

University of Victoria
Stellar Atmospheres

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CHAPTER OVERVIEW

1: Definitions of and Relations between Quantities used in Radiation Theory

Topic hierarchy
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1.1: Introduction to Radiation Theory

An understanding of any discipline must include a familiarity with and understanding of the words used within that discipline, and the theory of radiation is no exception. The theory of radiation includes such words as radiant flux, intensity, irradiance, radiance, exitance, source function and several others, and it is necessary to understand the meanings of these quantities and the relations between them. The meanings of most of the more commonly encountered quantities and the symbols recommended to represent them have been agreed upon and standardized by a number of bodies, including the International Union of Pure and Applied Physics, the International Commission on Radiation Units and Measurement, the American Illuminating Engineering Society, the Royal Society of London and the International Standards Organization. It is rather unfortunate that many astronomers appear not to follow these conventions, and frequent usages of words such as "flux" and "intensity", and the symbols and units used for them, are found in astronomical literature that differ substantially from usage that is standard in most other disciplines within the physical sciences.

In this chapter I use the standard terms, but I point out when necessary where astronomical usage sometimes differs. In particular I shall discuss the astronomical usage of the words "intensity" and "flux" (which differs from standard usage) in sections 1.12 and 1.14 . Standard usage also calls for SI units, although the older CGS units are still to be found in astronomical writings. Except when dealing with electrical units, this usually gives rise to little difficulty to anyone who is aware that $1 \text{ watt} = 10^7 \text{ erg s}^{-1}$. Where electrical units are concerned, the situation is much less simple.

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1.2: Radiant Flux or Radiant Power, ϕ or P

This is simply the rate at which energy is radiated from a source, in watts.

It is particularly unfortunate that, even with this most fundamental of concepts, astronomical usage is often different. When describing the radiant power of stars, it is customary for astronomers to use the word luminosity, and the symbol L . In standard usage, the symbol L is generally used for the quantity known as radiance, while in astronomical custom, the word "flux" has yet a different meaning. Particle physicists use the word "luminosity" in yet another quite different sense.

The radiant power ("luminosity") of the Sun is $3.85 \times 10^{26} \text{ W}$.

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1.3: Variation with Frequency or Wavelength

The radiant flux per unit frequency interval can be denoted by Φ_ν W Hz⁻¹, or per unit wavelength interval by Φ_λ W m⁻¹. The relations between them are

$$\Phi_\lambda = \frac{\nu^2}{c} \lambda_\nu; \quad \Phi_\nu = \frac{\lambda^2}{c} \Phi_\lambda \quad (1.3.1)$$

It is useful to use a subscript ν or λ to denote "per unit frequency or wavelength interval", but parentheses, for example $\alpha(\nu)$ or $\alpha(\lambda)$, to denote the value of a quantity at a given frequency or wavelength. In some contexts, where great clarity and precision of meaning are needed, it may not be overkill to use both, the symbol $I_\nu(\nu)$, for example, for the radiant intensity per unit frequency interval at frequency ν .

We shall be defining a number of quantities such as flux, intensity, radiance, etc., and establishing relations between them. In many cases, we shall omit any subscripts, and assume that we are discussing the relevant quantities integrated over all wavelengths. Nevertheless, very often the several relations between the various quantities will be equally valid if the quantities are subscripted with ν or λ .

The same applies to quantities that are weighted according to wavelength-dependent instrumental sensitivities and filters to define a *luminous* flux, which is weighted according to the photopic wavelength sensitivity of a defined standard human eye. The unit of luminous flux is the *lumen*. The number of lumens in a watt of monochromatic radiation depends on the wavelength (it is zero outside the range of sensitivity of the eye!), and for heterochromatic radiation the conversion between lumens and watts requires some careful computation. The number of lumens generated by a lightbulb per watt of power input is called the luminous efficiency of the lightbulb. This may seem at first to be a topic of very remote interest, if any, to astronomers, but those who would observe the faintest and most distant galaxies may well at some time in their careers have occasion to discuss the luminous efficiencies of lighting fixtures in the constant struggle against light pollution of the skies.

The topic of lumens versus watts is a complex and specialist one, and we do not discuss it further here, except for one brief remark. When dealing with visible radiation weighted according to the wavelength sensitivity of the eye, instead of the terms radiant flux, radiant intensity, irradiance and radiance, the corresponding terms that are used become luminous flux (expressed in lumens rather than watts), luminous intensity, illuminance and luminance. Further discussion of these topics can be found in section 1.10 and 1.12.

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1.4: Radiant Intensity, I

Not all bodies radiate isotropically, and a word is needed to describe how much energy is radiated in different directions. One can imagine, for example, that a rapidly-rotating star might be nonspherical in shape, and will not radiate isotropically. The *intensity* of a source towards a particular direction specified by spherical coordinates (θ, ϕ) is the radiant flux radiated per unit solid angle in that direction. It is expressed in W sr^{-1} , and the standard symbol is I . In astronomical custom, the word "intensity" and the symbol I are commonly used to describe a very different concept, to which we shall return later.

When dealing with *visible* radiation, we use the phrase *luminous* intensity rather than *radiant* intensity, and the unit is a lumen per steradian, or a candela. At one time, the standard of luminous intensity was taken to be that of a candle of defined design, though the present-day candela (which is one of the fundamental units of the SI system of units) has a different and more precise definition, to be described in section 1.12. The candela and the old standard candle are of roughly the same luminous intensity.

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1.5: "Per unit"

We have so far on three occasions used the phrase "per unit", as in flux per unit frequency interval, per unit wavelength interval, and per unit solid angle. It may not be out of place to reflect briefly on the meaning of "per unit".

The word *density* in physics is usually defined as "mass per unit volume" and is expressed in kilograms per cubic metre. But do we really mean the mass contained within a volume of a cubic metre? A cubic metre is, after all, a rather large volume, and the density of a substance may well vary greatly from point to point within that volume. Density, in the language of thermodynamics, is an *intensive* quantity, and it is defined *at a point*. What we really mean is the following. If the mass within a volume δV is δm , the *average density* in that volume is $\delta m / \delta V$. The density *at a point* is

$$\lim_{\delta V \rightarrow 0} \frac{\delta m}{\delta V}, \text{ i.e. } \frac{dm}{dV}. \quad (1.5.1)$$

Perhaps the short phrase "per unit mass" does not describe this concept with precision, but it is difficult to find an equally short phrase that does so, and the somewhat loose usage does not usually lead to serious misunderstanding.

Likewise, Φ_λ is described as the flux "per unit wavelength interval", expressed in W m^{-1} . But does it really mean the flux radiated in the absurdly large wavelength interval of a metre? Let $\delta\Phi$ be the flux radiated in a wavelength interval $\delta\lambda$. Then

$$\Phi_\lambda = \lim_{\delta\lambda \rightarrow 0} \frac{\delta\Phi}{\delta\lambda}; \text{ i.e. } \frac{d\Phi}{d\lambda}. \quad (1.5.2)$$

Intensity is flux "per unit solid angle", expressed in watts per steradian. Again a steradian is a very large angle. What is actually meant is the following. If $\delta\Phi$ is the flux radiated into an elemental solid angle $\delta\omega$ (which, in spherical coordinates, is $\sin\theta \delta\theta \delta\phi$) then the *average* intensity over the solid angle $\delta\omega$ is $\delta\Phi / \delta\omega$. The intensity *in a particular direction* (θ, ϕ) is

$$\lim_{\delta\omega \rightarrow 0} \frac{\delta\Phi}{\delta\omega}. \quad (1.5.3)$$

That is,

$$I = \frac{d\Phi}{d\omega}. \quad (1.5.4)$$

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1.6: Relation between Flux and Intensity

For an isotropic radiator,

$$\Phi = 4\pi I. \quad (1.6.1)$$

For an anisotropic radiator

$$\Phi = \int I d\omega, \quad (1.6.2)$$

the integral to be taken over an entire sphere. Expressed in spherical coordinates, this is

$$\Phi = \int_0^{2\pi} \int_0^\pi I(\theta, \phi) \sin \theta d\theta d\phi. \quad (1.6.3)$$

If the intensity is axially symmetric (i.e. does not depend on the azimuthal coordinate ϕ) equation 1.6.3 becomes

$$\Phi = 2\pi \int_0^\pi I(\theta) \sin \theta d\theta. \quad (1.6.4)$$

These relations apply equally to subscripted flux and intensity and to luminous flux and luminous intensity.

Example:

Suppose that the intensity of a light bulb varies with direction as

$$I(\theta) = 0.5I(0)(1 + \cos \theta) \quad (1.6.5)$$

(Note the use of parentheses to mean "at angle θ ".)

Draw this (preferably accurately by computer - it is a *cardioid*), and see whether it is reasonable for a light bulb. Note also that, if you put $\theta = 0$ in equation 1.6.5, you get $I(\theta) = I(0)$.

Show that the total radiant flux is related to the forward intensity by

$$\Phi = 2\pi I(0) \quad (1.6.6)$$

and also that the flux radiated between $\theta = 0$ and $\theta = \pi/2$ is

$$\Phi = \frac{3}{2}\pi I(0). \quad (1.6.7)$$

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1.7: Absolute Magnitude

The subject of magnitude scales in astronomy is an extensive one, which is not pursued at length here. It may be useful, however, to see how magnitude is related to flux and intensity. In the standard usage of the word flux, in the sense that we have used it hitherto in this chapter, flux is related to absolute magnitude or to intensity, according to

$$M_2 - M_1 = 2.5 \log(\Phi_1/\Phi_2) \quad (1.7.1)$$

or

$$M_2 - M_1 = 2.5 \log(I_1/I_2) \quad (1.7.2)$$

That is, the difference in magnitudes of two stars is related to the logarithm of the ratio of their radiant fluxes or intensities.

If we elect to define the zero point of the magnitude scale by assigning the magnitude zero to a star of a specified value of its radiant flux in watts or intensity in watts per steradian, equations 1.7.1 and 1.7.2 can be written

$$M = M_0 - 2.5 \log \Phi \quad (1.7.3)$$

or to its intensity by

$$M = M_0' - 2.5 \log I \quad (1.7.4)$$

If by Φ and I we are referring to flux and intensity integrated over all wavelengths, the absolute magnitudes in equations 1.7.1 to 1.7.4 are referred to as absolute *bolometric* magnitudes. Practical difficulties dictate that the setting of the zero points of the various magnitude scales are not quite as straightforward as arbitrarily assigning numerical values to the constants M_0 and M_0' and I do not pursue the subject further here, other than to point out that M_0 and M_0' must be related by

$$M_0' = M_0 - 2.5 \log 4\pi = M_0 - 2.748. \quad (1.7.5)$$

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1.8: Normal Flux Density F

The rate of passage of energy per unit area normal to the direction of energy flow is the normal flux density, expressed in W m^{-2} .

If a point source of radiation is radiating isotropically, the radiant flux being Φ , the normal flux density at a distance r will be Φ divided by the area of a sphere of radius r . That is

$$F = \Phi / (4\pi r^2) \quad (1.8.1)$$

If the source of radiation is not isotropic (or even if it is) we can express the normal flux density in some direction at distance r in terms of the intensity in that direction:

$$F = I / r^2 \quad (1.8.2)$$

That is, the normal flux density from a point source falls off inversely with the square of the distance.

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1.9: Apparent Magnitude

Although it is not the purpose of this chapter to discuss astronomical magnitude scales in detail, it should be evident that, just as intensity is related to absolute magnitude (both being intrinsic properties of a star, independent of the distance of an observer), so normal flux density is related to apparent magnitude, and they both depend on the distance of observer from star. The relationship is

$$m_2 - m_1 = 2.5 \log(F_1/F_2) \quad (1.9.1)$$

We could in principle set the zero point of the scale by writing

$$m = m_0 - 2.5 \log F \quad (1.9.2)$$

and assigning a numerical value to m_0 , so that there would then be a one-to-one correspondence between normal flux density in W m^{-2} and apparent magnitude. If we are dealing with normal flux density **integrated over all wavelengths**, the corresponding magnitude is called the apparent *bolometric* magnitude.

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1.10: Irradiance E

Suppose that some surface is being irradiated from a point source of radiation of intensity $I \text{ W sr}^{-1}$ at a distance r . The normal flux density ("normal" meaning normal to the direction of propagation), as we have seen, is I/r^2 . If the surface being irradiated is inclined so that its normal is inclined at an angle θ to the line joining it to the point source of radiation, the rate at which radiant energy is falling on unit area of the surface will be $I \cos \theta / r^2$.

In any case, the rate at which radiant energy is falling upon unit area of a surface is called the *irradiance* of that surface. It is denoted by the symbol E , and the units are W m^{-2} . In the simple geometry that we have described, the relation between the intensity of the source and the irradiance of the surface is

$$E = (I \cos \theta) / r^2 \quad (1.10.1)$$

If we are dealing with visible radiation, the number of lumens falling per unit area on a plane surface is called the *illuminance*, and is expressed in lumens per square metre, or *lux*. Recall that a lumen is the SI unit of luminous flux, and the candela is the unit of luminous intensity, and that an isotropic point source of light radiating with a luminous intensity of $I \text{ cd}$ (that is, $I \text{ lm sr}^{-1}$) emits a total luminous flux of $4\pi \text{ lm}$. The relation between the illuminance of a surface and the luminous intensity of a source of light is the same as the relation between irradiance and radiant intensity, namely, equation 1.10.1, or, if the surface is being illuminated normally, equation 1.8.2. If the luminous intensity of a source of light in some direction is one candela, the irradiance of a point on a surface that is closest to the source is 1 lm m^{-2} if the distance is one metre, 1 lm cm^{-2} if the distance is one cm, and 1 lm ft^{-2} if the distance is one foot. A lumen per square metre is a **lux**, and a lumen per square cm is a **phot**. A lumen per square foot is often (usually!) given the extraordinary name of a "foot-candle". This is a most illogical misuse of language, and is mentioned here only because the term is still in frequent use in non-scientific circles. Lumen, candela and lux are, respectively, the SI units of luminous flux, luminous intensity and illuminance. Phot and "foot-candle" are non-SI units of illuminance. The exact definition of the candela will be given in section 1.12; the lumen and lux are derived from the candela. Those who are curious about other strange-sounding units encountered in the quantitative measurement of the visible portion of radiation will also find the definition of "stilb" in section 1.12.

? Example 1.10.1

A table is being illuminated by a light bulb fixed at a distance h vertically above the table. The fixture is such that the socket is above the bulb, and the luminous intensity of the bulb varies as

$$I(\theta) = \frac{1}{2} I(0)(1 + \cos \theta) \quad (1.10.2)$$

where θ is the angle from the downward vertical from the bulb. Show that the illuminance at a point on the table at an angular distance θ from the sub-bulb point is

$$E(\theta) = \frac{1}{2} E(0) (\cos^3 \theta + \cos^4 \theta) \quad (1.10.3)$$

For what angle θ does the irradiance fall to half of the illuminance at the sub-bulb point??

? Example 1.10.2

If the table in the above problem is a circular table whose radius subtends an angle α at the bulb, show that the flux that it intercepts is

$$\Phi(\alpha) = \pi I(0) \left(1 - \cos \alpha + \frac{1}{2} \sin^2 \alpha \right) \quad (1.10.4)$$

What is this if $\alpha = 0$ and if $\alpha \rightarrow \pi/2$? Is this what you would expect? (Compare equation 1.6.7.)

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1.11: Exitance M

The **exitance** of an extended surface is the rate at which it is radiating energy (in all directions) per unit area. The usual symbol is M and the units are W m^{-2} . It is an intrinsic property of the radiating surface and is not dependent on the position of an observer.

Most readers will be aware that some property of a black body is equal to σT^4 . Technically it is the exitance (integrated over all wavelengths, with no subscript on the M) that is equal to σT^4 , so that, in our notation, the [Stefan-Boltzmann law](#) would be written

$$M = \sigma T^4, \quad (1.11.1)$$

where σ has the value $5.7 \times 10^{-8} \text{W m}^{-2} \text{K}^{-4}$.

Likewise the familiar Planck equation for a black body:

$$M_\lambda = \frac{2\pi hc^2}{\lambda^5 (e^{hc/kT} - 1)} \quad (1.11.2)$$

gives the exitance per unit wavelength interval.

The word "emittance" is an older word for what is now called exitance.

The **emissivity** of a radiating surface is the ratio of its exitance at a given wavelength and temperature to the exitance of a black body at that wavelength and temperature.

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1.12: Radiance L

The concept of exitance does nothing to describe a situation in which the brightness of an extended radiating (or reflecting) surface appears to vary with the direction from which it is viewed. For example, the centre of the solar disc is brighter than the limb (which is viewed at an oblique angle), particularly at shorter wavelengths, and the Moon is much brighter at full phase than at first or last quarter.

There are two concepts we can use to describe the directional properties of an extended radiating surface. I shall call them *radiance* L , and "surface brightness" B . I first define them, and then I determine the relationship between them. Please keep in mind the meaning of "per unit", or, as it is written in the next sentence, "from unit".

The radiance L of an extended source is the irradiance of an observer *from* unit solid angle of the extended source. It is an intrinsic property of the source and is independent of the distance of any observer. This is because, while irradiance of an observer falls off inversely as the square of the distance, the area included in unit solid angle increases as the square of the distance of the observer. While the radiance does not depend on the *distance* of the observer, it may well depend on the *direction* (θ, ϕ) from which the observer views the surface.

The *surface brightness* B of an extended source is the intensity (i.e. flux emitted *into* unit solid angle) from unit projected area of the source. "Projected" here means projected on a plane that is normal to the line joining the observer to a point on the surface. The solid angle referred to here is subtended at a point on the surface. Like radiance, surface brightness is a property intrinsic to the source and is independent of the distance (but not the direction) to the observer.

These concepts may become clearer as I try to explain the relationship between them. This I shall do by supposing that the surface brightness of a point on the surface is B in some direction; and I shall calculate the irradiance of an observer in that direction from unit solid angle around the point.

In figure I.1 I draw an elemental area and the vector $\delta\mathbf{A}$ representing that area. In some direction making an angle with the normal to $\delta\mathbf{A}$, the area projected on a plane at right angles to that direction is $\delta A \cos \theta$. We suppose the surface brightness to be B , and, since surface brightness is defined to be intensity per unit projected area, the intensity in the direction of interest is $B\delta A \cos \theta$. The irradiance of an observer at a distance r from the elemental area is $\delta E = \delta I / r^2 = B\delta A \cos \theta / r^2$. But $\delta A \cos \theta / r^2$ is the solid angle $\delta\omega$ subtended by the elemental area at the observer. Therefore, by definition, $\delta E / \delta\omega$ is L , the radiance. Thus $L = B$. We see, then, that radiance L and surface brightness B are one and the same thing. Henceforth we can use the one term *radiance* and the one symbol L for either, and either definition will suffice to define radiance.

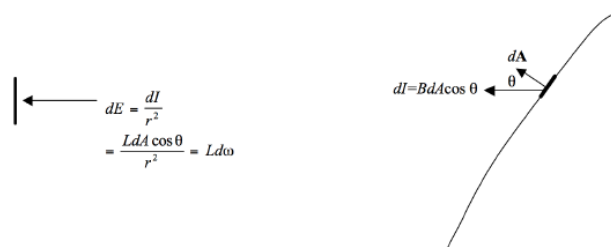


FIGURE I.1

In the figure the surface brightness at some point on a surface in a direction that makes an angle θ with the normal is B . The intensity radiated in that direction by an element of area dA is $dI = B dA \cos \theta$. The irradiance of a surface at a distance r away is $dE = dI / r^2 = B dA \cos \theta / r^2$. But $dA \cos \theta / r^2 = d\omega$, the solid angle subtended by dA . But the radiance L of a point on the right hand surface is the irradiance of the point in the left hand surface from unit solid angle of the former. Thus $L = B$, and we see that the two definitions, namely surface brightness and radiance, are equivalent, and will henceforth be called just radiance.

Radio astronomers usually use the term "surface brightness". In the literature of stellar atmospheres, however, the term used for radiance is often "specific intensity" or even just "intensity" and the symbol used is I . This is clearly a quite different usage of the word intensity and the symbol I that we have used hitherto. The use of the adjective "specific" does little to help, since in most contexts in physics, the adjective "specific" is understood to mean "per unit mass". It is obviously of great importance, in both reading and writing on the subject of stellar atmospheres, to be very clear as to the meaning intended by such terms as "intensity".

The radiance per unit frequency interval of a *black body* is often given the symbol B_ν , and the radiance per unit wavelength interval is given the symbol B_λ . We shall see later that these are related to the blackbody exitance functions (see equation 1.11.2

for M_λ) by $M_\nu = \pi B_\nu$ and $M_\lambda = \pi B_\lambda$. Likewise the integrated (over all wavelengths) radiance of a black body is sometimes written in the form $B = aT^4$. Here $a = \sigma/\pi$, σ being the Stefan-Boltzmann constant used in equation 1.11.1. (But see also section 1.17.)

Summary so far: The concepts "radiance" and "surface brightness", for which we started by using separate symbols, L and B , are identical, and the single name radiance and the single symbol L suffice, as also will either definition. The symbol B can now be reserved specifically for the radiance of a black body.

Although perhaps not of immediate interest to astronomers other than those concerned with light pollution, I now discuss the corresponding terms used when dealing with visible light. Instead of the terms radiant flux, radiant intensity, irradiance and radiance, the terms used are luminous flux, luminous intensity, illuminance and *luminance*. (This is the origin of the symbol L used for luminance and for radiance.) Luminous flux is expressed in *lumens*. Luminous intensity is expressed in lumens per steradian or *candela*. Illuminance is expressed in lumens per square metre, or *lux*. Luminance is expressed in $\text{lm m}^{-2}\text{sr}^{-1}$, or lux sr^{-1} , or cd m^{-2} or *nit*. The standard of luminous intensity was at one time the intensity of light from a candle of specified design burning at a specified rate. It has long been replaced by the candela, whose intensity is indeed roughly that of the former standard candle. The candela, when first introduced, was intended to be a unit of luminous intensity, equal approximately in magnitude to that of the former "standard candle", but making no reference to an actual real candle; it was defined such that the luminance of a black body at the temperature of melting platinum (2042 K) was exactly $600,000 \text{ cd m}^{-2}$. Since 1979 we have gone one step further, recognizing that obtaining and measuring the radiation from a black body at the temperature of melting platinum is a matter of some practical difficulty, and the current definition of the candela makes no mention of platinum or of a black body, and the candela is defined in such a manner that if a source of monochromatic radiation of frequency $5.4 \times 10^{14} \text{ Hz}$ has a radiant intensity of $1/683 \text{ W sr}^{-1}$ in that direction, then the luminous intensity is one candela. The reader may well ask what if the source is not monochromatic, or what if it is monochromatic but of a different frequency? Although it is not the intention here to treat this topic thoroughly, the answer, roughly, is that scientists involved in the field have prepared a table of a standard "photopic" relative sensitivity of a "standard" photopic human eye, normalized to unity at its maximum sensitivity at $5.4 \times 10^{14} \text{ Hz}$ (about 555 nm). For the conversion between watts and lumens for monochromatic light of wavelength other than 555 nm, one must multiply the conversion at 555 nm by the tabular value of the sensitivity at the wavelength in question. To calculate the luminance of a heterochromatic source, it is necessary to integrate over all wavelengths the product of the radiance per unit wavelength interval times the tabular value of the photopic sensitivity curve.

We have mentioned the word "photopic". The retina of the eye has two types of receptor cells, known, presumably from their shape, as "rods" and "cones". At high levels of illuminance, the cones predominate, but at low levels, the rods are quite insensitive, and the rods predominate. The sensitivity curve of the cones is called the "photopic" sensitivity, and that of the rods (which peaks at a shorter wavelength than the cones) is the "scotopic" sensitivity. It is the standard photopic curve that defines the conversion between radiance and luminance.

I make one last remark on this topic. Namely, together with the metre, kilogram, second, kelvin, ampère and mole, the *candela* is one of the fundamental base units of the *Système International des Unités*. The *lumen*, *lux* and *nit* are also SI units, but the *phot* is not. The SI unit of luminance is the *nit*, although in practice this word is rarely heard (lux sr^{-1} or cd m^{-2} serve). The non-SI unit known as the *stilb* is a luminance of one candela per square centimetre.

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1.13: Lambertian Surface

A *lambertian* radiating surface [Johann Heinrich Lambert 1728 - 1777] is one whose intensity varies with angle according to **Lambert's Law**;

$$I(\theta) = I(0) \cos \theta. \quad (1.13.1)$$

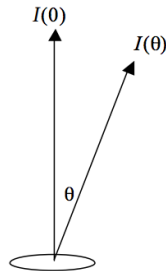


FIGURE I.2

Consider a small element δA of a lambertian radiating surface, such that the intensity radiated by this element in the normal direction is $I(0)$, and the normal radiance is therefore $I(0)/\delta A$. The radiance at angle θ is the intensity divided by the projected area:

$$\frac{I(0) \cos \theta}{\delta A \cos \theta} = \frac{I(0)}{\delta A} \quad (1.13.2)$$

Thus the radiance of a lambertian radiating surface is independent of the angle from which it is viewed. Lambertian surfaces radiate isotropically. The radiance of a black body is lambertian. Since the Sun exhibits limb-darkening; the Sun is not a black body, nor is it lambertian.

For a *reflecting* surface to be lambertian, it is required that the radiance be independent not only of the angle from which it is viewed, but also of the angle from which it is irradiated (or illuminated). In discussing the properties of reflecting surfaces, one often distinguishes between two extreme cases. At the one hand is the perfectly diffusing lambertian surface; blotting paper is sometimes cited as a near lambertian example. The other extreme is the perfectly reflecting surface, or specular reflection (Latin *speculum*, a mirror), in which the angle of reflection equals the angle of incidence. It might be noted that expensive textbooks are often printed on specularly reflecting paper and are difficult to read, whereas inexpensive textbooks are often printed on paper that is approximately lambertian and are consequently easy to read.

The full description of the reflecting properties of a surface requires a bidirectional reflectance distribution function, which is a function of the direction (θ_i, ϕ_i) of the incident light and the direction of the reflected (scattered) (θ_r, ϕ_r) light. Also included in the theory are the several albedoes (normal, geometric and Bond). These concepts are of great importance in the study of planetary physics, but are not pursued further here. Some further details may be found, for example, in Lester, P. L., McCall, M. L. and Tatum, J. B., *J. Roy. Astron. Soc. Can.*, **73**, 233 (1979).

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1.14: Relations between Flux, Intensity, Exitance, Irradiance

In this section I am going to ask, and answer, three questions.

i. (See figure I.3)

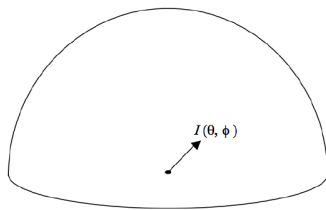


FIGURE I.3

A point source of light has an intensity that varies with direction as $I(\theta, \phi)$. What is the radiant flux radiated into the hemisphere $\theta < \pi/2$? This is easy; we already answered it for a complete sphere in equation 1.6.3. For a hemisphere, the answer is

$$\phi = \int_0^{2\pi} \int_0^{\pi/2} I(\theta, \phi) \sin \theta d\theta d\phi. \quad (1.14.1)$$

ii. At a certain point on an extended plane radiating surface, the radiance is $L(\theta, \phi)$. What is the emergent exitance M at that point?

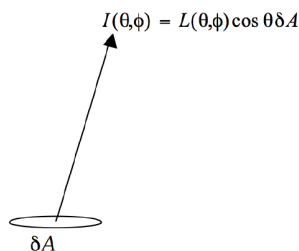


FIGURE I.4

Consider an elemental area δA (see figure I.4). The intensity $I(\theta, \phi)$ radiated in the direction (θ, ϕ) is the radiance times the projected area $\cos \theta \delta A$. Therefore the radiant power or flux radiated by the element into the hemisphere is

$$\delta \phi = \int_0^{2\pi} \int_0^{\pi/2} L(\theta, \phi) \cos \theta \sin \theta d\theta d\phi \delta A, \quad (1.14.2)$$

and therefore the exitance is

$$M = \int_0^{2\pi} \int_0^{\pi/2} L(\theta, \phi) \cos \theta \sin \theta d\theta d\phi \quad (1.14.3)$$

iii. A point O is at the centre of the base of a hollow radiating hemisphere whose radiance in the direction (θ, ϕ) is $L(\theta, \phi)$. What is the irradiance at that point O ? (See figure I.5.)

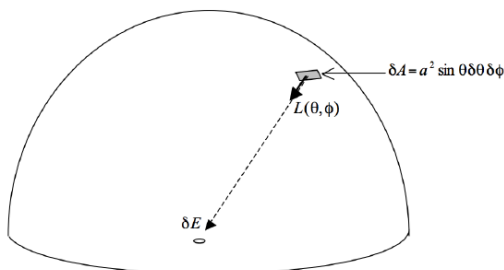


FIGURE I.5

Consider an elemental area $a^2 \sin \theta \delta \theta \delta \phi$ on the inside of the hemisphere at a point where the radiance is $L(\theta, \phi)$ (figure I.5). The intensity radiated towards O is the radiance times the area:

$$\delta I(\theta, \phi) = L(\theta, \phi) a^2 \sin \theta \delta \theta \delta \phi \quad (1.14.4)$$

The irradiance at O from this elemental area is (see equation (1.10.1))

$$\delta E = \frac{\delta I(\theta, \phi) \cos \theta}{a^2} = L(\theta, \phi) \cos \theta \sin \theta \delta \theta \delta \phi, \quad (1.14.5)$$

and so the irradiance at O from the entire hemisphere is

$$E = \int_0^{2\pi} \int_0^{\pi/2} L(\theta, \phi) \cos \theta \sin \theta \delta \theta \delta \phi. \quad (1.14.6)$$

The same would apply for any shape of inverted bowl - or even an infinite plane radiating surface (see figure I.6.)

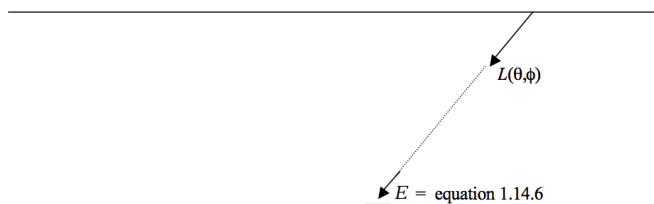


FIGURE I.6

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1.15: $A = \pi \pi B$

There are several occasions in radiation theory in which one quantity is equal to π times another, the two quantities being related by an equation of the form $A = \pi B$. I can think of three, and they are all related to the three questions asked and answered in section 1.14.

If the source in question i of Section 1.14 is an element of a lambertian surface, then $I(\theta, \phi)$ is given by Equation 1.13.1, and in that case Equation 1.14.1 becomes

$$\phi = \pi I(0) \quad (1.15.1)$$

If the element δA in question ii is lambertian, L is independent of θ and ϕ , and equation 1.14.3 becomes

$$M = \pi L \quad (1.15.2)$$

This, then is the very important relation between the exitance and the radiance of a lambertian surface. It is easy to remember which way round it is if you think of the units in which M and L are expressed and think of π as a solid angle.

If the hemisphere of question iii is uniformly lambertian (for example, if the sky is uniformly dull and cloudy) then L is the same everywhere in the sky, and the irradiance is

$$E = \pi L \quad (1.15.3)$$

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1.16: Radiation Density (u)

This is merely the radiation energy density per unit volume, expressed in J m^{-3} , and usually given the symbol u .

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1.17: Radiation Density and Irradiance

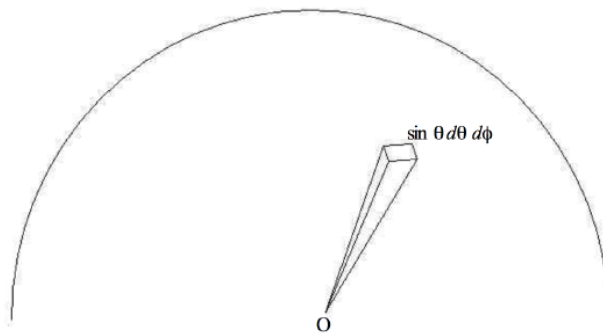


FIGURE I.7

Figure I.7 shows a hemisphere filled with radiation, the energy density being $u \text{ J m}^{-3}$. The motion of the photons is presumed to be isotropic, and all are moving at speed c . The centre of the base of the hemisphere, O, is being irradiated - i.e. bombarded with photons coming from all directions. How is the irradiance E at O related to the energy density? How much energy per unit area is arriving at O per unit time? I shall show that the answer is

$$E = uc/4. \quad (1.17.1)$$

Photons are arriving at O from all directions, but only a fraction

$$\frac{\sin \theta \delta \theta \delta \phi}{4\pi} \quad (1.17.2)$$

are coming from directions within the elemental solid angle between θ and $\theta + \delta \theta$ and ϕ and $\phi + \delta \phi$.

If there are n photons per unit volume, the rate at which photons (moving at speed c) are passing through an elemental area A at O from directions within the elemental solid angle $\sin \theta \delta \theta \delta \phi$ is

$$\frac{\sin \theta \delta \theta \delta \phi}{4\pi} \times nc \delta A \cos \theta. \quad (1.17.3)$$

(This is because the elemental area presents a projected area $\delta A \cos \theta$ to the photons arriving from that particular direction.)

The rate at which photons arrive per unit area (divide by δA) from the entire hemisphere above (integrate) is

$$\int_0^{2\pi} \int_0^{\pi/2} \frac{nc \sin \theta \cos \theta d\theta d\phi}{4\pi} \quad (1.17.4)$$

The rate at which energy arrives per unit area from the hemisphere above is

$$\int_0^{2\pi} \int_0^{\pi/2} \frac{uc \sin \theta \cos \theta d\theta d\phi}{4\pi} = uc/4, \quad (1.17.5)$$

which was to be demonstrated (Quod Erat Demonstrandum)

A more careful argument should convince the reader that it does not matter if all the photons do not carry the same energy. Just divide the population of photons into groups having different energies. The total energy is the sum of the energies of all the photons, whether these are equal or not.

I mentioned in section 1.12 that Stefan's law is sometimes written $L = aT^4$, where a is Stefan's constant divided by π . It is also sometimes written $u = a T^4$, and in this case $a = 4\sigma/c$.

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1.18: Radiation Pressure (P)

Photons carry momentum h/λ and hence exert pressure. Pressure is rate of change of momentum (i.e. force) per unit area.

The pressure P exerted by radiation (in N m^{-2} , or Pa) is related to the energy density u of radiation (in J m^{-3}) by

$$P = 2u \quad (1.18.1)$$

$$P = u \quad (1.18.2)$$

$$P = u/3 \quad (1.18.3)$$

or

$$P = u/6 \quad (1.18.4)$$

depending on the circumstances!

First, we may imagine a parallel beam of photons that have come a long way from their original source. For example, they might be photons that have arrived at a comet from the Sun, and they are about to push material out from the comet to form the tail of the comet. Each of them is travelling with speed c . We suppose that there are n of them per unit volume, and therefore the number of them per unit area arriving per unit time is nc . Each of them carries momentum h/λ . [As in section 1.17 they need not all carry the same momentum. The total momentum is the sum of each.] The rate of arrival of momentum per unit area is $nhc/\lambda = nh\nu$. But $h\nu$ is the energy of each photon, so the rate of arrival of momentum per unit area is equal to the energy density. (Verify that these are dimensionally similar.) If all the photons stick (i.e. if they are absorbed), the rate of change of momentum per unit area (i.e. the pressure) is just equal to the energy density (Equation 1.18.2); but if they are reflected elastically, the rate of change of momentum per unit area is twice the energy density (Equation 1.18.1).

If the radiation is isotropic, the situation is different. The radiation may be approximately isotropic deep in the atmosphere of a star, though I fancy not completely isotropic, because there is sure to be a temperature gradient in the atmosphere. I suppose for the radiation to be truly isotropic, you'd have to go to the very center of the star.

We'll start from Equation 1.17.4, which gives the rate at which photons arrive at a point per unit area. ("at a point per unit area"? This makes sense only if you bear in mind the meaning of "per unit"!) If the energy of each photon is E , the momentum of each is E/c . (This is the relation, from special relativity, between the energy and momentum of a particle of zero rest mass.) However, it is the normal component of the momentum which contributes to the pressure, and the normal component of each photon is $(E \cos \theta)/c$. The rate at which this normal component of momentum arrives per unit area is found by multiplying the integrand in Equation 1.17.4 by this. Bearing in mind that nE is the energy density u , we obtain

$$\frac{u}{4\pi} \int_0^{2\pi} \int_0^{\pi/2} \sin \theta \cos^2 \theta \, d\theta d\phi. \quad (1.18.5)$$

The pressure on the surface is the rate at which the normal component of this momentum is changing. If the photons stick, this is

$$\frac{u}{4\pi} \int_0^{2\pi} \int_0^{\pi/2} \sin \theta \cos^2 \theta \, d\theta d\phi = u/6. \quad (1.18.6)$$

But if they bounce, it is twice this, or $u/3$.

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CHAPTER OVERVIEW

2: Blackbody Radiation

This chapter briefly summarizes some of the formulas and theorems associated with blackbody radiation. A small point of style is that when the word "blackbody" is used as an adjective, it is usually written as a single unhyphenated word, as in "blackbody radiation"; whereas when "body" is used as a noun and "black" as an adjective, two separate words are used. Thus a black body emits blackbody radiation. The Sun radiates energy only very approximately like a black body. The radiation from the Sun is only very approximately blackbody radiation.

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[2.2: Radiation within a cavity enclosure](#)

[2.3: Kirchhoff's Law](#)

[2.4: An aperture as a black body](#)

[2.5: Planck's Equation](#)

[2.6: Wien's Law](#)

[2.7: Stefan's Law \(The Stefan-Boltzmann Law\)](#)

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[2.9: Dimensionless forms of Planck's equation](#)

[2.10: Derivation of Wien's and Stefan's Laws](#)

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2.1: Absorptance, and the Definition of a Black Body

If a body is irradiated with radiation of wavelength λ , and a fraction $a(\lambda)$ of that radiation is absorbed, the remainder being either reflected or transmitted, $a(\lambda)$ is called the *absorptance* at wavelength λ . Note that λ is written in parentheses, to mean "at wavelength λ ", not as a subscript, which would mean "per unit wavelength interval". The fractions of the radiation reflected and transmitted are, respectively, the *reflectance* and the *transmittance*. The sum of the absorptance, reflectance and transmittance is unity, unless you can think of anything else that might happen to the radiation.

A body for which $a(\lambda) = 1$ for all wavelengths is a black body.

A body for which a has the same value for all wavelengths, but less than unity, is a grey body.

(Caution: We may meet the word "absorbance" later. It is not the same as absorptance.)

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2.2: Radiation within a cavity enclosure

Consider two cavities at the same temperature. We'll suppose that the two cavities can be connected by a "door" that can be opened or closed to allow or to deny the passage of radiation between the cavities. We'll suppose that the walls of one cavity are bright and shiny with an absorptance close to zero, and the walls of the other cavity are dull and black with an absorptance close to unity. We'll also suppose that, because of the difference in nature of the walls of the two cavities, the radiation density in one is greater than in the other. Let us open the door for a moment. Radiation will flow in both directions, but there will be a net flow of radiation from the high-radiation-density cavity to the low-radiation-density cavity. As a consequence, the temperature of one cavity will rise and the temperature of the other will fall. The (now) hotter cavity can then be used as a source and the (now) colder cavity can be used as a sink in order to operate a heat engine which can then do external work, such work, for example, to be used for repeatedly opening and closing the door separating the two cavities. We have thus constructed a perpetual motion machine that can continue to do work without the expenditure of energy.

From this absurdity, we can conclude that, despite the difference in nature of the walls of the two cavities (which were initially at the same temperature), the radiation densities within the two cavities must be equal. We deduce the important principle that the radiation density inside an enclosure is determined solely by the temperature and is independent of the nature of the walls of the enclosure.

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2.3: Kirchhoff's Law

Kirchhoff's law, as well as his studies with Bunsen (who invented the Bunsen burner for the purpose) showing that every element has its characteristic spectrum, represents one of the most important achievements of mid-nineteenth century physics and chemistry. The principal results were published in 1859, the same year as Darwin's *The Origin of Species*, and it has been claimed that the publication of Kirchhoff's law was at least as influential in the advance of science as the Darwinian theory of evolution. It is therefore distressing that so few people can achieve the triple task of spelling his name, pronouncing it correctly, and properly stating his law. Kirchhoff and Bunsen laid the foundations of quantitative and qualitative spectroscopy.

Imagine an enclosure filled with radiation at some temperature such that the energy density per unit wavelength interval at wavelength λ is $u_\lambda(\lambda)$. Here I have used a subscript and parentheses, according to the convention described in Section 1.3, but, to avoid excessive pedantry, I shall henceforth omit the parentheses and write just u_λ . Imagine that there is some object, a football, perhaps, levitating in the middle of the enclosure and consequently being irradiated from all sides. The irradiance, in fact, per unit wavelength interval, is given by Equation 1.17.1

$$E_\lambda = u_\lambda c/4 \quad (2.4.1)$$

If the absorptance at wavelength λ is $a(\lambda)$, the body will absorb energy per unit area per unit wavelength interval at a rate $a(\lambda)E_\lambda$. The body will become warm, and it will radiate energy. Let the rate at which it radiates energy per unit area per unit wavelength interval (i.e. the exitance) be M_λ . When the body and the enclosure have reached an equilibrium state, the rates of absorption and emission of radiant energy will be equal:

$$M_\lambda = a(\lambda)E_\lambda. \quad (2.4.2)$$

But E and u are related through Equation 2.4.1, and u_λ is independent of the nature of the surface (of the walls of the enclosure or of any body within it), and so we see that the ratio of the exitance to the absorptance of any surface is independent of the nature of the surface. This is Kirchhoff's Law. (In popular parlance, "good emitters are good absorbers".) The ratio is a function only of temperature and wavelength. For a black body, the absorptance is unity, and the exitance is then the Planck function.

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2.4: An aperture as a black body

We consider an enclosure at some temperature and consequently filled with radiation of density u_λ per unit wavelength interval. The inside walls of the enclosure are being irradiated at a rate given by Equation 2.4.1. Now pierce a small hole in the side of the enclosure. Radiation will now pour out of the enclosure at a rate per unit area that is equal to the rate at which the walls are being radiated from within. In other words the exitance of the radiation emanating from the hole is the same as the irradiance within. Now irradiate the hole from outside. The radiation will enter the hole, and very little of it will get out again; the smaller the hole, the more nearly will all of the energy directed at the hole fail to get out again. The hole therefore absorbs like a black body, and therefore, by Kirchhoff's law, it also radiates like a black body. Put another way, a black body will radiate in the same way as will a small hole pierced in the side of an enclosure. Sometimes, indeed, a warm box with a small hole in it is used to emulate blackbody radiation and thus to calibrate the sensitivity of a radio telescope.

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2.5: Planck's Equation

The importance of Planck's equation in the early birth of quantum theory is well known. Its theoretical derivation is dealt with in courses on statistical mechanics. In this section I merely give the relevant equations for reference.

Planck's equation can be given in various ways, and here I present four. All will be given in terms of exitance. The radiance is the exitance divided by π . (Equation 1.15.2.). The four forms are as follows, in which I have made use of equations 1.3.1 and the expression $h\nu = hc/\lambda$ for the energy of a single photon.

The rate of emission of energy per unit area per unit time (i.e. the exitance) per unit wavelength interval:

$$M_\lambda = \frac{C_1}{\lambda^5 (e^{K_1/\lambda T} - 1)} \quad (2.6.1)$$

The rate of emission of photons per unit area per unit time per unit wavelength interval:

$$N_\lambda = \frac{C_2}{\lambda^4 (e^{K_1/\lambda T} - 1)} \quad (2.6.2)$$

The rate of emission of energy per unit area per unit time (i.e. the exitance) per unit frequency interval:

$$M_\nu = \frac{C_3 \nu^3}{e^{K_2 \nu/T} - 1} \quad (2.6.3)$$

The rate of emission of photons per unit area per unit time per unit frequency interval:

$$N_\nu = \frac{C_4 \nu^2}{e^{K_2 \nu/T} - 1} \quad (2.6.4)$$

The constants are:

$$C_1 = 2\pi h c^2 = 3.7418 \times 10^{-16} \text{ W m}^2 \quad (2.6.5)$$

$$C_2 = 2\pi c = 1.8837 \times 10^9 \text{ m s}^{-1} \quad (2.6.6)$$

$$C_3 = 2\pi h/c^2 = 4.6323 \times 10^{-50} \text{ kg s} \quad (2.6.7)$$

$$C_4 = 2\pi/c^2 = 6.9910 \times 10^{-17} \text{ m}^{-2} \text{ s}^2 \quad (2.6.8)$$

$$K_1 = hc/k = 1.4388 \times 10^{-2} \text{ m K} \quad (2.6.9)$$

$$K_2 = h/k = 4.7992 \times 10^{-11} \text{ s K} \quad (2.6.10)$$

Symbols:

h = Planck's constant

k = Boltzmann's constant

c = speed of light

T = temperature

λ = wavelength

ν = frequency

(2.5.2)

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2.6: Wien's Law

The wavelengths or frequencies at which these functions reach a maximum, and what these maximum values are, can be found by differentiation of these functions. They do not all come to a maximum at the same wavelength. For the four Planck functions discussed in Section 2.6 (Equations 2.6.1- 2.6.4), the wavelengths or frequencies at which the maxima occur are given by:

For Equation 2.6.1:

$$\lambda = W_1/T \quad (2.6.1)$$

For Equation 2.6.2:

$$\lambda = W_2/T \quad (2.6.2)$$

For Equation 2.6.3:

$$\nu = W_3 T \quad (2.6.3)$$

For Equation 2.6.4:

$$\nu = W_4 T \quad (2.6.4)$$

Any of these equations (but more usually the first one) may be referred to as *Wien's law*.

The constants are

$$W_n = \frac{hc}{kx_n}, \quad (n = 1, 2) \quad (2.6.5)$$

$$W_n = \frac{kx_n}{h}, \quad (n = 3, 4) \quad (2.6.6)$$

where the x_n are the solutions of

$$x_n = (6 - n) (1 - e^{-x_n}) \quad (2.6.7)$$

and have the values

$$x_1 = 4.965114 \quad (2.6.8)$$

$$x_2 = 3.920690 \quad (2.6.9)$$

$$x_3 = 2.821439 \quad (2.6.10)$$

$$x_4 = 1.593624 \quad (2.6.11)$$

The Wien constants then have the values

$$W_1 = 2.8978 \times 10^{-3} \text{ m K} \quad (2.6.12)$$

$$W_2 = 3.6697 \times 10^{-3} \text{ m K} \quad (2.6.13)$$

$$W_3 = 5.8790 \times 10^{10} \text{ Hz K}^{-1} \quad (2.6.14)$$

$$W_4 = 3.3206 \times 10^{10} \text{ Hz K}^{-1} \quad (2.6.15)$$

The maximum ordinates of the functions are given by

$$M_\lambda(\text{max}) = A_1 T^5 \quad (2.6.16)$$

$$N_\lambda(\text{max}) = A_2 T^4 \quad (2.6.17)$$

$$M_\nu(\text{max}) = A_3 T^3 \quad (2.6.18)$$

$$N_\nu(\text{max}) = A_4 T^2 \quad (2.6.19)$$

The constants A_n are given by

$$A_n = \frac{2\pi k^{6-n} y_n}{h^4 c^3}, \quad (n = 1, 2) \quad (2.6.20)$$

$$A_n = \frac{2\pi k^{6-n} y_n}{h^2 c^2}, \quad (n = 3, 4) \quad (2.6.21)$$

where the y_n are dimensionless numbers defined by

$$y_n = \frac{x_n^{6-n}}{e^{x_n} - 1} \quad (2.6.22)$$

That is,

$$y_1 = 21.20144 \quad (2.6.23)$$

$$y_2 = 4.779841 \quad (2.6.24)$$

$$y_3 = 1.421435 \quad (2.6.25)$$

$$y_4 = 0.6476102 \quad (2.6.26)$$

The constants A_n therefore have the values

$$A_1 = 1.2867 \times 10^{-5} \text{ W m}^{-2} \text{ K}^{-5} \text{ m}^{-1} \quad (2.6.27)$$

$$A_2 = 2.1011 \times 10^{17} \text{ ph s}^{-1} \text{ m}^{-2} \text{ K}^{-4} \text{ m}^{-1} \quad (2.6.28)$$

$$A_3 = 5.9568 \times 10^{-19} \text{ W m}^{-2} \text{ K}^{-3} \text{ Hz}^{-1} \quad (2.6.29)$$

$$A_4 = 1.9657 \times 10^4 \text{ ph s}^{-1} \text{ m}^{-2} \text{ K}^{-2} \text{ Hz}^{-1} \quad (2.6.30)$$

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2.7: Stefan's Law (The Stefan-Boltzmann Law)

The total exitance integrated over all wavelengths or frequencies can be found by integrating Equations 2.6.1 - 2.6.4. Integration of 2.6.1 over wavelengths or of 2.6.3 over frequencies each, of course, gives the same result:

$$M = \sigma T^4 \quad (2.7.1)$$

where

$$\sigma = \frac{2\pi^5 k^4}{15h^3 c^2} = 5.6705 \times 10^{-8} \text{ W m}^{-2} \text{K}^4 \quad (2.7.2)$$

Equation 2.7.1 is Stefan's Law, or the Stefan-Boltzmann law, and σ is *Stefan's constant*.

Integration of Equation 2.6.2 over wavelengths or of 2.6.4 over frequencies each, of course, gives the same result:

$$N = \rho T^3 \quad (2.7.3)$$

where

$$\rho = \frac{4\pi\zeta(3)k^3}{h^3 c^2} = 1.5205 \times 10^{-8} \text{ ph s}^{-1} \text{m}^{-2} \text{K}^{-3} \quad (2.7.4)$$

Here $\zeta(3)$ is the Riemann zeta-function:

$$\zeta(3) = 1 + \left(\frac{1}{2}\right)^3 + \left(\frac{1}{3}\right)^3 + \left(\frac{1}{4}\right)^3 + \dots = 1.202057 \quad (2.7.5)$$

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2.8: A Thermodynamical Argument

I have pointed out that Wien's and Stefan's laws can be derived by differentiation and integration respectively of Planck's equation. Readers should try that for themselves if only to convince themselves that neither is particularly easy, nor indeed is the derivation of Planck's equation to begin with. Those who succeed may justifiably congratulate themselves. Those who fail may console themselves with the thought that Stefan's law was derived from a simple thermodynamical argument long before the derivation of Planck's equation, and it is not necessary to know Planck's equation, let alone how to differentiate it or integrate it, in order to arrive at Stefan's law. You do, however, have to know a little thermodynamics.

Among the plethora of thermodynamical relations is to be found one that reads:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (2.8.1)$$

The derivation is usually started by writing entropy as a function of volume and temperature, and the derivation is commonly found as a preliminary to the derivation of the Joule effect for a nonideal gas. When Equation 2.8.1 is applied to the equation of state of a non-ideal gas (for example a van der Waals gas), it can be used to calculate the drop in temperature during a Joule expansion. We wish to apply it, however, to radiation in an enclosure.

We assume that the radiation is isotropic and in a steady state. Under such conditions, photons will presumably bounce rather than stick at the walls, otherwise they would rapidly become depleted - or, if they are absorbed, others are being emitted at the same rate. Either way, the radiation pressure is given by Equation 1.18.3, i.e. $P = u/3$. The energy density depends only on the temperature and not on the volume; therefore the term $(\partial U/\partial V)_T$ on the left hand side of equation 2.9.1 is just the energy density u . And since the pressure is $u/3$, the term $(\partial P/\partial T)_V$ is $\frac{1}{3}(du/dT)_V$.

Equation 2.8.1 therefore becomes

$$u = \frac{T}{3} \left(\frac{du}{dT} \right) - \frac{u}{3} \quad (2.8.2)$$

or

$$4u = T \frac{du}{dT}, \quad (2.8.3)$$

which yields Stefan's law upon integration.

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2.9: Dimensionless forms of Planck's equation

The Planck functions (of wavelength or frequency and temperature) can be collapsed on to dimensionless functions of a single variable if we express the exitance in units of the maximum exitance, and the wavelength or frequency in units of the wavelength or frequency at which the maximum occurs. Equations 2.7.1-4 and 16-20 will be needed to achieve this, and the reader might enjoy doing it as a challenge. (I said "might".) The results are

$$M_\lambda = \frac{b_1}{\lambda^5 (e^{x_1/\lambda} - 1)} \quad (2.10.1)$$

$$N_\lambda = \frac{b_2}{\lambda^4 (e^{x_2/\lambda} - 1)} \quad (2.10.2)$$

$$M_\nu = \frac{b_3 \nu^3}{e^{x_3 \nu} - 1} \quad (2.10.3)$$

$$N_\nu = \frac{b_4 \nu^2}{e^{x_4 \nu} - 1} \quad (2.10.4)$$

where

$$b_n = e^{x_n} - 1 \quad (n = 1, 2, 3, 4) \quad (2.10.5)$$

The numerical values of x_n are given in equations 2.7.8-11, and the values of b_n are

$$b_1 = 142.32492 \quad (2.10.6)$$

$$b_2 = 49.435253 \quad (2.10.7)$$

$$b_3 = 15.801016 \quad (2.10.8)$$

$$b_4 = 3.9215536 \quad (2.10.9)$$

The numbers x_n , y_n , b_n are independent of the values of any physical constants such as h , c or k , and will not change as our knowledge of these values improves. These functions, which are independent of temperature, are drawn in figures II.1,2,3,4 shown at the end of this chapter.

Example

Here is an example to show the use of the dimensionless functions to calculate the blackbody radiance quickly. What is the radiance per unit wavelength of a 5000 K black body at 400 nm? You may prefer to calculate this directly from equation 2.6.1, but let's try it using the dimensionless form. From equation 2.7.1 we find that the wavelength at which maximum exitance per unit wavelength occurs is 579.56 nm, and therefore our dimensionless wavelength to be inserted into equation 2.10.1 is 0.6902. This gives a radiance per unit wavelength interval (in units of the maximum) of 0.6832. But equation 2.7.16 gives the maximum radiance per unit wavelength interval as $4.0178 \times 10^{13} \text{ W m}^{-2} \text{ m}^{-1}$ and therefore the radiance at 400 nm is $2.745 \times 10^{13} \text{ W m}^{-2} \text{ m}^{-1}$.

I don't think there is much point in integrating the dimensionless functions 2.10.1-4 over all wavelengths and frequencies, but, for the record:

$$\int_0^\infty M_\lambda d\lambda = \frac{\pi^4 x_1}{15 y_1} = 1.52080 \quad (2.10.10)$$

$$\int_0^\infty N_\lambda d\lambda = \frac{2\zeta(3)x_2}{y_2} = 1.97199 \quad (2.10.11)$$

$$\int_0^\infty M_\nu d\nu = \frac{\pi^4}{15 x_3 y_3} = 1.61924 \quad (2.10.12)$$

$$\int_0^\infty N_\nu d\nu = \frac{2\zeta(3)}{x_4 y_4} = 2.32946 \quad (2.10.13)$$

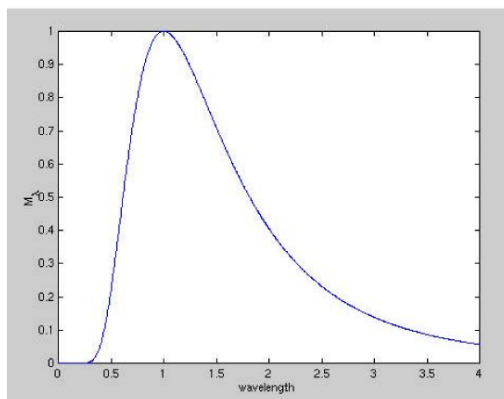


Figure II.1. Blackbody exitance per unit wavelength interval. The equation is equation 2.10.1, with constants given by equations 2.10.6 and 2.7.8. The maximum value is given by equations 2.7.16 and 2.7.27. It occurs at a wavelength given by equations 2.7.1 and 2.7.12.

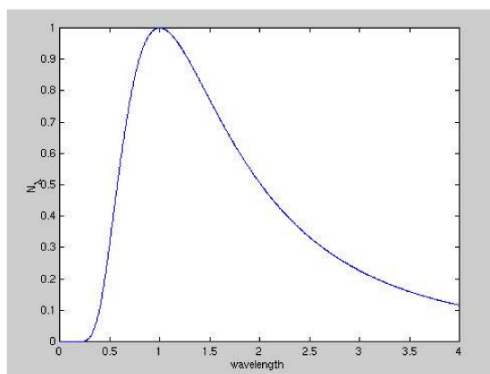


Figure II.2. Blackbody photon exitance per unit wavelength interval. The equation is equation 2.10.2 with constants given by equations 2.10.7 and 2.7.9. The maximum value is given by equations 2.7.17 and 2.7.28. It occurs at a wavelength given by equations 2.7.2 and 2.7.13.

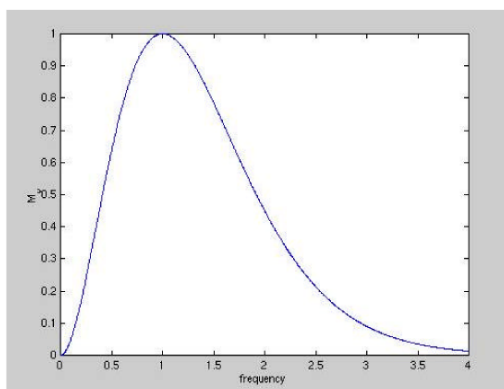


Figure II.3. Blackbody radiance per unit frequency interval. The equation is equation 2.10.3 with constants given by equations 2.10.8 and 2.7.10. The maximum value is given by equations 2.7.18 and 2.7.29. It occurs at a frequency given by equations 2.7.3 and 2.7.14.

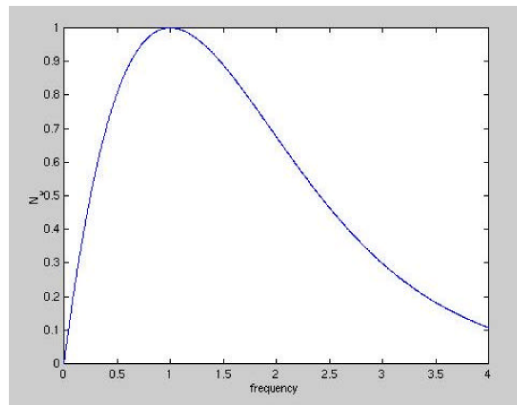


Figure II.4. Blackbody photon radiance per unit frequency interval. The equation is equation 2.10.4 with constants given by equations 2.10.9 and 2.7.11. The maximum value is given by equations 2.7.19 and 2.7.30. It occurs at a frequency given by equations 2.7.4 and 2.7.15.

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2.10: Derivation of Wien's and Stefan's Laws

Wien's and Stefan's Laws are found, respectively, by differentiation and integration of Planck's equation. Neither of these is particularly easy, and they are not found in every textbook. Therefore, I derive them here.

Wien's Law

Planck's equation for the exitance per unit wavelength interval (equation 2.6.1) is

$$\frac{M}{C} = \frac{1}{\lambda^5 (e^{K/\lambda T} - 1)}, \quad (2.11.1)$$

in which I have omitted some subscripts. Differentiation gives

$$\frac{1}{C} \frac{dM}{d\lambda} = -\frac{1}{(e^{K/\lambda T} - 1)^2} \cdot \left[5\lambda^4 \cdot (e^{K/\lambda T} - 1) + \lambda^5 \cdot \left(-\frac{K}{\lambda^2 T} \right) e^{K/\lambda T} \right]. \quad (2.11.2)$$

M is greatest when this is zero; that is, when

$$x = 5(1 - e^{-x}), \quad (2.11.3)$$

where

$$x = \frac{K}{\lambda T}. \quad (2.11.4)$$

Hence, with equation 2.6.9, the wavelength at which M is a maximum, is given by

$$\lambda = \frac{hc}{kxT}. \quad (2.11.5)$$

The maximum value of M is found by substituting this value of λ back into Planck's equation, to arrive at equation 2.7.16. The corresponding versions of Wien's Law appropriate to the other versions of Planck's equation are found similarly.

Stefan's Law

Integration of Planck's equation to arrive at Stefan's law is a bit more tricky.

It should be clear that $\int_0^\infty M_\lambda d\lambda = \int_0^\infty M_\nu d\nu$, and therefore I choose to integrate the easier of the functions, namely M_ν . To integrate M_λ , the first thing we would do anyway would be to make the substitution $\nu = c/\lambda$.

Planck's equation for the blackbody exitance per unit frequency interval is

$$M_\nu = C_3 \int_0^\infty \frac{\nu^3 d\nu}{e^{K_2\nu/T} - 1}. \quad (2.11.6)$$

Let $x = K_2\nu/T$; then

$$M_\nu = \frac{2\pi k^4 T^4}{c^2 h^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}, \quad (2.11.7)$$

And, except for the numerical value of the integral, we already have Stefan's law. The integral can be evaluated numerically, but not without difficulty, and there is an analytical solution for it.

Consider the indefinite integral and integrate it by parts:

$$\int \frac{x^3 dx}{e^x - 1} = x^3 \ln(1 - e^{-x}) - 3 \int x^2 \ln(1 - e^{-x}) dx + \text{const.} \quad (2.10.1)$$

Now put the limits in:

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = -3 \int_0^\infty x^2 \ln(1 - e^{-x}) dx. \quad (2.10.2)$$

Write down the Maclaurin expansion of the integrand:

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = 3 \int_0^\infty x^2 \left(e^{-x} + \frac{1}{2}e^{-2x} + \frac{1}{3}e^{-3x} + \dots \right) dx \quad (2.10.3)$$

and integrate term by term to obtain

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = 6 \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots \right). \quad (2.11.8)$$

We must now evaluate $1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots$

The series $\sum_1^\infty \frac{1}{n^m}$ is the Riemann ζ -function. For $m = 1$, it diverges. For $m = 3, 5, 7$, etc., it has to be evaluated numerically. For $m = 2, 4, 6$, etc., the sums can be written explicitly in terms of π . For example:

$$\zeta(2) = \frac{\pi^2}{6}, \quad (2.10.4)$$

$$\zeta(4) = \frac{\pi^4}{90}, \quad (2.10.5)$$

$$\zeta(6) = \frac{\pi^6}{945}. \quad (2.10.6)$$

One of the stages necessary in evaluating the ζ -function is to derive the infinite product

$$\frac{\sin \alpha \pi}{\alpha \pi} = [1 - \alpha^2] \left[1 - \left(\frac{1}{2} \alpha \right)^2 \right] \left[1 - \left(\frac{1}{3} \alpha \right)^2 \right] \dots \quad (2.11.9)$$

If we can do that, we are more than halfway there.

Let's start by considering the Fourier expansion of $\cos \theta x$:

$$\cos \theta x = \sum_0^\infty a_n \cos nx \quad (2.11.10)$$

In Equation 2.11.10 n is an integer, θ not necessarily so; we shall suppose that θ is some number between 0 and 1. There is no need to consider any sine terms, because $\cos \theta x$ is an even function of x . We work out what the Fourier coefficients are in the usual way, to get

$$a_n = (-1)^n \frac{2\theta \sin \theta \pi}{\theta^2 - n^2}, \quad n = 1, 2, 3, \dots \quad (2.11.11)$$

As usual, and for the usual reason, a_0 is an exception:

$$a_0 = \frac{\sin \theta \pi}{\theta \pi}. \quad (2.11.12)$$

We have therefore arrived at the Fourier expansion of $\cos \theta x$:

$$\cos \theta x = \frac{2\theta \sin \theta \pi}{\pi} \left(\frac{1}{2\theta^2} - \frac{\cos x}{\theta^2 - 1^2} + \frac{\cos 2x}{\theta^2 - 2^2} - \frac{\cos 3x}{\theta^2 - 3^2} + \dots \right). \quad (2.11.13)$$

Put $x = \pi$ and rearrange slightly:

$$\pi \cot \theta \pi - \frac{1}{\theta} = 2\theta \left(\frac{1}{\theta^2 - 1^2} + \frac{1}{\theta^2 - 2^2} + \dots \right). \quad (2.11.14)$$

Since we are assuming that θ is some number between 0 and 1, we shall re-write this so that the denominators are all positive:

$$\pi \cot \theta \pi - \frac{1}{\theta} = -\frac{2\theta}{1^2 - \theta^2} - \frac{2\theta}{2^2 - \theta^2} - \dots \quad (2.11.15)$$

Now multiply both sides by $d\theta$ and integrate from $\theta = 0$ to $\theta = \alpha$. The integration must be done with care. The indefinite integral of the left hand side is $\ln \sin \theta \pi - \ln \theta + \text{constant}$, i.e. $\ln \left(\frac{\sin \theta \pi}{\theta} \right) + \text{constant}$. The definite integral between 0 and α is $\ln \left(\frac{\sin \alpha \pi}{\alpha} \right) - \lim_{\theta \rightarrow 0} \ln \left(\frac{\sin \theta \pi}{\theta} \right)$.

The limit of the second term is $\ln \pi$, so the definite integral is $\ln \left(\frac{\sin \alpha \pi}{\alpha \pi} \right)$. Integrating the right hand side is a bit easier, so we arrive at

$$\ln \left(\frac{\sin \alpha \pi}{\alpha \pi} \right) = \ln \left(\frac{1^2 - \alpha^2}{1^2} \right) + \ln \left(\frac{2^2 - \alpha^2}{2^2} \right) + \dots \quad (2.11.16)$$

On taking the antilogarithm, we arrive at the required infinite product:

$$\frac{\sin \alpha \pi}{\alpha \pi} = [1 - \alpha^2] \left[1 - \left(\frac{1}{2} \alpha \right)^2 \right] \left[1 - \left(\frac{1}{3} \alpha \right)^2 \right] \dots \quad (2.11.17)$$

Now expand this as a power series in α^2 :

$$\frac{\sin \alpha \pi}{\alpha \pi} = 1 + ()\alpha^2 + ()\alpha^4 + ()\alpha^6 + \dots \quad (2.11.18)$$

The first one is easy, but subsequent ones rapidly get more difficult, but you do have to get at least as far as α^4 .

Now compare this expansion with the ordinary Maclaurin expansion:

$$\frac{\sin \alpha \pi}{\alpha \pi} = 1 - \frac{\pi^2}{3!} \alpha^2 + \frac{\pi^4}{5!} \alpha^4 - \dots \quad (2.11.19)$$

and we arrive at the correct expressions for the Riemann ζ -functions. We then get for Stefan's law:

$$M = \frac{2\pi^5 k^4}{15h^3 c^2} T^4 = \sigma T^4, \quad (2.11.20)$$

where $\sigma = 5.6705 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.

Questions

Finally, now that you have struggled through Riemann's zeta-function, let's just make sure that you have understood the really simple stuff, so here are a couple of easy questions – and you won't have to bother with zeta-functions.

1. By what factor should the temperature of a black body be increased so that

- The integrated radiance (over all frequencies) is doubled?
- The frequency at which its radiance is greatest is doubled?
- The spectral radiance per unit wavelength interval at its wavelength of maximum spectral radiance is doubled?

2. A block of shiny silver (absorptance = 0.23) has a bubble inside it of radius 2.2cm, and it is held at a temperature of 1200K.

A block of dull black carbon (absorptance = 0.86) has a bubble inside it of radius 4.3cm, and it is held at a temperature of 2300K,

Calculate the ratio

$$\frac{\text{Integrated radiation energy density inside the carbon bubble}}{\text{Integrated radiation energy density inside the silver bubble}}. \quad (2.10.7)$$

Answers. 1. a) 1.189 b) 2.000 c) 1.149

2. 13.5

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3: The Exponential Integral Function

Sooner or later (in particular in the next chapter) in the study of stellar atmospheres, we have need of the exponential integral function. This brief chapter contains nothing about stellar atmospheres or even astronomy, but it describes just as much as we need to know about the exponential integral function. It is not intended as a thorough exposition of everything that could be written about the function.

The exponential integral function of order n , written as a function of a variable a , is defined as

$$E_n(a) = \int_1^{\infty} x^{-n} e^{-ax} dx. \quad (3.1)$$

I shall restrict myself to cases where n is a non-negative integer and a is a non-negative real variable. For stellar atmosphere theory in the next chapter we shall have need of n up to and including 3.

Let us start by seeing what the values of the functions are when $a = 0$. We have

$$E_n(0) = \int_1^{\infty} x^{-n} dx \quad (3.2)$$

and this is infinite for $n = 0$ and for $n = 1$. For larger n it is $1/(n-1)$.

Thus $E_0(0) = \infty$, $E_1(0) = \infty$, $E_2(0) = 1$, $E_3(0) = \frac{1}{2}$, $E_4(0) = \frac{1}{3}$, etc.

Thereafter the functions (of whatever order) decrease monotonically as a increases, approaching zero asymptotically for large a .

The function $E_0(a)$ is easy to evaluate. It is

$$E_0(a) = \int_1^{\infty} e^{-ax} dx = \frac{e^{-a}}{a}. \quad (3.3)$$

The evaluation of the exponential integral function for $n > 0$ is less easy but it can be done by numerical (e.g. Simpson) integration. The upper limit of the integral in equation 3.1 is infinite, but this difficulty can be overcome by means of the substitution $y = 1/x$, from which the equation becomes

$$E_n(0) = \int_0^1 y^{n-2} e^{-a/y} dy. \quad (3.4)$$

Since both limits are finite, this can now in principle be integrated numerically in a straightforward way, for example by Simpson's rule or similar algorithm, except that, at the lower limit, a/y is infinite and it is necessary first to determine the limit of the integrand as $y \rightarrow 0$, which is zero.

There is, however, a way of evaluating the exponential integral function for $n \geq 2$ without the necessity of numerical integration. Consider, for example,

$$E_{n+1}(a) = \int_1^{\infty} x^{-(n+1)} e^{-ax} dx. \quad (3.5)$$

If this is integrated (very carefully!) by parts, we arrive at

$$E_{n+1}(a) = \frac{1}{n} [e^{-a} - aE_n(a)]. \quad (3.6)$$

Thus from this recurrence relation, once we have evaluated $E_1(a)$, we can evaluate $E_2(a)$ and hence $E_3(a)$ and so on.

The recurrence relation 3.6, however, holds only for $n \geq 1$ (as will become apparent during the careful partial integration), so there is no getting around the numerical integration for $n = 1$. Furthermore, for small values of a the functions for $n = 0$ or 1 become very large, becoming infinite as $a \rightarrow 0$, which makes them very sensitive when trying to compute the next function up. Thus for small a or for constructing a table it may in the end be less trouble to take the bull by the horns and integrate them all numerically.

It will afford good programming practice to prepare a table of $E_n(a)$ for $a = 0$ to 2, in steps of 0.01, for $n = 0, 1, 2, 3$. The table should ideally have five columns, the first being the 201 values of a , and the remaining four being $E_n(a)$, $n = 1$ to 4. A graph of these functions is shown in figure III.1.

In practice, in performing the calculations for figure III.1, this is what I found. The function for $n = 0$ was easy; it is given simply by equation 3.3. For $n = 1$, I integrated by Simpson's rule; 100 intervals in y was adequate to compute the function to nine decimal places. The function for $n = 2$ was unexpectedly difficult. The recurrence relation 3.6 was not useful at small a , as discussed above. I therefore attempted to integrate it using Simpson's rule, yet, although the function is, on the face of it, very simple:

$$E_2(a) = \int_0^1 e^{-a/y} dy, \quad (3.7)$$

Simpson's rule seemed inadequate to compute the function precisely even with as many as 1000 intervals in y . Neither the recurrence relation nor numerical integration was without problems! I had no difficulty, however, with integrating the function with $n = 3$, and so I then used the recurrence relation backwards to calculate the function for $n = 2$ and all was well.

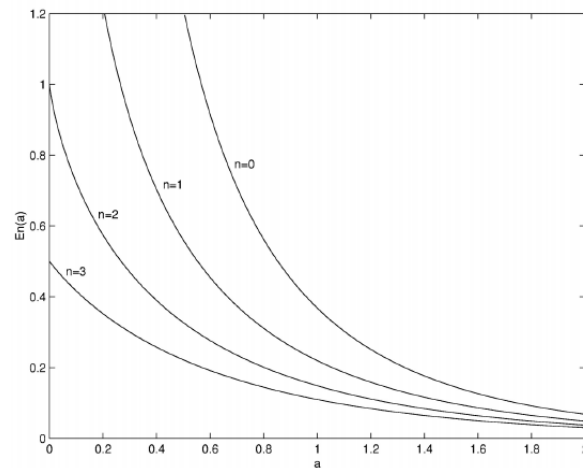


FIGURE III.1
The exponential integral function

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CHAPTER OVERVIEW

4: Flux, Specific Intensity and other Astrophysical Terms

Topic hierarchy

- [4.1: Introduction](#)
- [4.2: Luminosity](#)
- [4.3: Specific Intensity](#)
- [4.4: Flux](#)
- [4.5: Mean Specific Intensity](#)
- [4.6: Radiation Pressure](#)
- [4.7: Other Integrals](#)
- [4.8: Emission Coefficient](#)

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4.1: Introduction

In previous chapters we have used the definitions and symbols of the quantities in radiation theory as recommended by various bodies. We mentioned that, in the context of the special needs of stellar atmosphere theory, usage sometimes differs from the standard. In this chapter we introduce the definitions and symbols that are commonly used in stellar atmosphere theory, and we continue to use the astronomical usage henceforth.

In a later paragraph you will be asked to imagine a "horizontal" surface in the atmosphere of a star. Lest you are thinking of a star as a large, ball-shaped thing, and the word "horizontal" is puzzling, let me say that, at least for the time being, I am considering a "shallow" atmosphere; that is, an atmosphere whose depth is very small compared with the radius of the star. To that extent, the atmosphere can be considered as a plane parallel atmosphere. This will not do for a greatly extended atmosphere, such as that of an M supergiant; as to whether it is an appropriate model for a star like the Sun, remind yourself how sharply-defined the limb of the Sun is, and hence how rapidly the atmosphere becomes opaque.

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4.2: Luminosity

The most important differences between "standard" and "astrophysical" usages are in the meanings of flux and intensity. What we have hitherto called the "radiant flux" Φ of a source of radiation, expressed in watts, is generally called by astronomers, when describing the radiant flux from an entire star, the *luminosity* of the star, and the symbol used is L . While this can be expressed in watts, it is commonly expressed in units of the luminosity of the Sun, which is 3.85×10^{26} watts.

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4.3: Specific Intensity

Instead of the word "radiance", for which we have hitherto used the symbol L , the name commonly used in the context of stellar atmosphere theory is *specific intensity* and the symbol used is I . In most branches of physics, the word "specific" is used to mean "per unit mass", but that meaning is not intended in the present context. It might be noted that the word "specific" is often omitted, so that what we have hitherto called "radiance" L is now "intensity" I . Note also that this is not the same as what is meant in "standard" usage by "intensity", for which the symbol, in standard usage, is also I . In this and subsequent chapters, I shall always include the word "specific".

The quantity we have in earlier chapters called "radiance" was used to describe the brightness of an extended radiating surface, and the new term "specific intensity" can equally be used in a similar context. More often, however, you may need to imagine yourself embedded somewhere within a stellar atmosphere and you are looking around to see the watts per square metre per steradian arriving at you from various directions.

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4.4: Flux

The word "flux" in the context of stellar atmosphere theory differs from the "flux" of standard terminology. The symbol used is F , occasionally but not always printed in a special font. Let us imagine a horizontal surface embedded somewhere in a stellar atmosphere. It is being irradiated from below and above, but rather more from below than from above. Let us concentrate our attention for the time being on the radiation that is coming up from below. The rate of arrival of radiant energy per unit area from below from all directions would, in "standard" nomenclature, have been called the irradiance. After passage through the surface, it would be called the exitance. Now, using the nomenclature of stellar atmosphere theory, we call the rate of upward passage of radiant energy per unit area through a horizontal surface within the atmosphere the *upward* or the *outward flux*. The symbol is F_+ (sometimes printed in a special font), and the SI units would be W m^{-2} . Likewise, the rate of passage of radiant energy per unit area from above to below is the *downward* or *inward flux*, F_- . The net upward flux is

$$F = F_+ - F_- . \quad (4.4.1)$$

If you are standing upright, F_+ is the irradiance of the soles of your feet, while F_- is the irradiance of the top of your head. If we measure the spherical angle θ from a downwardly-directed z -axis, then, following equation 1.14.5, we have

$$F_+ = \int_0^{2\pi} \int_0^{\pi/2} I(\theta, \phi) \cos \theta \sin \theta \, d\theta d\phi \quad (4.4.2)$$

$$F_- = \int_0^{2\pi} \int_{\pi}^{\pi/2} I(\theta, \phi) \cos \theta \sin \theta \, d\theta d\phi \quad (4.4.3)$$

$$F = F_+ - F_- = \int_0^{2\pi} \int_0^{\pi} I(\theta, \phi) \cos \theta \sin \theta \, d\theta d\phi, \quad (4.4.4)$$

which is sometimes written for short

$$F = \int_{4\pi} I \cos \theta \, d\omega \quad (4.4.5)$$

or just

$$\int I \cos \theta \, d\omega \quad (4.4.6)$$

At the surface of the star (if there is such a thing!) $F_- = 0$, so that $F = F_+ = \pi I$. This is the same as equation 1.15.2. At the centre of the star, I is isotropic and $F = 0$.

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4.5: Mean Specific Intensity

Look around you again from your position somewhere in the middle of a stellar atmosphere. The specific intensity around you is not isotropic. It is quite large in the sky above you, but is much greater if you look towards the hell at your feet. The *mean specific intensity* J around the complete 4π steradians around you is

$$J = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi I(\theta) \sin \theta \, d\theta d\phi \quad (4.5.1)$$

or, for short

$$J = \frac{1}{4\pi} \int I d\omega. \quad (4.5.2)$$

At the centre of the star, where the specific intensity is isotropic, $J = I$.

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4.6: Radiation Pressure

Recall equation 1.18.5 and the conditions for which it is valid. It was derived for isotropic radiation. In the atmosphere, radiation is not isotropic; there is a net flux of radiation outwards. Therefore the radiation density must go inside the integral sign. We can also write the equation in terms of specific intensity, making use of equations 1.15.3 and 1.17.1. The equation for the radiation pressure then becomes

$$P = \frac{1}{c} \int_{4\pi} I \cos^2 \theta \, d\omega, \quad (4.6.1)$$

where by now we are used to the abbreviated notation.

If the radiation is isotropic, this is not zero; it is $4\pi/(3c)$. In the expressions for J and for P , the power of $\cos \theta$ is even (0 and 2 respectively) and one can see both physically and mathematically that neither of them is zero for isotropic radiation. On the other hand, the expression for F has an odd power of $\cos \theta$, and it is therefore zero for isotropic radiation, as expected.

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4.7: Other Integrals

Other integrals occurring in the theory of stellar atmospheres are (using the abbreviated notation)

$$H = \frac{1}{4\pi} \int I \cos \theta d\omega = F/(4\pi) \quad (4.7.1)$$

$$= 0 \text{ if isotropic} \quad (4.7.2)$$

$$K = \frac{1}{4\pi} \int I \cos^2 \theta d\omega = cP/(4\pi) \quad (4.7.3)$$

$$= J/3 \text{ if isotropic.} \quad (4.7.4)$$

The SI units for F are W m^{-2} . For I, J, H, K they are $\text{W m}^{-2} \text{ sr}^{-1}$. For P they are Pa.

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4.8: Emission Coefficient

This is the intensity emitted per unit volume of a gas. In this definition, the word “intensity” (without being preceded by the word “specific”) is intended to mean what is meant in section 1.4. The symbol used for emission coefficient is j , and the SI units are $\text{W sr}^{-1} \text{m}^{-3}$.

The *mass emission coefficient* j_m is the intensity per unit mass, and is related to the volume emission coefficient by $j = \rho j_m$. Not all authors are equally clear as to whether they are referring to a volume or a mass emission coefficient.

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CHAPTER OVERVIEW

5: Absorption, Scattering, Extinction and the Equation of Transfer

- [5.1: Introduction](#)
- [5.2: Absorption](#)
- [5.3: Scattering, Extinction and Opacity](#)
- [5.4: Optical Depth](#)
- [5.5: The Equation of Transfer](#)
- [5.6: The Source Function \(Die Ergiebigkeit\)](#)
- [5.7: A Series of Problems](#)
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- [5.9: More on the Equation of Transfer](#)

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5.1: Introduction

As radiation struggles to make its way upwards through a stellar atmosphere, it may be weakened by *absorption* and *scattering*. The combined effect of absorption and scattering is called *extinction*. Scattering may simply be by reflection from dust particles. If the radiation interacts with an *atom*, the atom may be excited to a higher energy level and almost immediately (typically on a time-scale of nanoseconds) the atom drops down to its original level and emits a photon of the same frequency as the one it absorbed. Such a process - temporary absorption followed almost immediately by re-emission without change in wavelength - is probably best described in the present context as scattering. Individual atoms in a stellar atmosphere generally radiate dipole radiation; however, since many randomly oriented atoms take place in the process, the scattering can be regarded as isotropic. If, however, the excited atom collides with another atom before re-emission, the collision may be super-elastic; as the atom falls to a lower state, the energy it gives up, instead of being radiated as a photon, goes to kinetic energy of the colliding atoms. The radiation has been converted to kinetic energy. This process is absorption.

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5.2: Absorption

To start with, let us suppose that the predominating mechanism is absorption with no scattering. We can define a *linear absorption coefficient* α as follows. Let the specific intensity at some level in an atmosphere be I . At a level in the atmosphere higher by a distance dx , the specific intensity has dropped, as a result of absorption, to $I + dI$. (Here dI , by the convention of differential calculus, means the increase in I , and it is in this case negative. The quantity $-dx$, which is positive, is the decrease in I .) The linear absorption coefficient α is defined such that the fractional decrease in the specific intensity over a distance dx is given by

$$-\frac{dI}{I} = \alpha dx \quad (5.2.1)$$

The coefficient is of dimension L^{-1} and the SI unit is m^{-1} . In general, α will depend on frequency or wavelength, and, at a particular wavelength, the Equation would be written

$$-\frac{dI_\nu}{I_\nu} = \alpha(\nu) dx \quad (5.2.2)$$

If Equation 5.2.1 is integrated over a finite distance, for a slab of atmosphere, say, between $x = 0$, where the specific intensity is I^0 , and $x = X$, where the specific intensity is I , it becomes

$$I = I^0 \exp \left[- \int_0^X \alpha(x) dx \right] \quad (5.2.3)$$

And if α is uniform and not a function of x , this becomes

$$I = I^0 \exp(-\alpha X) \quad (5.2.4)$$

Now let $\alpha_a = \alpha/n$, so that Equation 5.2.1 becomes

$$-dI/I = \alpha_a n dx \quad (5.2.5)$$

and Equation 5.2.4 becomes $I = I^0 \exp(-\alpha_a n X)$, where n is the number of atoms per unit volume. Then α_a is the *atomic absorption coefficient*, or *atomic absorption cross-section*. It is of dimension L^2 and the SI unit is m^2 .

In a similar manner, we can define $\alpha_m = \alpha/\rho$, where ρ is the mass density, as the *mass absorption coefficient*, with corresponding modifications in all the other equations. It is of dimension $L^2 M^{-1}$ and the SI unit is $m^2 kg^{-1}$.

We might also mention here that in laboratory chemistry, one comes across the word *absorbance* of a solution. This is the linear absorption coefficient divided by the concentration of the solute. While this word is not usually encountered in stellar atmosphere theory, it is mentioned here partly because it is very similar in concept to the several concepts discussed in this section, and also because of the similarity of the word to the rather different *absorptance* defined in Chapter 2. In chemical texts, the exponential decrease of intensity with distance is often referred to as the Lambert-Beer Law, or simply as Lambert's Law. This is mentioned here merely to point out that this is not at all related to the *Lambert's Law* discussed in Chapter 1.

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5.3: Scattering, Extinction and Opacity

If the predominating mechanism is scattering with no absorption, we can define in a similar manner linear, atomic and mass scattering coefficients, using the symbol σ rather than α . For the physical distinction between absorption and scattering, see [Section 5.1](#). And if both absorption and scattering are important, we can define linear, atomic and mass extinction coefficients, using the symbol κ , where

$$\kappa = \alpha + \sigma. \quad (5.3.1)$$

All the foregoing equations are valid, whether we use linear, atomic or mass absorption, scattering or extinction coefficients, and whether we refer to radiation integrated over all frequencies or whether at a particular wavelength or within a specified wavelength range.

The *mass extinction coefficient* is generally referred to as the *opacity*.

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5.4: Optical Depth

The product of linear extinction coefficient and distance, or, more properly, if the extinction coefficient varies with distance, the integral of the extinction coefficient with respect to distance,

$$\tau = \int \kappa(x) dx \quad (5.4.1)$$

is the *optical depth*, or *optical thickness*, τ . It is dimensionless. Specific intensity falls off with optical depth as

$$I = I^0 e^{-\tau}. \quad (5.4.2)$$

Thus optical depth can also be defined by $\ln(I^0/I)$. While the optical depth $\ln(I^0/I)$ is generally used to describe how opaque a stellar atmosphere or an interstellar cloud is, when describing how opaque a filter is, one generally uses $\log_{10}(I^0/I)$, which is called the *density* d of the filter. Density is 0.4343 times optical depth. If a star is hidden behind a cloud of optical depth τ it will be dimmed by 1.086τ magnitudes. If it is hidden behind a filter of density d it will be dimmed by $2.5d$ magnitudes. The reader is encouraged to verify these assertions.

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5.5: The Equation of Transfer

The equation of transfer deals with the transfer of radiation through an atmosphere that is simultaneously absorbing, scattering and emitting.

$$I_{\nu} \left| \begin{array}{c} dx \\ \alpha(\nu) \\ \sigma(\nu) \\ j_{\nu} \end{array} \right| I_{\nu} + dI_{\nu}$$

FIGURE V.1

Suppose that, between x and $x + dx$ the absorption coefficient and the scattering coefficient at frequency ν are $\alpha(\nu)$ and $\sigma(\nu)$, and the emission coefficient per unit frequency interval is $j_{\nu}d\nu$. In this interval, suppose that the specific intensity per unit frequency interval increases from I_{ν} to $I_{\nu} + dI_{\nu}$ (dI_{ν} might be positive or negative). The specific intensity will be reduced by absorption and scattering and increased by emission. Thus:

$$dI_{\nu} = -[I_{\nu}\alpha(\nu) + I_{\nu}\sigma(\nu) - j_{\nu}(\nu)]dx. \quad (5.5.1)$$

This is one form - the most basic form - of the *equation of transfer*. Notice that α and σ do not have a subscript.

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5.6: The Source Function (Die Ergiebigkeit)

This is the ratio of the emission coefficient to the extinction coefficient. A review of the dimensions of these will show that the dimensions of source function are the same as that of specific intensity, namely $\text{W m}^{-2} \text{sr}^{-1}$ (perhaps per unit wavelength or frequency interval). The usual symbol is S . Thus

$$S_\nu = \frac{j_\nu}{\alpha(\nu) + \sigma(\nu)} = \frac{j_\nu}{\kappa(\nu)} \quad (5.6.1)$$

Imagine a slice of gas of thickness dx . Multiply the numerator and denominator of the right hand side of equation 5.6.1 by dx . Observe that the numerator is now the specific intensity (radiance) of the slice, while the denominator is its optical thickness. Thus an alternative definition of source function is *specific intensity per unit optical thickness*. Later, we shall evaluate the source function in an atmosphere in which the extinction is pure absorption, in which it is purely scattering, and in which it is a bit of each.

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5.7: A Series of Problems

I am now going to embark upon a series of problems that at first sight may appear to be not very relevant to stellar atmospheres, but the reader is urged to be patient and look at them, partly because they make use of many of the ideas encountered up to this point, and also because they culminate in determining how the flux and the mean specific intensity in an atmosphere increase with optical depth in terms of the source function.

Problem 1

An infinite plane radiating surface has a uniform specific intensity (radiance) I . What is the flux (irradiance) at a point P, situated at a height h above the surface?

We have already answered that question in equation 1.15.3, and the answer, which, unsurprisingly since the plane is infinite in extent, is independent of h , is πI , so let's get on with

Problem 2

Same as Problem 1, except that this time the space between the radiating plane and the point P is filled with a uniform gas of absorption coefficient α . The specific intensity (radiance) of the surface, we are told, is, following astrophysical custom, I . Unfortunately I shall also be compelled to make use of "intensity" in the "standard" sense of Chapter 1, and for that I shall use the symbol \mathfrak{J} .

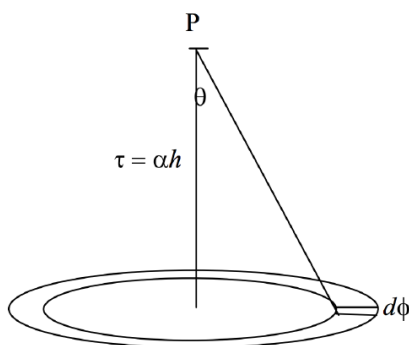


FIGURE V.2

The elemental area is $r dr d\phi$, or, since $r = h \tan \theta$, it is $h^2 \tan \theta \sec^2 \theta d\theta d\phi$. The intensity of the elemental area towards P is the specific intensity (radiance) times the projected area:

$$d\mathfrak{J} = I h^2 \tan \theta \sec^2 \theta d\theta d\phi \cos \theta \quad (5.7.1)$$

If there were no absorption, the irradiance of P by the elemental area would be

$$d\mathfrak{J} \cos \theta / (h^2 \sec^2 \theta), \quad (5.7.2)$$

which becomes

$$I \sin \theta \cos \theta d\theta d\phi. \quad (5.7.3)$$

But it is reduced by absorption by a factor $e^{-\tau \sec \theta}$, where $\tau = \alpha h$. Therefore the irradiance of P by the elemental area is

$$I e^{-\tau \sec \theta} \sin \theta \cos \theta d\theta d\phi. \quad (5.7.4)$$

For the irradiance at P (or "flux" in the astrophysics sense) by the entire infinite plane we integrate from $\phi = 0$ to 2π and $\theta = 0$ to $\pi/2$, to obtain

$$2\pi I \int_0^{\pi/2} e^{-\tau \sec \theta} \sin \theta \cos \theta d\theta \quad (5.7.5)$$

If we now write $x = \sec \theta$, this becomes

$$\text{Irradiance at P} = 2\pi I E_3(\tau), \quad (5.7.6)$$

and we hope that the reader has not forgotten the meaning of E_3 - if you have, as the game of snakes and ladders would say, Go back to Chapter 3. Note that, at $\tau = 0$, this becomes πI , as expected.

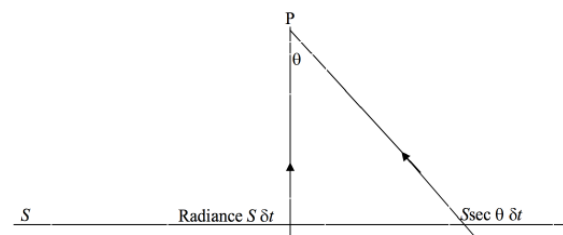


FIGURE V.3

A point P is situated at a height h above an infinite plane slice of gas of optical thickness $\delta\tau$ and source function S . There is nothing between P and the slice of gas. What is the flux (irradiance) at P?

At first glance this appears to be identical to Problem 1, except that the specific intensity of the slice is $S\delta t$. However, a more careful look at the diagram will reveal that the specific intensity of the slice is by no means uniform. It is darkest directly below P, and, when P looks farther from his nadir, the slice gets brighter and brighter, being $S \sec \theta \delta t$ at an angle θ . The upwards flux ("irradiance") at P is therefore

$$F_+ = 2\pi S\delta t \int_0^{\pi/2} \sec \theta \cos \theta \sin \theta d\theta = 2\pi S\delta t \quad (5.7.7)$$

Same as Problem 3, except that this time we'll place an absorbing gas of optical thickness t between P and the slice δt .

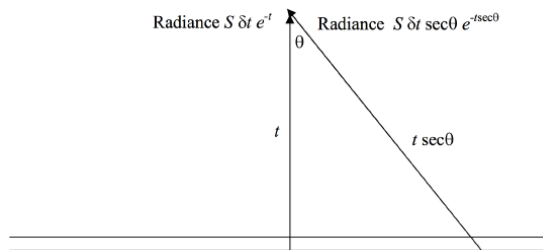


FIGURE V.4

In that case the flux (irradiance) at P from an element at an angle θ is reduced by $e^{-t \sec \theta}$ and consequently the flux at P from the entire slice is

$$F_+ = 2\pi S\delta t \int_0^{\pi/2} \sec \theta \cos \theta \sin \theta d\theta = 2\pi S\delta t. \quad (5.7.8)$$

If we write $x = \sec \theta$, we very soon see that this is

$$\text{Flux (irradiance) at P} = 2\pi S\delta t E_2(t) \quad (5.7.9)$$

Problem 5 (an important result in atmosphere theory)

Now consider a point P at an optical depth τ in a stellar atmosphere. (The use of the word "depth" will imply that τ is measured downwards from the surface towards the centre of the star.) We shall assume a plane parallel atmosphere i.e. a shallow atmosphere, or one that is shallow compared with the radius of the star, or we are not going to go very deep into the atmosphere. The point P is embedded in an absorbing, scattering, emitting gas. The flux coming up from below is equal to contributions from all the slices beneath P, from $t = \tau$ to $t = \infty$:

$$F_+ = 2\pi \int_{\tau}^{\infty} S(t) E_2(t - \tau) dt \quad (5.7.10)$$

The flux pouring down from above is the contribution from all the slices above, from $t = 0$ to $t = \tau$:

$$F_- = 2\pi \int_0^{\tau} S(t) E_2(\tau - t) dt \quad (5.7.11)$$

The net upward flux at a point P at an optical depth τ in an absorbing, scattering, emitting atmosphere is

$$F(\tau) = 2\pi \left[\int_{\tau}^{\infty} S(t)E_2(t-\tau)dt - \int_0^{\tau} S(t)E_2(\tau-t)dt \right] \quad (5.7.1)$$

The integral H is just $1/(4\pi)$ times this.

The reader is now asked to find the integrals $J(\tau)$ and $K(\tau)$. These should be given in the form of integrals that include a source function $S(t)$ and an exponential integral function $E(t-\tau)$ or $E(\tau-t)$. It is important to get the argument the right way round. One way is right; the other is wrong.

Problem 6

This is an easier problem, though the result is nevertheless important.

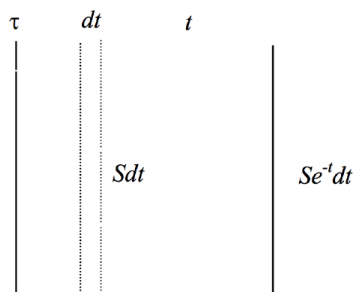


FIGURE V.5

Figure V.5 shows a slab of gas of optical thickness τ . The observer is supposed to be to the right of the slab, and optical depth is measured from the right hand face of the slab towards the left. At an optical depth t within the slab is a slice of optical thickness dt . The slab is supposed to have a uniform source function S throughout. Source function is specific intensity per unit optical thickness, so the specific intensity of the slice is Sdt . The emergent intensity from this slice, by the time that it reaches the right hand surface of the slab, is $Se^{-t}dt$. The emergent specific intensity of the entire slab is the sum of the contributions of all such slices throughout the slab; that is $\int_0^{\tau} Se^{-t}dt$. If the source function is uniform throughout the slab, so that S is not a function of t , we find that the emergent specific intensity of the slab is

$$I = S(1 - e^{-\tau}) \quad (5.7.2)$$

Problem. A quantity of hot gas is held in a box 50 cm long. The emission coefficient of the gas is $0.06 \text{ W sr}^{-1} \text{ m}^{-3}$ and the extinction coefficient is 0.025 cm^{-1} . What is the emergent specific intensity (radiance)? (I make it $1.71 \times 10^{-2} \text{ W m}^{-2} \text{ sr}^{-1}$.)

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5.8: Source function in scattering and absorbing atmospheres

Suppose that at some point in a stellar atmosphere the mean specific intensity per unit frequency interval surrounding it is J_ν . If all of the radiation arriving at that point is isotropically scattered, the emission coefficient j_ν will simply be $\sigma(\nu)J_\nu$. But from equation 5.6.1 we see that in a purely scattering atmosphere, the ratio of j_ν to $\sigma(\nu)$ is the source function. Thus we see that, for an atmosphere in which the extinction is due solely to scattering, the source function is just

$$S_\nu = J_\nu. \quad (5.8.1)$$

If on the other hand the extinction is all due to absorption, we have $S_\nu = j_\nu/\alpha(\nu)$. If we multiply top and bottom by dx , the numerator will be dI_ν , the increase in the specific intensity in a distance dx , while the denominator is the absorptance in a layer of thickness dx . Thus the source function in a purely absorbing atmosphere is the ratio of the specific intensity to the absorptance. But this ratio is the same for all surfaces, including that of a black body, for which the absorptance is unity. Thus in an atmosphere in which the extinction is due solely to absorption, the source function is equal to the specific intensity (radiance) of a black body, for which we shall use the symbol B . For a purely absorbing atmosphere, we have

$$S_\nu = B_\nu. \quad (5.8.2)$$

In an atmosphere in which extinction is by both scattering and absorption the source function is a linear combination of equations 5.8.1 and 5.8.2, in proportion to the relative importance of the two processes:

$$S_\nu = \frac{\alpha(\nu)}{\alpha(\nu) + \sigma(\nu)} B_\nu + \frac{\sigma(\nu)}{\alpha(\nu) + \sigma(\nu)} J_\nu \quad (5.8.3)$$

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5.9: More on the Equation of Transfer

Refer to equation 5.5.1. We see from what had been subsequently discussed that $[\alpha(\nu) + \sigma(\nu)]dx = d\tau(\nu)$ and that $j_\nu dx = d\tau(\nu)$. Therefore

$$\frac{dI_\nu}{d\tau(\nu)} = S_\nu - I_\nu, \quad (5.9.1)$$

and this is another form of the *equation of transfer*.

Now consider a spherical star with a shallow atmosphere ("plane parallel atmosphere"). In figure V.6, radial distance r is measured radially outwards from the centre of the star. Optical depth is measured from outside towards the centre of the star. The thickness of the layer is dr . The coordinate z is measured from the centre of the star towards the observer, and the path length through the atmosphere in that direction at angle θ is $dz = dr \sec \theta$. The equation of transfer can be written

$$dI_\nu(\theta) = -[\kappa(\nu)I_\nu(\theta) - j_\nu]dz. \quad (5.9.2)$$

Now $\kappa(\nu)dz = -\sec \theta d\tau(\nu)$ and $j_\nu = \kappa(\nu)S_\nu$. Therefore

$$\cos \theta \frac{dI_\nu(\theta)}{d\tau(\nu)} = I_\nu(\theta) - S_\nu \quad (5.9.3)$$

This is yet another form of the equation of transfer. The quantity $\cos \theta$ is often written μ , so that equation 5.9.3 is often written

$$\mu \frac{dI_\nu(\theta)}{d\tau(\nu)} = I_\nu(\theta) - S_\nu \quad (5.9.4)$$

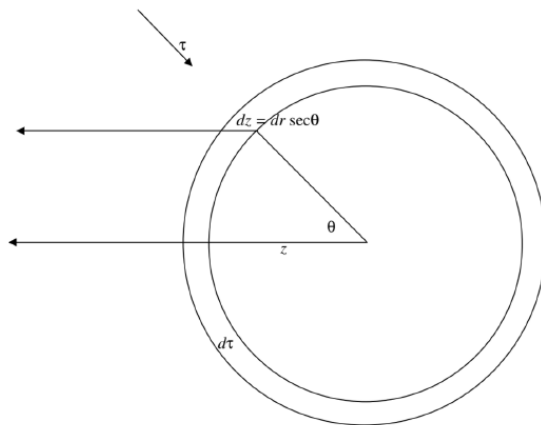


FIGURE V.6

Let us do $\frac{1}{4\pi} \oint d\omega$ to each term in equation 5.9.4. By \oint I mean integrate over 4π steradians. In spherical coordinates $d\omega = \sin \theta d\theta d\phi$. We obtain

$$\frac{1}{4\pi} \oint \frac{dI_\nu(\theta)}{d\tau(\nu)} \cos \theta d\omega = \frac{1}{4\pi} \oint I_\nu d\omega - \frac{1}{4\pi} \oint S_\nu d\omega \quad (5.9.5)$$

The left hand side is $dH_\nu/d\tau(\nu)$ and the first term on the right hand side is J_ν . (See the definitions - equations 4.5.2 and 4.7.1.) In the case of isotropic scattering, the source function is isotropic so that, in this case

$$\frac{dH_\nu}{d\tau(\nu)} = J_\nu - S_\nu, \quad (5.9.6)$$

and this is another form of the equation of transfer.

On the other hand, if we do $\frac{1}{4\pi} \oint \cos \theta d\omega$ to each term in equation 5.15, we obtain

$$\frac{1}{4\pi} \oint \frac{dI_\nu(\theta)}{d\tau(\nu)} \cos^2 \theta d\omega = \frac{1}{4\pi} \oint I_\nu \cos \theta d\omega - \frac{1}{4\pi} \oint S_\nu \cos \theta d\omega \quad (5.9.7)$$

In the case of isotropic scattering the last integral is zero, so that

$$\frac{dK_\nu}{d\tau(\nu)} = H_\nu, \quad (5.9.8)$$

and this is yet another form of the equation of transfer.

Now H_ν is independent of optical depth (why? - in a plane parallel atmosphere, this just expresses the fact that the flux (watts per square metre) is conserved), so we can integrate equation 5.9.8 to obtain

$$K_\nu = H_\nu \tau(\nu) + \text{constant} \quad (5.9.9)$$

Note also that $H_\nu = F_\nu/(4\pi)$, and, if the radiation is isotropic, $K_\nu = J_\nu/3$ so that,

$$J_\nu = \frac{3F_\nu \tau(\nu)}{4\pi} + J_\nu(0) \quad (5.9.10)$$

where $J_\nu(0)$ is the mean specific intensity (radiance) at the surface, which is half the specific intensity at the surface (since the radiance of the sky above the surface is zero). Thus

$$J_\nu(0) = \frac{1}{2} I_\nu(0) = F_\nu/(2\pi) \quad (5.9.11)$$

Therefore

$$J_\nu = \frac{F_\nu}{2\pi} \left(1 + \frac{3}{2} \tau(\nu) \right) \quad (5.9.12)$$

This shows, to this degree of approximation (which includes the approximation that the radiation in the atmosphere is isotropic - which can be the case exactly only at the centre of the star) how the mean specific intensity increases with optical depth.

Let T be the temperature at optical depth τ .

Let T_0 be the surface temperature.

Let T_{eff} be the effective temperature, defined by $F(0) = \sigma T_{\text{eff}}^4$,

We also have $\pi J = \sigma T^4$ and $\pi J(0) = \sigma T_0^4 = \frac{1}{2} F$.

From these we find the following relations between these temperatures:

$$T^4 = \left(1 + \frac{3}{2} \tau \right) T_0^4 = \frac{1}{2} \left(1 + \frac{3}{2} \tau \right) T_{\text{eff}}^4 \quad (5.9.13)$$

$$T_0^4 = \frac{2}{2 + 3\tau} T^4 = \frac{1}{2} T_{\text{eff}}^4 \quad (5.9.14)$$

$$T_{\text{eff}}^4 = \frac{4}{2 + 3\tau} T^4 = 2 T_0^4 \quad (5.9.15)$$

Note also that $T = T_{\text{eff}}$ at $\tau = 2/3$, and $T = T_0$ at $\tau = 0$.

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CHAPTER OVERVIEW

6: Limb Darkening

Limb darkening is an optical effect seen in stars (including the Sun), where the center part of the disk appears brighter than the edge or limb of the image.

Topic hierarchy

[6.1: Introduction. The Empirical Limb-darkening](#)

[6.2: Simple Models of the Atmosphere to Explain Limb Darkening](#)

Thumbnail: A filtered image of the Sun in visible light, showing the limb-darkening effect as a dimmer luminosity towards the edge or limb of the solar disk. The image was taken during the 2012 transit of Venus (seen here as the dark spot at the upper right). (CC BY 2.5; [Brocken Inaglory](#)).

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6.1: Introduction. The Empirical Limb-darkening

The Sun is not equally bright all over, but it is darkened towards the limb. The effect is more pronounced at the blue end of the spectrum and less pronounced at the red. A reasonably good empirical representation of the form of the limb darkening is given by an equation for the specific intensity of the form

$$I(r) = I(0) \left[1 - u \left(1 - \sqrt{\frac{a^2 - r^2}{a^2}} \right) \right] \quad (6.1.1)$$

Here, a is the radius of the solar disc, r is radial distance from the center of the disc and u is the *limb darkening coefficient*. This is often written in terms of θ (see Figure VI.1) or of $\mu = \cos \theta$:

$$I(\theta) = I(0) [1 - u(1 - \cos \theta)] \quad (6.1.2)$$

$$= I(0)[1 - u(1 - \mu)] \quad (6.1.3)$$

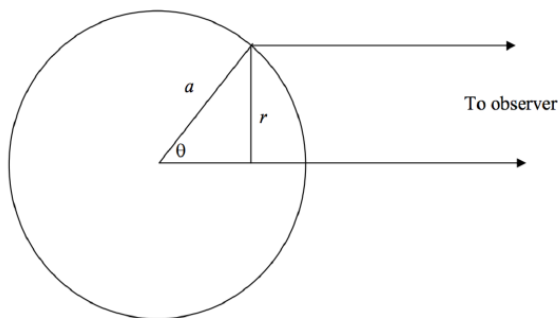


FIGURE VI.1

Whether written in the form of Equation 6.1.1 or 6.1.3, $I(0)$ is the specific intensity at the center of the disc. The specific intensity at the limb (where $r = a$ or $\theta = 90^\circ$) is $I(0)(1 - u)$. The limb darkening coefficient can be written as

$$u = \frac{I(\text{center}) - I(\text{limb})}{I(\text{center})}. \quad (6.1.4)$$

Equation 6.1.1 is shown in graphical form in figure VI.2 for different values of the limb darkening coefficient.

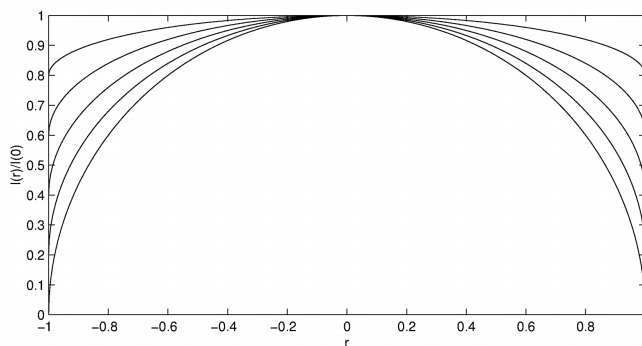


FIGURE VI.2. Equation 6.1.1 for six limb darkening coefficients, from the lowest curve upwards, $u = 1.0, 0.8, 0.6, 0.4, 0.2$ and 0.0 . The "curve" for the last of these (no limb darkening) is formed from three of the boundary lines. The curve for $u = 1$ is a circle. The radius of the disc is taken to be 1, $r = 0$ is the center of the disc and $r = \pm 1$ is the limb.

Limb-darkening is much greater in the violet and near ultraviolet than in the red. For example, at a wavelength of 600 nm, $u = 0.56$, whereas at 320 nm $u = 0.95$.

A slightly better empirical representation of the limb darkening can be obtained with two parameters, u' and ν' :

$$I(\theta) = I(0) [1 - u'(1 - \cos \theta) - \nu' \sin^2 \theta] \quad (6.1.5)$$

Why is the Sun darkened towards the limb?

We may perhaps imagine that the surface of the Sun radiates like a black body with uniform lambertian radiance, but it is surrounded by an absorbing atmosphere. Light from near the limb has to traverse a greater length of atmosphere than light from near the center of the disk and this accounts for the limb darkening. If that is the explanation, we should be able to calculate what form of limb darkening to expect, and see how well it agrees with what is observed. If the agreement is only moderately good, perhaps we could assume that the atmosphere is not only an absorbing atmosphere, but it also emits radiation of its own, and we could see if we could adjust the ratio of emission to extinction (the source function) to obtain good agreement with the model and the observations. Or perhaps, rather than thinking of a uniform radiating surface sharply separated from a surrounding atmosphere, we may imagine that there is no such sharp boundary, but, rather, the density and temperature of the solar gases increase continuously with depth. In that case, suppose that we can see everywhere to a given optical depth, say to $\tau = 1$. Near the limb, an optical depth of unity does not take us very deep (in terms of kilometers) into the atmosphere, because we are looking almost tangentially at the surface of the Sun, so we reach only relatively high levels in the atmosphere where the temperature is relatively cool. Near the center, on the other hand, where we are peering down perpendicularly into the Sun, an optical depth of one reaches deep down (in terms of kilometers) to places where the atmosphere is very hot. Thus the center appears brighter than the limb.

At any rate, the point is that, by making precise measurements of the form of the limb darkening and comparing these measurements with the predictions of different models, we should in principle be able to deduce something about the run of density and temperature with optical depth in the atmosphere.

One practical difficulty of doing this is that it turns out that it is necessary to make quite precise measurements of the exact form of the limb darkening very close to the limb to be able to distinguish convincingly between different models.

Are there any prospects of being able to measure the limb darkening of stars other than the Sun? The future will tell whether advances in technology, such as adaptive optics, may enable us to observe the limb darkening of other stars directly. Other methods are possible. For example, the detailed light curve of an eclipsing binary star undoubtedly gives us information on the limb darkening of the star that is being eclipsed. There are many factors that affect the form of the light curve of an eclipsing binary star, and the detailed interpretation of light curves is not at all easy - but no one ever claimed that astronomy was easy. In principle lunar or asteroidal occultations of stars might enable us to determine the limb darkening of a star. Another possible method is from a careful examination of the line profiles in the spectrum of a rotating star. If a star is of uniform brightness and is rotating rapidly, the intensity profiles of its spectrum lines are broadened and have a semi-elliptical profile. However, if the star is darkened towards the limb, the line profile is affected. If the star's disk is completely limb darkened ($u = 1$, so that the specific intensity at the limb is zero), it is an interesting exercise to show that the line profile is parabolic. For intermediate limb darkening, the profile is neither elliptical nor parabolic; an exact analysis of its shape could in principle tell us the limb darkening coefficient.

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6.2: Simple Models of the Atmosphere to Explain Limb Darkening

1. The Sun consists of a spherical body emitting continuous blackbody radiation of radiance (specific intensity) B_ν surrounded by a shallow ("plane parallel") atmosphere which absorbs light and is of optical thickness $\tau(\nu)$ but does not emit. See figure VI.3.

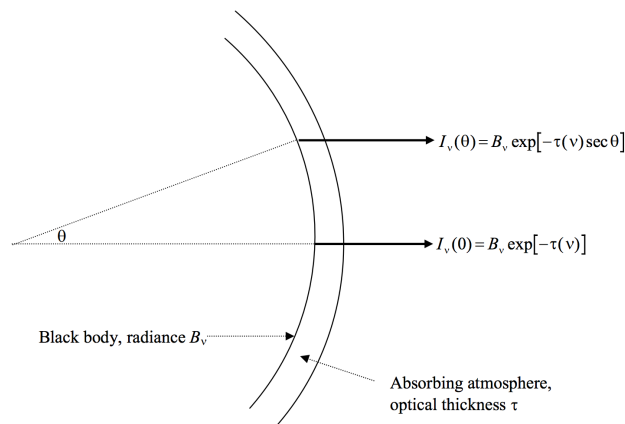


FIGURE VI.3

The emergent specific intensity at the centre of the disc is

$$I_\nu(0) = B_\nu e^{-\tau(\nu)} \quad (6.2.1)$$

and at a position on the disc given by θ is

$$I_\nu(\theta) = B_\nu e^{-\tau(\nu) \sec \theta} \quad (6.2.2)$$

so that the limb darkening is given by

$$I_\nu(\theta) = I_\nu(0) e^{-\tau(\nu)(\sec \theta - 1)} \quad (6.2.3)$$

If the limb darkening is indeed like this, then a graph of $\ln[I_\nu(\theta)/I_\nu(0)]$ versus $1 - \sec \theta$ will be a straight line whose slope will be the optical thickness of the atmosphere. However, in practice such a graph does not yield a straight line, and a comparison of Equation 6.2.3, which is shown in figure VI.4, with the observed limb darkening shown in figure VI.2, suggests that this is not at all a promising model.

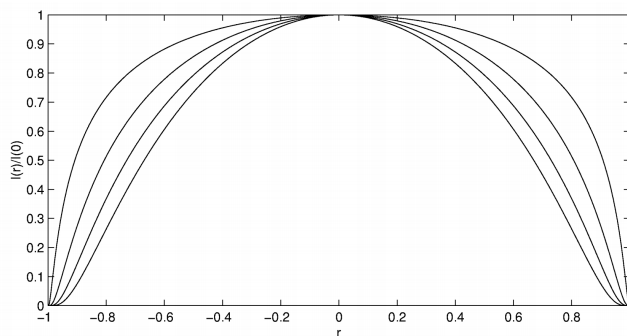


FIGURE VI.4

Equation 6.2.3 for four values of the optical thickness τ of the atmosphere. The curves are drawn for $\tau = 0.2, 0.4, 0.6$ and 0.8 . The curves do not greatly resemble the empirical, observed curves of figure VI.2, suggesting that this is not a very good atmospheric model.

2. This second model is similar to the first model, except that the atmosphere emits radiation as well as absorbing it. We suppose that the surface of the Sun is a black body of specific intensity B_1 . The subscript 1 refers to the surface of the Sun. I have omitted a subscript ν . The argument is the same whether we are dealing with the specific intensity per unit frequency interval (Planck function) or the integrated specific intensity (Stefan's law). Suppose that the atmosphere, of optical thickness τ , is an emitting, absorbing atmosphere, of source function B_2 , being a Planck function corresponding to a cooler temperature than the surface. The

emergent specific intensity will be the sum of the emergent intensity of the atmosphere (see Equation 5.7.2) and the specific intensity of the surface reduced by its passage through the atmosphere. At the centre of the disc, this will be

$$I(0) = B_1 e^{-\tau} + B_2 (1 - e^{-\tau}) \quad (6.2.4)$$

and at a position θ on the disc it will be

$$I(\theta) = B_1 e^{-\tau \sec \theta} + B_2 (1 - e^{-\tau \sec \theta}) \quad (6.2.5)$$

and so the limb darkening will be given by

$$\frac{I(\theta)}{I(0)} = \frac{(B_1 - B_2)e^{-\tau \sec \theta} + B_2}{(B_1 - B_2)e^{-\tau} + B_2} \quad (6.2.6)$$

In attempting to find a good fit between Equation 6.2.6 and the observed limb darkening, we now have two adjustable parameters, τ and the ratio B_2/B_1 . In figure VI.5 we show the limb darkening for $\tau = 0.5, 1.0, 1.5$ and 2.0 for a representative ratio $B_2/B_1 = 0.5$. If we are dealing with radiation integrated over all wavelengths, this would imply an atmospheric temperature equal to $(0.5)^{1/4} = 0.84$ times the surface temperature. There is no combination of the two parameters that gives a limb darkening very similar to the observed limb darkening, so this model is not a specially good one.

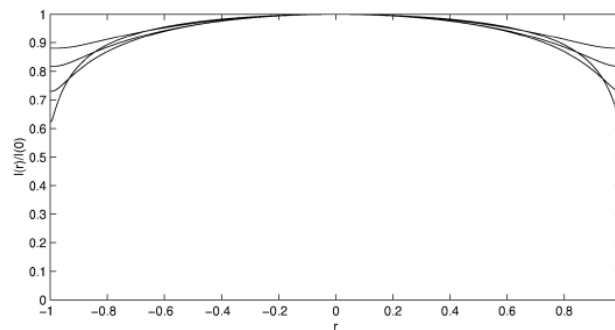


FIGURE VI.5

Equation 6.2.6 for $B_2/B_1 = 0.5$, and $\tau = 0.5, 1.0, 1.5$ and 2.0 .

3. In this model we do not assume a hard and fast photosphere surrounded by an atmosphere of uniform source function; rather, we suppose that the source function varies continuously with depth. In figure VI.6 we draw two levels in the atmosphere, at optical depths τ and $\tau + d\tau$. The reader should recall that we are dealing only with a "plane parallel" atmosphere - i.e. one that is shallow compared with the radius of the star. The geometric distance between the two levels is therefore much exaggerated in the figure.

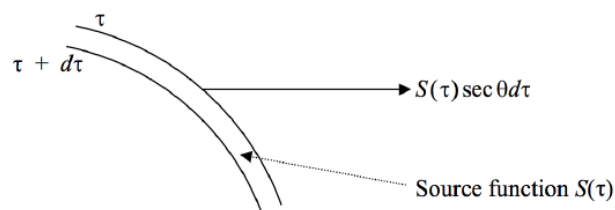


FIGURE VI.6

The source function of the shell between optical depths τ and $\tau + d\tau$ is $S(\tau)$. In the direction θ the radiance (specific intensity) of an elemental shell of optical thickness $d\tau$ is $S(\tau) \sec \theta d\tau$. (I have not explicitly indicated in this expression the dependence on frequency or wavelength of the source function or optical depth.) By the time the radiation from this shell reaches the outermost part of the atmosphere (i.e. where $\tau = 0$), it has been reduced by a factor $e^{-\tau \sec \theta}$. The specific intensity resulting from the addition of all such elemental shells is

$$I(\theta) = \sec \theta \int_0^\infty S(\tau) e^{-\tau \sec \theta} d\tau \quad (6.2.7)$$

This important Equation, attributed to Karl Schwarzschild, gives the limb darkening as a function of the way in which the source function varies with optical depth. The usual situation is that it is the limb darkening that is known and it is required to find $S(\tau)$,

so that Equation 6.2.7 has to be solved as an integral Equation. This, however, is not as difficult as it may first appear because it will be noticed that if we write $s = \sec \theta$, the Equation is merely a [Laplace Transform](#):

$$I(s) = sL[S(\tau)] \quad (6.2.8)$$

so that the source function is the inverse Laplace transform of the limb darkening.

If we assume that the source function can be expressed as a polynomial in the optical depth:

$$S(\tau) = I(0) (a_0 + a_1 \tau + a_2 \tau^2 \dots) \quad (6.2.9)$$

we find for the limb darkening (remembering that $1/s = \cos \theta$)

$$I(\theta) = I(0) (a_0 + a_1 \cos \theta + 2a_2 \cos^2 \theta \dots) \quad (6.2.10)$$

If we compare this with the empirical limb darkening Equation 6.1.3 we find the a coefficients in terms of the limb darkening coefficients, as follows:

$$a_0 = 1 - u' - \nu' \quad (6.2.11)$$

$$a_1 = u' \quad (6.2.12)$$

$$a_2 = \frac{1}{2} \nu' \quad (6.2.13)$$

If we extend this analysis a little further, we find that if the source function is given by

$$S(\tau) = I(0) \sum_0^N a_n \tau^n \quad (6.2.14)$$

the limb darkening is

$$I(\theta) = I(0) \sum_0^N u_n \mu^n \quad (6.2.15)$$

where $\mu = \cos \theta$ and it is left to the reader to determine a general relation between the a_n and the u_n .

? Exercise 6.2.1

If the limb darkening is given by Equation ???, calculate the mean specific intensity (radiance) \bar{I} over the solar disc in terms of $I(0)$ and u . If the limb darkening is given by Equation ???, what is the mean specific intensity in terms of $I(0)$, u' and ν' ? This is an important calculation because if, for example, you need to calculate the irradiance of a planet or a comet by the Sun, the intensity of the Sun is the mean radiance times the projected area of the solar disc

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CHAPTER OVERVIEW

7: Atomic Spectroscopy

Topic hierarchy

- 7.1: Introduction
- 7.2: A Very Brief History of Spectroscopy
- 7.3: The Hydrogen Spectrum
- 7.4: The Bohr Model of Hydrogen-like Atoms
- 7.5: One-dimensional Waves in a Stretched String
- 7.6: Vibrations of a Uniform Sphere
- 7.7: The Wave Nature of the Electron
- 7.8: Schrödinger's Equation
- 7.9: Solution of Schrödinger's Time-independent Equation for the Hydrogen Atom
- 7.10: Operators, Eigenfunctions and Eigenvalues
- 7.11: Spin
- 7.12: Electron Configurations
- 7.13: LS-coupling
- 7.14: States, Levels, Terms, Polyads, etc.
- 7.15: Components, Lines, Multiplets, etc.
- 7.16: Return to the Hydrogen Atom
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7.1: Introduction

Atomic spectroscopy is, of course, a vast subject, and there is no intention in this brief chapter of attempting to cover such a huge field with any degree of completeness, and it is not intended to serve as a formal course in spectroscopy. For such a task a thousand pages would make a good start. The aim, rather, is to summarize some of the words and ideas sufficiently for the occasional needs of the student of stellar atmospheres. For that reason this short chapter has a mere 26 sections.

Wavelengths of spectrum lines in the visible region of the spectrum were traditionally expressed in angstrom units (\AA) after the nineteenth century Swedish spectroscopist Anders Ångström, one \AA being 10^{-10}m . Today, it is recommended to use nanometres (nm) for visible light or micrometres (μm) for infrared. $1\text{ nm} = 10\text{ \AA} = 10^{-3}\mu\text{m} = 10^{-9}\text{m}$. The older word *micron* is synonymous with micrometre, and should be avoided, as should the isolated abbreviation μ . The usual symbol for wavelength is λ .

Wavenumber is the reciprocal of wavelength; that is, it is the number of waves per metre. The usual symbol is σ , although $\tilde{\nu}$ is sometimes seen. In SI units, wavenumber would be expressed in m^{-1} , although cm^{-1} is often used. The extraordinary illiteracy "a line of 15376 wavenumbers" is heard regrettably often. What is intended is presumably "a line of wavenumber 15376 cm^{-1} ." The kayser was an unofficial unit formerly seen for wavenumber, equal to 1 cm^{-1} . As some wag once remarked: "The Kaiser (kayser) is dead!"

It is customary to quote wavelengths below 200 nm as wavelengths *in vacuo*, but wavelengths above 200 nm in "standard air". Wavenumbers are usually quoted as wavenumbers *in vacuo*, whether the wavelength is longer or shorter than 200 nm. Suggestions are made from time to time to abandon this confusing convention; in any case it is incumbent upon any writer who quotes a wavelength or wavenumber to state explicitly whether s/he is referring to a vacuum or to standard air, and not to assume that this will be obvious to the reader. Note that, in using the formula $n_1\lambda_1 = n_2\lambda_2 = n_3\lambda_3$ used for overlapping orders, the wavelength concerned is neither the vacuum nor the standard air wavelength; rather it is the wavelength in the actual air inside the spectrograph.

If I use the symbols λ_0 and σ_0 for vacuum wavelength and wavenumber and λ and σ for wavelength and wavenumber in standard air, the relation between λ and σ_0 is

$$\lambda = \frac{1}{n\sigma_0} \quad (7.1.1)$$

"Standard air" is a mythical substance whose refractive index n is given by

$$(n-1) \cdot 10^7 = 834.213 + \frac{240603.0}{130 - \sigma_0^2} + \frac{1599.7}{38.9 - \sigma_0^2}, \quad (7.1.2)$$

where σ_0 is in μm^{-1} . This corresponds closely to that of dry air at a pressure of 760 mm Hg and temperature 15°C containing 0.03% by volume of carbon dioxide.

To calculate λ given σ_0 is straightforward. To calculate σ_0 given λ requires iteration. Thus the reader, as an exercise, should try to calculate the vacuum wavenumber of a line of standard air wavelength 555.5 nm. In any case, the reader who expects to be dealing with wavelengths and wavenumbers fairly often should write a small computer or calculator program that allows the calculation to go either way.

Frequency is the number of waves per second, and is expressed in hertz (Hz) or MHz or GHz, as appropriate. The usual symbol is ν , although f is also seen. Although wavelength and wavenumber change as light moves from one medium to another, frequency does not. The relation between frequency, speed and wavelength is

$$c = \nu\lambda_0 \quad (7.1.3)$$

where c is the speed *in vacuo*, which has the defined value $2.997\,924\,58 \times 10^8\text{ m s}^{-1}$.

A spectrum line results from a transition between two energy levels of an atom. The frequency of the radiation involved is related to the difference in energy levels by the familiar relation

$$h\nu = \Delta E, \quad (7.1.4)$$

where h is Planck's constant, $6.626075 \times 10^{-34}\text{ J s}$. If the energy levels are expressed in joules, this will give the frequency in Hz. This is not how it is usually done, however. What is usually tabulated in energy level tables is $E/(hc)$, in units of cm^{-1} . This quantity is known as the *term value* T of the level. Equation 7.1.4 then becomes

$$\sigma_0 = \Delta T \quad (7.1.5)$$

Thus the vacuum wavenumber is simply the difference between the two tabulated term values.

In some contexts it may also be convenient to express energy levels in electron volts, 1 eV being $1.60217733 \times 10^{-19}$ J. Energy levels of neutral atoms are typically of the order of a few eV. The energy required to ionize an atom from its ground level is called the *ionization energy*, and its SI unit would be the joule. However, one usually quotes the ionization energy in eV, or the *ionization potential* in volts.

It may be remarked that sometimes one hears the process of formation of a spectrum line as one in which an "electron" jumps from one energy level to another. This is quite wrong. It is true that there is an adjustment of the way in which the electrons are distributed around the atomic nucleus, but what is tabulated in tables of atomic energy levels or drawn in energy level diagrams is the energy of the *atom*, and in equation 7.1.4 ΔE is the change in energy of the *atom*. This includes the kinetic energy of all the particles in the atom as well as the mutual potential energy between the particles.

We have seen that the wavenumber of a line is equal to the difference between the term values of the two levels involved in its formation. Thus, if we know the term values of two levels, it is a trivial matter to calculate the wavenumber of the line connecting them. In spectroscopic analysis the problem is very often the converse - you have measured the wavenumbers of several spectrum lines; can you from these calculate the term values of the levels involved? For example, here are four (entirely hypothetical and artificially concocted for this problem) vacuum wavenumbers, in μm^{-1} :

1.96643
2.11741
2.28629
2.43727

The reader who is interested on spectroscopy, or in crossword puzzles or jigsaw puzzles, is very strongly urged to calculate the term values of the four levels involved with these lines, and to see whether this can or cannot be done without ambiguity from these data alone. Of course, you may object that there are six ways in which four levels can be joined in pairs, and therefore I should have given you the wavenumbers of six lines. Well, sorry to be unsympathetic, but perhaps two of the lines are too faint to be seen, or they may be forbidden by selection rules, or their wavelengths might be out of the range covered by your instrument. In any case, I have told you that four levels are involved, which is more information that you would have if you had just measured the wavenumbers of these lines from a spectrum that you had obtained in the laboratory. And at least I have helped by converting standard air wavelengths to vacuum wavenumbers. The exercise will give some appreciation of some of the difficulties in spectroscopic analysis.

In the early days of spectroscopy, in addition to flames and discharge tubes, common spectroscopic sources included arcs and sparks. In an arc, two electrodes with a hundred or so volts across them are touched, and then drawn apart, and an arc forms. In a spark, the potential difference across the electrodes is some thousands of volts, and it is not necessary to touch the electrodes together; rather, the electrical insulation of the air breaks down and a spark flies from one electrode to the other. It was noticed that the arc spectrum was usually very different from the spark spectrum, the former often being referred to as the "first" spectrum and the latter as the "second" spectrum. If the electrodes were, for example, of carbon, the arc or first spectrum would be denoted by C I and the spark or second spectrum by C II. It has long been known now that the "first" spectrum is mostly that of the neutral atom, and the "second" spectrum mostly that of the singly-charged ion. Since the atom and the ion have different electronic structures, the two spectra are very different. Today, we use the symbols C I, or Fe I, or Zr I, etc., to denote the spectrum of the neutral atom, regardless of the source, and C II, C III, C IV, etc., to denote the spectra of the singly-, doubly- triply-ionized atoms, C^+ , C^{++} , C^{+++} , etc. There are 4278 possible spectra of the first 92 elements to investigate, and many more if one adds the transuranic elements, so there is no want of spectra to study.

Hydrogen, of course, has only one spectrum, denoted by H I, since ionized hydrogen is merely a proton. The regions in space where hydrogen is mostly ionized are known to astronomers as "H II regions". Strictly, this is a misnomer, for there is no "second spectrum" of hydrogen, and a better term would be " H^+ regions", but the term "H II regions" is by now so firmly entrenched that it is unlikely to change. It is particularly ironic that the spectrum exhibited by an "H II region" is that of neutral hydrogen (e.g. the well-known Balmer series), as electrons and protons recombine and drop down the energy level ladder. On the other hand, apart from the 21 cm line in the radio region, the excitation temperature in regions where hydrogen is mostly neutral (and hence called, equally wrongly, "H I regions") is far too low to show the typical spectrum of neutral hydrogen, such as the Balmer series. Thus it can be accurately said that "H II regions" show the spectrum of H I, and "H I regions" do not. Lest it be thought that this is

unnecessary pedantry, it should be made clear at the outset that the science of spectroscopy, like those of celestial mechanics or quantum mechanics, is one in which meticulous accuracy and precision of ideas is an absolute necessity, and there is no room for vagueness, imprecision, or improper usage of terms. Those who would venture into spectroscopy would do well to note this from the beginning.

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7.2: A Very Brief History of Spectroscopy

Perhaps the first quantitative investigation that can be said to have a direct bearing on the science of spectroscopy would be the discovery of Snel's law of refraction in about 1621. I am not certain, but I believe the original spelling of the Dutch mathematician who discovered the law was Willebrod Snel or Willebrord Snel, whose name was latinized in accordance with the custom of learned scholars of the day to Snellius, and later anglicized to the more familiar spelling Snell.

Sir Isaac Newton's experiments were described in his *Opticks* of 1704. A most attractive illustration of the experiment, described in a work by Voltaire, is reproduced in Condon and Shortly's famous *Theory of Atomic Spectra* (1935). Newton showed that sunlight is dispersed by a prism into a band of colours, and the colours are recombined into white light when passed through an oppositely-oriented second prism. The infrared spectrum was discovered by Sir William Herschel in 1800 by placing thermometers beyond the red end of the visible spectrum. Johann Ritter the following year (and independently Wollaston) discovered the ultraviolet spectrum. In the period 1800-1803 Thomas Young demonstrated the wave nature of light with his famous double slit experiment, and he correctly explained the colours of thin films using the undulatory theory. Using Newton's measurements of this phenomenon, Young computed the wavelengths of Newton's seven colours and obtained the range 424 to 675 nm. In 1802 William Wollaston discovered dark lines in the solar spectrum, but attached little significance to them.

In 1814 Joseph Fraunhofer, a superb instrument maker, made a detailed examination of the solar spectrum; he made a map of 700 of the lines we now refer to as "Fraunhofer lines". (Spectrum lines in general are sometimes described as "Fraunhofer lines", but the term should correctly be restricted to the dark lines in the solar spectrum.) In 1817 he observed the first stellar spectra with an objective prism. He noted that planetary spectra resembled the solar spectrum, while many stellar spectra differed. Although the phenomenon of diffraction had been described as early as 1665 by Grimaldi, and Young had explained double-slit diffraction, Fraunhofer constructed the first *diffraction grating* by winding wires on two finely-cut parallel screws. With these gratings he measured the first wavelengths of spectrum lines, obtaining 588.7 for the line he had labelled D. We now know that this line is a close pair of lines of Na I, whose modern wavelengths are 589.0 and 589.6 nm. That different chemical elements produce their own characteristic spectra was noted by several investigators, including Sir John Herschel, (son of Sir William), Fox Talbot (pioneer in photography), Sir Charles Wheatstone (of Wheatstone Bridge fame), Anders Ångström (after whom the now obsolete unit the angstrom, Å, was named), and Jean Bernard Foucault (famous for his pendulum but also for many important studies in physical optics, including the speed of light) and especially by Kirchhoff and Bunsen. The fundamental quantitative law known as Kirchhoff's Law (see Chapter 2, section 2.4) was announced in 1859, and Kirchhoff and Bunsen conducted their extensive examination of the spectra of several elements. They correctly explained the origin of the solar Fraunhofer lines, investigated the chemical composition of the solar atmosphere, and laid the basic foundations of spectrochemical analysis. In 1868 Ångström published wavelengths of about 1000 solar Fraunhofer lines. In the 1870s, Rowland started to produce diffraction gratings of unparalleled quality and published extensive lists of solar wavelengths. New elements were being discovered spectroscopically:

Cs, Rb, Tl (1860-61); In (1863); He (1868 - in the chromosphere of the solar spectrum at the instants of second and third contact of a solar eclipse, by Lockyer); Ga (1875); Tm (1870); Nd, Pr (1885); Sm, Ho (1886); Lu, Yb (1907).

Michelson measured the wavelength of three Cd I lines with great precision in 1893, and Fabry and Pérot measured the wavelengths of other lines in terms of the Cd I standards. For many years the wavelength of a cadmium lines was used as a basis for the definition of the metre.

Although the existence of ultraviolet radiation had been detected by Richter, the first person actually to see an ultraviolet (UV) spectrum was Sir George Stokes (of viscosity and fluorescence fame), using a quartz prism (ordinary glass absorbs UV) and a fluorescent uranium phosphate screen. In 1906 Lyman made extensive investigations into ultraviolet spectra, including the hydrogen series now known as the Lyman series. Langley invented the bolometer in 1881, paving the way to the investigation of infrared spectra by Paschen. Balmer published his well-known formula for the wavelengths of the hydrogen Balmer series in 1885. Zeeman discovered magnetic splitting in 1896. Bohr's theory of the hydrogen atom appeared in 1913, and the wave mechanics of Schrödinger was developed in the mid 1920s.

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7.3: The Hydrogen Spectrum

In 1885, J. J. Balmer, a lecturer in a ladies' college in Switzerland, devised a simple formula relating the wavelengths of the lines in the visible region of the atomic hydrogen spectrum to the natural numbers, and these lines have since been referred to as the Balmer series and have been denoted by $H\alpha$, $H\beta$, $H\gamma$, ..., starting at the long wavelength end. The standard air wavelengths in nm and the vacuum wavenumbers in μm^{-1} are as follows:

	λ nm	σ_0 μm^{-1}
$H\alpha$	656.28	1.5233
$H\beta$	486.13	2.0565
$H\gamma$	434.05	2.3032
$H\delta$	410.17	2.4373
$H\epsilon$	397.01	2.5181

(7.3.1)

The series eventually converges to a series limit, the *Balmer limit*, at a standard air wavelength of 364.60 nm or a vacuum wavenumber of $2.7420 \mu\text{m}^{-1}$. In the way in which Balmer's formula is usually written today, the vacuum wavenumbers of the lines in the Balmer series are given by

$$\sigma_0 = R \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots \quad (7.3.2)$$

n being 3, 4, 5, etc., for $H\alpha$, $H\beta$, $H\gamma$, etc. The number R is called the *Rydberg constant for hydrogen*, and has the value $10.9679 \mu\text{m}^{-1}$.

Later, a similar series, to be named the *Lyman series*, was discovered in the ultraviolet, and several similar series were found in the infrared, named after Paschen, Brackett, Pfund, Humphreys, Hansen and Strong, and successively less famous people. Indeed in the radio region of the spectrum there are series named just for numbers; thus we may talk about the 109α line.

A single formula can be used to generate the wavenumbers of the lines in each of these series:

$$\sigma_0 = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_2 = n_1 + 1, n_1 + 2, \dots \quad (7.3.3)$$

Here $n_1 = 1, 2, 3, 4, 5, 6, \dots$ for the Lyman, Balmer, Paschen, Brackett, Pfund, Humphreys... series.

Similar (not identical) spectra are observed for other hydrogen-like atoms, such as He^+ , Li^{++} , Be^{+++} , etc., the Rydberg constants for these atoms being different from the Rydberg constant for hydrogen. Deuterium and tritium have very similar spectra and their Rydberg constants are very close to that of the ^1H atom.

Each "line" of the hydrogen spectrum, in fact, has fine structure, which is not easily seen and usually needs carefully designed experiments to observe it. This fine structure need not trouble us at present, but we shall later be obliged to consider it. An interesting historical story connected with the fine structure of hydrogen is that the quantity $e^2/(4\pi\epsilon_0\hbar c)$ plays a prominent role in the theory that describes it. This quantity, which is a dimensionless pure number, is called the *fine structure constant* α , and the reciprocal of its value is close to the prime number 137. Sir Arthur Eddington, one of the greatest figures in astrophysics in the early twentieth century, had an interest in possible connections between the fundamental constants of physics and the natural numbers, and became almost obsessed with the notion that the reciprocal of the fine structure constant should be *exactly* 137, even insisting on hanging his hat on a conference hall coatpeg number 137.

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7.4: The Bohr Model of Hydrogen-like Atoms

The model proposed in 1913 by the Danish physicist Niels Bohr (and later further developed by Arnold Sommerfeld) to describe the hydrogen spectrum was of great importance in the historical development of atomic theory. Even though it is very different from the modern description of an atom, it is difficult to avoid a summary of it in any introductory description of spectroscopy. In the simplest form, we could describe a model of an electron moving around a proton in a circular orbit. Here, however, we shall include in the theory such hydrogenlike atoms as He^+ , Li^{++} , Be^{+++} , etc. Furthermore, we shall not suppose that the electron moves around the nucleus; rather we assume that the nucleus has a charge Ze (Z = atomic number) and mass M , and the electron has a mass m , and the electron and nucleus move around their common centre of mass.

In Bohr's original model it was assumed that the electron could move round only in certain circular orbits (he and Sommerfeld later included the possibility of elliptic orbits in order to explain fine structure) such that the angular momentum is an integral multiple of Planck's constant divided by 2π . [The symbol \hbar is short for $h/(2\pi)$ and is a quantum unit of angular momentum.] This was an empirical assumption made only because it correctly predicted the appearance of the hydrogen spectrum.

Let us suppose that the hydrogen-like atom has a nucleus of charge $+Ze$ and mass M , and the electron has charge $-e$ and mass m , and that the distance between them is a . The distance of the nucleus from the centre of mass is $ma/(M+m)$ and the distance of the electron from the centre of mass is $Ma/(M+m)$. We'll suppose that the speed of the electron in its orbit around the centre of mass is v . It may not be immediately obvious, and the reader should take the trouble to derive it, that the angular momentum of the system is mva . Bohr's first assumption, then is that

$$mva = n\hbar, \quad (7.4.1)$$

where n is an integer.

The Coulomb force on the electron is equal to its mass times its centripetal acceleration:

$$\frac{Ze^2}{4\pi\epsilon_0 a^2} = \frac{mv^2}{Ma/(M+m)}. \quad (7.4.2)$$

If you eliminate v from these, you obtain an expression for the radius of the n th orbit:

$$a = \frac{4\pi\epsilon_0 \hbar^2 n^2}{Ze^2 \mu}, \quad (7.4.3)$$

where

$$\mu = \frac{mM}{m+M}. \quad (7.4.4)$$

The quantity represented by the symbol μ is called the *reduced mass* of the electron. It is slightly less than the actual mass of the electron. In the hydrogen atom, in which the nucleus is just a proton, the ratio M/m is about 1836, so that $\mu = 0.99946m$. For heavier hydrogen-like atoms it is closer to m .

Notice that the radius depends on n^2 , so that, for example, the radius of the $n = 2$ orbit is four times that of the $n = 1$ orbit. The reader should now calculate the radius of the first Bohr orbit for hydrogen. It should come to about 0.053 nm, so that the diameter of the hydrogen atom in its ground state is a little over one angstrom. Logically, I suppose, the symbol a_1 should be used for the first Bohr orbit, but in practice the usual symbol used is a_0 . If you wish to calculate the radius of the first Bohr orbit for some other hydrogen-like atom, such as D, or He^+ , or muonic hydrogen, note that for such atoms the only things that are different are the masses or charges or both, so there is no need to repeat the tedious calculations that you have already done for hydrogen. It would also be of interest to calculate the radius of the orbit with $n = 109$, in view of the observation of the radio line 109 α mentioned in section 7.3.

By eliminating a rather than v from equations 7.4.1 and 7.4.2 you could get an explicit expression for the speed of the electron in its orbit. Alternatively you can simply calculate v from equation 7.4.2 now that you know a . You should, for interest, calculate v , the speed of the electron in the first Bohr orbit, and see how large a fraction it is of the speed of light and hence to what extent our nonrelativistic analysis so far has been. You should also calculate the frequency of the orbital electron - i.e. how many times per second it orbits the nucleus. The explicit expression for v is

$$v = \frac{MZe^2}{4\pi\epsilon_0(M+m)\hbar n}. \quad (7.4.5)$$

The energy of the atom is the sum of the mutual potential energy between nucleus and electron and the orbital kinetic energies of the two particles. That is:

$$E = -\frac{Ze^2}{4\pi\epsilon_0 a} + \frac{1}{2}mv^2 + \frac{1}{2}M\left(\frac{mv}{M}\right)^2. \quad (7.4.6)$$

If we make use of equation 7.4.2 this becomes

$$\begin{aligned} E &= -\frac{m(M+m)v^2}{M} + \frac{1}{2}mv^2 + \frac{1}{2}\frac{m^2}{M}v^2 \\ &= -\frac{1}{2}m\left(\frac{M+m}{M}\right)v^2. \end{aligned}$$

Then, making use of equation 7.4.5, we obtain for the energy

$$E = -\frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \cdot \frac{1}{n^2}. \quad (7.4.7)$$

In deriving this expression for the energy, we had taken the potential energy to be zero at infinite separation of proton and nucleus, which is a frequent convention in electrostatics. That is, the energy level we have calculated for a bound orbit is expressed relative to the energy of ionized hydrogen. Hence the energy of all bound orbits is negative. In tables of atomic energy levels, however, it is more usual to take the energy of the ground state ($n = 1$) to be zero. In that case the energy levels are given by

$$E = \frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \cdot \left(1 - \frac{1}{n^2}\right). \quad (7.4.8)$$

Further, as explained in section 7.1, it is customary to tabulate *term values* T rather than energy levels, and this is achieved by dividing by hc . Thus

$$T = \frac{\mu Z^2 e^4}{2(4\pi\epsilon_0)^2 \hbar^2 hc} \cdot \left(1 - \frac{1}{n^2}\right). \quad (7.4.9)$$

The expression before the large parentheses is called the *Rydberg constant* for the atom in question. For hydrogen ($^1\text{H} : Z = 1$), it has the value $1.09679 \times 10^7 \text{ m}^{-1}$.

If we put $Z = 1$ and $\mu = m$ the resulting expression is called the *Rydberg constant for a hydrogen nucleus of infinite mass*; it is the expression one would arrive at if one neglected the motion of the nucleus. It is one of the physical constants whose value is known with greatest precision, its value being

$$R_\infty = 1.097\,373\,153\,4 \times 10^7 \text{ m}^{-1}.$$

(The gravitational constant G is probably the least precisely known.)

The term value equal to $1.097\,373\,153\,4 \times 10^7 \text{ m}^{-1}$, or the corresponding energy, which is $2.1799 \times 10^{-18} \text{ J}$ or 13.61 eV , is called a *rydberg*.

We can use equation 7.4.9 now to calculate the term values for the hydrogen atom. We use, of course, the Rydberg constant for the real hydrogen atom, not for infinite mass. We obtain:

n	$T \text{ (}\mu\text{m}^{-1}\text{)}$
∞	10.9679
6	10.6632
5	10.5292
4	10.2824
3	9.7492
2	8.2259
1	0.0000

Notice the large gap between $n = 1$ and $n = 2$, which corresponds to the line Lyman- α 75% of the way from the ground level ($n = 1$) to the ionization limit ($n = \infty$). The level $n = 3$ is 89% of the way, and $n = 4$ is 94% of the way.

You can now calculate the vacuum wavenumbers (and standard air or vacuum wavelengths) for all the series. The lower level for the Lyman series is $n = 1$, so the wavenumbers of the lines are just equal to the term values of the higher levels. The vacuum wavelengths of the Lyman lines, as well as the series limit, are therefore:

Ly α	121.57 nm
Ly β	102.57
Ly γ	97.25
Ly δ	94.97
Ly ϵ	93.78
Limit	91.18

The Lyman series limit corresponds to an ionization potential of 13.59 volts.

The lower level of the Balmer series is $n = 2$, so you can now verify the wavelengths and wavenumbers given in section 7.2. In a similar manner, you can calculate the wavelengths of the several infrared series.

Should you wish to calculate the wavelengths of corresponding lines in the spectra of other hydrogenlike atoms, such as D, or He^+ or muonic hydrogen, all you need do is to put the appropriate values of Z and μ in the expression for the Rydberg constant (see equation 7.4.9). The wavelengths of corresponding lines in the spectrum of deuterium are close to, but not exactly equal to, those of ^1H . The reader is strongly urged to calculate the term values for He^+ . Then draw two energy level diagrams, to scale, side-by-side, for H and He^+ , positioning them so that $n = 1$ for H is at the same horizontal level as $n = 2$ for He^+ . Please do this - it will take only a few minutes with pencil and paper, but it would take me all day to try and do it on this computer. In any case, you will understand it far better if you do it yourself. You will find that, for He^+ , $n = 1$ lies a long, long way below $n = 2$. The wavelength of the line, which corresponds to Ly α , is 30.38nm. You will find that the ionization potential for He^+ is 54.4 volts. You will find that the levels $n = 2, 4, 6$ of He^+ nearly coincide with the levels $n = 1, 2, 3$ of H, but that the odd-numbered levels of He^+ fall in between. The He II series whose lower level is $n = 3$ is called the Fowler series, and the wavelength of its first member is 468.6 nm. (The reference in which I looked this up did not say whether this was the vacuum or the standard air wavelength. Please, always, when you are writing your scientific material, be absolutely explicit about this; you cannot expect the reader to guess. For the time being, however, you have enough information to calculate the term values for He^+ and hence to calculate the vacuum wavenumber and the standard air wavelength yourself.) The series for which the lower level is $n = 4$ is called the Pickering series. You should be able to calculate the following standard air wavelengths:

656.02 nm
541.16
485.94
454.17
433.87
419.99
410.01

You will notice that half of these coincide closely with lines in the Balmer series of H I. These lines are important in the spectra of O stars.

The Bohr theory has been remarkably successful in enabling you to calculate the energy levels, wavelengths and series limits for hydrogenlike atoms, and consequently no apology need be offered for discussing it in such detail. Yet it has its limitations. It does not explain the fine structure (which we have yet to describe) that can be observed in hydrogenlike spectra, and is inadequate to deal with the spectra of more complex atoms, in which the "fine structure" is by no means as "fine" as it is in hydrogen. True, Bohr and Sommerfeld managed to refine the theory with some success by including the possibility of elliptical orbits. Yet a more unsatisfying aspect of Bohr theory is not so much its weakness in dealing with fine structure, but is the somewhat arbitrary and *ad hoc* nature of its assumptions. In classical electromagnetic theory, an electron in orbit around a proton will radiate away energy and will rapidly spiral in towards the nucleus. And the assumption that the only orbits possible are those in which the angular momentum of the system is an integral number of times $h/(2\pi)$, while it successfully predicts the spectrum, hardly explains it.

The development of wave mechanics not only copes better with fine structure, but the quantization of energy levels appears naturally and without the need for *ad hoc* assumptions.

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7.5: One-dimensional Waves in a Stretched String

The last sentence in the previous section may strike you as rather odd, because one sometimes has the impression that quantum mechanics is replete with *ad hoc* assumptions, peppered as it is with various quantum numbers which can assume only integral values for some mysterious reason that no one can understand. Therefore, before moving on to wave mechanics as applied to atomic spectra, it will be useful to remind ourselves of some aspects of the behaviour of waves in a taut, stretched string. By doing this, we may be able to take some of the "mystery" out of quantum mechanics, and to see that many of its assumptions are my no means *ad hoc*, and arise rather naturally from the elementary theory of waves.

We'll start by imagining a long, taut string, which is constrained so that it can vibrate only in a single plane. Let us suppose that it suffers a brief disturbance, such as by being struck or plucked. In that case a wave (not necessarily periodic) of the form

$$\Psi_1 = f_1(x - ct) \quad (7.5.1)$$

will travel down the string to the right (positive x -direction) with speed c (this is not intended to mean the speed of light - just the speed at which waves are propagated in the string, which depends on its mass per unit length and its tension), and another wave

$$\Psi_2 = f_2(x + ct) \quad (7.5.2)$$

will move to the left. The symbol Ψ is just the transverse displacement of the string. It can easily be verified by direct substitution that either of these satisfies a differential Equation of the form

$$c^2 \frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial^2 \Psi}{\partial t^2}. \quad (7.5.3)$$

Indeed it is also easy to verify that any linear combination such as

$$\Psi = A f_1(x - ct) + B f_2(x + ct) \quad (7.5.4)$$

also satisfies the differential Equation. Since Equation 7.5.3 is a second-order differential equation, there are just two arbitrary constants of integration, and, since there are two arbitrary constants in Equation 7.5.4, the latter is the most general solution of the differential Equation. The differential Equation is the general differential Equation for a wave in one dimension. Two points are worth noting. One, there is no minus sign in it. Two, if your memory fails you, you can easily determine which side of the Equation the c^2 is on by considering the dimensions.

If the function is periodic, it can be represented as the sum of a number (perhaps an infinite number) of sine and cosine terms with frequencies related to each other by rational fractions. Even if the function is not periodic, it can still be represented by sine and cosine functions, except that in this case there is a continuous distribution of component frequencies. The distribution of component frequencies is then the Fourier transform of the wave profile. (If you are shaky with Fourier transforms, do not worry - I promise not to mention them again in this chapter.) Because of this, I shall assume all waves to be sinusoidal functions.

Let us now assume that the string is fixed at both ends. (Until this point I had not mentioned whether the ends of the string were fixed or not, although I had said that the string was taut. I suppose it would be possible for those of mathematical bent to imagine a taut string of infinite length, though my imagination begins to falter after the first few parsecs.) If a sine wave travels down the string, when it reaches the end it reverses its direction, and it does so again at the other end. What happens is that you end up with two waves travelling in opposite directions:

$$\begin{aligned} \Psi &= a \sin k(x - ct) + a \sin k(x + ct) \\ &= a \sin(kx - \omega t) + a \sin(kx + \omega t). \end{aligned} \quad (7.5.5)$$

Here k is the propagation constant $2\pi/\lambda$ and ω is the angular frequency $2\pi\nu$.

By a trigonometric identity this can be written:

$$\Psi = 2a \cos \omega t \sin kx. \quad (7.5.6)$$

This is a stationary sin wave ($\sin kx$) whose amplitude ($2a \cos \omega t$) varies periodically with time. In other words, it is a stationary or standing wave system. Notice particularly that a stationary or standing wave system is represented by the *product of a function of space and a function of time*:

$$\Psi(x, t) = \Psi(x) \cdot \chi(t). \quad (7.5.7)$$

Because the string is fixed at both ends (these are *fixed boundary conditions*) the only possible wavelengths are such that there is a node at each fixed end, and consequently there can only be an integral number of antinodes or half wavelengths along the length of the string. If the length of the string is l , the fundamental mode of vibration has a wavelength $2l$ and a fundamental frequency of $c/(2l)$. Other modes (the higher harmonics) are equal to an integral number of times this fundamental frequency; that is $nc/(2l)$, where n is an integer. Note that the introduction of this number n , which is restricted to integral values (a "quantum number", if you will) is a consequence of the *fixed boundary conditions*.

Which modes are excited and with what relative amplitudes depends upon the *initial conditions* – that is, on whether the string is plucked (initially $\Psi \neq 0$, $\dot{\Psi} = 0$) or struck (initially $\Psi = 0$, $\dot{\Psi} \neq 0$), and where it was plucked or struck. It would require some skill and practice (ask any musician) to excite only one vibrational mode, unless you managed to get the initial conditions exactly right, and the general motion is a *linear superposition of the normal modes*.

I'll mention just one more thing here, which you should recall if you have studied waves at all, namely that the *energy* of a wave of a given frequency is proportional to the square of its amplitude.

Volumes could be written about the vibrations of a stretched string. I would ask the reader to take notice especially of these four points.

1. A stationary solution is the product of a function of space and a function of time.
2. Restriction to a discrete set of frequencies involving an integral number is a consequence of fixed boundary conditions.
3. The general motion is a linear combination of the normal modes.
4. The energy of a wave is proportional to the square of its amplitude.

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7.6: Vibrations of a Uniform Sphere

This is a three-dimensional problem and the wave equation is

$$c^2 \nabla^2 \Psi = \ddot{\Psi}. \quad (7.6.1)$$

The wave-function here, Ψ , which is a function of the coordinates and the time, can be thought of as the density of the sphere; it describes how the density of the sphere is varying in space and with time.

In problems of spherical symmetry it is convenient to write this in spherical coordinates. The expression for ∇^2 in spherical coordinates is fairly lengthy. You have probably not memorized it, but you will have seen it or know where to look it up. Stationary solutions are of the form

$$\Psi(r, \theta, \phi; t) = \psi(r, \theta, \phi) \cdot \chi(t). \quad (7.6.2)$$

Is it necessary to know the mathematical details of these functions? Probably not if it is not your intention to have a career in theoretical spectroscopy. If you *are* going to have a career in theoretical spectroscopy, it probably wouldn't hurt to do the detailed calculation - but in practice a great deal of calculation can be and is done without reference to the detailed algebra; all that is necessary to know and become familiar with are the properties of the functions and how they react to the several operators encountered in quantum mechanics. At this stage, we are just looking at some general principles, and need not worry about the details of the algebra, which can be fairly involved.

The spherical coordinates r, θ, ϕ are independent variables, and consequently the timeindependent part of the wave function can be written as the product of three functions:

$$\psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi). \quad (7.6.3)$$

Again, it is not immediately necessary to know the detailed forms of these functions - you will find them in various books on physics or chemistry or spectroscopy. The simplest is Φ - it is a simple sinusoidal function, usually written as $e^{-im\phi}$. The function Θ is a bit more complicated and it involves things called Legendre polynomials. The function R involves somewhat less-familiar polynomials called [Laguerre polynomials](#). But there are *boundary conditions*. Thus ϕ goes only from 0 to 2π , and in that interval there can only be an integral number of half waves. Likewise, θ goes only from 0 to π , and r goes only from 0 to a , where a is the radius of the sphere. All three of these functions have integral "quantum numbers" associated with them. There is nothing mysterious about this, nor is it necessary to see the detailed algebra to see why this must be so; it is one of the inevitable constraints of fixed boundary conditions. The function R , the radial part of the wavefunction, has associated with it an integer n , which can take only integral values 1, 2, 3, ... The function Θ , the meridional wavefunction, has associated with it an integer l , which, for a given radial function (i.e. a given value of n) can have only the n different integral values 0, 1, 2, ... $n-1$. Finally, the function Φ , the azimuthal wavefunction, has associated with it an integer m , which, for a given meridional function (i.e. a given value of l) can have only the $2l+1$ different integral values $-l, -l+1, \dots, 0, \dots, l-1, l$. Thus for a given n , the number of possible wavefunctions is

$$\sum_0^{n-1} 2l+1.$$

You will have to remember how to sum arithmetic series in order to evaluate this, so please do so. The answer is n^2 .

When I first came across these quantum numbers, it was in connection with the wave mechanics of the hydrogen atom, and I thought there was something very mysterious about atomic physics. I was reassured only rather later - as I hope you will be reassured now - that the introduction of these quantum numbers is nothing to do with some special mysterious properties of atoms, but comes quite naturally out of the classical theory of vibrating spheres. Indeed, if you come to think about it, it would be very difficult indeed to believe that the wavefunctions of vibrating spheres did not involve numbers that had to be integers with restrictions on them.

The time-independent part of the wavefunction can be written:

$$\psi_{lmn}(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \Phi_m(\phi). \quad (7.6.4)$$

Often the angular parts of the wavefunction are combined into a single function:

$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta) \cdot \Phi_m(\phi). \quad (7.6.5)$$

The functions Y_{lm} are known as *spherical harmonics*.

When performing various manipulations on the wavefunctions, very often all that happens is that you end up with a similar function but with different values of the integers ("quantum numbers"). Anyone who does a lot of such calculations soon gets used to this, and consequently, rather than write out the rather lengthy functions in full, what is done is merely to list the quantum number of a function between two special symbols known as a "ket". (That's one half of a bracket.) Thus a wavefunction may be written merely as $|lmn\rangle$. This is done frequently in the quantum mechanics of atoms. I have never seen it done in other, more "classical" branches of physics, but I see no reason why it should not be done, and I dare say that it is in some circles.

The problem of a vibrating sphere of uniform density is fairly straightforward. Similar problems face geophysicists or planetary scientists when discussing the interiors of the Earth or the Moon or other planets, or astrophysicists studying "helioseismology" or "asteroseismology" - except that you have to remember there that you are not dealing with *uniform* spheres.

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7.7: The Wave Nature of the Electron

In 1906 Barkla had shown that when "soft" (relatively long wavelength, low-energy) x-rays were scattered by carbon, they exhibited polarization phenomena in just the way one would expect if they were transverse waves. In 1913 the father-and-son team of W.H and W.L. Bragg had performed their experiments on the diffraction and interference of x-rays by crystals, and they showed that x-rays behaved just as one would expect for short wavelength electromagnetic waves. In 1919, Compton carried out his famous experiments on the scattering of x-rays by light atoms, including carbon, though he used higher energy ("harder") x-rays than in Barkla's experiments. Some of the x-rays were scattered without change of wavelength, as expected from classical Thomson scattering theory, and the wave nature of x-rays appeared to be very firmly established. Yet not all of the x-rays were scattered thus. Indeed when the scattering was from a light element such as carbon most of the scattered x-rays were found to have a longer wavelength than the incident x-rays. Most readers will be familiar with at least the broad outline of these experiments, and how Compton showed that the phenomenon could most easily be explained if, instead of being treated as waves of wavelength λ , they were treated as though they were particles of momentum h/λ . Thus x-rays appeared to have a "wave-particle duality", their behaviour in some circumstances being better treated as a wave phenomenon, and in others as though they were particles.

In 1924 de Broglie speculated that perhaps the electron, hitherto regarded, following the initial experiments in 1897 of J. J. Thomson, as a particle, might also exhibit "wave-particle duality" and in some circumstances, rather than be treated as a particle of momentum p might better be described as a wave of wavelength h/p . During the 1920s Davisson and Germer indeed did scattering experiments, in which electrons were scattered from a nickel crystal, and they found that electrons were selectively scattered in a particular direction just as they would if they were waves, and in a rather similar manner to the Bragg scattering of x-rays. Thus indeed it seemed that electrons, while in some circumstances behaving like particles, in others behaved like waves.

De Broglie went further and suggested that, if electrons could be described as waves, then perhaps in a Bohr circular orbit, the electron waves formed a standing wave system with an integral number of waves around the orbit:

$$n\lambda = 2\pi r. \quad (7.7.1)$$

Then, if $\lambda = h/(mv)$, we have

$$mvr = nh/(2\pi), \quad (7.7.2)$$

thus neatly "explaining" Bohr's otherwise *ad hoc* assumption, described by equation 7.4.1. From a modern point of view this "explanation" may look somewhat quaint, and little less "*ad hoc*" than Bohr's original assumption. One might also think that perhaps there should have been an integral number of *half*-wavelengths in a Bohr orbit. Yet it portended more interesting things to come. For example, one is reminded of the spherical harmonics in the solution to the vibrating sphere described in section 7.6, in which there is an integral number of antinodes between $\phi = 0$ and $\phi = 2\pi$.

For those who appreciate the difference between the *phase velocity* and the *group velocity* of a wave, we mention here that an electron moves with the group velocity of the wave that describes its behaviour.

We should also mention that the wave description of a particle is not, of course, restricted to an electron, but it can be used to describe the behaviour of any particle.

Finally, the equation $p = h/\lambda$ can also conveniently be written

$$p = \hbar k, \quad (7.7.3)$$

where $\hbar = h/(2\pi)$ and k is the propagation constant $2\pi/\lambda$. The propagation constant can also be written in the form $k = \omega/v$, since $\omega = 2\pi\nu = 2\pi v/\lambda = kv$.

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7.8: Schrödinger's Equation

If the behaviour of an electron can be described as if it were a wave, then it can presumably be described by the wave Equation:

$$v^2 \nabla^2 \Psi = \ddot{\Psi}. \quad (7.8.1)$$

Here v is the speed of the electron, or, rather, the group velocity of its wave manifestation.

Periodic solutions for Ψ are given by $\ddot{\Psi} = -\omega^2 \Psi$, and, since $\omega = kv$, Equation 7.8.1 can be written in the form

$$\nabla^2 \Psi + k^2 \Psi = 0. \quad (7.8.2)$$

The total energy E is the sum of the kinetic and potential energies $T + V$, and the kinetic energy is $p^2/(2m)$. This, of course, is the nonrelativistic form for the kinetic energy, and you can judge for yourself from the calculation you did just before we arrived at Equation 7.4.5 to what extent this is or is not justified. If, instead of p you substitute the de Broglie expression in the form of Equation 7.7.3, you arrive at Schrödinger's Equation:

$$\nabla^2 \Psi + \frac{2m}{\hbar^2} (E - V) \Psi = 0 \quad (7.8.3)$$

To describe the behaviour of a particle in any particular situation in which it finds itself -e.g. if it found itself confined to the interior of a box, or attached to the end of a spring, or circling around a proton - we have to put in the Equation how V depends on the coordinates. The stationary states of an atom, i.e. its energy levels, are described by standing, rather than progressive, waves, and we have seen that standing waves are described as a product of a function of space and a function of time:

$$\Psi(x, y, z; t) = \psi(x, y, z) \cdot \chi(t). \quad (7.8.4)$$

If you put this into Equation 7.8.3 (all you have to do is to note that $\nabla^2 \Psi = \chi \nabla^2 \psi$ and that $\Psi = \psi \chi$), you find that the time-independent part of Schrödinger's Equation satisfies

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0. \quad (7.8.5)$$

When we are dealing with time-varying situations - for example, when an atom is interacting with an electromagnetic wave (light), we must use the full Schrödinger Equation 7.8.3. When dealing with stationary states (i.e. energy levels), we deal with the time-independent Equation 7.8.5.

Let's suppose for a moment that we are discussing not something complicated like a hydrogen atom, but just a particle moving steadily along the x -axis with momentum p_x . We'll try and describe it as a progressive wave function of the form

$$\Psi = \text{constant} \times e^{i(kx - \omega t)}. \quad (7.8.6)$$

(That's just a compressed way of writing $a \cos(kx - \omega t) + b \sin(kx - \omega t)$.) This means that

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi \quad \text{and} \quad \frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi. \quad (7.8.7)$$

Now let us use $E = h\nu = \hbar\omega$ and $p = h/\lambda = \hbar k$ as well as the (nonrelativistic, note) relation between kinetic energy and momentum $E = p^2/(2m)$, and we arrive at

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi. \quad (7.8.8)$$

In three dimensions (i.e. if the particle were not restricted to the x axis but were moving in some arbitrary direction in space), this appears as:

$$i\hbar \dot{\Psi} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x, y, z; t) \Psi. \quad (7.8.9)$$

This is referred to as Schrödinger's *Time-dependent Equation*.

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7.9: Solution of Schrödinger's Time-independent Equation for the Hydrogen Atom

The Schrödinger equation is best written and solved for atoms in spherical coordinates. The expression for ∇^2 in spherical coordinates is lengthy and can be found in mathematical and many physics or chemistry texts. I am not going to reproduce it here. The expression for the potential energy of a hydrogen-like atom to be substituted for V in Schrödinger's equation is

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (7.9.1)$$

The full solution of the equation, written out in all its glory, is impressive to behold, and it can be seen in several texts - but I am not going to write it out just yet. This is not because it is not important, nor to discourage those who would like actually to work through the algebra and the calculus in detail to arrive at the result. Indeed I would encourage those who are interested to do so. Rather, however, I want to make some points about the solution that could be overlooked if one gets too heavily bogged down in the details of the algebra. The solution is, unsurprisingly, quite similar to the solution for a vibrating solid discussed in Section 7.6, to which you will probably want to refer from time to time.

Since the spherical coordinates r , θ , ϕ are independent variables, physically meaningful solutions are those in which $\psi(r, \theta, \phi)$ is a product of separate functions of r , θ and ϕ . Upon integration of the equation, constants of integration appear, and, as in the solution for the vibrations of a sphere, these constants are restricted to integral values and for the same reasons described in section 7.6. Thus the wavefunctions can be written as

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \Phi_m(\phi). \quad (7.9.2)$$

The quantum numbers are subject to the same restrictions as in section 7.6. That is, n is a positive integer; l is a nonnegative integer that can have any of the n integral values from 0 to $n-1$; m is an integer that can have any of the $2l+1$ integral values from $-l$ to $+l$. For a given n there are n^2 possible combinations of l and m , a result that you found shortly before you reached equation 7.6.4.

The only function that I shall write out explicitly is the function $\Phi_m(\phi)$. It is periodic with an integral number of antinodes between 0 and 2π and is usually written as a complex number:

$$\Phi = e^{im\phi}. \quad (7.9.3)$$

(You will recall that $e^{ix} = \cos x + i \sin x$, and the ease with which this relation allows us to deal with trigonometric functions.) Because Φ is usually written as a complex number, ψ is also necessarily complex.

Now in section 7.5 we discussed waves in a stretched string, and in that section the function $\Psi(x, t)$ was merely the transverse displacement of the string. It will be convenient to recall that, for a given frequency, the energy of the wave is proportional to the *square* of its amplitude. In section 7.6 we discussed the vibrations of a sphere, and in that case $\Psi(x, y, z; t)$ is the density, and how it varies in space and time. For a standing wave, $\psi(x, y, z)$ is the time-averaged mean density and how it varies with position. What meaning can be given to Ψ or to ψ when we are discussing the wave mechanics of a particle, or, in particular, the wavefunction that describes an electron in orbit around a proton? The interpretation that was given by Max Born is as follows. We'll start with the time-independent stationary solution ψ and we'll recall that we are writing it as a complex number. Born gives no immediate physical interpretation of ψ ; rather, he suggests the following physical interpretation of the real quantity $\psi\psi^*$, where the asterisk denotes the complex conjugate. Let $d\tau$ denote an element of volume. (In rectangular coordinates, $d\tau$ would be merely $dx dy dz$; in spherical coordinates, which we are using in our description of the hydrogen atom, $d\tau = r^2 \sin\theta dr d\theta d\phi$.) Then $\psi\psi^* d\tau$ is the probability that the electron is in that volume element $d\tau$. Thus $\psi\psi^*$ is the *probability density* function that describes the position of the electron, and ψ itself is the *probability amplitude*. Likewise, in a time-varying situation, $\psi\psi^* d\tau dt$ is the probability that, in a time interval dt , the electron is in the volume element $d\tau$.

Since $\psi\psi^* d\tau$ is a *probability* - i.e. a dimensionless number - it follows that ψ is a dimensioned quantity, having dimensions $L^{-3/2}$, and therefore when its numerical value is to be given it is essential that the units (in SI, $m^{-3/2}$) be explicitly stated. Likewise the dimensions of Ψ are $L^{-3/2}T^{-1/2}$ and the SI units are $m^{-3/2}s^{-1/2}$.

If ψ is a solution of Schrödinger's time-independent equation, that any constant multiple of ψ is also a solution. However, in view of the interpretation of $\psi\psi^*$ as a probability, the constant multiplier that is chosen, the so-called *normalization constant*, is chosen such as to satisfy

$$\int_0^{2\pi} \int_0^\pi \int_0^\infty \psi \psi^* r^2 \sin \theta dr d\theta d\phi = 1. \quad (7.9.4)$$

This just means that the probability that the electron is *somewhere* is unity. The function ψ is a complicated function of the coordinates and the quantum numbers, and the normalization constant is also a complicated function of the quantum numbers. For many purposes it is not necessary to know the exact form of the function, and I am tempted not to show the function at all. I shall now, however, write out in full the normalized wavefunction for hydrogen, though I do so for just two reasons. One is to give myself some practice with the equation editor of the computer program that I am using to prepare this document. The other is just to reassure the reader that there does indeed exist an actual mathematical expression for the function, even if we shall rarely, if ever in this chapter, have occasion to use it. The function, then, is

$$\psi_{lmn}(r, \theta, \phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} \cdot \sin^{|m|} \theta \cdot P_l^{|m|}(\cos \theta) \cdot \sqrt{\frac{4(n-l-1)!Z^3}{[(n+1)!]^3 n^4 a_0^3}} \cdot \left(\frac{2Zr}{na_0}\right)^l \cdot e^{-\frac{Zr}{na_0}} \quad (7.9.5)$$

$$\cdot L_{n+1}^{2l+1}\left(\frac{2Zr}{na_0}\right).$$

Here P and L are the associated Legendre and Laguerre polynomials respectively, and a_0 is given by equation 7.4.3 with $n = 1$, $Z = 1$ and $\mu = m$; that is, 0.0529 nm. You might at least like to check that the dimensions of ψ are correct. Obviously I have not shown how to *derive* this solution of the Schrödinger equation; mathematicians are paid good money to do things like that. I just wanted to show that a solution really does exist, and what it means.

The specific equations for $\Phi_m(\phi)$, $\Theta_{lm}(\theta)$, $R_{nl}(r)$ and their squares, and graphical drawings of them, for particular values of the quantum numbers, are given in many books. I do not do so here. I do make some remarks concerning them. For example some of the drawings of the function $[\Theta(\theta)]^2$ have various pleasing shapes, such as, for example, something that resembles a figure 8. It must not be thought, however, that such a figure represents the orbit that the electron pursues around the nucleus. Nor must it be thought that the drawing represents a volume of space within which an electron is confined. It represents a polar diagram showing the angular dependence of the probability density. Thus the probability that the electron is within angular distances θ and $\theta + d\theta$ of the z -axis is equal to $[\Theta(\theta)]^2$ times the solid angle subtended (at the nucleus) by the zone between θ and $\theta + d\theta$, which is $2\pi \sin \theta d\theta$. Likewise the probability that the distance of the electron from the nucleus is between r and $r + dr$ is $[R(r)]^2$ times the volume of the shell of radii r and $r + dr$, which is $4\pi r^2 dr$. It might be noted that the radial function for $n = 1$ goes through a maximum at a distance from the nucleus of $r = a_0$, the radius of the first Bohr orbit.

Although I have not reproduced the individual radial, meridional and azimuthal functions for particular values of the quantum numbers, this is not because they are not important, and those who have books that list those functions and show graphs of them will probably like to pore over them - but I hope they will do so with a greater understanding and appreciation of them following my brief remarks above.

? Exercise 7.9.1

Exercise: What are the dimensions and SI units of the functions R , Θ , and Φ ?

The wavefunction 7.9.5 is a complicated one. However, it is found by experience that many of the mathematical operations that are performed on it during the course of quantum mechanical calculations result in a very similar function, of the same form but with perhaps different values of the quantum numbers. Sometimes all that results is the very same function, with the same quantum numbers, except that the operation results merely in multiplying the function by a constant. In the latter case, the wavefunction is called an *eigenfunction* of the operator concerned, and the multiplier is the corresponding *eigenvalue*. We shall meet some examples of each. Because of this circumstance, it is often convenient, instead of writing out equation 7.9.5 in full every time, merely to list the quantum numbers of the function inside a "ket". Thus the right hand side of equation 7.9.5 may be written instead merely as $|lmn\rangle$. With practice (and usually with only a little practice) it becomes possible to manipulate these kets very quickly indeed. (It might be remarked that, if the practice is allowed to lapse, the skills also lapse!)

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7.10: Operators, Eigenfunctions and Eigenvalues

Sooner or later any books on quantum mechanics will bring in these words. There will also be discussions about whether certain pairs of operators do or do not commute. What is this all about?

Recall that Schrödinger's Equation is equation 7.8.5, and, for hydrogenlike atoms we use the Equation 7.9.1 for the potential energy. We might like to solve Equation 7.8.5 to find the wavefunctions. In fact mathematically-minded people have already done that for us, and I have reproduced the result as Equation 7.9.5. We might well also be interested to know the value of the total energy E for a given eigenfunction. Equation 7.8.5 can be rearranged to read:

$$\left(V - \frac{\hbar^2}{2m} \nabla^2 \right) \psi = E\psi. \quad (7.10.1)$$

This tells us that, if we operate on the wavefunction with the expression in parentheses, the result of the operation is that you end up merely with the same function, multiplied by E . Seen thus, we have an *eigenvalue problem*. The solution of the Schrödinger equation is tantamount to seeking a function that is an eigenfunction of the operator in parentheses. The operator in parentheses, for reasons that are as obvious to me as they doubtless would have been to the nineteenth century Scottish-Irish mathematician Sir William Hamilton, is called the *hamiltonian operator* H . Thus Equation 7.10.1 can be written as

$$H\psi = E\psi. \quad (7.10.2)$$

If we choose, instead of writing out the wavefunction in full, merely to list its quantum number inside a ket, Schrödinger's equation, written in operator-ket form becomes

$$H|lmn\rangle = E|lmn\rangle. \quad (7.10.3)$$

And what do we get for the eigenvalue of the hamiltonian operator operating on the hydrogenlike eigenfunction? We'll leave it to the mathematically inclined to work through the algebraic details, but what we get is the very same expression, Equation 7.4.7, that we got for the energy levels in Section 7.4 when we were dealing with the Bohr model - but this time without the arbitrary Bohr assumptions. This is exciting stuff! (Before we get too carried away, however, we'll note that, like the original Bohr model with circular orbits, this model predicts that the energy levels depend solely upon the one quantum number n . Fine structure of the lines, however, visible only with difficulty in hydrogenlike atoms, but much more obvious in more complex spectra, suggests that this isn't quite good enough yet. But we still don't deny that it is exciting so far.)

I hope this may have taken some of the mystery out of it - though there is a little more to come.

I used to love attending graduate oral examinations. After the candidate had presented his research with great confidence, one of my favorite questions would be: "What is the significance of pairs of operators that commute?" In case you ever find yourself in the same predicament, I shall try to explain here. Everyone knows what commuting operators are. If two operators A and B commute, then it doesn't matter in which order they are performed - you get the same result either way. That is, $AB\psi = BA\psi$. That is, the *commutator* of the two operators, $AB - BA$, or, as it is often written, $[A, B]$, is zero. So much anyone knows. But that is not the question. The question is: What is the *significance* of two operators that commute? Why are commuting pairs of operators of special interest? The significance is as follows:

If two operators commute, then there exists a function that is simultaneously an eigenfunction of each; conversely if a function is simultaneously an eigenfunction of two operators, then these two operators necessarily commute.

This is so easy to see that it is almost a truism. For example, let ψ be a function that is simultaneously an eigenfunction of two operators A and B , so that $A\psi = a\psi$ and $B\psi = b\psi$. Then

$$AB\psi = Ab\psi = bA\psi = ba\psi = ab\psi \quad (7.10.1)$$

and

$$BA\psi = Ba\psi = aB\psi = ab\psi. \quad (\text{Q.E.D.})$$

It therefore immediately becomes of interest to know whether there are any operators that commute with the hamiltonian operator, because then the wavefunction 7.9.5 will be an eigenfunction of these operators, too, and we'll want to know the corresponding eigenvalues. And any operators that commute with the hamiltonian operator will also commute with each other, and all will have

equation 7.9.5 as an eigenfunction. (I interject the remark here that the word "hamiltonian" is an adjective, and like similar adjectives named after scientists, such as "newtonian", "gaussian", etc., is best written with a small initial letter. Some speakers also treat the word as if it were a noun, talking about "the hamiltonian". This is an illiteracy similar to talking about "a spiral" or "an elliptical" or "a binary", or, as is heard in bird-watching circles, "an Orange-crowned". I hope the reader will not perpetuate such a degradation of the English language, and will always refer to "the hamiltonian operator".)

Let us return briefly to the wavefunction that describes a moving particle discussed at the end of section 7.8, and specifically to the time-dependent equation 7.8.9. The total energy of such a particle is the sum of its kinetic and potential energies, which, in nonrelativistic terms, is given by

$$E = \frac{p^2}{2m} + V. \quad (7.10.4)$$

If we compare this with equation 7.8.9 we see that we can write this in operator form if we replace E by the operator $i\hbar \frac{\partial}{\partial t}$ and \mathbf{p} by the operator $-i\hbar \nabla$ (or, in one dimension, p_x by $-i\hbar \frac{\partial}{\partial x}$).

(The minus sign for p is chosen to ensure that ψ is a periodic rather than an exponentially expanding function of x .)

Now let us return to the hydrogen atom and ask ourselves what is the orbital angular momentum \mathbf{l} of the electron. The angular momentum of a particle with respect to an origin (i.e. the nucleus) is defined by $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, where \mathbf{p} is the linear momentum and \mathbf{r} is the position vector with respect to the origin. In rectangular coordinates it is easy to write down the components of this vector product:

$$l_x = yp_z - zp_y, \quad (7.10.5)$$

$$l_y = zp_x - xp_z, \quad (7.10.6)$$

$$l_z = xp_y - yp_x. \quad (7.10.7)$$

Writing these equations in operator form, we have:

$$l_x \equiv -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (7.10.8)$$

and similar expressions for the operators \mathbf{l}_y and \mathbf{l}_z . Do any two of these commute? Try \mathbf{l}_x and \mathbf{l}_y . You'll find very soon that they do not commute, and in fact you should get

$$[l_x, l_y] \equiv i\hbar l_z \quad (7.10.9)$$

and two similar relations obtained by cyclic permutation of the subscripts. Indeed in the context of quantum mechanics any operator satisfying a relation like 7.10.9 is defined as being an angular momentum operator.

We have been using spherical coordinates to study the hydrogen atom, so the next thing we shall want to do will be to express the operators \mathbf{l}_x , \mathbf{l}_y and \mathbf{l}_z in spherical coordinates. This will take a little time, but if you do this, you will obtain two rather complicated expressions for the first two, but the third one turns out to be very simple:

$$l_z \equiv -i\hbar \frac{\partial}{\partial \phi}. \quad (7.10.10)$$

Now look at the wavefunction 7.9.5. Is this by any chance an eigenfunction for the operator 7.10.10? By golly – it is, too! Just carry out that simple operation, and you will immediately find that

$$l_z |lmn\rangle = m |lmn\rangle. \quad (7.10.11)$$

In writing this equation, we are expressing angular momentum in units of \hbar . Since $|lmn\rangle$ is an eigenfunction of the hamiltonian operator as well as of the z -component of the angular momentum operator, \mathbf{l}_z and H must commute.

We have just found that the function $|lmn\rangle$ is an eigenfunction of the operator \mathbf{l}_z and that the operator has the eigenvalue m , a number that, for a given l can have any of the $2l + 1$ integral values from $-l$ to $+l$.

If you are still holding on to the idea of a hydrogen atom being a proton surrounded by an electron moving in circular or elliptical orbits around it, you will conclude that the only orbits possible are those that are oriented in such a manner that the z -component of the angular momentum must be an integral number of times \hbar , and you will be entirely mystified by this magical picture. Seen

from the point of view of wave mechanics, however, there is nothing at all mysterious about it, and indeed it is precisely what one would expect. All we are saying is that the distribution of electrons around the nucleus is described by a probability amplitude function that must have an integral number of antinodes in the interval $\phi = 0$ to 2π , in exactly the same way that we describe the vibrations of a sphere. It is all very natural and just to be expected.

I shall not go further into the algebra, which you can either do yourself (it is very straightforward) or refer to books on quantum mechanics, but if you write out in full the operator L^2 (and you can work in either rectangular or spherical coordinates) you will soon find that it commutes with L_z and hence also with H , and hence $|lmn\rangle$ is an eigenfunction of it, too. The corresponding eigenvalue takes a bit more algebra, but the result, after a bit of work, is

$$L^2|lmn\rangle = l(l+1)|lmn\rangle. \quad (7.10.12)$$

As before, we are expressing angular momentum in units of \hbar .

There is much, much more of this fascinating stuff, but I'll just pause here to summarize the results.

The energy levels are given by equation 7.4.7, just as predicted from the Bohr model. They involve only the one quantum number (often called the "principal" quantum number) n , which can have any nonnegative integral value. Orbital angular momentum can take the values $\sqrt{l(l+1)}\hbar$, where, for a given n , l can have the n integral values from 0 to $n-1$. The z -component of angular momentum can have, for a given value of l , the $2l+1$ integral values from $-l$ to $+l$. For a given value of n there is a total of n^2 possible combinations of l and m .

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7.11: Spin

The model described in section 7.10 describes the hydrogen spectrum quite well, and, though it is much heavier mathematically than the Bohr model, it is much more satisfying because it does not have the *ad hoc* assumptions of the Bohr model. It is still not good enough, though. It predicts that all of the n^2 wavefunctions with a given value of n have the same energy, because the expression for the energy included only the single quantum number n . Careful measurements show, however, that the Balmer lines have fine structure, and consequently the energy levels have some fine structure and hence the energy is not a function of n alone. The fine structure is much more obvious in more complex atoms, so the form of the Schrödinger equation we have seen so far is inadequate to explain this structure. At the theoretical level, we obviously used the nonrelativistic expression $p^2/(2m)$ for the kinetic energy. This is good enough except for precise measurements, when it is necessary to use the correct relativistic expression.

This short chapter is not a textbook or formal course in quantum mechanics, and its intention is little more than to introduce the various words and ideas that are used in spectroscopy. At this stage, then, although there is a strong temptation to delve deeper into quantum mechanics and pursue further the ideas that we have started, I am merely going to summarize some of the results and the ways in which spectra are described. Anyone who wants to pursue the quantum theory of spectra further and in detail will sooner or later come across some quite forbidding terms, such as Clebsch-Gordan coefficients, Racah algebra, 3- j and 6- j symbols, and tensorial harmonics. What these are concerned with is the algebra of combining the wavefunctions of two or more electrons and calculating the resulting angular momenta. The 3- j and 6- j symbols are parentheses or braces in which various quantum numbers are displayed, and they are manipulated according to certain rules as two or more wavefunctions are combined. It is in fact great fun to use them, and you can do stupendous calculations at enormous speed and with very little thought - but only after you have overcome the initial steep learning process and only if you keep in constant practice. If you programme the manipulations for a computer to deal with, not only are the calculations done even faster, but it doesn't matter if you are out of practice - the computer's memory will not lapse!

It is found that the complete wavefunction that describes an electron bound in an atom requires not just three, but four quantum numbers. There are the three quantum numbers that we are already familiar with - n , l and m , except that the third of these now bears a subscript and is written m_l . The energy of a wavefunction depends mostly on n , but there is a small dependence also on l . Orbital angular momentum, in units of \hbar , is $\sqrt{l(l+1)}$ and its z -component is m_l . The additional quantum number necessary to describe an electron bound to an atom is denoted by the symbol m_s , and it can take either of two values, $+1/2$ and $-1/2$. For a given value of n , therefore, there are now $2n^2$ combinations of the quantum numbers - i.e. $2n^2$ wavefunctions. (Recall that, before we introduced the concept of electron spin, we had predicted just n^2 wavefunctions for a given n . See the discussion immediately following equation 7.9.2.)

In terms of a mechanical model of the electron, it is convenient to associate the extra quantum number with a *spin* angular momentum of the electron. The spin angular momentum of an electron, in units of \hbar , is $\sqrt{s(s+1)}$, where s has the only value $1/2$. In other words, the spin angular momentum of an electron, in units of \hbar , is $3/2$. Its z -component is m_s ; that is, $+1/2$ or $-1/2$.

The concept that an electron has an intrinsic spin and that its z -component is $+1/2$ or $-1/2$ arose not only from a study of spectra (including especially the splitting of lines when the source is placed in a magnetic field, known as the Zeeman effect) but also from the famous experiment of Stern and Gerlach in 1922. The totality of evidence from spectroscopy plus the Stern-Gerlach experiment led Goudsmit and Uhlenbeck in 1925 to propose formally that an electron has an intrinsic magnetic moment, and certainly if we think of an electron as a spinning electric charge we would indeed expect it to have a magnetic moment. A magnetic dipole may experience a torque if it is placed in a uniform magnetic field, but it will experience no net force. However, if a magnetic dipole is placed in a nonuniform magnetic field - i.e. a field with a pronounced spatial gradient in its strength, then it will indeed experience a force, and this is important in understanding the Stern-Gerlach experiment. Stern and Gerlach directed a beam of "electrons" (I'll explain the quote marks shortly) between the poles of a strong magnet in which one of the pole pieces was specially shaped so that the "electrons" passed through a region in which there was not only a strong transverse magnetic field but also a large transverse magnetic field gradient. One might have expected the beam to become broadened as the many electrons were attracted one way or another and to varying degrees, depending on the orientation of their magnetic moments to the field gradient. In fact the beam was split into two, with one half being pulled in the direction of the field gradient, and the other half being pushed in the opposite direction. This is because there were only two possible directions of the magnetic moment vector. (As a matter of experimental detail it was not actually a beam of electrons that Stern and Gerlach used. This would have completely spoiled the experiment, because an electron is electrically charged and an electron beam would have been deflected by the Lorentz force far more than by the effect of the field gradient on the dipole moment. As far as I recall they actually used a beam of silver atoms. These were not

accelerated in a particle accelerator of any sort (after all, they are neutral) but were just vaporized in an oven, and a beam was selected by means of two small apertures between the oven and the magnet. The silver atom has a number of paired electrons (with no resultant magnetic moment) plus a lone, unpaired electron in the outer shell, and this was the electron that supplied the magnetic moment.)

In some atoms the orbital angular momentum \mathbf{l} and the spin angular momentum \mathbf{s} are more strongly coupled to each other than they are to the z -axis. In that case m_l and m_s are no longer "good quantum numbers". The total angular momentum of the electron (orbit and spin combined) is given the symbol \mathbf{j} . Its magnitude, in units of \hbar , is $\sqrt{j(j+1)}$ and its z -component is called m . In that case the four "good quantum numbers" that describe the electron are n, l, j and m rather than n, l, m_l, m_s . Intermediate cases are possible, but we'll worry about that later. In any case the wavefunction that describes an electron is described by four quantum numbers, and of course no two wavefunctions (and hence no two electrons bound in an atom) have the same set of four quantum numbers. (If we return briefly to the vibrating sphere, each mode of vibration is described by three quantum numbers. It makes no sense to talk about two different modes having the same set of three quantum numbers.) The truism that no two electrons bound in an atom have the same set of four quantum numbers is called *Pauli's Exclusion Principle*.

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7.12: Electron Configurations

The several electrons that surround an atomic nucleus will have various orbital angular momenta - that is, each electron will have a certain value of the orbital angular momentum quantum number l .

An electron with $l = 0$ is called an s electron.

An electron with $l = 1$ is called a p electron.

An electron with $l = 2$ is called a d electron.

An electron with $l = 3$ is called an f electron.

This curious and admittedly illogical notation derives from the early study of the spectra of the alkali (e.g. Na, K) and alkali earth (e.g. Mg, Ca) elements in which four series of lines were noted, which, at the time, were called the "Sharp", "Principal", "Diffuse" and "Fundamental" series. Only later, when atomic structure was better understood, were these series associated with what we now know to be electrons with $l = 0, 1, 2, 3$. (San Francisco Police Department, SFPD, is NOT a good mnemonic to use in trying to remember them.) After $l = 2$, the letters go $g, h, i, k \dots$ etc., j being omitted.

An electron with, for example, $l = 1$, is often described as being "in a p -orbital". Bear in mind, however, the meaning of the shapes described by the wavefunctions as discussed in section 9.

Electrons with $n = 1, 2, 3, 4$, etc., are said to be in the " K, L, M, N , etc." shells. This almost as curious and not very logical notation derives from the early study of x-ray spectra, in which various observed absorption edges or groups of emission lines were labelled K, L, M, N , etc., and, with subsequent knowledge, these have since been associated with electrons with the principal quantum number being 1, 2, 3, 4. Presumably, since it wasn't initially known which x-ray absorption edge would ultimately prove to be the "first" one, it made good sense to start the notation somewhere near the middle of the alphabet.

The restrictions on the values of the quantum numbers together with the Pauli exclusion principle enable us to understand the *electron configurations* of the atoms. For example the electron configuration of copper, Cu, in its ground state is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s \quad (7.12.1)$$

This is usually pronounced, including by myself, "one-s-squared, two-s-squared, two-p-to-the-sixth..." etc, but we shall soon see that this is certainly not how it *ought* to be pronounced, and I shall not discourage the reader who wants to do it properly, while I continue with my slovenly ways.

What it means is as follows:

The 1 refers to electrons with $n = 1$; that is to K -shell electrons. The notation s^2 that follows indicates that there are two s -electrons; that is, two electrons with zero orbital angular momentum. (In a Bohr-Sommerfeld model presumably they'd either have to be motionless, or else move two and fro in a straight line through the nucleus! We don't have that difficulty in a wave-mechanical model.) Now recall that l can have integral values only up to $n - 1$, so that the only electrons possible in the K -shell are s -electrons with $l = 0$. Consequently the only possible value of m_l is zero. There are the two possible values for m_s , however, namely $+1/2$ and $-1/2$ so two s -electrons (but no more than two) are possible in the K -shell. Thus the K -shell is *full*, and the quantum numbers for the two K -shell electrons are:

n	l	m_l	m_s
1	0	0	$+1/2$
1	0	0	$-1/2$

(7.12.2)

Next we come to $2s^2 2p^6$. This indicates that there are two s -electrons in the L -shell and six p -electrons in the L -shell. Let's look at their quantum numbers:

$$\begin{array}{cccc}
 n & l & m_l & m_s \\
 \\
 2 & 0 & 0 & +1/2 \\
 2 & 0 & 0 & -1/2 \\
 2 & 1 & -1 & +1/2 \\
 2 & 1 & -1 & -1/2 \\
 2 & 1 & 0 & +1/2 \\
 2 & 1 & 0 & -1/2 \\
 2 & 1 & 1 & +1/2 \\
 2 & 1 & 1 & -1/2
 \end{array} \tag{7.12.3}$$

And so on, and so on and so on... Many physics and chemistry books give the configurations of the ground states of all the atoms in the periodic table, and such tables are well worth careful study. Recall that, for a given n , l can take values only up to $n - 1$, so that, for example, the N -shell ($n = 3$) can have only s , p , and d electrons. Within a given shell, there can be only two s -electrons, six p -electrons, ten d -electrons, $2(2l + 1)$ electrons with orbital angular momentum quantum number l . A given shell can hold only $2n^2$ electrons each having its unique set of four quantum numbers. You will observe that copper, in its ground configuration, has full K , L , and M shells, plus one outer electron in its N shell.

As said at the beginning of this chapter, we expect only to introduce some of the words and ideas encountered in spectroscopy. Careful study of more detailed textbooks will be necessary, and I strongly recommend trying yourself to build up the ground configurations of at least the first 30 elements, up to zinc. Compare your efforts with tables in the books, and you will find that the ground configurations of a very few of the first thirty elements may not be exactly what you predicted.

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7.13: LS-coupling

Each of the several electrons in an atom has an orbital angular momentum \mathbf{l} and a spin angular momentum \mathbf{s} , and there are numerous conceivable ways in which the various angular momenta can be coupled together to result in the total electronic angular momentum of the atom. (The total angular momentum of the atom may also include a small contribution from the nucleus. This contribution is usually quite tiny, but measurable. We'll ignore it for the time being; in any case, many nuclides (including most of those that have even numbers of protons and neutrons) have zero nuclear spin.

One of the simplest coupling schemes is called *LS-coupling* (or sometimes Russell-Saunders coupling). In this scheme (which may be regarded as one extreme of a host of conceivable coupling schemes), all the orbital angular momenta \mathbf{l} of the several electrons are strongly coupled together to form the total electronic orbital angular momentum of the atom, which is denoted by \mathbf{L} . This can be represented symbolically by

$$\sum \mathbf{l} = \mathbf{L}. \quad (7.13.1)$$

The summation indicated is a vector summation.

The magnitude of \mathbf{L} is $\sqrt{L(L+1)}\hbar$, and L can have nonnegative integral values, 0, 1, 2, 3, etc.

Similarly, all the spin angular momenta \mathbf{s} of the several electrons are strongly coupled together to form the total electronic spin angular momentum of the atom, which is denoted by \mathbf{S} . This can be represented symbolically by

$$\sum \mathbf{s} = \mathbf{S} \quad (7.13.2)$$

The magnitude of \mathbf{S} is $\sqrt{S(S+1)}\hbar$. If there is an even number of electrons in the atom, S can have nonnegative integral values. If there is an odd number of electrons in the atoms, the value of S is a positive odd integral number times $1/2$, such as $1/2$, $3/2$, $5/2$... etc.

The total electronic orbital angular momentum of the atom, \mathbf{L} , then couples weakly to the total electronic spin angular momentum of the atom, \mathbf{S} , to form the total (orbital plus spin) electronic angular momentum of the atom, denoted by \mathbf{J} . This is denoted symbolically by

$$\mathbf{L} + \mathbf{S} = \mathbf{J} \quad (7.13.3)$$

The magnitude of \mathbf{J} is $\sqrt{J(J+1)}\hbar$. If there is an even number of electrons, J can take any of the $2 \min\{L, S\} + 1$ nonnegative integral values from $|L - S|$ to $L + S$. If there is an odd number of electrons, J can have any of the $2 \min\{L, S\} + 1$ odd-half-integral values from $|L - S|$ to $L + S$. The z -component of \mathbf{J} is $M\hbar$. If J is integral (i.e. if there is an even number of electrons), M can have any of the $2J + 1$ integral values from $-J$ to $+J$. If J is odd-half-integral, M can have any of the $2J + 1$ odd-half-integral values from $-J$ to $+J$.

In many of the lighter elements near the beginning of the periodic table, the coupling of the angular momenta is close to that of ideal *LS-coupling*. There are appreciable departures from this simple scheme higher up in the periodic table. We shall discuss other coupling schemes a little later.

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7.14: States, Levels, Terms, Polyads, etc.

An *electron configuration* is a listing of the number of electrons in each *shell* and the orbital angular momentum of each. We gave an example of the lowest electron configuration of Cu I in section 7.12.

For a given electron configuration it is possible to predict the several (many) eigenfunctions that can exist. I shall not show how to do this, but I shall list, by way of example, the quantum numbers of the eigenfunctions that can arise from two *p* electrons in the same shell (i.e. having the same principal quantum number *n*.) If two *p* electrons are in the same shell, they are referred to as "equivalent" *p*-electrons, and the electron configuration is written p^2 . If they are in different shells (have different *n*) they are "nonequivalent" electrons, and the configuration is written *p.p*. We are going to deal, then with two equivalent *p*-electrons, p^2 . Without proof, I now list the 15 possible combinations of quantum numbers *LSJM* of the 15 *states* that arise from this configuration.

	L	S	J	M	Term	Level
1	0	0	0	0	1S	1S_0
2	1	1	0	0		3P_0
3	1	1	1	-1		
4	1	1	1	0		3P_1
5	1	1	1	1		
6	1	1	2	-2	3P	
7	1	1	2	-1		
8	1	1	2	0		3P_2
9	1	1	2	1		
10	1	1	2	2		
11	2	0	2	-2		
12	2	0	2	-1		
13	2	0	2	0	1D	1D_2
14	2	0	2	1		
15	2	0	2	2		

	L	S	J	M	Term	Level
1	0	0	0	0	1S	1S_0
2	1	1	0	0		3P_0
3	1	1	1	-1		
4	1	1	1	0		3P_1
5	1	1	1	1		
6	1	1	2	-2	3P	
7	1	1	2	-1		
8	1	1	2	0		3P_2
9	1	1	2	1		
10	1	1	2	2		
11	2	0	2	-2		
12	2	0	2	-1		
13	2	0	2	0	1D	1D_2
14	2	0	2	1		
15	2	0	2	2		

In principle we could write out in full the complete wavefunction for each of these states, though it is simpler to write the wavefunction in the form of a *ket* $|LSJM\rangle$, in which we merely list the quantum numbers - because most of the operators encountered in quantum mechanics when acting upon the spherical harmonics result in similar functions with at most a change in the quantum numbers. Thus the wavefunction for the first state in the list above would be written merely as $|0000\rangle$, and the wavefunction for the last one would be written $|2022\rangle$.

The totality of *states* with the same values of L and S is called a *term*. Thus the nine states 2 to 10 all have the same values of L and S and they comprise a term. The five states 11 to 15 also have the same values of L and S , and they also comprise a term. There is only one state with $L = 0$ and $S = 0$. This is a term that contains only one state.

A term is denoted by the letter S, P, D, F, G, H, I, K, ... according to whether its L -value is 0, 1, 2, 3, 4, 5, 6, 7, ... The value of $2S + 1$ is written as an upper left superscript. Thus the three terms are as follows:

$$\begin{array}{ll} \text{State 1:} & {}^1\text{S} \\ \text{States 2 - 10:} & {}^3\text{P} \\ \text{States 11 - 15:} & {}^1\text{D} \end{array} \quad (7.14.1)$$

These terms are generally pronounced "singlet-S, triplet-P, singlet-D".

The totality of states with the same values of L , S , and J is called a *level*. Thus the term ${}^3\text{P}$ has three levels, denoted by ${}^3\text{P}_0$, ${}^3\text{P}_1$ and ${}^3\text{P}_2$, in which the value of J is written as a bottom right subscript.

Except in the presence of an external magnetic or electric field, all states belonging to a given level have the same energy, and on an energy level diagram they would appear as a single horizontal line. The number of states in a given level is $2J + 1$ and this is called the *degeneracy* d of the level.

The number of levels in a term (see discussion following equation 7.13.3) is $2\min\{L, S\} + 1$. This is called the *multiplicity* g of the term. In all of the terms discussed above arising from the configuration p^2 , S is less than or equal to L , and therefore the multiplicity of these terms is $2S + 1$, which is equal to the upper left superscript. Consider, however, the terms ${}^3\text{S}$ and ${}^5\text{P}$, which occur in some other configurations. In these two cases, $L < S$, so the multiplicity is $2L + 1$. For ${}^3\text{S}$ we have $S = 1$ and $L = 0$; the multiplicity is 1 and the only level in the term has $J = 1$. For ${}^5\text{P}$, we have $S = 2$ and $L = 1$; the multiplicity is 3 and the three levels are ${}^5\text{P}_{1,2,3}$. Nevertheless it is customary to pronounce these terms "triplet-S, quintet-P".

The *statistical weight* ϖ of a level or a term is the number of states in it. The statistical weight of a level is the same as its degeneracy, and is $2J + 1$. The statistical weight of a term is the sum of the degeneracies of its constituent levels, and is $(2L + 1)(2S + 1)$, regardless of the relative sizes of L and S . You should verify this for each of the levels and terms in the configuration p^2 . The symbol ϖ , by the way, is a form of the Greek letter pi, and resembles the way in which pi is written in handwriting.

Exercise. Show that $\sum_{|L-S|}^{L+S} (2J + 1) = (2L + 1)(2S + 1)$ regardless of the relative sizes of L and S .

The reader might note that not all authors retain the distinction between degeneracy, multiplicity and statistical weight, or the symbols I am using to represent them. In particular, the symbol g is (regrettably) often used for the statistical weight or degeneracy of a level. It is not always clear what concept is being represented by a given symbol, and it is important in your own writing always to make it clear yourself and never to assume that your readers will understand what you intend if you not make it clear. Please also do not refer to the upper left superscript of a term as its "multiplicity". The multiplicity is $2\min\{L, S\} + 1$; the upper left superscript is $2S + 1$.

Parentage. We'll try to understand this word by means of an example, and we'll consider the neutral vanadium atom. The spectrum of vanadium is quite complex, and there are many lowlying terms. For example, among the many terms whose term values are within $3 \mu\text{m}^{-1}$ of the ground level are four ${}^6\text{D}$ terms. These are terms with $S = \frac{5}{2}$, $L = 2$. The multiplicity of such a term is 5, the J -values being $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$. The ground configuration of V_I is $KL3s^23p^63d^34s^2$. Here I have abbreviated the first ten electrons in the configuration with the letters KL , to indicate full K and L shells. In fact in the present discussion, I am not going to be specially interested in the first 18 electrons, and I am going to indicate the ground configuration merely by $3d^34s^2$. In fact, none of the four ${}^6\text{D}$ terms under discussion comes from this configuration. They all come from excited configurations. Specifically, in order of increasing energy, the configurations of these four ${}^6\text{D}$ terms are:

$$\begin{array}{l} 3d^44s \\ 3d^34s4p \\ 3d^44p \\ 3d^34s4p \end{array} \quad (7.14.2)$$

You will notice that two of them (the second and fourth) arise from the same configuration.

Let us consider how the several 6D terms arise. Consider the first of them. The configuration $3d^4$ of Ti_I (titanium is the element just before vanadium in the periodic table) gives rise to a great many terms (I believe it gives rise to 16 terms). In particular there is a 5D term. If you now add a $4s$ electron (to turn titanium into vanadium) to the 5D term of Ti_I , this gives rise to two V_I terms, one of which is the first of our 6D terms of interest. The 5D term of the $Ti_I 3d^4$ configuration is called the parent of this term, and, to make this clear, the configuration of the first $V_I {}^6D$ term is written

$$3d^4 ({}^5D) 4s \quad (7.14.3)$$

In a similar manner, the configurations of the other three 6D terms of V_I with their parents indicated are

$$\begin{aligned} 3d^3 4s ({}^5F) 4p \\ 3d^4 ({}^5D) 4p \\ 3d^3 4s ({}^5P) 4p \end{aligned} \quad (7.14.4)$$

Many terms of V_I have the same parent. Thus $3d^4 ({}^5D)$ is parent to eight terms in the lowest $3 \mu m^{-1}$ of term value. The totality of terms having the same parent is called a *polyad*.

Parity. The wavefunction that describes a particular term has the property that if it is inverted through the origin (this means, in spherical coordinates, that θ and ϕ are replaced by $\pi - \theta$ and $\pi + \phi$ respectively) the wavefunction is either unchanged or just changes in sign. In the former case the term is said to be of *even parity*; in the latter case it is of *odd parity*. This may sound like a rather obscure wavemechanical nicety, but it is of sufficient importance to a working spectroscopist that he or she needs to know the parity of each term. Because of this it is usual (in fact essential) to indicate a term of odd parity by means of the upper right superscript o . Terms of odd parity, for example, might be written ${}^3P^o$, ${}^4S^o$, etc. It is easy to know (if not to understand why) a given term has odd or even parity. If the (scalar) sum of the l -values of the configuration from which a term arises is even, the parity is even; if it is odd, the parity is odd. When we earlier considered the terms arising from p^2 , all the terms had even parity, because the sum of the l -values of the two p electrons is 2.

The reason why a working spectroscopist needs to know the parity of a term will become evident later in section 7.24 on *selection rules*.

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7.15: Components, Lines, Multiplets, etc.

An atom can make a transition from one level to another. This may be as a result of a collision with another atom. If one (or both) of the colliding atoms moves to a higher energy level, there will be a loss of kinetic energy; the collision is inelastic. If one (or both) moves to a lower level, there will be a gain in kinetic energy; the collision is superelastic. We are concerned here, however, with transitions from one level to another involving absorption or emission of radiation (or of a photon, depending on whether you prefer to think of light as waves or as particles). If a photon is absorbed and the atom moves up to a higher energy level, the process is called *photoexcitation* and an absorption line is formed. If an atom falls down to a lower level it may emit a photon of appropriate frequency or wavenumber ($h\nu = \Delta E$ or $\sigma = \Delta T$); this is *radiative de-excitation*. It is possible for a photon of the right frequency ($h\nu = \Delta T$) actually to stimulate a downward transition, thus amplifying the intensity of the original photon. This process is called *light amplification by stimulated emission of radiation*, generally abbreviated to *laser*. In any case, although the transition from one level to another may well result in a change of electron configuration, the energy levels concerned are those of the *atom*, and it is the *atom*, not "the electron" that makes a transition between energy levels. This point was discussed in section 7.1.

However, we have seen that a *level* (defined by LSJ) in fact consists of several $(2J + 1)$ *states*, all of which in the absence of an external magnetic or electric field, have the same energy. Evidently a *line* must be the totality of several transitions connecting the several states of which the two levels are composed. In the presence of a magnetic field (for example, in a sunspot) the various states within a level become separated in energy, and consequently the several components of a line become separated in wavelength. This is the *Zeeman effect*. There is a somewhat similar effect in the presence of an electric field, known as the *Stark effect*. However, stellar atmospheres are typically highly ionized plasmas and hence good electrical conductors that cannot sustain high electric potential differences, thus the Stark effect is not often met with in stellar atmosphere except on a microscopic scale when atom-atom interactions may give rise to *Stark broadening* of spectrum lines.

Before we proceed, just a reminder. A *term* is defined by LS . A term comprises $2 \min\{L, S\} + 1$ *levels*, each defined by LSJ . A *level* comprises $2J + 1$ *states*, each defined by $LSJM$.

Now for some more definitions. A (Zeeman) *component* is a transition between two *states*. (In most contexts, the two states will belong to different levels.)

A *line* is the totality of components connecting two *levels*. (In many, but not all, contexts, the two levels will belong to different terms.) Imagine two levels, one with $J = 2$ (and hence five states) and the other with $J = 3$ (and hence seven states). In principle there are 35 ways of connecting one of the five states in one level with one of the seven states in the other. In practice, the actual number of transitions possible is rather less than this, since some of the transitions have zero probability. This will be discussed later in section 7.24 on *selection rules*.

A *multiplet* is the totality of lines connecting two *terms*. Imagine two terms, for example a 5P term and a 5D term. The former has three levels, the latter five. (*Exercise*: What are the J -values for each?) In principle there are 15 ways of connecting one of the three levels of the former with one of the five of the latter. In practice, the *selection rules* (see later) preclude several of these.

In atomic spectroscopy, it is customary to indicate a line by writing the two levels with a dash between them, and the *lower level* is written first, whether the line is in emission or absorption. For example, a line might be $^5P_2 - ^5D_3$. If you want to specify an absorption line, you could use \rightarrow rather than a dash, or \leftarrow if you want to specify an emission line. In molecular spectroscopy it is customary to write the upper state first. A multiplet in atomic spectroscopy would be written $^5P - ^5D$.

The totality of terms connecting two polyads is a *supermultiplet*.

The totality of terms connecting two configurations is a *transition array*.

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7.16: Return to the Hydrogen Atom

We have until now talked about the "levels" $n = 1, 2, 3 \dots$ of hydrogen, and the Lyman and Balmer "lines" connecting them. This nomenclature is now suspect.

In its lowest configuration the sole electron in hydrogen is in the K -shell and has $n = 1$. The only possible l -value is zero, and hence the lowest configuration in hydrogen is $1s$. This single electron has $l = 0$ and $s = 1/2$, and hence for the atom $L = 0$ and $S = 1/2$. Thus the only term in the K -shell is 2S , and this has but a single level, $^2S_{1/2}$. (We are not considering here the very small contribution made by the spin of the nucleus; this is unimportant for most contexts in optical spectroscopy, but is important - VERY important - in the microwave region.)

In the L -shell, $n = 2$, and hence the electron can be in an s -orbital or a p -orbital. (See section 7.12 to recall the phrase "the electron is in a p -orbital".) That is, the configuration can be $2s$ or $2p$. In either case, of course, $s = 1/2$, so that the two possible terms in the L -shell are 2S (with one level, $^2S_{1/2}$) and 2P (with two levels, $^2P_{1/2}$ and $^2P_{3/2}$).

I leave it up to the honour and integrity of the reader to convince him/herself that the possible configurations for $n = 3$ are $3s$, $3p$ or $3d$. There are three terms: 2S , 2P and 2D , 5 levels (write down the J -levels of each) and 18 states.

In brief, although we have hitherto talked about the $n = 1, 2, 3$ levels, this is all right for $n = 1$, but $n = 2$ is three levels in two terms, and $n = 3$ is five levels in three terms.

The term values of the nine levels included in $n = 1, 2$ and 3 are as follows, in μm^{-1} . I have also written out the statistical weight $2J + 1$ of each level.

$3d\ ^2D_{\frac{5}{2}}$	9.7492342	6
$3d\ ^2D_{\frac{3}{2}}$	9.7492306	4
$3p\ ^2P_{\frac{3}{2}}^o$	9.7492306	4
$3s\ ^2S_{\frac{1}{2}}$	9.7492208	2
$3p\ ^2P_{\frac{1}{2}}^o$	9.7492198	2
(7.16.1)		
$2p\ ^2P_{\frac{3}{2}}^o$	8.2259272	4
$2s\ ^2S_{\frac{1}{2}}$	8.2258942	2
$2p\ ^2P_{\frac{1}{2}}^o$	8.2258907	2
$1s\ ^2S_{\frac{1}{2}}$	0.0000000	2

Notice that the statistical weights of the K , L and M shells ($n = 1, 2, 3$) are, respectively, 2, 8 and 18 - i.e $2n^2$, as explained in section 7.11. In section 7.9 (see especially immediately following equation 7.9.2), before the introduction of electron spin, we had deduced that the statistical weight of each shell was just n^2 ; the introduction of electron spin has doubled that.

So just how many transitions *are* there in the "line" $H\alpha$? We cannot answer that until we have familiarized ourselves with the *selection rules*, but I make it that $H\alpha$ comprises three transition arrays, three multiplets, seven lines, and I'm not sure just how many components! We'll come back to this in section 7.24..

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7.17: How to recognize LS-coupling

LS -coupling is in practice a good approximation in light atoms, but there are appreciable departures from LS -coupling in the heavier atoms. Generally the several lines in a multiplet in LS -coupling are fairly close together in wavelength for LS -coupling, but, as departures from LS -coupling become more pronounced, the lines in a multiplet may become more widely separated and may appear in quite different parts of the spectrum.

In LS -coupling, multiplets always connect terms with the same value of S . Thus, while $^3D - ^3P$ would be "allowed" for LS -coupling, $^3D - ^1P$ would not. $\Delta S = 0$ is a necessary condition for LS -coupling, but is not a sufficient condition. Thus while a multiplet with $\Delta S \neq 0$ certainly indicates departure from LS -coupling, $\Delta S = 0$ by no means guarantees that you have LS -coupling. In spectroscopy, the term "forbidden" generally refers to transitions that are forbidden to electric dipole radiation. Transitions that are forbidden merely to LS -coupling are usually referred to as "semi-forbidden", or as "intersystem" or "intercombination" transitions. We shall have more on selection rules in section 7.24.

The energies, or term values, of the levels (each defined by LSJ) within a term are given, for LS -coupling, by a simple formula:

$$T = \frac{1}{2}a[J(J+1) - L(L+1) - S(S+1)]. \quad (7.17.1)$$

Here a is the spin-orbit coupling coefficient, whose value depends on the electron configuration. What is the separation in term values between two adjacent levels, say between level J and $J-1$? Evidently (if you apply equation 7.17.1) it is just aJ . Hence Landé's Interval Rule, which is a good test for LS -coupling: *The separation between two adjacent levels within a term is proportional to the larger of the two J -values involved.* For example, in the $KL3s(^2S)3p^3P^o$ term of Mg_{I} (the first excited term above the ground term), the separation between the $J=2$ and $J=1$ levels is 4.07 mm^{-1} , while the separation between $J=1$ and $J=0$ is 2.01 mm^{-1} . Landé's rule is approximately satisfied, showing that the term conforms closely, but not exactly, to LS -coupling. It is true that for doublet terms (and all the terms in Na_{I} and K_{I} for example, are doublets) this is not of much help, since there is only one interval. There are, however, other indications. For example, the value of the spin-orbit coupling coefficient can be calculated from LS -theory, though I do not do that here. Further, the relative intensities of the several lines within a multiplet (or indeed of multiplets within a polyad) can be predicted from LS -theory and compared with what is actually observed. We discuss intensities in a later chapter.

The spin-orbit coupling coefficient a can be positive or negative. If it is positive, the level within a term with the largest J lies highest; such a term is called a *normal term*, though terms with negative a are in fact just as common as "normal" terms. If a is negative, the level with largest J lies lowest, and the term is called an *inverted term*. Within a shell (such as the L -shell) all the s electrons may be referred to as a subshell, and all the p electrons are another *subshell*. The subshell of s electrons can hold at most two electrons; the subshell of p electrons can hold at most six electrons. If the outermost subshell (i.e. the electrons responsible for the optical spectrum) is less than half full, a is positive and the terms are normal. If it is more than half full, a is negative and the terms are inverted. If the subshell is exactly half full, a is small, the term is compact and may be either normal or inverted. For example in Al_{I} , the term $3p^2\ ^4P$ (which has three levels - write down their J -values) is normal. There are only two p electrons out of six allowed in that subshell, so the subshell is less than half full. The term $2s2p^4\ ^4P$ of O_{II} has four p electrons, so the subshell is more than half full, and the term is inverted. The term $2s^22p^3\ ^2P^o$ of the same atom has a subshell that is exactly half full. The term happens to be normal, but the two levels are separated by only 0.15 mm^{-1} , which is relatively quite tiny.

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7.18: Hyperfine Structure

The levels and lines of many atoms have a hyperfine structure that is detectable only with high resolution, which may require not only interferometry but also a low temperature and low pressure source so that the intrinsic line width is small. Part of this very fine structure is due to the existence of several isotopes, and is not technically what is ordinarily meant by hyperfine structure, but is better referred to as isotope effects, which are dealt with in section 7.19. Hyperfine structure proper arises from the existence of *nuclear spin*, and it is this aspect that is dealt with in this section.

Protons and neutrons, the constituents of an atomic nucleus, collectively known as "nucleons", have, like the electron, a spin of $1/2$. That is to say, they possess an angular momentum

$$\sqrt{\frac{1}{2}(\frac{1}{2} + 1)}\hbar = \frac{1}{2}\sqrt{3}\hbar \quad (7.18.1)$$

oriented such that the component in some direction can have only one of the two values $\pm\frac{1}{2}\hbar$. Consequently a nucleus with an even number of nucleons must have an integral spin (which might be zero) while a nucleus with an odd number of nucleons must have an integral-plus-half spin, which cannot be zero. The spin quantum number of a nucleus is denoted by the symbol I . The magnitude of the nuclear angular momentum is $\sqrt{I(I+1)}\hbar$. It should be noted that different isotopes of a given element in general have different nuclear spins and consequently different hyperfine structure.

Whether the electrons in an atom are coupled by LS or jj or intermediate coupling, the coupling between the electrons is much stronger than the weak coupling between electrons and nucleus. Thus, in considering the coupling between the electrons and the nucleus, J can usually be regarded as a "good quantum number". To determine the total angular momentum of an atom, we have to add (vectorially, and by the rules of quantum mechanics) the nuclear angular momentum \mathbf{I} to the electronic angular momentum \mathbf{J} . This forms the total angular momentum of the atom, including nuclear spin, denoted by the symbol \mathbf{F} :

$$\mathbf{F} = \mathbf{J} + \mathbf{I}. \quad (7.18.1)$$

This equation is very similar to equation 7.13.3, except that, in equation 7.13.3, although S can be either integral or integral-plus-one-half, L is integral; whereas, in equation 7.18.1 both J and I have the possibility of being either integral or integral-plus-one-half. In any case, there are $2\min\{I, J\} + 1$ values of F , going from $|J - I|$ to $J + I$. If $J + I$ is integral, all values of F are integral; and if $J + I$ is integral-plus-one-half, so are all values of F . The magnitude of \mathbf{F} is $\sqrt{F(F+1)}\hbar$.

The nature of the interaction between \mathbf{J} and \mathbf{I} is the same as that between \mathbf{L} and \mathbf{S} in LS -coupling, and consequently the spacing of the term values of the hyperfine levels is similar to that described by equation 7.17.1 for the spacing of the levels within a term for LS -coupling namely:

$$T = \frac{1}{2}b[F(F+1) - J(J+1) - I(I+1)], \quad (7.18.2)$$

except that $b \ll a$. Landé's interval rule is obeyed; that is to say, the separation of two hyperfine levels within a level is proportional to the larger of the two F -values involved. There are similar selection rules for transitions between the hyperfine levels of one level and those of another, namely ΔF and $\Delta J = 0, \pm 1$ ($0 \leftrightarrow 0$) forbidden, and (naturally!) $\Delta I = 0$. Calculating the spacings and intensities in the hyperfine structure of a line is precisely like calculating the spacings and intensities of the lines within a multiplet in LS -coupling.

For nuclei with zero spin, the quantum number M was associated with the vector \mathbf{J} , which was oriented such that its z -component was $M\hbar$, where M could have any of the $2J + 1$ values from $-J$ to $+J$. (We are here describing the situation in the quasi-mechanical descriptive vector model, rather than in terms of the possible eigenvalues of the quantum-mechanical operators, which supplies the real reason for the restricted values of the quantum numbers.) With nuclear spin, however, the quantum number M is associated with the vector \mathbf{F} , which is oriented such that its z -component is $M\hbar$, where M can have any of the $2F + 1$ values from $-F$ to $+F$, these values being integral or integral-plus-one-half according to whether F is integral or integral-plus-one-half. Thus each level is split into $2\min\{J, I\} + 1$ hyperfine levels, and each hyperfine level is $(2F + 1)$ -fold degenerate. Thus the statistical weight of a level is $(2I + 1)(2J + 1)$. (For a derivation of this, recall the *Exercise* in Section 7.14 concerning the statistical weight of a term in LS -coupling.)

If the nuclear spin is zero, the statistical weight of a level is the same as its degeneracy, namely just $2J + 1$. For nonzero nuclear spin, the correct expression for the statistical weight is $(2I + 1)(2J + 1)$. Nevertheless, the statistical weight is often treated as

though it were merely $2J + 1$, and indeed there are many contexts in which this can be safely done. We shall return to this in Chapter 9 when discussing the Boltzmann and Saha equations.

Hyperfine structure of spectrum lines is not often evident in the visible spectrum of stars. Generally the resolution is too poor and the lines are so broadened by high temperature as to mask any hyperfine structure. However, the nuclear spin of, for example, the ${}^5\text{V}$ (vanadium) atom is $I = 7/2$, and the hyperfine structure of the lines, even if not fully resolved, is sufficient to make the lines noticeably broad. In the radio region, the most famous line of all is the 21-cm line of atomic hydrogen, and this involves hyperfine structure. The ground term of H I is $1s\,{}^2S$, which consists of the single level ${}^2S_{1/2}$. This level has $J = \frac{1}{2}$. The nuclear spin (spin of a proton) is $I = \frac{1}{2}$, so the level is split into two hyperfine levels with $F = 0$ and 1. The 21-cm line is the transition between these two hyperfine levels. The transition is forbidden to electric dipole radiation (there is no parity change) and so it involves magnetic dipole radiation. It is therefore intrinsically a very weak line, but there is an awful lot of space out there with an awful lot of hydrogen in it.

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7.19: Isotope effects

The existence of different isotopes of an element gives rise to what could be called hyperfine structure, except that we are restricting the use of the term hyperfine structure to the splitting caused by nuclear spin. There are two quite different isotope effects, which I refer to as the *mass effect* and the *volume effect*.

The effect of different isotopic masses is to displace the centre of mass between nucleus and electrons a small amount. In the hydrogen atom, for example, the term values (neglecting fine structure and referring to the Bohr model) are given by equation 7.4.9, in which the expression for the Rydberg constant includes the reduced mass $\mu = \frac{Mm}{M+m}$ of the electron. It becomes a simple matter to calculate the energy levels and Balmer wavelengths of D, He^+ , Li^{++} , etc., merely by exchanging the reduced mass in H by the reduced mass in the other species. I commend this exercise to the reader. For example, by how much does the wavelength of $\text{H}\alpha$ differ in the spectra of ordinary hydrogen and deuterium? For more complex atoms, the calculation of the isotope shift is more difficult, but the basic reason for the shift is the same.

It might well be thought that isotope shifts would be greatest for very light atoms, but would be negligible for heavier atoms, because the displacement of the position of the centres of mass in different isotopes of a heavy atoms such as, for example, iron, would be negligible. This is indeed the case for the mass isotope effect. It comes as something of a surprise, therefore, to learn that there are significant isotope shifts between isotopes of quite massive isotopes, such as lead, cadmium, gold, mercury, promethium and osmium, and that such shifts have even been observed in stellar spectra. The shift is a result of the relatively large *volumes* of these nuclei. There is no need to go into the detailed theory of the volume effect here, though it is at least useful to know of its existence and, to some extent, its cause. An allowed electric dipole line always involves a transition between two levels belonging to different configurations, and the volume effect is most marked for those transitions in which the two configurations have different numbers of *s*-electrons. These are electrons with zero orbital spin angular momentum, and, in the Bohr-Sommerfeld atomic model (mentioned briefly in section 7.4), these orbits would be ellipses that have degenerated into straight lines through the nucleus. In other words, we can understand that the volume effect is related to the penetration of the nuclei by *s*-electrons, and we can see why the effect is most marked in the largest nuclei.

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7.20: Orbiting and Spinning Charges

In the next section, section 7.21, we are going to look at the Zeeman effect, which is the symmetric splitting of spectrum lines in a magnetic field. Before we get to that, however, it will be useful to review some elementary principles of classical mechanics and electromagnetism in relation to orbiting and spinning electric charges. In particular, an orbiting or a spinning electric charge has *angular momentum* and also a *magnetic moment*. In this section we shall calculate both of these quantities for an orbiting charge and for a spinning charge. In particular we shall calculate for each the ratio of the magnetic moment to the angular momentum for each. This quantity should be called the *magnetogyric ratio*, though for some reason some people refer to it, entirely illogically, as the “gyromagnetic” ratio.

We shall start by considering a point electric charge of mass m and charge e moving with speed v in a circle of radius a . It is elementary classical mechanics that its *angular momentum* is mva . This may be seen either by thinking of angular momentum as synonymous with *moment of momentum* (in which case the moment of momentum is mv times a) or thinking of angular momentum as $I\omega$ (in which case it is ma^2 times v/a). The dimensions of angular momentum are ML^2T^{-1} , and the SI units are conveniently expressed as J s (joule seconds). You should check that the dimensions of J s are correct.

Before calculating the magnetic moment, it is worth while to consider what is *meant* by magnetic moment. This is because there are several different ways in which magnetic moment could be defined (I can think of twelve plausible definitions!) and it by no means clear what different authors think that they mean by the term. I shall use the following concept (which is standard SI). If a magnet is placed in an external magnetic field \mathbf{B} (of which the SI unit is tesla), the magnet will in general experience a *torque*. (I say “in general” because if the magnetic moment is parallel or antiparallel to the field, there will be no torque.) The magnitude of the torque depends on the orientation of the magnet with respect to the torque. There are two particular directions (opposite to each other - i.e. differing by 180°) in which the torque is a maximum. Definition: *The magnetic dipole moment is the maximum torque experienced in unit magnetic field \mathbf{B} .* It is a vector quantity, and I propose to use the symbol $\boldsymbol{\mu}$ for it, or μ for its magnitude, unless contexts arise in which μ might be confused with something else (such as permeability, for example). I shall warn if I need to use an alternative symbol. With that definition, the expression for the torque $\boldsymbol{\tau}$ on a magnet of moment $\boldsymbol{\mu}$ in a external field \mathbf{B} is

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B} \quad (7.20.1)$$

This equation alone will not define $\boldsymbol{\mu}$ uniquely, for (if you have experienced solutions of vector equations before) the equation cannot be solved uniquely for $\boldsymbol{\mu}$. However, in concert with the definition given in the italicized sentence above, the magnetic moment is defined uniquely and without ambiguity. The SI unit is N m T^{-1} . (J T^{-1} would also do in principle, except that joule does not suggest the concept of *torque* as well as N m does.) An example is usually given in introductory electricity courses for the torque on a plane, current-carrying coil, in which it is shown that the magnetic moment in that case is equal to the current times the area of the coil (times the number of turns if there are more than one). Thus equivalent and fully acceptable SI units are A m^2 . The dimensions of magnetic moment are IL^2 . (It will be noted that magnetic moment is often quoted in other units such as T m^3 or G cm^3 . If not actually wrong, these must describe dimensionally different definitions of what is meant by magnetic moment. T m^3 , for example, is not dimensionally the same as N m T^{-1} . I do not pursue this aspect here; I have given the standard SI treatment.)

With that introduction, we can now move to calculate the magnetic moment of a point electric charge e moving with speed v in a circle of radius a . The effective current is the charge divided by the period of the orbit, which is $e \div (2\pi a/v) = ev/(2\pi a)$. The area of the circle is πa^2 , so the magnetic moment is $eav/2$.

The ratio of the magnetic moment to the angular momentum, i.e. the *magnetogyric ratio*, is $\frac{e}{2m}$. The SI unit is C kg^{-1} . For an electron moving in a circle (of whatever radius and at whatever speed) its magnitude is $8.794 \times 10^{10} \text{ C kg}^{-1}$.

What about a spinning sphere of finite radius? Well, if the charge and the mass are both uniformly distributed throughout the sphere, or if they are not uniformly distributed but charge and mass are *equally* distributed throughout the sphere, then the magnetogyric ratio is again just $\frac{e}{2m}$, because every little element of the spinning sphere can be considered to be a point charge moving in a circle.

But what if the charge and mass densities are distributed differently? For example, if the sphere were a charged metal sphere, in which the mass is distributed uniformly through the sphere, but the charge is confined to the surface? In this case you would expect the magnetogyric ratio to be a good deal greater than $\frac{1}{2} \cdot \frac{e}{m}$. You will probably find it easy to calculate the *angular momentum* of a uniform sphere of mass m and radius a spinning at angular speed ω . It will be slightly more difficult, but a very good exercise, to

work out the *magnetic moment*, assuming that all the charge is on the surface. You should find that the magnetogyric ratio is $\frac{5}{6} \cdot \frac{e}{m}$, which, as expected, is a good deal larger than $\frac{1}{2} \cdot \frac{e}{m}$. From this it might be anticipated that, if we could somehow measure (perhaps from the Zeeman effect) the magnetogyric ratio of an electron (which, indeed, we can, and with quite extraordinary precision) we can get some information about how mass and charge are distributed throughout the electron. In fact it turns out that the magnetogyric ratio of a spinning electron is very close to e/m . This suggests not only that the charge is distributed near to the surface but that the mass is concentrated near to the centre. Is this true? It is true that we can measure the magnetogyric ratio spectroscopically, and it is true that it turns out to be very close to e/m . Whether deducing from this that an electron is a sphere in which the charge is held near the surface and the mass is centrally concentrated is a bit more problematical. It is not necessarily "wrong", but it may not be a very useful model to describe other properties of the electron beyond its magnetogyric ratio. Particle physicists generally regard an electron as a "lepton" without any discernible internal structure. Perhaps physics cannot say what an electron (or anything else) really "is"; we can describe its observable properties and use whatever models appear best to describe these and to predict its behaviour.

I move now to the question of what is the *potential energy* of a magnet of moment μ when it is situated in a magnetic field \mathbf{B} . When the angle between μ and \mathbf{B} is θ , there is a torque on the magnet of magnitude $\mu B \sin \theta$ (see equation 7.20.1). The work needed to increase θ by $d\theta$ is $\mu B \sin \theta d\theta$, and the work needed to go from θ_1 to θ_2 is therefore $\mu B (\cos \theta_1 - \cos \theta_2)$, which is the difference in potential energy between the two positions. We may choose the zero level for potential energy where we will. If, for example, we choose the potential energy to be zero when μ and \mathbf{B} are parallel, the potential energy at angle θ is $\mu B (1 - \cos \theta)$. If, on the other hand, we choose the potential energy to be zero when μ and \mathbf{B} are at right angles to each other (as is very often done), the potential energy at angle θ is $-\mu B \cos \theta$, or $-\mu \cdot \mathbf{B}$. With this convention, the potential energy is $-\mu B$, 0 or $+\mu B$ for μ and \mathbf{B} parallel, perpendicular or antiparallel.

One last topic before proceeding to the Zeeman effect. Those who have studied classical mechanics will appreciate that if a spinning body, of angular momentum \mathbf{L} is subjected to an external torque $\boldsymbol{\tau}$, it will *precess* with an angular speed $\boldsymbol{\Omega}$, and the three vectors are related by

$$\boldsymbol{\tau} = \boldsymbol{\Omega} \times \mathbf{L}. \quad (7.20.2)$$

Again, those familiar with vector equations will note that this equation cannot be solved uniquely for $\boldsymbol{\Omega}$, because we don't know the angle between $\boldsymbol{\tau}$ and \mathbf{L} . If, however, we are dealing with a nonvertical top spinning on a table, the torque is at right angles to the angular momentum vector and the rate of precession is $mg l / L$, where l is the distance between the bottom of the top (sorry for the choice of words) and the centre of mass. (Those who are very familiar with the theory of the top, will recognize that we are here referring to the rate of true or pseudo regular precession, after nutational motion has been damped out - but there is no need for such niceties here.)

Now consider a spinning magnet whose magnetic moment is μ and whose angular momentum is \mathbf{L} . Suppose it is placed in a magnetic field \mathbf{B} . It now experiences a torque $\boldsymbol{\tau} = \mu \times \mathbf{B}$. The result of this is that, regardless of the angle between \mathbf{L} and \mathbf{B} , \mathbf{L} will precess around \mathbf{B} at an angular speed $\mu B / L$. That is to say, at an angular speed equal to B times the magnetogyric ratio. In the case of a particle of charge e and mass m moving in a circle the angular speed of precession is $\frac{eB}{2m}$. This is called the *Larmor angular speed*, and $\frac{eB}{4\pi m}$ is the Larmor frequency. If e , B and m are expressed in C, T and kg respectively, the Larmor frequency will be in Hz.

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7.21: Zeeman effect

When a hot gas which is emitting or absorbing spectrum lines is placed in a magnetic field, the lines become split into several *components*. This is known as the *Zeeman effect*, discovered in 1896 by the Dutch spectroscopist P. Zeeman.

If we start by thinking of an atom with zero nuclear spin, it will be recalled that every energy level except those with $J = 0$ is *degenerate*. That is, there are $2J + 1$ wavefunctions, or eigenstates, or just *states*, each described by a quantum number M , which goes from $-J$ to $+J$, and each of these states has exactly the same energy. When the atom is placed in an external magnetic field, this degeneracy is removed, and each state has a slightly different energy. This happens to both levels involved in the formation of a line (unless one of the levels has $J = 0$), with the result that the line that joins the two levels is split up into a number of components. It will be recalled that a *line* joins two *levels*. In a similar manner a (Zeeman) *component* joins two *states*. Just as a *multiplet* is the totality of *lines* joining two *terms*, so a *line* is the totality of *components* joining two *levels*. In the absence of a magnetic field, all the states within a level have the same energy, and all the components that make up a line have the same wavelength. A *term* is described by LS . Its multiplicity is $2\min\{L, S\} + 1$ and its statistical weight is $(2L + 1)(2S + 1)$. A *level* is described by LSJ . Its degeneracy and statistical weight are $2J + 1$. A *state* is described by $LSJM$. It is not degenerate; its statistical weight is 1.

In sections 9, 10, and 11 of this chapter, I went to some trouble to persuade you that an electron is not a hard, spinning sphere that moves in a circular orbit around a nucleus. Rather I described electrons in terms of wavefunctions that describe the probability amplitude, and quantum numbers were eigenvalues of certain operators and were restricted to certain values as a result of boundary conditions. What model we use to describe the behaviour of atoms depends on our purpose, and, if our purpose was to obtain expertise in the intricacies of quantum mechanical calculations, we would have to become heavily involved in the algebra of kets, operators and eigenfunctions. Our present purpose, however, is to become acquainted in a rather descriptive way with spectroscopy, and in describing Zeeman phenomena without the intention of performing quantum mechanical calculations. It will be convenient to revert to a model of an electron, if not as a hard, spinning, orbiting particle, at least as an entity that possesses the attributes of orbital and spin angular momentum and consequently also of magnetic moment.

In particular, we recall that an orbiting electron has an orbital angular momentum $\sqrt{l(l+1)}\hbar$, where $\hbar = h/(2\pi)$ has the value 1.055×10^{-34} J s. Now, if we take the magnetogyric ratio of an orbiting electron to be $e/(2m)$, the magnetic moment of an orbiting electron is $\sqrt{l(l+1)} \cdot \frac{e\hbar}{2m}$. (Those who object to this simple treatment - and there are some rather obvious objections - will have no alternative but to do a proper quantum mechanical derivation, though the result is the same.) In any case, the quantity $\frac{e\hbar}{2m}$, a unit of magnetic moment, is called the *Bohr magneton*, and its value is 9.274×10^{-24} N m T⁻¹ or A m². I shall use the symbol μ_B to indicate the Bohr magneton. Thus the *orbital* angular momentum of an electron is $\sqrt{l(l+1)}\hbar$ and its magnetic moment is $\sqrt{l(l+1)}\mu_B$. The magnetogyric ratio of an orbiting electron (not taking into account the contribution to angular momentum and magnetic moment from its spin) is $\mu_B/\hbar = e/(2m) = 8.794 \times 10^{10}$ C kg⁻¹, or, if we agree to express angular momentum in units of \hbar and magnetic moment in units of Bohr magnetons, the magnetogyric ratio of an orbiting electron (still taking no account of the contributions of spin) is 1. The *spin* angular momentum of an electron is $\sqrt{s(s+1)}\hbar$, where $s = 1/2$, and its magnetic moment is (very close to) $2\sqrt{s(s+1)}\hbar$, so that its magnetogyric ratio is just e/m , or, in units of μ and \hbar , it is 2. (The exact value of the magnetogyric ratio, in units of μ_B/\hbar , is a little more than 2, and is one of the most precisely-known of the fundamental physical constants. Its value in the year 2000 is given as 2.002 319 304 374.)

In discussion of the Zeeman effect, we shall need to know the magnetogyric ratio of the *atom* in a given level, since this determines the way in which the levels are split in a magnetic field. The ratio of the magnetic moment *in units of* μ_B to the angular momentum *in units of* \hbar is known as the **Landé splitting factor**, and is generally denoted by the symbol g . It is the magnetogyric ratio in units of $e/(2m)$, or 8.794×10^{10} C kg⁻¹. The magnetogyric ratio, or Landé splitting factor, of an atom in a given level depends on the angle between the vectors \mathbf{L} and \mathbf{S} and hence on their resultant \mathbf{J} , and, though I do not do it here, it is not difficult to show that, in the case of LS -coupling, the Landé splitting factor has the value

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (7.21.1)$$

(This formula is calculated using the approximate value 2 for the magnetogyric ratio of the electron rather than the more accurate 2.00232. More accurately, it should be written

$$g = 1 + 1.00232 \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (7.21.2)$$

Formulas for the g -factor for other coupling schemes are available, but I do not give them here, since in practice the coupling between electron angular momenta in complex atoms is usually intermediate between idealized extremes, and the calculation has to be done numerically. In many of the lightest atoms, however, pure LS -coupling is a good approximation. The g -value can be found experimentally from observations of the Zeeman effect, and, in addition to Landé's interval rule mentioned earlier, this affords another good indication of how close a level is to LS -coupling.

Problem. The ${}^5P_1 - {}^5D_0^\circ$ line of Fe I at 617.33 nm is often used to investigate magnetic fields in sunspots. The strongest line of the multiplet that includes this line is ${}^5P_3 - {}^5D_4^\circ$. Calculate the g -factor for each of the four levels mentioned.

A small point to be made is as follows. From what we have said, the magnetic moment of an atom (excluding nuclear spin, if any) is of magnitude $\mu = g\mu_B \sqrt{J(J+1)}$. (This follows from the definition of g , which is the ratio of the magnetic moment in units of the Bohr magneton - i.e. μ/μ_B - to the angular momentum in units of \hbar .) In vector form this must be written $\boldsymbol{\mu} = -g\mu_B \mathbf{J}$, where \mathbf{J} is a dimensionless vector of magnitude $\sqrt{J(J+1)}$ and the minus sign arises because of the negative electron charge, the magnetic moment and angular momentum vectors being oppositely directed.

When the Zeeman effect was first investigated, lines were observed to be split into just three components, and this was referred to as the *normal Zeeman effect*. Later, more complex patterns were observed, and this was referred to as the *anomalous Zeeman effect*. As we now understand it, the so-called "normal" Zeeman effect is merely the Zeeman effect observed on lines joining levels with spin $S = 0$, which have a simpler Zeeman pattern than other lines. In addition to the Stern-Gerlach experiment, it was the study of "anomalous" Zeeman splitting that gave rise to the discovery of electron spin.

We are now in a position to start looking at how energy levels are split in the presence of a magnetic field. Let us consider, for example, a 1P_1 level ($L, S, J = 1, 0, 1$). The Landé factor is 1. (Note that for any level in which $S = 0$ and therefore in which J and L are necessarily equal, Equation 7.21.1 (or 7.21.2) shows that $g = 1$.)

The magnetic moment is $\boldsymbol{\mu} = -g\mu_B \mathbf{J} = -\mu_B \mathbf{J}$. The energy of a magnet in a magnetic field is $-\boldsymbol{\mu} \cdot \mathbf{B}$, so in this case it is $\mu_B \mathbf{J} \cdot \mathbf{B}$. But $\mathbf{J} \cdot \mathbf{B}$ is equal to B times the component of \mathbf{J} in the direction of \mathbf{B} , which is M . Thus the energy of the state M in the magnetic field is $\mu_B MB$. There are three values of M ($-1, 0, 1$). The splitting of the level into its three states is linearly proportional to the magnetic field B , and the separation between adjacent states is $\mu_B B$.

If we consider a 1D_2 level, again $g = 1$, and the states have just the same spacing, except that this time there are five states, with $M = -2$ to $+2$.

Now consider the line ${}^1P_1 - {}^1D_2$. This is the totality of all transitions connecting the three states in the one to the five states in the other. Not all transitions are possible, however, so there are not fifteen components to the line. Selection rules (to be dealt with in Section 7.24) limit the only possible transitions to those for which $\Delta M = 0$ or ± 1 . Figure VII.1 shows the energy levels of the eight states and the nine possible transitions that connect them.

It will be seen that the nine components are in three groups of three, and that, because the spacings in the two levels are the same (which in turn is a result of $S = 0$), all three lines in a given group have exactly the same wavelength (although I have drawn them slightly separated). Consequently, you will see in the spectrum apparently only three Zeeman components, the full

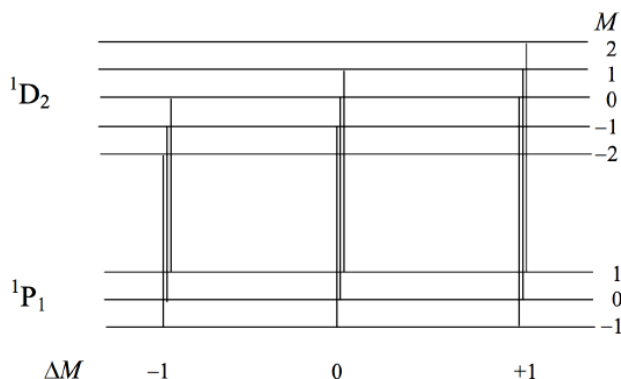


FIGURE VII.1

nine not being completely separated. This is what was called the "normal" Zeeman effect. However, as soon as $S \neq 0$, the g -values of the two levels will be different, spacings of the states in the two levels will be different, all the components will be fully separated, and we see the "anomalous" Zeeman effect, although there is nothing really at all anomalous about it. In a sense, the "normal" Zeeman effect is exceptional. In figure VII.2 I have drawn, schematically (with wavelength increasing linearly to the right), the Zeeman pattern for ${}^2S_{1/2} - {}^2P_{3/2}$. The splitting factors for the P and S levels are, respectively, 2 and $4/3$. It happens

that in this case all six Zeeman components are equally spaced, though this is not always the case; the exact pattern of Zeeman components varies from line to line

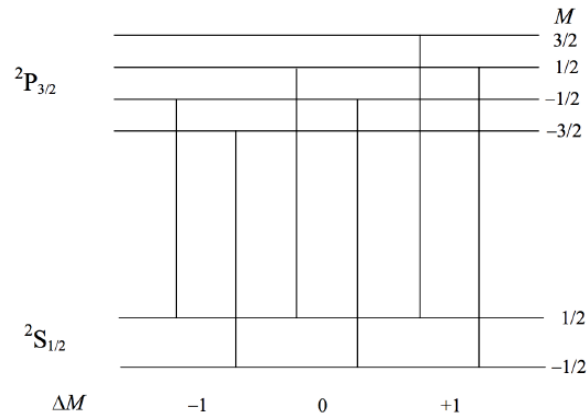


FIGURE VII.2

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7.22: Paschen-Back Effect

The description I have given so far of the way in which a level is split up and the states are separated in a magnetic field is good for relatively weak magnetic fields, but begins to break down for strong fields. What do I mean by "weak" and "strong"? The type of splitting I have described starts to break down when the energy separation of the states of a level becomes comparable to the separation of the levels within a multiplet. Stated otherwise, it breaks down when the strength of the coupling between **J** and **B** becomes comparable to the strength of the coupling between **L** and **S**. At that stage, the coupling between **L** and **S** breaks down, and *J* ceases to be a "good quantum number". **L** and **S** become separately coupled to, and precess separately around, **B**. The components of **L** and **S** in the direction of **B**, in units of \hbar , are M_L and M_S , with possible values from $-L$ to $+L$ and $-S$ to $+S$, respectively. The interaction energies between **L** and **B** and between **S** and **B**, are, respectively, $\mu_B M_L B$ and $2\mu_B M_S B$, and there will also be a relatively small remanent spin-orbit interaction between *L* and *S*, represented by $AM_L M_S$, so the total interaction energy, which determines the splitting of the level into separate states, is $(M_L + 2M_S)\mu_B B + AM_L M_S$. This gives rise to a quite different pattern of splitting of the levels into their constituent states, and consequently a quite different pattern of the splitting of a line into its components. This is the *Paschen-Back effect*. The Landé splitting factor can then no longer be defined as the ratio of the magnetic moment in Bohr magnetons to the angular momentum in units of \hbar . *L* and *S* are no longer coupled to each other, and *J* is no longer a good quantum number. Rather, the *g*-factor is the ratio of the sum of the components of the orbital and spin magnetic moments in the direction of **B** to the sum of the components of the orbital and spin angular momenta in that direction. That is

$$g = \frac{M_L + 2M_S}{M_L + M_S}. \quad (7.22.1)$$

? Exercise 7.22.1

The first excited term of Mg I is a $^3\text{P}_0$ term. The separation in term values between the levels $J = 0$ and $J = 1$ is 20 cm^{-1} and between $J = 1$ and $J = 2$ is 40 cm^{-1} , so that the multiplet evidently conforms to **Landé's interval rule** and hence to *LS*-coupling. How large a magnetic field, in tesla, would be necessary so that splitting of the states within the $^3\text{P}_1^o$ level is 20 cm^{-1} ?

(I make it about 29 T, which is a very strong field.)

Problem. On a sheet of graph paper, draw the three levels of a ^3P multiplet. Choose a scale so that the spin-orbit coupling coefficient (equation 7.17.1) $a =$ one inch, so that the energy levels of the three levels of the term are at -2 , -1 and $+1$ inches. The $J = 0$ level has only one state, and the *g*-values for the other two levels are each 1.5. Now apply a weak magnetic field, thus separating the states, and to the right of your zero-field energy level diagram of the three levels draw the energy levels for the nine states, such that the separation between adjacent states is one tenth of an inch. The $J = 0$ level, of course, is not split. The other two levels are split into three and five states. Mark the value of M_J against each state. (We have previously used the symbol *M*, but in the present context, let's call it M_J so as to be able to distinguish it from M_L and M_S .) You now have the Zeeman effect. Now apply a strong field. Since *S* and *L* are each 1, the projections of each can be -1 , 0 , $+1$, so there are nine combinations of M_L and M_S . For each of these, calculate $(M_L + 2M_S)\mu_B B + AM_L M_S$ supposing that (on the scale of your graph) $\mu_B B = 4$ inches and $A = 0.2$ inches. Here, I'll do it:

M_L	M_S	$(M_L + 2M_S)\mu_B B + AM_L M_S$	<i>J</i>	M_J
1	1	12.2	2	2
1	0	8.0	2	1
1	-1	3.8	2	0
0	1	4.0	1	1
0	0	0.0	1	0
0	-1	-4.0	2	-1
-1	1	-4.2	0	0
-1	0	-8.0	1	-1
-1	-1	-11.8	2	-2

These are the energies of the states in the Paschen-Back effect, so you can now draw them on your graph paper. Leave a gap of a couple of inches between the Zeeman energies and the Paschen-Back energies. You may be interested to know how the Zeeman states correlate with the Paschen-Back states. Well, a given value of M_J correlates with the same value of $M_S + M_L$, and that

gives you two of the correlations without ambiguity. For the rest, I have tabulated, in the last column above, the J and M_J values of the Zeeman state that correlates with each Paschen-Back state. You can now join each Zeeman state to its corresponding Paschen-Back state with a straight line. You can think of the horizontal scale as being increasing magnetic field. In reality, although the Zeeman splitting starts out by increasing linearly with magnetic field, it is not linear all the way to the corresponding Paschen-Back states; the detailed calculation has to be done numerically.

Of course, in *very* strong magnetic fields, even the coupling between the several \mathbf{l} s to form \mathbf{L} and the several \mathbf{s} s to form \mathbf{S} breaks down, and the individual \mathbf{l} s and \mathbf{s} s couple strongly with \mathbf{B} . You then have to be careful to be sure that no two electrons have the same set of values of n, l, m_l, m_s .. This complete breakdown of the coupling of the several angular momenta to each other in favour of coupling to the magnetic field is called the *complete Paschen-Back effect* - but that's another story, which I don't deal with here.

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7.23: Zeeman effect with nuclear spin

So far, I have described the splitting of the states within a level J on the assumption that there is no nuclear spin. Now I move to the case of an atom with nuclear spin I . We have seen in section 7.18, equation 7.18.1, that the electronic angular momentum \mathbf{J} combines with the nuclear spin angular momentum \mathbf{I} to form the total angular momentum \mathbf{F} for the atom, and we have seen, in equation 7.18.2, how the term values of the resulting hyperfine levels are spaced. Let us consider a level $J = 1$ in an atom whose nuclear spin is $I = 1$. The hyperfine levels are then spaced in exactly the same manner as the levels are placed in a ^3P term ($L = 1, S = 1$). Draw the three hyperfine levels on your graph paper, with the $F = 0, 1, 2$ hyperfine levels at $-0.2, -0.1$ and $+0.1$ inches respectively. Now, if you apply a very small magnetic field, each hyperfine level will be split up into $2F + 1$ equally-spaced states. But you must now bear in mind that the coupling between \mathbf{J} and \mathbf{I} is exceedingly weak (i.e. the spacings between the hyperfine levels is exceedingly small), so this Zeeman effect will obtain for only very tiny magnetic fields indeed. As soon as the magnetic field is at all appreciable, \mathbf{J} and \mathbf{I} uncouple from each other and they then couple independently with \mathbf{B} to form a Paschen-Back effect. Does this make life unbearably complicated? As it turns out - not at all! The separation of the states is given by exactly the same sort of expression as for the Paschen-Back effect earlier described, namely $(M_J + g_I M_I)\mu_B B + AM_J M_I$, except that the nuclear g -factor is not 2 as in the case of the electron, but is of order 10^{-3} . This makes a world of difference to the way the states are separated. Let us calculate the term values, as we did before with the Paschen-Back effect, and we'll use the same field strength as before so that $\mu_B B$ is represented by 4 inches, but this time, purely for illustrative purposes, we'll put $g_I = 0.002$ and $A = 0.0002$ inches. The result of the calculation (which you should carry out yourself - it is very quick with a programmable calculator, though tedious without) is as follows:

M_I	M_J	$(M_J + g_I M_I)\mu_B B + AM_J M_I$	F	M_F
1	1	4.01	2	2
1	0	0.01	2	1
1	-1	-3.99	2	0
0	1	4.00	1	1
0	0	0.00	1	0
0	-1	-4.00	2	-1
-1	1	3.99	0	0
-1	0	-0.01	1	-1
-1	-1	-4.01	2	-2

Now please do draw these out on your graph paper. You will find that the states are spaced in three widely-separated groups of three, with three closely-separated states in each group. You will not appreciate exactly what is happening unless you actually draw it out. But, if you do, you will see that, if your resolution is such that you cannot resolve the hyperfine structure in the zero-field situation, and you are unaware of or do not care about the nuclear spin, and you think that you have but a single level with $J = 1$, when you apply a magnetic field what happens is this: you will find that this level is apparently split into three "states" (which you cannot resolve into their several genuine states), and it will appear that you have a perfectly ordinary Zeeman effect in which the nuclear spin plays no role at all. Only with high-resolution, cold-source, interferometric resolution will you see the hyperfine structure of each component into hyperfine components.

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7.24: Selection rules

It will be recalled that a *multiplet* is the totality of transitions between two terms. For example, $^3P - ^3D^o$ is the multiplet connecting the two terms 3P and $^3D^o$. Each term has three levels, and therefore there are nine ways of connecting the levels of one term with the other, each transition resulting in a *line*. But in fact only six of these transitions are "allowed" or "permitted", the remaining three being "forbidden". This is because of certain "selection rules", or restrictions in the way some of the quantum number can change. Likewise there are restrictions on the number of multiplets that can connect the terms of two polyads, or on the number of Zeeman components that can connect the states of two levels. In all of these situations there are selection rules that restrict certain quantum numbers from changing by other than certain amounts. In this section we shall try to understand in a qualitative way how such selection rules arise. We shall list the various selection rules, and see how this will affect the number of lines in a multiplet, or the number of components in a line.

Everyone knows that when an electric dipole oscillates it radiates an electromagnetic wave. Likewise, if a dipole, rather than periodically oscillating, suddenly undergoes a change in its electric dipole moment – for example, if the distance between two opposite electric charges suddenly changes – a pulse of electromagnetic radiation will be radiated. While the radiation from a single atom will be radiated like that of a dipole, in a gas with enormous numbers of atoms oriented in completely random directions, the radiation will appear isotropic.

One reasonable way of explaining how an atom radiates a pulse (a quantum) of electromagnetic radiation when it changes from one state to another is that its dipole moment changes, and the energy radiated is related to the change in its dipole moment. Indeed in quantum mechanics, the amount of energy radiated when an atom changes from one state to another is determined by the square of a quantity known as the *transition moment*:

$$\int \psi_f^* \mu \psi_i d\tau. \quad (7.24.1)$$

Here $d\tau$ is the usual volume element, and ψ_i is the wavefunction of the initial state. μ is the *dipole moment operator*, which depends on the positions of all the electrons in the atom. ψ_f^* is the conjugate of the wavefunction of the final state. Those who have lots of practice in performing such calculations are experienced enough to know that the effect of the dipole moment operator is merely to produce a similar wavefunction with perhaps some changes in the quantum numbers. Therefore, in order to save writing out the complete expression for the wavefunction in full, they merely list the quantum numbers of the initial wavefunction in a ket, and of the conjugate of the final function in a bra, thus:

$$\langle L' S' J' M' | \mu | L S J M \rangle. \quad (7.24.2)$$

Again, those who do such calculations daily for a living soon recognize, from the very symmetries of the wavefunctions (group theory) and without having to worry greatly about the details of the functions, that this transition moment is zero unless there are certain relations between the initial and final quantum numbers. It is those transitions that result in a nonzero transition moment that are "allowed". If the transition moment is zero, which it is except for certain combinations of initial and final quantum numbers, the transition is "forbidden".

For example, if we are discussing the possible Zeeman components of a line, the only "allowed" transitions - i.e. the only nonzero transition moments - are those in which the initial and final values of M are either equal or differ by ± 1 . We say that the "selection rule" for the Zeeman effect is $\Delta M = 0, \pm 1$. We already took account of this restriction in drawing figures VII.1 and VII.2. In the former, instead of 15 possible components, there are only nine with nonzero transition moments and which satisfy the selection rule, and in figure VII.2 there are only six rather than eight.

Actually, when observing the Zeeman effect, if we view the light from a direction perpendicular to the magnetic field, we see that the components with $\Delta M = 0$ are plane polarized parallel to the magnetic field, and are called the *p*-components, and the ones with $\Delta M = \pm 1$ are plane polarized perpendicular to the magnetic field, and are called the *s*-components (German *senkrecht* - perpendicular). (It may appear that the symbols *s* and *p*, especially the former, are by now doing more than their fair share of work.) If the spectrum is viewed from a direction along the magnetic field, the *s*-components will be found to be circularly polarized in opposite senses, while the *p*-components are not visible at all.

Just as the number of Zeeman components of a line is limited by the selection rule $\Delta M = 0, \pm 1$ in a similar manner the number of possible lines in a multiplet is limited by a selection rule $\Delta J = 0, \pm 1$ ($0 \leftrightarrow 0$ forbidden). I already mentioned that a $^3P - ^3D^o$ multiplet has just six lines rather than nine. Figure VII.3 shows the possible transitions. (Unlike figures VII.1 and VII.2, in which

the horizontal scale was linear in wavelength with wavelength increasing to the right, the horizontal scale in figure VII.3 has no significance.)

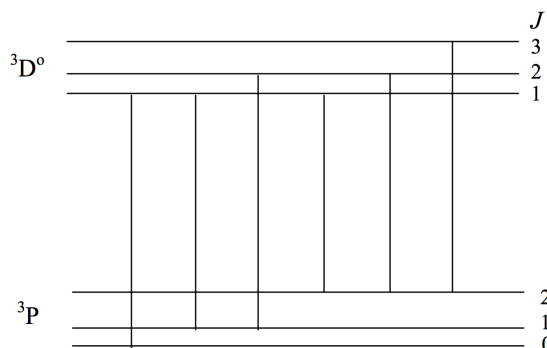


FIGURE VII.3

It may be that a line, or a component, is forbidden to dipole radiation and that, if μ is the electric dipole moment operator, the transition moment is zero. However, if we substitute for the dipole moment operator the operator for electric quadrupole or magnetic dipole moment, the transition moment is not zero. In that case a transition that is forbidden to electric dipole (E1) radiation may be permitted to electric quadrupole (E2) or magnetic dipole (M1) radiation. E2 and M1 transitions are very weak and are rarely observed under laboratory conditions (though they occur in astronomical sources for reasons that will be explained later). Therefore lines that are forbidden to electric dipole radiation are generally referred to merely as "forbidden" lines - even though they are not actually forbidden to E2 or M1 radiation. The carrier (atom) for a forbidden line is often written in brackets. For example, there is an E2 line in the spectrum of the aurora at 557.7 nm arising from the neutral oxygen atom, so the line is said to be a line of $[O_I]$.

Some multiplets are forbidden to electric dipole radiation only if the terms concerned conform strictly to LS -coupling, but may be allowed for electric dipole radiation if there are departures from LS -coupling. Such transitions are "semi-forbidden", and the carrier is sometimes written between a bracket and a parenthesis. Thus there is a semi-forbidden line at 345.3 nm due to $[Al_I]$. For LS -coupling, electric dipole radiation is allowed only if $\Delta S = 0$. That is to say, transitions are allowed between two triplet terms, or between two singlet terms, but not between a triplet or a singlet. (In this connection I am referring to a 3S term as a "triplet" term, even though it has just one level.) Not everyone uses this bracket-parenthesis convention.

In the neutral helium atom, there are singlet terms and triplet terms. LS -coupling is the norm, and, because of this, there are no transitions between any of the singlet terms and a triplet term. Indeed, it is as if there are two entirely independent sets of terms and two spectra, and indeed the singlet terms and the triplet terms are sometimes referred to as "para-helium" and "ortho-helium" respectively. Under such circumstances it is difficult (or impossible in the absence of additional independent evidence) to know the relative energies of the triplet and singlet terms, or to know which is the ground term of the atom - although we do now know that the ground term of helium is a 3S term.

Neutral calcium also has a set of singlet terms and a set of triplet terms, but there are departures from LS -coupling, and there are multiplets that connect singlet with triplet terms and *vice versa*. Such multiplets are called "intercombination" or "intersystem" multiplets. For example the line at 657.3 nm is a member of a $^1S - ^3P^o$ multiplet of $[Ca_I]$.

Here is a list of the various selection rules I can think of. I haven't included nuclear spin, but you may deduce what the rules are, given that the coupling between electron angular momentum and nuclear spin is generally pure JI -coupling (analogous to LS -coupling).

For Electric Dipole Transitions. Transitions take place between terms of different configurations, such that the l -value of one electron must change by ± 1 . It follows that allowed transitions are between terms of opposite parity. Lines within a multiplet are subject to the selection rule $\Delta J = 0, \pm 1$, except that 0 to 0 is forbidden. (These rules break down for electric dipole radiation in the presence of a strong external electric field, which need not concern us here, but needs to be considered with respect to the *Stark effect*.) Zeeman components of a line are subject to the selection rule $\delta M = 0, \pm 1$.

For LS -coupling, there are the following additional constraints. $\Delta S = 0$; that is to say, intersystem transitions are forbidden to electric dipole radiation. They are "semi-forbidden". $\Delta L = 0, \pm 1$, except that 0 to 0 is forbidden. Thus $S - S^o$,

$S - D^{\circ}$, $P - F^{\circ}$ multiplets would all be indicative of departures from LS -coupling. Transitions must also take place between terms of common parentage.

For Magnetic Dipole Transitions. Transitions take place between terms of a single configuration, and hence between terms of the same parity. Lines within a multiplet are subject to the selection rule $\Delta J = 0, \pm 1$, except that 0 to 0 is forbidden. Zeeman components of a line are subject to the selection rule $\Delta M = 0, \pm 1$, except that ΔJ and ΔM cannot both be zero.

For LS -coupling there are the additional constraints $\Delta S = 0$ and $\Delta L = 0$.

For Electric Quadrupole Transitions. Transitions take place either between terms of the same configuration or between configurations in which the l -value of one electron changes by ± 2 . In either case this implies that transitions take place between terms of the same parity. Lines within a multiplet are subject to the selection rule $\Delta J = 0, \pm 1, \pm 2$, except that $0 - 0, \frac{1}{2} - \frac{1}{2}, 0 - 1$ and $1 - 0$ are forbidden. This implies that $J' + J''$ must be at least 2 . Zeeman components of a line are subject to the selection rule $\Delta M = 0, \pm 1, \pm 2$.

For LS -coupling there are the additional constraints $\Delta S = 0$ and $\Delta L = 0, \pm 1, \pm 2$, except that $\Delta L = 0 - 0, 0 - 1, 1 - 0$ are forbidden. Transitions must also take place between terms of common parentage.

Exercise. In section 7.16 I listed the first ten levels for the hydrogen atom - i.e. the levels in the first three shells. I also asserted that $H\alpha$ comprises three transition arrays, three multiplets, seven lines and an unspecified number of Zeeman components. Now that you are familiar with selection rules, you are in a position to verify this. Therefore, as an exercise, list all of the arrays, multiplets and lines comprising $H\alpha$. (You should assume LS -coupling; obviously with just one electron there is no distinction between LS - and jj -coupling.) For example, $2p - 3d$ is one array. $2p^2 P^{\circ} - 3d^2 D$ is a multiplet. $2p^2 P^{\circ}_{\frac{3}{2}} - 3d^2 D_{\frac{5}{2}}$ is a line. In the table in section 7.16, I have listed the statistical weight of each level. For each level, list the possible M values, and then, using the Zeeman selection rules, determine how many Zeeman components there are for each level, and therefore for $H\alpha$ as a whole. How many of the Zeeman components have distinct wavelengths?

In the above exercise, perhaps you ignored the effect of nuclear spin. Now include nuclear spin ($I = 1/2$). You will see now that each of the eight levels involved in the formation of $H\alpha$ is split into two hyperfine levels with different values of F . Now, how many hyperfine and Zeeman are there?

Now answer the same questions with deuterium. One might hope that the deuterium nucleus (the "deuteron") has zero nuclear spin - but no such luck, for the spin of the deuteron is $I = 1$. Thus most of the levels are composed of three hyperfine levels. (Why did I say "most"? Some of the levels have just two hyperfine levels, don't they? Do you see why?) How many hyperfine and Zeeman components are allowed by the selection rules?

Of course, natural hydrogen includes both ^1H and a very small amount of ^2H , and the spectra of both will be exhibited. Truly $H\alpha$ is a much more complicated "line" than we envisaged in section 7.3! To add to the complication, we must not forget that under terrestrial conditions, hydrogen is molecular, and there are three possible isotopomers - H_2 , HD and D_2 - and those familiar with molecular spectra will recall that there are obvious differences between the spectra of homonuclear and heteronuclear molecules. One could clearly spend a lifetime studying the spectrum of hydrogen!

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7.25: Some forbidden lines worth knowing

The states in the ground level of an atom are the only stable states. Atoms may be raised to higher levels by collisions, but these excited states are not very stable, and an atom in an excited state will very soon de-excite by radiative emission of a photon. Lifetimes in the excited states are typically of the order of nanoseconds. However, the probability of de-excitation by emission of magnetic dipole or electric quadrupole radiation is much smaller than that for electric dipole radiation, and the lifetimes of excited states for M1 or E2 radiation may be seconds or even minutes. Such states are called *metastable* states. In normal laboratory conditions the interval between interatomic collisions (or collisions with the wall of the containing vessel) is very much shorter than the mean lifetime of a metastable level. (You can work out the inter-collision time from kinetic theory of gases.) Thus an atom will be knocked out of a metastable level by collision long before it has had a chance to emit M1 or E2 radiation. This is not so in very thin gases in some astronomical sources, such as the aurora or in emission nebulae. In such milieus collisions are few and far between, giving ample time for M1 or E2 radiative de-excitation.

It is worth noting, however, that the condition for the successful emission of M1 or E2 radiation is not quite as simple as supposing that the mean lifetime of a metastable level must be less than the intercollision interval. A collision may be inelastic, in which case some of the kinetic energy is absorbed and the metastable atom makes an upward transition; or it may be superelastic, in which case the metastable atom undergoes a radiationless downward transition, the excess energy going to increase the kinetic energy of the colliding particle; or the collision may be elastic, in which case there is no change in kinetic energy and the metastable atom remains in its metastable state. In order to determine the condition for emission or non-emission of "forbidden" radiation, it is necessary to take account of the probability of these several processes. In practice the probability that a collision will be inelastic or superelastic may be quite small, so that very few collisions result in removing an atom from its metastable state. Thus it is quite possible for M1 or E2 lines to be observed even if the mean time between collisions is appreciably less than the mean lifetime of a metastable state – though under laboratory conditions, the collision frequency is altogether far too high. In astronomical sources where "forbidden" lines can be emitted, they are still very weak – but we have the advantage of being able to look through sources of vast extent.

Now that we understand how forbidden lines can be observed in astronomical sources, I give some examples of a few forbidden lines worth knowing.

The first three terms of O_I are indicated schematically in figure VII.4. They arise from the same p^4 configuration, so the 3P term is an inverted term and none of the transitions are E1. The transitions I have drawn are all "forbidden". I have drawn E2 transitions as continuous lines and M1 transitions as dashed lines. You should verify this by reference to the selection rules.

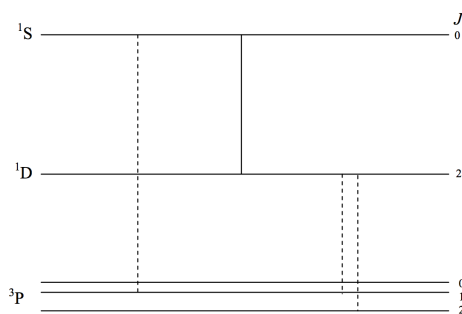


FIGURE VII.4

Starting from the left, the first two lines are at 297.2 and 557.7 nm. The mean lifetime of the 1S_0 level is of order about a second. The branching ratio is such that the ultraviolet M1 (dashed) transition is very much less likely than the green E2 transition at 557.5 nm. This green transition is usually the strongest auroral line, and you can even see that it is greenish in colour. The next time you look at an aurora you can reflect that electric quadrupole radiation is entering your eye! What a thrill! The 557.7 nm line also occurs in the short-lived trains left by meteors. The two dashed (magnetic dipole) lines at the right are at 636.3 and 630.0 nm, and are red. The mean lifetime of the 1D_2 level is more than a minute, and they also appear in the auroral spectrum, but much higher in the atmosphere, where the inter-collision time is longer. When you look at an aurora you can usually see a red glow higher than the green glow. You are seeing magnetic dipole as well as electric quadrupole radiation!

There are several somewhat similar magnetic dipole and electric quadrupole lines involving the first three terms of the spectra of $[O_{II}]$, $[O_{III}]$, $[N_I]$, $[N_{II}]$, $[N_{III}]$, which occur in the spectra of emission nebulae, including planetary nebulae. In figure VII.5 I

illustrate just three lines of $[\text{O III}]$. The configuration of all terms is p^2 and so the ^3P term is not inverted. The transitions $^3\text{P}_2 - ^1\text{D}_2$ and $^3\text{P}_2 - ^1\text{D}_2$ (notice - no parity change) are at 500.7 and 495.9 nm and are among the strongest observed in nebulae, and are often denoted by N_1 and N_2 , although they have nothing whatever to do with nitrogen, the letter N presumably signifying "nebular". I would strongly discourage such notation. The transition $^1\text{D}_2 - ^1\text{S}_0$ is at 436.3 nm. Before these lines were understood, they were referred to as "nebulium".

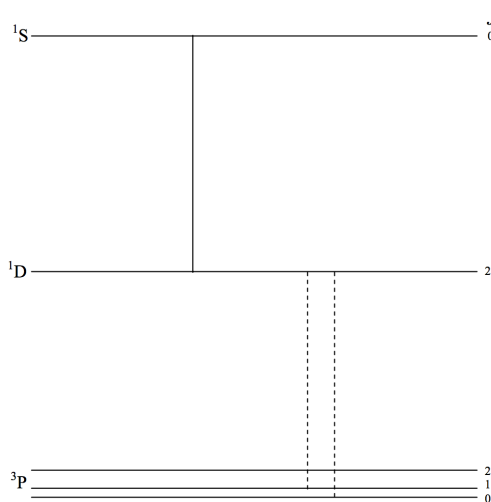


FIGURE VII.5

Before the spectrum of the solar corona was understood, the emission lines from the corona were ascribed to "coronium", but it is now known that they are "forbidden" lines from highly-ionized metals. The separation between levels within a single term is very large for highly-ionized atoms, and many of the observed lines in the coronal spectrum are magnetic dipole lines connecting two levels *within the same term*. For example, one of the strongest of the coronal lines, the green line at 530.3 nm, arises from the ion Fe^{13+} - that is to say the spectrum $[\text{Fe XIV}]$. This is isoelectronic with the neutral aluminium atom, and the ground term of the $KL3s^2(^1\text{S})3p$ configuration is a normal $^2\text{P}^o$ term with two levels - $J = \frac{1}{2}$ and $\frac{3}{2}$. In Al I the separation in term value of these levels is only 112 cm^{-1} , but they are much more widely spaced in Fe XIV so that, in this spectrum, the wavelength of $^2\text{P}_{\frac{1}{2}}^o - ^2\text{P}_{\frac{3}{2}}^o$ is 530.3 nm.

The last example is the famous 21-cm transition of neutral hydrogen, H I . Here, the lowest level is $^2\text{S}_{\frac{1}{2}}$, which is the one and only level is the ground term, ^2S . The level is split into two hyperfine levels as a result of the interaction between the total electronic angular momentum ($J = \frac{1}{2}$) and the nuclear spin ($I = \frac{1}{2}$), the F -values of the two hyperfine levels being 0 and 1. The 21-cm line is a magnetic dipole transition between these two hyperfine levels. The nuclear spin of deuterium is $I = 1$, and consequently the ground level of deuterium is split into hyperfine levels with $F = \frac{1}{2}$ and $\frac{3}{2}$. A transition between these two is predicted at 92 cm, but apparently there is as yet no unambiguous detection of it from an astronomical source.

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7.26: Stark Effect

The Stark effect concerns the separation of the states within a level as the result of the application of an external electric field, and the consequent splitting of lines into Stark components. The atmosphere of a star, being hot and highly ionized, is an electrical conductor and consequently cannot sustain electric potential gradients (fields). Thus the splitting of a line into its Stark components is not normally observed in stellar atmospheres, and for that reason I am not going into a detailed description of it or the theory of the effect here. There are just two small points that are probably worth mentioning.

The first point concerns the Balmer series of H_I . The details of the Stark pattern vary from line to line in the series, but it happens that in every even member of the series, that is to say $H\beta$, $H\delta$, etc., there is no central, undisplaced Stark component. Under some circumstances, even if the hydrogen lines are broad and the Stark components are unresolved, this may result in a small dip at the top of an emission line, or a small bump at the bottom of an emission line. There are other effects (see the chapter on line profiles) that can result in a dip at the top of an emission line or a bump at the bottom of an absorption line, but if the cause is Stark splitting, this may be recognized in that it affects only the even members of the Balmer series, and not the odd members ($H\alpha$, $H\gamma$, etc.).

The second point is that, although a stellar atmosphere cannot sustain a large macroscopic electric field, when two atoms approach each other in a near-collision, each induces a temporary electric dipole on the other. (This is the origin of the van der Waals forces, which fall off inversely as the sixth power of the interatomic distance.) The resulting electric field of one atom on the other, and the other on the one, results in a general broadening of the lines, often asymmetrically, as a result of Stark effect, and this effect obviously increases with pressure and is one of the components of the phenomenon of *pressure broadening*, to be discussed in a later chapter.

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CHAPTER OVERVIEW

8: Boltzmann's and Saha's Equations

Topic hierarchy

- 8.1: Introduction
- 8.2: Stirling's Approximation. Lagrangian Multipliers.
- 8.3: Some Thermodynamics and Statistical Mechanics
- 8.4: Boltzmann's Equation
- 8.5: Some Comments on Partition Functions
- 8.6: Saha's Equation
- 8.7: The Negative Hydrogen Ion
- 8.8: Autoionization and Dielectronic Recombination
- 8.9: Molecular Equilibrium
- 8.10: Thermodynamic Equilibrium

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8.1: Introduction

A measurement of the strength of a spectrum line can in principle enable us to determine the number of atoms *in the initial level of the transition* that produces it. For an emission line, that initial level is the upper level of the transition; for an absorption line it is the lower level. In order to determine the total number of atoms (in all energy levels) in the source, it is necessary to know, in addition to the number of atoms in a particular level, how the atoms are distributed, or partitioned, among their numerous energy levels. This is what Boltzmann's equation is concerned with. But even this will tell us only how many atoms there are in a particular ionization stage. If we are to determine the total abundance of a given element, we must also know how the atoms are distributed among their several ionization stages. This is what Saha's equation is concerned with.

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8.2: Stirling's Approximation. Lagrangian Multipliers.

In the derivation of Boltzmann's equation, we shall have occasion to make use of a result in mathematics known as Stirling's approximation for the factorial of a very large number, and we shall also need to make use of a mathematical device known as Lagrangian multipliers. These two mathematical topics are described in this section.

8.2i Stirling's Approximation

Stirling's approximation is

$$\ln N! \cong N \ln N - N. \quad (8.2.1)$$

Its derivation is not always given in discussions of Boltzmann's equation, and I therefore offer one here.

The gamma function is defined as

$$\Gamma(x+1) = \int_0^\infty t^x e^{-t} dt \quad (8.2.2)$$

or, what amounts to the same thing,

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt. \quad (8.2.3)$$

In either case it is easy to derive, by integration by parts, the recursion formula

$$\Gamma(x+1) = x\Gamma(x). \quad (8.2.4)$$

If x is a positive integer, N , this amounts to

$$\Gamma(N+1) = N!. \quad (8.2.5)$$

I shall start from equation 8.2.2. It is easy to show, by differentiation with respect to t , that the integrand $t^x e^{-t}$ has a maximum value of $(x/e)^x$ where $t = x$. I am therefore going to divide both sides of the equation by this maximum value, so that the new integrand is a function that has a maximum value of 1 where $t = x$:

$$\left(\frac{e}{x}\right)^x \Gamma(x+1) = \int_0^\infty \left(\frac{t}{x}\right)^x e^{-(t-x)} dt. \quad (8.2.6)$$

Now make a small change of variable. Let $s = t - x$, so that

$$\left(\frac{e}{x}\right)^x \Gamma(x+1) = \int_{-x}^\infty \left(1 + \frac{s}{x}\right)^x e^{-s} ds = \int_{-x}^\infty f(s) ds. \quad (8.2.7)$$

Bearing in mind that we aim to obtain an approximation for large values of x , let us try to obtain an expansion of $f(s)$ as a series in s/x . A convenient way of obtaining this is to take the logarithm of the integrand:

$$\ln f(s) = x \ln \left(1 + \frac{s}{x}\right) - s, \quad (8.2.8)$$

and, provided that $|s| < x$, the Maclaurin expansion is

$$\ln f(s) = x \left(\frac{s}{x} - \frac{1}{2} \cdot \left(\frac{s}{x}\right)^2 + \dots \right) - s. \quad (8.2.9)$$

If x is sufficiently large, this becomes

$$\ln f(s) = -\frac{s^2}{2x}, \quad (8.2.10)$$

so that

$$\left(\frac{e}{x}\right)^x \Gamma(x+1) = \int_{-\infty}^\infty \exp\left(-\frac{s^2}{2x}\right) ds. \quad (8.2.11)$$

While this integral is not particularly easy, it is at least well known (it occurs in the theory of the gaussian distribution, for example), and its value is $\sqrt{2\pi x}$. Thus we have, for large x ,

$$\Gamma(x+1) = \left(\frac{x}{e}\right)^x \sqrt{2\pi x} \quad (8.2.12)$$

or, if x is an integer,

$$N! = \left(\frac{N}{e}\right)^N \sqrt{2\pi N} \quad (8.2.13)$$

On taking logarithms of both sides, we obtain

$$\ln N! = \left(N + \frac{1}{2}\right) \ln N - N + \ln \sqrt{2\pi}, \quad (8.2.14)$$

or, since N is large:

$$\ln N! \cong N \ln N - N. \quad (8.2.15)$$

For very large N (i.e. if $\ln N \gg 1$), we can make the further approximation

$$\ln N! = N \ln N \quad (8.2.16)$$

or

$$\log N! = N \log N. \quad (8.2.17)$$

Any of equations 8.2.12 - 17 may be referred to as Stirling's approximation.

The largest value of N for which my hand calculator will return $N!$ is 69. For this, it gives

$$\ln N! = 226.2, \quad N \ln N - N = 223.2. \quad (8.2.1)$$

For very large numbers, the approximation will be much better. The extreme approximation represented by equations 8.2.16 or 8.2.17, however, becomes reasonable only for unreasonably large numbers, such as the number of protons in the Universe. We shall be making use of the much better approximation equation 8.2.15, which does not require such unimaginably huge numbers.

For smaller numbers that we commonly deal with in spectroscopy (where we are typically dealing with the number of atoms in a sample of gas) the following approximation is remarkably good:

$$\ln N! = \left(N + \frac{1}{2}\right) \ln N - N + \frac{1}{12N} + \ln \sqrt{2\pi} \quad (8.2.18)$$

This is almost the same as equation 8.2.14 except that, in deriving it, I have taken to expansion of equation 8.2.9 to one more term. Thus, to eight significant figures, $20! = 2.4329020 \times 10^{18}$, while equation 8.2.18 results in $2.432\,902\,9 \times 10^{18}$.

8.2ii Lagrangian Multipliers

This topic concerns the problem of determining where a function of several variables is a maximum (or a minimum) where the variables are not independent but are connected by one or more functional relations.

Let $\psi = \psi(x, y, z)$ be some function of x, y and z . Then, if x, y and z are independent variables, one would ordinarily understand that, where ψ is a maximum, the derivatives are zero:

$$\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial z} = 0. \quad (8.2.19)$$

However, if x, y and z are not completely independent, but are related by some constraining equation such as $f(x, y, z) = 0$, the situation is slightly less simple. An example from thermodynamics comes to mind. Entropy, S , is a function of state: $S = S(P, V, T)$. However, for a particular substance, P, V and T are related by an equation of state. In effect, we cannot determine S for the system at any point in P, V, T space, but we are restricted to explore only on the two-dimensional surface represented by the equation of state.

We return now to our function ψ . If we move by infinitesimal displacements dx, dy, dz from a point where ψ is a maximum, the corresponding changes in both ψ and f will be zero, and therefore both of the following equations must be satisfied:

$$d\psi = \frac{\partial\psi}{\partial x}dx + \frac{\partial\psi}{\partial y}dy + \frac{\partial\psi}{\partial z}dz = 0, \quad (8.2.20)$$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0. \quad (8.2.21)$$

Consequently any linear combination of ψ and f , such as $\phi = \psi + \lambda f$, where λ is an arbitrary constant, also satisfies a similar equation. The constant λ is sometimes called an "undetermined multiplier" or a "Lagrangian multiplier", although often some additional information in an actual problem enables the constant to be identified - and we shall see an example of this in the derivation of Boltzmann's equation.

In summary, the conditions that ψ is a maximum if x, y and z are related by a functional constraint $f(x, y, z) = 0$ are

$$\frac{\partial\phi}{\partial x} = 0, \quad \frac{\partial\phi}{\partial y} = 0, \quad \frac{\partial\phi}{\partial z} = 0, \quad (8.2.22)$$

where $\phi = \psi + \lambda f$.

Of course, if ψ is a function of many variables $x_1, x_2 \dots$, not just three, and the variables are subject to several constraints, such as $f = 0, g = 0, h = 0 \dots$, etc., where f, g, h , etc., are functions connecting all or some of the variables, the conditions for ψ to be a maximum (or minimum) are

$$\frac{\partial\psi}{\partial x_i} + \lambda \frac{\partial f}{\partial x_i} + \mu \frac{\partial g}{\partial x_i} + \nu \frac{\partial h}{\partial x_i} + \dots = 0, \quad i = 1, 2, 3, \dots \quad (8.2.23)$$

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8.3: Some Thermodynamics and Statistical Mechanics

Besides needing to know Stirling's approximation and the method of Lagrangian multipliers, before we can embark upon Boltzmann's equation we also need to remind ourselves of two small results from thermodynamics and statistical mechanics. I mention these only briefly here, with barely adequate explanations. Fuller treatments are given in courses or books on thermodynamics and statistical mechanics. If you are rusty on these topics, or perhaps have never studied them thoroughly, the only consequence is that you may not be able fully to understand the derivation of Boltzmann's equation. This will not matter a great deal and should not deter you from reading subsequent sections. It is more important to understand what Boltzmann's equation means and how to apply it, and this can be done even if you have missed some of the details of its derivation.

Most readers will either understand this section very well and will not need prolonged explanation, or will not understand it at all, and will be happy to skip over it. Therefore, for brevity's sake, I do little more than quote the results, and I do not even explain what many of the symbols mean.

Those who are familiar with thermodynamics will have no difficulty in recalling

$$dU = TdS - PdV. \quad (8.3.1)$$

The result that we shall be needing in Section 8.4 is $(\partial U / \partial S)_V = T$, or more likely its reciprocal:

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T}. \quad (8.3.2)$$

The relation we need from statistical mechanics is Boltzmann's relation between entropy and thermodynamic probability. Suppose we have an assembly of N particles that can be distributed or "partitioned" among m distinct states. If X is the number of ways in which this partition can be achieved, Boltzmann's equation for the entropy (indeed, his conception of entropy) is

$$S = k \ln X. \quad (8.3.3)$$

Here, k is Boltzmann's constant, $1.38 \times 10^{-23} \text{ J K}^{-1}$. Those who remember having seen this before might just like to be reminded of the gist of the argument leading to it. It presupposes some functional relation between S and X , and it notes that, if you have several assemblies, the total " X " for the ensemble as a whole is the product of the X 's of the individual assemblies, whereas the total entropy is the sum of the individual entropies, and therefore the entropy must be proportional to the logarithm of the number of possible configurations.

That was very brief, but it will do for the purposes of Section 8.4.

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8.4: Boltzmann's Equation

If we have a large number of atoms in a hot, dense gas, the atoms will constantly be experiencing collisions with each other, leading to excitation to the various possible energy levels. Collisional excitation will be followed, typically on timescales of the order of nanoseconds, by radiative deexcitation. If the temperature and pressure remain constant, there will exist a sort of dynamic equilibrium between collisional excitations and radiative de-excitations, leading to a certain distribution of the atoms among their various energy levels. Most of the atoms will be in low-lying levels; the number of atoms in higher levels will decrease exponentially with energy level. The lower the temperature, the faster will be the population drop at the higher levels. Only at very high temperatures will high-lying energy levels be occupied by an appreciable number of atoms. Boltzmann's Equation shows just what the distribution of the atoms will be among the various energy levels as a function of energy and temperature.

Let's imagine a box (constant volume) holding N atoms, each of which has m possible energy levels. Suppose that there are N_j atoms in energy level E_j . The total number N of atoms is given by

$$N = \sum_{i=1}^m N_i. \quad (8.4.1)$$

Here, i is a running integer going from 1 to m , including j as one of them.

The total internal energy U of the system is

$$U = \sum_{i=1}^m N_i E_i. \quad (8.4.2)$$

We now need to establish how many ways there are of arranging N atoms such that there are N_1 in the first energy level, N_2 in the second, and so on. We shall denote this number by X . To some, it will be intuitive that

$$X = \frac{N!}{N_1! N_2! \dots N_j! \dots N_m!} \quad (8.4.3)$$

That is,

$$X = \frac{N!}{\prod_{i=1}^m N_i!}. \quad (8.4.4)$$

I don't find it immediately obvious myself, and I am happier with at least a minimal proof. Thus, the number of ways in which N_1 atoms can be chosen from N to occupy the first level is $\binom{N}{N_1}$, where the parentheses denote the usual binomial coefficient. For each of these ways, we need to know the number of ways in which N_2 atoms can be chosen from the remaining $N - N_1$. This is, of course, $\binom{N - N_1}{N_2}$. Thus the number of ways of populating the first two levels is $\binom{N}{N_1} \binom{N - N_1}{N_2}$.

On continuing with this argument, we eventually arrive at

$$X = \binom{N}{N_1} \binom{N - N_1}{N_2} \binom{N - N_1 - N_2}{N_3} \dots \binom{N - \sum_{i=1}^{m-1} N_i}{N_m}. \quad (8.4.5)$$

If the binomial coefficients are written out in full (do it - don't just take my word for it), there will be lots of cancellations and you almost immediately arrive at Equation 8.4.3.

We now need to know the most probable partition - i.e. the most probable numbers N_1, N_2 , etc. The most probable partition is the one that maximizes X with respect to *each* of the N_j - subject to the constraints represented by Equations 8.4.1 and 8.4.2.

Mathematically it is easier to maximize $\ln X$, which amounts to the same thing. Taking the logarithm of Equation 8.4.3, we obtain

$$\ln X = \ln N! - \ln N_1! - \ln N_2! - \dots \quad (8.4.6)$$

Apply [Stirling's approximation](#) to the factorials of all the variables. (You'll see in a moment that it won't matter whether or not you also apply it to the constant term $\ln N!$) We obtain

$$\ln X \cong \ln N! - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2) - \dots \quad (8.4.7)$$

Let us now maximize $\ln X$ with respect to one of the variables, for example N_j , in a manner that is consistent with the constraints of Equations 8.4.1 and 8.4.2. Using the method of Lagrangian multipliers, we obtain, for the most probable occupation number of the j th level, the condition

$$\frac{\partial \ln X}{\partial N_j} + \lambda \frac{\partial N}{\partial N_j} + \mu \frac{\partial U}{\partial N_j} = 0. \quad (8.4.8)$$

Upon carrying out the differentiations, we obtain

$$-\ln N_j + \lambda + \mu E_j = 0. \quad (8.4.9)$$

That is to say:

$$N_j = e^{\lambda + \mu E_j} = C e^{\mu E_j}. \quad (8.4.10)$$

What now remains is to identify the Lagrangian multipliers λ (or $C = e^\lambda$) and μ . Multiply both sides of Equation 8.4.9 by N_j . Recall that i is a running subscript going from 1 to m , and that j is one particular value of i . Therefore now change the subscript from j to i , and sum from $i = 1$ to m , and Equation 8.4.9 now becomes

$$-\sum_{i=1}^m N_i \ln N_i + \lambda N + \mu U = 0, \quad (8.4.11)$$

where we have made use of Equations 8.4.1 and 8.4.2. From Equation 8.4.7, we see that

$$-\sum_{i=1}^m N_i \ln N_i = \ln X - \ln N! - N, \quad (8.4.12)$$

so that

$$\ln X = \ln N! - (\lambda + 1)N - \mu U. \quad (8.4.13)$$

Now apply Equation 8.3.3, followed by Equation 8.3.2, and we immediately make the identification

$$\mu = -\frac{1}{kT}. \quad (8.4.14)$$

Thus Equation 8.4.10 becomes

$$N_j = C e^{-E_j/(kT)}. \quad (8.4.15)$$

We still have to determine C . If we change the subscript in Equation 8.4.15 from j to i and sum from 1 to m , we immediately find that

$$C = \frac{N}{\sum_{i=1}^m e^{-E_i/(kT)}}. \quad (8.4.16)$$

Thus

$$\frac{N_j}{N} = \frac{e^{-E_j/(kT)}}{\sum e^{-E_i/(kT)}} \quad (8.4.17)$$

where I have omitted the summation limits (1 and m) as understood..

However, there is one factor we have not yet considered. Most energy levels in an atom are degenerate; that is to say there are several states with the same energy. Therefore, to find the population of a level, we have to add together the populations of the constituent states. Thus each term in Equation 8.4.17 must be multiplied by the statistical weight ϖ of the level. (This is unfortunately often given the symbol g . See section 7.14 for the distinction between d , g and ϖ . The symbol ϖ is a form of the Greek letter pi.) Thus we arrive at *Boltzmann's Equation*:

$$\frac{N_j}{N} = \frac{\varpi_j e^{-E_j/(kT)}}{\sum \varpi_i e^{-E_i/(kT)}} \quad (8.4.18)$$

The denominator of the expression is called the *partition function* (die Zustandsumme). It is often given the symbol u or Q or Z .

The statistical weight of a level of an atom with zero nuclear spin is $2J + 1$. If the nuclear spin is I , the statistical weight of a level is $(2I + 1)(2J + 1)$. However, the same factor $2I + 1$ occurs in the numerator and in every term of the denominator of equation 8.4.18 and it therefore cancels out from top and bottom. Consequently, in working with Boltzmann's equation, under most circumstances it is not necessary to be concerned about whether the atom has any nuclear spin, and the statistical weight of each level in equation 8.4.18 can usually be safely taken to be $(2J + 1)$.

In equation 8.4.18 we have compared the number of atoms in level j with the number of atoms in all level. We can also compare the number of atoms in level j with the number in the ground level 0:

$$\frac{N_j}{N_0} = \frac{\varpi_j e^{-E_j/(kT)}}{\varpi_0} \quad (8.4.19)$$

Or we could compare the number in level 2 to the number in level 1, where “2” represent any two level, 2 lying higher than 1:

$$\frac{N_2}{N_1} = \frac{\varpi_2}{\varpi_1} e^{-(E_2 - E_1)/(kT)} = \frac{\varpi_2}{\varpi_1} e^{-h\nu/(kT)}. \quad (8.4.20)$$

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8.5: Some Comments on Partition Functions

The topics we discuss in this section are

- i. Divergence of partition functions.
- ii. Metals and nonmetals.
- iii. Product of partition functions.
- iv. Particles in a box.

i. Divergence of Partition Functions

We can perhaps start by computing the partition function of atomic hydrogen. We have seen that each "level" (technically each *shell*) of hydrogen is actually a group of several terms, and that the total number of states in the shell - i.e. its statistical weight - is $2n^2$. See section 7.16. If we include nuclear spin, the statistical weight of each shell is actually $4n^2$ for ordinary hydrogen and $6n^2$ for deuterium. However, as agreed in section 8.4, we need not be concerned with nuclear spin, and we can take the statistical weight of each shell to be $2n^2$. The energy levels are given by equation 7.4.8:

$$E = \text{const.} \times \left(1 - \frac{1}{n^2}\right), \quad (8.5.1)$$

but how many "levels" are there? That is, what is the upper limit m of the sum in the partition function? Our first response is that there are an infinite number of energy levels converging towards the ionization limit at 13.6 eV. The same is true of other atoms; they, too, have infinite series of Rydberg levels. Evidently to calculate the partition function, we have to sum an infinite series, in this case, the series being

$$\sum_{n=1}^{\infty} 2n^2 \exp\left[-\left(1 - \frac{1}{n^2}\right) / (kT)\right]. \quad (8.5.2)$$

We can take anything that does not contain n outside the summation symbol and absorb it in the constant, and so we have to evaluate the sum

$$\sum_{n=1}^{\infty} n^2 \exp\left(\frac{1}{n^2 kT}\right). \quad (8.5.3)$$

Now we all remember that there are several tests to determine whether or not a series converges, and that, during an exam, all the tests that we remember fail, and the one test that we need is the one and only test that we cannot remember or never understood. Here is our chance now - Determine whether the above series converges or diverges!

I'll let you pause for a while you do that.

Darn it! The series diverges! The partition function is infinite! Although the uppermost "levels" have a high excitation potential and therefore cannot individually have high occupation numbers, there is an infinite number of them. The atoms are partitioned among an infinite number of levels, and the probability of any individual level being occupied approaches zero! Disaster!

This is a difficult subject, and not one in which I can claim much expertise, but a qualitative explanation goes something like this. The Coulomb potential of an isolated electric charge (in the present case we are thinking of the hydrogen nucleus; for heavier atoms we are thinking of the atom less the outermost, optical electron) is hyperbolic, approaching the ionization limit asymptotically, becoming horizontal as $r \rightarrow \infty$ if you draw a graph of the potential. In a partially ionized gas (which includes all stellar atmospheres) there are numerous charged particles - electrons and ions, and they all interact with one another. If two charged particles approach each other, the electric potential in the space between them becomes slightly lowered beneath the theoretical zero potential for an isolated charge. This is all one needs to resolve the difficulty. The ionization potential is lowered just a little (the exact amount will depend on the density of charged particles) and this eliminates the infinite number of Rydberg levels just beneath the ionization limit. There remains then a finite number of levels, and a finite number of terms in the partition function.

We do not, for our present purpose, necessarily need to know the exact amount of the lowering of the ionization potential, or how many "levels" remain, because we soon find that after the first few levels, the occupation numbers rapidly decrease and do not contribute much to the partition function. Where we choose to terminate the summation depends on the temperature and the precision we hope to achieve. Try calculating, for example, $\exp(-E/(kT))$ for $E = 10$ eV and $T = 20,000$ K. This should give you some idea.

Here is another insightful semiclassical guide. Consider the electron orbits in a Bohr model of the hydrogen atom. The radii of the orbits increase as n^2 . There comes a time when this radius becomes comparable to the average nearest-neighbour distance between atoms. If we assume an ideal gas equation of state, $P = NkT$, where N is the number of atoms per unit volume, we might take the nearest-neighbour distance to be $N^{-1/3}$, and we could equate this to the radius of the largest existing Bohr orbit. Presumably this will limit the number of Balmer lines we could see in a stellar atmosphere, and it will also tell us where to cut off the summation in calculating the partition function. Radio astronomers observe transitions involving very large quantum numbers - e.g. H 109 α . Presumably these come from hydrogen atoms in a region of space where the nearest neighbour distance is large enough to permit the existence of Bohr orbits of high quantum number.

ii. Metals and Nonmetals

There is a difference between calculating the partition functions of metals and of nonmetals - but first it is necessary to say what I mean by a "metal". It would be difficult to find two chemists or two physicists or two engineers who would agree on the exact definition of a metal. Among astronomers, however, there is near unanimity: the periodic table comprises hydrogen, helium, and all the remaining elements are "metals". This is a distressing misuse of the English language, and I strongly discourage it. I should make it plain that in this section - indeed in this chapter or book - this is not what I mean when I write the word "metal". Although, as I say, few scientists would agree on the precise definition, if I say "a metal is an element which, in the solid state, is hard, shiny, and conducts electricity", I should not be far off the mark. Almost everyone will find some immediate objection to that definition - but it is still not far off the mark, and certainly much better than the astronomers' "any element other than hydrogen and helium". In brief, elements that we think of in everyday life as being metals - such as iron, zinc, titanium, copper, lead, vanadium, tin, and so on - are metals. Neon, argon, chlorine, carbon, germanium, are not. From the spectroscopic point of view, a metal is characterized by having many, many energy levels, including many not far above the ground level. The calculation of the partition function is long and tedious, because so many levels, especially low-lying levels, must be taken into account. In the old days when these calculations were done by hand calculator, the levels were taken term by term, the statistical weight of each term being $(2S+1)(2L+1)$. The partition functions are fairly sensitive to temperature. Nonmetals, on the other hand, are characterized by typically having a large gap between the ground term and the first excited term. Consequently, the Boltzmann factors for terms other than the ground term are small, and, as a result, the partition function of a nonmetal is, to a good approximation, merely equal to the statistical weight of the ground term - and it hardly changes with temperature.

Now here is a question I used to enjoy asking students, both graduate and undergraduate. I would take particular pleasure in asking graduate students during a thesis defence. Think of a fairly hot star, such as Vega - say its temperature is something like 20,000 K. You will recall having seen the spectrum of Vega - it shows a beautiful development of the Balmer series of hydrogen. Obviously many of the higher "levels" are excited in the hot atmosphere; not all of neutral hydrogen atoms are still in the ground "level". The question is: At 20,000 K, what fraction of the neutral hydrogen atoms in the atmosphere remain in the ground "level"? And, just to make it clear that I was not expecting detailed precise calculations, I would give the question as a "multiple-choice" question, with just three alternatives:

- (a) Nearly all of them?
- (b) About half of them?
- (c) Hardly any of them?

Usually answers would be pretty evenly divided among the three. Have a go at it yourself. All the information you need is to be found in this chapter and chapter 7. It is important that you should have some feeling for the answer.

You will probably also be asking yourself how many of the hydrogen atoms are neutral, and how many are ionized. We shall come back to that when we have discussed Saha's equation. The answer will depend not only on the temperature but also on the pressure.

iii. Product of Partition Functions

In some systems, the total energy may be made up of several different sources of energy. Consider, for example, a simple diatomic molecule. Its energy may be the sum of the electronic excitation energy, energy of vibration, and kinetic energy of rotation. If these several sources of energy are independent of each other, the total energy will be merely the sum of the separate contributions:

$$E_{\text{tot.}} = E_{\text{el.}} + E_{\text{vib.}} + E_{\text{rot.}} \quad (8.5.4)$$

In practice, for real molecules, this is just a first approximation - in reality, there is some interaction between the several contributions to the energy, but the intention here is not to get bogged down in the finer details of molecular structure but merely to make a small point concerning partition functions, as follows. Provided that the several energy contributions are independent and

do not interact significantly and the energies are consequently additive, the total wavefunction is the product of the three wavefunctions:

$$\psi = \psi_{\text{el.}} \psi_{\text{vib.}} \psi_{\text{rot.}} \quad (8.5.5)$$

Here $\psi_{\text{vib.}}$ and $E_{\text{vib.}}$ are the wavefunctions and energy levels for a simple harmonic oscillator and $\psi_{\text{rot.}}$ and $E_{\text{rot.}}$ are the wavefunctions and energy levels of a rigid rotator. It will be easily understood that a molecule cannot simultaneously be a rigid rotator and a harmonic oscillator, which is why equations 8.5.4 and 8.5.5 are just first approximations. However, the vibrations of a molecule are generally far faster than the relatively slow and ponderous rotations, and electron motions are faster still, so the first approximation is not too bad. More to the point for our present purpose is that every term of the partition function is of the form $e^{-E/(kT)}$, and consequently, *if the total energy is the sum of the individual contributions, as in equation 8.5.4, the total partition function is the product of the partition functions of the individual contributions:*

$$u = u_{\text{el.}} u_{\text{vib.}} u_{\text{rot.}} \quad (8.5.6)$$

The extent to which this approximation is valid in real molecules is not the main subject of discussion here. I merely wished to establish that, provided equation 8.5.4 holds, then equation 8.5.6 follows.

iv. Particles in a Box

The reader may vaguely remember studying, in an introductory quantum mechanics course, perhaps without quite knowing why, something called "particle in a box". This was actually useful, and we shall need it before proceeding to the next section. Perhaps the topic would better have been called "waves in a box", because it was the wavefunctions that describe the wave aspect of a particle that were under discussion. If the particle (and its associated wave) is confined in a box, the wavefunctions are restricted to functions that have an integral number of antinodes between opposite walls, and consequently the energy levels can have only discrete values - another example of the inevitability of discrete energy levels resulting from boundary constraints. If the box is a cube of side a , the energy levels are given by

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2). \quad (8.5.7)$$

Problem: Verify that the above expression has the dimensions of energy.

If we have many particles in a box, we may be interested to know how the numerous particles are distributed or *partitioned* among the energy levels. In other words, we need to know the partition function, which is just

$$\sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \exp \left[-\frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8ma^2 kT} \right]. \quad (8.5.8)$$

If the box is very large, the energy levels are very close together and almost continuous. (If the box is infinitely large, there are no boundary constraints and hence there is a continuum of possible energies). If the levels are almost continuous, we can replace the summations with integrals:

$$\begin{aligned} \text{Partition function} &= \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \exp \left[-\frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8ma^2 kT} \right] dn_x dn_y dn_z \\ &= \left[\int_0^{\infty} \exp \left(-\frac{h^2 n^2}{8ma^2 kT} \right) dn \right]^3 \\ &= \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}} V, \end{aligned} \quad (8.5.9)$$

where $V = a^3$ is the volume of the box. We shall need this result in section 8.6.

Problem: What are the dimensions of the expression 8.5.9?

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8.6: Saha's Equation

Consider the reversible reaction



where A is a neutral atom and A^+ its first ion. Let N_0 , N_i , N_e be the numbers of neutral atoms, ions and electrons respectively, held in a box of volume V . Then

$$\frac{N_e N_i}{N_0} = S(T, P) \quad (8.6.2)$$

is the *Saha function*. It is a function of temperature and pressure, high temperature favouring ionization and high pressure favouring recombination. (Students of chemistry will recognize this as an application of Le Chatelier's principle.) The equation tells us the relative numbers of the three types of particle (i.e. the degree of ionization) in an equilibrium situation when the number of ionizations per second is equal to the number of recombinations per second.

Now the number of particles in a given energy level is proportional to the Boltzmann factor for that level, and the total number of particles is proportional to the sum of the Boltzmann factors for all the levels - i.e. to the partition function. Thus, using the symbol Q to denote partition functions, we have, for Saha's equation:

$$\frac{N_e N_i}{N_0} = \frac{Q_e Q_i}{Q_0}. \quad (8.6.3)$$

The partition function is the sum of the Boltzmann factors over all the states, translational and internal (electronic). The total energy of a particle is the sum of its translational and internal energies, so that total partition function is the product of its translational and internal partition functions, for which we shall use the symbol u . Therefore

$$\frac{N_e N_i}{N_0} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V \frac{u_e u_i}{u_0}. \quad (8.6.4)$$

Here $m = \frac{m_e m_i}{m_0}$, which is very little different from m_e .

The internal partition function of the electron is merely its statistical weight $2s + 1 = 2$. In calculating the internal partition functions of the atom and ion, it is, of course, essential to measure all energies from the same level - the ground level of the neutral atom, for example. You would not be so foolish, of course, as to calculate the partition function of the atom by using, in the Boltzmann sum, the energies of each level above the ground level of the atom, and then calculate the partition function of the ion by using the energies above some quite different level, such as the energy of the ground stage of the ion, would you? Most of us probably *would* be so foolish; we should, of course, add χ_i (the ionization energy) to each level of the ion. If we do calculate the partition function of the ion using energies above the ground level of the ion, we must then multiply the result, u_i , by $e^{-\chi_i/kT}$. Being even more careful, we should remember, from section 8.5, that the ionization energy is in practice lowered by a small amount $\Delta\chi_i$. Finally, let us now use the symbol n to denote number of particles per unit volume (so that $n = N/V$, and on no account to be confused with the quantum numbers n used in section 8.5) and we arrive at the usual form for Saha's equation:

$$\frac{n_e n_i}{n_0} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \frac{2u_i}{u_0} \exp\left(-\frac{(\chi_i - \Delta\chi_i)}{kT}\right). \quad (8.6.5)$$

It might be noted that $\Delta\chi_i$ is a function of n_e , which leads to a slight complication in the computation of Saha's equation, which we shall encounter in one of the problems that follow.

It should be remarked that Saha's equation played an extremely important role in the understanding of the stellar spectral sequence. As is well known, the sequence of spectral types OBAFG... is a result of the degree of ionization and excitation of the elements as a function of temperature, and the difference in the degree of ionization between main sequence stars and giants of a given temperature is the result of the higher degree of ionization in the relatively low pressure atmospheres of the giant stars. This could not be understood at a quantitative level until the development of Saha's equation and its application to stellar atmospheres by Saha, Fowler, Milne and Payne (later Payne-Gaposhkin) in the 1920s.

Problems.

Problem 1. Verify that equation 8.6.5 balances dimensionally.

Problem 2. In the bad old days, we did calculations using logarithm tables! You probably will never have to do that, but this exercise will nevertheless turn out to be useful. Show that Saha's equation can be written as

$$\log \frac{n_e n_i}{n_0} = A + \frac{3}{2} \log T + \log \frac{u_i}{u_0} - B \left(\frac{V_i - \Delta V_i}{T} \right) \quad (8.6.6)$$

and determine the numerical value of the constants A and B if n is expressed in m^{-3} , T is in K , V_i is the ionization potential in volts, and logarithms are common logarithms (i.e. to the base 10). I make them $A = 21.68$ and $B = 5039.7$. It is common also to write equation 8.6.6 in the form

$$\log \frac{n_e n_i}{n_0} = 27.24 - \frac{3}{2} \log \theta + \log \frac{u_i}{u_0} - \theta (V_i - \Delta V_i), \quad (8.6.7)$$

in which $\theta = 5039.7/T$.

Problem 3. You are going to calculate the Saha function for hydrogen, and so you need the partition functions for the electron, the neutral hydrogen atom and the hydrogen ion. The electron is easy. Its spin is $1/2$, so its partition function is 2, as already discussed and indeed already incorporated into Saha's equation. The partition function for neutral hydrogen can be taken to be the statistical weight of its $n = 1$ shell, which is $2n^2 = 2$. Now what about the statistical weight of the hydrogen ion? The hydrogen ion is a proton, which has spin $= 1/2$. Therefore, as for the electron, should the partition function be 2? The answer is no! When calculating the Saha equation for hydrogen, you should take the partition function of the proton to be 1. This probably seems entirely illogical and you are probably quite sure that I am wrong. But before coming to this conclusion, read again the last paragraph of section 8.4 and the first paragraph of section 8.5i. You can include the effect of the proton spin provided that you take it into account for both H and H^+ . If you insist that the statistical weight of the proton is 2, you must also insist that the statistical weight of the $n = 1$ shell of H is $4n^2 = 4$. As with the Boltzmann equation, you usually need not be concerned with nuclear spin - it cancels out in u_i/u_0 . There is nothing, however, to cancel out the factor 2 for the electron partition function.

Problem 4. A kilogram of water is contained in a box of volume one cubic metre. The box is made of material that won't melt or vaporize. (!) Draw a graph showing, as a function of temperature, from 10,000 K to 20,000 K, the logarithm of the numbers per unit volume of each of the species e , H, H^+ , O, O^+ . (Assume there are no higher ionization stages, and no molecules.)

This is going to be difficult, and will involve some computation. The first thing you are going to need to do is to calculate the Saha functions of the species involved as a function of temperature, and for this, you will need the partition functions. For the electron, the partition function is 2 and is already incorporated in the Saha equation. As discussed in Problem 3, the partition function of H^+ should be taken to be 1, and, as for the electron, it is mercifully independent of temperature. For neutral H, the statistical weight of the ground shell is 2, and, as you will already have discovered if you carried out the little calculation in section 8.5ii, you can probably take this to be the partition function at all temperatures between 10,000 and 20,000 K. The ground term of neutral oxygen is ^3P , and the first excited term is ^1D at a term value of 15868 cm^{-1} . Probably only the ground term contributes appreciably to the partition function, but you might want to check that. The ground term of O II is $^4\text{S}^o$ and the first excited term is a long way up. Thus, for all species, you can probably take the partition function to be the statistical weight of the ground term and independent of temperature. You are very lucky that I did not throw a metal into the mix!

The ionization limits of H and O are at 101678 and 109837 cm^{-1} respectively. We don't yet know by how much, $\Delta\chi_i$ the ionization energy is lowered, so we'll ignore $\Delta\chi_i$ to begin with. You now have enough information to calculate the Saha functions for hydrogen and for oxygen as a function of temperature.

We have been asked to calculate the numbers of five species and we are therefore going to need four equations. We started with one kilogram of water. We know that 18 grams of water contain A molecules, where A is Avogadro's number. (You may want to look up the exact molar mass of H_2O .) Thus, we started with $1000A/18$ molecules. Let's call that number N .

Now see if you agree with the following five equations.

$$N_{\text{H}} + N_{\text{H}^+} = 2N \quad (8.6.8)$$

$$N_{\text{O}} + N_{\text{O}^+} = N \quad (8.6.9)$$

$$N_{\text{H}^+} + N_{\text{O}^+} = N_e \quad (8.6.10)$$

$$N_e N_{\text{H}^+} = V S_{\text{H}} N_{\text{H}} \quad (8.6.11)$$

$$N_e N_{\text{O}^+} = V S_{\text{O}} N_{\text{O}} \quad (8.6.12)$$

We do indeed have five equations in the five unknowns, and all other quantities in the equations are known. The first two express the stoichiometry of the water molecule. The third expresses electrical neutrality. The last two are Saha's equations for hydrogen and oxygen. They five equations are not very difficult equations, although the last two are nonlinear, which makes them slightly awkward. We can make them a little easier. I am going to re-write them:

$$N_H + N_{H^+} - 2N = 0 \quad (8.6.13)$$

$$N_O + N_{O^+} - N = 0 \quad (8.6.14)$$

$$N_{H^+} + N_{O^+} - N_e = 0 \quad (8.6.15)$$

$$VS_H N_H - N_e N_{H^+} = 0 \quad (8.6.16)$$

$$VS_O N_O - N_e N_{O^+} = 0 \quad (8.6.17)$$

If we now, just for the moment, suppose that N_e is a quantity whose value is known. In that case, equations 8.6.13 to 8.6.17 would comprise five *linear* equations in just *four* unknowns. The condition for these equations to be consistent is that the determinant of the coefficients and the constant terms be zero:

$$\begin{vmatrix} 1 & 1 & 0 & 0 & -2N \\ 0 & 0 & 1 & 1 & -N \\ 0 & 1 & 0 & 1 & -N_e \\ VS_H & -N_e & 0 & 0 & 0 \\ 0 & 0 & VS_O & -N_e & 0 \end{vmatrix} = 0 \quad (8.6.18)$$

If I have done my algebra right (you might like to check this), this is a cubic equation in N_e :

$$N_e^3 + V(S_O + S_H)N_e^2 + V[VS_H S_O - (2S_H + S_O)N]N_e - 3V^2 S_H S_O N = 0. \quad (8.6.19)$$

You can now solve this for N_e . Remember, however, that, in calculating the Saha functions, you ignored the lowering of the ionization potential ΔV_i , so what you have found is but a first approximation for N_e . This is a function of the electron density. One rather old formula, due to Unsöld, is

$$\Delta V_i = 7 \times 10^{-5} n_e^{1/3}, \quad (8.6.20)$$

where V_i is in volts and $n_e (= N_e/V)$ is in m^{-3} (indicating that the lowering of the potential is proportional to the distance between the charged particles.). If you can find a more recent and perhaps better formula, by all means use it. You can use your first approximation for n_e to calculate the Saha functions, and then repeat the entire calculation and continue to iterate until you obtain an acceptably small change in n_e . It is probable that only one iteration will be necessary. Having found n_e (and N_e) it is then straightforward to find the remaining unknowns from equation 8.6.13 to 8.6.17. Just make sure that you make use of all five equations as a check for arithmetic mistakes.

Problem 5. A bottle of methyl cyanate CH_3CNO is held in a cylinder with a movable piston such that the pressure remains constant at one pascal. Heat it up to some temperature at which you can assume that the only species present are electrons and the neutral atoms and singly ionized stages of C, H, O and N - i.e. no higher ionization stages and no molecules. The cylinder and piston are not allowed to melt - they are required only to provide constant pressure conditions, in contrast to the previous problem in which you had a constant volume. You have nine unknowns, and you will need nine equations. In this problem you are asked merely to write down the nine required equations, not necessarily to solve them unless you particularly want to. There will be Saha equations for each element, an equation expressing electrical neutrality, and four equations reflecting the stoichiometry. You may assume the ideal gas equation $P = nkT$.

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8.7: The Negative Hydrogen Ion

The word "ion" in the gas phase is often thought of as the positively charged remnant of an atom that has lost one or more electrons. However, any electrically charged atom (or molecule or radical), whether positively charged (as a result of loss of an electron) or negatively charged (having an additional electron) can correctly be called an "ion". In this section, we are interested in the negative hydrogen ion, H^- , a bound system consisting of a proton and two electrons.

The formation of such an ion can be qualitatively described, in classical terms, as follows. A hydrogen atom, consisting of a proton and an electron, is approached by a second electron. The electric field of the second electron (which falls off with distance as r^{-2}) induces a dipole moment in the neutral hydrogen atom, with the two electrons then being at opposite sides of the proton. The induced dipole moment is proportional to the electric field of the polarizing electron, and hence to r^{-2} . The second electron now finds itself immersed in the electric field of the dipole that it has itself induced in the neutral H atom, and can be captured by it. The field of the dipole falls is proportional to p/r^3 , where p , the induced dipole moment, is already proportional to r^{-2} . Thus the force between the neutral (but dipolar) hydrogen atom and the intruding second electron falls off as r^{-5} , and the second electron moves in a potential varying as r^{-4} . Because of this, the energy level structure of H^- is very different from that of H. In H, the potential falls off as r^{-1} , which results in the familiar infinite Rydberg series of levels. For a potential of the form r^{-n} , if $n > 1$ the Schrödinger equation predicts a *finite* number of bound levels below the ionization limit, and, in the case of H^- , there is just *one* bound level, and it is a mere 0.7 eV below the ionization limit. The 0.7 eV can be called the *ionization potential* of the H^- ion or the *electron affinity* of the H atom. Perhaps the latter term is preferable, because it is a little odd to refer to removing an electron from the H^- ion (so that it is then no longer an ion) as "ionization"! As Professor Joad might have said: "It all depends what you mean by 'ionization'". In any case, an electron can easily be removed from H^- either by a mild collision or by any photon of (vacuum) wavelength shorter than about 1771 nm.

In the solar atmosphere, most hydrogen atoms are neutral and have the electron in the $n = 1$ shell (K shell). Only a few are in the form of H^+ or H^- . (I am not sure offhand which is more numerous, H^+ or H^- – that would make a good lunchtime discussion.) But because H^- is so readily stripped of an electron by almost any old photon, H^- makes an appreciable contribution to the continuous opacity of the solar atmosphere. The continuous absorption can be either by "bf" (bound-free) transitions or so-called "ff" (free-free) transitions. In the latter case the second electron is unbound, but it swerves in the field of the dipole that it has itself induced in the neutral H atom.

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8.8: Autoionization and Dielectronic Recombination

The ionization energy as discussed until this point has meant the energy required to remove an electron from an atom, initially in its ground level, leaving the removed electron with no kinetic energy. The neutral atom has a number of discrete energy levels below the ionization limit; above that limit, there is a continuum of energy states - which merely means that the electron is unbound and there are no restrictions on its kinetic energy.

However, it is possible for more than one electron in an atom to be excited, and in that case it is quite possible for an atom to exist in a discrete bound level whose energy is above the ionization limit as described in the previous paragraph. Although this is quite possible, an atom generally does not stay long in one of these highly excited levels. One of the electrons can easily slip away from the atom without the absorption of any additional energy, thereby leaving behind an ion in an excited state. Such a process is called *autoionization*, and the levels or states concerned are autoionization levels or states.

The converse process is quite possible. An ion in an excited state can capture a hitherto free electron, thus forming the neutral atom with two excited electrons. The process is *dielectronic recombination*. Downward transitions from these autoionization levels to lower discrete level can occur.

As mentioned above, the mean lifetime of the atom in one of these autoionization levels is rather short. As a consequence of Heisenberg's uncertainty principle, there is a corresponding uncertainty in the energy level that is inversely proportional to the lifetime. Stated otherwise, the autoionization energy levels are relatively broad. Consequently lines resulting from downward transitions originating from these autoionization levels are relatively broad, and indeed such lines are often recognized or at least suspected from their relatively diffuse appearance. Such lines are readily observed, for example, in the spectra of copper, zinc and cadmium among others.

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8.9: Molecular Equilibrium

The dissociation of diatomic molecules can be treated in a way that is very similar to Saha's equation for ionization. Consider, for example, the following reversible reaction



The equilibrium is governed by an equation that is essentially identical to the Saha equation:

$$\frac{n_A n_B}{n_{AB}} = K_{AB} = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \frac{u_A u_B}{u_{AB}} e^{-D_0^0/(kT)}. \quad (8.9.2)$$

Here K_{AB} is the equilibrium constant, m is $m_A m_B / (m_A + m_B)$, and D_0^0 is the dissociation energy. To a first approximation the partition function u_{AB} of the molecule is the product of the electronic, vibrational and rotational partition functions, although usually today more precise calculations are made. The equation is often written in terms of partial pressures:

$$\frac{p_A p_B}{p_{AB}} = K'_{AB} \quad (8.9.3)$$

in which $K'_{AB} = kT K_{AB}$ where the gases may be considered to be ideal.

Let us consider again Problem 5 of section 8.6, in which we have methyl cyanate CH_3CNO held at some pressure P , but this time we'll work at some temperature where we shall suppose that the only species to be expected would be neutral atoms and neutral diatomic molecules. The species concerned are C, H, O, N, C_2 , CN, CO, N_2 , H_2 , OH, NH, O_2 , NO, N_2 . We shall evidently need 14 equations. They are:

$$n_C + n_H + n_O + n_N + n_{\text{C}_2} + n_{\text{CH}} + n_{\text{CO}} + n_{\text{CN}} + n_{\text{H}_2} + n_{\text{OH}} + n_{\text{NH}} + n_{\text{O}_2} + n_{\text{NO}} + n_{\text{N}_2} = P/(kT), \quad (8.9.4)$$

$$n_C + 2n_{\text{C}_2} + n_{\text{CH}} + n_{\text{CO}} + n_{\text{CN}} = 2(n_N + n_{\text{CN}} + n_{\text{NH}} + n_{\text{NO}} + 2n_{\text{N}_2}), \quad (8.9.5)$$

$$n_H + n_{\text{CH}} + 2n_{\text{H}_2} + n_{\text{OH}} + n_{\text{NH}} = 3(n_N + n_{\text{CN}} + n_{\text{NH}} + n_{\text{NO}} + 2n_{\text{N}_2}), \quad (8.9.6)$$

$$n_O + n_{\text{CO}} + n_{\text{OH}} + 2n_{\text{O}_2} + n_{\text{NO}} = n_N + n_{\text{CN}} + n_{\text{NH}} + n_{\text{NO}} + 2n_{\text{N}_2}, \quad (8.9.7)$$

$$n_{\text{C}}^2 = K_{\text{C}_2} n_{\text{C}_2}, \quad n_{\text{C}} n_{\text{H}} = K_{\text{CH}} n_{\text{CH}}, \quad n_{\text{C}} n_{\text{O}} = K_{\text{CO}} n_{\text{CO}}, \quad n_{\text{C}} n_{\text{N}} = K_{\text{CN}} n_{\text{CN}}, \quad n_{\text{H}}^2 = K_{\text{H}_2} n_{\text{H}_2}, \quad (8.9.7-11)$$

$$n_{\text{O}} n_{\text{H}} = K_{\text{OH}} n_{\text{OH}}, \quad n_{\text{N}} n_{\text{H}} = K_{\text{NH}} n_{\text{NH}}, \quad n_{\text{O}}^2 = K_{\text{O}_2} n_{\text{O}_2}, \quad n_{\text{N}} n_{\text{O}} = K_{\text{NO}} n_{\text{NO}}, \quad n_{\text{N}}^2 = K_{\text{N}_2} n_{\text{N}_2}. \quad (8.9.12-16)$$

The first of these equations is the ideal gas equation. The next three express the stoichiometry of methyl cyanate. The remaining ten, which are nonlinear, are the equilibrium equations. Some skill and experience in the solution of multiple nonlinear simultaneous equations is necessary actually to solve these equations.

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8.10: Thermodynamic Equilibrium

Those who have studied thermodynamics will be familiar with such elementary and easy concepts as entropy, enthalpy, Gibbs free energy, chemical potential, activity and fugacity, and will have no difficulty in grasping their meaning. Much more difficult to grasp, however, is the very difficult concept of temperature. I have vague memories of something called the Zeroth Law of Thermodynamics which, I seem to recall, went something like this: "If two bodies are in thermodynamic equilibrium with each other, and each is in thermodynamic equilibrium with a third, then all three bodies are at the same temperature." I understood that this was a law of great profundity, though I was never quite sure whether any part of the Universe could ever truly be in thermodynamic equilibrium and that the Universe would be a pretty dull place if it were. This section may or may not (more likely the latter) make the concept of temperature any easier.

Let us try to imagine a system consisting of a hot gas with a solid body suspended in it.

Let us imagine that we are somehow able to measure the distribution of the translational speeds of the molecules in the case, and the distribution is found to conform to a Maxwell-Boltzmann distribution with a root-mean-square speed V . We could then calculate the quantity $mV^2/(3k)$ and call this quantity T . We could call this quantity the *kinetic temperature* of the gas. We might, for example, say that the kinetic temperature of the gas is 300 K. Some may think that it would be simpler merely to say how fast the molecules are moving. In any case, the *kinetic temperature* of the gas is merely a way of expressing what the root-mean-square speed of the molecules is.

Let us also imagine that we are able to determine how the molecules are partitioned among their numerous discrete energy levels. We may find that they are distributed according to the Boltzmann distribution with parameter T , and we could call that parameter the *excitation temperature*, which would then merely be a way of saying how fast or how slowly the occupation numbers of the levels fall off with energy.

We might also be able to determine the extent to which the atoms are ionized, and we could apply Saha's equation and hence define an *ionization temperature*.

Unless the molecules are single atoms, we might also be able to determine how the molecules are partitioned among their various vibrational levels or among their numerous rotational levels, and we could assign to these distributions a *vibrational temperature* and a *rotational temperature* respectfully.

If we look at the solid, it may be glowing with heat, and we may be able to determine how its exitance per unit wavelength interval varies with temperature, and we might observe that it conforms to Planck's radiation formula. We might be able to measure its total exitance, M . We could then pretend that it is a black body, and we could define $(M/\sigma)^{1/4}$, where σ is the Stefan-Boltzmann constant, as the *effective temperature*. Or we could note the wavelength at which the exitance per unit wavelength interval is greatest, and we could define W/λ_{max} as the *colour temperature* where W is Wien's constant.

Small wonder that "temperature" and "thermodynamic equilibrium" are such difficult concepts to grasp! However, I think it is fair to make the following statements: If the system is in thermodynamic equilibrium, then all of these various possible measures of "temperature" (kinetic, excitation, ionization, vibrational, rotational, effective, colour) are equal. If they are not equal, the system is not in thermodynamic equilibrium.

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CHAPTER OVERVIEW

9: Oscillator Strengths and Related Topics

Topic hierarchy

- 9.1: Introduction, Radiance, and Equivalent Width
- 9.2: Oscillator Strength. (die Oszillatorenstärke)
- 9.3: Einstein A Coefficient
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- 9.5: Line Strength
- 9.6: LS-coupling
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- 9.8: Zeeman Components
- 9.9: Summary of Relations Between f , A and S

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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 $I = \int_0^\infty I_\lambda d\lambda$. 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 nanometer from the line center.

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.

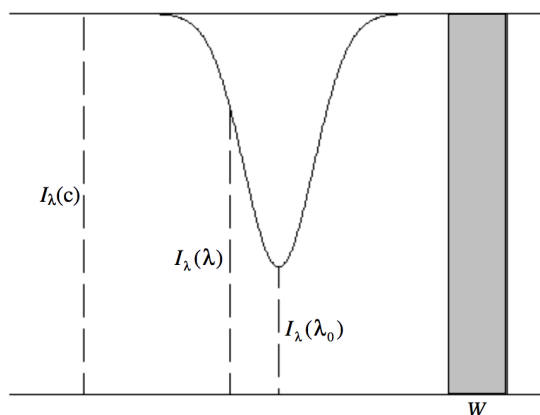
In the matter of notation, I am using:

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.

FIGURE IX.1



$I_\lambda(\lambda)$ 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 center.

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:

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

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.

? Exercise 9.1.1

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, $W \propto N_1$, 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.

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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

$$W = \frac{\mathcal{N} e^2 \lambda^2}{4 \epsilon_0 m c^2}. \quad (9.2.2)$$

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 meters.

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

$$W = \frac{\mathcal{N}_1 e^2 \lambda^2}{4 \epsilon_0 m c^2}. \quad (9.2.3)$$

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*:

Definition

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

$$W = \frac{\mathcal{N}_1 f_{12} e^2 \lambda^2}{4 \varepsilon_0 m c^2}. \quad (9.2.4)$$

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

$$W = \frac{\mathcal{N} e^2 \lambda^2 \varpi_1 f_{12} e^{-E_1/(kT)}}{4 \varepsilon_0 m c^2 u}. \quad (9.2.6)$$

In the above Equations I have used slightly different fonts for e , the electronic charge, and 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

$$W = \frac{\mathcal{N} e^2 \lambda^2 \varpi f e^{-E_1/(kT)}}{4 \varepsilon_0 m c^2 u}. \quad (9.2.8)$$

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

$$\log \frac{W}{\varpi f \lambda^2} = \log \frac{e^2}{4 \varepsilon_0 m c^2} + \log \mathcal{N} - \log u - \frac{e V_1}{k T} \log e. \quad (9.2.9)$$

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 (jtatum at uvic dot ca) if it's not right. Here W and λ are to be expressed in meters and N in atoms per square meter. 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 $\log\left(\frac{W}{\varpi f \lambda^2}\right)$ 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, $\varpi f(\text{line}) = \Sigma f(\text{components})$, 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 ϖf 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 "evaluate" of the electron or the " M -value" of the Sun. I suppose "weighted oscillator strength" could be used for ϖf .

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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 unit 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 9.3.3 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

$$L = \frac{\mathcal{N} h c \varpi_2 A_{21} e^{-E_2/(kT)}}{4\pi \lambda u}. \quad (9.3.8)$$

The common logarithm of this is

$$\log\left(\frac{L\lambda}{\varpi_2 A_{21}}\right) = \log \frac{hc}{4\pi} + \log \mathcal{N} - \log u - \frac{eV_2}{kT} \log e. \quad (9.3.9)$$

If everything is in SI units, this becomes

$$\log\left(\frac{L\lambda}{\varpi_2 A_{21}}\right) = -25.801 + \log \mathcal{N} - \log u - \theta V_2. \quad (9.3.10)$$

Thus a graph of $\log\left(\frac{L\lambda}{\varpi_2 A_{21}}\right)$ 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 $\varpi_2 A_{21}$, 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!

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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 $\varpi_1 f_{12}$. We followed this by defining an emission oscillator strength f_{21} by the equation $\varpi_2 f_{21} = \varpi_1 f_{12}$. Thereafter we defined a weighted oscillator strength ϖf to be used more or less as a single symbol equal to either $\varpi_2 f_{21}$ or $\varpi_1 f_{12}$. 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 $\varpi_2 A_{21}$. 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

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

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

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

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

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):

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

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

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

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

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

$$E_2 - E_1 = hc/\lambda. \quad (9.4.11)$$

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 $W L_{\lambda_{12}}$.

Therefore

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

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

$$B_{12}^a = \frac{e^2 \lambda^3}{4\epsilon_0 h m c^2} f_{12}. \quad (9.4.15)$$

It also follows from equations 9.4.13 and 9.4.15 that

$$\varpi_2 A_{21} = \frac{2\pi e^2}{\epsilon_0 m c \lambda^2} \varpi_1 f_{12}. \quad (9.4.16)$$

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

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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

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

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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:

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

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 $S(M)$, the *relative strengths of the multiplets* within the array, and for $S(L)$, 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 $J - 1$:

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

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

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

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

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

✓ Example 9.6.1

The multiplet $^3P - ^3D$. Here, we have $S = 1$, and $L = 2$.

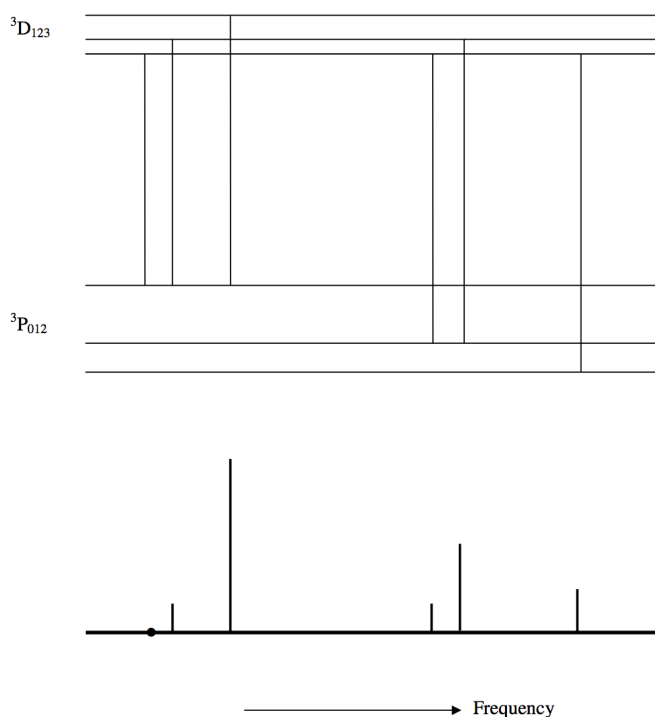
There are six lines. In what follows I list them, together with the J value to be substituted in the formulas, and the value of $S(L)$.

$^3P_0 - ^3D_1$	Main	$J = 1$	$S(L) = 1/9 = 0.11111$
$^3P_1 - ^3D_2$	Main	$J = 2$	$S(L) = 1/4 = 0.25000$
$^3P_1 - ^3D_1$	First satellite	$J = 1$	$S(L) = 1/12 = 0.08333$
$^3P_2 - ^3D_3$	Main	$J = 3$	$S(L) = 7/15 = 0.46667$
$^3P_2 - ^3D_2$	First satellite	$J = 2$	$S(L) = 1/12 = 0.08333$
$^3P_2 - ^3D_1$	Second satellite	$J = 1$	$S(L) = 1/180 = 0.00556$

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 ($^3P - ^3D$) 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	$J = 1$	$\mathcal{S}(L)$	=	0.150000	
${}^3D_2 - {}^3D_2$	Main	$J = 2$	$\mathcal{S}(L)$	=	0.231481	
${}^3D_3 - {}^3D_3$	Main	$J = 3$	$\mathcal{S}(L)$	=	0.414815	
${}^3D_2 - {}^3D_3$	Satellite	$J = 3$	$\mathcal{S}(L)$	=	0.051852	(9.6.8)
${}^3D_1 - {}^3D_2$	Satellite	$J = 2$	$\mathcal{S}(L)$	=	0.050000	
${}^3D_3 - {}^3D_2$	Satellite	$J = 3$	$\mathcal{S}(L)$	=	0.051852	
${}^3D_2 - {}^3D_1$	Satellite	$J = 2$	$\mathcal{S}(L)$	=	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.

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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	(9.7.1)
β	0.105	0.588	
γ	0.0387	0.220	
δ	0.0186	0.103	

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9.8: Zeeman Components

In this section I give $\mathcal{S}(C)$, 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 $M - 1$:

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

Components connecting M to $M + 1$:

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

Components in which M does not change:

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

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 9.8.1

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

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

Normalized to unity, these are

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

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

$$2 \ 6 \ 8 \ 8 \ 6 \ 2$$

or, normalized to unity,

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

Lines for which J does not change.

Components for which M changes by ± 1

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

Components for which M does not change:

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

✓ Example 9.8.2

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

$$M' \quad M'' \quad S(C)$$

-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

(9.8.6)

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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.

$$\varpi_2 A_{21} = \frac{8\pi hc}{\lambda^5} \varpi B = \frac{2\pi e^2}{\varepsilon_0 mc \lambda^2} \varpi f = \frac{16\pi^3}{3h\varepsilon_0 \lambda^3} S; \quad (9.9.1)$$

$$\varpi B = \frac{e^2 \lambda^3}{4h\varepsilon_0 mc^2} \varpi f = \frac{2\pi^2 \lambda^2}{3h^2 \varepsilon_0 c} S = \frac{\lambda^5}{8\pi hc} \varpi_2 A_{21}; \quad (9.9.2)$$

$$\varpi f = \frac{8\pi^2 mc}{3he^2 \lambda} S = \frac{\varepsilon_0 mc \lambda^2}{2\pi e^2} \varpi_2 A_{21} = \frac{4h\varepsilon_0 mc^2}{e^2 \lambda^3} \varpi B; \quad (9.9.3)$$

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

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.

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CHAPTER OVERVIEW

10: Line Profiles

Spectrum lines are not infinitesimally narrow; they have a finite width. A graph of radiance or intensity per unit wavelength (or frequency) versus wavelength (or frequency) is the *line profile*. There are several causes of line broadening, some internal to the atom, others external, and each produces its characteristic profile. Some types of profile, for example, have a broad core and small wings; others have a narrow core and extensive, broad wings. Analysis of the exact shape of a line profile may give us information about the physical conditions, such as temperature and pressure, in a stellar atmosphere.

[10.1: Natural Broadening \(Radiation Damping\)](#)

[10.2: Thermal Broadening](#)

[10.3: Microturbulence](#)

[10.4: Combination of Profiles](#)

[10.5: Pressure Broadening](#)

[10.6: Rotational Broadening](#)

[10.7: Instrumental Broadening](#)

[10.8: Other Line-Broadening Mechanisms](#)

[10.9: Appendix A- Convolution of Gaussian and Lorentzian Functions](#)

[10.10: APPENDIX B- Radiation Damping as Functions of Angular Frequency, Frequency and Wavelength](#)

[10.11: APPENDIX C- Optical Thinness, Homogeneity and Thermodynamic Equilibrium](#)

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10.1: Natural Broadening (Radiation Damping)

The classical oscillator model of the atom was described in Section 9.2. In this model, the motion of the optical electron, when subject to the varying electromagnetic field of a light wave, obeys the differential equation for forced, damped, oscillatory motion:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{e \hat{E}}{m} \cos \omega t. \quad (10.1.1)$$

Because the oscillating (hence accelerating) electron itself radiates, the system loses energy, which is equivalent to saying that the motion is damped, and γ is the damping constant. Electromagnetic theory tell us that the rate of radiation of energy from an accelerating electron is

$$\frac{2}{3} \cdot \frac{e^2 \ddot{x}^2}{4\pi\epsilon_0 c^3}. \quad (10.1.2)$$

(The reader, as always, should check the dimensions of this and all subsequent expressions.)

For an electron that is oscillating, the average rate of loss of energy per cycle is

$$\frac{2}{3} \cdot \frac{e^2 \overline{\ddot{x}^2}}{4\pi\epsilon_0 c^3}. \quad (10.1.3)$$

Here the bar denotes the average value over a cycle.

If the amplitude and angular frequency of the oscillation are a and ω_0 , the maximum acceleration is $a\omega_0^2$ and the mean square acceleration is $\frac{1}{2}a^2\omega_0^4$. The energy (kinetic plus potential) of the oscillating electron is

$$W = \frac{1}{2} m a^2 \omega_0^2. \quad (10.1.4)$$

Thus we can write for the average rate of loss per cycle of energy from the system by electromagnetic radiation:

$$\frac{2}{3} \cdot \frac{e^2 \omega_0^2}{4\pi\epsilon_0 m c^3} \cdot W \quad (10.1.5)$$

The energy therefore falls off according to

$$\dot{W} = -\frac{1}{3} \cdot \frac{e^2 \omega_0^2}{4\pi\epsilon_0 m c^3} \cdot W. \quad (10.1.6)$$

The radiated wavelength is given by $\lambda = 2\pi c/\omega_0$, so that Equation 10.1.6 becomes

$$\dot{W} = -\frac{2\pi e^2}{3\epsilon_0 m c \lambda^2} \cdot W. \quad (10.1.7)$$

It will be recalled from the theory of lightly damped oscillations that the solution to Equation 10.1.1 shows that the amplitude falls off with time as $\exp(-\frac{1}{2}\gamma t)$, and that the *energy* falls off as $\exp(-\gamma t)$. Thus we identify the coefficient of W on the right hand side of Equation 10.1.7 as the *classical radiation damping constant* γ :

$$\gamma = \frac{2\pi e^2}{3\epsilon_0 m c \lambda^2}. \quad (10.1.8)$$

Numerically, if γ is in s^{-1} and λ is in m,

$$\gamma = \frac{2.223 \times 10^{-5}}{\lambda^2}. \quad (10.1.9)$$

We are now going to calculate the rate at which energy is transported per unit area by an electromagnetic wave, and also to calculate the rate at which an optically thin slab of a gas of classical oscillators absorbs energy, and hence we are going to calculate the classical absorption coefficient. We start by recalling, from elementary electromagnetism, that the energy held per unit volume in an electric field is $\frac{1}{2} \mathbf{D} \cdot \mathbf{E}$ and the energy held per unit volume in a magnetic field is $\frac{1}{2} \mathbf{B} \cdot \mathbf{H}$. In an isotropic medium, these become $\frac{1}{2} \epsilon E^2$ and $\frac{1}{2} \mu H^2$, and, in *vacuo*, they become $\frac{1}{2} \epsilon_0 E^2$ and $\frac{1}{2} \mu_0 H^2$.

For an oscillating electric field of the form $E = \hat{E} \cos \omega t$, the average energy per unit volume per cycle is $\frac{1}{2} \epsilon_0 \overline{E^2} = \frac{1}{4} \epsilon_0 \hat{E}^2$. Similarly for an oscillating magnetic field, the average energy per unit volume per cycle is $\frac{1}{4} \mu_0 \hat{H}^2$. An electromagnetic wave consists of an electric and a magnetic wave moving at speed c , so the rate at which energy is transmitted across unit area is $\left(\frac{1}{4} \epsilon_0 \hat{E}^2 + \frac{1}{4} \mu_0 \hat{H}^2 \right) c$, and the two parts are equal, so that the rate at which energy is transmitted per unit area by a plane electromagnetic wave is $\frac{1}{2} \epsilon_0 \hat{E}^2 c$.

Now we are modelling the classical oscillator as an electron bound to an atom, and being subject to a periodic force $\frac{e\hat{E}}{m} \cos \omega t$ from an electromagnetic wave. The rate of absorption of energy by such an oscillator (see, for example, Chapter 12 of Classical Mechanics is

$$\frac{\gamma e^2 \hat{E}^2 \omega^2}{2m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}.$$

We imagine a plane electromagnetic wave arriving at (irradiating) a slab of gas containing \mathcal{N} classical oscillators per unit area, or n per unit volume. The rate of arrival of energy per unit area, we have seen, is $\frac{1}{2} \epsilon_0 \hat{E}^2 c$. The rate of absorption of energy per unit area is

$$\frac{\mathcal{N} \gamma e^2 \hat{E}^2 \omega^2}{2m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}.$$

The absorptance (see Chapter 2, section 2.2) is therefore

$$a = \frac{\mathcal{N} \gamma e^2 \omega^2}{m \epsilon_0 c [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}. \quad (10.1.10)$$

and the linear absorption coefficient is

$$\alpha = \frac{n \gamma e^2 \omega^2}{m \epsilon_0 c [(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}. \quad (10.1.11)$$

A reminder here might be in order. *Absorptance* a is defined in section 2.2, and in the notation of figure IX.1, the absorptance at wavelength λ would be $(I_\lambda(c) - I_\lambda(\lambda)) / I_\lambda(c)$. *Absorption coefficient* α is defined by equation 5.2.1: $-dI/I = \alpha dx$. For a thick slice of gas, of thickness t , this integrates, in the notation of figure IX.1, to $I_\lambda(\lambda) = I_\lambda(c) \exp(-\alpha t)$. But for an optically thin gas, which is what we are considering, unless stated otherwise, in this chapter, this becomes $(I_\lambda(c) - I_\lambda(\lambda)) / I_\lambda(c) = \alpha t$. Thus, *for an optically thin gas*, absorptance is just absorption coefficient times thickness of the gas. And the relation between particle density n and column density \mathcal{N} is $\mathcal{N} = nt$.

We can write $\omega_0^2 - \omega = (\omega_0 - \omega)(\omega_0 + \omega)$. Let us also write ω as $2\pi\nu$. Also, in the near vicinity of the line, let us make the approximation $\omega_0 + \omega = 2\omega$. We then obtain for the absorption coefficient, in the vicinity of the line,

$$\alpha = \frac{\gamma n e^2}{16\pi^2 m c \epsilon_0 \left[(\nu - \nu_0)^2 + \left(\frac{\gamma}{4\pi} \right)^2 \right]}. \quad (10.1.12)$$

? Exercise 10.1.1

Make sure that I have made no mistakes in deriving equations 10.1.10, 11 and 12, and check the dimensions of each expression as you go. Let me know if you find anything wrong.

Now the equivalent width in frequency units of an absorption line in an optically thin layer of gas of geometric thickness t is (see equation 9.1.6)

$$W^{(\nu)} = t \int_{-\infty}^{\infty} \alpha d(\nu - \nu_0). \quad (10.1.13)$$

? Exercise 10.1.2

- (a) For those readers who (understandably) object that expression 10.1.12 is valid only in the immediate vicinity of the line, and therefore that we cannot integrate from $-\infty$ to $+\infty$, integrate expression 10.1.11 from 0 to ∞ .
- (b) For the rest of us, integrate Equation 10.1.11 from $\nu - \nu_0 = -\infty$ to $+\infty$. A substitution $4\pi(\nu - \nu_0) = \gamma \tan \theta$ will probably be a good start.

We obtain

$$W^{(\nu)} = \frac{\mathcal{N}e^2}{4mc\varepsilon_0} = 2.654 \times 10^{-6} \mathcal{N}, \quad (10.1.14)$$

where $W^{(\nu)}$ is in Hz and \mathcal{N} is in m^{-2} . Thus the classical oscillator model predicts that the equivalent width in frequency units is independent of the frequency (and hence wavelength) of the line, and also independent of the damping constant. If we express the equivalent width in wavelength units (see equation 9.1.3), we obtain:

$$W = \frac{\mathcal{N}e^2\lambda^2}{4mc^2\varepsilon_0}. \quad (10.1.15)$$

This is the same as equation 9.2.2.

When we discussed this equation in Chapter 9, we pointed out that the equivalent widths of real lines differ from this prediction by a factor f_{12} , the absorption oscillator strength, and we also pointed out that \mathcal{N} has to be replaced by \mathcal{N}_1 , the column density of atoms in the initial (lower) level. Thus, from this point, I shall replace \mathcal{N} with $\mathcal{N}_1 f_{12}$. However, in this chapter we are not so much concerned with the equivalent width, but with the line profile and the actual width. The width of an emission line in this context is commonly expressed as the full width at half maximum (FWHM) and the width of an absorption line as the full width at half minimum (FWHM). (These are on no account to be confused with the *equivalent width*, which is discussed in section 9.1.) Note that some writers use the term “half-width”. It is generally not possible to know what a writer means by this.

In terms of the notation of figure IX.1 (in which “c” denotes “continuum”), but using a frequency rather than a wavelength scale, the absorptance at frequency ν is

$$a(\nu) = \frac{I_\nu(c) - I_\nu(\nu)}{I_\nu(c)}. \quad (10.1.16)$$

The profile of an absorption line is thus given by

$$I_\nu(\nu) = I_\nu(c) (1 - a(\nu)). \quad (10.1.17)$$

For radiation damping we have

$$a(\nu) = \frac{\gamma \mathcal{N}_1 f_{12} e^2}{16\pi^2 mc\varepsilon_0 \left[(\nu - \nu_0)^2 + \left(\frac{\gamma}{4\pi} \right)^2 \right]}. \quad (10.1.18)$$

The maximum value of the absorptance (at the line centre) is

$$a(\nu_0) = \frac{\mathcal{N}_1 f_{12} e^2}{mc\varepsilon_0 \gamma}. \quad (10.1.19)$$

This quantity is also $\frac{I_\nu(c) - I_\nu(\nu_0)}{I_\nu(c)}$ and it is also known as the *central depth* d of the line. (Be sure to refer to figure IX.1 to understand its meaning.) I shall use the symbol d or $a(\nu_0)$ interchangeably, according to context.

It is easy to see that the value of $\nu - \nu_0$ at which the absorptance is half its maximum value is $\gamma/(4\pi)$. That is to say, the full width at half maximum (FWHM) of the absorptance, which I denote as w , is, in frequency units:

$$w = \frac{\gamma}{2\pi}. \quad (10.1.20)$$

(In wavelength units, it is λ^2/c times this.) This is also the FWHM of the absorption profile.

Equation 10.1.18 can be written

$$\frac{a(\nu)}{a(\nu_0)} = \frac{1}{4\left(\frac{\nu-\nu_0}{w}\right)^2 + 1}. \quad (10.1.21)$$

The absorption line profile (see Equation 10.1.1) can be written

$$\frac{I_\nu(\nu)}{I_\nu(c)} = 1 - \frac{d}{4\left(\frac{\nu-\nu_0}{w}\right)^2 + 1}. \quad (10.1.22)$$

Notice that at the line centre, $I_\nu(\nu_0)/I_\nu(c) = 1$ minus the central depth; and a long way from the line centre, $I_\nu(\nu) = I_\nu(c)$, as expected. This type of profile is called a *Lorentz profile*.

From equations 10.1.14 (but with $\mathcal{N}_1 f_{12}$ substituted for \mathcal{N}), 10.1.19 and 10.1.20 we find that

$$\begin{aligned} \text{Equivalent width} &= \frac{\pi}{2} \times \text{central depth} \times \text{FWHM} \\ &= 1.571 \times \text{central depth} \times \text{FWHM}. \end{aligned} \quad (10.1.23)$$

This is true whether equivalent width and FWHM are measured in frequency or in wavelength units. (It is a pity that, for theoretical work, frequency is more convenient than wavelength, since frequency is proportional to energy, but experimentalists often (not invariably!) work with gratings, which disperse light linearly with respect to wavelength!)

Indeed the equivalent width of any type of profile can be written in the form

$$\text{Equivalent width} = \text{constant} \times \text{central depth} \times \text{FWHM}, \quad (10.1.24)$$

the value of the constant depending upon the type of profile.

In photographic days, the measurement of equivalent widths was a very laborious procedure, and, if one had good reason to believe that the line profiles in a spectrum were all Lorentzian, the equivalent width would be found by measuring just the FWHM and the central depth. Even today, when equivalent widths can often be determined by computer from digitally-recorded spectra almost instantaneously, there may be occasions where low-resolution spectra do not allow this, and all that can be honestly measured are the central depths and equivalent widths. The type of profile, and hence the value to be used for the constant in Equation 10.1.14 requires a leap of faith.

It is worth noting (consult equations 10.1.4, 10.1.19 and 10.1.20) that the equivalent width is determined by the column density of the absorbing atoms (or, rather, on $\mathcal{N}_1 f_{12}$), the FWHM is determined by the damping constant, but the central depth depends on both. You can determine the damping constant by measuring the FWHM.

The form of the Lorentz profile is shown in figure X.1 for two lines, one with a central depth of 0.8 and the other with a central depth of 0.4. Both lines have the same equivalent width, the product wd being the same for each. Note that this type of profile has a *narrow core, skirted by extensive wings*.

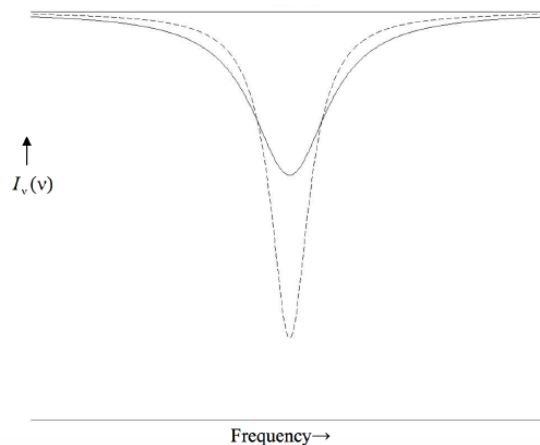


FIGURE X.1

Of course a visual inspection of a profile showing a narrow core and extensive wings, while suggestive, doesn't prove that the profile is strictly lorentzian. However, Equation 10.1.22 can be rearranged to read

$$\frac{I_\nu(c)}{I_\nu(c) - I_\nu(\nu)} = \frac{4}{w^2 d} (\nu - \nu_0)^2 + \frac{1}{d^2}. \quad (10.1.25)$$

This shows that if you make a series of measurements of $I_\nu(\nu)$ and plot a graph of the left hand side versus $(\nu - \nu_0)^2$, you should obtain a straight line if the profile is lorentzian, and you will obtain the central depth and equivalent width (hence also the damping constant and the column density) from the intercept and slope as a bonus. And if you don't get a straight line, you don't have a Lorentz profile.

It will be recalled that the purely classical oscillator theory predicted that the equivalent widths of all lines (in frequency units) of a given element is the same, namely that given by Equation 10.1.14. The obvious observation that this is not so led us to introduce the emission oscillator strength, and also to replace \mathcal{N} by \mathcal{N}_1 . Likewise, Equation 10.1.20 predicts that the FWHm (in wavelength units) is the same for all lines. (Equation 10.2.20 gives the FWHm in frequency units. To understand my caveat "in wavelength units", refer also to equations 10.1.8 and 10.1.9. You will see that the predicted FWHm in wavelength units is $\frac{e^2}{3\epsilon_0 mc^2} = 1.18 \times 10^{-14} \text{m}$, which is exceedingly small, and the core, at least, is beyond the resolution of most spectrographs.) Obviously the damping constants for real lines are much larger than this. For real lines, the classical damping constant γ has to be replaced with the *quantum mechanical damping constant* Γ .

At present I am describing in only a very qualitative way the quantum mechanical treatment of the damping constant. Quantum mechanically, an electromagnetic wave is treated as a perturbation to the hamiltonian operator. We have seen in section 9.4 that each level has a finite lifetime – see especially equation 9.4.7. The mean lifetime for a level m is $1/\Gamma_m$. Each level is not infinitesimally narrow. That is to say, one cannot say with infinitesimal precision what the energy of a given level (or state) is. The uncertainty of the energy and the mean lifetime are related through Heisenberg's uncertainty principle. The longer the lifetime, the broader the level. The energy probability of a level m is given by a Lorentz function with parameter Γ_m , given by equation 9.4.7 and equal to the reciprocal of the mean lifetime. Likewise a level n has an energy probability distribution given by a Lorentz function with parameter Γ_n . When an atom makes a transition between m and n , naturally, there is an energy uncertainty in the emitted or absorbed photon, and so there is a distribution of photons (i.e. a line profile) that is a Lorentz function with parameter $\Gamma = \Gamma_m + \Gamma_n$. This parameter Γ must replace the classical damping constant γ . The FWHm of a line, in frequency units, is now $\Gamma/(2\pi)$, which varies from line to line.

Unfortunately it is observed, at least in the spectrum of main sequence stars, if not in that of giants and supergiants, that the FWHms of most lines *are about the same*! How frustrating! Classical theory predicts that all lines have the same FWHm. We know classical theory is wrong, so we go to the trouble of doing quantum mechanical theory, which predicts different FWHms from line to line. And then we go and observe main sequence stars and we find that the lines all have the same FWHm (admittedly much broader than predicted by classical theory.)

The explanation is that, in main sequence atmospheres, lines are additionally broadened by *pressure broadening*, which also gives a Lorentz profile, which is generally broader than, and overmasks, radiation damping. (The pressures in the extended atmospheres of giants and supergiants are generally much less than in main sequence stars, and consequently lines are narrower.) We return to pressure broadening in a later section.

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10.2: Thermal Broadening

Let us start with an assumption that the radiation damping broadening is negligible, so that, for all practical purposes the spread of the frequencies emitted by a collection of atoms in a gas is infinitesimally narrow. The observer, however, will not see an infinitesimally thin line. This is because of the motion of the atoms in a hot gas. Some atoms are moving hither, and the wavelength will be blue-shifted; others are moving yon, and the wavelength will be red-shifted. The result will be a broadening of the lines, known as *thermal broadening*. The hotter the gas, the faster the atoms will be moving, and the broader the lines will be. We shall be able to measure the kinetic temperature of the gas from the width of the lines.

First, a brief reminder of the relevant results from the kinetic theory of gases, and to establish our notation.

Notation: c = speed of light
 \mathbf{V} = velocity of a particular atom $= u\hat{\mathbf{x}} + v\hat{\mathbf{y}} + w\hat{\mathbf{z}}$
 V = speed of that atom $= (u^2 + v^2 + w^2)^{\frac{1}{2}}$
 V_m = modal speed of all the atoms $= \sqrt{\frac{2kT}{m}} = 1.414\sqrt{\frac{kT}{m}}$
 \bar{V} = mean speed of all the atoms $= \sqrt{\frac{8kT}{\pi m}} = 1.596\sqrt{\frac{kT}{m}} = 1.128V_m$
 V_{RMS} = root mean square speed of all the atoms $= \sqrt{\frac{3kT}{m}} = 1.732\sqrt{\frac{kT}{m}} = 1.225V_m$

The Maxwell distribution gives the distribution of speeds. Consider a gas of N atoms, and let $N_V dV$ be the number of them that have speeds between V and $V + dV$. Then

$$\frac{N_V dV}{N} = \frac{4}{\sqrt{\pi} V_m^3} V^2 \exp\left(-\frac{u^2}{V_m^2}\right) dV. \quad (10.2.1)$$

More relevant to our present topic is the distribution of a velocity component. We'll choose the x -component, and suppose that the x -direction is the line of sight of the observer as he or she peers through a stellar atmosphere. Let $N_u du$ be the number of atoms with velocity components between u and du . Then the gaussian distribution is

$$\frac{N_u du}{N} = \frac{1}{\sqrt{\pi} V_m} \exp\left(-\frac{u^2}{V_m^2}\right) du, \quad (10.2.2)$$

which, of course, is symmetric about $u = 0$.

Now an atom with a line-of-sight velocity component u gives rise to a Doppler shift $\nu - \nu_0$, where (provided that $u^2 \ll c^2$) $\frac{\nu - \nu_0}{\nu_0} = \frac{u}{c}$. If we are looking at an emission line, the left hand side of Equation 10.2.2 gives us the line profile $I_\nu(\nu)/I_\nu(\nu_0)$ (provided the line is optically thin, as is always assumed in this chapter unless specified otherwise). Thus the line profile of an emission line is

$$\frac{I_\nu(\nu)}{I_\nu(\nu_0)} = \exp\left[-\frac{c^2}{V_m^2} \frac{(\nu - \nu_0)^2}{\nu_0^2}\right]. \quad (10.2.3)$$

This is a *gaussian*, or *Doppler*, profile.

It is easy to show that the full width at half maximum (FWHM) is

$$w = \frac{V_m \nu_0}{c} \sqrt{\ln 16} = 1.6651 \frac{V_m \nu_0}{c}. \quad (10.2.4)$$

This is also the full width at half minimum (FWHm) of an absorption line, in frequency units. This is also the FWHM or FWHm in wavelength units, provided that λ_0 be substituted for ν_0 .

The profile of an absorption line of central depth $d (= \frac{I_\nu(c) - I_\nu(\nu_0)}{I_\nu(c)})$ is

$$\frac{I_\nu(\nu)}{I_\nu(c)} = 1 - d \exp\left[-\frac{c^2}{V_m^2} \frac{(\nu - \nu_0)^2}{\nu_0^2}\right], \quad (10.2.5)$$

which can also be written

$$\frac{I_\nu(\nu)}{I_\nu(c)} = 1 - d \exp \left[-\frac{(\nu - \nu_0)^2 \ln 16}{w^2} \right]. \quad (10.2.6)$$

(Verify that when $\nu - \nu_0 = \frac{1}{2}w$, the right hand side is $1 - \frac{1}{2}d$. Do the same for equation 10.2.22.)

In figure X.2, I draw two gaussian profiles, each of the same equivalent width as the lorentzian profiles of figure X.1, and of the same two central depths, namely 0.4 and 0.8. We see that a gaussian profile is “all core and no wings”. A visual inspection of a profile may lead one to believe that it is probably gaussian, but, to be sure, one could write Equation 10.2.6 in the form

$$\ln \left[\frac{I_\nu(c) - I_\nu(\nu)}{I_\nu(c)} \right] = \ln d - \frac{(\nu - \nu_0)^2 \ln 16}{w^2} \quad (10.2.7)$$

and plot a graph of the left hand side versus $(\nu - \nu_0)^2$. If the profile is truly gaussian, this will result in a straight line, from which w and d can be found from the slope and intercept.

Integrating the Doppler profile to find the equivalent width is slightly less easy than integrating the Lorentz profile, but it is left as an exercise to show that

$$\begin{aligned} \text{Equivalent width} &= \sqrt{\frac{\pi}{\ln 16}} \times \text{central depth} \times \text{FWHM} \\ &= 1.064 \times \text{central depth} \times \text{FWHM}. \end{aligned} \quad (10.2.8)$$

Compare this with equation 10.2.23 for a Lorentz profile.

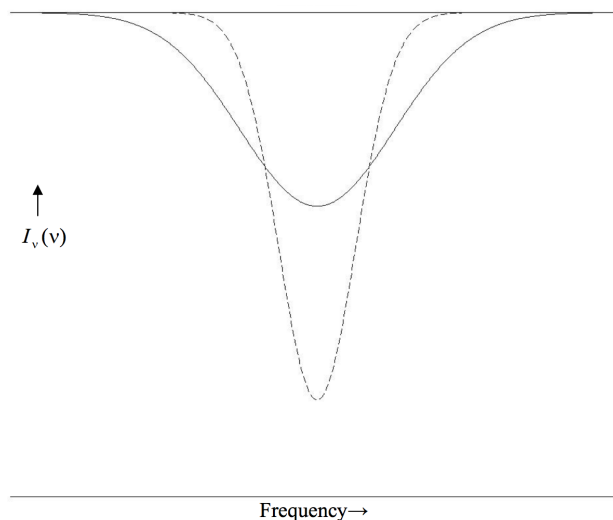


FIGURE X.2

Figure X.3 shows a lorentzian profile (continuous) and a gaussian profile (dashed), each having the same central depth and the same FWHm. The ratio of the lorentzian equivalent width to the gaussian equivalent width is $\frac{\pi}{2} \div \sqrt{\frac{\pi}{\ln 16}} = \sqrt{\pi \ln 2} = 1.476$.

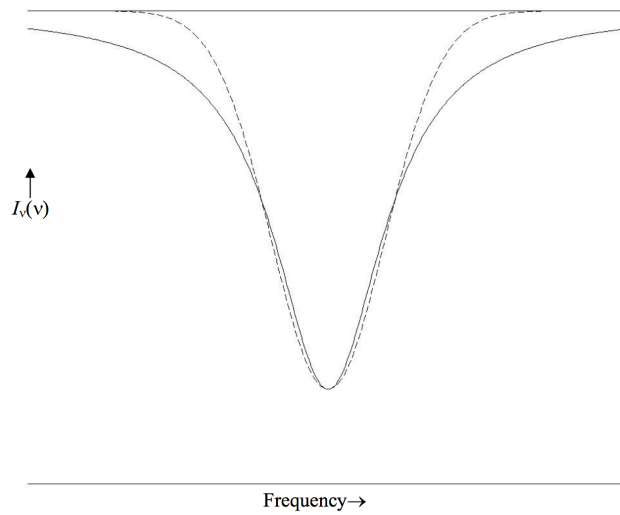


FIGURE X.3

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10.3: Microturbulence

In the treatment of microturbulence in a stellar atmosphere, we can suppose that there are many small cells of gas moving in random directions with a maxwellian distribution of speeds. The distinction between microturbulence and macroturbulence is that in microturbulence the size of the turbulent cells is very small compared with the optical depth, so that, in looking down through a stellar atmosphere we are seeing many cells of gas whose distribution of velocity components is gaussian. In macroturbulence the size of the cells is not very small compared with the optical depth, so that, in peering through the haze of an atmosphere, we can see at most only a very few cells.

If the distribution of velocity components of the microturbulent cells is supposed gaussian, then the line profiles will be just like that for thermal broadening, except that, instead of the modal speed $V_m = \sqrt{2kT/m}$ of the atoms we substitute the modal speed ξ_m of the microturbulent cells. Thus the line profile resulting from microturbulence is

$$\frac{I_\nu(\nu)}{I_\nu(\nu_0)} = 1 - d \exp \left[-\frac{c^2}{\xi_m^2} \frac{(\nu - \nu_0)^2}{\nu_0^2} \right]. \quad (10.3.1)$$

The FWHM in frequency units is

$$\frac{\xi_m \nu_0 \sqrt{\ln 16}}{c} \quad (10.3.2)$$

or, in wavelength units,

$$\frac{\xi_m \lambda_0 \sqrt{\ln 16}}{c}. \quad (10.3.3)$$

If the thermal and microturbulent broadening are comparable in size, we still get a gaussian profile, except that for V_m or ξ_m we must substitute

$$\sqrt{V_m^2 + \xi_m^2} = \sqrt{2kT/m + \xi_m^2}. \quad (10.3.4)$$

This actually requires formal proof, and this will be given as an exercise in Section 5.

Since either thermal broadening or microturbulence will result in a gaussian profile, one might think that it would not be possible to tell, from a spectrum exhibiting gaussian line profiles, whether the broadening was caused primarily by high temperature or by microturbulence. But a little more thought will show that in principle it is possible to distinguish, and to determine separately the kinetic temperature and the modal microturbulent speed. Think about it, and see if you can devise a way.

THINKING

The key is, in purely thermal broadening, the light atoms (such as lithium) move faster than the heavier atoms (such as cadmium), the speeds being inversely proportional to the square roots of their atomic masses. Thus the lines of the light atoms will be broader than the lines of the heavy atoms. In microturbulence all atoms move *en masse* at the same speed and are therefore equally broad. We have seen, beneath Equation 10.3.7, that the FWHM, in frequency units, is

$$w = \frac{\nu_0}{c} \sqrt{(2kT/m + \xi_m^2) \ln 16}. \quad (10.3.5)$$

If we form the quantity

$$X = \frac{w^2 c^2}{\nu_0^2 \ln 16} \quad (10.3.6)$$

for a lithium line and for a cadmium line, we will obtain

$$X_{\text{Li}} = \frac{2kT}{m_{\text{Li}}} + \xi_m^2 \quad \text{and} \quad X_{\text{Cd}} = \frac{2kT}{m_{\text{Cd}}} + \xi_m^2, \quad (10.3.7)$$

from which T and ξ_m are immediately obtained.

? Exercise 10.3.1

A Li line at 670.79 nm has a gaussian FWHM = 9 pm (picometres) and a Cd line at 508.58 nm has a gaussian FWHM = 3 pm. Calculate the kinetic temperature and the modal microturbulent speed.

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10.4: Combination of Profiles

Several broadening factors may be simultaneously present in a line. Two mechanisms may have similar profiles (e.g. thermal broadening and microturbulence) or they may have quite different profiles (e.g. thermal broadening and radiation damping). We need to know the resulting profile when more than one broadening agent is present. Let us consider an emission line, and let $x = \lambda - \lambda_0$. Let us suppose that the lines are broadened, for example, by thermal broadening, the thermal broadening function being $f(x)$. Suppose, however, that, in addition, the lines are also broadened by radiation damping, the radiation damping profile being $g(x)$. At a distance ξ from the line centre, the contribution to the line profile is the height of the function $f(\xi)$ weighted by the function $g(x - \xi)$. That is to say the resulting profile $h(x)$ is given by

$$h(x) = \int_{-\infty}^{\infty} f(\xi)g(x - \xi) d\xi. \quad (10.4.1)$$

The reader should convince him- or herself that this is exactly the same as

$$h(x) = \int_{-\infty}^{\infty} f(x - \xi)g(\xi) d\xi. \quad (10.4.2)$$

This profile is called the *convolution* of the two constituent profiles, and is often written symbolically

$$h = f * g. \quad (10.4.3)$$

Convoluting Two Gaussian Functions

Let us consider, for example, the convolution of two Gaussian functions, for example the convolution of thermal and microturbulent broadening.

Suppose one of the Gaussian functions is

$$G_1(x) = \frac{1}{g_1} \cdot \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{x^2 \ln 2}{g_1^2}\right) = \frac{0.46972}{g_1} \exp\left(-\frac{0.69315x^2}{g_1^2}\right). \quad (10.4.4)$$

Here $x = \lambda - \lambda_0$. The area under the curve is unity, the HWHM is g_1 and the peak is $\frac{1}{g_1} \sqrt{\frac{\ln 2}{\pi}}$. (Verify these.) Suppose that the second Gaussian function is

$$G_2(x) = \frac{1}{g_2} \cdot \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{x^2 \ln 2}{g_2^2}\right). \quad (10.4.5)$$

It can now be shown, using Equation 10.4.1 or 10.4.2 that the convolution of G_1 and G_2 is

$$G(x) = G_1(x) * G_2(x) = \frac{1}{g} \cdot \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{x^2 \ln 2}{g^2}\right), \quad (10.4.6)$$

where

$$g^2 = g_1^2 + g_2^2. \quad (10.4.7)$$

We used this result already in Section 10.4 when, in adding microturbulent to thermal broadening, we substituted $\sqrt{V_m^2 + \xi_m^2}$ for V_m . In case you find the integration to be troublesome, I have done it in an Appendix to this Chapter.

Convoluting Two Lorentzian Functions

Now let's consider the combination of two lorentzian functions. Radiation damping gives rise to a lorentzian profile, and we shall see later that pressure broadening can also give rise to a lorentzian profile. Let us suppose that the two lorentzian profiles are

$$L_1(x) = \frac{l_1}{\pi} \cdot \frac{1}{x^2 + l_1^2} \quad (10.4.8)$$

and

$$L_2(x) = \frac{l_2}{\pi} \cdot \frac{1}{x^2 + l_2^2}. \quad (10.4.9)$$

Here $x = \lambda - \lambda_0$. The area under the curve is unity, the HWHM is l_1 and the peak is $1/(\pi l)$. (Verify these.) It can be shown that

$$L(x) = L(x) * L_2(x) = \frac{1}{\pi} \cdot \frac{1}{x^2 + l^2}, \quad (10.4.10)$$

where

$$l = l_1 + l_2. \quad (10.4.11)$$

Details of the integration are in the Appendix to this Chapter.

Convoluting a Lorentzian Function with a Gaussian Function

Let us now look at the convolution of a Gaussian profile with a lorentzian profile; that is, the convolution of

$$G(x) = \frac{1}{g} \cdot \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{x^2 \ln 2}{g^2}\right) \quad (10.4.12)$$

with

$$L(x) = \frac{1}{\pi} \cdot \frac{1}{x^2 + l^2}. \quad (10.4.13)$$

We can find the convolution from either Equation 10.4.1 or from Equation 10.4.2 and we obtain either

$$V(x) = \frac{1}{g} \sqrt{\frac{\ln 2}{\pi^3}} \int_{-\infty}^{\infty} \frac{\exp(-[(\xi - x)^2 \ln 2]/g^2)}{\xi^2 + l^2} d\xi \quad (10.4.14)$$

or

$$V(x) = \frac{1}{g} \sqrt{\frac{\ln 2}{\pi^3}} \int_{-\infty}^{\infty} \frac{\exp[-(\xi^2 \ln 2)/g^2]}{(\xi - x)^2 + l^2} d\xi. \quad (10.4.15)$$

The expression 10.4.14 or 10.4.15 which is a convolution of a Gaussian and a lorentzian profile, is called a *Voigt profile*. (A rough attempt at pronunciation would be something like *Focht*.)

A useful parameter to describe the “gaussness” or “lorentzness” of a Voigt profile might be

$$k_G = \frac{g}{g + l}, \quad (10.4.16)$$

which is 0 for a pure lorentz profile and 1 for a pure Gaussian profile. In figure X.4 I have drawn Voigt profiles for $k_G = 0.25, 0.5$ and 0.75 (continuous, dashed and dotted, respectively). The profiles are normalized so that all have the same area. A nice exercise for those who are more patient and competent with computers than I am would be to draw 1001 Voigt profiles, with k_G going from 0 to 1 in steps of 0.001, perhaps normalized all to the same height rather than the same area, and make a movie of a Gaussian profile gradually morphing to a lorentzian profile. Let me know if you succeed!

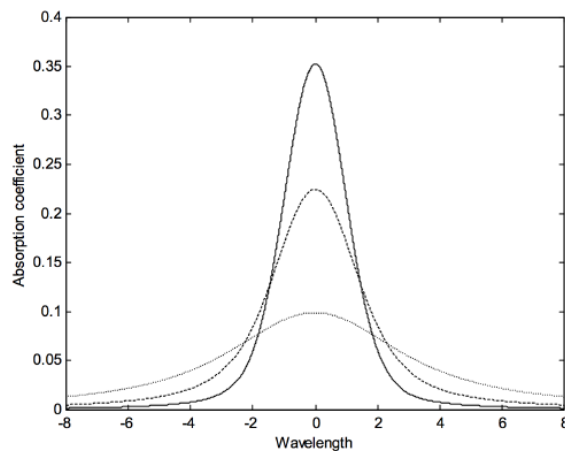


FIGURE X.4

As for the gauss-gauss and lorentz-lorentz profiles, I have appended some details of the integration of the gauss-lorentz profile in the Appendix to this Chapter.

The FWHM or FWHm in wavelength units of a Gaussian profile (i.e. $2g$) is

$$w_G = \frac{(2kT/m + \xi_m^2)^{\frac{1}{2}} \lambda_0 \sqrt{\ln 16}}{c} = \frac{1.665 (2kT/m + \xi_m^2)^{\frac{1}{2}} \lambda_0}{c}. \quad (10.4.17)$$

The FWHM or FWHm in frequency units of a lorentzian profile is

$$w_L = \Gamma/(2\pi) = 0.1592\Gamma, \quad (10.4.18)$$

Here Γ is the sum of the radiation damping constant (see section 2) and the contribution from pressure broadening $2/\bar{t}$ (see section 6). For the FWHM or FWHm in wavelength units (i.e. $2l$), we have to multiply by λ_0^2/c .

Integrating a Voigt Profile

The area under Voigt profile is $2 \int_0^\infty V(x) dx$, where $V(x)$ is given by Equation 10.4.14 which itself had to be evaluated with a numerical integration. Since the profile is symmetric about $x = 0$, we can integrate from 0 to ∞ and multiply by 2. Even so, the double integral might seem like a formidable task. Particularly troublesome would be to integrate a nearly lorentzian profile with extensive wings, because there would then be the problem of how far to go for an upper limit. However, it is not at all a formidable task. The area under the curve given by Equation 10.4.14 is unity! This is easily seen from a physical example. The profile given by Equation 10.4.14 is the convolution of the lorentzian profile of Equation 10.4.13 with the Gaussian profile of Equation 10.4.12 both of which were normalized to unit area. Let us imagine that an emission line is broadened by radiation damping, so that its profile is lorentzian. Now suppose that it is further broadened by thermal broadening (Gaussian profile) to finish as a Voigt profile. (Alternatively, suppose that the line is scanned by a spectrophotometer with a Gaussian sensitivity function.) Clearly, as long as the line is always optically thin, the additional broadening does not affect the integrated intensity.

Now we mentioned in sections 2 and 3 of this chapter that the equivalent width of an absorption line can be calculated from $c \times \text{central depth} \times \text{FWHM}$, and likewise the area of an emission line is $c \times \text{height} \times \text{FWHM}$, where c is $1.064 (= \sqrt{\pi/\ln 16})$ for a Gaussian profile and $1.571 (= \pi/2)$ for a lorentzian profile. We know that the integral of $V(x)$ is unity, and it is a fairly straightforward matter to calculate both the height and the FWHM of $V(x)$. From this, it becomes possible to calculate the constant c as a function of the Gaussian fraction k_G . The result of doing this is shown in figure X.4A.

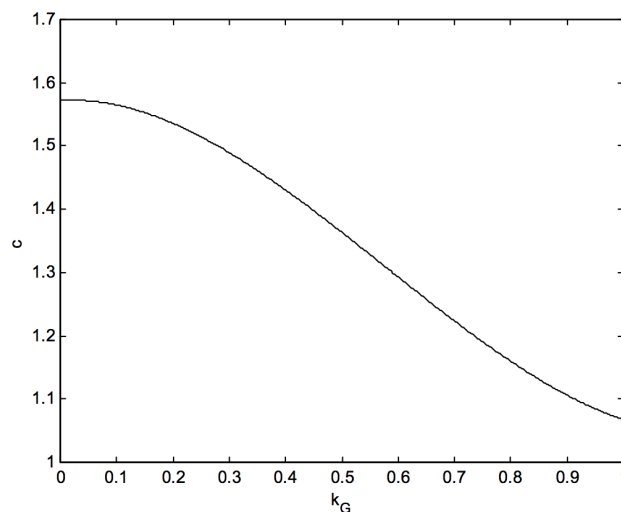


FIGURE X.4A

This curve can be fitted with the empirical Equation

$$c = a_0 + a_1 k_G + a_2 k_G^2 + a_3 k_G^3, \quad (10.4.19)$$

where $a_0 = 1.572$, $a_1 = 0.05288$, $a_2 = -1.323$ and $a_3 = 0.7658$. The error incurred in using this formula nowhere exceeds 0.5%; the mean error is 0.25%.

The Voigt Profile in Terms of the Optical Thickness at the Line Center.

Another way to write the Voigt profile that might be useful is

$$\tau(x) = Cl\tau(0) \int_{-\infty}^{\infty} \frac{\exp[-(\xi - x)^2 \ln 2 / g^2]}{\xi^2 + l^2} d\xi. \quad (10.4.20)$$

Here $x = \lambda - \lambda_0$ and ξ is a dummy variable, which disappears when the definite integral is performed. The Gaussian HWHM is $g = \lambda_0 V_m \sqrt{\ln 2} / c$, and the lorentzian HWHM is $l = \lambda_0^2 \Gamma / (4\pi c)$. The optical thickness at $\lambda - \lambda_0 = x$ is $\tau(x)$, and the optical thickness at the line centre is $\tau(0)$. C is a dimensionless coefficient, whose value depends on the Gaussian fraction $k_G = g / (g + l)$. C is clearly given by

$$Cl \int_{-\infty}^{\infty} \frac{\exp[-\xi^2 \ln 2 / g^2]}{\xi^2 + l^2} d\xi = 1. \quad (10.4.21)$$

If we now let $l = l'g / \sqrt{\ln 2}$ and $\xi = \xi'g / \sqrt{\ln 2}$, and also make use of the symmetry of the integrand about $\xi = \xi' = 0$, this becomes

$$2Cl' \int_0^{\infty} \frac{\exp(-\xi'^2)}{\xi'^2 + l'^2} d\xi' = 1. \quad (10.4.22)$$

On substitution of $\xi' = \frac{2l't}{1-t^2}$ (in order to make the limits finite), we obtain

$$4C \int_0^1 \frac{\exp[-\{2l't / (1-t^2)\}^2]}{1+t^2} dt = 1, \quad (10.4.23)$$

which can readily be numerically integrated for a given value of l' . Recall that $l/g = 1/k_G - 1$ and hence that $l' = (1/k_G - 1)\sqrt{\ln 2}$. The results of the integration are as follows. The column C_{approx} is explained following figure X.4B.

k_G	C	C_{approx}
0.05	8.942 417	9.325 6
0.10	4.264 473	4.288 9
0.15	2.719 106	2.716 4
0.20	1.957 257	1.956 6
0.25	1.508 719	1.511 1
0.30	1.216 486	1.219 6
0.35	1.013 114	1.015 3
0.40	0.864 815	0.865 5
0.45	0.752 806	0.751 9
0.50	0.665 831	0.663 9
0.55	0.596 758	0.594 3
0.60	0.540 859	0.538 6
0.65	0.494 893	0.493 4
0.70	0.456 569	0.456 2
0.75	0.424 227	0.425 1
0.80	0.396 642	0.398 5
0.85	0.372 889	0.375 3
0.90	0.352 263	0.354 2
0.95	0.334 214	0.334 5
1.00	0.318 310	0.315 3

The last entry, the value of C for $k_G = 1$, a pure Gaussian profile, is $1/\pi$. These data are graphed in figure X.4B.

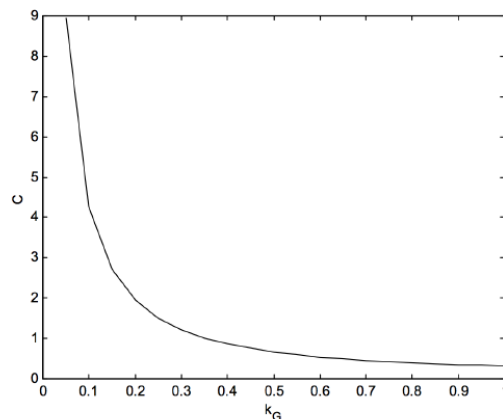


FIGURE X.4B

The empirical formula

$$C_{\text{approx}} = ak_G^{-b} + c_0 + c_1k_G + c_2k_G^2 + c_3k_G^3, \quad (10.4.24)$$

where

$$\begin{aligned} a &= +0.309031 & b &= +1.132747 & c_0 &= +0.16510 \\ c_1 &= -0.82999 & c_2 &= +1.21782 & c_3 &= -0.54665 \end{aligned}$$

fits the curve tolerably well within (but not outside) the range $k_G = 0.15$ to 1.00 .

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10.5: Pressure Broadening

This is a fairly difficult subject, and I am no expert in it. The reader will forgive me if I accordingly treat it rather briefly and descriptively.

The phenomena of pressure broadening (also known as collisional broadening) are often divided into effects resulting from the short time interval between atomic collisions, and effects resulting at the moment of collision. I shall begin by describing the first of these phenomena.

The only possible absolutely monochromatic unbroadened infinitesimally narrow line with a single, uniquely defined frequency is a sine wave of infinite extent. A sine wave of finite length is not a true sine wave of a single frequency, but it has a spread of component frequencies, which can be determined by Fourier analysis. This, by the way, is the reason behind Heisenberg's uncertainty principle (*Unschärferprinzip*). If the wavefunction that describes a particle is very limited in extent, then the position of the particle is relatively well determined. On the other hand, the limited extent of the wavefunction means that it has a correspondingly broad Fourier spread of constituent wavelengths, and hence the momentum is correspondingly uncertain.

The atmospheres of giant and supergiant stars are relatively thin; pressure broadening is slight and lines tend to be narrow. In the atmospheres of main sequence stars, however, collisions between atoms are frequent. The frequent occurrence of collisions interrupts the wave trains and divides them into short wave-packets, with a corresponding spread of component frequencies. Thus the spectrum lines are broadened.

The Fourier distribution of amplitudes of component frequencies of a sine wave that is truncated by a box function is the same as the Fourier distribution of amplitudes of a light wave that is diffracted by a single slit. That is to say it is a sinc function of the form $(\sin \Delta\nu)/\Delta\nu$ and the intensity distribution is the square of this. The shorter the intercollision time, the wider the spread of constituent frequencies, just as a narrow slit produces a wide diffraction pattern. Thus one might expect the profile of a pressure broadened line to resemble a single slit diffraction pattern, which, it will be recalled, looks like figure X.5.

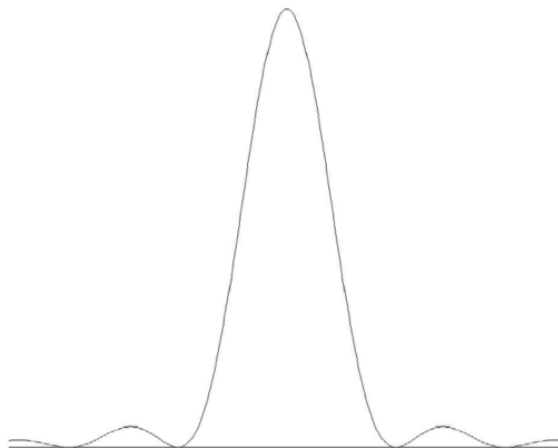


FIGURE X.5

The profile would indeed look like that if all intercollision times were exactly equal and all wave-train fragments were of exactly the same length. There is, however, a Poisson distribution of intercollision times, and so the above profile has to be convolved with this Poisson distribution. While I don't do the calculation here, the resulting profile is a Lorentz profile except that the damping constant Γ is replaced by $2/\bar{t}$, where \bar{t} is the mean time between collisions. The mean time between collisions is given, from kinetic theory of gases, by

$$\bar{t} = \frac{1}{nd^2} \sqrt{\frac{m}{16\pi kT}}. \quad (10.5.1)$$

Here m , d and n are, respectively, the masses, diameters and number density of the atoms. Hence, if the kinetic temperature is independently known, the number density of the particles can be determined from the FWHM of a pressure-broadened line.

It will be recalled that classical radiation damping theory predicts the same FWHM for all lines, with a classical damping constant γ . Quantum mechanical theory predicts a damping constant Γ and hence FWHM that differs from line to line. Yet in the spectrum

of a main sequence star, one quite often finds that all lines of a given element have the same FWHm and hence the same effective damping constant. This is because the width of a Lorentz profile is determined more by pressure broadening than by radiation damping.

There are further broadening effects caused by interactions that take place at the moment of collision. If an atom is approached by an electron or an ion, it will temporarily be in an electric field, and consequently the lines will be broadened by Stark effect, which may be either linear (proportional to the electric field E) or quadratic ($\propto E^2$), or neutral-neutral reactions give rise to interactions between temporarily induced dipole moments (van der Waals forces), and these all have different dependences on interatomic distance. Neutral magnesium is very sensitive to quadratic Stark effect, and hydrogen is sensitive to linear Stark effect. The entire subject is quite difficult, and I leave it here except to point out two small details. Very often the broadening is not symmetric, lines typically having wider wings to the long wavelength side than on the short wavelength side. This is because the effect of the interactions is to lower and broaden the energy levels of a transition, the lower energy level generally being lowered more than the upper. A second point is that the hydrogen Balmer lines are often much broadened by linear Stark effect, and this can be recognized because the Stark pattern for the Balmer series is such that there are no undisplaced Stark components for even members of the series – $H\beta$, $H\delta$, $H\zeta$, etc. Thus results in a central dip to these lines in an emission spectrum or a central bump in an absorption line.

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10.6: Rotational Broadening

The lines in the spectrum of a rotating star are broadened because light from the receding limb is redshifted and light from the approaching limb is blueshifted. It may be remarked that early-type stars (type F and earlier) tend to be much faster rotators than later-type stars, and consequently early-type stars show more rotational broadening. It should also be remarked that pole-on rotators do not, of course, show rotational broadening (even early-type fast rotators).

I shall stick to astronomical custom and refer to a “redshift” as a shift towards a longer wavelength, even though for an infrared line a “redshift” in this sense would be a shift away from the red! A “longward” shift doesn’t quite solve the problem either, for the following reason. While it is true that relativity makes no distinction between a moving source and a moving observer, in the case of the Doppler effect in the context of sound in air, if the *observer* is moving, there may be a change in the pitch of the perceived sound, but there is no change in wavelength!

We shall start by considering a star whose axis of rotation is in the plane of the sky, and which is of uniform radiance across its surface. We shall then move on to oblique rotators, and then to limb-darkened stars. A further complication that could be considered would be non-uniform rotation. Thus, the Sun does not rotate as a solid body, but the angular speed at low latitudes is faster than at higher latitudes – the so-called “equatorial acceleration”.

In figure X.6, on the left hand we see the disc of a star as seen on the sky by an observer. PQ is the axis of rotation, supposed to be in the plane of the sky, and AB is the equator. X is a point on the surface of the star at coordinates (x, y) , latitude θ . The star is supposed to be rotating with an equatorial speed v_e . What we are going to show is that all points on the chord LMN have the same radial velocity away from or towards the observer, and consequently all light from points on this chord has the same Doppler shift.

The right hand part of the figure shows the star seen from above the pole P. The small circle is the parallel of latitude CD shown on the left hand part of the figure.

M is a point on the equator and also on the chord LMN. Its speed is v_e and the radial component of its velocity is $v_e \sin \alpha$. The speed of the point M is $v_e \cos \theta$, and its radial velocity is $v_e \cos \theta \sin \alpha$. But $x = PM \sin \alpha = a \sin \alpha$ and $x = PX \sin \alpha = a \cos \theta \sin \alpha$. Therefore $\cos \theta \sin \alpha = \sin \alpha$. Therefore the radial velocity of X is $v_e \sin \alpha$, which is the same as that of M, and therefore all points on the chord LMN have radial velocity $v_e \sin \alpha = v_e x / a$.

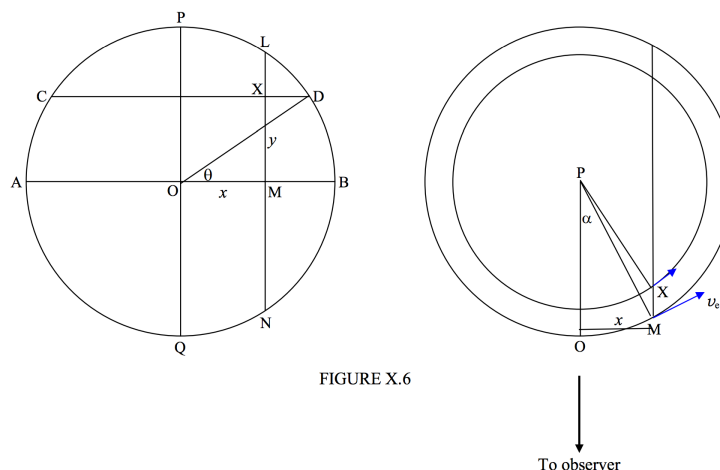


FIGURE X.6

Therefore all points on the chord $x = \text{constant}$ are subject to the same Doppler shift

$$\frac{\Delta \lambda}{\lambda} = \frac{v_e x}{ac}. \quad (10.6.1)$$

The ordinate of an emission line profile at Doppler shift $\Delta \lambda$ compared with its ordinate at the line center is equal to the ratio of the length of the chord $x = \text{constant}$ to the diameter $2a$ of the stellar disk:

$$\frac{I_{\lambda}(\Delta\lambda)}{I_{\lambda}(0)} = \left(1 - \frac{x^2}{a^2}\right)^{\frac{1}{2}} = \left(1 - \frac{c^2(\Delta\lambda)^2}{v_e^2 \lambda^2}\right)^{\frac{1}{2}}. \quad (10.6.2)$$

In the above, we have assumed that the axis of rotation is in the plane of the sky, or that the inclination i of the equator to the plane of the sky is 90° . If the inclination is not 90° , the only effect is that all radial velocities are reduced by a factor of $\sin i$, so that Equation 10.6.2 becomes

$$\frac{I_{\lambda}(\Delta\lambda)}{I_{\lambda}(0)} = \left(1 - \frac{c^2(\Delta\lambda)^2}{v_e^2 \sin^2 i \lambda^2}\right)^{\frac{1}{2}}, \quad (10.6.3)$$

and this is the line profile. It is an ellipse, and if we write $\frac{I_{\lambda}(\Delta\lambda)}{I_{\lambda}(0)} = X$ and $\frac{\Delta\lambda}{\lambda} = Y$ Equation 10.6.3 can be written

$$\frac{x^2}{\left(\frac{v_e \sin i}{c}\right)^2} + \frac{y^2}{1^2} = 1. \quad (10.6.4)$$

The basal width of the line (which has no asymptotic wings) is $\frac{2v_e \sin i}{c}$ and the FWHM is $\frac{\sqrt{3}v_e \sin i}{c}$. The profile of an absorption line of central depth d is

$$\frac{I_{\lambda}(\Delta\lambda)}{I_{\lambda}(0)} = 1 - d \left(1 - \frac{c^2(\Delta\lambda)^2}{v_e^2 \sin^2 i \lambda^2}\right)^{\frac{1}{2}}, \quad (10.6.5)$$

It is left as an exercise to show that

$$\text{Equivalent width} = \frac{\pi}{\sqrt{12}} \times \text{central depth} \times \text{FWHM} = 0.9069dw. \quad (10.6.6)$$

From the width of a rotationally broadened line we can determine $v_e \sin i$, but we cannot determine v_e and i separately without additional information. Likewise, we cannot determine the angular speed of rotation unless we know the radius independently.

It might be noted that, for a rotating *planet*, visible only by reflected light, the Doppler effect is doubled by reflection, so the basal width of a rotationally broadened line is

$$\frac{4v_e \sin i}{c}.$$

Now let us examine the effect of limb darkening. I am going to use the words *intensity* and *radiance* in their strictly correct senses as described in Chapter 1, and the symbols I and L respectively. That is, radiance = intensity per unit projected area. For spectral intensity and spectral radiance – i.e. intensity and radiance per unit wavelength interval, I shall use a subscript λ .

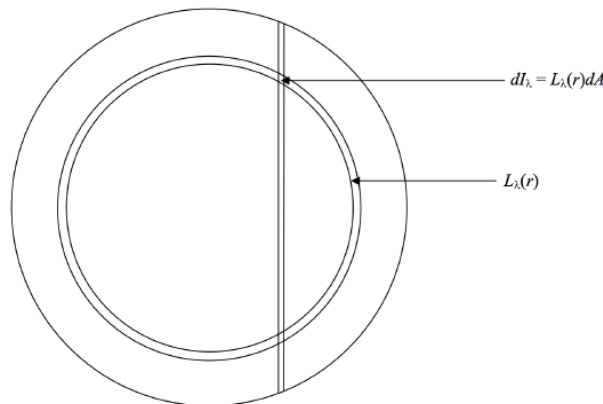


FIGURE X.7

We suppose that the spectral radiance at a distance r from the center of the disc is $L_{\lambda}(r)$. The intensity from an elemental area dA on the disc is $dI_{\lambda} = L_{\lambda}(r)dA$. The area between the vertical strip and the annulus in figure X.7 is a little parallelogram of length dy and width dx , so that $dA = dx dy$. Here $y^2 = r^2 - x^2$, so that

$$dy = \frac{rdr}{y} = \frac{rdr}{\sqrt{r^2 - x^2}}.$$

Therefore $dA = \frac{rdrdx}{\sqrt{r^2 - x^2}}$. The total intensity from the strip of width dx , which is $dI_\lambda(\Delta\lambda)$, where $\frac{\Delta\lambda}{\lambda} = \frac{v_e \sin i}{ac}$, is

$$dI_\lambda(\Delta\lambda) = 2 \int_x^a \frac{L_\lambda(r)rdr}{\sqrt{r^2 - x^2}} dx. \quad (10.6.7)$$

The (emission) line profile is

$$\frac{I_\lambda(\Delta\lambda)}{I_\lambda(0)} = \frac{\int_x^a \frac{L_\lambda(r)rdr}{\sqrt{r^2 - x^2}}}{\int_0^a L_\lambda(r)dr}, \quad (10.6.8)$$

which is the line profile. As an exercise, see if you can find an expression for the line profile if the limb-darkening is given by $L_\theta = L(0)[1 - u(1 - \cos \theta)]$, and show that if the limb-darkening coefficient $u = 1$, the profile is parabolic.

Equation 10.6.8 enables you to calculate the line profile, given the limb darkening. The more practical, but more difficult, problem, is to invert the Equation and, from the observed line profile, find the limb darkening. Examples of this integral, and its inversion by solution of an integral equation, are given by Tatum and Jaworski, J. Quant. Spectr. Rad. Transfer, 38, 319, (1987).

Further pursuit of this problem would be to calculate the line profile of a uniform star that is rotating faster at the equator than at the poles, and then for a star that is both limb-darkened and equatorially accelerated – and then see if it is possible to invert the problem uniquely and determine both the limb darkening and the equatorial acceleration from the line profile. That would be quite a challenge.

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10.7: Instrumental Broadening

Even if the radiation damping profile of a line is negligible and if it is subject to negligible thermal, pressure and rotational broadening, it still has to suffer the indignity of instrumental broadening. Almost any type of spectrograph will broaden a line. The broadening produced by a prism is inversely proportional to the size of the prism, and the broadening produced by a grating is inversely proportional to the number of grooves in the grating. After a spectrum is produced (and broadened) by a spectrograph, it may be scanned by a further instrument such as a microphotometer, or even if it is recorded digitally, it is still further broadened by the point spread function. The instrumental broadening can in principle be determined experimentally by measuring the instrumentally-produced profile of an intrinsically very narrow line. Then, when the instrument is used to examine a broad line, the observed profile is the [convolution](#) of the true profile and the instrumental profile. We can write this symbolically as

$$O = T * I. \quad (10.7.1)$$

Here O , T and I are respectively the observed, true and instrumental profiles, and the asterisk denotes the convolution. The mathematical problem is to deconvolve this equation so that, given the instrumental profile and the observed profile it is possible to recover the true profile. This is done by making use of a mathematical theorem known as **Borel's theorem**, which is that the Fourier transform of the convolution of two functions is equal to the product of the Fourier transforms of each. That is

$$\bar{O} = \bar{T} \times \bar{I}, \quad (10.7.2)$$

where the bar denotes the Fourier transform. Numerical fast Fourier transform computer programs are now readily available, so the procedure is to calculate the Fourier transforms of the observed and instrumental profile, divide the former by the latter to obtain \bar{T} , and then calculate the inverse Fourier transform to obtain the true profile. This procedure is well known in radio astronomy, in which the observed map of a sky region is the convolution of the true map with the beam of the radio telescope, though, unlike the one-dimensional spectroscopic problem the corresponding radio astronomy problem is two-dimensional.

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10.8: Other Line-Broadening Mechanisms

I just briefly mention here one or two additional sources of line-broadening.

Lines may be broadened by unresolved or smeared Zeeman splitting, particularly for lines involving levels with large Landé g -factors. By “smeared” I mean the situation that arises if there is a large range of magnetic field strength through the line of sight or because (as is always the case with stars other than the Sun) you are looking at a whole-disc spectrum. Since the splitting depends on the field strength, the lines will obviously be smeared rather than cleanly divided into a number of discrete Zeeman components. Zeeman smearing is often large in the spectrum of white dwarf stars, where magnetic fields can be large and the observer looks through a large range of magnetic field strength.

Different Zeeman components are plane or circularly polarized according to the direction of the magnetic field. Thus in principle one should be able to recognize Zeeman effect, even if smeared or not fully resolved, by its changing appearance in different polarization directions. However, this will be true only if the magnetic field is uniform in direction, as it may mostly be in, for example, a sunspot. For a whole-disc spectrum there will be a variety of different directions of the magnetic field, and so the polarization information will be lost.

Broad lines are sometimes the result of unresolved hyperfine structure in elements with a large nuclear spin such as vanadium, or unresolved isotopic lines in elements with several isotopes of comparable abundance such as tin, copper or chlorine.

Another source of line broadening is autoionization (in absorption spectra) or dielectronic recombination (in emission spectra) in elements such as copper. These mechanisms were described in section 8.8.

One last remark might be made, namely that line broadening, whether instrumental, thermal, rotational, etc., does not change the equivalent width of a line, provided that the line is everywhere optically thin. This does not apply, however, if the line is not everywhere optically thin.

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10.9: Appendix A- Convolution of Gaussian and Lorentzian Functions

Equation 10.5.6 is

$$G(x) = G_1(x) * G_2(x) = \frac{1}{g_1 g_2} \frac{\ln 2}{\pi} \int_{-\infty}^{\infty} \exp\left(-\frac{\xi^2 \ln 2}{g_1^2}\right) \exp\left(-\frac{(\xi - x)^2 \ln 2}{g_2^2}\right) d\xi. \quad (10.A.1)$$

The integration is straightforward, if taken slowly and carefully, provided you know the integral $\int_{-\infty}^{\infty} \exp(-kx^2) dx = \sqrt{\frac{\pi}{k}}$. It goes thus:

$$G(x) = \frac{1}{g_1 g_2} \frac{\ln 2}{\pi} \int_{-\infty}^{\infty} \exp[-(a\xi^2 + b\xi + c)] d\xi, \quad (10.A.2)$$

where

$$a = \frac{(g_1^2 + g_2^2) \ln 2}{g_1^2 g_2^2}, \quad b = -\frac{x \ln 4}{g_2^2}, \quad c = \frac{x^2 \ln 2}{g_2^2}.$$

$$G(x) = \frac{1}{g_1 g_2} \frac{\ln 2}{\pi} \int_{-\infty}^{\infty} \exp[-a(\xi^2 + 2B\xi + C)] d\xi, \quad (10.A.3)$$

where

$$B = b/(2a), \quad C = c/a. \quad (10.9.1)$$

$$G(x) = \frac{1}{g_1 g_2} \frac{\ln 2}{\pi} \int_{-\infty}^{\infty} \exp[-a\{(\xi + B)^2 + C - B^2\}] d\xi \quad (10.A.4)$$

$$= \frac{1}{g_1 g_2} \frac{\ln 2}{\pi} \int_{-\infty}^{\infty} \exp[-a(\zeta^2 + C - B^2)] d\zeta \quad (10.A.5)$$

$$= \frac{K \ln 2}{\pi g_1 g_2} \int_{-\infty}^{\infty} \exp(-a\zeta^2) d\zeta = \frac{K \ln 2}{g_1 g_2 \sqrt{\pi a}}, \quad (10.A.6)$$

where

$$K = \exp[-a(C - B^2)]. \quad (10.9.2)$$

We have now completed the integration, except that we now have to remember what a, C and B were. When we do this, after a bit more careful algebra we arrive at the result

$$G(x) = G_1(x) * G_2(x) = \frac{1}{g} \cdot \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\frac{x^2 \ln 2}{g^2}\right). \quad (10.A.7)$$

In a similar manner, equation 10.5.10 is

$$L(x) = L_1(x) * L_2(x) = \frac{l_1 l_2}{\pi^2} \int_{-\infty}^{\infty} \frac{1}{\xi^2 + l_1^2} \frac{1}{(\xi - x)^2 + l_2^2} d\xi. \quad (10.A.8)$$

Resolve the integrand into partial fractions:

$$\frac{1}{\xi^2 + l_1^2} \frac{1}{(\xi - x)^2 + l_2^2} = \frac{A\xi}{\xi^2 + l_1^2} + \frac{B}{\xi^2 + l_1^2} + \frac{C(\xi - x)}{(\xi - x)^2 + l_2^2} + \frac{D}{(\xi - x)^2 + l_2^2}. \quad (10.A.9)$$

Evaluation of the constants is straightforward, if slightly tedious, by the usual method of partial fractions:

$$A = -C = 2x\alpha, \quad (10.A.10)$$

$$B = (x^2 + l_2^2 - l_1^2)\alpha, \quad (10.9.3)$$

$$D = (x^2 - l_2^2 + l_1^2)\alpha, \quad (10.9.4)$$

$$\text{where } \alpha = 1/[(x^2 + l_2^2 + l_1^2)^2 - 4l_1^2 l_2^2]. \quad (10.9.5)$$

Now

$$L(x) = \frac{l_1 l_2}{\pi^2} \left(A \int_{-\infty}^{\infty} \frac{\xi d\xi}{\xi^2 + l_1^2} + B \int_{-\infty}^{\infty} \frac{d\xi}{\xi^2 + l_1^2} + C \int_{-\infty}^{\infty} \frac{(\xi - x) d\xi}{(\xi - x)^2 + l_2^2} + D \int_{-\infty}^{\infty} \frac{d\xi}{(\xi - x)^2 + l_2^2} \right). \quad (10.A.11)$$

From symmetry considerations, this is:

$$L(x) = \frac{2l_1 l_2}{\pi^2} \left(B \int_0^{\infty} \frac{d\xi}{\xi^2 + l_1^2} + D \int_0^{\infty} \frac{d\xi}{\xi^2 + l_2^2} \right). \quad (10.A.12)$$

$$L(x) = \frac{2l_1 l_2}{\pi^2} \left(\frac{\pi B}{2l_1} + \frac{\pi D}{2l_2} \right) = (l_2 B + l_1 D) / \pi. \quad (10.A.13)$$

We have now completed the integration, except that we now have to remember what B and D were. When we do this, after a bit more careful algebra we arrive at the result

$$L(x) = \frac{l}{\pi} \cdot \frac{1}{x^2 + l^2}, \quad (10.A.14)$$

where

$$l = l_1 + l_2. \quad (10.9.6)$$

The Voigt profile is given by equation 10.5.14:

$$V(x) = \frac{l}{g} \sqrt{\frac{\ln 2}{\pi^2}} \int_{-\infty}^{\infty} \frac{\exp(-[(\xi - x)^2 \ln 2] / g^2)}{\xi^2 + l^2} d\xi. \quad (10.A.15)$$

For short, I am going to write the ratio l/g as a . The relation between this ratio and the gaussian fraction k_G is $a = (1 - k_G)/k_G$, $k_G = 1/(1 + a)$. In the above equation, $x = \lambda - \lambda_0$, and I am going to choose a wavelength scale such that $g = 1$; in other words wavelength interval is to be expressed in units of g . Thus I shall write the equation as

$$V(x) = a \sqrt{\frac{\ln 2}{\pi^3}} \int_{-\infty}^{\infty} \frac{\exp(-(\xi - x)^2 \ln 2)}{\xi^2 + a^2} d\xi. \quad (10.A.16)$$

The integration has to be done numerically, and there is a problem in that the limits are infinite. We can deal with this with the change of variable $\xi = a \tan \theta$, when the integral becomes

$$V(x) = \sqrt{\frac{\ln 2}{\pi^3}} \int_{-\pi/2}^{\pi/2} \exp[-(a \tan \theta - x)^2 \ln 2] d\theta. \quad (10.A.17)$$

The limits are now finite, and the integrand is zero at each limit. Computing time will be much diminished by the further substitution $t = \tan \frac{1}{2} \theta$, when the expression becomes

$$V(x) = \sqrt{\frac{\ln 16}{\pi^3}} \int_{-1}^1 \frac{\exp[-\{2at/(1 - t^2) - x\}^2 \ln 2]}{1 + t^2} dt \quad (10.A.18)$$

This is faster than the previous expression because one avoids having to compute the trigonometric function \tan . It could also have been arrived at in one step by means of the substitution $\xi = \frac{2at}{1 - t^2}$, though such a substitution may not have been immediately obvious. Like the previous expression, the limits are finite, and the integrand is zero at each end. Numerical integration would now seem to be straightforward, although there may yet be some difficulty. Suppose one is integrating, for example, by Simpson's method. A question might arise as to how many intervals should be used. Simpson's method is often very effective with a remarkably small number of intervals, but, for high precision, one may nevertheless wish to use a fine interval. If one uses a fine interval, however, as one approaches either limit, the expression $t/(1 - t^2)$ becomes very large, and, even though the integrand then becomes small, a computer may be reluctant to return a value for the exp function, and it may deliver an error message. The best way to deal with that difficulty is to set the integrand equal to zero whenever the absolute value of the argument of the exp function exceeds some value below which the computer is happy.

One might be tempted to reduce the amount of computation by saying that $\int_{-1}^1 = 2 \int_0^1$, but this is not correct, for, while the Voigt profile is symmetric about $x = 1$, the integrand is not symmetric about $t = 0$. However, if

$$V(x) = \int_{-1}^1, \text{ and } V_1(x) = \int_{-1}^0, \text{ and } V_2(x) = \int_0^1, \quad (10.9.7)$$

it is true that $V(x) = V_1(x) + V_2(x)$ and $V_1(x) = V_2(-x)$, and hence that $V(x) = V_1(x) + V_1(-x)$ and this can be used to economise to a small extent. It is still necessary to calculate $V_1(x)$ for all values of x , both positive and negative, but the number of integration steps for each point can be halved.

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10.10: APPENDIX B- Radiation Damping as Functions of Angular Frequency, Frequency and Wavelength

It occurred to me while preparing this Chapter as well as the preceding and following ones, that sometimes I have been using angular frequency as argument, sometimes frequency, and sometimes wavelength. In this Appendix, I bring together the salient formulas for radiation damping in terms of $\Delta\omega = \omega - \omega_0$, $\Delta\nu = \nu - \nu_0$ and $\Delta\lambda = \lambda - \lambda_0$. I reproduce equation 10.2.11 for the absorption coefficient for a set of forced, damped oscillators, except that I replace n , the number per unit volume of oscillators with $n_1 f_{12}$, the effective number of atoms per unit volume in the lower level of a line, and I replace the classical damping constant γ with Γ , which may include a pressure broadening component.

$$\alpha = \frac{n_1 f_{12} \Gamma e^2 \omega^2}{m \epsilon_0 c [(\omega^2 - \omega_0^2)^2 + \Gamma^2 \omega^2]} \quad \text{m}^{-1}. \quad (10.B.1)$$

You should check that the dimensions of this expression are L^{-1} , which is appropriate for linear absorption coefficient. You may note that $[e^2/\epsilon_0] \equiv \text{ML}^3\text{T}^{-2}$ and $[\Gamma] \equiv \text{T}^{-1}$. Indeed check the dimensions of all expressions that follow, at each stage.

We can write $\omega^2 - \omega_0^2 = (\omega - \omega_0)(\omega + \omega_0) = \Delta\omega(2\omega_0 + \Delta\omega)$, and the equation becomes

$$\alpha = \frac{n_1 f_{12} \Gamma e^2 (\omega_0 + \Delta\omega)^2}{m \epsilon_0 c [(\Delta\omega)^2 (2\omega_0 + \Delta\omega)^2 + \Gamma^2 (\omega_0 + \Delta\omega)^2]} \quad \text{m}^{-1}. \quad (10.B.2)$$

Now I think it will be owned that the width of a spectrum line is very, very much smaller than its actual wavelength, except perhaps for extremely Stark-broadened hydrogen lines, so that, in the immediate vicinity of a line, $\Delta\omega$ can be neglected compared with ω_0 ; and a very long way from the line, where this might not be so, the expression is close to zero anyway. (Note that you can neglect $\Delta\omega$ *only with respect to* ω ; you cannot just put $\Delta\omega = 0$ where it lies alone in the denominator!) In any case, I have no compunction at all in making the approximation

$$\alpha(\Delta\omega) = \frac{n_1 f_{12} \Gamma e^2}{4m \epsilon_0 c [(\Delta\omega)^2 + (\frac{1}{2}\Gamma)^2]} \quad \text{m}^{-1}. \quad (10.B.3)$$

The maximum of the $\alpha(\Delta\omega)$ curve is

$$\alpha(0) = \frac{e^2 n_1 f_{12}}{m \epsilon_0 c \Gamma} \quad \text{m}^{-1}. \quad (10.B.4)$$

The optical thickness at the line centre (whether or not the line is optically thin) is

$$\tau(0) = \frac{e^2 \mathcal{N}_1 f_{12}}{m \epsilon_0 c \Gamma}. \quad (10.B.5)$$

\mathcal{N}_1 is the number of atoms in level 1 per unit area in the line of sight, whereas n_1 is the number per unit volume.

The HWHM of $\alpha(\Delta\omega)$ curve is

$$\text{HWHM} = \frac{1}{2}\Gamma \quad \text{rad s}^{-1}. \quad (10.B.6)$$

The area under the $\alpha(\Delta\omega)$ curve is

$$\text{Area} = \frac{\pi e^2 n_1 f_{12}}{2m \epsilon_0 c} \quad \text{m}^{-1} \text{rad s}^{-1}. \quad (10.B.7)$$

As expected, the area does not depend upon Γ .

To express the absorption coefficient as a function of *frequency*, we note that $\omega = 2\pi\nu$, and we obtain

$$\alpha(\Delta\nu) = \frac{n_1 f_{12} \Gamma e^2}{16\pi^2 m \epsilon_0 c [(\Delta\nu)^2 + (\frac{\Gamma}{4\pi})^2]} \quad \text{m}^{-1}. \quad (10.B.8)$$

The maximum of this is (of course) the same as equation 10.B.4.

The HWHM of the $\alpha(\Delta\nu)$ curve is

$$\text{HWHM} = \Gamma / (4\pi) \quad \text{s}^{-1}. \quad (10.B.9)$$

The area under the $\alpha(\Delta\nu)$ curve is

$$\text{Area} = \frac{e^2 n_1 f_{12}}{4m\varepsilon_0 c} \quad \text{m}^{-1} \text{s}^{-1}. \quad (10.B.10)$$

$$\alpha = \frac{n_1 f_{12} \Gamma e^2}{m\varepsilon_0 c} \cdot \left(\frac{\lambda_0^4}{4\pi^2 c^2 (\lambda_0^2 - \lambda^2)^2 + \lambda^2 \lambda_0^4 \Gamma^2} \right) \quad \text{m}^{-1}. \quad (10.B.11)$$

In a manner similar to our procedure following equation 10.B.12, we write $\lambda_0^2 - \lambda^2 = (\lambda_0 - \lambda)(\lambda_0 + \lambda)$, and $\lambda = \lambda_0 + \Delta\lambda$, and neglect $\Delta\lambda$ with respect to λ_0 , and we obtain:

$$\alpha(\Delta\lambda) = \frac{n_1 f_{12} \Gamma e^2}{16\pi^2 m\varepsilon_0 c^3} \cdot \left(\frac{\lambda_0^4}{(\Delta\lambda)^2 + \frac{\lambda_0^4 \Gamma^2}{16\pi^2 c^2}} \right) \quad \text{m}^{-1}. \quad (10.B.12)$$

The maximum of this is (of course) the same as equation 10.B.4. (Verifying this will serve as a check on the algebra.)

The HWHM of the $\alpha(\Delta\lambda)$ curve is

$$\text{HWHM} = \frac{\lambda_0^2 \Gamma}{4\pi c} \quad \text{m}. \quad (10.B.13)$$

The area under the $\alpha(\Delta\lambda)$ curve is

$$\text{Area} = \frac{\lambda_0^2 e^2 n_1 f_{12}}{4m\varepsilon_0 c^2}. \quad (10.B.14)$$

Did I forget to write down the units after this equation?

These results for α might be useful in tabular form. For τ , replace n_1 by N_1 .

	$\Delta\omega$	$\Delta\nu$	$\Delta\lambda$
	$\frac{\Gamma e^2 n_1 f_{12}}{4m\varepsilon_0 c [(\Delta\omega)^2 + (\frac{1}{2}\Gamma)^2]}$	$\frac{\Gamma e^2 n_1 f_{12}}{16\pi^2 m\varepsilon_0 c [(\Delta\nu)^2 + (\frac{\Gamma}{4\pi})^2]}$	$\frac{\Gamma e^2 \lambda_0^4 n_1 f_{12}}{16\pi^2 m\varepsilon_0 c^3 [(\Delta\lambda)^2 + \frac{\lambda_0^4 \Gamma^2}{16\pi^2 c^2}]}$
Height	$\frac{e^2 n_1 f_{12}}{m\varepsilon_0 c \Gamma}$	$\frac{e^2 n_1 f_{12}}{m\varepsilon_0 c \Gamma}$	$\frac{e^2 n_1 f_{12}}{m\varepsilon_0 c \Gamma}$
Area	$\frac{\pi e^2 n_1 f_{12}}{2m\varepsilon_0 c}$	$\frac{e^2 n_1 f_{12}}{4m\varepsilon_0 c}$	$\frac{\lambda_0^2 e^2 n_1 f_{12}}{4m\varepsilon_0 c^2}$
HWMH	$\frac{1}{2} \Gamma$	$\Gamma / (4\pi)$	$\frac{\lambda_0^2 \Gamma}{4\pi c}$

(10.10.1)

It is to be noted that if the radiation damping profile is thermally broadened, the height of the absorption coefficient curve diminishes, while the area is unaltered provided that the line is optically thin. The optically thick situation is dealt with in the following chapter. It might also be useful to note that a gaussian profile of the form

$$\alpha(\Delta\lambda) = \alpha(0) \exp \left(-\frac{c^2 (\Delta\lambda)}{V_m^2 \lambda_0^2} \right) \quad (10.B.15)$$

has an area of $\frac{\lambda_0^2 e^2 n_1 f_{12}}{4m\varepsilon_0 c^2}$ if

$$\alpha(0) = \frac{\lambda_0 e^2 n_1 f_{12}}{4\sqrt{\pi} m\varepsilon_0 c V_m}. \quad (10.B.16)$$

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10.11: APPENDIX C- Optical Thinness, Homogeneity and Thermodynamic Equilibrium

It has also occurred to me while preparing these chapters that some of the equations are valid only under certain conditions, such as that the gas is *optically thin*, or is *homogeneous* or is in *thermodynamic equilibrium*, or some combination of these, or none of them. It would be tedious to spell out all of the conditions after each equation. Yet it is important to know under what conditions each is valid. In this Appendix I try to give some guidance. For example, most of the equations in this Chapter deal with line profiles in an optically thin gas, whereas in the next Chapter the gas is no longer optically thin. In the end, however, the only way of being sure of what conditions apply to each equation is to understand the basic physics behind each rather than attempting to memorize which conditions apply to which equations.

The linear absorption coefficient α at a point within a gas is proportional to the local number density n_1 of absorbers. (The subscript 1 refers to “atoms in the lower level of the line concerned”.) The optical thickness of a slab of gas of thickness D is related to the absorption coefficient (which may or may not vary throughout the slab) by $\tau = \int_0^D \alpha(x) dx$. This is so whether or not the gas is optically thin or whether it is homogeneous. Likewise, the column density N_1 of absorbers is related to the number density by $N_1 = \int_0^D n_1(x) dx$. If the gas is homogeneous in the sense that n_1 is not a function of x , and consequently α is not a function of x either, then these equations become simply $\tau = \alpha D$ and $N_1 = n_1 D$, and this is so whether or not the gas is optically thin.

Whether optically thin or thick, and whether homogeneous or not, the optical thickness is proportional to the column density N , just as the absorption coefficient is proportional to n_1 .

If a layer of gas of thickness D is not homogeneous, the optical thickness is related to the absorption coefficient and the thickness of the gas by $\tau = \int_0^D \alpha(x) dx$. If the gas is homogeneous so that α is independent of x , then the relation is merely $\tau = \alpha D$. Neither of these equations requires the gas to be optically thin. That is, they are valid whether the gas is optically thin or thick. The absorption coefficient at a point within the gas is proportional to the local density (number of absorbers per unit volume there.) The optical thickness is proportional to the column density of absorbers along the line of sight, whether or not the gas is optically thin and whether or not it is homogeneous.

However, the *equivalent width* and *central depth* of an absorption line, or the *intensity* or *radiance*, or *central intensity* or *radiance per unit wavelength interval* of an emission line, are proportional to the column density of atoms only if the gas is optically thin. Indeed this simple proportionality can serve as a good definition of what is meant by being optically thin.

The equivalent width of an absorption line is given by $W = \int [1 - \exp\{-\tau(\lambda)\}] d\lambda$. If the gas is homogeneous, this becomes $W = \int [1 - \exp\{-D\alpha(\lambda)\}] d\lambda$. If, in addition, the gas is optically thin at all wavelengths within the line, this becomes (by Maclaurin expansion), merely $W = D \int \alpha(\lambda) d\lambda$. Note that, if λ and D are expressed in m and if α is expressed in m^{-1} , the equivalent width will be in m. If, however, you choose to express wavelengths in angstroms and the thickness of a cloud in parsecs, that is your problem, and you are on your own.

Any equations in which we have gone from n , the total number of atoms per unit volume in all levels to n_1 via Boltzmann's equation, implies an assumption of thermodynamic equilibrium. An example would be going from equation 9.2.4 (which does not imply thermodynamic equilibrium) to equations 9.2.6-10 (which do imply thermodynamic equilibrium). If a gas is truly in thermodynamic equilibrium, this implies that the gas will be at a single, homogenous temperature – otherwise there will be heat flow and no equilibrium. It is doubtful if anything in the Universe is truly in thermodynamical equilibrium in the very strictest use of the term. However, even in an atmosphere in which the temperature is different from point to point, we may still have *local* thermodynamic equilibrium (LTE), in the sense that, at any point, it is all right to calculate the distribution of atoms among their energy levels by Boltzmann's equation, or the degree of ionization by Saha's equation, or the atomic speeds by the Maxwell-Boltzmann equation, or the radiation energy density by Planck's equation – and you may even be able to use the same temperature for each. This may be all right within a small volume of an atmosphere; only when considered over large ranges of space and time will it be evident that the atmosphere is not in true thermodynamic equilibrium.

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CHAPTER OVERVIEW

11: Curve of Growth

It will be part of the aim of this chapter to predict the curve of growth for gaussian and lorentzian profiles, and also for Voigt profile for different Gauss/Lorentz ratios. The curve of growth (die Wachstumskurve) is a graph showing how the equivalent width of an absorption line, or the radiance of an emission line, increases with the number of atoms producing the line.

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11.1: Introduction to Curve of Growth

The *curve of growth* (**die Wachstumskurve**) is a graph showing how the equivalent width of an absorption line, or the radiance of an emission line, increases with the number of atoms producing the line.

In an *optically thin* gas, the equivalent width of an absorption line, or the radiance of an emission line, is linearly proportional to the number of atoms in the initial level of the line. Let us imagine, for example, that we have a continuous source of radiation, and, in front of it, we have a homogeneous, isothermal slab of gas, and that there are \mathcal{N}_1 atoms per unit area in the line of sight in the lower level of some absorption line. We could double \mathcal{N}_1 either by doubling the thickness of the slab, or by doubling the density of the gas within the slab. Either way, if doubling the number of atoms per unit area (the column density) in level 1 results in a doubling of the equivalent width of the line, then the gas is said to be optically thin. More precisely, the *line* is optically thin – for there may well be other lines in the spectrum which are not optically thin. I suppose one could say that a gas is optically thin at the wavelength of a particular line if you can see all of the atoms – even those at the back. In Chapter 9, where we were developing formulas for the equivalent width of a line, and in Chapter 10, where we were studying line profiles, we were limiting our attention to optically thin lines. We shall depart from this assumption in this Chapter, although we shall still assume that our slab of gas is homogeneous (same temperature and pressure throughout) and in thermodynamic equilibrium.

We can see, by referring to figure XI.1, why it is that the equivalent width of an absorption line cannot continue to increase indefinitely and linearly as the column density increases. The figure represents the profile of an absorption line. (Strictly speaking, the ordinate should read “radiance per unit wavelength interval”, rather than “intensity”.) Profile *a* is a weak line (actually a gaussian profile) that is optically thin. In profile *b*, we have greatly increased the column density \mathcal{N}_1 , and we see that the intensity at the centre of the line is almost zero. Hardly any of the background light from the continuous source is getting through. At this wavelength, the background is black. Increasing the column density will make no difference at all to the central intensity, and hardly any change in the equivalent width. Thus a graph of equivalent width versus column density will no longer be a linearly increasing function, but will be almost horizontal.

But it will not remain horizontal. As we see in profile *c*, when yet further atoms have been added, although the central depth does not and cannot become any deeper, the wings of the profile start to add to the equivalent width, so that the equivalent width starts to increase again, although rather more slowly than during the optically thin stage. Thus we might expect three stages in the curve of growth. At first, the equivalent width increases linearly with the column density of absorbers. Then there will be a stage in which the equivalent width is scarcely increasing. Finally, there will be a third stage in which the equivalent width increases, but not as rapidly as in the optically thin case.

It will also be noticed that, as soon as the profile (which was gaussian when it was optically thin) ceases to be optically thin, the profile becomes distorted and is no longer the same as it was in the optically thin region.

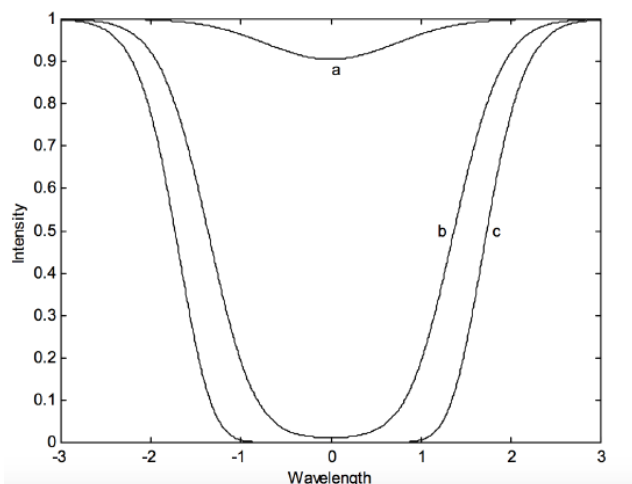


FIGURE XI.1

From our qualitative description of the curve of growth, it will be evident that the form of the curve of growth will depend on the form of the original line profile. For example, it will be recalled that the gaussian profile is “all core and no wings”, whereas the lorentzian profile is “narrow core and extensive wings”. Thus the onset of the third stage of the curve of growth will occur sooner

for a lorentzian profile than for a gaussian profile. We shall find, as we proceed, that for a pure gaussian profile, the third stage of the classic curve of growth is scarcely evident, whereas for a pure lorentzian profile, the second stage is scarcely evident. The classic three-stage curve of growth is exhibited for a Voigt profile in which the gaussian and lorentzian contributions are comparable.

It will be part of the aim of this chapter to predict the curve of growth for gaussian and lorentzian profiles, and also for Voigt profile for different Gauss/Lorentz ratios.

This by itself will be an interesting intellectual exercise – but can it be taken further? Yes it can. Imagine a situation in which we have a spectrum in which the resolution is not sufficient to measure the profiles of individual lines with any great precision. No great imagination is in fact needed, for this will usually be the case with a stellar spectrum. If we can somehow construct a curve of growth, we might be able to deduce the line profiles, or at least the FWHm (full width at half minimum) of the gaussian component (which will tell us the kinetic temperature) and of the lorentzian component (which will tell us the mean time between collisions and hence the pressure). We cannot, of course, change the column density of a stellar atmosphere. However, some lines of a given element will be weak (because they have a high excitation potential, or a small oscillator strength, or both) and others will be strong (because they have a low excitation potential, or a large oscillator strength, or both), and perhaps a curve of growth can be constructed from many lines of a given atom, and so we will be able to deduce the temperature and the pressure, even though we cannot resolve the details of individual line profiles.

So far, I have discussed the curve of growth for an absorption line. What about an emission line? We understand that the intensity of the centre of an absorption line cannot drop below the “floor” corresponding to zero intensity. But is there a “ceiling” that will stop the growth of the centre of an emission line, or can we go on increasing the intensity of an emission line indefinitely? The answer is that, for a gas in thermodynamic equilibrium, there is indeed a “ceiling”, and that occurs when the radiance per unit wavelength interval of the centre of the emission line reaches the ordinate of the Planck blackbody curve having a blackbody temperature equal to the kinetic and excitation temperature of the gas. When the line centre is completely optically thick, it radiates like a black body at that wavelength. Adding more atoms to the column density will not increase the central intensity. What happens is that photons emitted by atoms near the back of the slab of gas are re-absorbed as they struggle forward towards the front.

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11.2: A Review of Some Terms

Before continuing, a review of some terms such as *absorption coefficient*, *absorptance*, *central depth* and *optical thickness* may be of some use.

Imagine a thin slice of absorbing gas of thickness δx . At one side of the slice, suppose that the specific intensity (radiance) per unit wavelength interval wavelength λ is $I_\lambda(\lambda)$ and that, after passage of the radiation through the slice, the specific intensity is now only $I_\lambda + \delta I_\lambda$. (δI_λ is negative.) The fractional decrease in the specific intensity is proportional to δx :

$$-\frac{\delta I_\lambda(\lambda)}{I_\lambda(\lambda)} = \alpha(\lambda)\delta x. \quad (11.2.1)$$

$\alpha(\lambda)$ is the *linear absorption coefficient*, and is of dimension L^{-1} . Now let imagine that, rather than an infinitesimally thin slice of gas, we have a slab of gas of finite thickness D and that it is sitting in front of a continuum source of specific intensity (radiance) per unit wavelength interval $I_\lambda(c)$, where “c” indicates “continuum”. The radiance after passage through the slice is given by integrating Equation 11.2.1:

$$I_\lambda(\lambda) = I_\lambda(c) \exp \left[- \int_0^D \alpha(\lambda) dx \right], \quad (11.2.2)$$

The quantity

$$\tau(\lambda) = \int_0^D \alpha(\lambda) dx \quad (11.2.3)$$

is the *optical thickness* of the slab. It is dimensionless. If the slab of gas is *homogeneous*, in the sense that $\alpha(\lambda)$ is the same throughout the slab and is not a function of x , this becomes simply

$$\tau(\lambda) = D\alpha(\lambda). \quad (11.2.4)$$

Let us suppose that, after passage through the slab of gas, the specific intensity (radiance) of the gas at wavelength λ , which was initially $I_\lambda(c)$, is now $I_\lambda(\lambda)$. The fraction of the radiance that has been absorbed is the *absorptance* at wavelength λ , $a(\lambda)$:

$$a(\lambda) = \frac{I_\lambda(c) - I_\lambda(\lambda)}{I_\lambda(c)} \quad (11.2.5)$$

It is dimensionless. The relation between absorptance and optical thickness is evidently

$$a(\lambda) = 1 - e^{-\tau(\lambda)}, \quad \tau(\lambda) = -\ln(1 - a(\lambda)). \quad (11.2.6 \text{ a,b})$$

For a gas of very small optical thickness, in which only a tiny fraction of the radiation has been absorbed (which will not in general be the case in this chapter), Maclaurin expansion of either of these Equations will show that

$$a(\lambda) \approx \tau(\lambda). \quad (11.2.7)$$

If, in addition, the slab of gas is homogeneous,

$$a(\lambda) \approx D\alpha(\lambda). \quad (11.2.8)$$

The *absorptance at the line centre* is

$$a(\lambda_0) = \frac{I_\lambda(c) - I_\lambda(\lambda_0)}{I_\lambda(c)}, \quad (11.2.9)$$

and we have also called this, in Chapter 10, the *central depth* d .

The *absorption coefficient* of a gas at the wavelength of an absorption line is proportional to n_1 , the number of atoms per unit volume in the initial (lower) level of the transition. This is so whether the slab of gas is optically thin or not; we are concerned here with the absorption coefficient and the number density *at a point within the gas*, not with the slab as a whole. The optical thickness of a slab of gas is proportional to \mathcal{N}_1 , the number of atoms per unit area in the line of sight (column density) in the initial level. This is so whether or not the slab is homogeneous. In the sense in which the words *intensive* and *extensive* are used in thermodynamics, it could be said that absorption coefficient is an intensive quantity and optical thickness and absorptance are

extensive quantities. While the optical thickness is proportional to \mathcal{N}_1 , the radiance per unit wavelength interval and the equivalent width are not linearly proportional to \mathcal{N}_1 unless the gas is optically thin.

For the terms such as atomic and mass absorption coefficient, opacity, and the distinction between absorption, scattering and extinction, see Chapter 5.

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11.3: Theory of the Curve of Growth

Let us think again of our homogeneous slab of gas in front of a continuum source. Let $I_\lambda(c)$ be the radiance per unit wavelength interval of the continuum at wavelength λ . Let $\tau(x)$ be the optical thickness in the vicinity of a line and $x = \lambda - \lambda_0$. If the slab is of thickness D , the emergent radiance per unit wavelength as a function of wavelength will be

$$I_\lambda(x) = I_\lambda(c) \exp[-\tau(x)]. \quad (11.3.1)$$

The equivalent width W is given by

$$WI_\lambda(c) = \int_{-\infty}^{\infty} (I_\lambda(c) - I_\lambda(x)) dx, \quad (11.3.2)$$

or, by making use of Equation 11.3.1,

$$W = \int_{-\infty}^{\infty} [1 - \exp\{-\tau(x)\}] dx. \quad (11.3.3)$$

If the line is symmetric, this may be evaluated as

$$W = 2 \int_0^{\infty} [1 - \exp\{-\tau(x)\}] dx. \quad (11.3.4)$$

In former days, gallant efforts were made to find, using various approximations in the different regimes of the curve of growth, algebraic expressions for evaluating this integral. The availability of modern computers enables us to carry out the integration numerically.

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11.4: Curve of Growth for Gaussian Profiles

By “gaussian profile” in the title of this section, I mean profiles that are gaussian in the optically-thin case; as soon as there are departures from optical thinness, there are also departures from the gaussian profile. Alternatively, the *absorption coefficient* and the *optical depth* are gaussian; the *absorptance* is not.

For an optically-thin thermally-broadened line, the optical thickness as a function of wavelength is given by

$$\tau(x) = \tau(0) \exp\left(-\frac{x^2 \ln 2}{g^2}\right), \quad (11.4.1)$$

where the HWHM is

$$g = \frac{V_m \lambda_0 \sqrt{\ln 2}}{c}. \quad (11.4.2)$$

Here V_m is the modal speed. (See Chapter 10 for details.) The line profiles, as calculated from equations 11.3.4 and 11.4.1, are shown in figure XI.2 for the following values of the optical thickness at the line centre: $\tau(0) = \frac{1}{16}, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}, 1, 2, 4, 8$.

On combining equations 11.3.4 and 11.4.1 and 11.4.2 we obtain the following expression for the equivalent width:

$$W = 2 \int_0^\infty \left(1 - \exp\left\{-\tau(0) e^{-x^2 \ln 2 / g^2}\right\}\right) dx, \quad (11.4.3)$$

or

$$W = \frac{2V_m \lambda_0}{c} \int_0^\infty \left(1 - \exp\left\{-\tau(0) e^{-\Delta^2}\right\}\right) d\Delta, \quad (11.4.4)$$

where

$$\Delta = \frac{x \sqrt{\ln 2}}{g} = \frac{cx}{V_m \lambda_0}. \quad (11.4.5)$$

The half-width at half maximum (HWHM) of the expression 11.4.1 for the optical thickness corresponds to $\Delta = \sqrt{\ln 2} = 0.8326$. For the purposes of practical numerical integration of Equation 11.4.4, I shall integrate from $\Delta = -5$ to $+5$ that is to say from ± 6 times the HWHM. One can appreciate from figure XI.2 that going outside these limits will not contribute significantly to the equivalent width. I shall calculate the equivalent width for central optical depths ranging from $1/20 (\log \tau(0) = -1.3)$ to $10^5 (\log \tau(0) = 5.0)$

What we have in figure XI.3 is a curve of growth for thermally broadened lines (or lines that, in the optically thin limit, have a gaussian profile, which could include a thermal and a microturbulent component). I have plotted this from $\log \tau(0) = -1.3$ to $+5.0$; that is $\tau(0) = 0.05$ to 10^5 .

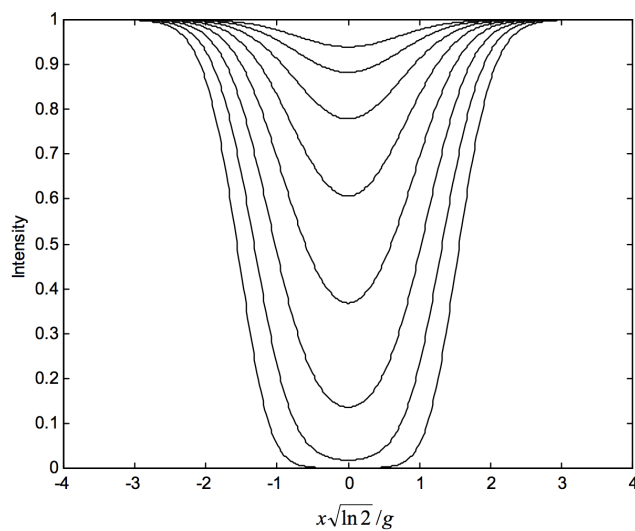


FIGURE XI.2

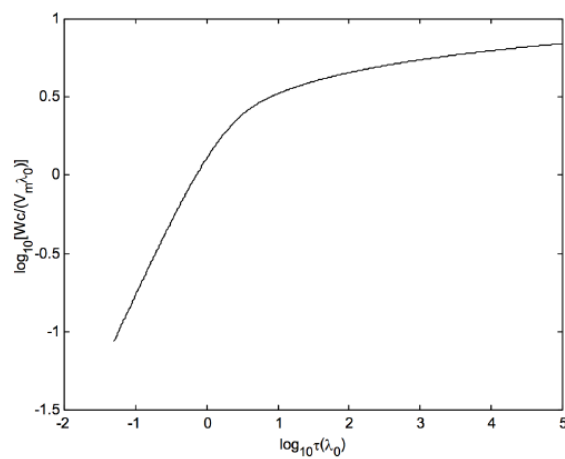


FIGURE XI.3

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11.5: Curve of Growth for Lorentzian Profiles

The optical depth of a line broadened by radiation damping is given, as a function of wavelength, by

$$\tau(x) = \tau(0) \frac{l^2}{x^2 + l^2}, \quad (11.5.1)$$

where the HWHM is

$$l = \frac{\Gamma \lambda_0^2}{4\pi c} \quad (11.5.2)$$

and the optical thickness at the line center is

$$\tau(0) = \frac{e^2 \mathcal{N}_1 f_{12}}{m \epsilon_0 c \Gamma}. \quad (11.5.3)$$

Here $x = \lambda - \lambda_0$, and the damping constant Γ may include a contribution from pressure broadening. As in Section 11.4, in figure XI.4 I draw line profiles for optical thicknesses at the line center $\tau(0) = \frac{1}{16}, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}, 1, 2, 4, 8$.

We see that the wings continue to add to the equivalent width as soon as, and indeed before, the central depth has reached unity. On combining equations 11.3.4, 11.5.1, 2 and 3, we obtain the following expression for the equivalent width:

$$W = \frac{\Gamma \lambda_0^2}{2\pi c} \int_0^\infty \left(1 - \exp \left\{ -\frac{\tau(0)}{y^2 + 1} \right\} \right) dy, \quad (11.5.4)$$

in which $y = x/l$ - i.e. distance from the line center in units of the HWHM.

If we now substitute $y = \tan \theta$, the expression for the equivalent width becomes

$$W = \frac{\Gamma \lambda_0^2}{2\pi c} \int_0^{\pi/2} \frac{1 - \exp[-\tau(0) \cos^2 \theta]}{\cos^2 \theta} d\theta. \quad (11.5.5)$$

Now that we have a finite upper limit, the expression can be integrated numerically without artificial and unjustified truncation. As described in the Appendix to Chapter 10, calculation of the trigonometric function \cos can be avoided, and hence the integration much speeded up, by the substitution of $t = \tan(\frac{1}{2}\theta)$. Although the denominator of the integrand is obviously zero at the upper limit, so is the numerator, and the value of the integrand at the upper limit is finite and equal to $\tau(0)$. Figure XI.5 shows the equivalent width, in units of $\frac{\Gamma \lambda_0^2}{2\pi c}$ as a function of $\tau(0)$.

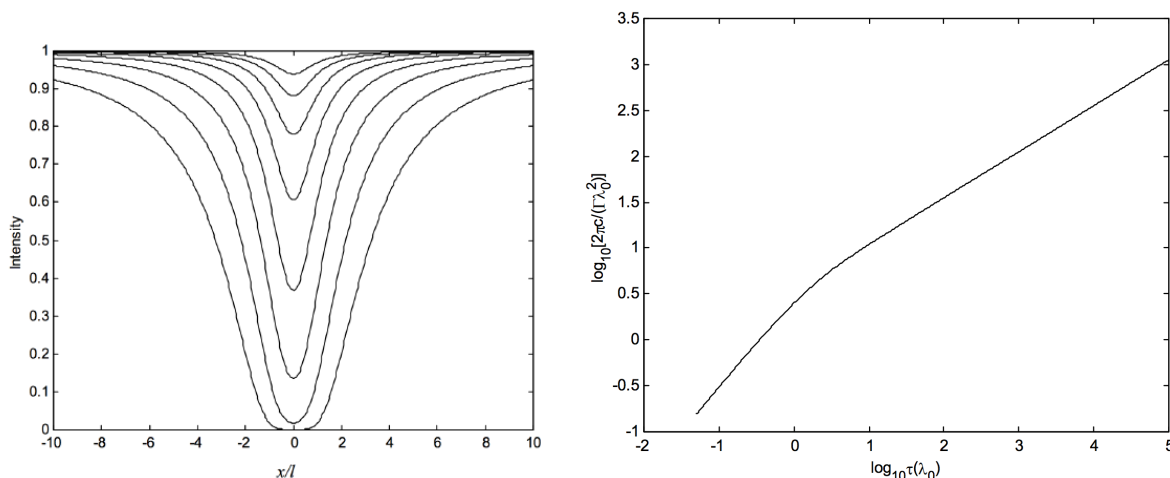


FIGURE XI.4 FIGURE XI.5

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11.6: Curve of Growth for Voigt Profiles

Our next task is to construct curves of growth for Voigt profiles for different values of the ratio of the lorentzian and gaussian HWHMs, l/g , which is

$$\frac{l}{g} = \frac{\Gamma \lambda_0}{4\pi V_m \sqrt{\ln 2}} = \frac{\Gamma \lambda_0}{V_m \pi \sqrt{\ln 65536}} = \frac{\Gamma \lambda_0}{34.841 V_m}, \quad (11.6.1)$$

or, better, for different values of the gaussian ratio $k_G = \frac{g}{l+g}$. These should look intermediate in appearance between figures XI.3 and 5.

The expression for the equivalent width in wavelength units is given by Equation 11.3.4:

$$W = 2 \int_0^\infty [1 - \exp\{-\tau(x)\}] dx. \quad (11.3.4)$$

combined with Equation 10.5.20

$$\tau(x) = Cl\tau(0) \int_{-\infty}^\infty \frac{\exp[-(\xi-x)^2 \ln 2/g^2]}{\xi^2 + l^2} d\xi. \quad (10.5.20)$$

That is:

$$W = 2 \int_0^\infty \left(1 - \exp \left\{ -Cl\tau(0) \int_{-\infty}^\infty \frac{\exp[-(\xi-x)^2 \ln 2/g^2]}{\xi^2 + l^2} d\xi \right\} \right) dx. \quad (11.6.2)$$

Here

- $x = \lambda - \lambda_0$, l is the Lorentzian HWHM $= \lambda_0^2 \Gamma / (4\pi c)$ (where Γ may include a pressure-broadening contribution),
- g is the gaussian HWHM $= V_m \lambda_0 \sqrt{\ln 2} / c$ (where V_m may include a microturbulence contribution), and
- W is the equivalent width, all of dimension L .

The symbol ξ , also of dimension L , is a dummy variable, which disappears after the definite integration. $\tau(0)$ is the optical thickness at the line centre. C is a dimensionless number given by Equation 10.5.23 and tabulated as a function of gaussian fraction in Chapter 10. The reader is urged to check the dimensions of Equation 11.6.2 carefully. The integration of Equation 11.6.2 is discussed in Appendix A.

Our aim is to calculate the equivalent width as a function of $\tau(0)$ for different values of the gaussian fraction $k_G = g/(l+g)$. What we find is as follows. Let $W' = W\sqrt{\ln 2}/g$; that is, W' is the equivalent width *expressed in units of* $g/\sqrt{\ln 2}$. For $\tau(0)$ less than about 5, where the wings contribute relatively little to the equivalent width, we find that W' is almost independent of the gaussian fraction. The difference in behaviour of the curve of growth for different profiles appears only for large values of $\tau(0)$, when the wings assume a larger role. However, for any profile which is less gaussian than about k_G equal to about 0.9, the behaviour of the curve of growth (for $\tau(0) > 5$) mimics that for a lorentzian profile. For that reason I have drawn curves of growth in figure XI.6 only for $k_G = 0.9, 0.99, 0.999$ and 1. This corresponds to $l/g = 0.1111, 0.0101, 0.0010$ and 0 or to $\Gamma \lambda_0 / V_m = 1.162, 0.1057, 0.0105$ and 0 respectively.

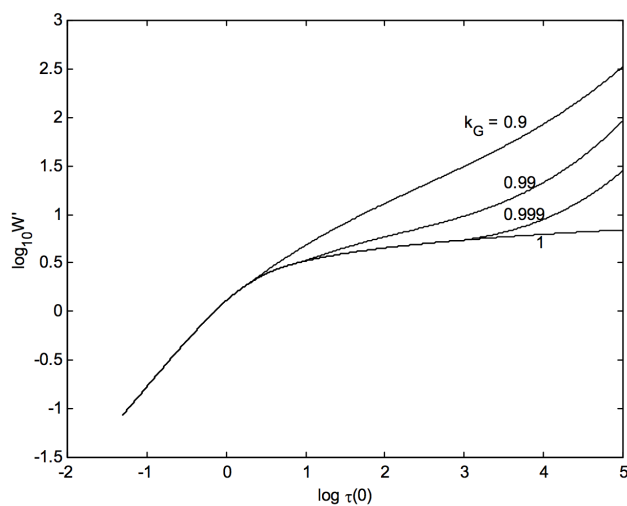


FIGURE XI.6

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11.7: Observational Curve of Growth

Equation 11.6.2 and figure XI.6 show how the equivalent width of a line will grow as the optical thickness is increased, which can be achieved either by increasing the geometrical thickness of the gas under study or by increasing the number density of the absorbers (atoms). Of course, if you are looking at the spectrum of a stellar atmosphere, you cannot do either of these things, but you might be able to construct a curve of growth by looking at many lines from the same element (such as an element from the iron group, which has lots of lines of a wide range of equivalent widths.) Then, by comparing the form of the observed curve of growth with one of the theoretical curves, you could deduce the gaussian and lorentzian HWHm, g and l , of your lines (and hence possibly the temperature and pressure) even if your resolution were not sufficient to determine the individual line profiles with any precision. You will notice the word “possibly” – because it has to be remembered that g includes both a thermal and a microturbulent component, and l includes both a radiation damping and pressure broadening component. Provided that the gas under study is homogeneous and of a uniform temperature throughout (I suppose this rules out a stellar atmosphere!) g should be the same for all lines of a given element. (The microturbulent component of g should be the same for all elements.) The radiation damping component of l will vary from line to line, but in practice, at least in the atmosphere of a main sequence star (but not necessarily of a giant, where the atmospheric pressure is much lower), the pressure broadening component of l will be much greater than the radiation damping component, and hence l will be the same for all lines of a given element. The theories of thermal, microturbulent, radiation damping and pressure broadening are all covered in Chapter 10.

It is all very well to say plot $\log W'$ versus $\log \tau(0)$ for many lines of an iron-group element, but we immediately discover that we don't know either. The dimensionless quantity W' is given by

$$W' = W \sqrt{\ln 2} / g, \quad (11.7.1)$$

and we don't know g – indeed one of our aims is to find it. The optical depth at the line centre is given by

$$\tau(0) = \frac{\mathcal{N}_1 f_{12} e^2}{m c \epsilon_0 \Gamma}, \quad (11.7.2)$$

and we don't know Γ – again, one of our aims is to find it. However, these equations can be written in the form

$$\log W' = \log W + \text{constant} \quad (11.7.3)$$

and

$$\log \tau(0) = \log \mathcal{N}_1 f_{12} + \text{constant}. \quad (11.7.4)$$

Also, from Boltzmann's equation (where applicable!), we have

$$\ln \mathcal{N}_1 = \ln(\mathcal{N}/u) - E_1/(kT) + \ln \varpi_1, \quad (11.7.5)$$

from which

$$\log \mathcal{N}_1 = \log \varpi_1 + C(E_1) \quad (11.7.6)$$

where the “constant” is a function of E_1 , the excitation energy of the lower level of the line. From this, we obtain

$$\log \tau(0) = \log \varpi f + C(E_1). \quad (11.7.7)$$

Thus, provided we take a set of lines all having the same lower excitation level (or at least the same lower term, provided that departures from LS -coupling are not so severe as to scatter the levels widely), we can construct a partial curve of growth by plotting $\log W$ versus $\log \varpi f$ for these lines. These will be displaced both vertically and horizontally from the theoretical curves of figure XI.6 by arbitrary amounts, which will not affect the shape of the curve.

We can then take another set of lines, having a different common lower excitation level (or term), and plot another partial curve of growth. It will be displaced horizontally (but not vertically) from the first fragment, and it must be slid horizontally until it meshes in with the first fragment. And so we continue, building up partial curves of growth from sets of lines with a common lower term, sliding them horizontally until they all mesh with each other in a single continuous curve, which we can then compare with the shapes of the theoretical curves to obtain g and l and hence the temperature and pressure.

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11.8: Interpreting an Optically Thick Profile

This chapter has been concerned with optically thick lines and with the curve of growth – and how one might recover the parameters g and l from the curve of growth even if the profiles of individual lines are not resolved. This section is written rather as an afterthought, albeit an important one, and it does not concern the curve of growth. It discusses how one might analyse the profile of a line that is well resolved, but is not optically thin. I use as an example a line that is thermally broadened and which, if optically thin, would have a gaussian profile. The optically thick line is no longer gaussian, but can one recover g (and hence T) from it? Just for a change, and because it is a while since we used the term “source function”, I’ll deal with an emission line.

As discussed in Section 5.7, the radiance of a slab of gas of source function S is given by

$$I_{\lambda}(x) = S \int_0^{\tau(x)} e^{-\tau} d\tau = S(1 - e^{-\tau(x)}). \quad (11.8.1)$$

Here, $x = \lambda - \lambda_0$. For a thermally-broadened line, this becomes

$$I_{\lambda}(x) = S [1 - \exp \{ -\tau(0) \exp(-x^2 \ln 2 / g^2) \}], \quad (11.8.2)$$

where $g = V_m \lambda_0 / \sqrt{\ln 2}$.

In figure XI.7, I draw two such profiles, in which the line strength of one is A times the *line strength* of the other. The lines, perhaps, belong to the same multiplet and the ratio of the line strengths is known. (I am here using the term line strength in the technical sense of Chapter 7.) Figure XI.7 was drawn with $A = 2$, but since the lines are not optically thin, neither the ratio of their areas nor the ratio of their heights is two.

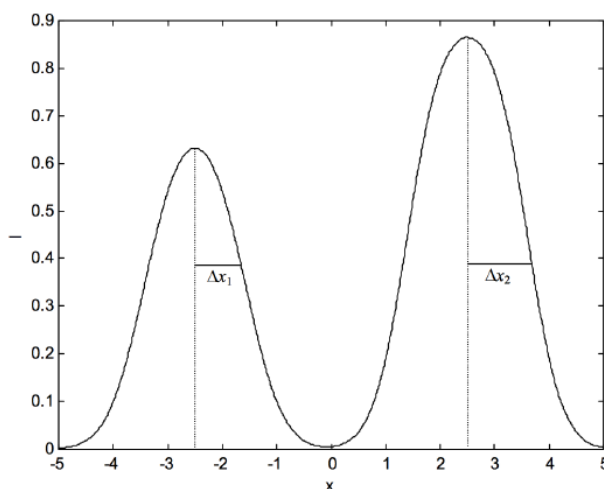


FIGURE XI.7

We can measure the half widths Δx_1 and Δx_2 of the two profiles *at the same height*.

Then:

$$S[1 - \exp \{ -\tau(0) \exp(-(\Delta x_1)^2 \ln 2 / g^2) \}] = S[1 - \exp \{ -A\tau(0) \exp(-(\Delta x_2)^2 \ln 2 / g^2) \}], \quad (11.8.3)$$

after which

$$\frac{(\Delta x_1) \ln 2}{g^2} = \frac{(\Delta x_2) \ln 2}{g^2} - \ln A, \quad (11.8.4)$$

and hence

$$g^2 = \frac{[(\Delta x_1)^2 - (\Delta x_2)^2]}{\ln A}. \quad (11.8.5)$$

The same technique can be used for lorentzian profiles.

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11.9: APPENDIX A- Evaluation of the Voigt Curve of Growth Integral

We wish to evaluate the equivalent width as given by equation 11.6.2:

$$W = 2 \int_0^\infty \left(1 - \exp \left\{ -Cl\tau(0) \int_{-\infty}^\infty \frac{\exp[-(\xi-x)^2 \ln 2/g^2]}{\xi^2 + l^2} d\xi \right\} \right) dx. \quad (11.A.1)$$

We slightly simplify it by introducing dimensionless variables W' , x' , ξ' and l' defined by $X' = \frac{Xc}{\lambda_0 V_m} = \frac{X\sqrt{\ln 2}}{g}$, where X is any of W , x , ξ or l . That is, we are expressing lengths in units of $g/\sqrt{\ln 2}$. Then:

$$W' = 2 \int_0^\infty \left(1 - \exp \left\{ -Cl'\tau(0) \int_{-\infty}^\infty \frac{\exp[-(\xi' - x')^2]}{\xi'^2 + l'^2} d\xi' \right\} \right) dx'. \quad (11.A.2)$$

We shall eventually want to evaluate the integral as a function of the gaussian ratio k_G , and we note that $l' = \left(\frac{1}{k_G} - 1 \right) \sqrt{\ln 2}$. Since ξ' is a dummy variable, we could in principle dispense with the prime as superfluous, but it is probably helpful to retain the prime. The limits of the inner integral can be made finite by means of a change of variable. The substitution $\xi' = l' \tan \theta$ will achieve this, but the introduction of a trigonometric function will increase the computing time. An alternative is $\xi' = \frac{2l't}{1-t^2}$, which looks clumsier but is rather faster. The equation becomes

$$W' = 2 \int_0^\infty \left(1 - \exp \left\{ -2C\tau(0) \int_{-1}^1 \frac{\exp[-(\frac{2l't}{1-t^2} - x')^2]}{1+t^2} dt \right\} \right) dx'. \quad (11.A.3)$$

This integral is not particularly easy, and I do not advise merely putting it into a prepackaged integration program without critical examination. (Indeed I never advocate that!) One is faced with the usual problems of numerical integration: What should be the step size and number of steps? And, in the case of the outer integral, how far should we take the upper limit? One way to determine the necessary number of intervals (and step size) is to try, say 100 intervals, and then try 1000, and see if it makes any difference. Similarly with determining the upper limit to the outer integration, try integrating to $x' = 5$, and then to 10, and see if it makes any difference. But this integral has some problems of its own.

Some insight into the problems can be obtained by looking at the behaviour of the inner integrand. This function, $\frac{\exp[-(\frac{2l't}{1-t^2} - x')^2]}{1+t^2}$, is shown as a function of t for four different values of x' in figure XI.A1. The value of l' for the figure is $1/(4\pi)$, which has no particular significance, since the figure is intended solely for illustrative purposes.

For $x' = 0$, the function is symmetric about $t = 0$, but not for other values of x' . For small values of x' , there is no particular difficulty with the integration, either by Simpson's rule or by seven-point integration (see my Web notes on Celestial Mechanics, Chapter 1).

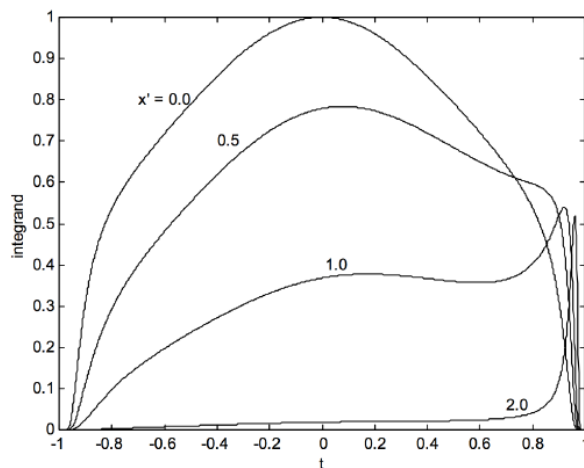


FIGURE XI.A1

However, for large x' , the integrand is close to zero for most of the range between $t = -1.0$ and 0.0 , but, close to $t = 1.0$, the integrand exhibits a sharp spike, becoming almost a delta-function for larger x' . A coarse interval for integration may miss the spike altogether, while a very fine interval will use massive amounts of computer time to no good purpose over most of the range of t . Fortunately, the area under the spike is progressively smaller and smaller for larger and larger x' but the nagging question still remains, when may one stop integrating? One useful, efficient and effective technique is to adjust the size of the interval for integration according to the slope of the function. A coarse interval is quite adequate while the graph is near-horizontal, but a much finer integration step kicks in as soon as the slope becomes large. This requires a certain amount of programming legerdemain, but is frequently resorted to in such situations.

The part of equation 11.A.2:

$$\exp \left\{ -Cl\tau(0) \int_{-\infty}^{\infty} \frac{\exp[-(\xi - x)^2 \ln 2 / g^2]}{\xi^2 + l^2} d\xi \right\} \quad (11.A.4)$$

represents the optically thick Voigt profile. This is shown for $l' = 1/(4\pi)$ for several $\tau(0)$ in figure XI.A.2. The value $l' = 1/(4\pi)$ has no particular significance; figure XI.A.2 was drawn solely for illustrative purposes.

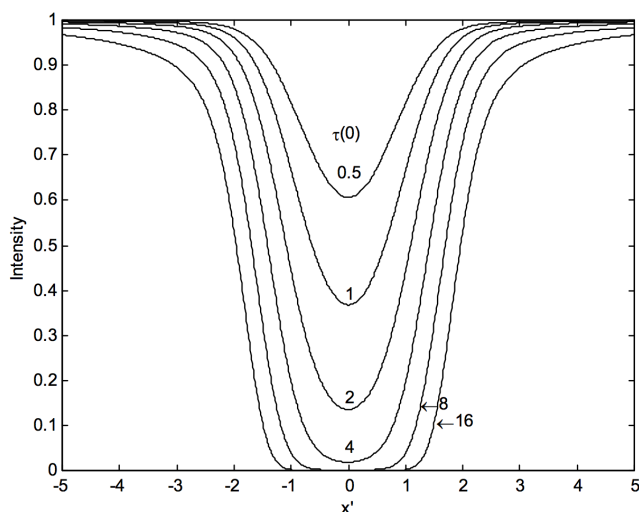


FIGURE XI.A.2

The equivalent width (equation 11.A.1) is the area above these curves, and it can be seen again that determining the upper limit for x' is a problem.

We can, however, remember that the profile that we are integrating is the convolution of a gaussian and a lorentzian, and that x' is $\lambda - \lambda_0$ in units of $2g/\sqrt{\ln 2}$. The gaussian component has very small wings, whereas the lorentzian profile has extensive wings. The ratio of the gaussian component to the ordinate to the lorentzian component is $\left(\frac{l'^2 + x'^2}{l'^2} \right) \exp(-x'^2)$, where $l' = (1/k_G - 1)\sqrt{\ln 2}$. The value of x' at which this ratio drops to 0.0001 is shown as a function of k_G in figure XI.A.1a. Beyond this point one can treat the wings of the profile as lorentzian.

Thus equation 11.A.2 can be integrated by treating the optically thin profile as a Voigt function up to some $x' = a$ and as a lorentzian function thereafter. That is, I have written equation 11.A.2 as

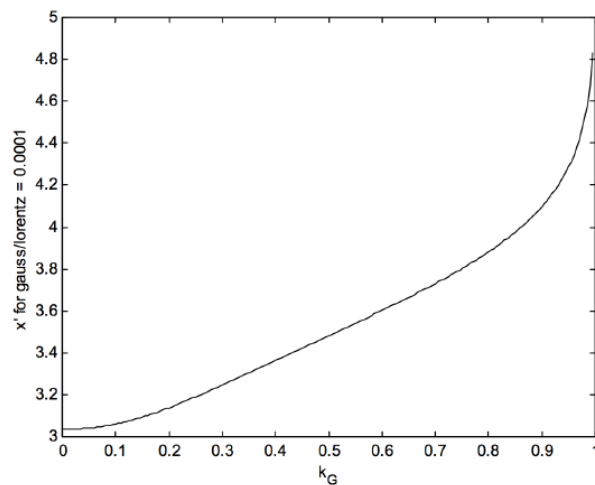


FIGURE XI.A.1A

$$W' = 2 \int_0^a \left(1 - \exp \left\{ -Cl' \tau(0) \int_{-\infty}^{\infty} \frac{\exp[-(\xi' - x')^2]}{\xi'^2 + l'^2} d\xi' \right\} \right) dx' \quad (11.9.1)$$

$$+ 2 \int_a^{\infty} \left(1 - \exp \left\{ -\frac{\tau(0)}{x'^2 + l'^2} \right\} \right) dx'. \quad (11.9.2)$$

On substitution of $\xi' = \frac{2l't}{1-t^2}$ in the first integral and $x' = l' \tan \theta$ in the second, this becomes

$$W' = 2 \int_0^a \left(1 - \exp \left\{ -2C\tau(0) \int_{-1}^1 \frac{\exp[-(\frac{2l't}{1-t^2} - x')^2]}{1+t^2} dt \right\} \right) dx' \quad (11.9.3)$$

$$+ 2l' \int_{\alpha}^{\pi/2} \frac{(1 - \exp \{ -\tau(0) \cos^2 \theta \})}{\cos^2 \theta} d\theta, \quad (11.9.4)$$

where $\tan \alpha = l'/a$. The dreaded symbol ∞ has now gone and, further, there is no problem at the upper limit of the second integral, for the value of the integrand when $\theta = \pi/2$ is unity.

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