

14.5: The Kinetics of Photon Absorption and Emission

The Phenomenological Rate Laws

Before closing this chapter, it is important to emphasize the context in which the transition rate expressions obtained here are most commonly used. The perturbative approach used in the above development gives rise to various contributions to the overall rate coefficient for transitions from an initial state Φ_i to a final state Φ_f ; these contributions include the electric dipole, magnetic dipole, and electric quadrupole first order terms as well contributions arising from second (and higher) order terms in the perturbation solution.

In principle, once the rate expression

$$R_{i,f} = 2\pi g(\omega_{f,i}) |\alpha_{f,i}|^2$$

has been evaluated through some order in perturbation theory and including the dominant electromagnetic interactions, one can make use of these **state-to-state rates**, which are computed on a per-molecule basis, to describe the time evolution of the populations of the various energy levels of the molecule under the influence of the light source's electromagnetic fields.

For example, given two states, denoted i and f , between which transitions can be induced by photons of frequency $\omega_{f,i}$, the following kinetic model is often used to describe the time evolution of the numbers of molecules n_i and n_f in the respective states:

$$\begin{aligned}\frac{dn_i}{dt} &= -R_{i,f}n_i + R_{f,i}n_f \\ \frac{dn_f}{dt} &= -R_{f,i}n_f + R_{i,f}n_i.\end{aligned}$$

Here, $R_{i,f}$ and $R_{f,i}$ are the rates (per molecule) of transitions for the $i \rightarrow f$ and $f \rightarrow i$ transitions respectively. As noted above, these rates are proportional to the intensity of the light source (i.e., the photon intensity) at the resonant frequency and to the square of a matrix element connecting the respective states. This matrix element square is $|\alpha_{i,f}|^2$ in the former case and $|\alpha_{f,i}|^2$ in the latter. Because the perturbation operator whose matrix elements are $\alpha_{i,f}$ and $\alpha_{f,i}$ is Hermitian (this is true through all orders of perturbation theory and for all terms in the long-wavelength expansion), these two quantities are complex conjugates of one another, and, hence $|\alpha_{i,f}|^2 = |\alpha_{f,i}|^2$, from which it follows that $R_{i,f} = R_{f,i}$. This means that the state-to-state absorption and stimulated emission rate coefficients (i.e., the rate per molecule undergoing the transition) are identical. This result is referred to as the principle of **microscopic reversibility**.

Quite often, the states between which transitions occur are members of levels that contain more than a single state. For example, in rotational spectroscopy a transition between a state in the $J = 3$ level of a diatomic molecule and a state in the $J = 4$ level involve such states; the respective levels are $2J+1 = 7$ and $2J+1 = 9$ fold degenerate, respectively.

To extend the above kinetic model to this more general case in which degenerate levels occur, one uses the number of molecules in each **level** (N_i and N_f for the two levels in the above example) as the time dependent variables. The kinetic equations then governing their time evolution can be obtained by summing the state-to-state equations over all states in each level

$$\begin{aligned}\sum_{i \text{ in level } I} \left(\frac{dn_i}{dt} \right) &= \frac{dN_I}{dt} \\ \sum_{f \text{ in level } F} \left(\frac{dn_f}{dt} \right) &= \frac{dN_F}{dt}\end{aligned}$$

and realizing that each state within a given level can undergo transitions to all states within the other level (hence the total rates of production and consumption must be summed over all states to or from which transitions can occur). This generalization results in a set of rate laws for the populations of the respective levels:

$$\begin{aligned}\frac{dN_i}{dt} &= -g_f R_{i,f} N_i + g_i R_{f,i} N_f \\ \frac{dN_f}{dt} &= -g_i R_{f,i} N_f + g_f R_{i,f} N_i.\end{aligned}$$

Here, g_i and g_f are the degeneracies of the two levels (i.e., the number of states in each level) and the $R_{i,f}$ and $R_{f,i}$, which are equal as described above, are the state-to-state rate coefficients introduced earlier.

Spontaneous and Stimulated Emission

It turns out (the development of this concept is beyond the scope of this text) that the rate at which an excited level can emit photons and decay to a lower energy level is dependent on two factors:

- the rate of **stimulated** photon emission as covered above and
- the rate of **spontaneous** photon emission.

The former rate $g_f R_{i,f}$ (per molecule) is proportional to the light intensity $g(\omega_{f,i})$ at the resonance frequency. It is conventional to separate out this intensity factor by defining an intensity independent rate coefficient $B_{i,f}$ for this process as:

$$g_f R_{i,f} = g(\omega_{f,i}) B_{i,f}.$$

Clearly, $B_{i,f}$ embodies the final-level degeneracy factor g_f , the perturbation matrix elements, and the 2π factor in the earlier expression for $R_{i,f}$. The spontaneous rate of transition from the excited to the lower level is found to be **independent** of photon intensity, because it deals with a process that does not require collision with a photon to occur, and is usually denoted $A_{i,f}$. The rate of photon-stimulated upward transitions from state f to state i ($g_i R_{f,i} = g_i R_{i,f}$ in the present case) is also proportional to $g(\omega_{f,i})$, so it is written by convention as:

$$g_i R_{f,i} = g(\omega_{f,i}) B_{f,i}.$$

An important relation between the $B_{i,f}$ and $B_{f,i}$ parameters exists and is based on the identity $R_{i,f} = R_{f,i}$ that connects the state-to-state rate coefficients:

$$\frac{(B_{i,f})}{(B_{f,i})} = \frac{(g_f R_{i,f})}{(g_i R_{f,i})} = \frac{g_f}{f_i}.$$

This relationship will prove useful in the following sections.

Saturated Transitions and Transparency

Returning to the kinetic equations that govern the time evolution of the populations of two levels connected by photon absorption and emission, and adding in the term needed for spontaneous emission, one finds (with the initial level being of the lower energy):

$$\begin{aligned}\frac{dN_i}{dt} &= -gB_{i,f}N_i + (A_{f,i} + gB_{f,i})N_f \\ \frac{dN_f}{dt} &= -(A_{f,i} + gB_{f,i})N_f + gB_{i,f}N_i\end{aligned}$$

where $g = g(\omega)$ denotes the light intensity at the resonance frequency. At steady state, the populations of these two levels are given by setting

$$\begin{aligned}\frac{dN_i}{dt} &= \frac{dN_f}{dt} = 0 : \\ \frac{N_f}{N_i} &= \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}.\end{aligned}$$

When the light source's intensity is so large as to render $gB_{f,i} \gg A_{f,i}$ (i.e., when the rate of spontaneous emission is small compared to the stimulated rate), this population ratio reaches $(B_{i,f}/B_{f,i})$, which was shown earlier to equal (g_f/g_i) . In this case, one says that the populations have been **saturated** by the intense light source. Any further increase in light intensity will result in **zero** increase in the rate at which photons are being absorbed. Transitions that have had their populations saturated by the application of intense light sources are said to display optical **transparency** because they are unable to absorb (nor emit) any further photons because of their state of saturation.

Equilibrium and Relations Between A and B Coefficients

When the molecules in the two levels being discussed reach **equilibrium** (at which time the $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$ also holds) with a photon source that itself is in **equilibrium** characterized by a temperature T , we must have:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} e^{\frac{-(E_f - E_i)}{kT}} = \frac{g_f}{g_i} e^{\frac{\hbar\omega}{kT}}$$

where g_f and g_i are the degeneracies of the states labeled f and i . The photon source that is characterized by an equilibrium temperature T is known as a **black body** radiator, whose intensity profile $g(\omega)$ (in $\text{erg cm}^{-3} \text{ sec}$) is known to be of the form:

$$g(\omega) = \frac{2(\hbar\omega)^3}{\pi c^3 \hbar^2} \left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^{-1}.$$

Equating the kinetic result that must hold at equilibrium:

$$\frac{N_f}{N_i} = \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}$$

to the thermodynamic result:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} e^{\frac{\hbar\omega}{kT}},$$

and using the above black body $g(\omega)$ expression and the identity

$$\frac{B_{i,f}}{B_{f,i}} = \frac{g_f}{g_i},$$

one can solve for the $A_{f,i}$ rate coefficient in terms of the $B_{f,i}$ coefficient. Doing so yields:

$$A_{f,i} = B_{f,i} \frac{2(\hbar\omega)^3}{\pi^3 \hbar^2}$$

Summary

In summary, the so-called **Einstein A and B rate coefficients** connecting a lower-energy initial state i and a final state f are related by the following conditions:

$$B_{i,f} = \frac{g_f}{g_i} B_{f,i}$$

and

$$A_{f,i} = \frac{2(\hbar\omega)^3}{\pi c^3 \hbar^2} B_{f,i}.$$

These phenomenological level-to-level rate coefficients are related to the state-to-state $R_{i,f}$ coefficients derived by applying perturbation theory to the electromagnetic perturbation through

$$g_f R_{i,f} = g(\omega_{f,i}) B_{i,f}.$$

The A and B coefficients can be used in a kinetic equation model to follow the time evolution of the populations of the corresponding levels:

$$\begin{aligned} \frac{dN_i}{dt} &= -gB_{i,f}N_i + (A_{f,i} + gB_{f,i})N_f \\ \frac{dN_f}{dt} &= -(A_{f,i} + gB_{f,i})N_f + gB_{i,f}N_i. \end{aligned}$$

These equations possess steady state solutions

$$\frac{N_f}{N_i} = \frac{(gB_{i,f})}{(A_{f,i} + gB_{f,i})}$$

which, for large $g(\omega)$, produce saturation conditions:

$$\frac{N_f}{N_i} = \frac{(B_{i,f})}{(B_{f,i})} = \frac{g_f}{g_i}.$$

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