Second Year Atomic Physics 2019/20
Part II - Radiation

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5   The Einstein A & B coefficients

The way that we know most information about atoms is through the radiation that they absorb and emit. For atoms this is mainly in the visible and UV regions of the spectrum, where we can use the eye, photographic film, CCD cameras, photomultipliers, photodiodes etc to detect the light. However, there are also interactions with X-rays and microwaves that we can investigate. In this lecture we will look at general features of the way that atoms interact with light – i.e. the conditions under which they absorb and emit light. This is governed by the *Einstein A and B coefficients*, which you came across briefly in the first year *Quantum Physics* course.

5.1   Dirac notation

First we need to introduce the Dirac notation used in quantum mechanics. It is used here mainly as a shorthand notation in order to make the equations simpler to read and write. However, Dirac notation is in fact much more powerful than is implied by the way I use it here, and it is not just an efficient way to write equations.

We write the wavefunction $\phi_i(\mathbf{r})$ as $|i\rangle$ and its complex conjugate $\phi_i^*(\mathbf{r})$ as $\langle i|$. More generally, an atom in a state described by the quantum numbers n, l, j, m_j is written as $|nljm_j\rangle$. The expectation value of some operator $\hat{O}$ in a state i,

$$\langle \hat{O} \rangle = \int \phi_i^*(\mathbf{r})\hat{O}\phi_i(\mathbf{r})d^3\mathbf{r} \tag{5.1}$$

we write simply as $\langle i|\hat{O}|i\rangle$ and the *matrix element*

$$\int \phi_j^*(\mathbf{r})\hat{O}\phi_i(\mathbf{r})d^3\mathbf{r} \tag{5.2}$$

we write as $\langle j|\hat{O}|i\rangle$. If we leave out the operator in this expression we recover the standard orthogonality relation $\langle j|i\rangle = \int \phi_j^*(\mathbf{r})\phi_i(\mathbf{r})d^3\mathbf{r} = \delta_{ji}$.

This is all you need to know about Dirac notation in order to take advantage of its usefulness in writing equations in quantum mechanics. In these lectures I will slip between conventional and Dirac notation as appropriate.

5.2   The two-level atom

We start with an idealised system much beloved of atomic theoreticians, the *two-level atom* (see Figure 1). We assume an atomic system with only two energy levels of interest, call them $|1\rangle$ (the *ground state*), with energy E_1 and $|2\rangle$ (the excited state) with energy E_2. The energy difference between these states we will call $E_{21} = E_2 - E_1$. We assume that the atom can decay radiatively from the excited state to the ground state. This follows from the fact that atoms
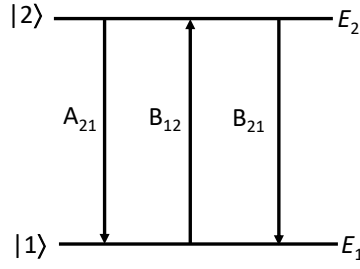
Figure 1: The two-level atom, showing the three processes described by the Einstein coefficients.

emit light at specific wavelengths. Later we will find out how to calculate the rate at which this happens for a given atom. For the moment we just assume that an excited atomic state $|2\rangle$ will have a finite radiative lifetime, call it τ_2. Our two-level atom will emit light at a frequency of $\nu_{21} = \omega_{21}/2\pi = E_{21}/h = (E_2 - E_1)/h$.

Although hugely simplified, this is a good way to study the general features of the interaction of light and matter, so long as there are no other energy levels close by.

5.3   The Einstein coefficients

You should have seen the Einstein coefficients before in the "*Quantum Physics*" course in the first year, but we will review them again here. There are three Einstein coefficients, corresponding to three distinct process that can take place when light interacts with matter. We consider a population of $N = N_1(t) + N_2(t)$ two-level atoms, where $N_1(t)$ and $N_2(t)$ are the populations of states $|1\rangle$ and $|2\rangle$ at time t.

Spontaneous emission. The first coefficient, A_{21}, represents spontaneous emission arising from the decay of an atom from state $|2\rangle$ down to state $|1\rangle$ by emission of a photon at angular frequency ω_{21}. We know that this sort of process takes place because we see light emitted from excited atoms, for instance the typical yellow colour of a flame is generally due to radiation of light from sodium atoms around $589\,\text{nm}$. We define the lifetime of the excited state to be $\tau_2 = 1/A_{21}$ so the population of the excited state decays exponentially:

$$N_2(t) = N_2(0)e^{-A_{21}t} = N_2(0)e^{-t/\tau_2}, \tag{5.3}$$

or equivalently

$$\frac{dN_2(t)}{dt} = -\frac{dN_1(t)}{dt} = -N_2(t)A_{21}, \tag{5.4}$$

where $N_2(t)$ is the population of state $|2\rangle$ at time t. This is a bit like radioactive decay: we don't know when a particular atom is going to decay but we know the overall decay rate. Notice that the last equation implies that all the population lost from state $|2\rangle$ goes to state $|1\rangle$: the total population (N) is constant.

Absorption. The next process is absorption of light at angular frequency ω_{21}. This takes an atom initially in state $|1\rangle$ up to state $|2\rangle$. The atom gains energy from the radiation field. The rate at which this occurs is proportional to the amount of light present at the correct frequency (called the *spectral energy density*), which we write as $\rho(\omega_{21})$. It is defined as the amount of electromagnetic energy per unit volume and per unit angular frequency interval around ω_{21}. This is expressed in units of Jm^{-3}s. The rate of absorption of light (or the rate of excitation of the atoms) is then given by

$$\frac{dN_2(t)}{dt} = -\frac{dN_1(t)}{dt} = N_1(t)B_{12}\rho(\omega_{21}), \tag{5.5}$$

and this serves to define the Einstein absorption coefficient B_{12}.

Now if these were the only two processes that took place, we can show that there would be an unphysical consequence. Imagine that the radiation density increased more and more. The

above equations show that nearly all the population would be driven into state $|2\rangle$, but this is not observed in practice. In equilibrium, the population of states at higher energy is *always* lower that those at lower energy, so this inversion of population cannot occur in equilibrium. (In fact this would theoretically correspond to a *negative temperature*.) Einstein therefore realised from this thought experiment that there must be a third process which acted to equalise the populations:

Stimulated emission. The final process is emission of light that is driven by the same radiation field. This takes an atom initially in state $|2\rangle$ down to state $|1\rangle$. The atom gives energy to the radiation field. The rate at which this occurs is also proportional to the amount of light present and it is given by

$$\frac{dN_2(t)}{dt} = -\frac{dN_1(t)}{dt} = -N_2(t)B_{21}\rho(\omega_{21}). \tag{5.6}$$

This defines the third Einstein coefficient, B_{21}. We will see in the next section that in the limit of infinite radiation density we would now have behaviour that makes more sense physically. Stimulated emission is fundamental to the operation of lasers.

Combining the three processes, we can write that the total rate of change of the population is

$$\frac{dN_2(t)}{dt} = -\frac{dN_1(t)}{dt} = -N_2(t)A_{21} + [N_1(t)B_{12} - N_2(t)B_{21}]\rho(\omega_{21}). \tag{5.7}$$

5.4 Thermal equilibrium

Thermal equilibrium occurs when the system of atoms is in contact with a thermal bath at a fixed temperature (here the black body radiation field) and the populations of the atomic states are all constant. For example, imagine that you have an atomic gas inside a sealed opaque cell at a uniform temperature T. We can learn more about the Einstein coefficients in a very elegant way simply by considering what happens in this steady state. In this case we can set $\frac{dN_2(t)}{dt} = -\frac{dN_1(t)}{dt} = 0$, and adding together the effects of all three processes above then leads to

$$N_1 B_{12}\rho(\omega_{21}) = N_2[A_{21} + B_{21}\rho(\omega_{21})], \tag{5.8}$$

which can be rewritten as

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\omega_{21})}{A_{21} + B_{21}\rho(\omega_{21})}. \tag{5.9}$$

What we mean by thermal equilibrium is that the different parts of a system are in equilibrium with each other at a uniform and constant temperature. In this case we can investigate the equilibrium between our atom and radiation that is at a fixed temperature – i.e. blackbody radiation. The density of radiation at temperature T is given by (*Note: you do not need to learn this expression*):

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \cdot \frac{1}{\exp\left(\hbar\omega/k_B T\right) - 1}. \tag{5.10}$$

(You will have seen this expression in your *Statistical Physics* course.) We also know from statistical physics that in thermal equilibrium at temperature T the ratio of the populations must be given by $N_2/N_1 = \exp\left(-\hbar\omega_{21}/k_B T\right)$, so combining all these equations we find (*Note: you do not need to learn this expression*):

$$\frac{N_2}{N_1} = \exp\left(-\hbar\omega_{21}/k_B T\right) = \frac{B_{12}}{A_{21}[\exp\left(\hbar\omega_{21}/k_B T\right) - 1]\pi^2 c^3/\hbar\omega_{21}^3 + B_{21}}. \tag{5.11}$$

Now this expression has to be true for all values of the temperature T. This fixes the relations between A_{21}, B_{21} and B_{12}. Consider first the low-temperature limit. At very low temperatures

the exponential term dominates the denominator of equation 5.11, so we can neglect the other terms. This can be shown to lead to the relation (*Note: you do not need to learn this expression*):

$$A_{21}\pi^2 c^3 / \hbar \omega_{21}^3 = B_{12}. \tag{5.12}$$

At high temperatures the exponentials tend towards the value 1 so the term B_{21} dominates the denominator of equation 5.11, and this implies that $B_{21} = B_{12}$.

Note that these relations are fixed and do not only apply in thermal equilibrium. Note also that simply from considerations of general principles, we have derived links between atomic properties without knowledge of any of the properties of the particular atom.

Here we assumed we only had a two-level atom. All real atoms are much more complicated than this, but it can easily be shown that when degeneracy of the atomic levels is included, the results are very similar. It can also be shown that these relations apply for any transition in any atom.

5.5 Natural lifetime

In the absence of any driving radiation $\rho(\omega)$ we see that

$$\frac{dN_2(t)}{dt} = -N_2(t)A_{21} \tag{5.13}$$

which has the solution

$$N_2(t) = N_2(0)e^{-A_{21}t} = N_2(0)e^{-t/\tau_2} \tag{5.14}$$

where the *natural lifetime* of state $|2\rangle$ is τ_2.

If a state $|j\rangle$ can decay to several states $|i\rangle$ (all lower in energy of course), then the lifetime becomes

$$\tau_j = \frac{1}{\sum_j A_{ji}}. \tag{5.15}$$

As we shall see later, the typical atomic lifetime for optically excited states in atoms is $\sim 10^{-8}\,\text{s}$ ($\sim 10\,\text{ns}$).

A sample of atoms all excited to state $|j\rangle$ at $t = 0$ decays exponentially with a lifetime of τ_j. The intensity of light $I(t)$ emitted at time t on *any* of the transitions $|j\rangle$ to $|i\rangle$ is proportional to $N_j(t)$ so we find that

$$I(t) = I(0)e^{-t/\tau_j}. \tag{5.16}$$

If you take the Fourier transform of this decay you find the spectral lineshape, which in this case is a *Lorentzian*:

$$I(\omega) = I(\omega_0) \cdot \frac{(\gamma/2)^2}{(\gamma/2)^2 + (\omega - \omega_0)^2}, \tag{5.17}$$

where ω_0 is the angular frequency of the transition and $\gamma = 1/\tau_j$ is called the *natural linewidth* in angular frequency units. This expression (5.17) represents light centred at an angular frequency ω_0 (here equal to ω_{ji}) but with a spectral frequency width proportional to γ. This width can be seen as a consequence of the classical bandwidth theorem, or in quantum mechanical terms it can be related to the energy/time uncertainty relation. In frequency units the natural linewidth is equal to $\gamma/2\pi$. The typical value in frequency units is $10\,\text{MHz}$.

In general, when both upper and lower states have a finite lifetime, the natural linewidth of the transition from state j to state i is given by

$$\gamma = \frac{1}{\tau_j} + \frac{1}{\tau_i}, \tag{5.18}$$

where τ_j is the lifetime of the upper state and τ_i is the lifetime of the lower state. (If this is the ground state of the atom, which cannot decay, then $\tau_i = \infty$ and so $\gamma = 1/\tau_j$.)

5.6 The Doppler effect

(The details of this section are not examinable, but you need to know how the Doppler width arises, the fact that it gives a Gaussian lineshape (equation 5.20) and the typical Doppler linewidth.)

For completeness we will also derive the broadening of a spectral line due to the Doppler effect. We start with the distribution of velocities (v_z) along a given direction of observation for atoms of mass M in a gas at temperature T:

$$P(v_z) \propto \exp(-Mv_z^2/2k_BT). \tag{5.19}$$

(This expression is a general result from statistical physics considerations.) If the atom is moving towards the observer at a velocity v_z the observed frequency of light emitted at angular frequency ω_0 is shifted by the Doppler effect to $\omega = \omega_0(1 + v_z/c)$, which we can write as a frequency shift of $\omega - \omega_0 = v_z\omega_0/c$. The Gaussian distribution of velocities (v_z) therefore gives rise to a Gaussian distribution of observed frequencies (ω) given by

$$I(\omega) \propto \exp[-(\omega - \omega_0)^2/\Delta\omega^2] \tag{5.20}$$

where $\Delta\omega$, which is a measure of the width of the Doppler-broadened lineshape, is given by $\Delta\omega = (\omega_0/c)\sqrt{2k_BT/M}$. The Doppler width is usually expressed as the *Full Width at Half Maximum (FWHM)* of the profile, which is given by $\Delta\omega_{FWHM} = 2\sqrt{\ln 2}\,\Delta\omega$. For a typical atom at room temperature, the Doppler width (in frequency units) is around $1\,\text{GHz}$ in the visible region.

In the presence of both a natural width and a Doppler width, the final profile of a spectral line is a convolution of the Lorentzian and Gaussian profiles in equations 5.17 and 5.20 and is called a *Voigt profile*.

5.7 Summary

- We find out about atoms mainly through the radiation they absorb and emit

- We use the two-level atom as a simple model to give us general statements about radiation

- Einstein postulated three radiative processes described by the coefficients A_{21}, B_{21} and B_{12}

- Consideration of what happens in thermal equilibrium gives us general relations between these coefficients

- The natural lifetime of a state leads to a broadening of a transition described by a Lorentzian function

- The Doppler effect due to the thermal velocity distribution leads to a convolution of this natural broadening with a Gaussian distribution

6 Radiation of light from atoms

In this lecture we will see how to work out which transitions are allowed to take place between the energy levels of an atom, and how to estimate the rate at which these transitions occur.

6.1 Introduction

The Bohr model allows us to find stable (or *stationary*) energy states of hydrogen. However, according to classical electromagnetism, any accelerating charged particle should radiate electromagnetic energy continuously at a rate given by (*Note: you do not need to learn this expression*):

$$\frac{dE}{dt} = -\frac{1}{4\pi\epsilon_0} \cdot \frac{2e^2}{3c^3}\,\overline{\ddot{x}^2}. \tag{6.1}$$

Here dE/dt is the rate of loss of energy and $\overline{\ddot{x}^2}$ is the mean square acceleration of the particle. (This equation can be used to describe synchrotron radiation from a high energy particle storage ring or radiation from an RF antenna.)

In the Bohr model, we postulate that this does not occur for the stationary states of the atom, in order to fit the observation that the electron does not spiral into the nucleus.

However, we observe that excited states of hydrogen actually do decay, not by continuously changing their energy but by jumping from one stationary state to another by emitting a photon of a specific frequency. In fact, we can use the above formula to estimate the order of magnitude of excited state lifetimes in hydrogen, even though the Bohr model does not describe radiation well. We will do this before we do a proper calculation.

For an electron in a Bohr atom, $\ddot{x} = -\omega^2 x$. Putting in parameters corresponding to $n = 2$ in hydrogen, and setting $dE/dt = -E_0/\tau$ we obtain a typical lifetime τ of around 2.5 ns. This is only a very approximate estimate but it is a useful guide and gives roughly the correct order of magnitude for the lifetime.

6.2 Result of the quantum mechanical calculation

In order to perform a quantum mechanical calculation of the atomic lifetimes in hydrogen, we have to start from the perturbation corresponding to the interaction of the radiation field with the atom. The most important part of this concerns the atom's *electric dipole moment*. Since the electron has a charge $-e$, the atom has an instantaneous electric dipole moment of $\mathbf{d} = -e\mathbf{r}$ when the electron is at position $\mathbf{r}$. This interacts with the electric field of the radiation, $\mathbf{E} = \mathbf{E}_0 \cos \omega t$. The perturbation is therefore written as $\mathcal{H}_1 = -\mathbf{d}.\mathbf{E} = e\mathbf{r}.\mathbf{E}_0 \cos \omega t$ and the process it drives is called *electric dipole radiation*. This counts as a weak perturbation because we know that the atomic lifetimes are very long compared to the oscillation frequencies in the atom.

Consider a two-level atom again. At any time during the radiation process, the atom will be in a coherent superposition of its stationary states, i.e. $|\psi(t)\rangle = c_j(t)|j\rangle + c_i(t)|i\rangle$. Using time-dependent perturbation theory we can show that this perturbation $\mathcal{H}_1$ causes the amplitudes of the components in the superposition to change with time so that an atom that starts in the excited state $|j\rangle$ will, under the influence of the interaction with the radiation field, gradually acquire a component of the ground state $|i\rangle$ in its wavefunction. The result we find is that the probability of occupation of the excited state decays exponentially at a rate given by

$$\frac{dN_j(t)}{dt} = -A_{ji}N_j(t) \tag{6.2}$$

where now $N_j(t) = |c_j(t)|^2$ is the occupation probability of state $|j\rangle$ at time t and A_{ji}, the Einstein A-coefficient, is given by (*Note: you do not need to learn this expression*):

$$A_{ji} = \frac{1}{4\pi\epsilon_0} \cdot \frac{4}{3} \cdot \frac{\omega_{ji}^3 e^2}{\hbar c^3} \cdot |\langle j|\mathbf{r}|i\rangle|^2. \tag{6.3}$$

where $\hbar\omega_{ji}$ is the energy of the photon emitted. The rate of energy loss is therefore

$$\frac{dE}{dt} = \hbar\omega_{ji}\frac{dN_j(t)}{dt} = -A_{ji}\hbar\omega_{ji}N_j(t) \tag{6.4}$$

The term $\langle j|\mathbf{r}|i\rangle$ is referred to as the *electric dipole matrix element* of the transition between state $|j\rangle$ and state $|i\rangle$ and is a measure of the magnitude of the atomic dipole during the decay. Here j stands for the complete set of quantum numbers for the initial state and i stands for all the quantum numbers of the final state. The matrix element can also be written as

$$\langle j|\mathbf{r}|i\rangle = \int \psi_j^*(\mathbf{r})\mathbf{r}\psi_i(\mathbf{r})d^3\mathbf{r}. \tag{6.5}$$

To find the total rate of decay, equation 6.3 has to be summed over all possible values of the magnetic quantum number m of the final state.

This is a general formula but if we apply it to the first excited state of hydrogen (the 2p state) we find that $A_{21} = 6 \times 10^8\,\mathrm{s}^{-1}$, making the lifetime for decay to the ground (1s) state equal to 1.6 ns. In the process of this decay the atom will emit a photon at 121 nm.

The important thing about the expression for A_{ji} is that

$$A_{ji} \propto \omega_{ji}^3|\langle j|\mathbf{r}|i\rangle|^2, \tag{6.6}$$

that is, the transition rate is proportional to the cube of the frequency of the transition and the square of the matrix element. States that decay via UV transitions (high frequency) therefore tend to have shorter lifetimes than those that decay via visible or infrared transitions (low frequency).

Once we have calculated A_{ji}, we can then also calculate B_{ji} and B_{ij} using the general formulae for these coefficients that we discussed in the last lecture. Therefore we can calculate the rate at which transitions will be driven by an external source of radiation (e.g. a laser). This is very important for laser spectroscopy and related fields.

6.3 Selection rules in hydrogen

It turns out that the lifetimes of atomic states vary enormously, and it is the electric dipole matrix element $\langle j|\mathbf{r}|i\rangle$ that determines which transitions take place in an atom in practice. We can use arguments based on symmetry and other basic principles to make general statements about which transitions can take place. For certain combinations of quantum numbers, we find that $\langle j|\mathbf{r}|i\rangle$ is equal to zero, in which case the transition is said to be *forbidden*.

6.3.1 Parity

Remember that j is a label here that stands for all the excited state quantum numbers (n', l', j', m_j') and i stands for all the quantum numbers of the ground state (n, l, j, m_j). Ignoring spin for the moment, we can write the state $|i\rangle$ as

$$|i\rangle \equiv \psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_{lm_l}(\theta, \phi). \tag{6.7}$$

Now the *parity* of Y_{lm_l} is $(-1)^l$, i.e.

$$Y_{lm_l}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm_l}(\theta, \phi). \tag{6.8}$$

So all s and d states have *even parity* and all p and f states have *odd parity*. The parity of $\mathbf{r}$ is odd. The integral is over all space, so if the integrand is odd, the integral must be zero, whereas if the integrand is even, the integral can be non-zero. Therefore the parity of the states $|i\rangle$ and $|j\rangle$ must be different for the matrix element to be non-zero. In other words, the change in l, which we write as $\Delta l = l' - l$, must be an odd number.

Furthermore, we know that the photon carries away one unit of angular momentum because it has a spin of unity. This means, by conservation of angular momentum, that $|\Delta l| \leq 1$.

Combining these results, we find that Δl can be $+1$ or -1 but not zero. This is called the *selection rule* for the quantum number l.
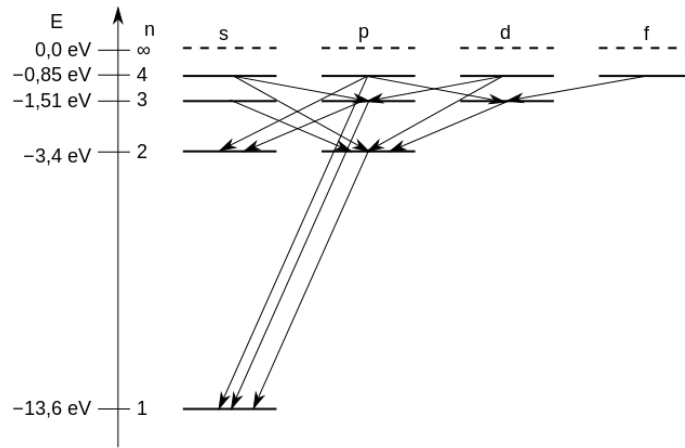
Figure 2: Energy levels and allowed transitions in hydrogen

6.3.2 Conservation of total angular momentum

The total angular momentum of the atom is defined as $\mathbf{j} = \boldsymbol{\ell} + \mathbf{s}$. The photon carries away one unit of angular momentum, so this restricts the change of the quantum number j, which we write as $\Delta j = j' - j$. Classically we could use vectors to express the initial and final angular momentum values for the atom and the angular momentum of the photon. The conservation of angular momentum would be guaranteed if the three angular momenta form a triangle so that the initial angular momentum of the atom is equal to its final angular momentum added to that of the photon emitted. When this classical picture is translated into a quantum mechanical description, it requires that Δj can only equal ± 1 or zero, because the photon carries away one unit of angular momentum. This *triangle rule* therefore determines the selection rule for j. [For completeness, we note here that the triangle rule forbids a transition from $j' = 0$ to $j = 0$ because angular momentum conservation cannot be satisfied in this case. However, this situation does not arise in hydrogen because j only takes half-integer values. But this additional rule will become important when we look at helium.]

6.3.3 Conservation of angular momentum projection

By an extension of the previous argument, it can be shown that there is a similar restriction on the change in m_j, which we define as $\Delta m_j = m'_j - m_j$. We find that Δm_j is equal to ± 1 or zero. When it is ± 1, the light emitted is polarised perpendicular to the z-axis, and is referred to as σ-polarised light, and when $\Delta m_j = 0$, the light is polarised along the z-axis and is referred to as π-polarisation.

In order to simplify the discussion we have written the matrix element in a general form without specifying which component of the vector $\mathbf{r}$ we are interested in. If we want to look at the polarisation of the light emitted or absorbed, we need to consider the appropriate component of $\mathbf{r}$ (i.e., x, y or z) and the appropriate values of Δm_j. For example, the electric field of π-polarised light is directed along z, so the matrix element that has to be evaluated in this case is $\langle j|z|i \rangle$ where $|j\rangle$ and $|i\rangle$ both have the same value of m_j. For σ-polarised light we would need to calculate $\langle j|x|i \rangle$ or $\langle j|y|i \rangle$.

6.3.4 Principal quantum number

There are no restrictions on the change in the principal quantum number n, so $\Delta n = n' - n$ can take any value. This quantum number is not related to any angular momentum properties of the atom.

6.3.5 Allowed transitions

Armed with these selection rules, we can determine which transitions are allowed and which are forbidden, simply by looking at the values of the quantum numbers of the initial and final states (see Figure 2 for a diagram showing the allowed transitions in hydrogen). An allowed transition must satisfy all of the above selection rules. However, in order to find out the actual rate of a transition, if it is allowed in principle by these rules, we need to perform a detailed calculation of a matrix element using the atomic wavefunctions. In general, these calculations are very complex but we can make some general statements about the expected results. First, the radial part of the matrix element $\langle j|\mathbf{r}|i\rangle$ will typically have a value similar to the size of the atom (i.e. the extent of the radial wavefunctions). Second, the angular part of the matrix element will give a result of order unity, unless the selection rules are not satisfied, in which case it will be zero. The atomic lifetimes for states which have allowed transitions to lower states in the visible region of the spectrum are typically of the order of 1 to 10 ns. If the transitions are in the UV (e.g. for highly-charged ions), the lifetimes are much shorter.

6.4 Zeeman effect for radiative transitions

In section 4 we looked at the effect that a magnetic field has on the energy levels of an atom, and we calculated that the different m_j states split in energy according to

$$\Delta E_{m_j} = g_j \mu_B B m_j \quad \text{where} \quad g_j = \frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \tag{6.9}$$

Now we want to see how the magnetic field affects a spectral line. Consider a transition from the m_{j_2} state of the upper level $|2\rangle$ to the m_{j_1} state of the lower level $|1\rangle$. Since in general both levels are split by the magnetic field, the frequency of the transition depends on both m_{j_1} and m_{j_2}. The energy of the upper state is $E_2 + g_{j_2} m_{j_2} \mu_B B$ and the energy of the lower state is $E_1 + g_{j_1} m_{j_1} \mu_B B$, so the energy of the photon is

$$\Delta E = h\nu_{m_{j_2} m_{j_1}} = E_2 + g_{j_2} m_{j_2} \mu_B B - E_1 - g_{j_1} m_{j_1} \mu_B B = E_2 - E_1 + (g_{j_2} m_{j_2} - g_{j_1} m_{j_1})\mu_B B, \tag{6.10}$$

so the transition from m_{j_2} to m_{j_1} is shifted from the unperturbed frequency $\nu_{21} = (E_2 - E_1)/h$ by

$$\Delta \nu_{m_{j_2} m_{j_1}} = (g_{j_2} m_{j_2} - g_{j_1} m_{j_1})\mu_B B/h. \tag{6.11}$$

This can be calculated for all components of the transition, bearing in mind that the π components have $\Delta m_j = m_{j_2} - m_{j_1} = 0$ and the σ components have $\Delta m_j = m_{j_2} - m_{j_1} = \pm 1$. Note that μ_B/h is equal to $14\,\text{GHz/T}$, giving an easy way to find the values of $\Delta \nu_{m_{j_2} m_{j_1}}$.

6.5 Metastable states

Sometimes we find an excited state of an atom which has no allowed transitions at all to lower energy states via the electric dipole transitions that we have been considering. This is then called a *metastable state* of the atom. In this case the state must decay via other, higher-order processes. For example, it may be that the perturbation that drives the transition is not the interaction of an atomic electric dipole moment with the radiation field, but an atomic *magnetic dipole* moment. These transitions have a different set of selection rules, and as a general rule, allowed magnetic dipole transitions have rates which are typically a factor of order $\alpha^2 \sim 10^{-4}$ slower than electric dipole transitions. Another possibility is where the transition is driven by an *electric quadrupole* process, in which case the transition is also typically a factor of order α^2 slower than electric dipole processes. In this case, the photon carries away two units of angular momentum so some quantum numbers can now change by 0, ± 1, or ± 2. Metastable state lifetimes usually range from microseconds up to seconds. The Yb$^+$ ion has one excited

state which can only decay via a very slow *octupole* process, and therefore has a lifetime of several years, but this is extremely unusual.

In hydrogen the only metastable state is the 2s state, which has a lifetime of the order of 0.15 s. The decay of this state is actually forbidden for most types of decay process and the only way it can decay is by emitting two photons simultaneously. This *two-photon decay* is very slow because it has to proceed through a virtual state.

6.6   Summary

- Excited atomic states decay by emitting radiation in a quantum mechanical analogue of radiation from a classical accelerating charged particle

- The interaction between the atomic electric dipole moment and the electric field of the radiation leads to an electric dipole decay, resulting in typical atomic lifetimes of the order of 1 to 10 ns

- The electric dipole transition rate is proportional to the radiation frequency cubed and the matrix element squared

- Selection rules for l, j and m_j determine which transitions can take place

- The Zeeman splitting of a transition can be found by considering the energy splittings of the upper and lower levels of the transition

- Where no electric dipole transition is possible, other, slower, process will lead to atomic decay