipole oscillator discussed in Section 3.1. We assume that the atom is irradiated with light, and makes a jump from level 1

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[1] This is sometimes written in the shorthand **Dirac notation** as $M_{12} \equiv \langle 2|H'|1\rangle$.

[2] In solid-state physics, we consider transitions between electron *bands* rather than between discrete states. We then have to consider the density of electron states as well as the density of photon states when we calculate the transition rate. This point is covered in other courses, e.g. PHY475: Optical properties of solids.

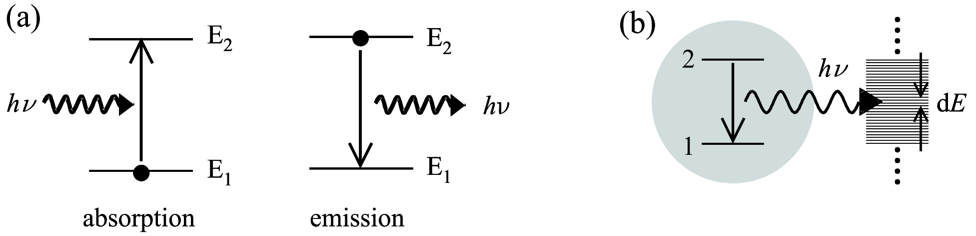

Figure 3.2: (a) Absorption and emission transitions in an atom. (b) Emission into a continuum of photon modes during a radiative transition between discrete atomic states.

to 2 by absorbing a photon. The interaction energy between an electric dipole $\boldsymbol{p}$ and an external electric field $\boldsymbol{\mathcal{E}}$ is given by

$$E = -\boldsymbol{p}\cdot\boldsymbol{\mathcal{E}}\,. \tag{3.6}$$

We presume that the nucleus is heavy, and so we only need to consider the effect on the electron. Hence the electric dipole perturbation is given by:

$$H' = +e\boldsymbol{r}\cdot\boldsymbol{\mathcal{E}}\,, \tag{3.7}$$

where $\boldsymbol{r}$ is the position vector of the electron and $\boldsymbol{\mathcal{E}}$ is the electric field of the light wave. This can be simplified to:

$$H' = e(x\mathcal{E}_x + y\mathcal{E}_y + z\mathcal{E}_z)\,, \tag{3.8}$$

where $\mathcal{E}_x$ is the component of the field amplitude along the x axis, etc. Now atoms are small compared to the wavelength of light, and so the amplitude of the electric field will not vary significantly over the dimensions of an atom. We can therefore take $\mathcal{E}_x$, $\mathcal{E}_y$, and $\mathcal{E}_z$ in Eq. 3.8 to be constants in the calculation, and just evaluate the following integrals:

$$\begin{aligned} M_{12} &\propto \int \psi_1\, x\, \psi_2\, \mathrm{d}^3\boldsymbol{r} && x\text{−polarized light}\,, \\ M_{12} &\propto \int \psi_1\, y\, \psi_2\, \mathrm{d}^3\boldsymbol{r} && y\text{−polarized light}\,, \\ M_{12} &\propto \int \psi_1\, z\, \psi_2\, \mathrm{d}^3\boldsymbol{r} && z\text{−polarized light}\,. \end{aligned} \tag{3.9}$$

Integrals of this type are called **dipole moments**. The dipole moment is thus the key parameter that determines the transition rate for the electric dipole process.

At this stage it is helpful to give a hand-waving explanation for why electric dipole transitions lead to the emission of light. To do this we need to to consider the time-dependence of the quantum mechanical wave functions. This naturally drops out of the *time-dependent* Schrödinger equation:

$$\hat{H}(\boldsymbol{r})\Psi(\boldsymbol{r},t) = \mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{r},t)\,, \tag{3.10}$$

where $\hat{H}(\boldsymbol{r})$ is the Hamiltonian of the system. The solutions of Eq. 3.10 are of the form:

$$\Psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}Et/\hbar}\,, \tag{3.11}$$

where $\psi(\boldsymbol{r})$ satisfies the *time-independent* Schrödinger equation:

$$\hat{H}(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\,. \tag{3.12}$$

During a transition between two quantum states of energies E_1 and E_2, the electron will be in a superposition state with a mixed wave function given by

$$\begin{aligned} \Psi(\boldsymbol{r},t) &= c_1\Psi_1(\boldsymbol{r},t) + c_2\Psi_2(\boldsymbol{r},t) \\ &= c_1\psi_1(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}E_1t/\hbar} + c_2\psi_2(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}E_2t/\hbar}\,, \end{aligned} \tag{3.13}$$

where c_1 and c_2 are the mixing coefficients. The expectation value $\langle x\rangle$ of the position of the electron is given by:

$$\langle x\rangle = \int \Psi^*\, x\, \Psi\, \mathrm{d}^3\boldsymbol{r}\,. \tag{3.14}$$

Quantum number	Selection rule	
parity	changes	
l	$\Delta l = \pm 1$	
m	$\Delta m = 0, \pm 1$	unpolarized light
	$\Delta m = 0$	linear polarization $\parallel z$
	$\Delta m = \pm 1$	linear polarization in (x, y) plane
	$\Delta m = +1$	σ^+ circular polarization
	$\Delta m = -1$	σ^- circular polarization
s	$\Delta s = 0$	
m_s	$\Delta m_s = 0$	

Table 3.1: **Electric dipole selection rules** for the quantum numbers of the states involved in the transition.

With Ψ given by Eq. 3.13 we obtain:

$$\begin{aligned} \langle x \rangle &= c_1^* c_1 \int \psi_1^* \, x \, \psi_1 \, \mathrm{d}^3\boldsymbol{r} + c_2^* c_2 \int \psi_2^* \, x \, \psi_2 \, \mathrm{d}^3\boldsymbol{r} \\ &+ c_1^* c_2 \mathrm{e}^{-\mathrm{i}(E_2 - E_1)t/\hbar} \int \psi_1^* \, x \, \psi_2 \, \mathrm{d}^3\boldsymbol{r} \; + \; c_2^* c_1 \mathrm{e}^{-\mathrm{i}(E_1 - E_2)t/\hbar} \int \psi_2^* \, x \, \psi_1 \, \mathrm{d}^3\boldsymbol{r} \, . \end{aligned} \tag{3.15}$$

This shows that if the dipole moment defined in Eq. 3.9 is non-zero, then the electron wave-packet oscillates in space at angular frequency $(E_2 - E_1)/\hbar$. The oscillation of the electron wave packet creates an oscillating electric dipole, which then radiates light at angular frequency $(E_2 - E_1)/\hbar$. Hey presto!

3.4 Selection rules for E1 transitions

Electric dipole transitions can only occur if the **selection rules** summarized in Table 3.1 are satisfied. Transitions that obey these E1 selection rules are called **allowed** transitions. If the selection rules are not satisfied, the matrix element (i.e. the dipole moment) is zero, and we then see from Eq. 3.4 that the transition rate is zero. The origins of these rules are discussed below.

Parity

The parity of a function refers to the sign change under inversion about the origin. Thus if $f(-x) = f(x)$ we have even parity, whereas if $f(-x) = -f(x)$ we have odd parity. Now atoms are spherically symmetric, which implies that

$$|\psi(-\boldsymbol{r})|^2 = |\psi(+\boldsymbol{r})|^2 \, . \tag{3.16}$$

Hence we must have that

$$\psi(-\boldsymbol{r}) = \pm \psi(+\boldsymbol{r}) \, . \tag{3.17}$$

In other words, the wave functions have either even or odd parity. The dipole moment of the transition is given by Eq. 3.9. x, y and z are odd functions, and so the product $\psi_1 \psi_2$ must be an odd function if M_{12} is to be non-zero. Hence ψ_1 and ψ_2 must have different parities.

The orbital quantum number l

The parity of the spherical harmonic functions is equal to $(-1)^l$. Hence the parity selection rule implies that Δl must be an odd number. Detailed evaluation of the overlap integrals tightens this rule to $\Delta l = \pm 1$. This can be seen as a consequence of the fact that the angular momentum of a photon is $\pm\hbar$, with the sign depending on whether we have a left or right circularly polarized photon. Conservation of angular momentum therefore requires that the angular momentum of the atom must change by one unit.

The magnetic quantum number m

The dipole moment for the transition can be written out explicitly:

$$M_{12} \propto \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \Psi^*_{n',l',m'} \, \boldsymbol{r} \, \Psi_{n,l,m} \; r^2 \sin\theta \, \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi \, . \tag{3.18}$$

We consider here just the ϕ part of this integral:

$$M_{12} \propto \int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m'\phi} \, \boldsymbol{r} \, \mathrm{e}^{\mathrm{i}m\phi} \, \mathrm{d}\phi \, , \tag{3.19}$$

where we have made use of the fact that (see Eq. 2.44 or Table 2.1):

$$\Psi_{n,l,m}(r,\theta,\phi) \propto \mathrm{e}^{\mathrm{i}m\phi} \, . \tag{3.20}$$

Now for z-polarized light we have from Eq. 3.9:

$$M_{12} \propto \int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m'\phi} \, z \, \mathrm{e}^{\mathrm{i}m\phi} \, \mathrm{d}\phi \propto \int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m'\phi} \cdot 1 \cdot \mathrm{e}^{\mathrm{i}m\phi} \, \mathrm{d}\phi \, , \tag{3.21}$$

because $z = r\cos\theta$. Hence we must have that $m' = m$ if M_{12} is to be non-zero. If the light is polarized in the (x, y) plane, we have integrals like

$$M_{12} \propto \int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m'\phi} \, x \, \mathrm{e}^{\mathrm{i}m\phi} \, \mathrm{d}\phi \propto \int_0^{2\pi} \mathrm{e}^{-\mathrm{i}m'\phi} \cdot \mathrm{e}^{\pm\mathrm{i}\phi} \cdot \mathrm{e}^{\mathrm{i}m\phi} \, \mathrm{d}\phi \, . \tag{3.22}$$

This is because $x = r\sin\theta\cos\phi = r\sin\theta\frac{1}{2}(\mathrm{e}^{+\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi})$, and similarly for y. This give $m' - m = \pm 1$. This rule can be tightened up a bit by saying that $\Delta m = +1$ for σ^+ circularly polarized light and $\Delta m = -1$ for σ^- circularly polarized light. If the light is unpolarized, then all three linear polarizations are possible, and we can have $\Delta m = 0, \pm 1$.

Spin

The photon does not interact with the electron spin. Therefore, the spin state of the atom does not change during the transition. This implies that the spin quantum numbers s and m_s are unchanged.

3.5 Higher order transitions

How does an atom de-excite if E1 transitions are forbidden by the selection rules? In some cases it may be possible for the atom to de-excite by alternative methods. For example, the 3s → 1s transition is forbidden, but the atom can easily de-excite by two allowed E1 transitions, namely 3s → 2p, then 2p → 1s. However, this may not always be possible, and in these cases the atom must de-excite by making a **forbidden** transition. The use of the word "forbidden" is somewhat misleading here. It really means "electric-dipole forbidden". The transitions are perfectly possible, but they just occur at a slower rate.

After the electric-dipole interaction, the next two strongest interactions between the photon and the atom give rise to **magnetic dipole** (M1) and **electric quadrupole** (E2) transitions. There have different selection rules to E1 transitions (e.g. parity is conserved), and may therefore be allowed when when E1 transitions are forbidden. M1 and E2 transitions are second-order processes and have much smaller probabilities than E1 transitions.

In extreme cases it may happen that all types of radiative transitions are forbidden. In this case, the excited state is said to be **metastable**, and must de-excite by transferring its energy to other atoms in collisional processes or by multi-photon emission.

3.6 Radiative lifetimes

An atom in an excited state has a spontaneous tendency to de-excite by a radiative transition involving the emission of a photon. This follows from statistical physics: atoms with excess energy tend to want to get rid of it. This process is called **spontaneous emission**. Let us suppose that there are N_2 atoms

Transition	Einstein A coefficient	Radiative lifetime
E1 allowed	$10^8 - 10^9$ s^{-1}	1 – 10 ns
E1 forbidden (M1 or E2)	$10^3 - 10^6$ s^{-1}	1 μs – 1 ms

Table 3.2: Typical transition rates and radiative lifetimes for allowed and forbidden transitions at optical frequencies.

in level 2 at time t. We use quantum mechanics to calculate the transition rate from level 2 to level 1, and then write down a rate equation for N_2 as follows:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -AN_2\,. \tag{3.23}$$

This merely says that the total number of atoms making transitions is proportional to the number of atoms in the excited state and to the quantum mechanical probability. The parameter A that appears in eqn 3.23 is called the **Einstein A coefficient** of the transition.[3]

Equation 3.23 has the following solution:

$$\begin{aligned} N_2(t) &= N_2(0)\exp(-At) \\ &= N_2(0)\exp(-t/\tau)\,, \end{aligned} \tag{3.24}$$

where

$$\tau = \frac{1}{A}\,. \tag{3.25}$$

Equation 3.24 shows that if the atoms are excited into the upper level, the population will decay due to spontaneous emission with a time constant τ. τ is thus called the **natural radiative lifetime** of the excited state.

The values of the Einstein A coefficient and hence the radiative lifetime τ vary considerably from transition to transition. Allowed E1 transitions have A coefficients in the range $10^8 - 10^9\,\mathrm{s}^{-1}$ at optical frequencies, giving radiative lifetimes of $\sim 1 - 10\,$ns. Forbidden transitions, on the other hand, are much slower because they are higher order processes. The radiative lifetimes for M1 and E2 transitions are typically in the millisecond or microsecond range. This point is summarized in Table 3.2.

3.7 The width and shape of spectral lines

The radiation emitted in atomic transitions is not perfectly monochromatic. The shape of the emission line is described by the **spectral line shape function** $g(\nu)$. This is a function that peaks at the line centre defined by

$$h\nu_0 = (E_2 - E_1)\,, \tag{3.26}$$

and is normalized so that:

$$\int_0^\infty g(\nu)\,\mathrm{d}\nu = 1\,. \tag{3.27}$$

The most important parameter of the line shape function is the **full width at half maximum** (FWHM) $\Delta\nu$, which quantifies the width of the spectral line. We shall see below how the different types of line broadening mechanisms give rise to two common line shape functions, namely the **Lorentzian** and **Gaussian** functions.

In a gas of atoms, spectral lines are broadened by three main processes:

- natural broadening,
- collision broadening,
- Doppler broadening.

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[3] When we study laser physics in the second part of the course, we shall encounter the Einstein B coefficients that describe the processes of stimulated emission and absorption.

We shall look at each of these processes separately below. A useful general division can be made at this stage by classifying the broadening as either **homogeneous** or **inhomogeneous**.

- **Homogeneous** broadening affects all the individual atoms in the same way. Natural lifetime and collision broadening are examples of homogeneous processes. All the atoms are behaving in the same way, and each atom produces the same emission spectrum.

- **Inhomogeneous** broadening affects different individual atoms in different ways. Doppler broadening is the standard example of an inhomogeneous process. The individual atoms are presumed to behave identically, but they are moving at different velocities, and one can associate different parts of the spectrum with the subset of atoms with the appropriate velocity. Inhomogeneous broadening is also found in solids, where different atoms may experience different local environments due to the inhomogeneity of the medium.

3.8 Natural broadening

We have seen in Section 3.6 that the process of spontaneous emission causes the excited states of an atom to have a finite lifetime. Let us suppose that we somehow excite a number of atoms into level 2 at time $t = 0$. Equation 3.23 shows us that the rate of transitions is proportional to the instantaneous population of the upper level, and eqn 3.24 shows that this population decays exponentially. Thus the rate of atomic transitions decays exponentially with time constant τ. For every transition from level 2 to level 1, a photon of angular frequency $\omega_0 = (E_2 - E_1)/\hbar$ is emitted. Therefore a burst of light with an exponentially-decaying intensity will be emitted for $t > 0$:

$$I(t) = I(0)\exp(-t/\tau)\,. \tag{3.28}$$

This corresponds to a time dependent electric field of the form:

$$\begin{array}{lrcl} t < 0: & \mathcal{E}(t) & = & 0\,, \\ t \geq 0: & \mathcal{E}(t) & = & \mathcal{E}_0\,\mathrm{e}^{\mathrm{i}\omega_0 t}\,\mathrm{e}^{-t/2\tau}\,. \end{array} \tag{3.29}$$

The extra factor of 2 in the exponential in eqn 3.29 compared to eqn 3.28 arises because $I(t) \propto \mathcal{E}(t)^2$. We now take the Fourier transform of the electric field to derive the frequency spectrum of the burst:

$$\mathcal{E}(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\mathcal{E}(t)\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t\,. \tag{3.30}$$

The emission spectrum is then given by:

$$I(\omega) \propto \left|\mathcal{E}(\omega)^2\right| \propto \frac{1}{(\omega-\omega_0)^2 + (1/2\tau)^2}\,. \tag{3.31}$$

Remembering that $\omega = 2\pi\nu$, we find the final result for the spectral line shape function:

$$g(\nu) = \frac{\Delta\nu}{2\pi}\,\frac{1}{(\nu-\nu_0)^2 + (\Delta\nu/2)^2}\,, \tag{3.32}$$

where the full width at half maximum is given by

$$\Delta\nu = \frac{1}{2\pi\tau}\,. \tag{3.33}$$

The spectrum described by eqn 3.32 is called a **Lorentzian** line shape. This function is plotted in Fig. 3.3. Note that we can re-write eqn 3.33 in the following form:

$$\Delta\nu\cdot\tau = \frac{1}{2\pi}\,. \tag{3.34}$$

By multiplying both sides by h, we can recast this as:

$$\Delta E\cdot\tau = h/2\pi\,. \tag{3.35}$$

If we realize that τ represents the average time the atom stays in the excited state (i.e the uncertainty in the time), we can interpret this as the **energy–time uncertainty principle**.

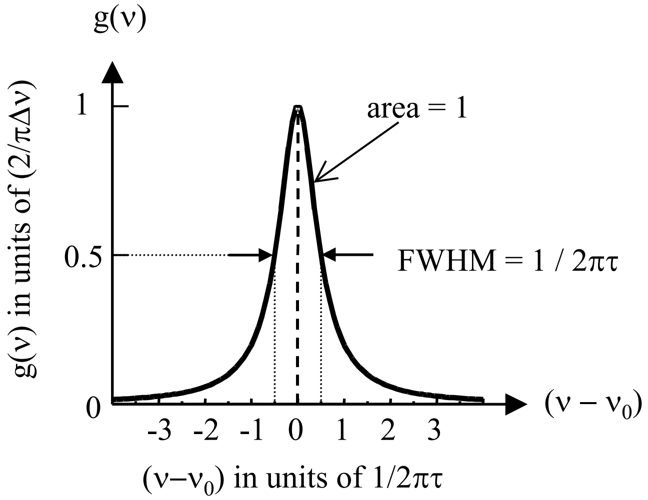

Figure 3.3: **The Lorentzian line shape**. The functional form is given in eqn 3.32. The function peaks at the line centre ν_0 and has an FWHM of $1/2\pi\tau$. The function is normalized so that the total area is unity.

3.9 Collision (Pressure) broadening

The atoms in a gas jostle around randomly and frequently collide into each other and the walls of the containing vessel. This interrupts the process of light emission and effectively shortens the lifetime of the excited state. This gives additional line broadening through the uncertainty principle, as determined by eqn 3.33 with τ replaced by τ_c, where τ_c is the mean time between collisions.

It can be shown from the kinetic theory of gases that the time between collisions in an ideal gas is given by:

$$\tau_c \sim \frac{1}{\sigma_s P}\left(\frac{\pi m k_B T}{8}\right)^{1/2}, \tag{3.36}$$

where σ_s is the collision cross-section, and P is the pressure. The collision cross-section is an effective area which determines whether two atoms will collide or not. It will be approximately equal to the size of the atom. For example, for sodium atoms we have:

$$\sigma_s \sim \pi r_{\text{atom}}^2 \sim \pi \times (0.2\,\text{nm})^2 = 1.2 \times 10^{-19}\,\text{m}^2\,.$$

Thus at S.T.P we find $\tau_c \sim 6 \times 10^{-10}$ s, which gives a line width of ~ 1 GHz. Note that τ_c is much shorter than typical radiative lifetimes. For example, the strong yellow D-lines in sodium have a radiative lifetime of 16 ns, which is nearly two orders of magnitude larger.

In conventional atomic discharge tubes, we reduce the effects of pressure broadening by working at low pressures. We see from eqn 3.36 that this increases τ_c, and hence reduces the linewidth. This is why we tend to use “low pressure” discharge lamps for spectroscopy.

3.10 Doppler broadening

The spectrum emitted by a typical gas of atoms in a low pressure discharge lamp is usually found to be much broader than the radiative lifetime would suggest, even when everything is done to avoid collisions. For example, the radiative lifetime for the 632.8 nm line in neon is 2.7×10^{-7} s. Equation 3.33 tells us that we should have a spectral width of 0.54 MHz. In fact, the line is about three orders of magnitude broader, and moreover, does not have the Lorentzian lineshape given by eqn 3.32.

The reason for this discrepancy is the thermal motion of the atoms. The atoms in a gas move about randomly with a root-mean-square thermal velocity given by:

$$\tfrac{1}{2} m v_x^2 = \tfrac{1}{2} k_B T\,, \tag{3.37}$$

where k_B is Boltzmann’s constant. At room temperature the thermal velocities are quite large. For example, for sodium with a mass number of 23 we find $v_x \sim 330\,\text{ms}^{-1}$ at 300 K. This random thermal

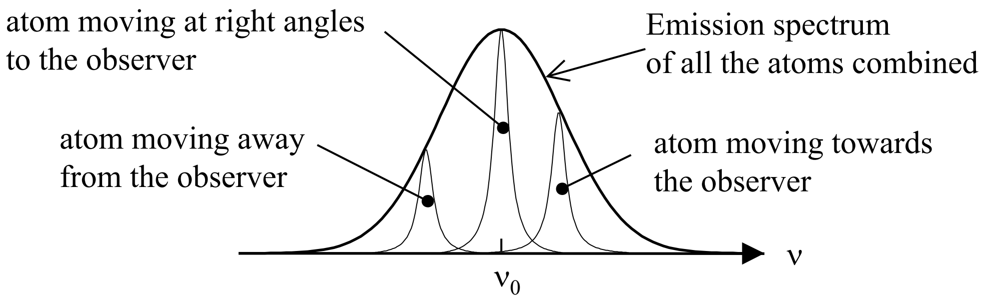

Figure 3.4: The Doppler broadening mechanism. The thermal motion of the atoms causes their frequency to be shifted by the Doppler effect.

motion of the atoms gives rise to Doppler shifts in the observed frequencies, which then cause line broadening, as illustrated in Fig. 3.4. This is Doppler line broadening mechanism.

Let us suppose that the atom is emitting light from a transition with centre frequency ν_0. An atom moving with velocity v_x will have its observed frequency shifted by the Doppler effect according to:

$$\nu = \nu_0 \left(1 \pm \frac{v_x}{c}\right) , \tag{3.38}$$

where the + and − sign apply to motion towards or away from the observer respectively. The number of atoms with a particular velocity $N(v_x)$ is given by the Maxwell-Boltzmann distribution:

$$N(v_x) = N_0 \left(\frac{2k_\mathrm{B}T}{\pi m}\right)^{1/2} \exp\left(-\frac{\frac{1}{2}mv_x^2}{k_\mathrm{B}T}\right) . \tag{3.39}$$

We can combine eqns 3.38 and 3.39, to find the number of atoms emitting at frequency ν:

$$N(\nu) = N_0 \left(\frac{2k_\mathrm{B}T}{\pi m}\right)^{1/2} \exp\left(-\frac{mc^2(\nu-\nu_0)^2}{2k_\mathrm{B}T\nu_0^2}\right) . \tag{3.40}$$

The frequency dependence of the light emitted is therefore given by:

$$I(\nu) \propto \exp\left(-\frac{mc^2(\nu-\nu_0)^2}{2k_\mathrm{B}T\nu_0^2}\right) . \tag{3.41}$$

This gives rise to a **Gaussian** line shape with $g(\nu)$ given by:

$$g(\nu) \propto \exp\left(-\frac{mc^2(\nu-\nu_0)^2}{2k_\mathrm{B}T\nu_0^2}\right) , \tag{3.42}$$

with a full width at half maximum equal to:

$$\Delta\nu_\mathrm{D} = 2\nu_0 \left(\frac{(2\ln 2)k_\mathrm{B}T}{mc^2}\right)^{1/2} = \frac{2}{\lambda}\left(\frac{(2\ln 2)k_\mathrm{B}T}{m}\right)^{1/2} . \tag{3.43}$$

The Doppler linewidth in a gas at S.T.P is usually several orders of magnitude larger than the natural linewidth. For example, the Doppler line width of the 632.8 nm line of neon at 300 K works out to be 1.3 GHz, i.e. three orders of magnitude larger than the broadening due to spontaneous emission. The dominant broadening mechanism in the emission spectrum of gases at room temperature is usually Doppler broadening, and the line shape is closer to Gaussian than Lorentzian. [4]

3.11 Atoms in solids

In laser physics we shall frequently be interested in the emission spectra of atoms in crystals. The spectra will be subject to lifetime broadening as in gases, since this is a fundamental property of radiative

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[4] Since $\Delta\nu_\mathrm{D}$ is proportional to $\sqrt{T}$, we can reduce its value by cooling the gas. Cooling also reduces the collision broadening because $P \propto T$, and therefore $\tau_\mathrm{c} \propto T^{-1/2}$. (See eqn 3.36.) Laser cooling techniques can produce temperatures in the micro-Kelvin range, where we finally observe the natural line shape of the emission line.

emission. However, the atoms are locked in a lattice, and so collisional broadening is not relevant. Doppler broadening does not occur either, for the same reason. On the other hand, the emission lines can be broadened by other mechanisms.

In some cases it may be possible for the atoms to de-excite from the upper level to the lower level by making a **non-radiative transition**. One way this could happen is to drop to the lower level by emitting phonons (ie heat) instead of photons. To allow for this possibility, we must re-write eqn 3.23 in the following form:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = -AN_2 - \frac{N_2}{\tau_{\mathrm{NR}}} = -\left(A + \frac{1}{\tau_{\mathrm{NR}}}\right) N_2 = -\frac{N_2}{\tau}\,, \tag{3.44}$$

where τ_{NR} is the non-radiative transition time. This shows that non-radiative transitions shorten the lifetime of the excited state according to:

$$\frac{1}{\tau} = A + \frac{1}{\tau_{\mathrm{NR}}}\,. \tag{3.45}$$

We thus expect additional lifetime broadening according to eqn 3.33. The phonon emission times in solids are often very fast, and can cause substantial broadening of the emission lines. This is the solid-state equivalent of collisional broadening.

Another factor that may cause line broadening is the inhomogeneity of the host medium, for example when the atoms are doped into a glass. If the environment in which the atoms find themselves is not entirely uniform, the emission spectrum will be affected through the interaction between the atom and the local environment. This is an example of an inhomogeneous broadening mechanism.

Reading

Demtröder, W., *Atoms, Molecules and Photons*, §7.1 – §7.4.
Haken, H. and Wolf, H.C., *The Physics of Atoms and Quanta*, chapter 16.
Smith, F.G. and King, T.A., *Optics and Photonics*, sections 13.1–4, 20.1–2
Beisser, A., *Concepts of Modern Physics*, sections 6.8–9
Eisberg, R. and Resnick, R., *Quantum Physics*, section 8.7.