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 ith electron in the atom. The expectation value of this quantity over the initial (i)and final (f) *states* of a transition is

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

or, as it is usually written

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

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 $\mathrm{C\ m}$, 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 debye = 10^{-18} cgs esu = 0.3935 atomic units = 3.336×10^{-30} $\mathrm{C\ m}$

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

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 of 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:

$$\varpi_2 A_{21} = \frac{16\pi^3}{3h\varepsilon_0\lambda^3} S_{E1}. \tag{9.5.3}$$

For electric quadrupole radiation:

$$\varpi_2 A_{21} = \frac{8\pi^5}{5\varepsilon_0 h\lambda^5} S_{E2}. \tag{9.5.4}$$

For magnetic dipole radiation:

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

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 $\mathrm{C}^2\ \mathrm{m}^2$, $\mathrm{C}^2\ \mathrm{m}^4$ and $\mathrm{A}^2\ \mathrm{m}^4$ 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

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