

CHAPTER 9 OSCILLATOR STRENGTHS AND RELATED TOPICS

9.1 Introduction. Radiance and Equivalent Width.

If we look at a hot, glowing gas, we can imagine that we could measure its *radiance* in $\text{W m}^{-2} \text{sr}^{-1}$. If we disperse the light with a spectrograph, we may see that it is made up of numerous discrete emission lines. These lines are not infinitesimally narrow, but have a finite width and a measurable profile. At any particular wavelength within the wavelength interval covered by the line, let us suppose that the radiance per unit wavelength interval is $I_\lambda \text{ W m}^{-2} \text{sr}^{-1} \text{m}^{-1}$. Here, we are using the symbol I for radiance, which is customary in astronomy, rather than the symbol L , which we used in chapter 1. We insist, however, on the correct use of the word "radiance", rather than the often too-loosely used "intensity". We might imagine that we could measure I_λ by comparing the radiance per unit wavelength interval in the spectrum of the gas with the radiance per unit wavelength interval of a black body at a known temperature (or of any other body whose emissivity is known), observed under the same conditions with the same spectrograph.

The radiance I of the whole line is given by $I = \int I_\lambda d\lambda$. In principle, the integration limits are 0 and ∞ , although in practice for most lines the integration need be performed only within a few tenths of a nanometre from the line centre.

The radiance of an emission line depends, among other things, upon the number of atoms per unit area in the line of sight (the "column density") in the initial (i.e. upper) level of the line.

You will have noticed that I wrote "depends upon", rather than "is proportional to". We may imagine that the number of atoms per unit area in the line of sight could be doubled either by doubling the density (number of atoms per unit volume), or by doubling the depth of the layer of gas. If doubling the column density results in a doubling of the radiance of the line, or, expressed otherwise, if the radiance of a line is linearly proportional to the column density, the line is said to be *optically thin*. Very often a line is not optically thin, and the radiance is not proportional to the number of atoms per unit area in the upper level. We shall return to this topic in the chapter on the curve of growth. In the meantime, in this chapter, unless stated otherwise, we shall be concerned entirely with optically thin sources, in which case $I \propto \mathcal{N}_2$, where \mathcal{N} is the column density and the subscript denotes the upper level. We shall also suppose that the gas is homogenous and of a single, uniform temperature and pressure throughout.

In the matter of notation, I am using:

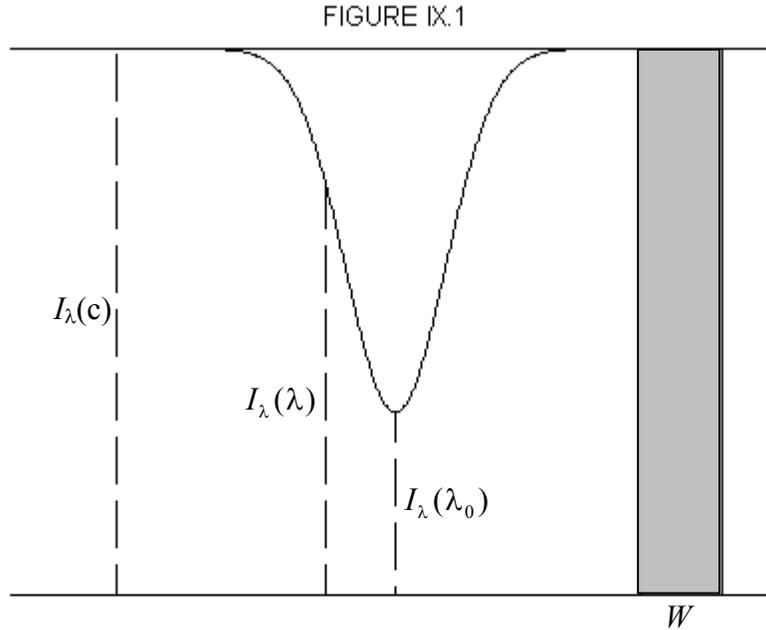
n = number of atoms per unit volume

\mathcal{N} = column density

N = number of atoms

Thus in a volume V , $N = nV$, and in a layer of thickness t , $\mathcal{N} = nt$.

Most lines in stellar spectra are *absorption* lines seen against a brighter continuum. In an analogous laboratory situation, we may imagine a uniform layer of gas seen against a continuum. We'll suppose that the radiance per unit wavelength interval of the background continuum source is $I_\lambda(c)$. We shall establish further notation by referring to figure IX.1, which represents an absorption line against a continuum. The radiance per unit wavelength interval is plotted against wavelength horizontally.



$I_\lambda(\lambda)$ is the radiance per unit wavelength interval at some wavelength within the line profile, and $I_\lambda(\lambda_0)$ is the radiance per unit wavelength interval at the line centre.

The *equivalent width* W (die Äquivalentbreite) of an absorption line is the width of the adjacent continuum that has the same area as is taken up by the absorption line. Expressed as a defining equation, this means:

$$WI_\lambda(c) = \int [I_\lambda(c) - I_\lambda(\lambda)] d\lambda. \quad 9.1.1$$

Again in principle the integration limits are 0 to ∞ , although in practice a few tenths of a nanometre will suffice. Equivalent width is expressed in nm (or in Å). It must be stressed that equivalent width is a measure of the strength of an absorption line, and is in no way related to the actual width (or full width at half minimum) of the line. In figure IX.1, the width W of the continuum has the same area as the absorption line.

In principle, the equivalent width could also be expressed in frequency units (Hz), via a defining equation:

$$W^{(\nu)} I_{\nu}(c) = \int [I_{\nu}(c) - I_{\nu}(\nu)] d\nu. \quad 9.1.2$$

This is sometimes seen in theoretical discussions, but in practice equivalent width is usually expressed in wavelength units. The two are related by

$$W^{(\nu)} = \frac{c}{\lambda^2} W^{(\lambda)}, \quad W^{(\lambda)} = \frac{c}{\nu^2} W^{(\nu)}. \quad 9.1.3$$

Unless otherwise specified, I shall omit the superscript (λ) , and W will normally mean equivalent width expressed in wavelength units, as in equation 9.1.1.

Problem. A layer of cool gas lies above an extended source of continuous radiation, and an absorption line formed in the gas layer has an equivalent width W . If the temperature of the extended continuous source is now increased so that its spectral radiance at the wavelength of the line is doubled, what will now be the equivalent width of the line?

The equivalent width of an absorption line depends, among other things, upon the number of atoms per unit area in the line of sight (the "column density") in the initial (i.e. lower) level of the line. If the gas is optically thin, $W \propto \mathcal{N}_1$, where the subscript indicates the lower level of the line.

If the absorption coefficient at wavelength λ is $\alpha(\lambda)$ and has the same value throughout the gas, and if the thickness of the gas layer is t , $I_{\lambda}(\lambda)$ and $I_{\lambda}(c)$ are related by

$$I_{\lambda}(\lambda) = I_{\lambda}(c) \exp[-\alpha(\lambda)t]. \quad 9.1.4$$

Thus equation 9.1.1 can be written

$$W = \int [1 - \exp(-\alpha(\lambda)t)] d\lambda, \quad 9.1.5$$

and this equation is sometimes cited as the *definition* of the equivalent width. The *definition*, however, is equation 9.1.1. Equation 9.1.4 can be used to *calculate* it, but only if $\alpha(\lambda)$ is uniform throughout the gas. In the optically thin limit, the first term in the Maclaurin expansion of $1 - \exp(-\alpha(\lambda)t)$ is $\alpha(\lambda)t$, so that, for an optically thin homogeneous gas,

$$W = t \int \alpha(\lambda) d\lambda. \quad 9.1.6$$

The reader should verify, as ever, the dimensional correctness of all of the foregoing equations.

We have seen that the radiance of an emission line or the equivalent width of an absorption line depends, *among other things*, on the column density of atoms in the initial state. In fact, in a homogeneous optically thin gas, the radiance or equivalent width is linearly proportional to the product of two things. One is the column density of atoms in the initial state. The other is an intrinsic property of the atom, or rather of the two atomic levels involved in the formation of the line, which determines how much energy a *single atom* emits or absorbs. There are three quantities commonly used to describe this property, namely *oscillator strength*, *Einstein coefficient* and *line strength*.

All three of these quantities are related by simple equations, but *oscillator strength* is particularly appropriate when discussing absorption lines, *Einstein coefficient* is particularly appropriate when discussing emission lines, while *line strength* is a quantum mechanical quantity particularly useful in theoretical work. Because of this very technical usage of the term *line strength*, the term should not be used merely to describe how "intense" a particular line appears to be.

9.2 *Oscillator Strength*. (die Oszillatorenstärke)

The concept of oscillator strength arises from a classical electromagnetic model of the absorption of radiation by an atom. While a detailed understanding of each step in the derivation requires an understanding and recall of some results from classical mechanics and electromagnetic theory, it is not at all difficult to understand qualitatively the meaning of oscillator strength and at least the general gist of the argument that follows.

An atom consists of a nucleus surrounded by electrons - but not all of the electrons are equally strongly bound. We are going to think of an atom as having, for the purposes of this model, just two parts of interest, namely an outer loosely bound electron, and the rest of the atom. If this system is set into vibration, we'll suppose that it has a natural frequency ω_0 , but that the oscillations are damped. An oscillating dipole does, of course, radiate electromagnetic waves. That is to say, it loses energy. That is to say, the oscillations are damped. If the atom is placed in an oscillating electric field (i.e. if you shine a light on the atom) given by $\hat{E} \cos \omega t$, the electron will experience a force per unit mass $\frac{e\hat{E}}{m} \cos \omega t$. The equation of motion is

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{e\hat{E}}{m} \cos \omega t. \quad 9.2.1$$

This is the differential equation that describes forced, damped oscillations. The solutions to this equation are well known, but I shall defer detailed consideration of it until the chapter on line profiles. Suffice it to say, for our present purposes, that it is possible to determine, from analysis of this equation, how much energy is absorbed.

If a periodic force is applied to a mass attached to a fixed point by a spring, and the motion is damped, either by viscous forces (for example, if the mass were immersed in a fluid) or by internal stresses in the spring, not all of the work done by the periodic force goes into setting the mass in motion; some of it is dissipated as heat. In a way, we are imagining the atom to consist of an electron attached by some sort of force to the rest of the atom; not all of the work done by the forcing electromagnetic wave goes into setting the electron in motion. Some of the work is absorbed or degraded into a non-mechanical form. Perhaps the energy is lost because the accelerating electron radiates away energy into space. Or perhaps, if you believe in discrete energy levels, the atom is raised to a higher energy level. It does not matter a great deal what you believe happens to the energy that is "lost" or "absorbed"; the essential point for the present is that equation 9.2.1 allows us to calculate (and I do promise to do this in the chapter on line profiles) just how much energy is lost or absorbed, and hence, if the atom is irradiated by a continuum of wavelengths, it enables us to calculate the equivalent width of the resulting spectrum line. The result obtained is

$$W = \frac{\mathcal{N}e^2\lambda^2}{4\varepsilon_0mc^2}. \quad 9.2.2$$

W = equivalent width in wavelength units.

\mathcal{N} = column density (number per unit area in the line of sight) of absorbing atoms.

λ = wavelength of the line.

ε_0 = permittivity of free space.

e, m = charge and mass of the electron.

c = speed of light.

The reader should, as ever, check that the above expression has the dimensions of length. If every quantity on the right hand side is expressed in SI units, the calculated equivalent width will be in metres.

The reader may well object that s/he is not at all satisfied with the above argument. An atom is not at all like that, it will be said. Besides, equation 9.2.2 says that the equivalent width depends only on the wavelength, and that all lines of the same wavelength have the same equivalent width. This is clearly nonsense. Let us deal with these two objections in turn.

First: Atoms are not at all like that. For a start, an atom is an entity that can exist only in certain discrete energy levels, and the only atoms that will absorb radiation of a given frequency are those that are in the lower level of the two levels that are involved in a line. Thus \mathcal{N} in equation 9.2.2 must be replaced by \mathcal{N}_1 , the column density (number per unit area in the line of sight) *of just those atoms that are in the lower level of the line involved*. Thus equation 9.2.2 should be replaced by

$$W = \frac{\mathcal{N}_1e^2\lambda^2}{4\varepsilon_0mc^2}. \quad 9.2.3$$

Second: The equivalent width of a line obviously does not depend only on its wavelength. Many lines of very nearly the same wavelength can have almost any equivalent width, and the equivalent

width can vary greatly from line to line. We therefore now come to the *definition of oscillator strength*:

The absorption oscillator strength f_{12} of a line is the ratio of its observed equivalent width to the equivalent width (wrongly) predicted on the basis of the classical oscillator model and given by equation 9.2.3.

Thus the expression for the equivalent width becomes

$$W = \frac{\mathcal{N}_1 f_{12} e^2 \lambda^2}{4 \epsilon_0 m c^2}. \quad 9.2.4$$

The oscillator strength for a given line must be determined either experimentally or theoretically before the column density of a particular atom in, for example, a stellar spectrum can be determined from the observed equivalent width of a line. In principle, the oscillator strength of a line could be measured in the laboratory if one were able, for example, to measure the equivalent width of a line produced in an absorbing gas in front of a continuum source, and if one were able independently to determine \mathcal{N}_1 . Other experimental methods can be devised (see section 9.3 on Einstein coefficients), and theoretical methods are also available (see section 9.5 on line strengths).

It should be emphasized that equation 9.2.4 applies only to an optically thin layer of gas. As far as I can see, there is no reason why equation 9.2.4 is restricted either to a homogeneous layer of gas of uniform temperature and pressure, or to a gas in thermodynamic equilibrium - but it does require the layer to be optically thin.

We shall now restrict ourselves to an optically thin layer that is in *thermodynamic equilibrium* and of *uniform temperature* throughout. In that case, \mathcal{N}_1 is given by Boltzmann's equation (see equation 8.4.18):

$$\frac{\mathcal{N}_1}{\mathcal{N}} = \frac{\varpi_1 e^{-E_1/(kT)}}{u}. \quad 9.2.5$$

Here \mathcal{N} is the total number of atoms per unit area in all levels, ϖ_1 is the statistical weight $2J + 1$ of the lower level, and u is the partition function. Thus equations 9.2.4 and 9.2.5 combined become

$$W = \frac{\mathcal{N} e^2 \lambda^2 \varpi_1 f_{12} e^{-E_1/(kT)}}{4 \epsilon_0 m c^2 u}. \quad 9.2.6$$

In the above equations I have used slightly different fonts for e , the electronic charge, and \mathbf{e} , the base of natural logarithms.

The quantity f_{12} is called the *absorption oscillator strength*. An *emission oscillator strength* f_{21} can be defined by

$$\varpi_1 f_{12} = \varpi_2 f_{21}, \quad 9.2.7$$

and either side of this equation is usually given the symbol ϖf . Indeed, it is more usual to tabulate the quantity ϖf than f_{12} or f_{21} alone. I should also point out that the notation seen in the literature is very often gf rather than ϖf . However, in chapter 7 I went to considerable trouble to distinguish between statistical weight, degeneracy and multiplicity, and I do not wish to change the notation here. In any case, the value of ϖ (a form of the Greek letter pi) for an atomic energy level is $2J+1$. (We pointed out in chapter 7 why it is not usually necessary to include the further factor $2I + 1$ for an atom with nonzero nuclear spin.) Equation 9.2.6 is usually written

$$W = \frac{\mathcal{N}e^2\lambda^2\varpi f e^{-E_1/(kT)}}{4\epsilon_0 mc^2 u}. \quad 9.2.8$$

If we take the common logarithm of equation 9.2.8, we obtain

$$\log \frac{W}{\varpi f \lambda^2} = \log \frac{e^2}{4\epsilon_0 mc^2} + \log \mathcal{N} - \log u - \frac{eV_1}{kT} \log e. \quad 9.2.9$$

If everything is in SI units, this is

$$\log \frac{W}{\varpi f \lambda^2} = -14.053 + \log \mathcal{N} - \log u - \theta V_1. \quad 9.2.10$$

I'd be happy for the reader to check my arithmetic here, and let me know (universe@uvvm.uvic.ca) if it's not right. Here W and λ are to be expressed in metres and \mathcal{N} in atoms per square metre. V_1 is the excitation potential of the lower level of the line in volts, and θ is $5039.7/T$, where T is the excitation temperature in kelvin. *Thus, if we measure the equivalent widths of several lines from an optically thin gas, and plot $\log\left(\frac{W}{\varpi f \lambda^2}\right)$ versus the excitation potential of the lower level of each line, we should get a straight line whose slope will give us the excitation temperature, and, provided that we know the partition function, the intercept will give us the column density of the neutral atoms (in all levels) or of a particular ionization state.*

Often it will happen that some points on the graph fall nowhere near the regression line. This could be because of a wildly-erroneous oscillator strength, or because of a line misidentification. Sometimes, especially for the resonance lines (the strongest lines arising from the lowest level or term) a line lies well below the regression line; this may be because these lines are not optically thin. Indeed, equation 9.2.10 applies only for optically thin lines.

Equation 9.2.10 shows how we can make use of Boltzmann's equation and plot a straight-line graph whose slope and intercept will give us the excitation temperature and the column density of

the atoms. We can go further and make use of Saha's equation. If we plot $\log\left(\frac{W}{\pi f \lambda^2}\right)$ versus the lower excitation potential for atomic lines and do the same thing separately for ionic lines, we should obtain two straight lines of the same slope (provided that the gas is in thermodynamic equilibrium so that the excitation temperatures of atom and ion are the same). From the difference between the intercepts of the two lines we can get the electron density. Here's how it works.

If we set up equation 9.2.9 or equation 9.2.10 for the atomic lines and for the ionic lines, we see that the difference between the intercepts will be equal to $\log\left(\frac{\mathcal{N}_a u_i}{\mathcal{N}_i u_a}\right)$, and, if the gas is optically thin, this is also equal to $\log\left(\frac{n_a u_i}{n_i u_a}\right)$. Here the subscripts denote atom and ion, \mathcal{N} is column density and n is particles per unit volume. Then from equation 8.6.7 we see that

$$\log\left(\frac{n_a u_i}{n_i u_a}\right) = \text{difference between intercepts} = 27.24 - \frac{3}{2} \log \theta - \theta(V - \Delta V) - \log n_e. \quad 9.2.11$$

Here θ is $5039.7/T$, where T is the ionization temperature and, in assuming that this is the same as the excitation temperatures obtained from the slopes of the lines, we are assuming thermodynamic equilibrium. V is the ionization potential of the atom. Thus we can obtain the electron density n_e – except for one small detail. ΔV is the lowering of the excitation potential, which itself depends on n_e . We can first assume it is zero and hence get a first approximation for n_e ; then iterate to get a better V in the same manner that we did in solving Problem 4 of section 8.6.

So far we have discussed the equivalent width of a *line*. A line, however, is the sum of several Zeeman *components*, with (in the absence of an external magnetic field) identical wavelengths. It is possible to define an oscillator strength of a Zeeman *component*. Is the oscillator strength of a line equal to the sum of the oscillator strengths of its components? The answer is *no*. Provided the line and all of its components are optically thin, the *equivalent width* of a line is equal to the sum of the *equivalent widths* of its components. Thus equation 9.2.8 shows that the πf value of a line is equal to the sum of the πf values of its components. A further point to make is that, for a component, the statistical weight of each state of the component is unity. (A review from chapter 7 of the meanings of line, level, component, state, etc., might be in order here.) Thus, for a component there is no distinction between absorption and emission oscillator strength, and one can use the isolated symbol f with no subscripts, and the unqualified phrase "oscillator strength" (without a "absorption" or "emission" prefix) when discussing a component. One can accurately say that the πf value of a line is equal to the sum of the f values of its components. In other words, $\pi f(\text{line}) = \sum f(\text{components})$, so that one could say that the oscillator strength of a line is the *average* of the oscillator strength of its components. Of course, this doesn't tell you, given the πf value of a line, what the f -values of the individual components are. We defer discussion of that to a later section of this chapter.

The phrase "*f*-value" is often used instead of "oscillator strength". I was rather forced into that in the previous paragraph, when I needed to talk about \overline{mf} values versus *f*-values. However, in general, I would discourage the use of the phrase "*f*-value" and would encourage instead the phrase "oscillator strength". After all, we never talk about the "*e*-value" of the electron or the "*M*-value" of the Sun. I suppose "weighted oscillator strength" could be used for \overline{mf} .

9.3 Einstein *A* Coefficient

Although either oscillator strength or Einstein *A* coefficient could be used to describe either an emission line or an absorption line, oscillator strength is more appropriate when talking about absorption lines, and Einstein *A* coefficient is more appropriate when talking about emission lines.

We think of an atom as an entity that can exist in any of a number of discrete energy levels. Only the lowest of these is stable; the higher levels are unstable with lifetimes of the order of nanoseconds. When an atom falls from an excited level to a lower level, it emits a quantum of electromagnetic radiation of frequency ν given by

$$h\nu = \Delta E, \quad 9.3.1$$

where $\Delta E = E_2 - E_1$, E_2 and E_1 respectively being the energies of the upper (initial) and lower (final) levels. The number of downward transitions per unit time is supposed to be merely proportional to the number of atoms, N_2 , at a given time in the upper level. The number of downward transitions per unit time is $-\dot{N}_2$, since \dot{N}_2 in calculus means the rate at which N_2 is *increasing*. Thus

$$-\dot{N}_2 = A_{21}N_2. \quad 9.3.2$$

The proportionality constant A_{21} is the *Einstein coefficient for spontaneous emission* for the transition from E_2 to E_1 . It is equivalent to what, in the study of radioactivity, would be called the *decay constant*, usually given the symbol λ . It has dimensions T^{-1} and SI units s^{-1} . Typically for electric dipole transitions, it is of order $10^8 s^{-1}$. As in radioactivity, integration of the above equation shows that if, at time zero, the number of atoms in the upper level is $N_2(0)$, the number remaining after time t will be

$$N_2(t) = N_2(0)e^{-A_{21}t}. \quad 9.3.3$$

Likewise, as will be familiar from the study of radioactivity (or of first-order chemical reactions, if you are a chemist), the mean lifetime in the upper level is $1/A_{21}$ and the half-life in the upper level is $(\ln 2)/A_{21}$. This does presume, however, that there is only *one* lower level below E_2 . We return to this point in a moment, when we consider the situation when there is a choice of more than one lower level to which to decay from E_2 .

Since there are $A_{21}N_2$ downward transitions per units time from E_2 to E_1 , and each transition is followed by emission of an energy quantum $h\nu$, the rate of emission of energy from these N_2 atoms, i.e. the *radiant power or radiant flux* (see chapter 1) is

$$\Phi = N_2 A_{21} h\nu \quad \text{watts.} \quad 9.3.4$$

(For absolute clarity, we could append the subscript 21 to the frequency ν in order to make clear that the frequency is the frequency appropriate to the transition between the two energy levels; but a surfeit of subscripts might be too distracting to the point of actually making it less clear.) Provided the radiation is emitted isotropically, the *intensity* is

$$I = \frac{N_2 A_{21} h\nu}{4\pi} \quad \text{W sr}^{-1}. \quad 9.3.5$$

The *emission coefficient* (intensity per unit volume) is

$$j = \frac{n_2 A_{21} h\nu}{4\pi} \quad \text{W m}^{-3} \text{ sr}^{-1}. \quad 9.3.6$$

If we are looking at a layer, or slice, or slab, of gas, the *radiance* is

$$L = \frac{\mathcal{N}_2 A_{21} h\nu}{4\pi}. \quad \text{W m}^{-2} \text{ sr}^{-1}. \quad 9.3.7$$

Here, I have been obliged to use I and L correctly for *intensity* and *radiance*, rather than follow the unorthodox astronomical custom of using I for *radiance* and calling it "intensity". I hope that, by giving the SI units, I have made it clear, though the reader may want to refer again to the definitions of the various quantities described in chapter 1. I am using the symbols described in section 9.1 of the present chapter for N , n and \mathcal{N} . I should also point out that equations 9.3.4-7 require the gas to be optically thin.

Equation 9.3.2 and 3 assume that the atom, starting from level 2, can decay to only one lower level. This may sometimes be the case, or, even if it is not, transitions to one particular lower level are far more likely than decay to any or all of the others. But in general, there will be a choice (with different branching ratios) of several lower levels. The correct form for the decay constant under those circumstances is $\lambda = \sum A_{21}$, the sum to be taken over all the levels below E_2 to which the atom can decay, and the mean lifetime in level 2 is $1/\sum A_{21}$. Nowadays it is possible to excite a particular energy level selectively and follow electronically on a nanosecond timescale the rate at which the light intensity falls off with time. This tells us the lifetime (and hence the sum of the relevant Einstein coefficients) in a given level, with great precision without having to measure absolute intensities or the number of emitting atoms. This is a great advantage, because the measurement of absolute intensities and determination of the number of emitting atoms are both matters of great experimental difficulty, and are among the greatest sources of error in laboratory determinations of oscillator strengths. The method does not by itself, however, give the Einstein coefficients of individual lines, but only the sum of the Einstein coefficients of several possible

downward transitions. Measurements of (or theoretical calculations of) *relative* oscillator strengths or branching ratios (which do not require absolute intensity measurements or determinations of the number of emitting or absorbing atoms), combined with lifetime measurements, however, can result in relatively reliable absolute oscillator strengths or Einstein coefficients.

We shall deal in section 9.4 with the relation between oscillator strength and Einstein coefficient.

If the optically thin layer of gas described by equation 9.3.7 is in thermodynamic equilibrium, then \mathcal{N}_2 is given by Boltzmann's equation, so that equation 9.3.7 becomes

$$L = \frac{\mathcal{N}hc\varpi_2A_{21}e^{-E_2/(kT)}}{4\pi\lambda u}. \quad 9.3.8$$

The common logarithm of this is

$$\log\left(\frac{L\lambda}{\varpi_2A_{21}}\right) = \log\frac{hc}{4\pi} + \log\mathcal{N} - \log u - \frac{eV_2}{kT}\log e. \quad 9.3.9$$

If everything is in SI units, this becomes

$$\log\left(\frac{L\lambda}{\varpi_2A_{21}}\right) = -25.801 + \log\mathcal{N} - \log u - \theta V_2. \quad 9.3.10$$

Thus a graph of $\log\left(\frac{L\lambda}{\varpi_2A_{21}}\right)$ versus the upper excitation potential V_2 will yield (for optically thin lines) the temperature and the column density of atoms from the slope and intercept. I leave it to the reader to work out the procedure for determining the electron density in a manner similar to how we did this for absorption lines in developing equation 9.2.11.

The radiance of a line is, of course, the sum of the radiances of its Zeeman components, and, since the radiance is proportional to ϖ_2A_{21} , one can say, following a similar argument to that given in the penultimate paragraph of section 9.2, that the Einstein coefficient of a line is equal to the *average* of the Einstein coefficients of its components.

At this stage, you may be asking yourself if there is a relation between oscillator strength and Einstein coefficient. There is indeed, but I crave your patience a little longer, and I promise to address this in section 9.4.

“*Transition Probability*” (die Übergangswahrscheinlichkeit.) The expression “transition probability” is often used for the Einstein A coefficient, and it is even sometimes defined as “the probability per second that an atom will make a spontaneous downward transition from level 2 to level 1”. Both are clearly wrong.

In probability theory (especially in the theory of Markov chains) one sometimes has to consider a system that can exist in any of several states (as indeed an atom can) and the system, starting from one state, can make a transition to any of a number of other possible states. The probability of making a particular transition is called, not unnaturally, the *transition probability*. The transition probability so defined is a dimensionless number in the range zero to one inclusive. The sum of the transition probabilities to all possible final states is, of course unity. “Branching ratio” is another term often used to describe this concept, although perhaps “branching fraction” might be better. In any case, the reader must be aware that in many papers on spectroscopy, the phrase “transition probability” is used when what is intended is the Einstein A coefficient.

The reader will have no difficulty in showing (from equation 9.3.3) that the probability that an atom, initially in level 2, will make a spontaneous downward transition to level 1 in time t , is $1 - e^{-A_{21}t}$, and that the probability that it will have made this transition in a second is $1 - e^{-A_{21}}$. With A_{21} being typically of order 10^8 s^{-1} , this probability is, unsurprisingly, rather close to one!

9.4 Einstein B Coefficient

In section 9.2 on oscillator strengths, we first defined what we meant by absorption oscillator strength f_{12} . We then showed that the equivalent width of a line is proportional to $\omega_{12} f_{12}$. We followed this by defining an emission oscillator strength f_{21} by the equation $\omega_{21} f_{21} = \omega_{12} f_{12}$. Thereafter we defined a weighted oscillator strength ωf to be used more or less as a single symbol equal to either $\omega_{21} f_{21}$ or $\omega_{12} f_{12}$. Can we do a similar sort of thing with Einstein coefficient? That is, we have defined A_{21} , the Einstein coefficient for spontaneous emission (i.e. downward transition) without any difficulty, and we have shown that the intensity or radiance of an emission line is proportional to $\omega_{21} A_{21}$. Can we somehow define an Einstein absorption coefficient A_{12} ? But this would hardly make any sense, because atoms do not make spontaneous upward transitions! An upward transition requires either absorption of a photon or collision with another atom.

For absorption lines (upwards transitions) we can define an *Einstein B coefficient* such that the rate of upward transitions from level 1 to level 2 is proportional to the product of two things, namely the number of atoms N_1 currently in the initial (lower) level and the amount of radiation that is available to excite these upward transitions. The proportionality constant is the Einstein coefficient for the transition, B_{12} . There is a real difficulty in that by “amount of radiation” different authors mean different things. It could mean, for example, any of the four things:

u_λ the energy density per unit wavelength interval at the wavelength of the line, expressed in $\text{J m}^{-3} \text{ m}^{-1}$;

u_ν the energy density per unit frequency interval at the frequency of the line, expressed in $\text{J m}^{-3} \text{ Hz}^{-1}$;

L_λ radiance (unorthodoxly called “specific intensity” or even merely “intensity” and given the symbol I by many astronomers) per unit wavelength interval at the wavelength of the line, expressed in $\text{W m}^{-2} \text{sr}^{-1} \text{m}^{-1}$;

L_ν radiance per unit frequency interval at the frequency of the line, expressed in $\text{W m}^{-2} \text{sr}^{-1} \text{Hz}^{-1}$.

Thus there are at least four possible definitions of the Einstein B coefficient and it is rarely clear which definition is intended by a given author. It is essential in all one’s writings to make this clear and always, in numerical work, to state the units. If we use the symbols B_{12}^a , B_{12}^b , B_{12}^c , B_{12}^d for these four possible definitions of the Einstein B coefficient, the SI units and dimensions for each are

$$B_{12}^a : \text{ s}^{-1} (\text{J m}^{-3} \text{ m}^{-1})^{-1} \quad \text{M}^{-1} \text{L}^2 \text{T}$$

$$B_{12}^b : \text{ s}^{-1} (\text{J m}^{-3} \text{ Hz}^{-1})^{-1} \quad \text{M}^{-1} \text{L}$$

$$B_{12}^c : \text{ s}^{-1} (\text{W m}^{-2} \text{ sr}^{-1} \text{ m}^{-1})^{-1} \quad \text{M}^{-1} \text{L T}^2$$

$$B_{12}^d : \text{ s}^{-1} (\text{W m}^{-2} \text{ sr}^{-1} \text{ Hz}^{-1})^{-1}. \quad \text{M}^{-1} \text{T}$$

You can, of course, find equivalent ways of expressing these units (for example, you could express B_{12}^b in metres per kilogram if you thought that that was helpful!), but the ones given make crystal clear the meanings of the coefficients.

The relations between them are (omitting the subscripts 12):

$$B^a = \frac{\lambda^2}{c} B^b = \frac{c}{4\pi} B^c = \frac{\lambda^2}{4\pi} B^d ; \quad 9.4.1$$

$$B^b = \frac{v^2}{4\pi} B^c = \frac{c}{4\pi} B^d = \frac{v^2}{c} B^a ; \quad 9.4.2$$

$$B^c = \frac{\lambda^2}{c} B^d = \frac{4\pi}{c} B^a = \frac{4\pi\lambda^2}{c^2} B^b ; \quad 9.4.3$$

$$B^d = \frac{4\pi v^2}{c^2} B^a = \frac{4\pi}{c} B^b = \frac{v^2}{c} B^c ; \quad 9.4.4$$

For the derivation of these, you will need to refer to equations 1.3.1, 1.15.3 and 1.17.12,

From this point henceforth, unless stated otherwise, I shall use the first definition without a superscript, so that the Einstein coefficient, when written B_{12} , will be understood to mean B_{12}^a . Thus the rate of radiation-induced upward transitions from level 1 to level 2 will be taken to be B_{12} times N_1 times u_λ .

Induced downward transitions.

The Einstein B_{12} coefficient and the oscillator strength f_{12} (which are closely related to each other in a manner that will be shown later this section) are concerned with the forced upward transition of an atom from a level 1 to a higher level 2 by radiation of a wavelength that corresponds to the energy difference between the two levels. The Einstein A_{21} coefficient is concerned with the spontaneous downward decay of an atom from a level 2 to a lower level 1.

There is another process. Light of the wavelength that corresponds to the energy difference between levels 2 and 1 may *induce a downward transition* from an atom, initially in level 2, to the lower level 1. When it does so, the light is not absorbed; rather, the atom emits another photon of that wavelength. Of course the light that is irradiating the atoms induces upward transitions from level 1 to level 2, as well as inducing downward transitions from level 2 to level 1, and since, for any finite positive temperature, there are more atoms in level 1 than in level 2, there is a net absorption of light. (The astute reader will note that there may be more atoms in level 2 than in level 1 if it has a larger statistical weight, and that the previous statement should refer to states rather than levels.) If, however, the atoms are not in thermodynamic equilibrium and there are more atoms in the higher levels than in the lower (the atom is “top heavy”, corresponding to a negative excitation temperature), there will be *Light Amplification by Stimulated Emission of Radiation* (LASER). In this section, however, we shall assume a Boltzmann distribution of atoms among their energy levels and a finite positive excitation temperature. The number of induced downward transitions per unit time from level 2 to level 1 is given by $B_{21}N_2u_\lambda$. Here B_{21} is the Einstein coefficient for induced downward transition.

Let m denote a particular atomic level. Let n denote any level lower than m and let n' denote any level higher than m . Let N_m be the number of atoms in level m at some time. The rate at which N_m decreases with time as a result of these processes is

$$-\dot{N}_m = N_m \sum_n A_{mn} + N_m \sum_n B_{mn} u_{\lambda_{mn}} + N_m \sum_{n'} B_{mn'} u_{\lambda_{mn'}}. \quad 9.4.5$$

This equation describes only the rate at which N_m is depleted by the three radiative processes. It does not describe the rate of replenishment of level m by transitions from other levels, nor with its depletion or replenishment by collisional processes. Equation 9.4.5 when integrated results in

$$N_m(t) = N_m(0)e^{-\Gamma_m t}. \quad 9.4.6$$

Here
$$\Gamma_m = \sum_n A_{mn} + \sum_n B_{mn} u_{\lambda_{mn}} + \sum_{n'} B_{mn'} u_{\lambda_{mn'}} \quad 9.4.7$$

(Compare equation 9.3.3, which dealt with a two-level atom in the absence of stimulating radiation.)

The reciprocal of Γ_m is the mean lifetime of the atom in level m .

Consider now just two levels – a level 2 and a level below it, 1. The rate of spontaneous and induced downward transitions from m to n is equal to the rate of forced upward transitions from n to m :

$$A_{21}N_2 + B_{21}N_2u_\lambda = B_{12}N_1u_\lambda. \quad 9.4.8$$

I have omitted the subscripts 21 to λ , since there is only one wavelength involved, namely the wavelength corresponding to the energy difference between the levels 2 and 1. Let us assume that the gas and the radiation field are in thermodynamic equilibrium. In that case the level populations are governed by Boltzmann's equation (equation 8.4.19), so that equation 9.4.8 becomes

$$(A_{21} + B_{21}u_\lambda)N_0 \frac{\varpi_2}{\varpi_0} e^{-E_2/(kT)} = B_{12}u_\lambda N_0 \frac{\varpi_1}{\varpi_0} e^{-E_1/(kT)}, \quad 9.4.9$$

from which
$$u_\lambda = \frac{A_{21}\varpi_2}{B_{12}\varpi_1 e^{hc/(\lambda kT)} - B_{21}\varpi_2}, \quad 9.4.10$$

where I have made use of $E_2 - E_1 = hc/\lambda$. 9.4.11

Now, still assuming that the gas and photons are in thermodynamic equilibrium, the radiation distribution is governed by Planck's equation (equations 2.6.4, 2.6.5, 2.6.9; see also equation 2.4.1):

$$u_\lambda = \frac{8\pi hc}{\lambda^5 (e^{hc/(\lambda kT)} - 1)}. \quad 9.4.12$$

On comparing equations 9.4.10 and 9.4.12, we obtain

$$\varpi_1 B_{12} = \varpi_2 B_{21} = \frac{\lambda^5}{8\pi hc} \varpi_2 A_{21}. \quad 9.4.13$$

A reminder here may be appropriate that the B here is B^a as defined near the beginning of this section. Also, in principle there would be no objection to defining an ϖB such that $\varpi B = \varpi_1 B_{12} = \varpi_2 B_{21}$, just as was done for oscillator strength, although I have never seen this done.

Einstein B_{12} coefficient and Equivalent width.

Imagine a continuous radiant source of radiance per unit wavelength interval L_λ , and in front of it an optically thin layer of gas containing N_1 atoms per unit area in the line of sight in level 1. The number of upward transitions per unit area per unit time to level 2 is $B_{12}^c \mathcal{N}_1 L_{\lambda_{12}}$, and each of these absorbs an amount hc/λ_{12} of energy. The rate of absorption of energy per unit area per unit solid angle is therefore $\frac{1}{4\pi} \times B_{12}^c \mathcal{N}_1 L_{\lambda_{12}} \times \frac{hc}{\lambda_{12}}$. This, by definition of equivalent width (in wavelength units), is equal to $WL_{\lambda_{12}}$.

$$\text{Therefore} \quad W = \frac{B_{12}^c \mathcal{N}_1 hc}{4\pi \lambda_{12}} = \frac{h}{\lambda_{12}} \mathcal{N}_1 B_{12}^a. \quad 9.4.14$$

If we compare this with equation 9.2.4 we obtain the following relation between B_{12}^a and f_{12} :

$$B_{12}^a = \frac{e^2 \lambda^3}{4\varepsilon_0 h m c^2} f_{12}. \quad 9.4.15$$

It also follows from equations 9.4.13 and 9.4.15 that

$$\varpi_2 A_{21} = \frac{2\pi e^2}{\varepsilon_0 m c \lambda^2} \varpi_1 f_{12}. \quad 9.4.16$$

I shall summarize the various relations between oscillator strength, Einstein coefficient and line strength in section 9.9.

9.5 Line Strength

The term *line strength*, although often loosely used to indicate how prominent or otherwise a spectrum line is, has acquired in theoretical spectroscopy a rather definite specialist meaning, which is discussed in this section.

In discussing the intensities of emission lines, the Einstein A is an appropriate parameter to use, whereas in discussing the equivalent widths of absorption lines the appropriate parameter is oscillator strength f . Either of these can be determined experimentally in the laboratory. The

Einstein coefficient and the oscillator strength are related (I summarize the relations in section 9.9) and either could in principle be used whether discussing an emission or an absorption line.

In theoretical studies one generally uses yet another parameter, called the *line strength*.

The theoretical calculation of line strengths is a specialized study requiring considerable experience in quantum mechanics, and is not treated in any detail here. Instead I give just a short qualitative description, which I hope will be sufficient for the reader to understand the meaning of the term line strength without actually being able to calculate it. Absolute line strengths can be calculated in terms of explicit algebraic formulas (albeit rather long ones) for hydrogen-like atoms. For all others, approximate numerical methods are used, and it is often a matter of debate whether theoretically calculated line strengths are more or less preferable to experimentally determined oscillator strengths, Einstein coefficients or lifetimes. As a general rule, the more complex the atom, unsurprisingly the more difficult (and less reliable?) are the theoretical calculations, whereas for light atoms theoretical line strengths may be preferable to experimental oscillator strengths.

Energy levels of atoms are found from the eigenvalues of the time-independent wave equation. For the interaction of electromagnetic radiation with an atom, however, solutions of the time-dependent equation are required. The effect of the electromagnetic radiation is to impose a time-dependent perturbation on the wavefunctions. In the formation of *permitted* lines, the electromagnetic wave interacts with the *electric dipole moment* of the atom. This is a vector quantity given by $\sum e_i \mathbf{r}_i$, where \mathbf{r}_i is the position vector of the i th electron in the atom. The expectation value of this quantity over the initial (i) and final (f) states of a transition is

$$\int \psi_f^* \boldsymbol{\mu} \psi_i d\tau, \quad 9.5.1$$

or, as it is usually written

$$\langle n' L' S' J' M' | \boldsymbol{\mu} | n L S J M \rangle. \quad 9.5.2$$

Here, for permitted lines, $\boldsymbol{\mu}$ is the *electric dipole moment operator*. For forbidden lines it is replaced with either the *magnetic dipole moment operator* or the *electric quadrupole moment operator*, or, in principle, moments of even higher order. In any case, the above quantity is called the *transition moment*. In the case of electric dipole (permitted) lines, its SI unit is C m, although it is more commonly expressed in units of $a_0 e$ ("atomic unit") or, in older literature, cgs esu, or, in some chemical literature, debye.

$$1 \text{ debye} = 10^{-18} \text{ cgs esu} = 0.3935 \text{ atomic units} = 3.336 \times 10^{-30} \text{ C m}$$

$$1 \text{ atomic unit} = 8.478 \times 10^{-30} \text{ C m.}$$

The square of the transition moment is called the *line strength*. Oscillator strengths and Einstein coefficients of Zeeman components (i.e. of transitions between states) are proportional to their line strengths, or to the squares of their transition moments. The symbol generally used for line strength is S . Line strengths are additive. That is to say the strength of a *line* is equal to the sum of

the strengths of its *Zeeman components*. In this respect it differs from oscillator strength or Einstein coefficient, in which the oscillator strength or Einstein coefficient of a line is equal to the average oscillator strength or Einstein coefficient of its components. Furthermore, line strength is symmetric with respect to emission and absorption, and there is no need for distinction between S_{12} and S_{21} . Intensities of emission lines are proportional to their line strengths S or to their *weighted Einstein coefficients* $\varpi_2 A_{21}$. Equivalent widths of absorption lines are proportional to their line strengths or to their *weighted oscillator strengths* $\varpi_1 f_{12}$.

I dwell no more on this subject in this section other than to state, without derivation, the relations between Einstein coefficient and line strength. The formulas below, in which ϵ_0 and μ_0 are the “rationalized” permittivity and permeability of free space, are valid for any *coherent* set of units; in particular they are suitable for SI units.

For electric dipole radiation:

$$\varpi_2 A_{21} = \frac{16\pi^3}{3h\epsilon_0\lambda^3} S_{E1}. \quad 9.5.3$$

For electric quadrupole radiation:

$$\varpi_2 A_{21} = \frac{8\pi^5}{5\epsilon_0 h\lambda^5} S_{E2}. \quad 9.5.4$$

For magnetic dipole radiation:

$$\varpi_2 A_{21} = \frac{16\pi^3\mu_0}{3h\lambda^3} S_{M1}. \quad 9.5.5$$

The subscripts E1, E2, M1 to the symbol S indicate whether the line strength is for electric dipole, electric quadrupole or magnetic dipole radiation. Although I have not derived these equations, you should check to see that they are dimensionally correct. The dimensional analysis will have to use the four dimensions of electromagnetic theory, and you must note that the SI units for line strength are $C^2 m^2$, $C^2 m^4$ and $A^2 m^4$ for electric dipole, electric quadrupole and magnetic dipole radiation respectively. Please let me know (jtatum@uvic.ca) if you find any discrepancies. In equation 9.5.5, μ_0 is the permeability of free space.

By making use of equation 9.4.16, we also find, for electric dipole radiation, that

$$\varpi_1 f_{12} = \varpi f = \frac{8\pi^2 mc}{3he^2\lambda} S_{E1}. \quad 9.5.6$$

9.6 *LS-coupling*

The expression 9.5.2 gives the transition moment for a component, and its square is the strength of the component. For the strength of a line, one merely adds the strengths of the components. In general it is very hard to calculate the transition moment accurately in absolute units.

In *LS-coupling*, the strength of a line can be written as the product of three factors:

$$S = \mathbf{S(M)}\mathbf{S(L)}\sigma^2. \quad 9.6.1$$

Here σ^2 is the strength of the *transition array*, and is given by

$$\sigma^2 = \frac{e^2}{4l^2 - 1} \left(\int_0^\infty r^3 R_i R_f dr \right)^2. \quad 9.6.2$$

Here l is the larger of the two azimuthal quantum numbers involved in the transition. R_i and R_f are the radial parts of the initial and final wavefunctions (each of which has dimension $L^{-3/2}$). The reader should verify that the expression 9.6.2 has dimensions of the square of electric dipole moment. In general σ^2 (which is the only dimensioned term on the right hand side of equation 9.6.1) is difficult to calculate, and it determines the absolute scale of the line strengths. Unless the strength of the transition array can be determined (in $C^2 m^2$ or equivalently in atomic units of $a_0^2 e^2$), absolute values of line strengths will remain unknown. However, for *LS-coupling*, there exist explicit algebraic expressions for $\mathbf{S(M)}$, the *relative strengths of the multiplets* within the array, and for $\mathbf{S(L)}$, the *relative strengths of the lines* within a multiplet. In this section I give the explicit formulas for the relative strengths of the lines within a multiplet.

In *LS-coupling* there are two types of multiplet – those in which L changes by 1, and those in which L does not change. I deal first with multiplets in which L changes by 1. In the following formulas, L is the *larger* of the two orbital angular momentum quantum numbers involved. For multiplets connecting two *LS-coupled* terms, S is the same in each term. The selection rule for J is $\Delta J = 0, \pm 1$. The lines in which J changes in the same way as L (i.e. if L increases by 1, J also increases by 1) are the strongest lines in the multiplet, and are called the main lines or the principal lines. The lines in which J does not change are weaker (“satellite” lines), and the lines in which the change in J is in the opposite sense to the change in L are the weakest (“second satellites”). Some of the following formulas include the factor $(-1)^2$. This is included so that the transition moment (the square root of the line strength) can be recovered if need be.

Multiplet L to $L - 1$.

Main lines, J to $J - 1$:

$$\mathbf{S(L)} = \frac{(J + L - S - 1)(J + L - S)(J + L + S + 1)(J + L + S)}{4JL(4L^2 - 1)(2S + 1)} \quad 9.6.3$$

First satellites (weaker lines), no change in J :

$$\mathbf{S}(L) = \frac{(2J+1)(J+L-S)(J-L+S+1)(J+L+S+1)(-J+L+S)}{4J(J+1)L(4L^2-1)(2S+1)} \quad 9.6.4$$

Second satellites (weakest lines), J to $J+1$:

$$\mathbf{S}(L) = \frac{(-1)^2(J-L+S+1)(-J+L+S)(J-L+S+2)(-J+L+S-1)}{4(J+1)L(4L^2-1)(2S+1)} \quad 9.6.5$$

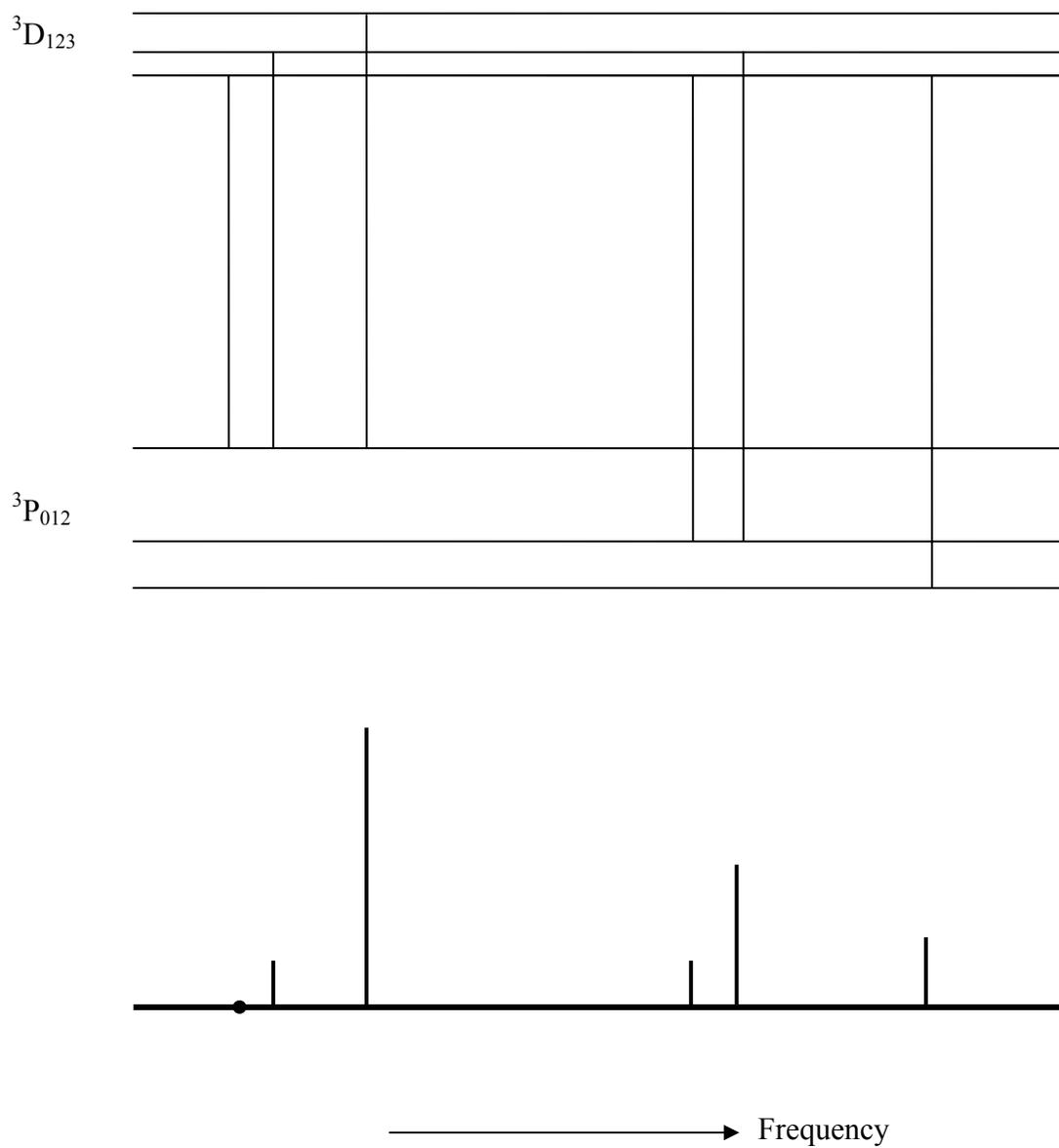
Example: The multiplet ${}^3\text{P} - {}^3\text{D}$. Here, we have $S = 1$, and $L = 2$.

There are six lines. In what follows I list them, together with the J value to be substituted in the formulas, and the value of $\mathbf{S}(L)$.

${}^3\text{P}_0 - {}^3\text{D}_1$	Main	$J = 1$	$\mathbf{S}(L) = 1/9$	$= 0.11111$
${}^3\text{P}_1 - {}^3\text{D}_2$	Main	$J = 2$	$\mathbf{S}(L) = 1/4$	$= 0.25000$
${}^3\text{P}_1 - {}^3\text{D}_1$	First satellite	$J = 1$	$\mathbf{S}(L) = 1/12$	$= 0.08333$
${}^3\text{P}_2 - {}^3\text{D}_3$	Main	$J = 3$	$\mathbf{S}(L) = 7/15$	$= 0.46667$
${}^3\text{P}_2 - {}^3\text{D}_2$	First satellite	$J = 2$	$\mathbf{S}(L) = 1/12$	$= 0.08333$
${}^3\text{P}_2 - {}^3\text{D}_1$	Second satellite	$J = 1$	$\mathbf{S}(L) = 1/180$	$= 0.00556$

The transitions and the positions and intensities of the lines are illustrated in figure IX.2. It was mentioned in Chapter 7 that one of the tests for LS -coupling was Hund's interval rule, which governs the spacings of the levels within a term, and hence the wavelength spacings of the lines within a multiplet. Another test is that the relative intensities of the lines within a multiplet follow the line strength formulas for LS -coupling. The characteristic spacings and intensities form a "fingerprint" by which LS -coupling can be recognized. It is seen in the present case (${}^3\text{P} - {}^3\text{D}$) that there are three main lines, the strongest of which has two satellites, and the second strongest has one satellite.

FIGURE IX.2



The second type of multiplet is the *symmetric* multiplet, in which there is no change in L – for example, ${}^3P - {}^3P$. The strongest lines (main lines) are those in which there is no change in J .

The formulas for the relative line strengths within a symmetric multiplet are:

Main lines, no change in J :

$$S(L) = \frac{(2J+1)[J(J+1)+L(L+1)-S(S+1)]^2}{4J(J+1)L(L+1)(2L+1)(2S+1)} \quad 9.6.6$$

Satellite lines, J changes by ± 1 ; in the following formula, J is the *larger* of the two J -values:

$$S(L) = \frac{(-1)^2(J+L-S)(J-L+S)(J+L+S+1)(-J+L+S+1)}{4JL(L+1)(2L+1)(2S+1)} \quad 9.6.7$$

Example: ${}^3D - {}^3D$:

${}^3D_1 - {}^3D_1$	Main	$J = 1$	$S(L) = 0.150000$
${}^3D_2 - {}^3D_2$	Main	$J = 2$	$S(L) = 0.231481$
${}^3D_3 - {}^3D_3$	Main	$J = 3$	$S(L) = 0.414815$
${}^3D_2 - {}^3D_3$	Satellite	$J = 3$	$S(L) = 0.051852$
${}^3D_1 - {}^3D_2$	Satellite	$J = 2$	$S(L) = 0.050000$
${}^3D_3 - {}^3D_2$	Satellite	$J = 3$	$S(L) = 0.051852$
${}^3D_2 - {}^3D_1$	Satellite	$J = 2$	$S(L) = 0.050000$

I leave it to the reader to draw a figure analogous to figure IX.2 for a symmetric multiplet. Remember that the spacings of the levels within a term are given by equation 7.17.1, and you can use different coupling coefficients for the two terms. It should be easier for you to draw the levels and the transitions with pencil and ruler than for me to struggle to draw it with a computer.

Tabulations of these formulae are available in several places. Today, however, it is often quicker to calculate them with either a computer or hand calculator than to find one of the tabulations and figure out how to read it. (Interesting thought: It is quicker to draw an energy level diagram with pencil and paper than with a computer, but it is quicker to calculate line strengths by computer than to look them up in tables.)

The relative strengths of hyperfine components within a line can be calculated with the same formulae by substituting JIF for LSJ , since JI -coupling is usual.

9.7 Atomic hydrogen

What is meant by the oscillator strength of $H\alpha$? This question may well be asked, recalling that $H\alpha$ technically is not a single line, but consists of three transition arrays, three multiplets, seven lines, and I don't think we ever worked out quite how many Zeeman and hyperfine components.

The hydrogen atom is a two-body system, and for such a system the wavefunction and its eigenvalues (energy levels) can be worked out explicitly in algebraic terms. The same is true of the transition moments and hence the strengths of each Zeeman and hyperfine component. The strength of the entire "line" of $H\alpha$ is then merely the sum of the strengths of all the Zeeman and hyperfine components of which it is composed. Then the weighted oscillator strength of $H\alpha$ is merely calculated from equation 9.5.6. As for the question: What is ϖ ? – the question need not arise, since all one is likely to need is the product ϖf . However if this has been worked out by adding the strengths of all the Zeeman and hyperfine components, it would be $4n^2$, which, for the lower level of $H\alpha$, is 8.

For the record, here are the weighted oscillator strengths, ϖf , for the first four "lines" of the Lyman and Balmer series for H.

	Lyman	Balmer
α	0.555	3.139
β	0.105	0.588
γ	0.0387	0.220
δ	0.0186	0.103

9.8 Zeeman components

In this section I give $S(C)$, the relative strengths of Zeeman components within a line.

I consider first lines for which J changes by 1, and then lines for which J does not change.

Lines connecting J to $J - 1$.

Components connecting M to $M - 1$:

$$S(C) = (J + M_>)(J + M_<) \quad 9.8.1$$

Components connecting M to $M+1$:

$$S(C) = (J - M_{<})(J - M_{>}). \quad 9.8.2$$

Components in which M does not change:

$$S(C) = 4(J + M)(J - M). \quad 9.8.3$$

In these equations J is the larger of the two J -values involved in the line; $M_{>}$ and $M_{<}$ are, respectively, the larger and the smaller of the two M -values involved in the component. Note that these formulas are not normalized to a sum of unity. In order to do so, the strength of each component should be divided by the sum of the strengths of all the components – i.e. by the strength of the line.

Example. Consider the Zeeman pattern of figure VII.1. The strength factors for each of the nine components, reading from left to right in the figure, will be found to be

$$0 \quad 2 \quad 6 \quad 12 \quad 16 \quad 12 \quad 6 \quad 2 \quad 0$$

Normalized to unity, these are

$$0.0000 \quad 0.0357 \quad 0.1071 \quad 0.2143 \quad 0.2857 \quad 0.2143 \quad 0.1071 \quad 0.0357 \quad 0.0000$$

As described in section 7.27 in connection with figure VII.1, the components within each group of three are unresolved, so the relative strengths of the three groups are $\frac{1}{7}$ $\frac{5}{7}$ $\frac{1}{7}$.

Consider also the Zeeman pattern of figure VII.2. The strength factors for each of the six components, reading from left to right in the figure, will be found to be

$$2 \quad 6 \quad 8 \quad 8 \quad 6 \quad 2,$$

or, normalized to unity,

$$\frac{1}{16} \quad \frac{3}{16} \quad \frac{4}{16} \quad \frac{4}{16} \quad \frac{3}{16} \quad \frac{1}{16}.$$

Lines for which J does not change.

Components for which M changes by ± 1

$$S(C) = (J + M_{<})(J - M_{>}). \quad 9.8.4$$

Components for which M does not change:

$$S(C) = 4M^2. \quad 9.8.5$$

Example. For a line $J - J = 2 - 2$, the relative strengths of the components are

M'	M''	$S(C)$
-2	-2	16
-2	-1	4
-1	-2	4
-1	-1	4
-1	0	6
0	-1	6
0	0	0
0	1	6
1	0	6
1	1	4
1	2	4
2	1	4
2	2	16

9.9 Summary of Relations Between f , A and S .

In this section I use ϖf to mean either $\varpi_1 f_{12}$ or $\varpi_2 f_{21}$, since these are equal; likewise I use ϖB to mean either $\varpi_1 B_{12}$ or $\varpi_2 B_{21}$. The Einstein A coefficient is used exclusively in connection with emission spectroscopy. The B coefficient is defined here in terms of radiation energy density per unit wavelength interval; that is, it is the B^a of section 9.4. The relations between the possible definitions of B are given in equations 9.4.1-4.

The following relations for electric dipole radiation may be useful. In these, ϵ_0 is the “rationalized” definition of free space permittivity, and the formulas are suitable for use with SI units.

$$\varpi_2 A_{21} = \frac{8\pi hc}{\lambda^5} \varpi B = \frac{2\pi e^2}{\epsilon_0 mc \lambda^2} \varpi f = \frac{16\pi^3}{3h\epsilon_0 \lambda^3} S; \quad 9.9.1$$

$$\varpi B = \frac{e^2 \lambda^3}{4h\epsilon_0 mc^2} \varpi f = \frac{2\pi^2 \lambda^2}{3h^2 \epsilon_0 c} S = \frac{\lambda^5}{8\pi hc} \varpi_2 A_{21}; \quad 9.9.2$$

$$\varpi f = \frac{8\pi^2 mc}{3he^2 \lambda} S = \frac{\epsilon_0 mc \lambda^2}{2\pi e^2} \varpi_2 A_{21} = \frac{4h\epsilon_0 mc^2}{e^2 \lambda^3} \varpi B; \quad 9.9.3$$

$$S = \frac{3h\varepsilon_0\lambda^3}{16\pi^3} \varpi_2 A_{21} = \frac{3h^2\varepsilon_0c}{2\pi^2\lambda^2} \varpi B = \frac{3he^2\lambda}{8\pi^2mc} \varpi f. \quad 9.9.4$$

For electric quadrupole radiation:

$$\varpi_2 A_{21} = \frac{8\pi^5}{5\varepsilon_0 h\lambda^5} S. \quad 9.9.5$$

For magnetic dipole radiation:

$$\varpi_2 A_{21} = \frac{16\pi^3\mu_0}{3h\lambda^3} S, \quad 9.9.6$$

in which μ_0 is the free space permeability. 9.9.7