

## APPENDIX I

### A. Definitions Einstein coefficients

We consider here processes of emission and absorption of line radiation in atoms. In a formal sense, these can be described (and their rates or probabilities calculated) through time-dependent quantum mechanics applied to the interaction of the internal field of an atom with the external radiation field. Some aspects of this interaction can also be treated classically by analogy with the radiation of a damped harmonic oscillator. For a good treatment of the classical theory, see Chapters 14–17 of Jackson (*Classical Electrodynamics*). The book *Radiative Processes in Astrophysics* by Rybicki and Lightman is a good introduction to all kinds of radiative processes, including those involving line spectra of atoms. In this appendix, we will try to apply the following molecular convention to states of both atoms and molecules: the quantum numbers that label the upper state of a transition are indicated with a single-prime (e.g.  $n'$ ), while the lower state is denoted by a double-prime (e.g.  $n''$ ).

Consider a transition between states  $n'$  and  $n''$ : the spontaneous transition probability is  $A_{n'n''}$   $s^{-1}$  for a downward transition  $n' \rightarrow n''$  at a frequency  $\nu = (E_{n'} - E_{n''})/h$ . The mean lifetime against spontaneous decay of the upper state  $n'$  is related to the sum of such  $A$ -values over all possible transitions to lower states by

$$\tau_{n'}^{-1} = \sum_{n''} A_{n'n''} \quad s^{-1}. \quad (A.1)$$

Einstein (1917, *Phys. Zeits.*, **18**, 121) defined two other coefficients that describe the interaction of an atom and the radiation field. The radiation field is said to have an *intensity*  $I_\nu d\nu$  [ergs  $s^{-1} \text{ cm}^{-2} \text{ sr}^{-1}$ ] in the frequency interval  $d\nu$  about a frequency  $\nu$ . Implicitly, the specific intensity may also be a function of direction. The absorption coefficient  $B_{n''n'}$  gives the rate at which upward transitions  $n'' \rightarrow n'$  are induced in an atom by the radiation field at transition frequency  $\nu$

$$\mathcal{N}(n'') B_{n''n'} I_\nu \quad s^{-1} \quad (A.2)$$

where  $\mathcal{N}(n'')$  is the number of atoms in the initial (lower) state  $n''$ . [Note: the letter “N” is used in these notes for many purposes; we will try typically to use  $\mathcal{N}$  for an number of atoms,  $N$  for a column density (projected number of atoms along a column per unit of surface), and  $n$  for a number density (number of atoms per unit of volume). The distinction between density  $n$  and quantum number  $n$  should usually be clear from context and dimensions.] The radiation field can also induce downward transitions  $n' \rightarrow n''$  at the same frequency by a process called *stimulated emission*, whose rate is

$$\mathcal{N}(n') B_{n'n''} I_\nu \quad s^{-1}. \quad (A.3)$$

Note that the two  $B$  coefficients are distinguished by the order of their subscripts, which is part of the reason that we take the pains to introduce a convention for the labelling of upper and lower states. For unpolarized radiation and for atoms not exposed to any external fields other than the radiation itself, the spontaneous transition probability  $A_{n'n''}$  and the absorption probability  $B_{n''n'}$  can be considered to be isotropic, that is, independent of direction. This is not true of the coefficient of stimulated emission: the stimulated photon proceeds in the same direction as the stimulating

photon. These considerations are usually not important except for very intense or highly directional radiation fields, such as those in lasers and masers.

The Einstein coefficients  $A_{n'n''}$ ,  $B_{n'n''}$ , and  $B_{n''n'}$  are inherent properties of an atom that are independent of the nature of any external radiation field. Thus we can choose some arbitrarily convenient radiation field to evaluate the rates of absorption and stimulated emission processes and thus to derive the relationships among the three atomic coefficients. For this purpose, we assume complete thermodynamic equilibrium (TE): this means that a single physical parameter, the temperature  $T$ , characterizes (i) the energy density and spectrum of the radiation, (ii) the internal state distributions of all atoms, and (iii) the distribution of random motions of all atoms. Specifically, in TE the intensity of the radiation field is given by the Planck function:

$$I_\nu = B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/kT) - 1} . \quad (\text{A.4})$$

In TE, the relative populations of internal energy states are given by the Boltzmann formula

$$\frac{\mathcal{N}(n')}{\mathcal{N}(n'')} = \frac{g_{n'}}{g_{n''}} \exp[-(E_{n'} - E_{n''})/kT] \quad (\text{A.5})$$

where  $g_n$  is the *statistical weight* of state  $n$ . The statistical weight is ordinarily the degeneracy of the state; for example, a hydrogenic state of principal quantum number  $n$  has  $g_n = 2n^2$  if hyperfine structure is ignored. An individual level of total angular momentum  $J$  in LS coupling has  $g = (2J + 1)$ , to account for the number of degenerate magnetic sublevels. Now, we apply the *principle of detailed balance*, which requires for any particular state that the rate of all upward transitions exactly equal the rate of all downward transitions. In the present case, this yields the following rate equation for  $n' \leftrightarrow n''$ :

$$\mathcal{N}(n'')B_{n''n'}I_\nu = \mathcal{N}(n')\left[A_{n'n''} + B_{n'n''}I_\nu\right] \text{ s}^{-1}. \quad (\text{A.6})$$

From these considerations, it is possible to derive explicit relations between  $B_{n'n''}$  and  $B_{n''n'}$  and between  $A_{n'n''}$  and  $B_{n'n''}$ , which must be independent of  $T$  and thus intrinsic atomic properties:

$$g_{n'}B_{n'n''} = g_{n''}B_{n''n'} \quad (\text{A.7a})$$

$$A_{n'n''} = \frac{2h\nu^3}{c^2}B_{n'n''} . \quad (\text{A.7b})$$

The absorption coefficient, as defined above, must have dimensions of  $[\text{ergs}^{-1} \text{ cm}^2 \text{ Hz sr}]$  in order that the product  $I_\nu B_{n''n'}$  will have dimensions of an absorption rate per atom in  $[\text{s}^{-1}]$ . This absorption coefficient refers to the total rate of absorption in a transition whose central frequency is  $\nu_{n'n''}$ ; it can also be related to a frequency-dependent absorption cross section  $\sigma_{\text{abs}}(\nu)$  whose dimension is area:

$$\sigma_{\text{abs}}(\nu) \equiv \frac{\text{energy absorbed (unit frequency)}^{-1}}{\text{incident flux (unit frequency)}^{-1}} \text{ cm}^2. \quad (\text{A.8})$$

Then

$$\frac{h\nu}{4\pi}B_{n''n'} = \int_0^\infty \sigma_{\text{abs}}(\nu)d\nu \text{ cm}^2 \text{ Hz}. \quad (\text{A.9})$$

The most common way of describing the absorption probability of an atomic or molecular transition is in terms of the *oscillator strength*. The original meaning of the oscillator strength was the number of classical electron harmonic oscillators at the transition frequency that would be required to produce the same total absorption as the actual transition. In other words, the oscillator strength or  $f$ -value can be thought of as the ratio of integrated absorption cross sections of quantum mechanical and classical oscillators

$$f_{n''n'} = \frac{\int_0^\infty \sigma_{\text{abs}}^{\text{QM}} d\nu}{\int_0^\infty \sigma_{\text{abs}}^{\text{CL}} d\nu} . \quad (\text{A.10})$$

It can be shown that

$$\int_0^\infty \sigma_{\text{abs}} d\nu = \frac{\pi e^2}{m_e c} f_{n''n'} \quad (\text{A.11a})$$

so that

$$\frac{h\nu}{4\pi} B_{n''n'} = \frac{\pi e^2}{m_e c} f_{n''n'} , \quad (\text{A.11b})$$

which implies the general relation between transition probability and oscillator strength

$$A_{n'n''} = \frac{8\pi^2 e^2}{m_e c} \left(\frac{\nu}{c}\right)^2 \frac{g_{n''}}{g_{n'}} f_{n''n'} = 0.66702 \left(\frac{\nu}{c}\right)^2 \frac{g_{n''}}{g_{n'}} f_{n''n'} . \quad (\text{A.12})$$

## B. Multipole expansion of the radiation field

In the semi-classical theory of radiation, the atom is treated quantum mechanically, but the radiation field is described classically. The is specified in terms of a vector potential  $\vec{A}$  that can be written in terms of plane waves

$$\vec{A}(\vec{r}, \omega) = \vec{A}(\omega) e^{i\vec{k}\cdot\vec{r}} \quad (\text{A.13})$$

and that enters the interaction hamiltonian as

$$\mathcal{H}_{\text{int}} = \frac{e}{m_e c} \vec{A} \cdot \vec{p} = -\frac{ie\hbar}{m_e c} \vec{A} \cdot \sum_j \nabla_j \quad (\text{A.14})$$

and thus contributes to the total hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{rad}} + \mathcal{H}_{\text{atom}} + \mathcal{H}_{\text{int}} . \quad (\text{A.15})$$

The probability of a transition per unit time is given by

$$W_{a \rightarrow b} = \frac{4\pi^2 e^2}{m_e^2 c^2} |A(\omega_{ba})|^2 | \langle b | e^{i\vec{k}\cdot\vec{r}} \sum_j \nabla_j | a \rangle |^2 \quad (\text{A.16})$$

where

$$D_{ba} = \langle b | e^{i\vec{k}\cdot\vec{r}} \sum_j \nabla_j | a \rangle \quad (\text{A.17})$$

is called the transition matrix element.

The *multipole expansion* consists in expanding the exponential function of the plane wave and retaining the leading terms

$$e^{i\vec{k}\cdot\vec{r}} \approx 1 + i\vec{k}\cdot\vec{r} - \frac{(\vec{k}\cdot\vec{r})^2}{2} - i\frac{(\vec{k}\cdot\vec{r})^3}{6} + \dots \quad (\text{A.18})$$

The matrix elements  $D_{ba}$  are best evaluated one at a time. Assume also for a moment that  $j = 1$ . If the radiation field is assumed to be linearly polarized in the  $z$  direction, then the  $x$ -component becomes

$$(D_{ba})_x = \langle b | e^{ikx} \frac{\partial}{\partial x} | a \rangle \quad . \quad (\text{A.19})$$

The *electric dipole approximation* retains only the first term of the multipole expansion (A.18). Thus for an electric dipole transition, the matrix element (A.19) becomes

$$(D_{ba})_x = \langle b | \frac{\partial}{\partial x} | a \rangle \quad . \quad (\text{A.20})$$

This can be rewritten in terms of the *dipole moment operator* through use of the relation

$$\langle b | \frac{\partial}{\partial x} | a \rangle = -\frac{m_e}{\hbar}(E_b - E_a) \langle b | x | a \rangle \quad . \quad (\text{A.21})$$

Generalizing this result to the other spatial components, and using  $\omega_{ba} = (E_b - E_a)/\hbar$ , we find

$$W_{a \rightarrow b} = \frac{\omega^2}{c^2 \hbar^2} |A(\omega_{ba})|^2 |\langle b | \vec{d} | a \rangle|^2 \quad (\text{A.22})$$

where the electric dipole operator is defined as

$$\vec{d} \equiv e \sum_j \vec{r}_j \quad . \quad (\text{A.23})$$

In cases where the matrix elements of the electric dipole operator vanish, it is necessary to retain terms of successively higher order in the multipole expansion (eq. A.18). For example, if the term  $ikz$  is included, we find the  $x$ -component of the matrix element to be

$$(D_{ba})_x \propto \langle b | z \frac{\partial}{\partial x} | a \rangle \quad . \quad (\text{A.24})$$

To evaluate this term, we divide it into two parts, and add and subtract terms involving  $x\partial/\partial z$ . Thus

$$(D_{ba})_x \propto \frac{1}{2} [\langle b | z \frac{\partial}{\partial x} + x \frac{\partial}{\partial z} | a \rangle + \langle b | z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} | a \rangle] \quad . \quad (\text{A.25})$$

Through use of relation (A.21), the first term can be shown to be the  $xz$ -component of the quadrupole moment tensor of the atom

$$\langle b | z \frac{\partial}{\partial x} + x \frac{\partial}{\partial z} | a \rangle = -\frac{m_e}{\hbar} \omega_{ba} \langle b | xz | a \rangle \quad . \quad (\text{A.26})$$

The second term in (A.25) has the form of an angular momentum operator, so that

$$\langle b | z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} | a \rangle \propto i \langle b | \mu_y | a \rangle \quad , \quad (\text{A.27})$$

where  $\mu_y$  is the  $y$ -component of the magnetic dipole moment. Thus, the second-order terms in the multipole expansion give rise to part of the electric quadrupole and all of the magnetic dipole radiation. Since they arise from the same expansion term, they are fundamentally the same order of magnitude.

In summary, in the multipole expansion of  $e^{i\vec{k}\cdot\vec{r}}$ , the first term, the *electric dipole* term, yields matrix elements of the form:

$$E_1 : \quad \langle b | \sum_j \vec{r}_j | a \rangle \quad . \quad (A.28)$$

The next term gives both *magnetic dipole* transition matrix elements

$$M_1 : \quad \langle b | \sum_j \vec{\mu}_j | a \rangle \quad (A.29)$$

and *electric quadrupole* matrix elements

$$E_2 : \quad \langle b | \sum_j Q_j | a \rangle \quad (A.30)$$

where the electric quadrupole moment operator is

$$\vec{Q} = \vec{r}\vec{r} - \frac{1}{3}r^2\delta_{ij} \quad . \quad (A.31)$$

Transitions of even higher order are sometimes observed: e.g., electric hexadecapole transitions in solid hydrogen are seen in the laboratory and it is always possible that some astronomical context for these will be found someday.