

Fig. 2.16a–c. Continuous “bound–free” and discrete “bound–bound” fluorescence transitions of the NaK molecule observed upon laser excitation at $\lambda = 488$ nm: (a) part of the spectrum; (b) enlargement of three discrete vibrational bands; (c) level scheme [2.18]

2.7 Transition Probabilities

The intensities of spectral lines depend not only on the population density of the molecules in the absorbing or emitting level but also on the transition probabilities of the corresponding molecular transitions. If these probabilities are known, the population density can be obtained from measurements of line intensities. This is very important, for example, in astrophysics, where spectral lines represent the main source of information from the extraterrestrial world. Intensity measurements of absorption and emission lines allow the concentration of the elements in stellar atmospheres or in interstellar space to be determined. Comparing the intensities of different lines of the same element (e.g., on the transitions $E_i \rightarrow E_k$ and $E_e \rightarrow E_k$ from different upper levels E_i , E_e to the same lower level E_k) furthermore enables us to derive the temperature of the radiation source from the relative population densities N_i , N_e in the levels E_i and E_e at thermal equilibrium according to (2.18). *All these experiments, however, demand a knowledge of the corresponding transition probabilities.*

There is another aspect that makes measurements of transition probabilities very attractive with regard to a more detailed knowledge of molecular structure. Transition probabilities derived from computed wave functions of upper and lower states are much more sensitive to approximation errors in

these functions than are the energies of these states. Experimentally determined transition probabilities are therefore well suited to test the validity of calculated approximate wave functions. A comparison with computed probabilities allows theoretical models of electronic charge distributions in excited molecular states to be improved [2.19, 2.20].

2.7.1 Lifetimes, Spontaneous and Radiationless Transitions

The probability \mathcal{P}_{ik} that an excited molecule in the level E_i makes a transition to a lower level E_k by spontaneous emission of a fluorescence quantum $h\nu_{ik} = E_i - E_k$ is, according to (2.17), related to the Einstein coefficient A_{ik} by

$$d\mathcal{P}_{ik}/dt = A_{ik} .$$

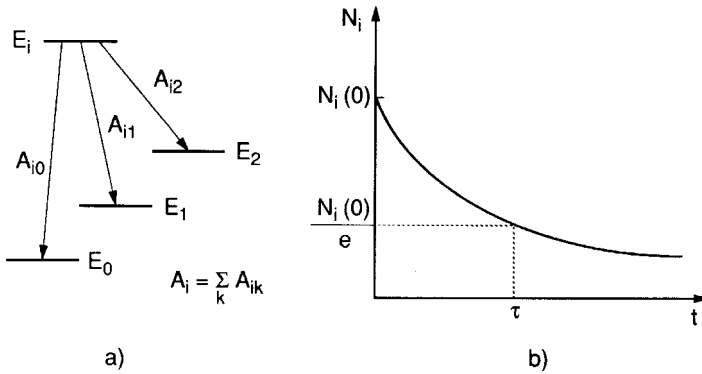


Fig. 2.17a,b. Radiative decay of the level $|i\rangle$: (a) Level scheme; (b) decay curve $N_i(t)$

When several transition paths from E_i to different lower levels E_k are possible (Fig. 2.17), the total transition probability is given by

$$A_i = \sum_k A_{ik} . \quad (2.46)$$

The decrease dN_i of the population density N_i during the time interval dt due to radiative decay is then

$$dN_i = -A_i N_i dt . \quad (2.47)$$

Integration of (2.47) yields

$$N_i(t) = N_{i0} e^{-A_i t} , \quad (2.48)$$

where N_{i0} is the population density at $t = 0$.

After the time $\tau_i = 1/A_i$ the population density N_i has decreased to $1/e$ of its initial value at $t = 0$. The time τ_i represents the *mean spontaneous lifetime*

of the level E_i as can be seen immediately from the definition of the mean time

$$\bar{t}_i = \int_0^{\infty} t \mathcal{P}_i(t) dt = \int_0^{\infty} t A_i e^{-A_i t} dt = \frac{1}{A_i} = \tau_i, \quad (2.49)$$

where $\mathcal{P}_i(t) dt$ is the probability that one atom in the level E_i makes a spontaneous transition within the time interval between t and $t + dt$.

The *radiant power* emitted from N_i molecules on the transition $E_i \rightarrow E_k$ is

$$P_{ik} = N_i h \nu_{ik} A_{ik}. \quad (2.50)$$

If several transitions $E_i \rightarrow E_k$ from the same upper level E_i to different lower levels E_k are possible, the radiant powers of the corresponding spectral lines are proportional to the product of the Einstein coefficient A_{ik} and the photon energy $h \nu_{ik}$. The relative radiation intensities in a certain direction may also depend on the spatial distribution of the fluorescence, which can be different for the different transitions.

The level E_i of the molecule A can be depopulated not only by spontaneous emission but also by collision-induced *radiationless* transitions (Fig. 2.18). The probability $d\mathcal{P}_{ik}^{\text{coll}}/dt$ of such a transition depends on the density N_B of the collision partner B , on the mean relative velocity \bar{v} between A and B , and on the collision cross section $\sigma_{ik}^{\text{coll}}$ for an inelastic collision that induces the transition $E_i \rightarrow E_k$ in the molecule A

$$d\mathcal{P}_{ik}^{\text{coll}}/dt = \bar{v} N_B \sigma_{ik}^{\text{coll}}. \quad (2.51)$$

When the excited molecule $A(E_i)$ is exposed to an intense radiation field, the *induced emission* may become noticeable. It contributes to the depopulation

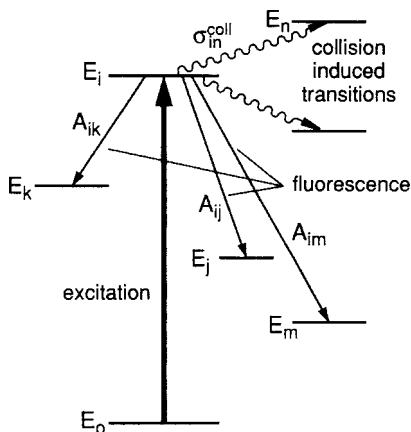


Fig. 2.18. Fluorescence- and collision-induced decay channels of an excited level $|i\rangle$

of level E_i in a transition $|i\rangle \rightarrow |k\rangle$ with the probability

$$d\mathcal{P}_{ik}^{\text{ind}}/dt = \rho(v_{ik})B_{ik}. \quad (2.52)$$

The total transition probability that determines the effective lifetime of a level E_i is then the sum of spontaneous, induced, and collisional contributions, and the mean lifetime τ_i^{eff} becomes

$$\frac{1}{\tau_i^{\text{eff}}} = \sum_k [A_{ik} + \rho(v_{ik})B_{ik} + N_B \sigma_{ik} \bar{v}]. \quad (2.53)$$

Measuring the effective lifetime τ_i^{eff} as a function of the exciting radiation intensity and also its dependence on the density N_B of collision partners (Stern–Vollmer plot) allows one to determine the three transition probabilities separately (Vol. 2, Sect. 8.3).

2.7.2 Semiclassical Description: Basic Equations

In the semiclassical description, the radiation incident upon an atom is described by a classical electromagnetic (EM) plane wave

$$\mathbf{E} = E_0 \cos(\omega t - kz). \quad (2.54a)$$

The atom, on the other hand, is treated quantum-mechanically. In order to simplify the equations, we restrict ourselves to a two-level system with the eigenstates E_a and E_b (Fig. 2.19).

Until now laser spectroscopy was performed in spectral regions where the wavelength λ was large compared to the diameter d of an atom (e.g., in the visible spectrum λ is 500 nm, but d is only about 0.5 nm). For $\lambda \gg d$, the phase of the EM wave does not change much within the volume of an atom because $kz = (2\pi/\lambda)z \ll 1$ for $z \leq d$. We can therefore neglect the spatial derivatives of the field amplitude (dipole approximation). In a coordinate system with its origin in the center of the atom, we can assume $kz \simeq 0$ within the

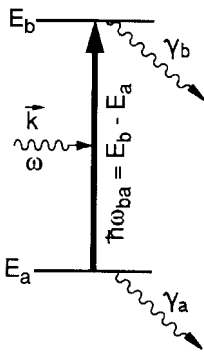


Fig. 2.19. Two-level system with open decay channels into other levels interacting with an EM field

atomic volume, and write (2.54a) in the form

$$\mathbf{E} = \mathbf{E}_0 \cos \omega t = \mathbf{A}_0(e^{i\omega t} + e^{-i\omega t}) \quad \text{with} \quad |\mathbf{A}_0| = \frac{1}{2}E_0. \quad (2.54b)$$

The Hamiltonian operator

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}, \quad (2.55)$$

of the atom interacting with the light field can be written as a sum of the unperturbed Hamiltonian \mathcal{H}_0 of the free atom without the light field plus the perturbation operator \mathcal{V} , which describes the interaction of the atom with the field and which reduces in the *dipole approximation* to

$$\mathcal{V} = \mathbf{p} \cdot \mathbf{E} = \mathbf{p} \cdot \mathbf{E}_0 \cos \omega t, \quad (2.56)$$

where \mathcal{V} is the scalar product of the dipole operator $\mathbf{p} = -e \cdot \mathbf{r}$ and the electric field \mathbf{E} .

The radiation field causes transitions in the atom. This means that the eigenfunctions of the atom become time-dependent. The general solution $\psi(\mathbf{r}, t)$ of the time-dependent Schrödinger equation

$$\mathcal{H}\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (2.57)$$

can be expressed as a linear superposition

$$\psi(\mathbf{r}, t) = \sum_{n=1}^{\infty} c_n(t) u_n(\mathbf{r}) e^{-iE_n t/\hbar}, \quad (2.58)$$

of the eigenfunctions of the unperturbed atom

$$\phi_n(\mathbf{r}, t) = u_n(\mathbf{r}) e^{-iE_n t/\hbar}. \quad (2.59)$$

The spatial parts $u_n(\mathbf{r})$ of these eigenfunctions are solutions of the time-independent Schrödinger equation

$$\mathcal{H}_0 u_n(\mathbf{r}) = E_n u_n(\mathbf{r}), \quad (2.60)$$

and satisfy the orthogonality relations¹

$$\int u_i^* u_k d\tau = \delta_{ik}. \quad (2.61)$$

For our two-level system with the eigenstates $|a\rangle$ and $|b\rangle$ and the energies E_a and E_b , (2.58) reduces to a sum of two terms

$$\psi(\mathbf{r}, t) = a(t) u_a e^{-iE_a t/\hbar} + b(t) u_b e^{-iE_b t/\hbar}. \quad (2.62)$$

¹ Note that in (2.58–2.60) a nondegenerate system has been assumed.

The coefficients $a(t)$ and $b(t)$ are the time-dependent *probability amplitudes* of the atomic states $|a\rangle$ and $|b\rangle$. This means that the value $|a(t)|^2$ gives the probability of finding the system in level $|a\rangle$ at time t . Obviously, the relation $|a(t)|^2 + |b(t)|^2 = 1$ must hold at all times t , if decay into other levels is neglected.

Substituting (2.62) and (2.55) into (2.57) gives

$$i\hbar\dot{a}(t)u_a e^{-iE_a t/\hbar} + i\hbar\dot{b}(t)u_b e^{-iE_b t/\hbar} = a\mathcal{V}u_a e^{-iE_a t/\hbar} + b\mathcal{V}u_b e^{-iE_b t/\hbar}, \quad (2.63)$$

where the relation $\mathcal{H}_0 u_n = E_n u_n$ has been used to cancel equal terms on both sides. Multiplication with u_n^* ($n = a, b$) and spatial integration results in the following two equations

$$\dot{a}(t) = -(i/\hbar)[a(t)V_{aa} + b(t)V_{ab}e^{i\omega_{ab}t}], \quad (2.64a)$$

$$\dot{b}(t) = -(i/\hbar)[b(t)V_{bb} + a(t)V_{ba}e^{-i\omega_{ab}t}], \quad (2.64b)$$

with $\omega_{ab} = (E_a - E_b)/\hbar = -\omega_{ba}$ and with the spatial integral

$$V_{ab} = \int u_a^* \mathcal{V} u_b d\tau = -eE \int u_a^* \mathbf{r} u_b d\tau. \quad (2.65a)$$

Since \mathbf{r} has odd parity, the integrals V_{aa} and V_{bb} vanish when integrating over all coordinates from $-\infty$ to $+\infty$. The quantity

$$\mathbf{D}_{ab} = \mathbf{D}_{ba} = -e \int u_a^* \mathbf{r} u_b d\tau, \quad (2.65b)$$

is called the atomic *dipole matrix element*. It depends on the stationary wave functions u_a and u_b of the two states $|a\rangle$ and $|b\rangle$ and is determined by the charge distribution in these states.

The expectation value \mathbf{D}_{ab} of the dipole matrix element for our two-level system should be distinguished from the expectation value of the dipole moment in a specific state $|\psi\rangle$

$$\mathbf{D} = -e \int \psi^* \mathbf{r} \psi d\tau = 0 \quad (2.66a)$$

which is zero because the integrand is an odd function of the coordinates. Using (2.62) and the abbreviation $\omega_{ba} = (E_b - E_a)/\hbar = -\omega_{ab}$, this can be expressed by the coefficients $a(t)$ and $b(t)$, and by the matrix element \mathbf{D}_{ab} as

$$\mathbf{D} = -\mathbf{D}_{ab}(a^* b e^{-i\omega_{ba}t} + ab^* e^{+i\omega_{ba}t}) = D_0 \cos(\omega_{ba}t + \varphi), \quad (2.66b)$$

with

$$D_0 = D_{ab} |a^* b| \quad \text{and} \quad \tan \varphi = -\frac{\text{Im}\{a^* b\}}{\text{Re}\{a^* b\}}.$$

Even without the external field, the expectation value of the atomic dipole moment oscillates with the eigenfrequency ω_{ba} and the amplitude $|a^* \cdot b|$ if the

wavefunction of the atomic system can be represented by the superposition (2.65). The time average of this oscillation's dipole moment is zero!

Using (2.54b) for the EM field and the abbreviation

$$\Omega_{ab} = D_{ab}E_0/\hbar = 2D_{ab}A_0/\hbar = \Omega_{ba} \quad (2.67)$$

which depends on the field amplitude E_0 and the dipole matrix element D_{ab} , (2.64) reduces to

$$\dot{a}(t) = -(i/2)\Omega_{ab}(e^{i(\omega-\omega_{ba})t} + e^{-i(\omega+\omega_{ba})t})b(t), \quad (2.68a)$$

$$\dot{b}(t) = -(i/2)\Omega_{ab}(e^{-i(\omega-\omega_{ba})t} + e^{i(\omega+\omega_{ba})t})a(t). \quad (2.68b)$$

where $\omega_{ba} = -\omega_{ab} > 0$.

These are the basic equations that must be solved to obtain the probability amplitudes $a(t)$ and $b(t)$. The frequency Ω_{ab} is called the Rabi frequency. Its physical interpretation will be discussed in Sect. 2.7.6.

2.7.3 Weak-Field Approximation

Suppose that at time $t = 0$, the atoms are in the lower state E_a , which implies that $a(0) = 1$ and $b(0) = 0$. We assume the field amplitude A_0 to be sufficiently small so that for times $t < T$ the population of E_b remains small compared with that of E_a , i.e., $|b(t < T)|^2 \ll 1$. Under this *weak-field condition* we can solve (2.68) with an iterative procedure starting with $a = 1$ and $b = 0$. Using thermal radiation sources, the field amplitude A_0 is generally small enough to make the first iteration step already sufficiently accurate.

With these assumptions the first approximation of (2.68) gives

$$\dot{a}(t) = 0, \quad (2.69a)$$

$$\dot{b}(t) = -(i/2)\Omega_{ba}(e^{i(\omega_{ba}-\omega)t} + e^{i(\omega_{ba}+\omega)t}). \quad (2.69b)$$

With the initial conditions $a(0) = 1$ and $b(0) = 0$, integration of (2.69) from 0 to t yields

$$a(t) = a(0) = 1, \quad (2.70a)$$

$$b(t) = \left(\frac{\Omega_{ab}}{2}\right) \left(\frac{e^{i(\omega-\omega_{ba})t} - 1}{\omega - \omega_{ba}} - \frac{e^{i(\omega+\omega_{ba})t} - 1}{\omega + \omega_{ba}} \right). \quad (2.70b)$$

For $E_b > E_a$ the term $\omega_{ba} = (E_b - E_a)/\hbar$ is positive. In the transition $E_a \rightarrow E_b$, the atomic system absorbs energy from the radiation field. Noticeable absorption occurs, however, only if the field frequency ω is close to the eigenfrequency ω_{ba} . In the optical frequency range this implies that $|\omega_{ba} - \omega| \ll \omega_{ba}$. The second term in (2.70b) is then small compared to the

first one and may be neglected. This is called the *rotating-wave approximation* for only that term is kept in which the atomic wave functions and the field waves with the phasors $\exp(-i\omega_{ab}t)$ and $\exp(-i\omega t)$ rotate together.

In the rotating-wave approximation we obtain from (2.70b) for the probability $|b(t)|^2$ that the system is at time t in the upper level E_b

$$|b(t)|^2 = \left(\frac{\Omega_{ab}}{2} \right)^2 \left(\frac{\sin(\omega - \omega_{ba})t/2}{(\omega - \omega_{ba})/2} \right)^2. \quad (2.71)$$

Since we had assumed that the atom was at $t = 0$ in the lower level E_a , (2.71) gives the transition probability for the atom to go from E_a to E_b during the time t . Figure 2.20a illustrates this transition probability as a function of the detuning $\Delta\omega = \omega - \omega_{ba}$. Equation (2.71) shows that $|b(t)|^2$ depends on the absolute value of the detuning $\Delta\omega = |\omega - \omega_{ba}|$ of the field frequency ω from the eigenfrequency ω_{ba} . When tuning the frequency ω into resonance with the atomic system ($\omega \rightarrow \omega_{ba}$), the second factor in (2.71) approaches the value t^2 because $\lim_{x \rightarrow 0}[(\sin^2 xt)/x^2] = t^2$. The transition probability at resonance,

$$|b(t)|^2_{\omega=\omega_{ba}} = \left(\frac{\Omega_{ab}}{2} \right)^2 t^2, \quad (2.72)$$

increases proportionally to t^2 . The approximation used in deriving (2.71) has, however, anticipated that $|b(t)|^2 \ll 1$. According to (2.72) and (2.67), this assumption for the resonance case is equivalent to

$$\left(\frac{\Omega_{ab}}{2} \right)^2 t^2 \ll 1 \quad \text{or} \quad t \ll T = \frac{2}{\Omega_{ab}} = \frac{\hbar}{D_{ab}E_0}. \quad (2.73)$$

Our small-signal approximation only holds if the interaction time t of the field (amplitude E_0) with the atom (matrix element D_{ab}) is restricted to $t \ll T = \hbar/(D_{ab}E_0)$. Because the spectral analysis of a wave with the finite detection time T gives the spectral width $\Delta\omega \simeq 1/T$ (see also Sect. 3.2), we

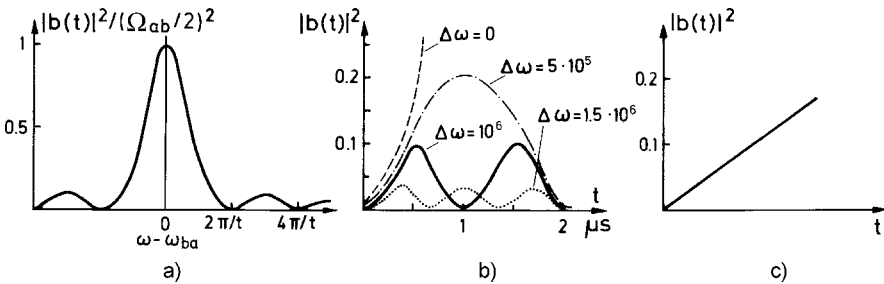


Fig. 2.20. (a) Normalized transition probability for monochromatic excitation as a function of the detuning $(\omega - \omega_{ba})$ in the rotating-wave approximation; (b) probability of a transition to the upper level as a function of time for different detuning; (c) $|b(t)|^2$ under broadband excitation and weak fields

cannot assume monochromaticity, but have to take into account the frequency distribution of the interaction term.

2.7.4 Transition Probabilities with Broad-Band Excitation

In general, thermal radiation sources have a bandwidth $\delta\omega$, which is much larger than the Fourier limit $\Delta\omega = 1/T$. Therefore, the finite interaction time imposes no extra limitation. This may change, however, when lasers are considered (Sects. 2.7.5 and 3.4).

Instead of the field amplitude E_0 (which refers to a unit frequency interval), we introduce the spectral energy density $\rho(\omega)$ within the frequency range of the absorption line by the relation, see (2.30),

$$\int \rho(\omega) d\omega = \epsilon_0 E_0^2 / 2 = 2\epsilon_0 A_0^2.$$

We can now generalize (2.71) to include the interaction of broadband radiation with our two-level system by integrating (2.71) over all frequencies ω of the radiation field. This yields the total transition probability $\mathcal{P}_{ab}(t)$ within the time T . If $\mathbf{D}_{ab} \parallel \mathbf{E}_0$, we obtain with $\Omega_{ab} = D_{ab}E_0/\hbar$

$$\mathcal{P}_{ab}(t) = \int |b(t)|^2 d\omega = \frac{(\mathbf{D}_{ab})^2}{2\epsilon_0 \hbar^2} \int \rho(\omega) \left(\frac{\sin(\omega_{ba} - \omega)t/2}{(\omega_{ba} - \omega)/2} \right)^2 d\omega. \quad (2.74)$$

For thermal light sources or broadband lasers, $\rho(\omega)$ is slowly varying over the absorption line profile. It is essentially constant over the frequency range where the factor $[\sin^2(\omega_{ba} - \omega)t/2]/[(\omega_{ba} - \omega)/2]^2$ is large (Fig. 2.20a). We can therefore replace $\rho(\omega)$ by its resonance value $\rho(\omega_{ba})$. The integration can then be performed, which gives the value $\rho(\omega_{ba})2\pi t$ for the integral because

$$\int_{-\infty}^{\infty} \frac{\sin^2(xt)}{x^2} dx = 2\pi t.$$

For broadband excitation, the transition probability for the time interval between 0 and t

$$\mathcal{P}_{ab}(t) = \frac{\pi}{\epsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba}) t, \quad (2.75)$$

is linearly dependent on t (Fig. 2.20c).

For broadband excitation the *transition probability per second*

$$\frac{d}{dt} \mathcal{P}_{ab} = \frac{\pi}{\epsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba}), \quad (2.76)$$

becomes independent of time!

To compare this result with the Einstein coefficient B_{ab} derived in Sect. 2.3, we must take into account that the blackbody radiation was isotropic, whereas the EM wave (2.54) used in the derivation of (2.76) propagates into one direction. For randomly oriented atoms with the dipole moment \mathbf{p} , the averaged component of \mathbf{p}^2 in the z -direction is $\langle p_z^2 \rangle = p^2 \langle \cos^2 \theta \rangle = p^2/3$.

In the case of isotropic radiation, the interaction term $D_{ab}^2 \rho(\omega_{ba})$ therefore has to be divided by a factor of 3. A comparison of (2.16) with the modified equation (2.76) yields

$$\frac{d}{dt} \mathcal{P}_{ab} = \frac{\pi}{3\epsilon_0 \hbar^2} \rho(\omega_{ba}) D_{ab}^2 = \rho(\omega_{ba}) B_{ab}. \quad (2.77)$$

With the definition (2.65) for the dipole matrix element D_{ik} , the Einstein coefficient B_{ik} of induced absorption $E_i \rightarrow E_k$ finally becomes

$$B_{ik}^\omega = \frac{\pi e^2}{3\epsilon_0 \hbar^2} \left| \int u_i^* \mathbf{r} u_k d\tau \right|^2 \quad \text{and} \quad B_{ik}^\nu = B_{ik}^\omega / 2\pi. \quad (2.78)$$

Equation (2.78) gives the Einstein coefficient for a one-electron system where $\mathbf{r} = (x, y, z)$ is the vector from the nucleus to the electron, and $u_n(x, y, z)$ denotes the one-electron wave functions.² From (2.78) we learn that the **Einstein coefficient B_{ik} is proportional to the squared transition dipole moment.**

So far we have assumed that the energy levels E_i and E_k are not degenerate, and therefore have the statistical weight factor $g = 1$. In the case of a degenerate level $|k\rangle$, the total transition probability ρB_{ik} of the transition $E_i \rightarrow E_k$ is the sum

$$\rho B_{ik} = \rho \sum_n B_{ik_n},$$

over all transitions to the sublevels $|k_n\rangle$ of $|k\rangle$. If level $|i\rangle$ is also degenerate, an additional summation over all sublevels $|i_m\rangle$ is necessary, taking into account that the population of each sublevel $|i_m\rangle$ is only the fraction N_i/g_i .

The Einstein coefficient B_{ik} for the transition $E_i \rightarrow E_k$ between the two degenerate levels $|i\rangle$ and $|k\rangle$ is therefore

$$B_{ik} = \frac{\pi}{3\epsilon_0 \hbar^2} \frac{1}{g_i} \sum_{m=1}^{g_i} \sum_{n=1}^{g_k} |D_{i_m k_n}|^2 = \frac{\pi}{3\epsilon_0 \hbar^2 g_i} S_{ik}. \quad (2.79)$$

The double sum is called the *line strength* S_{ik} of the atomic transition $|i\rangle \leftarrow |k\rangle$.

² Note that when using the frequency $\nu = \omega/2\pi$ instead of ω , the spectral energy density $\rho(\nu)$ per unit frequency interval is larger by a factor of 2π than $\rho(\omega)$ because a unit frequency interval $d\nu = 1 \text{ Hz}$ corresponds to $d\omega = 2\pi \text{ [Hz]}$. The right-hand side of (2.78) must then be divided by a factor of 2π , since $B_{ik}^\nu \rho(\nu) = B_{ik}^\omega \rho(\omega)$.

2.7.5 Phenomenological Inclusion of Decay Phenomena

So far we have neglected the fact that the levels $|a\rangle$ and $|b\rangle$ are not only coupled by transitions induced by the external field but may also decay by spontaneous emission or by other relaxation processes such as collision-induced transitions. We can include these decay phenomena in our formulas by adding phenomenological decay terms to (2.68), which can be expressed by the decay constant γ_a and γ_b (Fig. 2.19). A rigorous treatment requires quantum electrodynamics [2.23].

In the rotating-wave approximation, for which the term with the frequency $(\omega_{ba} + \omega)$ is neglected, (2.68) then becomes

$$\dot{a}(t) = -\frac{1}{2}\gamma_a a - \frac{i}{2}\Omega_{ab} e^{-i(\omega_{ba}-\omega)t} b(t), \quad (2.80a)$$

$$\dot{b}(t) = -\frac{1}{2}\gamma_b b - \frac{i}{2}\Omega_{ab} e^{+i(\omega_{ba}-\omega)t} a(t). \quad (2.80b)$$

When the field amplitude E_0 is sufficiently small, see (2.73), we can use the weak-signal approximation of Sect. 2.7.3. This means that $|a(t)|^2 = 1$, $|b(t)|^2 \ll 1$, and also $aa^* - bb^* \simeq 1$. With this approximation, one obtains in a similar way as in the derivation of (2.71) the transition probability

$$\mathcal{P}_{ab}(\omega) = |b(t, \omega)|^2 = \int \gamma_{ab} e^{-\gamma_{ab}t} |b(t)|^2 dt = \frac{1}{2} \frac{\Omega_{ab}^2}{(\omega_{ba} - \omega)^2 + (\frac{1}{2}\gamma_{ab})^2}. \quad (2.80c)$$

This is a Lorentzian line profile (Fig. 2.21) with a full halfwidth $\gamma_{ab} = \gamma_a + \gamma_b$.

After taking the second-time derivative of (2.66b) and using (2.80), the equation of motion for the dipole moment D of the atom under the influence of a radiation field, becomes

$$\begin{aligned} \ddot{D} + \gamma_{ab} \dot{D} + (\omega_{ba}^2 + \gamma_{ab}^2/4) D \\ = (\Omega_{ab}) [(\omega_{ba} + \omega) \cos \omega t + (\gamma_{ab}/2) \sin \omega t]. \end{aligned} \quad (2.81a)$$

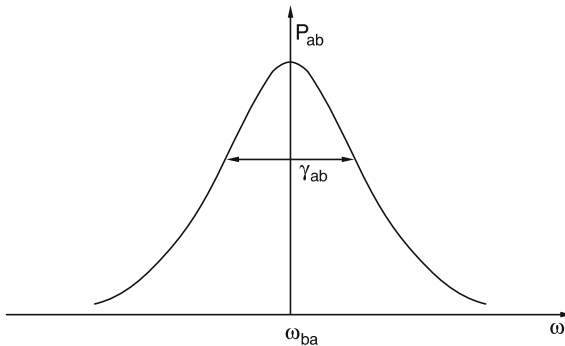


Fig. 2.21. Transition probability of a damped system under weak broadband excitation

The homogeneous equation

$$\ddot{D} + \gamma_{ab}\dot{D} + (\omega_{ba}^2 + \gamma_{ab}^2/4)D = 0, \quad (2.81b)$$

which describes the atomic dipoles without the driving field ($\Omega_{ab} = 0$), has the solution for weak damping ($\gamma_{ab} \ll \omega_{ba}$)

$$D(t) = D_0 e^{(-\gamma_{ab}/2)t} \cos \omega_{ba} t. \quad (2.82)$$

The inhomogeneous equation (2.81a) shows that the induced dipole moment of the atom interacting with a monochromatic radiation field behaves like a driven damped harmonic oscillator with $\omega_{ba} = (E_b - E_a)/\hbar$ for the eigenfrequency and $\gamma_{ab} = (\gamma_a + \gamma_b)$ for the damping constant oscillating at the driving field frequency ω .

Using the approximation $(\omega_{ba} + \omega) \simeq 2\omega$ and $\gamma_{ab} \ll \omega_{ba}$, which means weak damping and a close-to-resonance situation, we obtain solutions of the form

$$D = D_1 \cos \omega t + D_2 \sin \omega t, \quad (2.83)$$

where the factors D_1 and D_2 include the frequency dependence,

$$D_1 = \frac{\Omega_{ab}(\omega_{ba} - \omega)}{(\omega_{ba} - \omega)^2 + (\gamma_{ab}/2)^2}, \quad (2.84a)$$

$$D_2 = \frac{\frac{1}{2}\Omega_{ab}\gamma_{ab}}{(\omega_{ba} - \omega)^2 + (\gamma_{ab}/2)^2}. \quad (2.84b)$$

These two equations for D_1 and D_2 describe dispersion and absorption of the EM wave. The former is caused by the phase lag between the radiation field and the induced dipole oscillation, and the latter by the atomic transition from the lower level E_a to the upper level E_b and the resultant conversion of the field energy into the potential energy $(E_b - E_a)$.

The macroscopic polarization \mathbf{P} of a sample with N atoms/cm³ is related to the induced dipole moment \mathbf{D} by $\mathbf{P} = N\mathbf{D}$.

2.7.6 Interaction with Strong Fields

In the previous sections we assumed weak-field conditions where the probability of finding the atom in the initial state was not essentially changed by the interaction with the field. This means that the population in the initial state remains approximately constant during the interaction time. In the case of broadband radiation, this approximation results in a *time-independent transition probability*. Also the inclusion of weak-damping terms with $\gamma_{ab} \ll \omega_{ba}$ did not affect the assumption of a constant population in the initial state.

When intense laser beams are used for the excitation of atomic transitions, the weak-field approximation is no longer valid. In this section, we therefore consider the “strong-field case.” The corresponding theory, developed by

Rabi, leads to a time-dependent probability of the atom being in either the upper or lower level. The representation outlined below follows that of [2.21].

We consider a monochromatic field of frequency ω and start from the basic equations (2.68) for the probability amplitudes in the rotating wave approximation with $\omega_{ba} = -\omega_{ab}$

$$\dot{a}(t) = \frac{i}{2}\Omega_{ab} e^{-i(\omega_{ba}-\omega)t} b(t), \quad (2.85a)$$

$$\dot{b}(t) = \frac{i}{2}\Omega_{ab} e^{+i(\omega_{ba}-\omega)t} a(t). \quad (2.85b)$$

Inserting the trial solution

$$a(t) = e^{i\mu t} \Rightarrow \dot{a}(t) = i\mu e^{i\mu t},$$

into (2.85a) yields

$$b(t) = \frac{2\mu}{\Omega_{ab}} e^{i(\omega_{ba}-\omega+\mu)t} \Rightarrow \dot{b}(t) = \frac{2i\mu(\omega_{ba}-\omega+\mu)}{\Omega_{ab}} e^{i(\omega_{ba}-\omega+\mu)t}.$$

Substituting this back into (2.85b) gives the relation

$$2\mu(\omega_{ba}-\omega+\mu) = \Omega_{ab}^2/2.$$

This is a quadratic equation for the unknown quantity μ with the two solutions

$$\mu_{1,2} = -\frac{1}{2}(\omega_{ba}-\omega) \pm \frac{1}{2}\sqrt{(\omega_{ba}-\omega)^2 + \Omega_{ab}^2}. \quad (2.86)$$

The general solutions for the amplitudes a and b are then

$$a(t) = C_1 e^{i\mu_1 t} + C_2 e^{i\mu_2 t}, \quad (2.87a)$$

$$b(t) = (2/\Omega_{ab}) e^{i(\omega_{ba}-\omega)t} (C_1 \mu_1 e^{i\mu_1 t} + C_2 \mu_2 e^{i\mu_2 t}). \quad (2.87b)$$

With the initial conditions $a(0) = 1$ and $b(0) = 0$, we find for the coefficients

$$\begin{aligned} C_1 + C_2 &= 1 \quad \text{and} \quad C_1 \mu_1 = -C_2 \mu_2, \\ \Rightarrow C_1 &= -\frac{\mu_2}{\mu_1 - \mu_2} \quad C_2 = +\frac{\mu_1}{\mu_1 - \mu_2}. \end{aligned}$$

From (2.86) we obtain $\mu_1 \mu_2 = -\Omega_{ab}^2/4$. With the shorthand

$$\Omega = \mu_1 - \mu_2 = \sqrt{(\omega_{ba}-\omega)^2 + \Omega_{ab}^2},$$

we get the probability amplitude

$$b(t) = i(\Omega_{ab}/\Omega) e^{i(\omega_{ba}-\omega)t/2} \sin(\Omega t/2). \quad (2.88)$$

The probability $|b(t)|^2 = b(t)b^*(t)$ of finding the system in level E_b is then

$$|b(t)|^2 = (\Omega_{ab}/\Omega)^2 \sin^2(\Omega t/2), \quad (2.89)$$

where

$$\Omega = \sqrt{(\omega_{ba} - \omega)^2 + (\mathbf{D}_{ab} \cdot \mathbf{E}_0 / \hbar)^2} \quad (2.90)$$

is called the general “*Rabi flopping frequency*” for the nonresonant case $\omega \neq \omega_{ba}$. Equation (2.89) reveals that the transition probability is a periodic function of time. Since

$$|a(t)|^2 = 1 - |b(t)|^2 = 1 - (\Omega_{ab}/\Omega)^2 \sin^2(\Omega t/2), \quad (2.91)$$

the system oscillates with the frequency Ω between the levels E_a and E_b , where the level-flopping frequency Ω depends on the detuning $(\omega_{ba} - \omega)$, on the field amplitude E_0 , and the matrix element D_{ab} (Fig. 2.20b).

The general Rabi flopping frequency Ω gives the frequency of population oscillation in a two-level system in an electromagnetic field with amplitude E_0 .

Note: In the literature often the term “Rabi frequency” is restricted to the resonant case $\omega = \omega_{ba}$.

At resonance $\omega_{ba} = \omega$, and (2.89) and (2.91) reduce to

$$|a(t)|^2 = \cos^2(\mathbf{D}_{ab} \cdot \mathbf{E}_0 t / 2\hbar), \quad (2.92a)$$

$$|b(t)|^2 = \sin^2(\mathbf{D}_{ab} \cdot \mathbf{E}_0 t / 2\hbar). \quad (2.92b)$$

After a time

$$T = \pi\hbar / (\mathbf{D}_{ab} \cdot \mathbf{E}_0) = \pi / \Omega_{ab}, \quad (2.93)$$

the probability $|b(t)|^2$ of finding the system in level E_b becomes unity. This means that the population probability $|a(0)|^2 = 1$ and $|b(0)|^2 = 0$ of the initial system has been inverted to $|a(T)|^2 = 0$ and $|b(T)|^2 = 1$ (Fig. 2.22).

Radiation with the amplitude A_0 , which resonantly interacts with the atomic system for exactly the time interval $T = \pi\hbar / (\mathbf{D}_{ab} \cdot \mathbf{E}_0)$, is called a π -pulse because it changes the phases of the probability amplitudes $a(t)$, $b(t)$ by π , see (2.87, 2.88).

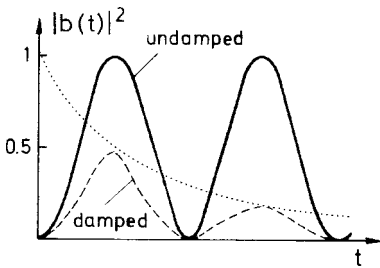


Fig. 2.22. Population probability $|b(t)|^2$ of the levels E_b altering with the Rabi flopping frequency due to the interaction with a strong field. The resonant case is shown without damping and with damping due to decay channels into other levels. The decaying curve represents the factor $\exp[-(\gamma_{ab}/2)t]$

We now include the damping terms γ_a and γ_b , and again insert the trial solution

$$a(t) = e^{i\mu t} ,$$

into (2.80a, 2.80b). Similar to the procedure used for the undamped case, this gives a quadratic equation for the parameter μ with the two complex solutions

$$\mu_{1,2} = -\frac{1}{2} \left(\omega_{ba} - \omega - \frac{i}{2} \gamma_{ab} \right) \pm \frac{1}{2} \sqrt{\left(\omega_{ba} - \omega - \frac{i}{2} \gamma \right)^2 + \Omega_{ab}^2} ,$$

where

$$\gamma_{ab} = \gamma_a + \gamma_b \quad \text{and} \quad \gamma = \gamma_a - \gamma_b . \quad (2.94)$$

From the general solution

$$a(t) = C_1 e^{i\mu_1 t} + C_2 e^{i\mu_2 t} ,$$

we obtain from (2.80a) with the initial conditions $|a(0)|^2 = 1$ and $|b(0)|^2 = 0$ the transition probability

$$|b(t)|^2 = \frac{\Omega_{ab}^2 e^{(-\gamma_{ab}/2)t} [\sin(\Omega/2)t]^2}{(\omega_{ba} - \omega)^2 + (\gamma/2)^2 + \Omega_{ab}^2} . \quad (2.95)$$

This is a damped oscillation (Fig. 2.22) with the damping constant $\frac{1}{2} \gamma_{ab} = (\gamma_a + \gamma_b)/2$, the Rabi flopping frequency

$$\Omega = \mu_1 - \mu_2 = \sqrt{\left(\omega_{ba} - \omega + \frac{i}{2} \gamma \right)^2 + \Omega_{ab}^2} , \quad (2.96)$$

and the envelope $\Omega_{ab}^2 e^{-(\gamma_{ab}/2)t} / [(\omega_{ba} - \omega)^2 + (\gamma/2)^2 + \Omega_{ab}^2]$. The spectral profile of the transition probability is Lorentzian (Sect. 3.1), with a half-width depending on $\gamma = \gamma_a - \gamma_b$ and on the strength of the interaction. Since $\Omega_{ab}^2 = (\mathbf{D}_{ab} \cdot \mathbf{E}_0 / \hbar)^2$ is proportional to the intensity of the electromagnetic wave, the linewidth *increases* with increasing intensity (saturation broadening, Sect. 3.5). Note, that $|a(t)|^2 + |b(t)|^2 < 1$ for $t > 0$, because the levels a and b can decay into other levels.

In some cases the two-level system may be regarded as isolated from its environment. The relaxation processes then occur only between the levels $|a\rangle$ and $|b\rangle$, but do not connect the system with other levels. This implies $|a(t)|^2 + |b(t)|^2 = 1$. Equation (2.80) then must be modified as

$$\dot{a}(t) = -\frac{1}{2} \gamma_a a(t) + \frac{1}{2} \gamma_b b(t) + \frac{i}{2} \Omega_{ab} e^{-i(\omega_{ba} - \omega)t} b(t) , \quad (2.97a)$$

$$\dot{b}(t) = -\frac{1}{2} \gamma_b b(t) + \frac{1}{2} \gamma_a a(t) + \frac{i}{2} \Omega_{ab} e^{+i(\omega_{ba} - \omega)t} a(t) . \quad (2.97b)$$

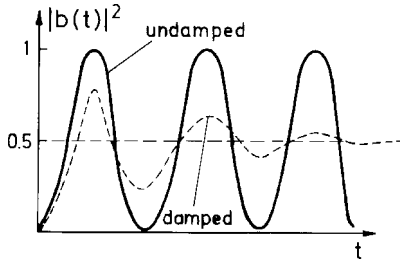


Fig. 2.23. Population of level $|b\rangle$ for a closed two-level system where the relaxation channels are open only for transitions between $|a\rangle$ and $|b\rangle$

The trial solution $a = \exp(i\mu t)$ yields, for the resonance case $\omega = \omega_{ba}$, the two solutions

$$\mu_1 = \frac{1}{2}\Omega_{ab} + \frac{i}{2}\gamma_{ab}, \quad \mu_2 = -\frac{1}{2}\Omega_{ab},$$

and for the transition probability $|b(t)|^2$, one obtains with $|a(0)|^2 = 1$, $|b(0)|^2 = 0$ a damped oscillation that approaches the steady-state value

$$|b(t = \infty)|^2 = \frac{1}{2} \frac{\Omega_{ab}^2 + \gamma_a \gamma_b}{\Omega_{ab}^2 + (\frac{1}{2}\gamma_{ab})^2}. \quad (2.98)$$

This is illustrated in Fig. 2.23 for the special case $\gamma_a = \gamma_b$ where $|b(\infty)|^2 = 1/2$, which means that the two levels become equally populated.

For a more detailed treatment see [2.21–2.24].

2.7.7 Relations Between Transition Probabilities, Absorption Coefficient, and Line Strength

In this section we will summarize important relations between the different quantities discussed so far.

The absorption coefficient $\alpha(\omega)$ for a transition between levels $|i\rangle$ and $|k\rangle$ with population densities N_i and N_k and statistical weights g_i , g_k is related to the absorption cross section $\sigma_{ik}(\omega)$ by

$$\alpha(\omega) = [N_i - (g_i/g_k)N_k]\sigma_{ik}(\omega). \quad (2.99)$$

The Einstein coefficient for absorption B_{ik} is given by

$$B_{ik} = \frac{c}{\hbar\omega} \int_0^\infty \sigma_{ik}(\omega) d\omega = \frac{c \bar{\sigma}_{ik}}{\hbar\omega} \int_0^\infty g(\omega - \omega_0) d\omega \quad (2.100)$$

where $g(\omega - \omega_0)$ is the line profile of the absorbing transition at center frequency ω_0 . The transition probability per second according to (2.15) is then

$$P_{ik} = B_{ik} \cdot \mathcal{Q} = \frac{c}{\hbar\omega \cdot \Delta\omega} \int \mathcal{Q}(\omega) \cdot \sigma_{ik}(\omega) d\omega, \quad (2.101)$$

where $\Delta\omega$ is the spectral linewidth of the transition.

The line strength S_{ik} of a transition is defined as the sum

$$S_{ik} = \sum_{m_i, m_k} |D_{m_i, m_k}|^2 = |D_{ik}|^2, \quad (2.102)$$

over all dipole-allowed transitions between all subcomponents m_i , m_k of levels $|i\rangle$, $|k\rangle$. The oscillator strength f_{ik} gives the ratio of the power absorbed by a molecule on the transition $|i\rangle \rightarrow |k\rangle$ to the power absorbed by a classical oscillator on its eigenfrequency $\omega_{ik} = (E_k - E_i)/\hbar$.

Some of these relations are compiled in Table 2.2.

Table 2.2. Relations between the transition matrix element D_{ik} and the Einstein coefficients A_{ik} , B_{ik} , the oscillator strength f_{ik} , the absorption cross section σ_{ik} , and the line strength S_{ik} . The numerical values are obtained, when λ [m], B_{ik} [$\text{m}^3\text{s}^{-2}\text{J}^{-1}$], D_{ik} [As m], m_c [kg]

$A_{ki} = \frac{1}{g_k} \frac{16\pi^3 \nu^3}{3\epsilon_0 \hbar c^3} D_{ik} ^2$ $= \frac{2.82 \times 10^{45}}{g_k \cdot \lambda^3} D_{ik} ^2 \text{ s}^{-1}$	$B_{ik}^{(v)} = \frac{1}{g_i} \frac{2\pi^2}{3\epsilon_0 \hbar^2} D_{ik} ^2$ $= 6 \times 10^{31} \lambda^3 \frac{g_i}{g_k} A_{ki}$	$B_{ik}^{(\omega)} = \frac{1}{g_i} \frac{\pi}{3\epsilon_0 \hbar^2} D_{ik} ^2$ $= \frac{g_k}{g_i} B_{ki}$
$f_{ik} = \frac{1}{g_i} \frac{8\pi^2 m_e \nu}{e^2 \hbar} D_{ik} ^2$ $= \frac{g_k}{g_i} \cdot 4.5 \times 10^4 \lambda^2 A_{ki}$	$S_{ik} = D_{ik} ^2$ $= (7.8 \times 10^{-21} g_i \lambda) f_{ik}$	$\sigma_{ik} = \frac{1}{\Delta \nu} \frac{2\pi^2 \nu}{3\epsilon_0 \hbar g_i} \cdot S_{ik}$ $B_{ik} = \frac{c}{h\nu} \int_0^\infty \sigma_{ik}(\nu) d\nu$

2.8 Coherence Properties of Radiation Fields

The radiation emitted by an extended source S generates a total field amplitude A at the point P that is a superposition of an infinite number of partial waves with the amplitudes A_n and the phases ϕ_n emitted from the different surface elements dS (Fig. 2.24), i.e.,

$$A(P) = \sum_n A_n(P) e^{i\phi_n(P)} = \sum_n [A_n(0)/r_n^2] e^{i(\phi_{n0} + 2\pi r_n/\lambda)}, \quad (2.103)$$

where $\phi_{n0}(t) = \omega t + \phi_n(0)$ is the phase of the n th partial wave at the surface element dS of the source. The phases $\phi_n(r_n, t) = \phi_{n,0}(t) + 2\pi r_n/\lambda$ depend on the distances r_n from the source and on the angular frequency ω .

If the phase differences $\Delta\phi_n = \phi_n(P, t_1) - \phi_n(P, t_2)$ at a given point P between two different times t_1 , t_2 are nearly the same for all partial waves, the radiation field at P is *temporally coherent*. The maximum time interval $\Delta t = t_2 - t_1$ for which $\Delta\phi_n$ for all partial waves differ by less than π is termed the *coherence time* of the radiation source. The path length $\Delta s_c = c\Delta t$ traveled by the wave during the coherence time Δt is the *coherence length*.