

Section 5 Time Dependent Processes

Chapter 14

The interaction of a molecular species with electromagnetic fields can cause transitions to occur among the available molecular energy levels (electronic, vibrational, rotational, and nuclear spin). Collisions among molecular species likewise can cause transitions to occur. Time-dependent perturbation theory and the methods of molecular dynamics can be employed to treat such transitions.

I. The Perturbation Describing Interactions With Electromagnetic Radiation

The full N-electron non-relativistic Hamiltonian H discussed earlier in this text involves the kinetic energies of the electrons and of the nuclei and the mutual coulombic interactions among these particles

$$H = \sum_{a=1, M} \left(-\frac{\hbar^2}{2m_a} \right) \nabla_a^2 + \sum_j \left[\left(-\frac{\hbar^2}{2m_e} \right) \nabla_j^2 - \sum_a Z_a e^2 / r_{j,a} \right] \\ + \sum_{j < k} e^2 / r_{j,k} + \sum_{a < b} Z_a Z_b e^2 / R_{a,b}.$$

When an electromagnetic field is present, this is not the correct Hamiltonian, but it can be modified straightforwardly to obtain the proper H.

A. The Time-Dependent Vector $\mathbf{A}(\mathbf{r}, t)$ Potential

The only changes required to achieve the Hamiltonian that describes the same system in the presence of an electromagnetic field are to replace the momentum operators \mathbf{P}_a and \mathbf{p}_j for the nuclei and electrons, respectively, by $(\mathbf{P}_a - Z_a e/c \mathbf{A}(R_{a,t}))$ and $(\mathbf{p}_j - e/c \mathbf{A}(r_j, t))$. Here $Z_a e$ is the charge on the a^{th} nucleus, $-e$ is the charge of the electron, and c is the speed of light.

The vector potential \mathbf{A} depends on time t and on the spatial location \mathbf{r} of the particle in the following manner:

$$\mathbf{A}(\mathbf{r}, t) = 2 \mathbf{A}_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}).$$

The circular frequency of the radiation ω (radians per second) and the wave vector \mathbf{k} (the magnitude of \mathbf{k} is $|\mathbf{k}| = 2\pi / \lambda$, where λ is the wavelength of the light) control the temporal

and spatial oscillations of the photons. The vector \mathbf{A}_0 characterizes the strength (through the magnitude of \mathbf{A}_0) of the field as well as the direction of the \mathbf{A} potential; the direction of propagation of the photons is given by the unit vector $\mathbf{k}/|\mathbf{k}|$. The factor of 2 in the definition of \mathbf{A} allows one to think of \mathbf{A}_0 as measuring the strength of both $\exp(i(\omega t - \mathbf{k} \cdot \mathbf{r}))$ and $\exp(-i(\omega t - \mathbf{k} \cdot \mathbf{r}))$ components of the $\cos(\omega t - \mathbf{k} \cdot \mathbf{r})$ function.

B. The Electric $\mathbf{E}(\mathbf{r},t)$ and Magnetic $\mathbf{H}(\mathbf{r},t)$ Fields

The electric $\mathbf{E}(\mathbf{r},t)$ and magnetic $\mathbf{H}(\mathbf{r},t)$ fields of the photons are expressed in terms of the vector potential \mathbf{A} as

$$\mathbf{E}(\mathbf{r},t) = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = -\frac{1}{c} \omega \mathbf{A}_0 \sin(\omega t - \mathbf{k} \cdot \mathbf{r})$$

$$\mathbf{H}(\mathbf{r},t) = \nabla \times \mathbf{A} = \mathbf{k} \times \mathbf{A}_0 \sin(\omega t - \mathbf{k} \cdot \mathbf{r}).$$

The \mathbf{E} field lies parallel to the \mathbf{A}_0 vector, and the \mathbf{H} field is perpendicular to \mathbf{A}_0 ; both are perpendicular to the direction of propagation of the light $\mathbf{k}/|\mathbf{k}|$. \mathbf{E} and \mathbf{H} have the same phase because they both vary with time and spatial location as $\sin(\omega t - \mathbf{k} \cdot \mathbf{r})$. The relative orientations of these vectors are shown below.



C. The Resulting Hamiltonian

Replacing the nuclear and electronic momenta by the modifications shown above in the kinetic energy terms of the full electronic and nuclear-motion hamiltonian results in the following additional factors appearing in H:

$$H_{\text{int}} = \sum_j \left\{ \left(i e \hbar / m_e c \right) \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{p}_j + \left(e^2 / 2 m_e c^2 \right) |\mathbf{A}(\mathbf{r}_j, t)|^2 \right\} \\ + \sum_a \left\{ \left(i Z_a e \hbar / m_a c \right) \mathbf{A}(\mathbf{R}_a, t) \cdot \mathbf{p}_a + \left(Z_a^2 e^2 / 2 m_a c^2 \right) |\mathbf{A}(\mathbf{R}_a, t)|^2 \right\}.$$

These so-called interaction perturbations H_{int} are what induces transitions among the various electronic/vibrational/rotational states of a molecule. The one-electron additive nature of H_{int} plays an important role in determining the kind of transitions that H_{int} can induce. For example, it causes the most intense electronic transitions to involve excitation of a single electron from one orbital to another (recall the Slater-Condon rules).

II. Time-Dependent Perturbation Theory

A. The Time-Dependent Schrödinger Equation

The mathematical machinery needed to compute the rates of transitions among molecular states induced by such a time-dependent perturbation is contained in time-dependent perturbation theory (TDPT). The development of this theory proceeds as follows. One first assumes that one has in-hand all of the eigenfunctions $\{ \psi_k \}$ and eigenvalues $\{ E_k^0 \}$ that characterize the Hamiltonian H^0 of the molecule in the absence of the external perturbation:

$$H^0 \psi_k = E_k^0 \psi_k.$$

One then writes the time-dependent Schrödinger equation

$$i \hbar \partial / \partial t \psi = (H^0 + H_{\text{int}}) \psi$$

in which the full Hamiltonian is explicitly divided into a part that governs the system in the absence of the radiation field and H_{int} which describes the interaction with the field.

B. Perturbative Solution

By treating H^0 as of zeroth order (in the field strength $|\mathbf{A}_0|$), expanding order-by-order in the field-strength parameter:

$$= 0 + 1 + 2 + 3 + \dots,$$

realizing that H_{int} contains terms that are both first- and second- order in $|\mathbf{A}_0|$

$$H^1_{\text{int}} = \sum_j \left\{ (ie\hbar/m_e c) \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{p}_j \right\}$$

$$+ \sum_a \left\{ (i Z_a e \hbar / m_a c) \mathbf{A}(\mathbf{R}_a, t) \cdot \mathbf{p}_a \right\},$$

$$H^2_{\text{int}} = \sum_j \left\{ (e^2/2m_e c^2) |\mathbf{A}(\mathbf{r}_j, t)|^2 \right\}$$

$$+ \sum_a \left\{ (Z_a^2 e^2 / 2m_a c^2) |\mathbf{A}(\mathbf{R}_a, t)|^2 \right\},$$

and then collecting together all terms of like power of $|\mathbf{A}_0|$, one obtains the set of time-dependent perturbation theory equations. The lowest order such equations read:

$$i\hbar \frac{d}{dt} \psi^0 = H^0 \psi^0$$

$$i\hbar \frac{d}{dt} \psi^1 = (H^0 + H^1_{\text{int}}) \psi^0$$

$$i\hbar \frac{d}{dt} \psi^2 = (H^0 + H^2_{\text{int}}) \psi^0 + H^1_{\text{int}} \psi^1.$$

The zeroth order equations can easily be solved because H^0 is independent of time. Assuming that at $t = -\infty$, $\psi = \psi_i$ (we use the index i to denote the initial state), this solution is:

$$\psi^0 = \psi_i \exp(-i E_i^0 t / \hbar).$$

The first-order correction to ψ^0 , ψ^1 can be found by (i) expanding ψ^1 in the complete set of zeroth-order states $\{\psi_f\}$:

$$\psi^1 = \sum_f \langle \psi_f | \psi^1 \rangle \psi_f = \sum_f C_f^1 \psi_f,$$

(ii) using the fact that

$$H^0 \psi_f = E_f^0 \psi_f,$$

and (iii) substituting all of this into the equation that $\psi^{(1)}$ obeys. The resultant equation for the coefficients that appear in the first-order equation can be written as

$$i \hbar \frac{d C_f^{(1)}}{dt} = \sum_k \{ E_k^{(0)} C_k^{(1)} \}_{f,k} + \langle f | H_{int}^{(1)} | i \rangle \exp(-i E_i^{(0)} t / \hbar),$$

or

$$i \hbar \frac{d C_f^{(1)}}{dt} = E_f^{(0)} C_f^{(1)} + \langle f | H_{int}^{(1)} | i \rangle \exp(-i E_i^{(0)} t / \hbar).$$

Defining

$$C_f^{(1)}(t) = D_f^{(1)}(t) \exp(-i E_f^{(0)} t / \hbar),$$

this equation can be cast in terms of an easy-to-solve equation for the $D_f^{(1)}$ coefficients:

$$i \hbar \frac{d D_f^{(1)}}{dt} = \langle f | H_{int}^{(1)} | i \rangle \exp(i [E_f^{(0)} - E_i^{(0)}] t / \hbar).$$

Assuming that the electromagnetic field $\mathbf{A}(\mathbf{r},t)$ is turned on at $t=0$, and remains on until $t = T$, this equation for $D_f^{(1)}$ can be integrated to yield:

$$D_f^{(1)}(t) = (i \hbar)^{-1} \int_0^T \langle f | H_{int}^{(1)} | i \rangle \exp(i [E_f^{(0)} - E_i^{(0)}] t' / \hbar) dt'.$$

C. Application to Electromagnetic Perturbations

1. First-Order Fermi-Wentzel "Golden Rule"

Using the earlier expressions for $H_{int}^{(1)}$ and for $\mathbf{A}(\mathbf{r},t)$

$$H_{int}^{(1)} = \sum_j \{ (ie \hbar / m_e c) \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{p}_j \}$$

$$+ \sum_a \{ (i Z_a e \hbar / m_a c) \mathbf{A}(\mathbf{R}_a, t) \cdot \mathbf{p}_a \}$$

and

$$2 \mathbf{A}_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}) = \mathbf{A}_0 \{ \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r})] + \exp[-i(\omega t - \mathbf{k} \cdot \mathbf{r})] \},$$

it is relatively straightforward to carry out the above time integration to achieve a final expression for $D_f^1(t)$, which can then be substituted into $C_f^1(t) = D_f^1(t) \exp(-i E_f^0 t / \hbar)$ to obtain the final expression for the first-order estimate of the probability amplitude for the molecule appearing in the state $f \exp(-i E_f^0 t / \hbar)$ after being subjected to electromagnetic radiation from $t = 0$ until $t = T$. This final expression reads:

$$\begin{aligned} C_f^1(T) = & (i \hbar)^{-1} \exp(-i E_f^0 T / \hbar) \{ \langle f | j \{ (ie \hbar / m_e c) \exp[-i \mathbf{k} \cdot \mathbf{r}_j] \mathbf{A}_0 \cdot \mathbf{e}_j \\ & + \sum_a (i Z_a e \hbar / m_a c) \exp[-i \mathbf{k} \cdot \mathbf{R}_a] \mathbf{A}_0 \cdot \mathbf{e}_a | i \rangle \} \frac{\exp(i(\omega_{fi} + \omega) T) - 1}{i(\omega_{fi} + \omega)} \\ & + (i \hbar)^{-1} \exp(-i E_f^0 T / \hbar) \{ \langle f | j \{ (ie \hbar / m_e c) \exp[i \mathbf{k} \cdot \mathbf{r}_j] \mathbf{A}_0 \cdot \mathbf{e}_j \\ & + \sum_a (i Z_a e \hbar / m_a c) \exp[i \mathbf{k} \cdot \mathbf{R}_a] \mathbf{A}_0 \cdot \mathbf{e}_a | i \rangle \} \frac{\exp(i(-\omega_{fi} + \omega) T) - 1}{i(-\omega_{fi} + \omega)}, \end{aligned}$$

where

$$\omega_{fi} = [E_f^0 - E_i^0] / \hbar$$

is the resonance frequency for the transition between "initial" state i and "final" state f .

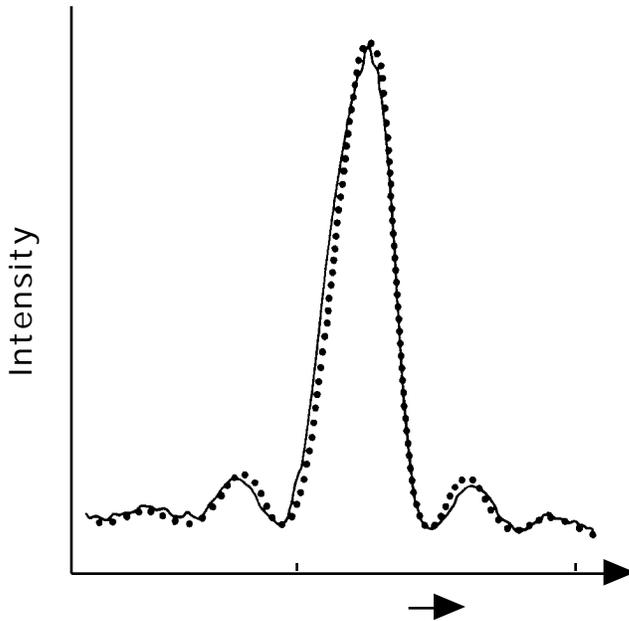
Defining the time-independent parts of the above expression as

$$\begin{aligned} f_{f,i} = & \langle f | j \{ (e \hbar / m_e c) \exp[-i \mathbf{k} \cdot \mathbf{r}_j] \mathbf{A}_0 \cdot \mathbf{e}_j \\ & + \sum_a (Z_a e \hbar / m_a c) \exp[-i \mathbf{k} \cdot \mathbf{R}_a] \mathbf{A}_0 \cdot \mathbf{e}_a | i \rangle, \end{aligned}$$

this result can be written as

$$\begin{aligned} C_f^1(T) = & \exp(-i E_f^0 T / \hbar) \{ f_{f,i} \frac{\exp(i(\omega_{fi} + \omega) T) - 1}{i(\omega_{fi} + \omega)} \\ & + f_{f,i} \frac{\exp(-i(\omega_{fi} - \omega) T) - 1}{-i(\omega_{fi} - \omega)} \}. \end{aligned}$$

grows with T. Physically, this means that when the molecules are exposed to the light source for long times (large T), the sinc function emphasizes values near ω_i (i.e., the on-resonance values). These properties of the sinc function will play important roles in what follows.



In most experiments, light sources have a "spread" of frequencies associated with them; that is, they provide photons of various frequencies. To characterize such sources, it is common to introduce the spectral source function $g(\omega) d\omega$ which gives the probability that the photons from this source have frequency somewhere between ω and $\omega + d\omega$. For narrow-band lasers, $g(\omega)$ is a sharply peaked function about some "nominal" frequency ω_0 ; broader band light sources have much broader $g(\omega)$ functions.

When such non-monochromatic light sources are used, it is necessary to average the above formula for $|C_f^1(T)|^2$ over the $g(\omega) d\omega$ probability function in computing the probability of finding the molecule in state f after time T, given that it was in i up until $t = 0$, when the light source was turned on. In particular, the proper expression becomes:

$$|C_f^1(T)|_{\text{ave}}^2 = 4 |C_{f,i}^1|^2 \int g(\omega) \frac{\sin^2(1/2(\omega - \omega_{f,i})T)}{(\omega - \omega_{f,i})^2} d\omega$$

$$= 2 |f_{i,i}|^2 T \int_{-\infty}^{\infty} g(\omega) \frac{\sin^2(1/2(\omega - \omega_{f,i})T)}{1/4T^2(\omega - \omega_{f,i})^2} d\omega \quad T/2 .$$

If the light-source function is "tuned" to peak near $\omega = \omega_{f,i}$, and if $g(\omega)$ is much broader (in ω -space) than the $\frac{\sin^2(1/2(\omega - \omega_{f,i})T)}{(\omega - \omega_{f,i})^2}$ function, $g(\omega)$ can be replaced by its value at the peak of the $\frac{\sin^2(1/2(\omega - \omega_{f,i})T)}{(\omega - \omega_{f,i})^2}$ function, yielding:

$$|C_f^1(T)|_{\text{ave}}^2 = 2 g(\omega_{f,i}) |f_{f,i}|^2 T \int_{-\infty}^{\infty} \frac{\sin^2(1/2(\omega - \omega_{f,i})T)}{1/4T^2(\omega - \omega_{f,i})^2} d\omega \quad T/2$$

$$= 2 g(\omega_{f,i}) |f_{f,i}|^2 T \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} dx = 2 g(\omega_{f,i}) |f_{f,i}|^2 T .$$

The fact that the probability of excitation from ω_i to ω_f grows linearly with the time T over which the light source is turned on implies that the rate of transitions between these two states is constant and given by:

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

this is the so-called first-order Fermi-Wentzel "**golden rule**" expression for such transition rates. It gives the rate as the square of a transition matrix element between the two states involved, of the first order perturbation multiplied by the light source function $g(\omega)$ evaluated at the transition frequency $\omega_{f,i}$.

2. Higher Order Results

Solution of the second-order time-dependent perturbation equations,

$$i \hbar \frac{d^2}{dt^2} = (H^0 + H_{\text{int}}^2 + H_{\text{int}}^0 + H_{\text{int}}^1) \quad (1)$$

which will not be treated in detail here, gives rise to two distinct types of contributions to the transition probabilities between i and f :

i. There will be matrix elements of the form

$$\langle f | j \{ (e^2/2m_e c^2) |\mathbf{A}(\mathbf{r}_j, t)|^2 \} + a \{ (Z_a^2 e^2/2m_a c^2) |\mathbf{A}(\mathbf{R}_a, t)|^2 \} | i \rangle$$

arising when H_{int}^2 couples i to f .

ii. There will be matrix elements of the form

$$\langle k | f | j \{ (ie \hbar / m_e c) \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{j} \} + a \{ (i Z_a e \hbar / m_a c) \mathbf{A}(\mathbf{R}_a, t) \cdot \mathbf{j}_a \} | k \rangle$$

$$\langle k | j \{ (ie \hbar / m_e c) \mathbf{A}(\mathbf{r}_j, t) \cdot \mathbf{j} \} + a \{ (i Z_a e \hbar / m_a c) \mathbf{A}(\mathbf{R}_a, t) \cdot \mathbf{j}_a \} | i \rangle$$

arising from expanding $H_{int}^1 = \sum_k C_k^1 H_{int}^1 | k \rangle$ and using the earlier result for the first-order amplitudes C_k^1 . Because both types of second-order terms vary quadratically with the $\mathbf{A}(\mathbf{r}, t)$ potential, and because \mathbf{A} has time dependence of the form $\cos(\omega t - \mathbf{k} \cdot \mathbf{r})$, these terms contain portions that vary with time as $\cos(2\omega t)$. As a result, transitions between initial and final states i and f whose transition frequency is ω_{fi} can be induced when $2\omega = \omega_{fi}$; in this case, one speaks of coherent two-photon induced transitions in which the electromagnetic field produces a perturbation that has twice the frequency of the "nominal" light source frequency ω .

D. The "Long-Wavelength" Approximation

To make progress in further analyzing the first-order results obtained above, it is useful to consider the wavelength λ of the light used in most visible/ultraviolet, infrared, or microwave spectroscopic experiments. Even the shortest such wavelengths (ultraviolet) are considerably longer than the spatial extent of all but the largest molecules (i.e., polymers and biomolecules for which the approximations we introduce next are not appropriate).

In the definition of the essential coupling matrix element f_{fi}

$$f_{fi} = \langle f | j \{ (e / m_e c) \exp[-i\mathbf{k} \cdot \mathbf{r}_j] \mathbf{A}_0 \cdot \mathbf{j} \}$$

$$+ a \{ (Z_a e / m_a c) \exp[-i\mathbf{k} \cdot \mathbf{R}_a] \mathbf{A}_0 \cdot \mathbf{j}_a \} | i \rangle,$$

the factors $\exp[-i\mathbf{k}\cdot\mathbf{r}_j]$ and $\exp[-i\mathbf{k}\cdot\mathbf{R}_a]$ can be expanded as:

$$\exp[-i\mathbf{k}\cdot\mathbf{r}_j] = 1 + (-i\mathbf{k}\cdot\mathbf{r}_j) + 1/2 (-i\mathbf{k}\cdot\mathbf{r}_j)^2 + \dots$$

$$\exp[-i\mathbf{k}\cdot\mathbf{R}_a] = 1 + (-i\mathbf{k}\cdot\mathbf{R}_a) + 1/2 (-i\mathbf{k}\cdot\mathbf{R}_a)^2 + \dots$$

Because $|\mathbf{k}| = 2\pi/\lambda$, and the scales of \mathbf{r}_j and \mathbf{R}_a are of the dimension of the molecule, $\mathbf{k}\cdot\mathbf{r}_j$ and $\mathbf{k}\cdot\mathbf{R}_a$ are less than unity in magnitude, within this so-called "long-wavelength" approximation.

1. Electric Dipole Transitions

Introducing these expansions into the expression for $f_{f,i}$ gives rise to terms of various powers in $1/\lambda$. The lowest order terms are:

$$f_{f,i}(E1) = \langle f | \sum_j (e/m_e c) \mathbf{A}_0 \cdot \mathbf{r}_j + \sum_a (Z_a e/m_a c) \mathbf{A}_0 \cdot \mathbf{R}_a | i \rangle$$

and are called "electric dipole" terms, and are denoted E1. To see why these matrix elements are termed E1, we use the following identity (see Chapter 1) between the momentum operator $-i\hbar\nabla$ and the corresponding position operator \mathbf{r} :

$$\mathbf{r}_j = - (m_e/\hbar^2) [H, \mathbf{r}_j]$$

$$\mathbf{R}_a = - (m_a/\hbar^2) [H, \mathbf{R}_a].$$

This derives from the fact that H contains ∇_j^2 and ∇_a^2 in its kinetic energy operators (as ∇_j^2 and ∇_a^2).

Substituting these expressions into the above $f_{f,i}(E1)$ equation and using $H|i\rangle = E_i|i\rangle$ or $H|f\rangle = E_f|f\rangle$, one obtains:

$$\begin{aligned} f_{f,i}(E1) &= (E_f^0 - E_i^0) \mathbf{A}_0 \cdot \langle f | \sum_j (e/\hbar^2 c) \mathbf{r}_j + \sum_a (Z_a e/\hbar^2 c) \mathbf{R}_a | i \rangle \\ &= \sum_j f_{f,i} \mathbf{A}_0 \cdot \langle f | \sum_j (e/\hbar c) \mathbf{r}_j + \sum_a (Z_a e/\hbar c) \mathbf{R}_a | i \rangle \\ &= \langle f | \boldsymbol{\mu} | i \rangle, \end{aligned}$$

where μ is the electric dipole moment operator for the electrons and nuclei:

$$\mu = \sum_j e \mathbf{r}_j + \sum_a Z_a e \mathbf{R}_a.$$

The fact that the E1 approximation to $\Gamma_{f,i}$ contains matrix elements of the electric dipole operator between the initial and final states makes it clear why this is called the electric dipole contribution to $\Gamma_{f,i}$; within the E1 notation, the E stands for electric moment and the 1 stands for the first such moment (i.e., the dipole moment).

Within this approximation, the overall rate of transitions is given by:

$$\begin{aligned} R_{i,f} &= 2 \sum_{\mathbf{k}} g(\mathbf{k}) |\langle f | \mu | i \rangle|^2 \\ &= 2 \sum_{\mathbf{k}} g(\mathbf{k}) \left(\frac{1}{\hbar c} \right)^2 |\mathbf{A}_0 \cdot \langle f | \mu | i \rangle|^2. \end{aligned}$$

Recalling that $\mathbf{E}(\mathbf{r},t) = -1/c \nabla \phi = -1/c \mathbf{A}_0 \sin(\omega t - \mathbf{k} \cdot \mathbf{r})$, the magnitude of \mathbf{A}_0 can be replaced by that of \mathbf{E} , and this rate expression becomes

$$R_{i,f} = (2/\hbar^2) \sum_{\mathbf{k}} g(\mathbf{k}) |\mathbf{E}_0 \cdot \langle f | \mu | i \rangle|^2.$$

This expresses the widely used E1 approximation to the Fermi-Wentzel golden rule.

2. Magnetic Dipole and Electric Quadrupole Transitions

When E1 predictions for the rates of transitions between states vanish (e.g., for symmetry reasons as discussed below), it is essential to examine higher order contributions to $\Gamma_{f,i}$. The next terms in the above long-wavelength expansion vary as $1/\omega^2$ and have the form:

$$\begin{aligned} \Gamma_{f,i}(E2+M1) &= \sum_{\mathbf{k}} \sum_j \left(\frac{e}{m_e c} \right) [-i\mathbf{k} \cdot \mathbf{r}_j] \mathbf{A}_0 \cdot \langle f | \mathbf{L}_j | i \rangle \\ &+ \sum_a \left(\frac{Z_a e}{m_a c} \right) [-i\mathbf{k} \cdot \mathbf{R}_a] \mathbf{A}_0 \cdot \langle f | \mathbf{L}_a | i \rangle. \end{aligned}$$

For reasons soon to be shown, they are called electric quadrupole (E2) and magnetic dipole (M1) terms. Clearly, higher and higher order terms can be so generated. Within the long-wavelength regime, however, successive terms should decrease in magnitude because of the successively higher powers of $1/\omega^2$ that they contain.

To further analyze the above E2 + M1 factors, let us label the propagation direction of the light as the z-axis (the axis along which \mathbf{k} lies) and the direction of \mathbf{A}_0 as the x-axis. These axes are so-called "lab-fixed" axes because their orientation is determined by the direction of the light source and the direction of polarization of the light source's \mathbf{E} field, both of which are specified by laboratory conditions. The molecule being subjected to this light can be oriented at arbitrary angles relative to these lab axes.

With the x, y, and z axes so defined, the above expression for $f_{f,i}(\text{E2+M1})$ becomes

$$f_{f,i}(\text{E2+M1}) = -i (A_0^2 / c) \langle f | j (e / m_e c) z_j / x_j + a (Z_a e / m_a c) z_a / x_a | i \rangle.$$

Now writing (for both z_j and z_a)

$$z / x = 1/2 (z / x - x / z + z / x + x / z),$$

and using

$$j = - (m_e / \hbar^2) [H, \mathbf{r}_j]$$

$$a = - (m_a / \hbar^2) [H, \mathbf{R}_a],$$

the contributions of $1/2 (z / x + x / z)$ to $f_{f,i}(\text{E2+M1})$ can be rewritten as

$$f_{f,i}(\text{E2}) = -i \frac{(A_0^2 e^2)}{c \hbar} \langle f | j z_j x_j + a Z_a z_a x_a | i \rangle.$$

The operator $z_j x_j + z_a x_a$ that appears above is the z,x element of the electric quadrupole moment operator $Q_{z,x}$; it is for this reason that this particular component is labeled E2 and denoted the electric quadrupole contribution.

The remaining $1/2 (z / x - x / z)$ contribution to $f_{f,i}(\text{E2+M1})$ can be rewritten in a form that makes its content more clear by first noting that

$$1/2 (z / x - x / z) = (i/2\hbar) (z p_x - x p_z) = (i/2\hbar) L_y$$

contains the y-component of the angular momentum operator. Hence, the following contribution to $\rho_{f,i}(E_2+M_1)$ arises:

$$\rho_{f,i}(M_1) = \frac{A_0^2 e}{2 c \hbar} \langle f | \sum_j L_{y_j} / m_e + \sum_a Z_a L_{y_a} / m_a | i \rangle.$$

The magnetic dipole moment of the electrons about the y axis is

$$\mu_{y, \text{electrons}} = \sum_j (e/2m_e c) L_{y_j};$$

that of the nuclei is

$$\mu_{y, \text{nuclei}} = \sum_a (Z_a e / 2m_a c) L_{y_a}.$$

The $\rho_{f,i}(M_1)$ term thus describes the interaction of the magnetic dipole moments of the electrons and nuclei with the magnetic field (of strength $|H| = A_0 k$) of the light (which lies along the y axis):

$$\rho_{f,i}(M_1) = \frac{|H|}{\hbar} \langle f | \mu_{y, \text{electrons}} + \mu_{y, \text{nuclei}} | i \rangle.$$

The total rate of transitions from $|i\rangle$ to $|f\rangle$ is given, through first-order in perturbation theory, by

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

where $\rho_{f,i}$ is a sum of its E1, E2, M1, etc. pieces. In the next chapter, molecular symmetry will be shown to be of use in analyzing these various pieces. It should be kept in mind that the contributions caused by E1 terms will dominate, within the long-wavelength approximation, unless symmetry causes these terms to vanish. It is primarily under such circumstances that consideration of M1 and E2 transitions is needed.

III. The Kinetics of Photon Absorption and Emission

A. 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 i to a final state 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

$$R_{i,f} = 2 \operatorname{Re} \langle f, i | \hat{V} | i, i \rangle^2$$

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 $\nu_{f,i}$, 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:

$$\frac{dn_i}{dt} = -R_{i,f} n_i + R_{f,i} n_f$$

$$\frac{dn_f}{dt} = -R_{f,i} n_f + R_{i,f} n_i$$

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 $|\langle f, i | \hat{V} | i, i \rangle|^2$ in the former case and $|\langle f, i | \hat{V} | i, i \rangle|^2$ in the latter. Because the perturbation operator whose matrix elements are $\langle f, i | \hat{V} | i, i \rangle$ and $\langle f, i | \hat{V} | i, i \rangle$ 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 $|\langle f, i | \hat{V} | i, i \rangle|^2 = |\langle f, i | \hat{V} | i, i \rangle|^2$, 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

$$i \text{ in level I } \left(\frac{dn_i}{dt} \right) = \frac{dN_I}{dt}$$

$$f \text{ in level F } \left(\frac{dn_f}{dt} \right) = \frac{dN_F}{dt}$$

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:

$$\frac{dN_i}{dt} = -g_f R_{i,f} N_i + g_i R_{f,i} N_f$$

$$\frac{dN_f}{dt} = -g_i R_{f,i} N_f + g_f R_{i,f} N_i .$$

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.

B. 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: (i) the rate of **stimulated** photon emission as covered above, and (ii) the rate of **spontaneous** photon emission. The former rate $g_f R_{i,f}$ (per molecule) is proportional to the light intensity $g(f_i)$ 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:

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

Clearly, $B_{i,f}$ embodies the final-level degeneracy factor g_f , the perturbation matrix elements, and the 2 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 $g(f,i)$, so it is written by convention as:

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

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:

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

This relationship will prove useful in the following sections.

C. 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):

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

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

where $g = g(\nu)$ denotes the light intensity at the resonance frequency.

At steady state, the populations of these two levels are given by setting $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$:

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

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 (or emit) any further photons because of their state of saturation.

D. 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:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} \exp(-(E_f - E_i)/kT) = \frac{g_f}{g_i} \exp(-h\nu/kT)$$

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 $g(\nu)$ (in $\text{erg cm}^{-3} \text{ sec}^{-1}$) is known to be of the form:

$$g(\nu) = \frac{2(h\nu)^3}{c^3 h^2} (\exp(h\nu/kT) - 1)^{-1} .$$

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:

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} \exp(-h\nu/kT),$$

and using the above black body $g(\nu)$ 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:

$$A_{f,i} = B_{f,i} \frac{2(h\nu)^3}{c^3 h^2}.$$

E. 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

$$A_{f,i} = \frac{2(h\nu)^3}{c^3 h^2} B_{f,i}.$$

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

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

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:

$$\frac{dN_i}{dt} = -g_{B_{i,f}} N_i + (A_{f,i} + g_{B_{f,i}}) N_f$$

$$\frac{dN_f}{dt} = - (A_{f,i} + g_{B_{f,i}}) N_f + g_{B_{i,f}} N_i .$$

These equations possess steady state solutions

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

which, for large g (), produce saturation conditions:

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