

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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