COURSE 1

ATOMS IN STRONG RESONANT FIELDS

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Contents

Balian et al., ed. Les Houches, Session XXVII, 1975 – Aux frontières de la spectroscopie laser / Frontiers in laser spectroscopy

1. General introduction

1.1. What questions do we try to answer in this course?

How do atoms behave in strong resonant (or quasi-resonant) light beams? What kind of light do they emit? (intensity, polarization, spectral distribution ...).

1.2. Why do we study these problems?

Spectroscopic interest. A lot of spectroscopic information (g factors, fine or hyperfine structures, radiative lifetimes ...) is obtained by looking at the fluorescence light reemitted by free atoms irradiated by a resonant light beam. It is important to have a quantitative theory connecting the detection signals to the atomic parameters, and giving in particular the perturbation associated with the light beam (radiative broadenings, light-shifts ...).

Theoretical interest. How are the lowest order QED predictions modified at high intensities? Comparison between various theoretical approaches providing a better understanding of the interaction processes between atoms and photons.

1.3. Concrete examples of experiments we are dealing with

Fig. 1a: Atoms in a resonance cell are irradiated by a polarized laser beam. One measures with a photomultiplier the total intensity L_F of the fluorescence light reemitted with a given polarization in a given direction. One slowly sweeps a static magnetic field B_0 applied to the atoms and one records the variations of L_F with B_0 (level crossing resonances).

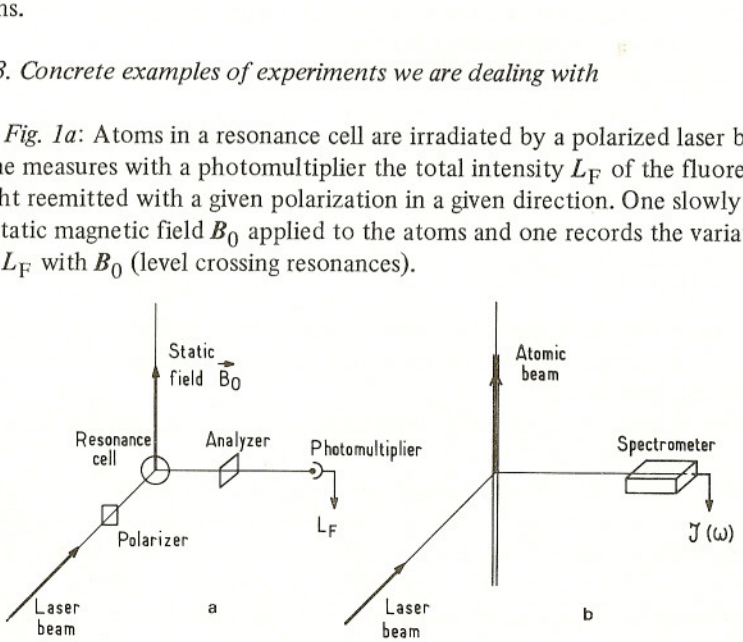

Fig. 1.

What kind of variations do we get? How does the shape of the curve change when we increase the laser intensity? What kind of information can we extract from these curves?

Possible variants: Double resonance, quantum beats, ...

Fig. 1b: An atomic beam is irradiated at right angle by a laser beam (no Doppler effect). In the third perpendicular direction, a spectrometer records the spectral distribution $\mathcal{I}(\omega)$ of the fluorescence light.

Is the scattering elastic or inelastic? What are the changes observed on $\mathcal{I}(\omega)$ when the laser intensity increases?

1.4. What effects do we neglect? Why?

We neglect interferences between light waves scattered by different atoms. These atoms are randomly distributed, separated by distances large compared to λ, and we look at the fluorescence light reemitted *not in the forward but in a lateral direction.* Consequently the relative phases of the light waves scattered by different atoms are random and the coherence area of the scattered light is negligible.

We neglect any coupling between atoms due to collisions or to a common coupling to the radiation field (superradiance, multiple scattering ...). We only consider very dilute vapors or atomic beams.

We neglect the reaction of atoms on the incident beam (for the same reason).

To summarize, we calculate the light scattered by each atom from a *given* incident light beam, and we add the *intensities* corresponding to the various atoms.

1.5. Brief survey of the course

We start with a simple problem: spectral distribution $\mathcal{I}(\omega)$ of the fluorescence light emitted by a two-level atom, and we try two approaches for dealing with this problem.

(i) We recall lowest order QED predictions and we try to calculate some higher order corrections.

(ii) We treat to all orders the coupling between the atoms and the incident light, and we consider only one single spontaneous emission process calculated by Fermi's golden rule. We discuss the difficulties encountered in these two approaches.

Because of these difficulties, we change our philosophy. Instead of calculating the detailed temporal development of the whole system atom + radia-

tion field, we try to relate the detection signals ($L_F(t)$, $\mathcal{I}(\omega)$) to some simple quantities characterizing the radiating atoms. We find that $L_F(t)$ is related to the average of some atomic observables evaluated at time t (one-time averages), whereas $\mathcal{I}(\omega)$ is related to some correlation functions of the atomic dipole moment (two-time averages).

One-time averages of atomic observables are easily calculated if one knows the master equation describing the evolution of the reduced atomic density matrix. We first derive the terms of such a master equation which describe the effect of spontaneous emission and we discuss their physical meaning.

Then, we establish the terms of the master equation which describe the effect of the coupling with the incident light beam in two cases:

(i) Pure monochromatic field with well-defined phase and amplitude.

(ii) Broad-line excitation (spectral lamps or free-running multimode lasers which have a spectral width $\Delta\nu$ much larger than the frequency ω_1 characterizing the coupling of atoms to the light beam).

We solve the master equation for simple atomic transitions ($J = 0 \leftrightarrow J = 1$, $J = \frac{1}{2} \leftrightarrow J = \frac{1}{2}$) and we discuss some important physical effects: optical pumping, level crossing resonances radiative broadenings, saturation resonances, Zeeman detuning ... .

We show from a Langevin equation approach how two-time averages may be calculated from the master equation giving one-time averages (quantum regression theorem). This gives the possibility of calculating the spectral distribution of the fluorescence light for the two types of incident light beams considered above. We discuss the importance of the fluctuations of the atomic dipole moment.

Finally, we discuss briefly what happens with other types of light beams and intensity and photon correlations.

A lot of papers, both theoretical and experimental, have been devoted to the interaction of atoms with resonant fields. It is obviously impossible, in these lectures, to present a detailed review of all this work. We have preferred to focus on some particular topics and to discuss in detail some difficult points. We apologize for the inadequacies of this presentation and for the non-exhaustive character of our bibliography.

2. Discussion of a simple problem. Presentation of several theoretical approaches

We discuss the experiment of fig. 1b, assuming that atoms have only two levels g (ground) and e (excited). We will come back to this problem in sect. 7 where several references are given.

2.1. Very low intensity limit – lowest order QED predictions [1,2]

2.1.1. Basic lowest order diagram for resonance fluorescence

Absorption of one impinging photon ω_L. Propagation of the intermediate excited state e. Spontaneous emission of the fluorescence photon ω.

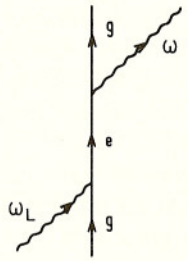

Fig. 2.

What is neglected? Processes where several interactions with the incident light beam occur. Induced emission processes. This is valid for very low intensities of the light beam.

Scattering amplitude. Contains two important factors.

$\delta(\omega - \omega_L)$: conservation of energy ,

$\dfrac{1}{\omega_L - \omega_0 + \frac{1}{2}i\Gamma}$: resonant behaviour of the scattering amplitude ,

with

$\omega_0 = E_e - E_g$: atomic frequency ,

Γ : natural width of the excited state .

2.1.2. Predicted shape of the fluorescence spectrum

(a) Monochromatic excitation. Because of $\delta(\omega - \omega_L)$, the fluorescence is also monochromatic with the same frequency as the excitation (fig. 3)

$$\mathcal{I}(\omega) = \delta(\omega - \omega_L) . \tag{2.1}$$

(b) Broad-line excitation. The incident light beam contains photons with all frequencies forming a white continuous spectrum. Each individual photon ω is scattered elastically with an efficiency given by

$$\left|\frac{1}{\omega-\omega_0+\frac{1}{2}i\Gamma}\right|^2=\frac{1}{(\omega-\omega_0)^2+(\frac{1}{2}\Gamma)^2}.$$

Consequently, the fluorescence spectrum $\mathcal{I}(\omega)$ is a Lorentzian curve, centred on $\omega=\omega_0$ (atomic frequency), with a half-width $\frac{1}{2}\Gamma$ (fig. 4)

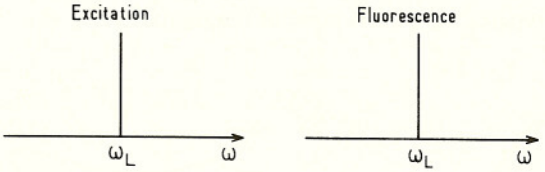

Fig. 3.

$$\mathcal{I}(\omega)\sim\frac{1}{(\omega-\omega_0)^2+(\frac{1}{2}\Gamma)^2}. \tag{2.2}$$

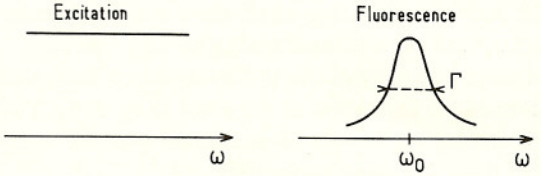

Fig. 4.

2.1.3. Scattering of a wave packet

As we know the scattering amplitude for each energy ω, we can study the scattering of an incident wave packet,

$$\phi_{\text{inc}}(s)=\int g(\omega)e^{-i\omega s}\,d\omega \quad \text{with} \quad s=t-r/c\,, \tag{2.3}$$

which becomes after the scattering

$$\phi_{\text{sc}}(s)=\int g(\omega)\frac{e^{-i\omega s}}{\omega-\omega_0+\frac{1}{2}i\Gamma}\,d\omega \tag{2.4}$$

(we do not write any angular or polarization dependence). We find that $\phi_{\text{sc}}(s)$ is given by the convolution of $\phi_{\text{inc}}(s)$ by $e^{-i\omega_0 s}e^{-\Gamma s/2}\theta(s)$ (θ: heaviside func-

tion), which is the Fourier transform of $1/(\omega - \omega_0 + \frac{1}{2}i\Gamma)$. This gives the possibility of studying a lot of time-dependent problems.

(i) Time dependence of the counting rate of a photomultiplier detecting the fluorescence light emitted by an atom excited by a short pulse of resonant or quasi-resonant light. From (2.4) one deduces that, if $g(\omega)$ has a large width and contains ω_0 (short resonant pulse), $\phi_{sc}(s)$ has a long tail varying as $e^{-i\omega_0 s}e^{-\Gamma s/2}$ (fig. 5). This clearly shows the exponential decay of an excited atomic state prepared by a short pulse of resonant light.

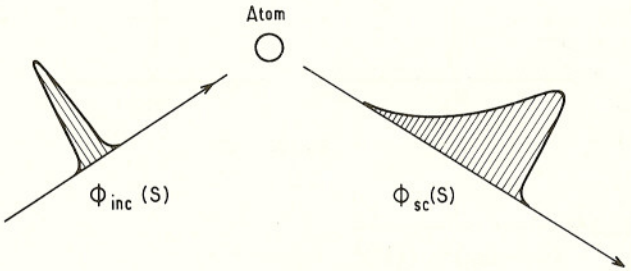

Fig. 5.

(ii) Quantum beats [3] appearing where there is a structure in e, for example two sublevels e_1 and e_2, separated from g by ω_{01} and ω_{02}.

The incident wave packet gives rise to two scattered wave packets corresponding to intermediate excitation of the atom to e_1 or e_2. The quantum beat signal, at frequency $\omega_{01} - \omega_{02}$, is associated with the interference between the tails of these two wave packets (fig. 6).

$$|A_1 e^{-i\omega_{01}s}e^{-\Gamma s/2} + A_2 e^{-i\omega_{02}s}e^{-\Gamma s/2}|^2$$

$$= |A_1|^2 e^{-\Gamma s} + |A_2|^2 e^{-\Gamma s} + 2\,\mathrm{Re}\, A_1 A_2^* e^{-i(\omega_{01}-\omega_{02})s}e^{-\Gamma s}\,. \quad (2.5)$$

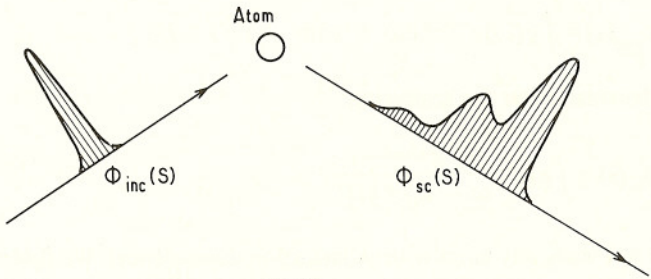

Fig. 6.

2.1.4. Higher order corrections – perturbative approach

We come back to a monochromatic excitation (at frequency ω_L) and we study higher order diagrams involving two interactions with the light beam (instead of only one). Diagrams 7a and 7b represent the scattering of two impinging photons ω_L, ω_L into two scattered photons ω_A, ω_B. They differ by the order of emission of ω_A and ω_B.

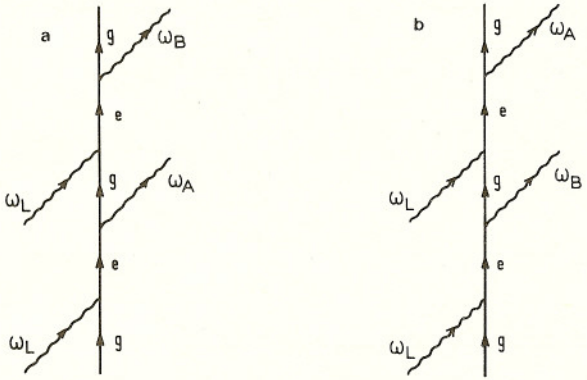

Fig. 7.

What does conservation of energy imply?

$$\omega_L + \omega_L = \omega_A + \omega_B \,, \tag{2.6}$$

and *not* necessarily $\omega_L = \omega_A = \omega_B$. Only the lowest order diagram (fig. 2) predicts *elastic scattering*. At high intensities, non-linear scattering processes involving several photons of the incident light beam give rise to *inelastic scattering*.

How are ω_A and ω_B distributed? Let us write down the energy denominators associated with the three intermediate states of diagrams 5a and 5b. (The numerators are the same for 5a and 5b, and proportional to the incident light intensity as they involve two ω_L interactions.) Adding to the energy ω_0 of e an imaginary term $-\frac{1}{2}i\Gamma$ which describes the radiative damping of e, we get

diagram 7a: $$\frac{1}{2\omega_L-\omega_A-\omega_0+\frac{1}{2}i\Gamma}\,\frac{1}{\omega_L-\omega_A+i\epsilon}\,\frac{1}{\omega_L-\omega_0+\frac{1}{2}i\Gamma}\,, \tag{2.7a}$$

diagram 7b: $$\frac{1}{2\omega_L-\omega_B-\omega_0+\frac{1}{2}i\Gamma}\,\frac{1}{\omega_L-\omega_B+i\epsilon}\,\frac{1}{\omega_L-\omega_0+\frac{1}{2}i\Gamma}\,, \tag{2.7b}$$

where ϵ is an infinitesimal positive quantity. Adding (2.7a) and (2.7b), and using $2\omega_L = \omega_A + \omega_B$, one gets for the total amplitude of the non-linear process $\omega_L + \omega_L \to \omega_A + \omega_B$,

$$\frac{1}{(\omega_L - \omega_0 + \frac{1}{2}i\Gamma)(\omega_A - \omega_0 + \frac{1}{2}i\Gamma)(\omega_A - 2\omega_L + \omega_0 - \frac{1}{2}i\Gamma)}. \tag{2.8}$$

One of the two photons is distributed over an interval $\frac{1}{2}\Gamma$ around $\omega = \omega_0$. As $\omega_B = 2\omega_L - \omega_A$, the second photon is symmetrically distributed over an interval $\frac{1}{2}\Gamma$ around $2\omega_L - \omega_0$.

Shape of the fluorescence spectrum (for $\omega_L \neq \omega_0$).

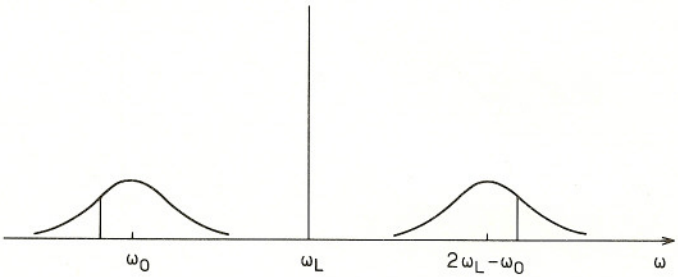

Fig. 8.

The δ function at $\omega = \omega_L$ is the elastic component given by the lowest order QED diagram. It is proportional to the light intensity I. The two Lorentz curves centred at ω_0 and $2\omega_L - \omega_0$ are the inelastic components. The total area below these curves is proportional to I^2 (non-linear scattering processes). The two photons are distributed over finite intervals but are strongly correlated ($\omega_A + \omega_B = 2\omega_L$).

It would not be a good idea to consider higher and higher order diagrams for understanding the behaviour of atoms in strong resonant fields. The perturbation series would not converge and the situation would be the more difficult, the nearer ω_L is to ω_0. So we are tempted to try another approach where the coupling of the atom to the laser beam is treated to all orders.

2.2. Very high intensity limit – the "dressed atom" approach

We now try to treat to all orders the coupling between the atom and the laser beam, using either a classical or a quantum treatment of this laser beam.

2.2.1. Classical treatment of the laser field

Atomic Hamiltonian ($\hbar = c = 1$) H_a,

$$H_a = \begin{pmatrix} \omega_0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{2.9}$$

Coupling with the laser:

$$V = -D\mathcal{E}\cos\omega_L t\,, \tag{2.10}$$

where D is the atomic electric dipole operator (odd) and $\mathcal{E}$ is the amplitude of the light wave,

$$D = \begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix}. \tag{2.11}$$

We assume $d = \langle e|D|g\rangle$ real. Let us put

$$\boxed{\omega_1 = -d\mathcal{E}}\,, \tag{2.12}$$

where ω_1 is a frequency characterizing the strength of the coupling

$$V = \omega_1\cos\omega_L t\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \underbrace{\tfrac{1}{2}\omega_1\begin{pmatrix} 0 & e^{-i\omega_L t} \\ e^{i\omega_L t} & 0 \end{pmatrix}}_{V_1} + \underbrace{\tfrac{1}{2}\omega_1\begin{pmatrix} 0 & e^{i\omega_L t} \\ e^{-i\omega_L t} & 0 \end{pmatrix}}_{V_2}. \tag{2.13}$$

Interaction representation:

$$V \to \tilde{V} = \underbrace{\tfrac{1}{2}\omega_1\begin{pmatrix} 0 & e^{i(\omega_0-\omega_L)t} \\ e^{-i(\omega_0-\omega_L)t} & 0 \end{pmatrix}}_{\tilde{V}_1} + \underbrace{\tfrac{1}{2}\omega_1\begin{pmatrix} 0 & e^{i(\omega_0+\omega_L)t} \\ e^{-i(\omega_0+\omega_L)t} & 0 \end{pmatrix}}_{\tilde{V}_2} \tag{2.14}$$

Spin-$\frac{1}{2}$ representation: A fictitious spin-$\frac{1}{2}$ $\mathcal{S}$ can be associated with any two-level system,

$$|e\rangle \to |+\rangle\,, \quad |g\rangle \to |-\rangle\,, \quad H_a - \tfrac{1}{2}\omega_0 \to \omega_0\mathcal{S}_z\,, \quad V \to 2\omega_1\cos\omega_L t\,\mathcal{S}_x\,. \tag{2.15}$$

$H_a \rightarrow$ Larmor precession of $\mathcal{S}$ around a magnetic field $\mathcal{B}_0$ parallel to $0z$ and such that $\omega_0 = -\gamma \mathcal{B}_0$ (γ: gyromagnetic ratio). $V \rightarrow$ Larmor precession of $\mathcal{S}$ around a magnetic field $\mathcal{B}_1 \cos \omega_L t$ parallel to $0x$ and such that $2\omega_1 = -\gamma \mathcal{B}_1$.

Rotating wave approximation (r.w.a.). $\mathcal{B}_1 \cos \omega_L t$ may be decomposed into two right and left circular components of amplitude $B_1 = \frac{1}{2}\mathcal{B}_1$ (decomposition of V into V_1, and V_2 in (2.13)). r.w.a. amounts to keep only the component rotating around $\mathcal{B}_0$ in the same sense as $\mathcal{S}$. Mathematically, we keep only V_1 since V_2 is rapidly oscillating in interaction representation (see (2.14)). When doing r.w.a., we neglect Bloch-Siegert type shifts (which are very small in optical range) and which are due to V_2. Note that we do not exclude "light shifts" produced by V_1 when the irradiation is quasi-resonant: $\Gamma < |\omega_L - \omega_0| \ll \omega_0$ (see next paragraph).

Reference frame $0XYZ$ rotating at ω_L around $0z = 0Z$ (fig. 9). In $0XYZ$, $\boldsymbol{B}_1$ becomes static and parallel to $0X$. The Larmor precession around $0Z$ is reduced from ω_0 to $\omega_0 - \omega_L$. Finally, the spin $\boldsymbol{S}$ in this new reference frame only sees two static fields: $\boldsymbol{B}_0$ parallel to $0Z$ and proportional to $\omega_0 - \omega_L$, and $\boldsymbol{B}_1$ parallel to $0X$ and proportional to ω_1. Physical interpretation of ω_1: Rabi nutation frequency of the spin at resonance ($B_0 = 0$).

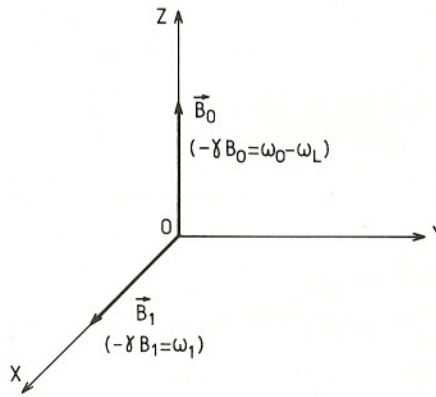

Fig. 9.

Summary. We have now a geometrical representation of the internal energy of the atom (precession around $\boldsymbol{B}_0$), of the coupling with the laser (precession around $\boldsymbol{B}_1$). The problems which remain are: How to describe spontaneous emission (i.e. the coupling with the empty modes of the quantized electromagnetic field)? How to compute $L_F(t)$, $\mathcal{I}(\omega)$ ... (i.e. the detection signals)?

2.2.2. Quantum treatment of the laser field – "dressed atom" approach [5–8]

(i) Definition of the "dressed atom". Total isolated system atom + impinging photons interacting together. (Physical picture of an atom surrounded by photons and interacting with them.)

(ii) Hamiltonian of the dressed atom. (We replace the two-level atom by the equivalent fictitious spin $\frac{1}{2}$.)

$$H = H_a + H_{laser} + V\,,$$

$$H_a = \omega_0 S_z\,, \qquad H_{laser} = \omega_L a^+ a\,, \qquad V = \lambda S_x (a + a^+)\,, \tag{2.16}$$

where a^+, a are the creation and annihilation operators of a ω_L photon; λ is the coupling constant; $a + a^+$ is the electric field operator (in the dipole approximation).

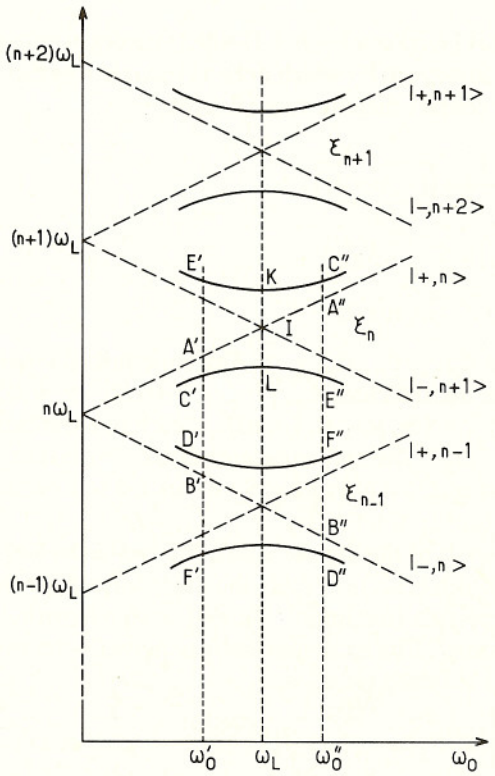

Fig. 10.

(iii) Energy levels of the uncoupled Hamiltonian $\mathcal{H}_0 = \mathcal{H}_a + \mathcal{H}_{laser}$,

$$\mathcal{H}_0|\pm, n\rangle = (\pm\tfrac{1}{2}\omega_0 + n\omega_L)|\pm, n\rangle\,, \tag{2.17}$$

where $|\pm, n\rangle$ is the atom in the + or − state in the presence of $n\omega_L$ photons. The unperturbed energy levels are represented by the dotted lines of fig. 10 which give their variation with ω_0, ω_L being fixed. At resonance ($\omega_0 = \omega_L$) degeneracy between pair of levels. For example at point I, the two levels $|+, n\rangle$ and $|-, n+1\rangle$ are degenerate.

(iv) Coupling V,

$$V = \underbrace{\tfrac{1}{2}\lambda(S_+a + S_-a^+)}_{V_1} + \underbrace{\tfrac{1}{2}\lambda(S_+a^+ + S_-a)}_{V_2}\,, \tag{2.18}$$

where V_1 couples $|+, n\rangle$ and $|-, n+1\rangle$ which are degenerate at resonance. The r.w.a. amounts to neglect V_2 which does not couple together these two degenerate levels. V_2 couples them to very far levels,

$$\boxed{|+, n\rangle} \overset{V_1}{\longleftrightarrow} \boxed{|-, n+1\rangle}\,. \tag{2.19}$$

$$V_2 \updownarrow \qquad\qquad \updownarrow V_2$$

$$|-, n-1\rangle \qquad |+, n+2\rangle$$

Multiplicities $\mathcal{E}_{n+1}$, $\mathcal{E}_n$, $\mathcal{E}_{n-1}$ ... . The unperturbed levels group into two-dimensional multiplicities $\mathcal{E}_{n+1} = \{|+, n+1\rangle, |-, n+2\rangle\}$, $\mathcal{E}_n = \{|+, n\rangle, |-, n+1\rangle\}$, $\mathcal{E}_{n-1} = \{|+, n-1\rangle, |-, n\rangle\}$... , each of them being degenerate at resonance ($\omega_0 = \omega_L$). The only non-zero matrix elements of V_1 are between the two states of such a multiplicity. So we are led to a series of two-level problems.

(v) Energy levels of the dressed atom. The two unperturbed levels $|+, n\rangle$ and $|-, n+1\rangle$ which cross in I repel each other when V is taken into account and form an hyperbola (full lines of fig. 10). Such a hyperbola is sometimes called "anticrossing". The minimum distance between the two branches of the hyperbola is obtained for $\omega_0 = \omega_L$,

$$KL = 2\langle +, n|V_1|-, n+1\rangle = \tfrac{1}{2}\lambda\langle +|S_+|-\rangle\langle n|a|n+1\rangle$$

$$= \tfrac{1}{2}\lambda\sqrt{n+1} \sim \tfrac{1}{2}\lambda\sqrt{n} \quad \text{as} \quad n \gg 1\,. \tag{2.20}$$

Physical interpretation of $\frac{1}{2}\lambda\sqrt{n}$: If at resonance ($\omega_0 = \omega_L$) one starts at $t = 0$ from $|-, n+1\rangle$, the probability of finding, at a later time, the system in $|+, n\rangle$ is modulated at the Bohr frequency $\frac{1}{2}\lambda\sqrt{n}$ of the dressed atom. This frequency is nothing but the Rabi nutation frequency of the classical approach, Finally, we get the relation

$$\omega_1 = \tfrac{1}{2}\lambda\sqrt{n} \tag{2.21}$$

between the parameters ω_1, λ, n of the classical and quantum approaches.

(vi) Periodical structure of the energy diagram. As $n \gg 1$, the shape of the various hyperbolas corresponding to $\mathcal{E}_{n+1}$, $\mathcal{E}_n$, $\mathcal{E}_{n-1}$ ... is the same. There is a periodicity in the energy diagram when n is varied within a range $\Delta n \ll n$. For a coherent state,

$$\langle \Delta n \rangle = \sqrt{\langle n \rangle} \gg 1 ,$$

$$\frac{\langle \Delta n \rangle}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}} \ll 1 . \tag{2.22}$$

The dispersion of n is large in absolute value, but very small in relative value. Therefore, when the field is in a coherent state we can consider the energy diagram of the dressed atom as periodical.

(vii) Light shifts [9–12]. They appear clearly in fig. 10. (a) Non-resonant irradiation $\omega_0' < \omega_L$: Unperturbed atomic frequency $\omega_0' = A'B'$. Perturbed atomic frequency $\overline{\omega_0'} = C'D' < \omega_0'$. (b) Non-resonant irradiation $\omega_0'' > \omega_L$: Unperturbed atomic frequency $\omega_0'' = A''B''$. Perturbed atomic frequency $\overline{\omega_0''} = C''D'' > \omega_0''$.

Conclusion: Atomic frequencies are perturbed when atoms are irradiated by a non-resonant light beam. The light shift is proportional to the light intensity I (near the asymptotes, $A'C'$, $B'D'$, $A''C''$, $B''D''$ are proportional to the square of the matrix element of V, i.e. to n, i.e. to I), provided that ω_1 is not too large ($\omega_1 < |\omega_0 - \omega_L|$) so that the hyperbola is near its asymptotes. The sign of the light shifts is the same as the sign of $\omega_0 - \omega_L$. Note that this light shift can be observed only if one irradiates the spin-$\frac{1}{2}$ system with a *second* probing RF field.

(viii) Bloch-Siegert shifts [13,14]. We take V_2 into account by perturbation theory. Due to the non-resonant V_2 coupling of $|+, n\rangle$ to $|-, n-1\rangle$ which is far below $|+, n\rangle$, the $|+, n\rangle$ level (dotted line in fig. 11) is shifted upward to a new position (interrupted line). Due to the non-resonant V_2 coupling of $|-, n+1\rangle$ to $|+, n+2\rangle$ which is far above $|-, n+1\rangle$, the $|-, n+1\rangle$ state (dotted line) is shifted downward to a new position (inter-

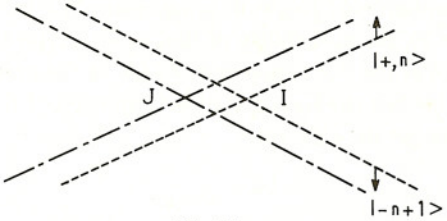

Fig. 11.

rupted line). It follows that the crossing point I between $|+, n\rangle$ and $|-, n+1\rangle$ is shifted from I to J. J is the centre of the anticrossing which appears when the coupling induced by V_1 between the two displaced levels is introduced.

IJ is the Bloch-Siegert shift, of the order of ω_1^2/ω_0, which is very simply calculated in the dressed atom approach by elementary second order time-independent perturbation theory. Strictly speaking, we have also to take into account the contribution of atomic levels others than e and g since the two-level approximations break down when one considers such non-resonant processes.

2.2.3. How to treat spontaneous emission in the dressed atom approach?

2.2.3.1. Fermi's golden rule treatment. The dressed atom jumps from a stationary state $|\psi_\alpha\rangle$ with energy E_α to a lower state $|\psi_\beta\rangle$ with energy E_β, emitting a photon $\omega = E_\alpha - E_\beta$ with a probability per unit time given by $|\langle\psi_\alpha|D|\psi_\beta\rangle|^2$ where D is the atomic electric dipole operator.

Conclusion: The frequencies of the various components of the fluorescence spectrum are the *Bohr frequencies* $E_\alpha - E_\beta$ of the dressed atom corresponding to *allowed transitions* ($\langle\psi_\alpha|D|\psi_\beta\rangle \neq 0$).

2.2.3.2. Application: *Predicted fluorescence spectrum at resonance.* In fig. 13, we have represented in the left part the multiplicities $\mathcal{C}_{n+1}$, $\mathcal{C}_n$ of unperturbed

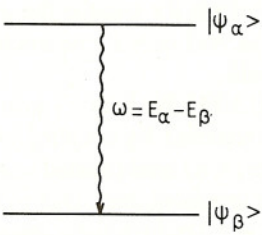

Fig. 12.

levels, in the right part the perturbed levels $|\psi^{\pm}_{n+1}\rangle$, $|\psi^{\pm}_{n}\rangle$ which appear when V_1 is taken into account. We suppose $\omega_L = \omega_0$ and $\omega_1 \gg \Gamma$. The allowed transitions starting from $|\psi^{\pm}_{n+1}\rangle$ are represented by the wavy vertical lines in fig. 13. The numbers indicated near each of these lines are the Bohr frequency of the transition and the matrix element of D between the two levels of the transition (we have put $\langle +|D|-\rangle = d$). All other transitions to lower levels belonging to $\mathcal{E}_{n-1}$, $\mathcal{E}_{n-2}$ are forbidden when r.w.a. is done. For the free atom the transition probability Γ is proportional to $|\langle +|D|-\rangle|^2 = d^2$. For the dressed atom, we see in fig. 13 that all allowed transitions have the same transition probability, $\frac{1}{4}\Gamma$ (all the matrix elements of D have the same absolute value, $\frac{1}{2}d$). It follows that the total probability of emission of a photon (of any frequency) from any level of the dressed atom is the same and equal to $\frac{1}{4}\Gamma + \frac{1}{4}\Gamma = \frac{1}{2}\Gamma$. All levels of the dressed atom have the same natural width $\frac{1}{2}\Gamma$.

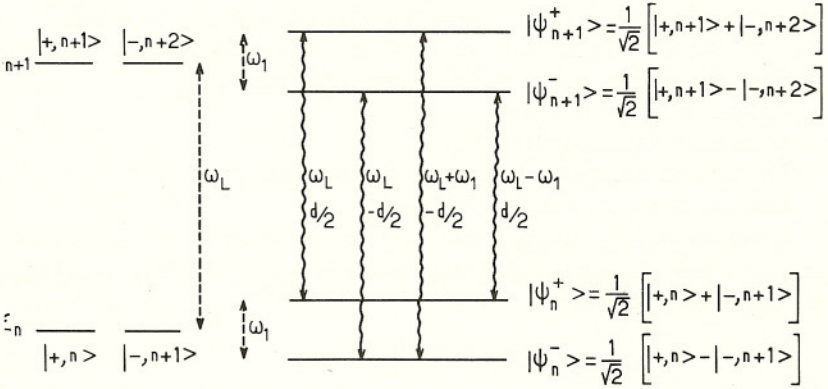

Fig. 13.

Conclusion: One predicts three lines in the fluorescence spectrum. For ω_L, the total probability is $\frac{1}{4}\Gamma + \frac{1}{4}\Gamma = \frac{1}{2}\Gamma$. The transitions connect two levels of natural width $\frac{1}{2}\Gamma$. It follows that the half-width of the component ω_L is $\frac{1}{2}(\frac{1}{2}\Gamma + \frac{1}{2}\Gamma) = \frac{1}{2}\Gamma$. For $\omega_L \pm \omega_1$, the total probability is $\frac{1}{4}\Gamma$. Same half-width as the ω_L component since all levels have the same natural width $\frac{1}{2}\Gamma$.

We have represented in fig. 14 the three lines at ω_L, $\omega_L + \omega_1$, $\omega_L - \omega_1$ with the same half-width $\frac{1}{2}\Gamma$, the height of the central component being two times greater than the one of the two sidebands. Although qualitatively correct, this prediction is not quantitatively exact as we will show later.

Remark: What happens for $\omega_L \neq \omega_0$? From fig. 10 one predicts one component at ω_L (transitions $E'D'$ and $C'F'$), one component at ω'_0 (transition

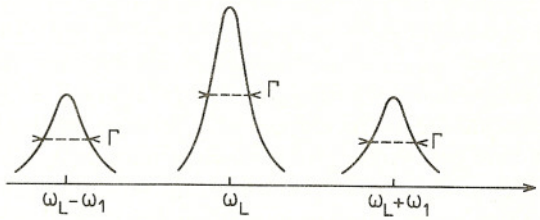

Fig. 14.

$C'D'$), one component at $2\omega_L - \overline{\omega'_0}$ (transition $E'F'$). We get qualitatively the results predicted from perturbation theory (see fig. 8), except that the atomic frequency ω'_0 is corrected by the light shift. We do not calculate here the height and the width of these three components as Fermi's golden rule approach to this problem is not sufficient as shown in the next paragraph.

2.2.3.3. The difficulty of cascades. We cannot consider only a single spontaneous emission process. Let us give some orders of magnitude.

Atomic velocity $\sim 10^3$ m/sec.

Laser beam diameter $\sim 10^{-3}$ m.

Transit time through the laser beam $T \sim 10^{-6}$ sec.

Lifetime of excited state $\tau \sim 10^{-8}$ sec.

It follows that the average number of spontaneous emission processes for an atom flying through the laser beam and saturated by this laser beam (spending half of its time in e) is

$$N \sim \frac{1}{2}\frac{T}{\tau} \sim 50 \gg 1 .$$

The situation is more exactly described by fig. 15 than by fig. 12. To simplify, we have considered only $N = 3$ spontaneous emission processes. In fig. 15a, the dressed atom is cascading downwards the energy diagram, from ψ^-_{n+1} to ψ^+_n, then from ψ^+_n to ψ^-_{n-1}, finally from ψ^-_{n-1} to ψ^-_{n-2} successively emitting photons $\omega_A \sim \omega_L - \omega_1$, $\omega_B \sim \omega_L + \omega_1$, $\omega_C \sim \omega_L$. Other possibilities exist, differing by the order of emission of the three photons ω_A, ω_B, ω_C (figs. 15b, 15c) and we can make the following remarks:

(i) The three cascades represented in fig. 15 start from the same initial level ψ^-_{n+1} and end at the same final level ψ^-_{n-2}.

(ii) We cannot decide which is the quantum path followed by the system. Being interested in a precise measurement of the frequencies ω_A, ω_B, ω_C, we cannot simultaneously determine their time of emission and, consequently, their order of emission (time and frequency are complementary quantities).

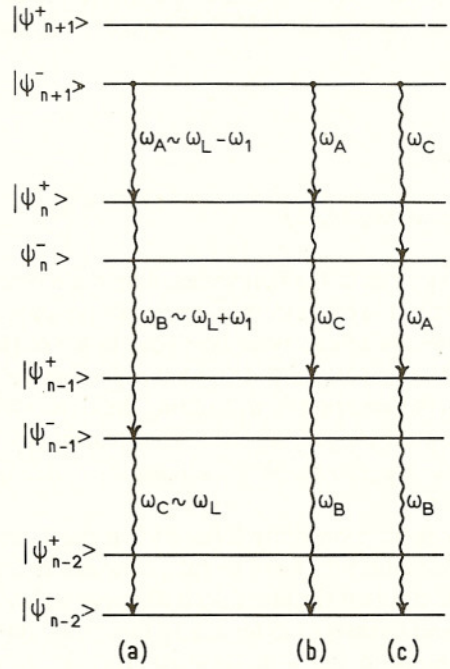

Fig. 15.

(iii) The three amplitudes are simultaneously large. This is due to the periodical structure of the energy diagram. We can find intermediate states which approximately satisfy the conservation of energy.

Conclusion: The quantum amplitudes associated to different cascades interfere and this modifies the height and the width of the various components of the fluorescence spectrum. (Similar difficulties are encountered when one studies spontaneous emission from a harmonic oscillator which has also a periodical energy diagram. See ref. [2] p. 47.)

Correct way of pursuing the calculations. For all values of N, calculate the $N!$ cascading amplitudes. Deduce from them the N-fold probability distribution $\mathcal{P}^{(N)}$ $(\omega_A \omega_B \ldots \omega_N)$ for having N emitted photons with frequencies $\omega_A, \omega_B \ldots \omega_N$. After several integrations, deduce from the $\mathcal{P}^{(N)}$, a reduced one-photon probability distribution $\mathcal{P}(\omega)$ giving the probability for any individual photon to have the frequency ω, which is the measured spectral distribution.

Criticisms: This method is correct but too ambitious and too indirect. We do

not measure the $\mathcal{P}^{(N)}$ but $\mathcal{I}(\omega)$. Would it not be possible to calculate directly $\mathcal{I}(\omega)$ without passing through the $\mathcal{P}^{(N)}$? This leads us to the problem of detection signals.

3. Detection signals

3.1. Method of calculation [14,15]

We put a detecting atom in the field radiated by the resonance cell or by the atomic beam of fig. 1. This detecting atom has a ground state a and an excited state b, separated by an energy ω which can be tuned (by a magnetic field for example). The natural width Γ' of b is supposed very small so that we can neglect spontaneous emission from b during the time θ of observation ($\tau' = 1/\Gamma' \gg \theta$). The precision in frequency measurement is $1/\theta$ and is supposed much smaller than the frequencies characterizing the radiating atoms: ω_0, Γ, $\omega_1 \gg 1/\theta$.

What we measure is the probability $\mathcal{P}(\omega, \theta)$ that the detecting atom is excited from a to b after a time θ. (For example, we measure a photocurrent produced by the ionisation of the atom from its upper state b.) We repeat the experiment for different values of ω by tuning the energy difference between a and b. $\mathcal{P}(\omega, \theta)$ is proportional to the spectral distribution $\mathcal{I}(\omega)$ of the fluorescence light. We will use perturbation theory for calculating $\mathcal{P}(\omega, \theta)$. We can always put a neutral filter before the detecting atom in order to reduce the incident light intensity to a sufficiently low value (we avoid any saturation of the detector). We also neglect the reaction of the detecting atoms or the radiating atoms (they are far from each other).

3.2. Hamiltonian

$$H = H_R + H_D + W\,, \tag{3.1}$$

where H_R is the Hamiltonian of radiating atoms + radiation field coupled together; H_D is the Hamiltonian of the detecting atom; W is the $-\mathcal{D}E$ interaction between the detecting atom and the radiation field ($\mathcal{D}$ is the electric dipole of the detecting atom).

Let us use interaction representation with respect to $H_R + H_D$. In this representation, the electric field operator $E(r, t)$ is just the Heisenberg electric field operator of the radiating atoms + radiation field system (without detecting atoms). In this representation, W becomes

$$\tilde{W}(t) = -[\mathcal{D}^{(+)} e^{i\omega t} E^{(+)}(r, t) + \mathcal{D}^{(-)} e^{-i\omega t} E^{(-)}(r, t)] , \tag{3.2}$$

where $\mathcal{D}^{(+)} = \delta |b\rangle\langle a|$ and $\mathcal{D}^{(-)} = \delta |a\rangle\langle b|$ are the raising and lowering parts of $\mathcal{D}$ ($\delta = \langle a| \mathcal{D} |b\rangle$ is assumed to be real) and $E^{(+)}$ and $E^{(-)}$ are the positive and negative frequency parts of the electric field operator $E(r, t)$.

3.3. Calculation of $\mathcal{P}(\omega, \theta)$

At $t = 0$, the density matrix $\rho(0)$ of the total system in interaction representation is

$$\rho(0) = |a\rangle\langle a| \otimes \rho_R , \tag{3.3}$$

where ρ_R is the density matrix of the radiating atoms + radiation field system.

As

$$\frac{d\rho}{dt} = -i [\tilde{W}(t), \rho] , \tag{3.4}$$

we obtain from perturbation theory

$$\rho(\theta) = \rho(0) - i \int_0^\theta dt\, [\tilde{W}(t), \rho] - \int_0^\theta dt \int_0^t dt' [\tilde{W}(t), [\tilde{W}(t'), \rho(0)]] . \tag{3.5}$$

We are interested in

$$\mathcal{P}(\omega, \theta) = \mathrm{Tr}_{R,D} |b\rangle\langle b| \rho(\theta) , \tag{3.6}$$

where Tr_R is trace over radiating atoms + radiation field variables and Tr_D is trace over detecting atom variables.

From (3.2), (3.3) and (3.5) the first non-zero term of (3.6) is

$$\mathcal{P}(\omega, \theta) = \mathrm{Tr}_{R,D} \int_0^\theta dt \int_0^t dt' |b\rangle\langle b| [\tilde{W}(t) \rho(0) \tilde{W}(t') + \tilde{W}(t') \rho(0) \tilde{W}(t)]$$

$$= \delta^2 \mathrm{Tr}_R \int_0^\theta dt \int_0^t dt' \{ e^{i\omega(t-t')} E^{(+)}(r, t) \rho_R E^{(-)}(r, t')$$

$$+ e^{+i\omega(t'-t)} E^{(+)}(r, t') \rho_R E^{(-)}(r, t)\} . \tag{3.7}$$

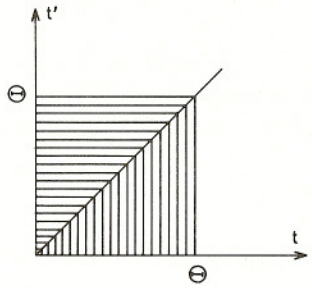

Fig. 16.

Changing, in the last term of (3.7), t into t' and t' into t and using (see fig. 16)

$$\int_0^\theta \mathrm{d}t \int_0^t \mathrm{d}t' + \int_0^\theta \mathrm{d}t' \int_0^{t'} \mathrm{d}t = \int_0^\theta \mathrm{d}t \int_0^\theta \mathrm{d}t' \,, \tag{3.8}$$

we get after a circular permutation of the three operators to be traced

$$\mathcal{P}(\omega, \theta) \sim \int_0^\theta \mathrm{d}t \int_0^\theta \mathrm{d}t' \langle E^{(-)}(r, t) E^{(+)}(r, t') \rangle \mathrm{e}^{-i\omega(t-t')} \,. \tag{3.9}$$

We recognize the Fourier transform of the correlation function of the positive frequency part of the electric field operator at the position r where the detector is. In (3.9), $E^{(+)}(r, t)$ and $E^{(-)}(r, t')$ are Heisenberg operators of the radiating atoms + radiation field system. The average value is taken within the whole quantum state of this system.

Remark: If we take into account the vectorial character of the electric field and if we detect the light reemitted with a polarization $\hat{\epsilon}_d$, we must replace in (3.9) $\langle E^{(-)}(r, t) E^{(+)}(r, t') \rangle$ by

$$\langle (\hat{\boldsymbol{\varepsilon}}_d \cdot \boldsymbol{E}^{(-)}(r, t))(\hat{\boldsymbol{\varepsilon}}_d \cdot \boldsymbol{E}^{(+)}(r, t')) \rangle \,. \tag{3.10}$$

3.4. Calculation of the total intensity of the fluorescence light

Suppose we have atoms with all frequencies ω in the detector. Integrating (3.9) with respect to ω gives a $\delta(t - t')$ function, so that the total photocurrent recorded by the detector from 0 to θ is

$$\int \mathrm{d}\omega \mathcal{P}(\omega, \theta) = \int_0^\theta \mathrm{d}t \langle E^{(-)}(r, t) E^{(+)}(r, t) \rangle \,. \tag{3.11}$$

The counting rate at time t, $L_F(t)$, is

$$L_F(t) \sim \langle E^{(-)}(r, t)E^{(+)}(r, t)\rangle . \tag{3.12}$$

When polarization is taken into account, we use (3.10) with $t' = t$,

$$L_F(t) \sim \langle (\hat{\varepsilon}_d \cdot E^{(-)}(r, t))(\hat{\varepsilon}_d \cdot E^{(+)}(r, t))\rangle . \tag{3.13}$$

Conclusion: $L_F(t)$ is given by one-time averages; $\mathcal{I}(\omega)$ is given by two-time averages (more difficult).

Remark: For calculating $L_F(t)$, we can also take an atom with a continuum of excited states (photoelectric effect) rather than an ensemble of atoms with a discrete excited state b having all possible atomic frequencies ω (see ref. [14]).

3.5. Expression of the signals in terms of atomic observables [16]

In Heisenberg representation, the quantum operator $E(r, t)$ satisfies Maxwell's equation: As $E(r, t)$ is radiated by the atomic dipole moment (we suppose the detector outside the incident laser beam), we have the following relation between operators (which may be derived from Maxwell's equation in the same way as in classical theory):

$$E^{(\pm)}(r, t) \sim \frac{\omega_0^2}{r} D^{(\mp)}\left(t - \frac{r}{c}\right), \tag{3.14}$$

where r is the distance between the radiating atoms and the detector, and $D^{(+)} = d|e\rangle\langle g|$ and $D^{(-)} = d|g\rangle\langle e|$ (with $d = \langle e|D|g\rangle$) are the raising and lowering parts of D. Neglecting the propagation time r/c, we get

$$\mathcal{I}(\omega) \sim \int_0^{} dt \int_0^{} dt' \langle D^{(+)}(t)D^{(-)}(t')\rangle e^{-i\omega(t-t')} , \tag{3.15}$$

$$L_F(t) \sim \langle D^{(+)}(t)D^{(-)}(t)\rangle , \tag{3.16}$$

$$\langle (\hat{\varepsilon}_d \cdot D^{(+)}(t))(\hat{\varepsilon}_d \cdot D^{(-)}(t'))\rangle$$

when we take into account polarization effects.

In terms of the fictitious spin-$\frac{1}{2}$ S in the rotating reference frame we can make the substitution

$$\langle D^{(+)}(t)D^{(-)}(t')\rangle \to \langle S^{+}(t)S^{-}(t')\rangle e^{i\omega_L(t-t')}\,, \tag{3.17}$$

where

$$S^{\pm} = S_x \pm iS_y\,. \tag{3.18}$$

4. Master equation treatment of spontaneous emission

4.1. General problem of the evolution of a small system coupled to a large reservoir [4,15,17–21]

4.1.1. Formulation of the problem

A small system A, of Hamiltonian H_A, is coupled by V to a large "reservoir" R, of Hamiltonian H_R. Our problem is to describe the evolution of A.

Hamiltonian:

$$H = H_A + H_R + V\,. \tag{4.1}$$

All system variables commute with reservoir variables.

Density operator ρ of the total system:

$$\frac{d\rho}{dt} = \frac{1}{i\hbar}[H,\rho]\,, \tag{4.2}$$

$$\langle G\rangle = \mathrm{Tr}_{A,R}\, G\rho = \sum_{m,\alpha}\langle m,\alpha|G\rho|m,\alpha\rangle\,. \tag{4.3}$$

where $\mathrm{Tr}_A(\mathrm{Tr}_R)$ is the trace over $A(R)$ variables; $\{|m\rangle\}$ is an orthonormal basis in the space of A states $\mathcal{E}_A$ (Latin indices for A); $\{|\alpha\rangle\}$ is an orthonormal basis in the space of R states $\mathcal{E}_R$ (Greek indices for R).

Suppose we are interested only in system A variables: G_A,

$$\langle G_A\rangle = \mathrm{Tr}_{A,R}\, G_A\rho = \sum_{\substack{m,\alpha\\ m',\alpha'}} \underbrace{\langle m,\alpha|G_A|m'\alpha'\rangle}_{\langle m|G_A|m'\rangle\delta_{\alpha\alpha'}}\langle m',\alpha'|\rho|m,\alpha\rangle$$

$$= \sum_{m,m'}\langle m|G_A|m'\rangle \sum_{\alpha}\langle m',\alpha|\rho|m,\alpha\rangle\,. \tag{4.4}$$

From ρ, operator of $\mathcal{E}_A \otimes \mathcal{E}_R$, we can deduce an operator of $\mathcal{E}_A$, σ_A, given by

$$\langle m'|\sigma_A|m\rangle = \sum_{\alpha} \langle m'\alpha|\rho|m\alpha\rangle . \tag{4.5}$$

Here, σ_A is called the "*reduced density operator*" of A, obtained by "*tracing ρ over R*"

$$\rho \Rightarrow \sigma_A = \mathrm{Tr}_R\ \rho . \tag{4.6}$$

From (4.5) and (4.4), one deduces

$$\langle G_A \rangle = \sum_{m,m'} \langle m|G_A|m'\rangle\langle m'|\sigma_A|m\rangle = \mathrm{Tr}_A\, G_A\, \sigma_A . \tag{4.7}$$

All system averages can be done with the reduced operator σ_A in the $\mathcal{E}_A$ space. If we are interested only in A variables, it is better to try to derive an equation of evolution of σ_A from (4.2), rather than solving (4.2) which is much more complicated (as it gives also information on R),

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{1}{i\hbar}\,[H, \rho] \Rightarrow \frac{\mathrm{d}\sigma_A}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Tr}_R\ \rho = ? \tag{4.8}$$

The equation giving $\mathrm{d}\sigma_A/\mathrm{d}t$ is called "*master equation of A*" and describes the evolution of A due to its coupling with R.

It is important to realize that, although the evolution of ρ can be described by a Hamiltonian H, this is not in general true for σ_A. In other words, it is impossible to find an hermitian operator $\mathcal{H}_A$ of $\mathcal{E}_A$ such that $(\mathrm{d}/\mathrm{d}t)\sigma_A = (1/i\hbar)\,[\mathcal{H}_A, \sigma_A]$. This is due to the fact that V depends on both A and R variables: when tracing over R the right member of (4.2), one gets a difficult term $\mathrm{Tr}_R\,[V, \rho]$ which cannot be expressed simply in terms of σ_A. This non-Hamiltonian character of the evolution of σ_A introduces some irreversibility in the behaviour of A.

In this paragraph, we try to derive a master equation for σ_A in conditions where a perturbation treatment of V is possible. More precisely, we will show that, when the correlation time τ_C of the force exerted by R upon A is sufficiently short, it is possible to consider only one interaction process between A and R during this time τ_C.

These general considerations will then be applied in subsects. 4.2 and 4.3 to spontaneous emission.

4.1.2. Derivation of the master equation

Here we give the main steps of the derivation of the master equation giving $d\sigma_A/dt$. A certain number of approximations will be done which will be then discussed in § 4.1.3. The results will be interpreted in § 4.1.4.

Interaction representation (all quantities in IR are labelled by a tilde).

$$\rho(t) \rightarrow \tilde{\rho}(t) = e^{i(H_A+H_R)t/\hbar}\,\rho(t)\,e^{-i(H_A+H_R)t/\hbar}\,, \tag{4.9a}$$

$$\sigma_A(t) \rightarrow \tilde{\sigma}_A(t) = e^{iH_A t/\hbar}\,\sigma_A(t)\,e^{-iH_A t/\hbar}\,, \tag{4.9b}$$

$$V \rightarrow \tilde{V}(t) = e^{i(H_A+H_R)t/\hbar}\,V\,e^{-i(H_A+H_R)t/\hbar}\,. \tag{4.9c}$$

One can easily show from (4.9) that

$$\sigma_A(t) = \mathrm{Tr}_R\ \rho(t) \Rightarrow \tilde{\sigma}_A(t) = \mathrm{Tr}_R\ \tilde{\rho}(t)\,. \tag{4.10}$$

Equation of evolution of $\tilde{\rho}(t)$:

$$\frac{d}{dt}\tilde{\rho}(t) = \frac{1}{i\hbar}\,[\tilde{V}(t), \tilde{\rho}(t)]\,. \tag{4.11}$$

Two hypotheses concerning the initial density operator $\rho(0)$ at $t = 0$.

(i) $\rho(0)$ factorizes

$$\rho(0) = \tilde{\rho}(0) = \sigma_A(0) \otimes \sigma_R(0)\,. \tag{4.12}$$

(ii) $\sigma_R(0)$ commutes with H_R,

$$[\sigma_R(0), H_R] = 0\,. \tag{4.13}$$

It follows that $\sigma_R(0)$ and H_R can be simultaneously diagonalized. An important example is a reservoir in thermodynamical equilibrium, in which case $\sigma_R(0) \sim \exp\{-H_R/kT\}$.

We will see in § 4.1.3 that the factorization of $\rho(0)$ is not a very restrictive hypothesis.

Iterative solution of the equation of evolution of ρ. Integrating (4.11), we get

$$\tilde{\rho}(t) = \tilde{\rho}(0) + \frac{1}{i\hbar}\int_0^t dt'\,[\tilde{V}(t'), \tilde{\rho}(t')]\,. \tag{4.14}$$

Introducing (4.14) in the right member of (4.11) gives the *exact* equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\tilde{\rho} = \frac{1}{i\hbar}\,[\tilde{V}(t), \tilde{\rho}(0)] + \frac{1}{(i\hbar)^2}\int_0^t \mathrm{d}t'\,[\tilde{V}(t), [\tilde{V}(t'), \tilde{\rho}(t')]]\,. \tag{4.15}$$

A first hypothesis concerning V. We assume that V has no diagonal elements in the basis where H_R is diagonal. As $\sigma_R(0)$ has only diagonal elements in this basis [see (4.13)], it follows that

$$\mathrm{Tr}_R\,[\sigma_R(0)\,\tilde{V}(t)] = 0\,. \tag{4.16}$$

Consequently, if we trace over R the right member of (4.15), the first term gives (with (4.12))

$$\mathrm{Tr}_R\,[\tilde{V}(t), \tilde{\rho}(0)] = [\mathrm{Tr}_R(\sigma_R(0)\,\tilde{V}(t)), \sigma_A(0)] = 0\,. \tag{4.17}$$

Physical interpretation: $\mathrm{Tr}_R(\sigma_R(0)\,\tilde{V}(t))$ is an operator of $\mathcal{E}_A$ which represents the energy of A in the average potential exerted by R upon A when R is in the state $\sigma_R(0)$ (some sort of "Hartree potential"). So, we assume this average potential is 0. If this were not the case, it would be easy to add, in the master equation, a commutator describing the effect of this "Hartree potential".

Finally, by tracing (4.15) over R, we get

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\tilde{\sigma}_A(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t'\,\mathrm{Tr}_R\,[\tilde{V}(t), [\tilde{V}(t'), \tilde{\rho}(t')]]\,. \tag{4.18}$$

Approximation 1: Factorization of $\tilde{\rho}(t)$. Introducing $\tilde{\sigma}_A(t') = \mathrm{Tr}_R\,\tilde{\rho}(t')$, we can always write

$$\tilde{\rho}(t') = \tilde{\sigma}_A(t')\,\sigma_R(0) + \Delta\tilde{\rho}(t')\,. \tag{4.19}$$

We insert (4.19) in (4.18) and neglect the contribution of $\Delta\tilde{\rho}(t')$, so that the exact equation (4.18) is replaced by the approximate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\tilde{\sigma}_A(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t'\,\mathrm{Tr}_R\,[\tilde{V}(t), [\tilde{V}(t'), \tilde{\sigma}_A(t')\,\sigma_R(0)]]\,. \tag{4.20}$$

The error we have made is given by

$$-\frac{1}{\hbar^2}\int_0^t \mathrm{Tr}_R\,[\tilde{V}(t),\,[\tilde{V}(t'),\,\Delta\tilde{\rho}(t')]]\,, \tag{4.21}$$

and will be estimated in § 4.1.3.

Explicit form of V. We will assume that V is a product (or a sum of products) of reservoir and system operators,

$$V = AR\,,\quad (\text{or } V = \sum_p A^p R^p)\,, \tag{4.22}$$

where A is an hermitian operator of $\mathcal{E}_A$, R an hermitian operator of $\mathcal{E}_R$,

$$\tilde{V}(t) = \tilde{A}(t)\tilde{R}(t)\,, \tag{4.23}$$

$$\tilde{A}(t) = \mathrm{e}^{iH_A t/\hbar} A\, \mathrm{e}^{-iH_A t/\hbar}\,,$$

$$\tilde{R}(t) = \mathrm{e}^{iH_R t/\hbar} R\, \mathrm{e}^{-iH_R t/\hbar}\,. \tag{4.24}$$

Let us insert (4.23) in (4.20), change from the variable t' to the variable $\tau = t - t'$, expand the double commutator, use the invariance of a trace in a circular permutation. We get

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{\sigma}_A(t) = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}\tau\,\{\mathrm{Tr}_R\,\tilde{\sigma}_R(0)\tilde{R}(t)\tilde{R}(t-\tau)\}$$

$$\times\,\{\tilde{A}(t)\tilde{A}(t-\tau)\tilde{\sigma}_A(t-\tau) - \tilde{A}(t-\tau)\tilde{\sigma}_A(t-\tau)\tilde{A}(t)\}$$

$$+\,\text{hermit. conjug.} \tag{4.25}$$

The reservoir only appears in the number

$$G(\tau) = \mathrm{Tr}_R\,\sigma_R(0)\tilde{R}(t)\tilde{R}(t-\tau)\,, \tag{4.26}$$

which is a *correlation function* of the reservoir. $G(\tau)$ only depends on τ because $\sigma_R(0)$ commutes with H_R. All other quantities appearing in the second bracket of (4.25) are system operators. Eq. (4.25) is an *integro-differential equation.* The rate of variation of $\tilde{\sigma}_A$ at time t depends on the whole previous story of A i.e. on $\tilde{\sigma}_A(t-\tau)$ with $0 \leqslant \tau \leqslant t$.

Approximation 2: Short memory of the reservoir. We will see that $G(\tau) \to 0$

if $\tau \gg \tau_C$, where τ_C is the *correlation time* of the reservoir. We will assume that τ_C is much shorter than the characteristic time T of the system, i.e. of $\tilde{\sigma}_A$. In the interval of time $0 \leqslant \tau \lesssim \tau_C$ where $G(\tau)$ is not zero, $\tilde{\sigma}_A(t-\tau)$ does not vary appreciably, so that we can replace $\tilde{\sigma}_A(t-\tau)$ by $\tilde{\sigma}_A(t)$ in (4.25). If $t \gg \tau_C$, we can also replace the upper limit of the integral by $+\infty$.

If we come back from the interaction representation to the Schrödinger representation, we finally get

$$\frac{\mathrm{d}\sigma_A}{\mathrm{d}t} = \frac{1}{i\hbar}[H_A, \sigma_A] - \frac{1}{\hbar^2}\int_0^\infty \mathrm{d}\tau G(\tau)$$

$$\times [A\,\mathrm{e}^{-iH_A\tau/\hbar} A\,\mathrm{e}^{iH_A\tau/\hbar}\sigma_A(t) - \mathrm{e}^{-iH_A\tau/\hbar} A\,\mathrm{e}^{iH_A\tau/\hbar}\sigma_A(t)A]$$

$$+ \text{hermit. conjug. of the second line.} \qquad (4.27)$$

For the matrix elements of σ_A, we get a set of coupled linear first-order differential equations with time-independent coefficients.

If we skip the index A for σ_A, and if we take the basis of eigenstates of H_A, (4.27) may be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{ij} = -i\omega_{ij}\sigma_{ij} + \sum_{lm} R_{ijlm}\sigma_{lm}\,, \qquad (4.28)$$

where $\omega_{ij} = (E_i - E_j)/\hbar$ is a Bohr frequency of A, and the R_{ijlm} are time-independent coefficients which can be calculated from (4.27) and which will be explicited and discussed in § 4.1.4.

Approximation 3: Secular approximation. In absence of damping σ_{ij} and σ_{lm} evolve at frequencies ω_{ij} and ω_{lm}. Let Γ be the order of magnitude of the coupling coefficients R_{ijlm}. If $\Gamma \ll |\omega_{ij} - \omega_{lm}|$, we can neglect the coupling between σ_{ij} and σ_{lm}, the error being of the order of $|\Gamma/(\omega_{ij} - \omega_{lm})| \ll 1$. The argument for proving this point is the same as in perturbation theory: the coupling V_{ab} induced by V between two states $|a\rangle$ and $|b\rangle$ of energies E_a and E_b has a small effect if $|V_{ab}| \ll |E_a - E_b|$. Finally, with the secular approximation, (4.28) may be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{ij} = -i\omega_{ij}\sigma_{ij} + \sum_{lm} R_{ijlm}\sigma_{lm}\,, \qquad (4.29)$$

with $|\omega_{lm} - \omega_{ij}| < \Gamma$.

4.1.3. Discussion of the approximations

Correlation time of the reservoir. Let us explicit the correlation function $G(\tau)$ given in (4.26). Introducing an orthonormal basis $\{|\alpha\rangle\}$ of eigenstates of H_R [in which σ_R is diagonal according to (4.13)], and putting

$$P_\alpha = \langle\alpha|\sigma_R(0)|\alpha\rangle \tag{4.30}$$

(probability for the reservoir R to be in state α),

$$\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar \tag{4.31}$$

(Bohr frequency of the reservoir), we get

$$G(\tau) = \sum_{\alpha\beta} p(\alpha)|\langle\alpha|R|\beta\rangle|^2 \mathrm{e}^{i\omega_{\alpha\beta}\tau}$$

$$= \int \mathrm{d}\omega\, g(\omega)\mathrm{e}^{i\omega\tau}\,, \tag{4.32}$$

where

$$g(\omega) = \sum_{\alpha\beta} p(\alpha)|\langle\alpha|R|\beta\rangle|^2 \delta(\omega - \omega_{\alpha\beta})\,. \tag{4.33}$$

We see therefore that $G(\tau) \to 0$ if $\tau \gg \tau_C$ where τ_C is the inverse of the width of $g(\omega)$; τ_C is the *correlation time* of the reservoir. The force exerted by R upon A is a random force with a *memory* characterized by τ_C.

The larger the width of $g(\omega)$, the shorter the correlation time τ_C.

Parameter v characterizing the strength of the coupling between A and R. To characterize this coupling, we can first take the average of V in the initial state $\rho(0)$,

$$\mathrm{Tr}_A\, \rho(0)\, V = \mathrm{Tr}_A(\sigma_A(0)\mathrm{Tr}_R\, \sigma_R(0)\, V)\,, \tag{4.34}$$

which is equal to 0 according to (4.16). So we take the average of V^2 and we put, using (4.22),

$$v^2 = \mathrm{Tr}_{AR}\, \rho(0)\, V^2 = (\mathrm{Tr}_A\, \sigma_A(0)A^2)(\mathrm{Tr}_R\, \sigma_R(0)R^2)\,. \tag{4.35}$$

Order of magnitude of the damping time T. Suppose the condition of validity of (4.27) is fulfilled. What is the order of magnitude of the coefficient Γ of $\sigma_A(t)$? ($\Gamma = 1/T$.) We can take

$$G(\tau) \simeq G(0)\mathrm{e}^{-\tau/\tau_C} \simeq (\mathrm{Tr}\ \sigma_R(0)R^2)\mathrm{e}^{-\tau/\tau_C} . \tag{4.36}$$

On the other hand,

$$A\ \mathrm{e}^{-iH_A\tau/\hbar} A\ \mathrm{e}^{iH_A\tau/\hbar} \simeq (\mathrm{Tr}\ \sigma_A(0)A^2)\mathrm{e}^{i\omega_0\tau} , \tag{4.37}$$

where ω_0 is a typical Bohr frequency of A, so that we finally have

$$\Gamma \sim \frac{1}{\hbar^2}\int_0^\infty \underbrace{\mathrm{d}\tau(\mathrm{Tr}\ \sigma_R(0)R^2)(\mathrm{Tr}\ \sigma_A(0)A^2)}_{v^2}\mathrm{e}^{-\tau/\tau_C}\ \mathrm{e}^{i\omega_0\tau}$$

$$\simeq \frac{1}{\hbar^2}\ \frac{v^2\tau_C}{1+\omega_0^2\tau_C^2} . \tag{4.38}$$

Neglecting $\omega_0\tau_C$ in the denominator gives an upper value of Γ,

$$\Gamma \lesssim \frac{v^2\tau_C}{\hbar^2} . \tag{4.39}$$

Condition of validity of approximation 2. This condition is, as we have mentioned above, that the characteristic time of evolution of $\tilde{\sigma}_A$, i.e. $T = 1/\Gamma$, must be much longer than τ_C,

$$T = 1/\Gamma \gg \tau_C . \tag{4.40}$$

Using (4.39), we see that we must have

$$\frac{v^2\tau_C^2}{\hbar^2} \ll 1 . \tag{4.41}$$

The condition $v\tau_C/\hbar \ll 1$ means that the effect of the coupling between A and R during the correlation time τ_C of R is very small.

Condition of validity of approximation 1. Taking the time derivative of (4.19) and using (4.15) and (4.18) we get the following equation of evolution for $\Delta\tilde{\rho}(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Delta\tilde{\rho}=\frac{1}{i\hbar}[\tilde{V}(t),\tilde{\rho}(0)]-\frac{1}{\hbar^2}\int_0^t \mathrm{d}t'[\tilde{V}(t),[\tilde{V}(t'),\tilde{\rho}(t')]]$$

$$-\frac{1}{\hbar^2}\sigma_R(0)\mathrm{Tr}_R\int_0^t \mathrm{d}t'[\tilde{V}(t),[\tilde{V}(t'),\tilde{\rho}(t')]]\,. \tag{4.42}$$

We can integrate (4.42) and introduce the value so obtained for $\Delta\tilde{\rho}$ into eq. (4.21) which gives the error introduced by approximation 1. As we expect this correction to be small, we only need an approximate expression $\Delta\tilde{\rho}$, so that we will replace in the right member of (4.42) $\tilde{\rho}(t')$ by $\tilde{\sigma}_A(t')\tilde{\sigma}_R(0)$. We assume that the average value of an odd number of operators R is zero [generalization of (4.16)], so that the first term of the right member of (4.42) does not contribute. We will not explicit the contribution of the last two terms of (4.42). But it is easy to see that they will lead to corrections of the damping coefficients Γ given by triple integrals of four $\tilde{V}$ operators. The order of magnitude of these triple integrals is

$$\frac{v^4\tau_C^3}{\hbar^4}=\frac{v^2\tau_C}{\hbar^2}\,\frac{v^2\tau_C^2}{\hbar^2}\sim\Gamma\frac{v^2\tau_C^2}{\hbar^2}\ll\Gamma \tag{4.43}$$

according to (4.41). These corrections represent the effect of more than one interaction occuring during the correlation time τ_C. So, if approximation 2 is justified, approximation 1 is also justified.

We see also that we can forget $\Delta\tilde{\rho}(t')$ in (4.19) since keeping this term in (4.18) does not appreciably change the master equation. So, it is a good approximation to consider that the density matrix factorizes at each time in $\tilde{\sigma}_A(t)\tilde{\sigma}_R(0)$, so that hypothesis 1 assuming such a factorization at $t=0$ is not very restrictive. We must not forget however that, even when replacing $\tilde{\rho}(t')$ by $\tilde{\sigma}_A(t')\tilde{\sigma}_R(0)$ in (4.18), we take into account the correlations which appear between A and R in the interval (t', t). Because of the correlation function $G(\tau)$ of R, this interval is in fact limited to $(t-\tau_C, t)$, so that the master equation derived above includes the effect of the correlations appearing between A and R during a time τ_C. A and R cannot remain correlated during a time longer than τ_C.

To summarize, the condition of validity of the master equation (4.27) is (4.41) which means that the correlation time τ_C of the reservoir is so small that the effect of the coupling between A and R during τ_C is very small and can be treated by perturbation theory. Eq. (4.27) describes the effect on A of

a *single* interaction process with R occurring during the correlation time τ_C. From (4.42) we can, by iteration, calculate the effect of multiple interaction processes occurring during τ_C, an effect which is smaller by a factor $v^2\tau_C^2/\hbar^2$. We finally note that the order of magnitude of Γ is not $v/\hbar$, but $v^2\tau_C/\hbar^2 = (v/\hbar)v\tau_C/\hbar$, which is smaller than $v/\hbar$ by a factor $v\tau_C/\hbar$. This means that the fluctuations of R are so fast, that their effect on A is reduced by a "*motional narrowing*" factor which is precisely $v\tau_C/\hbar$.

4.1.4. Explicit form of the master equation. Physical interpretation

4.1.4.1. Simplification. To simplify, we will assume that A has discrete non-degenerate energy levels and that the distance between any two pairs of levels is large compared to the damping coefficients Γ,

$$|\omega_{ij}| \gg \Gamma \quad \text{when } i \neq j\,. \tag{4.44}$$

In this case, because of the secular approximation, the diagonal elements σ_{ii}, i.e. the populations of energy levels of A, are only coupled to themselves, and not to the off-diagonal elements of σ,

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{ii} = \sum_j R_{iijj}\,\sigma_{jj}\,. \tag{4.45}$$

An off-diagonal element σ_{ij} which corresponds to a non-degenerate Bohr frequency ω_{ij} of A (i.e. no other Bohr frequency ω_{kl} exists with $|\omega_{ij} - \omega_{kl}| \lesssim \Gamma$) is only coupled to itself. Only off-diagonal elements corresponding to the same Bohr frequency (within Γ) are coupled together.

4.1.4.2. Rate equations for the populations. Pauli equations. Let us first calculate the coefficient R_{iiii} (coupling of σ_{ii} to itself). Starting from the second line of (4.27), taking the matrix element of the two operators between $|i\rangle$ and $\langle i|$, keeping only the contribution of σ_{ii}, and using expression (4.32) of $G(\tau)$, we get

$$R_{iiii} = -\frac{1}{\hbar^2}\int_0^\infty \mathrm{d}\tau\, G(\tau)\left(\sum_l A_{il}A_{li}\,\mathrm{e}^{i\omega_{il}\tau} - A_{ii}A_{ii}\right) + \text{hermit. conjug.}$$

$$= -\frac{1}{\hbar^2}\sum_\alpha\sum_\beta\sum_{l\neq i} p(\alpha)|R_{\alpha\beta}|^2|A_{il}|^2\int_0^\infty \mathrm{e}^{i(\omega_{\alpha\beta}+\omega_{il})\tau}\,\mathrm{d}\tau$$

$$+ \text{hermit. conjug.} \tag{4.46}$$

(Note that the term $l = i$ disappears.) Now we use

$$\int_0^\infty e^{i\omega\tau}\,d\tau = \lim_{\epsilon\to 0+}\int_0^\infty e^{i(\omega+i\epsilon)\tau}\,d\tau = \lim_{\epsilon\to 0+}\frac{i}{\omega+i\epsilon} = i\mathcal{P}\frac{1}{\omega} + \pi\delta(\omega)\,. \tag{4.47}$$

As all other quantities are real, the contribution of the principal part $i\mathcal{P}[1/(\omega_{\alpha\beta}+\omega_{il})]$ vanishes when we add the hermitian conjugate and we get

$$R_{iiii} = -\sum_{l\neq i}\Gamma_{i\to l}\,,$$

with

$$\Gamma_{i\to l} = \frac{2\pi}{\hbar}\sum_\alpha p(\alpha)\sum_\beta |\langle\alpha i|V|\beta l\rangle|^2\,\delta(E_{\alpha i}-E_{\beta l})\,, \tag{4.48}$$

where $E_{\alpha i}$ ($E_{\beta l}$) is the unperturbed energy of the combined state $|\alpha i\rangle$ ($|\beta l\rangle$) of the total system $A+R$ and where we have used (4.22).

$\Gamma_{i\to l}$ has a very simple interpretation. It represents the transition rate (given by Fermi's golden rule) of the total system $A+R$ from the initial state $|\alpha, i\rangle$, weighted by the probability $p(\alpha)$ of finding the reservoir R in the state $|\alpha\rangle$, to any final state $|\beta, l\rangle$ where A is in the state l, the δ function expressing the energy conservation for the total system $A+R$. In other words, $\Gamma_{i\to l}$ is the probability per unit time that A makes a transition from $|i\rangle$ to $|l\rangle$ under the effect of the coupling with R.

Let us now calculate R_{iijj} (coupling of σ_{ii} to σ_{jj}) A calculation similar to the previous one gives

$$R_{iijj} = \Gamma_{j\to i}\,. \tag{4.49}$$

Finally we get for $\dot{\sigma}_{ii}$ (Pauli's equations)

$$\dot{\sigma}_{ii} = -\left(\sum_{l\neq i}\Gamma_{i\to l}\right)\sigma_{ii} + \sum_{j\neq i}\Gamma_{j\to i}\,\sigma_{jj}\,. \tag{4.50}$$

Physical interpretation: the population of level $|i\rangle$ decreases because of transitions from $|i\rangle$ to other levels $|l\rangle$, and increases because of transitions from other levels $|j\rangle$ to $|i\rangle$.

In steady state, the populations of two levels N_i and N_j usually satisfy

$$N_i\,\Gamma_{i\to j} = N_j\,\Gamma_{j\to i}\,. \tag{4.51}$$

The number of transitions from $|i\rangle$ to $|j\rangle$ must compensate the number of transitions from $|j\rangle$ to $|i\rangle$.

Particular case of a reservoir R in thermodynamic equilibrium at T. In this case, we have

$$\frac{p(\alpha)}{p(\beta)} = \mathrm{e}^{-(E_\alpha - E_\beta)/kT} . \tag{4.52}$$

Let us write (4.48) in the following way

$$\Gamma_{i\to l} = \frac{2\pi}{\hbar} \sum_\alpha \sum_\beta p(\beta) \frac{p(\alpha)}{p(\beta)} |\langle \alpha i | V | \beta l \rangle|^2 \delta (E_{\alpha i} - E_{\beta l}) . \tag{4.53}$$

But, because of the δ function which expresses that $E_\alpha + E_i = E_\beta + E_l$, i.e. that $E_\alpha - E_\beta = E_l - E_i$, we have

$$\frac{p(\alpha)}{p(\beta)} = \mathrm{e}^{-(E_\alpha - E_\beta)/kT} = \mathrm{e}^{-(E_l - E_i)/kT} . \tag{4.54}$$

We can therefore take $p(\alpha)/p(\beta)$ out of $\Sigma_\alpha \Sigma_\beta$ and obtain, after some rearrangements,

$$\Gamma_{i\to l} = \mathrm{e}^{-(E_l - E_i)/kT} \frac{2\pi}{\hbar} \sum_\beta p(\beta) \sum_\alpha |\langle \beta l | V | \alpha i \rangle|^2 \delta (E_{\beta l} - E_{\alpha i})$$

$$= \mathrm{e}^{-(E_l - E_i)/kT} \Gamma_{l\to i} . \tag{4.55}$$

In other words,

$$\mathrm{e}^{-E_i/kT} \Gamma_{i\to l} = \mathrm{e}^{-E_l/kT} \Gamma_{l\to i} . \tag{4.56}$$

Comparing (4.56) and (4.51), we see that when the system A reaches a steady state, the population of any level i is proportional to $\exp(-E_i/kT)$. By interacting with a reservoir R in thermodynamic equilibrium at temperature T, the small system A itself reaches the thermodynamic equilibrium.

4.1.4.3. Evolution of an off-diagonal element of σ corresponding to a non-degenerate Bohr frequency. We have only to calculate R_{ijij}. The calculations are similar to the previous ones and give

$$\dot{\sigma}_{ij} = -i\omega_{ij}\sigma_{ij} - \left(\Gamma_{ij} + i\frac{\Delta_{ij}}{\hbar}\right)\sigma_{ij} , \tag{4.57}$$

where Γ_{ij} is the damping rate of σ_{ij}; Δ_{ij} is a shift of the energy separation between $|i\rangle$ and $|j\rangle$. Let us first give the expressions of Γ_{ij}. One finds that Γ_{ij} is the sum of a "non-adiabatic" and of an "adiabatic" contribution,

$$\Gamma_{ij} = \Gamma_{ij}^{\text{non-adiab}} + \Gamma_{ij}^{\text{adiab}}, \tag{4.58}$$

where

$$\Gamma_{ij}^{\text{non-adiab}} = \frac{1}{2}\left[\sum_{l \neq i} \Gamma_{i \to l} + \sum_{m \neq j} \Gamma_{j \to m}\right]. \tag{4.59}$$

$\Gamma_{ij}^{\text{non-adiab}}$ is half of the sum of the total transition rates from i to levels l other than i, and from j to levels m other than j. $\Gamma_{ij}^{\text{adiab}}$ is given by

$$\Gamma_{ij}^{\text{adiab}} = \frac{2\pi}{\hbar} \sum_{\alpha} p(\alpha) \sum_{\beta} \delta(E_\beta - E_\alpha)$$

$$\times \{\tfrac{1}{2}|\langle \alpha i|V|\beta i\rangle|^2 + \tfrac{1}{2}|\langle \alpha j|V|\beta j\rangle|^2 - \langle \alpha i|V|\beta i\rangle\langle \beta j|V|\alpha j\rangle\}. \tag{4.60}$$

The first term of the bracket of (4.60) represents the destruction of "coherence" between i and j due to an "elastic collision" with R during which $A + R$ transits from $|\alpha i\rangle$ to $|\beta i\rangle$ (this "collision" is "elastic" because $E_\alpha = E_\beta$) (see fig. 17a). Similarly, the second term of the bracket of (4.60) represents the effect of elastic collisions $|\alpha j\rangle \to |\beta j\rangle$ (fig. 17b). The last term represents a "restitution of coherence" due to elastic collisions which transfer a linear superposition of $|\alpha i\rangle$ and $|\alpha j\rangle$ to a linear superposition of $|\beta i\rangle$ and $|\beta j\rangle$ (fig. 17c).

The transitions which appear in $\Gamma_{ij}^{\text{non-adiab}}$ are such that $E_\beta \neq E_\alpha$ contrary to the transitions which appear in $\Gamma_{ij}^{\text{adiab}}$ for which $E_\alpha = E_\beta$. This is the origin

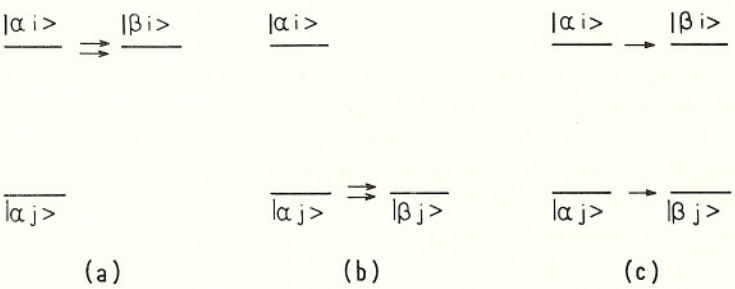

Fig. 17.

of the denominations adiabatic and non-adiabatic. When the diagonal elements of the A operator appearing in $V = AR$ are zero, $\Gamma_{ij}^{\text{adiab}} = 0$.

Let us now come to Δ_{ij}. We find

$$\Delta_{ij} = \Delta_i - \Delta_j \,, \tag{4.61}$$

with

$$\Delta_i = \mathcal{P} \sum_l \sum_\alpha \sum_\beta p(\alpha) \frac{|\langle \alpha i | V | \beta l \rangle|^2}{E_{\alpha i} - E_{\beta l}} \,. \tag{4.62}$$

Here Δ_i is a second order shift due to virtual transitions of the total system $A + R$ from state $|\alpha, i\rangle$ (weighted by $p(\alpha)$) to *all* other states $|\beta, l\rangle$. The singularity of the energy denominator for $E_{\alpha i} = E_{\beta l}$ is eliminated by the principal part.

4.1.4.4. Evolution of a set of off-diagonal elements of σ corresponding to a degenerate Bohr frequency. We find

$$\dot{\sigma}_{ij} = -i\omega_{ij}\,\sigma_{ij} - \left(\Gamma_{ij} + i\frac{\Delta_{ij}}{\hbar}\right)\sigma_{ij} + \sum_{k,l} \Gamma_{kl\to ij}\,\sigma_{kl} \,, \tag{4.63}$$

with $|\omega_{kl} - \omega_{ij}| \lesssim \Gamma$. We have already given Γ_{ij} and Δ_{ij}. We have for $\Gamma_{kl\to ij}$

$$\Gamma_{kl\to ij} = \frac{2\pi}{\hbar} \sum_\alpha \sum_\beta p(\alpha) \langle \beta i | V | \alpha k \rangle \langle \alpha l | V | \beta j \rangle \delta(E_{\alpha k} - E_{\beta i}) \,. \tag{4.64}$$

Here $\Gamma_{kl\to ij}$ corresponds to "collisions" with R (not elastic as $E_\alpha - E_\beta \neq 0$) which transfer a coherent superposition of $|\alpha k\rangle$ and $|\alpha l\rangle$ to a coherent superposition of $|\beta i\rangle$ and $|\beta j\rangle$ (fig. 18).

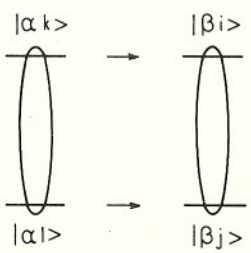

Fig. 18.

4.2. Application to spontaneous emission. General considerations [20]

4.2.1. What is A? What is R?

A is an atom. R is the quantized electromagnetic field which has an infinite number of degrees of freedom (infinite number of "modes").

4.2.2. What is V?

$$V = -\boldsymbol{D} \cdot \boldsymbol{E} = \sum_{a=x,y,z} D_a E_a \,, \tag{4.65}$$

where $\boldsymbol{D}$ is the atomic dipole moment operator; $\boldsymbol{E}$ is the electric field operator evaluated at the position $\boldsymbol{r}$ of the atom (taken at the origin $\boldsymbol{r} = \boldsymbol{0}$);

$$\tilde{E}_a(t) = \tilde{E}_a^{(+)}(t) + \tilde{E}_a^{(-)}(t) \,,$$

where $\tilde{E}_a^{(+)}$ is the positive frequency part of E_a in interaction representation $\tilde{E}_a^{(-)} = (\tilde{E}_a^{(+)})^+$,

$$\tilde{E}_a^{(+)}(t) = \sum_{\boldsymbol{k}} \sum_{\boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}' \perp \boldsymbol{k}} \epsilon_a \mathcal{E}_k a_{\boldsymbol{k}\boldsymbol{\varepsilon}} \, \mathrm{e}^{-i\omega t} \,, \tag{4.66}$$

where $\boldsymbol{\varepsilon}$ is one of two unit vectors $\boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}'$ perpendicular to $\boldsymbol{k}$ ($\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}' = 0$), $\boldsymbol{k}$ being the wave vector.

$$\mathcal{E}_k = i \sqrt{\frac{\hbar\omega}{2\epsilon_0 L^3}} \quad (L^3 = \text{quantization volume}) \,, \tag{4.67}$$

$a_{\boldsymbol{k}\boldsymbol{\varepsilon}}$ ($a^+_{\boldsymbol{k}\boldsymbol{\varepsilon}}$) is the annihilation (creation) operator of one photon $\boldsymbol{k}\boldsymbol{\varepsilon}$,

$$[a_{\boldsymbol{k}\boldsymbol{\varepsilon}}, a^+_{\boldsymbol{k}'\boldsymbol{\varepsilon}'}] = \delta_{\boldsymbol{k}\boldsymbol{k}'} \delta_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}'} \,. \tag{4.68}$$

4.2.3. What is $\sigma_R(0)$?

$$\sigma_R(0) = |0\rangle\langle 0| \quad \text{where } |0\rangle = \text{vacuum state} \,. \tag{4.69}$$

In the vacuum, there is no photon present. All modes are empty. In this state, the reservoir R, i.e. the quantized electromagnetic field, can be considered as in thermodynamic equilibrium at temperature $T = 0$.

As $|0\rangle$ is an eigenstate of H_R, condition (4.13) is fulfilled.

As $\mathrm{Tr}\, a_{k\varepsilon}\, \sigma_R(0) = \langle 0|a_{k\varepsilon}|0\rangle = 0 = \langle 0|a^+_{k\varepsilon}|0\rangle$, we have $\mathrm{Tr}_R(V\sigma_R(0)) = 0$ and condition (4.16) is fulfilled.

4.2.4. Correlation time of the reservoir

Let us calculate

$$G_{ab}(\tau) = \mathrm{Tr}\, \sigma_R(0)\tilde{E}_a(t)\tilde{E}_b(t-\tau) = \langle 0|\tilde{E}_a(t)\tilde{E}_b(t-\tau)|0\rangle\,. \tag{4.70}$$

Using (4.65), (4.66) and (4.68), we immediately get

$$G_{ab}(\tau) = \sum_{k;\varepsilon,\varepsilon' k} \epsilon_a \epsilon_b |\mathcal{E}_k|^2\, \mathrm{e}^{-i\omega\tau}\,.$$

Summation over the two unit vectors $\boldsymbol{\varepsilon}$, $\boldsymbol{\varepsilon}'$: Using the completeness relation for the three orthonormal vectors $\boldsymbol{\varepsilon}$, $\boldsymbol{\varepsilon}'$, $\boldsymbol{\kappa} = \boldsymbol{k}/k$, we get

$$\epsilon_a \epsilon_b + \epsilon'_a \epsilon'_b + \kappa_a \kappa_b = \delta_{ab}\,,$$

so that

$$\sum_{\varepsilon,\varepsilon' \perp k} \epsilon_a \epsilon_b = \epsilon_a \epsilon_b + \epsilon'_a \epsilon'_b = \delta_{ab} - \kappa_a \kappa_b = \delta_{ab} - \frac{\kappa_a \kappa_b}{k^2}\,. \tag{4.71}$$

Transformation from a discrete sum to an integral:

$$\sum_k = \frac{L^3}{(2\pi)^3}\int \mathrm{d}^3 k = \frac{L^3}{(2\pi)^3}\int \mathrm{d}\Omega\, k^2\, \mathrm{d}k\,. \tag{4.72}$$

Summation over angles:

$$\int \mathrm{d}\Omega \left(\delta_{ab} - \frac{\kappa_a \kappa_b}{k^2}\right) = \tfrac{2}{3}\delta_{ab}\,. \tag{4.73}$$

Finally, we get

$$G_{ab}(\tau) = \frac{\hbar c}{3\epsilon_0}\,\frac{1}{(2\pi)^3}\,\delta_{ab}\int \mathrm{d}\omega\, \frac{\omega^3}{C^4}\,\mathrm{e}^{-i\omega\tau}\,. \tag{4.74}$$

We see that the correlation time of the "vacuum fluctuations" is extremely short, certainly shorter than the optical period $1/\omega_0$ of the atom A,

$$\tau_C < 1/\omega_0 \,. \tag{4.75}$$

4.2.5. Order of magnitude of the damping coefficient Γ. *Validity of the master equation*

Calculating Γ by Fermi's golden rule, we find that

$$\Gamma/\omega_0 \sim \alpha^3 \,, \tag{4.76}$$

where ω_0 is the optical frequency and $\alpha = e^2/4\pi\epsilon_0\hbar c = 1/137$ is the fine structure constant. Comparing (4.75) and (4.76), we see that the damping time $T = 1/\Gamma$ satisfies

$$T = 1/\Gamma \gg 1/\omega_0 > \tau_C \,. \tag{4.77}$$

As the damping time is much longer than the correlation time, this shows that the master equation can be used for describing spontaneous emission.

4.2.6. Some important relations satisfied by the $\Gamma_{i\to l}$

As R is in the ground state $|\alpha\rangle = |0\rangle$, all other states $|\beta\rangle$ which are connected to $|\alpha\rangle$ by V have a higher energy. These states correspond to one photon in a given mode $|\beta\rangle = |\boldsymbol{k}\boldsymbol{\varepsilon}\rangle$,

$$E_\beta - E_\alpha > 0 \,. \tag{4.78}$$

Consequently, the atom A can only go from a state $|i\rangle$ to another state $|l\rangle$ such that

$$E_l - E_i = E_\alpha - E_\beta < 0 \,. \tag{4.79}$$

Therefore

$$\Gamma_{i\to l} = 0 \quad \text{if} \quad E_l - E_i > 0 \,. \tag{4.80}$$

By spontaneous emission, an atom can only decay to lower states. The steady state corresponds to the atom in the ground state (thermodynamic equilibrium at $T = 0$). For the same reason [see expression (4.64)]

$$\Gamma_{kl\to ij} = 0 \quad \text{if} \quad E_i - E_k = E_j - E_l > 0 \,. \tag{4.81}$$

As D is an odd operator, it has no diagonal elements in the atomic basis and

$$\Gamma_{ij}^{\text{adiab}} = 0 \,. \tag{4.82}$$

4.2.7. Signification of the Δ_i

Δ_i is the "Lamb shift" of level i due to the coupling of the atom to the electromagnetic field. We will not consider here the problem of the renormalization of the Δ_i's, and will suppose that the Δ_i's are incorporated in the atomic Hamiltonian. Let us just remark that we have not used r.w.a. and that the master equation approach gives simultaneously the Lamb shifts of the two states e and g of an atomic transition. This is not the case in the Wigner-Weisskopf approach where the Lamb shift of the final state is more difficult to derive.

4.3. Explicit form of the master equation describing spontaneous emission in some particular cases

4.3.1. Two-level atom. $E_e - E_g = \hbar\omega_0$

Let us put: $\Gamma_{e\to g} = \Gamma$. We have seen that $\Gamma_{g\to e} = 0$ and that $\Gamma_{eg}^{\text{adiab}} = 0$, so that the master equation can be written

$$\dot{\sigma}_{ee} = -\Gamma\sigma_{ee} \,, \qquad \dot{\sigma}_{eg} = -i\omega_0\,\sigma_{eg} - \tfrac{1}{2}\Gamma\sigma_{eg} \,,$$

$$\dot{\sigma}_{gg} = \Gamma\sigma_{ee} \,, \qquad \dot{\sigma}_{ge} = (\dot{\sigma}_{eg})^* = i\omega_0\sigma_{ge} - \tfrac{1}{2}\Gamma\sigma_{ge} \,. \tag{4.83}$$

Spontaneous emission is sometimes described by a "non-hermitian Hamiltonian" obtained by just adding an imaginary term, $-\frac{1}{2}i\Gamma$, to the unperturbed energy of e. Let us remark that it is impossible, with such an approach, to derive the second equation (4.83) which describes the transfer of atoms from e to g.

If we consider the fictitious spin $\frac{1}{2}\boldsymbol{S}$ associated with this two-level problem, we have

$$\langle S_z\rangle = \tfrac{1}{2}(\sigma_{ee} - \sigma_{gg}) \,, \quad \langle S_+\rangle = \sigma_{ge} \,, \quad \langle S_-\rangle = \sigma_{eg} \,, \tag{4.84}$$

so that the master equation can also be written as

$$\langle \dot{S}_z\rangle = -\Gamma(\langle S_z\rangle + \tfrac{1}{2}) \,, \quad \langle \dot{S}_\pm\rangle = -\tfrac{1}{2}\Gamma\langle S_\pm\rangle \pm i\omega_0\langle S_\pm\rangle \,. \tag{4.85}$$

We have used $\sigma_{ee} + \sigma_{gg} = 1$ for the first equation. This equation means that $\langle S_z\rangle$ reaches its steady state value, $-\frac{1}{2}$, corresponding to the spin in the $|-\rangle$ state, with a rate Γ. The second equation means that $\langle S_\pm\rangle$ are damped to zero with a rate $\frac{1}{2}\Gamma$.

4.3.2. Harmonic oscillator

As the matrix elements of $D = eX$ are non-zero only between two adjacent states $|n\rangle$ and $|n-1\rangle$ and are proportional to $\sqrt{n}$, we have

$$\Gamma_{n\to m} = n\Gamma\delta_{m,n-1}\,, \tag{4.86}$$

where

$$\Gamma = \Gamma_{1\to 0}\,.$$

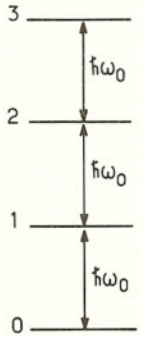

Fig. 19.

As the levels are equidistant, we have a coupling between σ_{pq} and σ_{mn} when $p - q = m - n$. Using (4.64), we immediately find that $\Gamma_{pq\to mn}$ is proportional to the product of the matrix elements of X between p and m, and between q and n. Furthermore, as m must be lower than p, we have

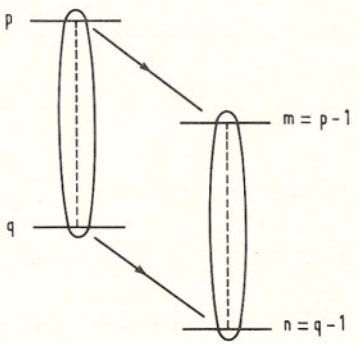

Fig. 20.

$$\Gamma_{pq\to mn} = \sqrt{pq}\,\Gamma\,\delta_{m,p-1}\,\delta_{n,q-1}\,. \tag{4.87}$$

Finally, we get the following master equation:

$$\begin{aligned}
\dot{\sigma}_{n,n} &= -n\Gamma\sigma_{n,n} + (n+1)\Gamma\sigma_{n+1,n+1}\,,\\
\dot{\sigma}_{m,n} &= -i(m-n)\omega_0\,\sigma_{m,n}\\
&\quad -\tfrac{1}{2}(m+n)\Gamma\sigma_{m,n} + \sqrt{(m+1)(n+1)}\,\Gamma\sigma_{m+1,n+1}\,.
\end{aligned} \tag{4.88}$$

We now show from (4.88) that the mean energy $\langle H\rangle - \frac{1}{2}\hbar\omega$, $\langle a\rangle$, $\langle a^+\rangle$ are damped with rates equal to Γ, $\frac{1}{2}\Gamma$, $\frac{1}{2}\Gamma$, respectively.

Evolution of $\langle H\rangle - \frac{1}{2}\hbar\omega = \hbar\omega\,\Sigma_{n=0}^{\infty}\, n\sigma_{n,n}$. Using (4.88), we get

$$\sum_{n=0}^{\infty} n\dot{\sigma}_{nn} = \Gamma\left[-\sum_{n=0}^{\infty} n^2\sigma_{nn} + \sum_{n=0}^{\infty} n(n+1)\sigma_{n+1,n+1}\right]. \tag{4.89}$$

But

$$\sum_{n=0}^{\infty} n(n+1)\sigma_{n+1,n+1} = \sum_{n=0}^{\infty}\,[(n+1)^2 - (n+1)]\sigma_{n+1,n+1}$$

$$= \sum_{n=1}^{\infty}\,(n^2-n)\sigma_{nn} = \sum_{n=0}^{\infty}\,(n^2-n)\sigma_{nn}\,,$$

so that

$$\sum_{n=0}^{\infty} n\dot{\sigma}_{nn} = -\Gamma\sum_{n=0}^{\infty} n\sigma_{nn}\,,$$

which may be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle H\rangle - \tfrac{1}{2}\hbar\omega) = -\Gamma(\langle H\rangle - \tfrac{1}{2}\hbar\omega)\,. \tag{4.90}$$

Evolution of $\langle a^+\rangle = \Sigma_{n=1}^{\infty}\,\sqrt{n}\,\sigma_{n-1,n}$. Using (4.88), we get

$$\sum_{n=1}^{\infty} \sqrt{n}\, \dot{\sigma}_{n-1,n} = i\omega_0 \left(\sum_{n=1}^{\infty} \sqrt{n}\, \sigma_{n-1,n} \right)$$

$$+ \Gamma \left[- \sum_{n=1}^{\infty} \tfrac{1}{2}(2n-1)\sqrt{n}\, \sigma_{n-1,n} + \sum_{n=1}^{\infty} n\sqrt{n+1}\, \sigma_{n,n+1} \right] . \quad (4.91)$$

But,

$$\sum_{n=1}^{\infty} n\sqrt{n+1}\, \sigma_{n,n+1} = \sum_{n=0}^{\infty} n\sqrt{n+1}\, \sigma_{n,n+1} = \sum_{n=1}^{\infty} (n-1)\sqrt{n}\, \sigma_{n-1,n} .$$

The second line of (4.91) can therefore be written as

$$-\Gamma \sum_{n=1}^{\infty} \sqrt{n}\, \sigma_{n-1,n} \underbrace{[\tfrac{1}{2}(2n-1) - (n-1)]}_{\frac{1}{2}} = -\tfrac{1}{2}\Gamma \sum_{n=1}^{\infty} \sqrt{n}\, \sigma_{n-1,n} .$$

Finally, we have

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle a^+ \rangle = (i\omega_0 - \tfrac{1}{2}\Gamma) \langle a^+ \rangle , \quad (4.92a)$$

and consequently

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle a \rangle = (-i\omega_0 - \tfrac{1}{2}\Gamma) \langle a \rangle . \quad (4.92b)$$

As $\langle X \rangle$ and $\langle P \rangle$ are linear combinations of $\langle a \rangle$ and $\langle a^+ \rangle$, we also conclude that $\langle X \rangle$ and $\langle P \rangle$ are damped by spontaneous emission to zero with a rate $\frac{1}{2}\Gamma$. These results clearly show the importance of the coupling coefficients $\Gamma_{m+1\ n+1 \to m,n}$. If we forget these terms in (4.88), we are tempted to consider that σ_{mn} is damped with a rate $\frac{1}{2}(m+n)\Gamma$. Such a mistake would lead us to the prediction that, the higher the initial excitation of the oscillator, the faster is the damping of $\langle X \rangle$. In fact the coherence which leaves the couple of states $m+1, n+1$ is not lost; it is transferred partially to m, n and this explains why the damping of $\langle X \rangle$ is independent of the initial excitation, and consequently why the spectral distribution of the light emitted by the oscillator has a width Γ independent of the initial state.

4.3.3. Dressed atom of § 2.2.3

We come back to the dressed atom studied in § 2.2.3, and we study what

happens for a strong resonant irradiation ($\omega_L = \omega_0$, $\omega_1 \gg \Gamma$). What we have neglected in § 2.2.3.2 is the transfer of coherence from one pair of levels to another one corresponding to the same Bohr frequency, $\omega_0 + \omega_1$, ω_0, $\omega_0 - \omega_1$. As we suppose $\omega_1 \gg \Gamma$ we can, because of the secular approximation, neglect any coupling between ω_0 and $\omega_0 \pm \omega_1$, $\omega_0 + \omega_1$ and $\omega_0 - \omega_1$. The important transfers are represented below (fig. 21). The numbers near the arrows are the matrix elements of D between the two connected levels which may be calculated from the wave functions given in fig. 13. Remember that $\Gamma = [\langle g|D|e\rangle]^2 \sim d^2$.

Let us recall that we have established that the total transition rate from any level is the same and equal to $\frac{1}{2}\Gamma$. So the rate of disparition of any coherence is $\frac{1}{2}(\frac{1}{2}\Gamma + \frac{1}{2}\Gamma) = \frac{1}{2}\Gamma$. Let us now calculate the transfer of coherence corresponding to figs. 21a, b, c, d, and which were neglected above in § 2.2.3. We have just to multiply the two numbers shown near the arrows for a given transfer and use $d^2 \sim \Gamma$.

If we put

$$\langle \psi_n^{\epsilon} | \sigma | \psi_{n'}^{\epsilon'} \rangle = \sigma_{nn'}^{\epsilon\epsilon'} , \tag{4.93}$$

we get

$$\text{fig. a} \rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\sigma_{n,n-1}^{+-} = -i(\omega_0 + \omega_1)\sigma_{n,n-1}^{+-} - \tfrac{1}{2}\Gamma\sigma_{n,n-1}^{+-} - \tfrac{1}{4}\Gamma\sigma_{n+1,n}^{+-} ,$$

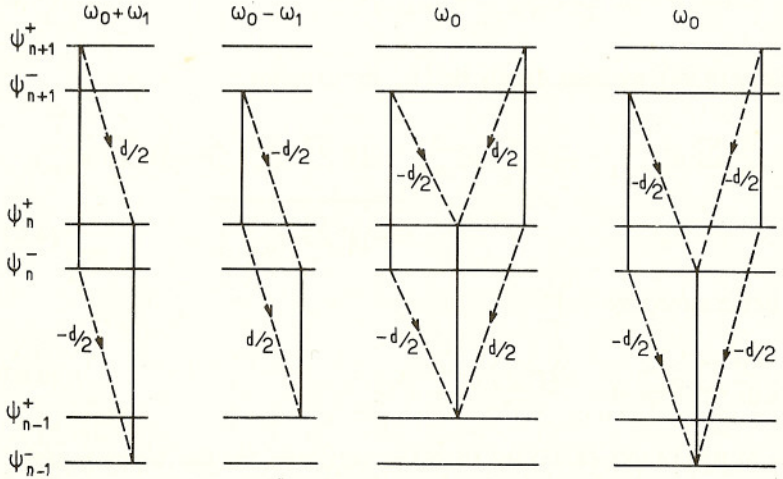

Fig. 21.

$$\text{fig. b} \rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\sigma^{-+}_{n,n-1} = -i(\omega_0-\omega_1)\sigma^{-+}_{n,n-1} - \tfrac{1}{2}\Gamma\sigma^{-+}_{n,n-1} - \tfrac{1}{4}\Gamma\sigma^{-+}_{n+1,n},$$

$$\text{fig. c} \rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\sigma^{++}_{n,n-1} = -i\omega_0\,\sigma^{++}_{n,n-1} - \tfrac{1}{2}\Gamma\sigma^{++}_{n,n-1} + \tfrac{1}{4}\Gamma\sigma^{++}_{n+1,n} + \tfrac{1}{4}\Gamma\sigma^{--}_{n+1,n},$$

$$\text{fig. d} \rightarrow \frac{\mathrm{d}}{\mathrm{d}t}\sigma^{--}_{n,n-1} = -i\omega_0\,\sigma^{--}_{n,n-1} - \tfrac{1}{2}\Gamma\sigma^{--}_{n,n-1} + \tfrac{1}{4}\Gamma\sigma^{++}_{n+1,n} + \tfrac{1}{4}\Gamma\sigma^{--}_{n+1,n}. \tag{4.94}$$

Subtracting the two last equations, we get

$$\frac{\mathrm{d}}{\mathrm{d}t}(\sigma^{++}_{n,n-1} - \sigma^{--}_{n,n-1}) = (-i\omega_0 - \tfrac{1}{2}\Gamma)(\sigma^{++}_{n,n-1} - \sigma^{--}_{n,n-1}). \tag{4.95}$$

Let us now use eqs. (4.94) and (4.95) for determining the damping rates of the components of $\langle D\rangle$ oscillating at $\omega_0+\omega_1$, $\omega_0-\omega_1$, ω. We get for the negative frequency parts

$$\langle D(\omega_0+\omega_1)\rangle = -\tfrac{1}{2}d\sum_n \sigma^{+-}_{n,n-1},$$

$$\langle D(\omega_0-\omega_1)\rangle = -\tfrac{1}{2}d\sum_n \sigma^{-+}_{n,n-1},$$

$$\langle D(\omega_0)\rangle = \tfrac{1}{2}d\sum_n (\sigma^{++}_{n,n-1} - \sigma^{--}_{n,n-1}). \tag{4.96}$$

Using (4.94), we immediately find for the damping

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_n \sigma^{+-}_{n,n-1} = -\tfrac{1}{2}\Gamma\sum_n \sigma^{+-}_{n,n-1} \underbrace{-\tfrac{1}{4}\Gamma\sum_n \sigma^{+-}_{n+1,n}}_{\simeq -\frac{1}{4}\Gamma\sum_n \sigma^{+-}_{n,n-1}} = -\tfrac{3}{4}\Gamma\sum_n \sigma^{+-}_{n,n-1}, \tag{4.97}$$

and in the same way

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_n \sigma^{-+}_{n,n-1} = -\tfrac{3}{4}\Gamma\sum_n \sigma^{-+}_{n,n-1}. \tag{4.98}$$

From (4.97), (4.98), (4.95) and (4.96) we conclude that the damping rate of $\langle D(\omega_0+\omega_1)\rangle$ is $\frac{3}{4}\Gamma$; that of $\langle D(\omega_0-\omega_1)\rangle$ is $\frac{3}{4}\Gamma$, and that of $\langle D(\omega_0)\rangle$ is $\frac{1}{2}\Gamma$.

We see now that the spectrum given in fig. 14 is not quantitatively correct: the two sidebands have a width which is not equal to $2 \times \frac{1}{2}\Gamma = \Gamma$ but to $2 \times \frac{3}{4}\Gamma = \frac{3}{2}\Gamma$. As the height is inversely proportional to the width, we see that the height must be reduced by a factor $(\frac{1}{2}\Gamma)/(\frac{3}{4}\Gamma) = \frac{2}{3}$. So the two sidebands have a half-width $\frac{3}{4}\Gamma$ and a height three times smaller than the height of the central component.

We will derive again this result in a next section by calculating the correlation function of the dipole. But we see how the transfer of coherences in the master equation approach can describe the effect of interferences between cascades discussed in § 2.2.3.

4.3.4. Atomic transition between two states e and g of angular momentum J_e and J_g [9,10,22]

The atomic density matrix has the following form:

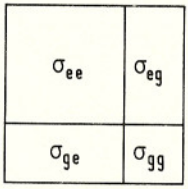

Fig. 22.

The Zeeman sublevels of a are called $|J_e, m_e\rangle$ $(-J_e \leqslant m_e \leqslant J_e)$, those of g are called $|J_g, m_g\rangle$ $(-J_g \leqslant m_g \leqslant J_g)$; σ_g is a $(2J_g + 1) \times (2J_g + 1)$ matrix, σ_e a $(2J_e + 1) \times (2J_e + 1)$ matrix; σ_{eg} has $2J_e + 1$ rows and $2J_g + 1$ columns; $\sigma_{ge} = \sigma_{eg}^{+}$. The diagonal elements $\sigma_{m_e m_e}$ and $\sigma_{m_g m_g}$ of σ_e and σ_g are the populations of the Zeeman sublevels of e and g. The off-diagonal elements $\sigma_{m_e m'_e}$ and $\sigma_{m_g m'_g}$ of σ_e and σ_g are called "Zeeman coherences".

σ_{eg} consists only of off-diagonal elements $\sigma_{m_e m_g}$ which are called "*optical coherences*". Because of the secular approximation $(\omega_0 \gg \Gamma)$, σ_e is only coupled to σ_e and not to σ_{eg} (σ_e is not coupled to σ_g because $\Gamma_{g \to e} = 0$; see (4.80)); σ_g is coupled to σ_e, σ_{eg} is coupled to σ_{eg}.

Because V is a sum of products of atomic and field operators (see (4.65)) we must replace in (4.27) $G(\tau)$ by $G_{ab}(\tau)$ and the two A operators by D_a and D_b and sum over a and b. But as G_{ab} contains δ_{ab} (see (4.74)), we have just to add a subscript a to the two D operators and to sum over a.

(i) Damping of σ_e. From the previous remark and eq. (4.27), we get for the damping term of σ_e

$$\frac{d\sigma_e}{dt} = -\frac{1}{\hbar^2}\sum_a \int_0^\infty G_{aa}(\tau) P_e D_a P_g \, e^{-iH_A\tau/\hbar} D_a \, e^{iH_A\tau/\hbar} P_e \sigma_e \, d\tau$$

$$+ \text{hermit. conj.}, \tag{4.99}$$

where P_e and P_g are the projectors into e and g. Using

$$P_g \, e^{-iH_A\tau/\hbar} D_a \, e^{iH_A\tau/\hbar} P_e = e^{i\omega_0\tau} P_g D_a P_e ,$$

$$P_e \, e^{-iH_A\tau/\hbar} D_a \, e^{+iH_A\tau/\hbar} P_e = e^{-i\omega_0\tau} P_e D_a P_g , \tag{4.100}$$

(we suppose that e and g are degenerate, i.e. that there is no magnetic field), we get

$$\frac{d}{dt}\sigma_e = -\frac{1}{\hbar^2}\sum_a \int_0^\infty G_{aa}(\tau) P_e D_a P_g D_a P_e \, \sigma_e(t) e^{i\omega_0\tau} \, d\tau$$

$$+ \text{hermit. conjug.} \tag{4.101}$$

$G_{aa}(\tau)$ does not depend on a (see (4.74)). The operator $\Sigma_a P_e D_a P_g D_a P_e$ is obviously scalar in the e space (the scalar product $\Sigma_a D_a D_a$ is scalar and P_g is also scalar). One easily finds

$$\sum_a P_e D_a P_g D_a P_e = \frac{1}{2J_e+1} |\langle e \| D \| g \rangle|^2 P_e , \tag{4.102}$$

where $\langle e \| D \| g \rangle$ is the reduced matrix element of $\boldsymbol{D}$ between e and g.

Using expression (4.74) of $G_{aa}(\tau)$, integrating over τ, we get

$$\frac{d\sigma_e}{dt} = -\Gamma_{e\to g}\sigma_e , \tag{4.103}$$

where Γ is a number given by (q is the charge of the electron: $\boldsymbol{D} = q\boldsymbol{r}$),

$$\Gamma_{e\to g} = \frac{2\pi}{\hbar}\frac{q^2}{\epsilon_0}\left(\frac{1}{2J_e+1}\right)^2 |\langle e \| r \| g \rangle|^2 \, \frac{\omega_0^3}{(2\pi c)^3} . \tag{4.104}$$

We note that all matrix elements of σ_e are damped at the same rate. This is

due to the *isotropy of spontaneous emission.* The atom interacts with all modes of the electromagnetic field, having all wave vectors and all polarizations.

(ii) Damping of σ_{eg}. We always start from (4.27) and get

$$\frac{\mathrm{d}\sigma_{eg}}{\mathrm{d}t} = -i\omega_0\sigma_{eg} - \frac{1}{\hbar^2}\sum_a \int_0^\infty P_e D_a P_g D_a P_e \, \sigma_{eg} G_{aa}(\tau) \mathrm{e}^{i\omega_0\tau}\,\mathrm{d}\tau$$

$$-\frac{1}{\hbar^2}\sum_a \int_0^\infty \sigma_{eg} P_g D_a P_e D_a P_g \, G^*_{aa}(\tau)\mathrm{e}^{-i\omega_0\tau}\,\mathrm{d}\tau\,, \tag{4.105}$$

from which we derive, using (4.74), (4.102) and (4.104),

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{eg} = (-i\omega_0 - \tfrac{1}{2}\Gamma_{e\to g})\sigma_{eg} \tag{4.106}$$

(remember we have included the Lamb shift in H_A).

(iii) Evolution of σ_g. The same calculations give

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_g = \frac{1}{\hbar^2}\int_0^\infty \mathrm{d}\tau \sum_a G_{aa}(\tau) P_g D_a P_e \, \sigma_e(t) P_e D_a P_g \, \mathrm{e}^{i\omega_0\tau}$$

$$+ \text{hermit. conjug.}\,, \tag{4.107}$$

which can be transformed into

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_g = \frac{2}{\hbar^2}\left(\mathcal{R}e \int_0^\infty G(\tau)\mathrm{e}^{i\omega_0\tau}\,\mathrm{d}\tau\right)\sum_a P_g D_a P_e \, \sigma_e(t) P_e D_a P_g\,. \tag{4.108}$$

If we introduce the standard components of $\boldsymbol{D}$,

$$D_{+1} = -\sqrt{\tfrac{1}{2}}(D_x + iD_y)\,, \quad D_0 = D_z\,, \quad D_{-1} = \sqrt{\tfrac{1}{2}}(D_x - iD_y)\,, \tag{4.109}$$

we can write

$$\sum_{a=x,y,z} P_g D_a P_e \, \sigma_e P_e D_a P_g$$

$$= \sum_{q=-1,0,+1} (-1)^q P_g D_q P_e \, \sigma_e P_e D_{-q} P_g\,. \tag{4.110}$$

Using the Wigner-Eckart theorem,

$$\langle J_e, m_e | D_q | J_g, m_g \rangle = \frac{1}{\sqrt{2J_e+1}} \langle e \| D \| g \rangle \langle J_e, m_e | J_g, 1, m_g, q \rangle, \quad (4.111)$$

where

$$\langle J_e, m_e | J_g, 1, m, q \rangle$$

is a Clebsch-Gordan coefficient, we get after simple calculations

$$\frac{\mathrm{d}}{\mathrm{d}t} \sigma_{m_g m'_g} = \Gamma_{e \to g} \sum_{q=-1,0,+1} \sigma_{m_e = m_g + q, m'_e = m'_g + q}$$

$$\times \langle J_e, m_{g+q} | J_g, 1, m_g, q \rangle \langle J_e, m'_g + q | J_g, 1, m'_g, q \rangle . \quad (4.112)$$

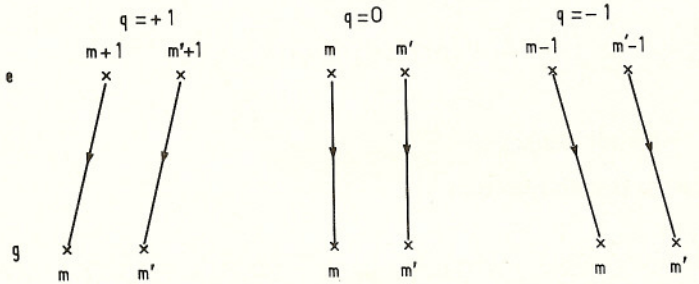

Fig. 23.

The different arrows represent Clebsch-Gordan coefficients, the product of which appears in the transfer coefficients.

Examples. (i) $J_e = 1 \to J_g = 0$ transition (we put $\Gamma = \Gamma_{e \to g}$)

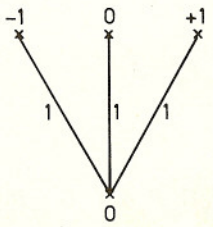

Fig. 24.

$$\frac{d\sigma_e}{dt} = -\Gamma\sigma_e\,, \qquad \frac{d\sigma_{eg}}{dt} = -\tfrac{1}{2}\Gamma\sigma_{eg}\,,$$

$$\frac{d}{dt}\sigma^g_{00} = \Gamma(\sigma^e_{+1,+1} + \sigma^e_{00} + \sigma^e_{-1,-1})\,. \tag{4.113}$$

(ii) $J_e = \frac{1}{2} \to J_g = \frac{1}{2}$ transition

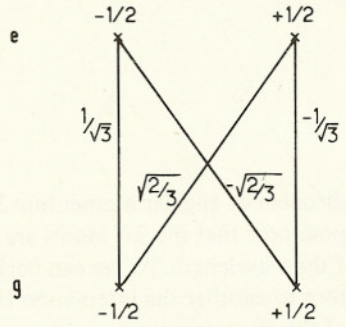

Fig. 25.

$$\frac{d\sigma_e}{dt} = -\Gamma\sigma_e\,, \qquad \frac{d}{dt}\sigma_{eg} = -\tfrac{1}{2}\Gamma\sigma_{eg}\,,$$

$$\frac{d}{dt}\sigma^g_{++} = \Gamma(\tfrac{1}{3}\sigma^e_{++} + \tfrac{2}{3}\sigma^e_{--})\,,$$

$$\frac{d}{dt}\sigma^g_{--} = \Gamma(\tfrac{1}{3}\sigma^e_{--} + \tfrac{2}{3}\sigma^e_{++})\,,$$

$$\frac{d}{dt}\sigma^g_{+-} = -\Gamma\,\tfrac{1}{3}\sigma^e_{+-}\,. \tag{4.114}$$

Here again, note the isotropy of spontaneous emission. Populations of σ_g are only coupled to populations of σ_e, Zeeman coherence of σ_g is only coupled to Zeeman coherence of σ_e.

Remarks. (i) If g is not the ground state, the transfer from e to g described by eq. (4.112) remains unchanged. In (4.103), $\Gamma_{e\to g}$ must be replaced by $\Gamma_e = \Sigma_j \Gamma_{e\to j}$, and in (4.106) by $\frac{1}{2}(\Gamma_e + \Gamma_g)$ where $\Gamma_g = \Sigma_l \Gamma_{g\to l}$.

(ii) The master equation describing spontaneous emission can be expanded on a set of irreducible tensor operators [22].

4.3.5. Angular momentum. Connection with superradiance [20]

Let us consider an ensemble of $2N$ identical atoms. If $\boldsymbol{S}_i$ is the fictitious spin-$\frac{1}{2}$ associated with atom i, the atomic Hamiltonian H_a may be written as

$$H_a = \sum_{i=1} \omega_0 S_z^i = \omega_0 S_z \,, \tag{4.115}$$

with

$$\boldsymbol{S} = \sum_{i=1}^{2N} \boldsymbol{S}_i \,. \tag{4.116}$$

It looks like the Hamiltonian of angular momentum $\boldsymbol{S}$ in a static magnetic field parallel to $0z$. Suppose now that the $2N$ atoms are in a volume small compared to the cube of the wavelength. As we can neglect the variations of $\exp(i\boldsymbol{k} \cdot \boldsymbol{R}_i)$ from one atom to another the interaction Hamiltonian of these $2N$ atoms with a mode of the electromagnetic field may be rewritten as

$$V \sim \sum_i (S_+^i a + S_-^i a^+) = S_+ a + S_- a^+ \,. \tag{4.117}$$

It looks like the interaction Hamiltonian of angular momentum $\boldsymbol{S}$ with the same electromagnetic field. Suppose that we start with all atoms in the upper state. The initial state is the completely symmetric vector

$$\underbrace{|+ +, \ldots +\rangle}_{2N} = |J = 2N, M = J\rangle \,. \tag{4.118}$$

As H_a and V are symmetric, the state vector remains completely symmetric at any later time, i.e. remains in the $J = 2N$ subspace. We have therefore the following simple result: Spontaneous emission from a system of $2N$ identical atoms, initially excited and contained in a volume small compared to λ^3 is a problem mathematically equivalent to the spontaneous emission of an angular momentum $J = 2N$ starting from its upper level $|J, M = J\rangle$. Applying the general expressions (4.48) and (4.64) we get for an angular momentum $J = 2N$

$$\Gamma_{M \to N} = \Gamma \delta_{N,M-1} [J(J+1) - M(M-1)] \,, \tag{4.119}$$

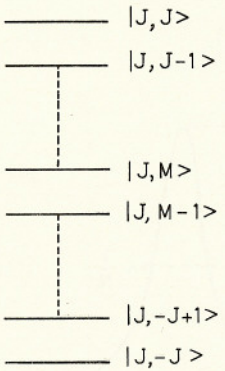

Fig. 26.

$$\Gamma_{PQ\to MN} = \Gamma \delta_{M,P-1}\, \delta_{N,Q-1}$$

$$\times \sqrt{[J(J+1) - P(P-1)]\,[J(J+1) - Q(Q-1)]}\,, \qquad (4.120)$$

where Γ is a constant. We will not write down the master equation in such a case (let us just mention that $\langle J_z \rangle$ and $\langle J_\pm \rangle$ are not eigenvectors of this equation), but we will restrict ourselves to a qualitative discussion. According to (4.119), we see that, when $M \sim J = 2N$,

$$\Gamma_{M\to M-1} \sim \Gamma J \sim 2N\Gamma\,. \qquad (4.121)$$

At the beginning of the decay of the $2N$ atoms, the decay rate is proportional to $2N$. When $M \sim 0$, i.e. when half of the initial excitation has been radiated, we see from (4.119) that

$$\Gamma_{M\to M-1} \sim \Gamma J^2 \sim 4N^2\Gamma\,. \qquad (4.122)$$

The radiation rate is considerably higher. Finally, when $M = -J$, all atoms are in the lower state and the system does not radiate any longer.

We expect therefore that, as a function of time, the radiation is not emitted at a constant rate, but as a short burst.

The total area under the curve of fig. 27 is of course proportional to N (initial total energy). As the height of the maximum is proportional to N^2, we expect that the width of the superradiant pulse is proportional to $1/N$.

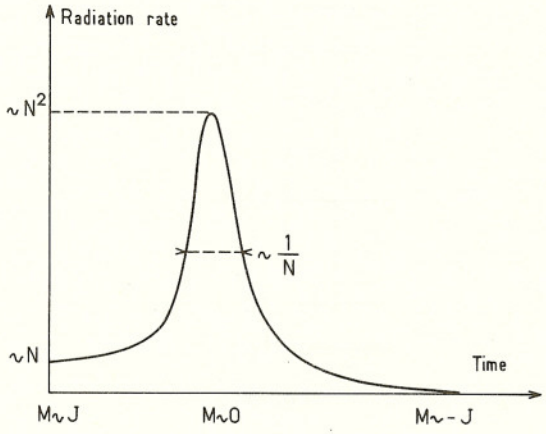

Fig. 27.

5. Master equation describing the interaction with a light beam in two particular cases

5.1. Coherent monochromatic light beam

5.1.1. How to describe spontaneous emission in presence of a light beam

Let us come back to figs. 13 and 21. If $\omega_1 \ll \omega_0$, we can, when we calculate the transition rate between two levels of the dressed atom, consider that the density of final states of the spontaneously emitted photons is the same for the three frequencies ω_0, $\omega_0 + \omega_1$, $\omega_0 - \omega_1$. From (4.74), we see that this density is proportional to ω^3, so that this approximation is equivalent to

$$\omega^3 \sim (\omega_0 + \omega_1)^3 \sim (\omega_0 - \omega_1)^3 , \qquad \text{when } \omega_1 \ll \omega_0 . \tag{5.1}$$

This means that, when studying spontaneous emission, we can neglect the splittings which appear as a consequence of the coupling with the light beam, if these splittings are sufficiently small compared to the optical frequency. In other words, we can add independently in the master equation the terms describing spontaneous emission (which have been calculated in sect. 4) and those which describe the coupling with the light beam.

Physically, condition $\omega_1 \ll \omega_0$ means that $1/\omega_1 \gg 1/\omega_0 > \tau_C$, i.e. that the correlation time of the vacuum fluctuations is much shorter than the characteristic time $1/\omega_1$ of the coupling between the atoms and the laser beam.

During the correlation time τ_C of an elementary spontaneous emission process, we can therefore neglect this coupling. Between two spontaneous emission processes, separated by times of the order of $1/\Gamma$, this coupling plays an important role and we must, of course, take it into account by adding the corresponding terms in the master equation.

The same argument shows that, if there is a magnetic field giving rise to a Zeeman splitting ω_Z, and if $\omega_Z \ll \omega_0$, we have just to add the terms $(1/i\hbar)[H_Z, \sigma_e]$, $(1/i\hbar)[H_Z, \sigma_g]$, $(1/i\hbar)[H_Z, \sigma_{eg}]$ to the three equations (4.103), (4.112), (4.106) (H_Z being the Zeeman Hamiltonian).

5.1.2. Classical treatment of the light beam

To simplify, we will adopt a classical treatment of the incident light beam. It can be shown that this leads to the same results as a quantum treatment. We will call $\mathcal{E}\,\hat{\varepsilon}_0 \cos \omega_L t$ the incident electric field of frequency ω_L, polarization $\hat{\varepsilon}_0$, amplitude $\mathcal{E}$. In the rotating wave approximation, the coupling with the atom is described by the following interaction Hamiltonian:

$$2V = -\mathcal{E}\,\hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg} e^{-i\omega_L t} - \mathcal{E}^* \hat{\boldsymbol{\varepsilon}}_0^* \cdot \boldsymbol{D}_{ge} e^{i\omega_L t} . \tag{5.2}$$

We suppose that the light beam is in resonance (or quasi-resonance) with an atomic transition $e \to g$ connecting two levels of angular momentum J_e and J_g · D_{eg} represents $P_e D P_g$ where $\boldsymbol{D}$ is the atomic dipole operator and P_e and P_g are the projectors into e and g.

5.1.3. Generalized Bloch equations [23,24]

$(\mathrm{d}/\mathrm{d}t)\sigma$ is given by a sum of three terms describing

(i) Free evolution due to the atomic (H_a) and Zeeman (H_Z) Hamiltonians

$$-\frac{i}{\hbar}\,[H_a, \sigma] - \frac{i}{\hbar}\,[H_Z, \sigma] .$$

(ii) Spontaneous emission. Terms calculated in § 4.3.4. To simplify, we will call $\mathcal{T}(\sigma_e)$ the terms appearing in σ_g and describing the transfer from e to g (see eqs. (4.112)).

(iii) Coupling with the light beam, $(-i/\hbar)[V, \sigma]$. We will put

$$\sigma_{eg} = \rho_{eg} e^{-i\omega_L t} , \tag{5.3}$$

(equivalent to the transformation to the rotating reference frame). This eliminates all time dependences in the coefficients of the equations. Finally, we get

$$
\begin{array}{l|l|l|l}
\frac{\mathrm{d}}{\mathrm{d}t}\sigma_e = & -\frac{i}{\hbar}[H_Z, \sigma_e] & -\Gamma\sigma_e & +\frac{i}{\hbar}[\mathcal{C}\,\hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg}\rho_{ge} - \mathcal{C}^*\rho_{eg}\hat{\boldsymbol{\varepsilon}}_0^* \cdot \boldsymbol{D}_{ge}], \\
\frac{\mathrm{d}}{\mathrm{d}t}\sigma_g = & -\frac{i}{\hbar}[H_Z, \sigma_g] & +\mathcal{T}(\sigma_e) & +\frac{i}{\hbar}[\mathcal{C}^*\hat{\boldsymbol{\varepsilon}}_0^* \cdot \boldsymbol{D}_{ge}\rho_{eg} - \mathcal{C}\rho_{ge}\hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg}], \\
\frac{\mathrm{d}}{\mathrm{d}t}\rho_{eg} = & i(\omega_L - \omega_0)\rho_{eg} - \frac{i}{\hbar}[H_Z, \rho_{eg}] & -\tfrac{1}{2}\Gamma\rho_{eg} & +\frac{i}{\hbar}\mathcal{C}[\hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg}\sigma_g - \sigma_e\hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg}]. \\
 & \text{free evolution} & \text{spontaneous emission} & \text{coupling with the light beam}
\end{array}
\tag{5.4}
$$

5.1.4. Explicit form of Bloch equations in some particular cases

(i) Two-level atom. We have just to add to eqs. (4.85) the terms describing the coupling with the laser, i.e. the terms describing the Larmor precession around the field $\boldsymbol{B}_1$ of fig. 9 (we also use the transformation to the rotating reference frame, which amounts to change in eq. (4.85) ω_0 by $\omega_0 - \omega_L$). Finally, we get

$$
\begin{array}{l|l|l|l}
\langle \dot{S}_Z \rangle = & & -\Gamma(\langle S_Z \rangle + \tfrac{1}{2}) & +\tfrac{1}{2}i\omega_1(\langle S_- \rangle - \langle S_+ \rangle), \\
\langle \dot{S}_\pm \rangle = & \pm i(\omega_0 - \omega_L)\langle S_\pm \rangle & -\tfrac{1}{2}\Gamma\langle S_\pm \rangle & \mp i\omega_1\langle S_Z \rangle. \\
 & \text{free evolution} & \text{spontaneous emission} & \text{coupling with the laser}
\end{array}
\tag{5.5}
$$

(ii) $J_g = 0 \leftrightarrow J_e = 1$ transition with a σ-polarized excitation. We suppose $\hat{\epsilon}_0 = \hat{e}_x$, $0Z$ being the axis of quantization along which the static magnetic

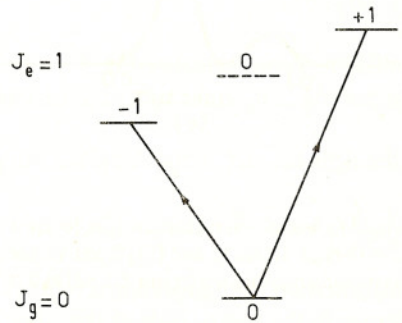

Fig. 28.

field B_0 is applied. With this polarization, only sublevels $m = \pm 1$ of the $J_e = 1$ upper state are excited and we can forget the $m = 0$ excited sublevel so that σ takes the following form:

$$\begin{array}{|c|c|}\hline \sigma_e & \sigma_{eg} \\ \hline \sigma_{ge} & \sigma_g \\ \hline \end{array} = \begin{array}{|ccc|}\hline \sigma_{++} & \sigma_{+-} & \sigma_{+0} \\ \sigma_{-+} & \sigma_{--} & \sigma_{-0} \\ \hline \sigma_{0+} & \sigma_{0-} & \sigma_{00} \\ \hline \end{array} \tag{5.6}$$

When explicited, eqs. (5.4) become

$$\begin{array}{|lll|}\hline
\dot{\sigma}_{++} = & -\Gamma\sigma_{++} & -iv(\rho_{0+}-\rho_{+0}) , \\
\dot{\sigma}_{--} = & -\Gamma\sigma_{--} & +iv(\rho_{0-}-\rho_{-0}) , \\
\dot{\sigma}_{-+} = 2i\Omega_e\sigma_{-+} & -\Gamma\sigma_{-+} & +iv(\rho_{0+}+\rho_{-0}) , \\
\dot{\sigma}_{00} = & +\Gamma(\sigma_{++}+\sigma_{--}) & +iv(\rho_{-0}-\rho_{+0}+\rho_{0+}-\rho_{0-}) , \\
\dot{\rho}_{0+} = i(\omega_0-\omega_L+\Omega_e)\rho_{0+} & -\tfrac{1}{2}\Gamma\rho_{0+} & -iv(\sigma_{++}-\sigma_{-+}-\sigma_{00}) , \\
\dot{\rho}_{0-} = i(\omega_0-\omega_L-\Omega_e)\rho_{0-} & -\tfrac{1}{2}\Gamma\rho_{0-} & +iv(\sigma_{--}-\sigma_{+-}-\sigma_{00}) . \\
\hline
\text{free evolution} & \text{spontaneous emission} & \text{coupling with the light beam} \\
\hline
\end{array} \tag{5.7}$$

Here Ω_e is the Zeeman frequency in e (the energies of sublevels +1 and −1 are $\omega_0 + \Omega_e$ and $\omega_0 - \Omega_e$); v is a coupling parameter proportional to the product of the atomic dipole moment by the amplitude $\mathcal{E}$ of the light wave. More precisely,

$$v^2 = 3\,\mathcal{E}^2 e^2 f_{ge}/16 m\hbar\omega_0 , \tag{5.8}$$

where f_{ge} is the oscillator strength of the transition g–e, while e, m are the charge and mass of the electron.

5.2. Broad line excitation [9,10,23,25,26]

As in subsect. 5.1, we add independently in the master equation the terms describing spontaneous emission and the other ones. We also treat classically the incident light beam.

5.2.1. Description of the light beam

The light beam is supposed to result from the superposition of parallel plane waves having all the same polarization $\hat{e}_0$ but different (complex) amplitudes $\mathcal{E}_\mu$ and frequencies ω_μ. The positive frequency part $\boldsymbol{\mathcal{E}}^{(+)}(t)$ of the electric field is given by

$$\hat{e}_0 \, \mathcal{E}^{(+)}(t) = \hat{e}_0 \sum_\mu \mathcal{E}_\mu \, e^{-i\omega_\mu t} \, .$$

Fig. 29 shows the intensities $|\mathcal{E}_\mu|^2$ of the various waves forming the light beam. In the case of a spectral lamp, the frequencies ω_μ of these waves form a continuum. If we have a laser beam, we suppose that the laser oscillates on a great number of modes. In both cases, we will assume that the width Δ of the spectral interval covered by the frequencies ω_μ (see fig. 29) is very large compared to the Doppler width $\Delta\nu_D$ and the natural width Γ of the atomic line, and that the spacing $\delta\omega$ between modes is small compared to Γ,

$$\Delta \gg \Delta\nu_D, \Gamma \, , \qquad \delta\omega < \Gamma \, . \tag{5.10}$$

In this case, the different "Bennett holes" burnt by the various modes in the Doppler profile overlap, and it is easy to understand that the response of an atom does not depend on its velocity, so that σ refers to internal variables only.

The relative phases of the various modes are assumed to be random: we have a "free-running" multimode laser and not a "phase locked" one. The instantaneous electric field $\mathcal{E}(t)$ of the light wave (see eq. (5.9)) may be con-

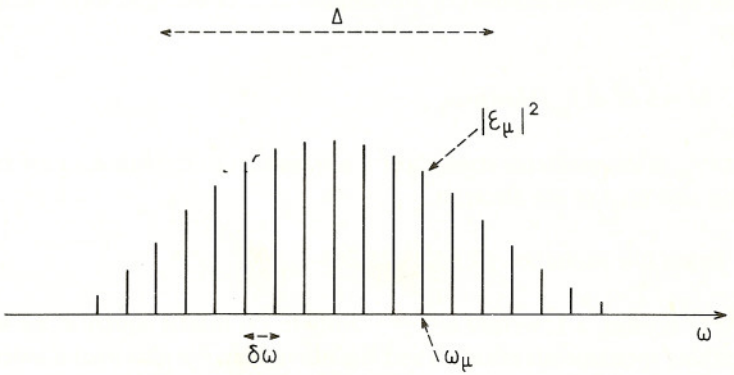

Fig. 29.

sidered as a stationary random function. The correlation function $\overline{\mathcal{E}^{(-)}(t)\,\mathcal{E}^{(+)}(t-\tau)}$ of $\mathcal{E}(t)$ only depends on τ and tends to zero when τ is larger than the correlation time τ_C' of the light wave which is of the order of $1/\Delta$ [27].

Relation between the correlation function of $\mathcal{E}$ and the spectral distribution $I(\omega)$ of the incident light. Putting $\mathcal{E}_\mu = |\mathcal{E}_\mu| e^{i\phi\mu}$ and assuming that the ϕ_μ's are random, we easily calculate the correlation function of $\mathcal{E}^{(+)}$, $\overline{\mathcal{E}^{(-)}(t)\,\mathcal{E}^{(+)}(t-\tau)}$, and show that it is proportional to the Fourier transform of $I(\omega)$ (Wiener-Khintchine relations; see ref. [19])

$$\overline{\mathcal{E}^{(-)}(t)\,\mathcal{E}^{(+)}(t-\tau)} = \sum_{\mu,\mu'} |\mathcal{E}_\mu||\mathcal{E}_{\mu'}| \overline{e^{i(\phi_{\mu'}-\phi_\mu)}}$$

$$\times\, e^{i\omega_\mu t} e^{-i\omega_{\mu'}(t-\tau)} . \tag{5.11}$$

But

$$\overline{e^{i(\phi_{\mu'}-\phi_\mu)}} = \delta_{\mu\mu'}$$

so that (5.11) may be written as

$$\overline{\mathcal{E}^{(-)}(t)\,\mathcal{E}^{(+)}(t-\tau)} = \sum_\mu |\mathcal{E}_\mu|^2 e^{i\omega_\mu \tau} \simeq \int_{-\infty}^{+\infty} d\omega\, I(\omega) e^{i\omega\tau} , \tag{5.12}$$

and consequently

$$I(\omega) \simeq \int_{-\infty}^{+\infty} d\tau\, e^{-i\omega\tau}\, \overline{\mathcal{E}^{(-)}(t)\,\mathcal{E}^{(+)}(t-\tau)} . \tag{5.13}$$

The strength of the coupling between the atom and the light wave may be characterized by a parameter v which is the product of the atomic electric dipole moment d by an electric field amplitude and which gives an order of magnitude of the evolution frequency of $\tilde{\sigma}$,

$$v = d \cdot [\overline{|\mathcal{E}(t)|^2}]^{1/2} = d \cdot \left[\sum_\mu |\mathcal{E}_\mu|^2 \right]^{1/2} . \tag{5.14}$$

5.2.2. "Coarse grained" rate of variation of σ

Let T_p be the time characterizing the evolution of σ under the effect of the coupling with the light beam. We will assume in the following that the in-

tensity is sufficiently low so that T_p is much longer than the correlation time $\tau'_C = 1/\Delta$ of the light wave,

$$T_p \gg \tau'_C = 1/\Delta \,. \tag{5.15}$$

Let us consider a time interval Δt such that

$$T_p \gg \Delta t \gg \tau'_C \,. \tag{5.16}$$

As $\Delta t \ll T_p$, $\tilde{\sigma}(t + \Delta t) - \tilde{\sigma}(t)$ is very small and can be calculated by perturbation theory. We show in this paragraph that the average variation of $\tilde{\sigma}$, $\overline{\tilde{\sigma}(t + \Delta t) - \tilde{\sigma}(t)}$ (the average is taken over all possible values of the random function $\mathcal{E}(t)$) is proportional to Δt and only depends on $\tilde{\sigma}(t)$,

$$\frac{\overline{\tilde{\sigma}(t + \Delta t) - \tilde{\sigma}(t)}}{\Delta t} = \frac{\Delta \tilde{\sigma}(t)}{\Delta t} = \mathcal{F}[\tilde{\sigma}(t)] \,, \tag{5.17}$$

where $\Delta \tilde{\sigma}(t)/\Delta t$ is a "coarse grained" rate of variation of $\tilde{\sigma}$ since we consider the variation of $\tilde{\sigma}$ over an interval Δt longer than the correlation time of the light wave which drives the atoms.

In interaction representation and with the rotating wave approximation, the interaction Hamiltonian $\tilde{V}(t)$ may be written as

$$\tilde{V}(t) = -\mathcal{E}^{(+)}(t) e^{i\omega_0 t}\, \hat{\boldsymbol{\varepsilon}}_0 \cdot \boldsymbol{D}_{eg} - \mathcal{E}^{(-)}(t) e^{-i\omega_0 t}\, \hat{\boldsymbol{\varepsilon}}_0^* \cdot \boldsymbol{D}_{ge} \,. \tag{5.18}$$

Applying perturbation theory, we get

$$\tilde{\sigma}(t + \Delta t) - \tilde{\sigma}(t) = \text{spont. emission terms} \tag{5.19}$$

$$+ \frac{1}{i\hbar} \int_t^{t+\Delta t} dt' [\tilde{V}(t'), \tilde{\sigma}(t)] - \frac{1}{\hbar^2} \int_t^{t+\Delta t} dt' \int_t^{t'} dt'' [\tilde{V}(t'), [\tilde{V}(t''), \tilde{\sigma}(t)]] \,.$$

Let us now take the average over the random function $\mathcal{E}(t)$. As $\tilde{\sigma}(t)$ is driven by $\tilde{V}(t)$, $\tilde{V}(t')$ and $\tilde{\sigma}(t)$ are correlated and we cannot in general consider that

$$\overline{\tilde{V}(t')\tilde{\sigma}(t)} = \overline{\tilde{V}(t')}\,\overline{\tilde{\sigma}(t)} \,,$$

$$\overline{\tilde{V}(t')\tilde{V}(t'')\tilde{\sigma}(t)} = \overline{\tilde{V}(t')\tilde{V}(t'')}\,\overline{\tilde{\sigma}(t)} \,, \tag{5.20}$$

except if

$$t' - t \gtrsim \tau_C \,, \qquad t'' - t \gtrsim \tau_C \,. \tag{5.21}$$

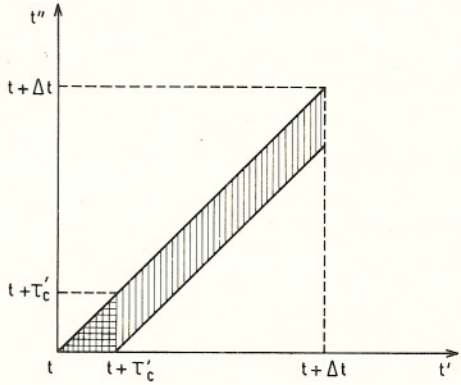

Fig. 30.

But the intervals of variation of t' and t'' in expression (5.19) are $[t, t+\Delta t]$, much longer than τ_C since $\Delta t \gg \tau_C$, so that the error made in writing (5.20) is negligible, of the order of $\tau'_C/\Delta t \ll 1$ according to (5.16) (see fig. 30). It follows that the first term of the second line of (5.19) is zero since $\overline{\tilde{V}(t')} \sim \overline{\mathcal{E}(t')} = 0$.

For evaluating the double integral, we note that $\overline{\tilde{V}(t')\tilde{V}(t'')}$ only depends on $\tau = t' - t''$. If we change from the variables $\{t', t''\}$ to the variables $\{\tau = t' - t'', t'\}$, the integral over t' is trivial since the integrand does not depend on t' and gives a multiplicative factor Δt which shows that $\overline{\tilde{\sigma}(t+\Delta t) - \tilde{\sigma}(t)}$ is proportional to Δt. After doing the integral over τ (the upper limit of the integral, Δt, can be extended to $+\infty$ since $\Delta t \gg \tau'_C$), we get a rate equation coupling $\Delta\overline{\tilde{\sigma}(t)}/\Delta t$ to $\overline{\tilde{\sigma}(t)}$ [to simplify, we do not write $\overline{\tilde{\sigma}(t)}$ but simply $\tilde{\sigma}(t)$] which we now calculate in detail.

Calculation of $\Delta\overline{\tilde{\sigma}_e}/\Delta t$. Writing $\boldsymbol{D} = e\boldsymbol{r}$, separating the angular and the radial part of $\boldsymbol{r}$, and putting $\hat{r} = \boldsymbol{r}/r$, $r_{ge} = \langle g \| r \| e \rangle$, we get

$$\frac{\Delta\overline{\tilde{\sigma}_e}}{\Delta t} = \text{spont. em. terms} - \frac{e^2|r_{eg}|^2}{\hbar^2}$$

$$\times \int_0^{+\infty} \overline{\mathcal{E}^{(+)}(t')\,\mathcal{E}^{(-)}(t'-\tau)}\, e^{i\omega_0\tau}\, d\tau \left[(\hat{\boldsymbol{\varepsilon}}_0 \cdot \hat{r}_{eg})(\hat{\boldsymbol{\varepsilon}}_0^* \cdot \hat{r}_{ge})\overline{\tilde{\sigma}_e(t)}\right.$$

$$\left. - (\hat{\boldsymbol{\varepsilon}}_0 \cdot \hat{r}_{eg})\overline{\tilde{\sigma}_g(t)}(\hat{\boldsymbol{\varepsilon}}_0^* \cdot \hat{r}_{ge})\right] + \text{hermit. conjug.} \qquad (5.22)$$

Using (5.12) and (4.47), we transform the integral over τ into

$$\int_0^\infty d\tau \int_{-\infty}^{+\infty} d\omega\, I(\omega) e^{-i(\omega-\omega_0)\tau} = \pi I(\omega_0) - i\mathcal{P}\int \frac{I(\omega)\,d\omega}{\omega-\omega_0}. \tag{5.23}$$

Introducing the two parameters

$$\frac{1}{2T_p} = \frac{1}{\hbar^2}\pi I(\omega_0) e^2 |r_{eg}|^2 ,$$

$$\Delta E'/\hbar = \frac{1}{\hbar^2}\mathcal{P}\int \frac{I(\omega)e^2|r_{eg}|^2}{\omega-\omega_0}\,d\omega , \tag{5.24}$$

and the operator B_e acting inside the e multiplicity,

$$B_e = (\hat{\varepsilon}_0 \cdot \hat{r}_{eg})(\hat{\varepsilon}_0^* \cdot \hat{r}_{ge}) , \tag{5.25}$$

we finally get for $\Delta\tilde{\sigma}_e/\Delta t$,

$$\frac{\Delta\tilde{\sigma}_e}{\Delta t} = \text{spont. em. terms} - \frac{1}{2T_p}\{B_e, \tilde{\sigma}_e(t)\}_+ + i\frac{\Delta E'}{\hbar}[B_e, \tilde{\sigma}_e(t)]$$

$$+ \frac{1}{T_p}(\hat{\varepsilon}_0 \cdot \hat{r}_{eg})\tilde{\sigma}_g(t)(\hat{\varepsilon}_0^* \cdot \hat{r}_{ge}) , \tag{5.26}$$

where $\{U, V\}_+ = UV + VU$ is the anticommutator of U and V.

Calculation of $\Delta\tilde{\sigma}_g/\Delta t$. Similar calculations give

$$\frac{\Delta\tilde{\sigma}_g}{\Delta t} = \text{spont. em. terms} - \frac{1}{2T_p}\{B_g, \tilde{\sigma}_g(t)\}_+ - \frac{i\Delta E'}{\hbar}[B_g, \tilde{\sigma}_g(t)]$$

$$+ \frac{1}{T_p}(\hat{\varepsilon}_0^* \cdot \hat{r}_{ge})\tilde{\sigma}_e(t)(\hat{\varepsilon}_0 \cdot \hat{r}_{eg}) , \tag{5.27}$$

where B_g is an operator acting inside g and is given by

$$B_g = (\hat{\varepsilon}_0^* \cdot \hat{r}_{ge})(\hat{\varepsilon}_0 \cdot \hat{r}_{eg}) . \tag{5.28}$$

(Note the change of sign of the $\Delta E'$ term from (5.26) to (5.27).)

Calculation of $\Delta\tilde{\sigma}_{eg}/\Delta t$. Because of the secular approximation, we neglect the coupling between $\tilde{\sigma}_{eg}$ and $\tilde{\sigma}_{ge}$ and we get

$$\frac{\Delta\tilde{\sigma}_{eg}}{\Delta t} = \text{spont. em. terms} - \left(\frac{1}{2T_p} - i\Delta E'\right) B_e \tilde{\sigma}_{eg}(t)$$

$$- \left(\frac{1}{2T_p} - i\Delta E'\right) \tilde{\sigma}_{eg}(t) B_g \,. \tag{5.29}$$

Collecting all the above results, coming back to the Schrödinger picture and writing $d\sigma/dt$ instead of $\Delta\sigma/\Delta t$, we finally get

$$\frac{d\sigma_e}{dt} = \underbrace{-\frac{i}{\hbar}[H_Z, \sigma_e]}_{\text{free evolution}} \underbrace{-\Gamma\sigma_e}_{\text{spontaneous emission}}$$

$$+ \frac{1}{T_p}(\hat{\varepsilon}_0 \cdot \hat{r}_{eg})\sigma_g(\hat{\varepsilon}_0^* \cdot \hat{r}_{ge}) \qquad - \frac{1}{2T_p}\{B_e, \sigma_e\}_+ + \frac{i\Delta E'}{\hbar}[B_e, \sigma_e]\,, \tag{5.30a}$$

$$\frac{d}{dt}\sigma_g = -\frac{i}{\hbar}[H_Z, \sigma_g] \qquad + \Gamma(\sigma_e)$$

$$- \frac{1}{2T_p}\{B_g, \sigma_g\}_+ - i\frac{\Delta E'}{\hbar}[B_g, \sigma_g] \qquad + \frac{1}{T_p}(\hat{\varepsilon}_0^* \cdot \hat{r}_{ge})\sigma_e(\hat{\varepsilon}_0 \cdot \hat{r}_{eg})\,, \tag{5.30b}$$

$$\frac{d}{dt}\sigma_{eg} = -i\omega_0\sigma_{eg} - \frac{i}{\hbar}[H_Z, \sigma_{eg}] \qquad -\tfrac{1}{2}\Gamma\sigma_{eg}$$

$$\underbrace{-\left(\frac{1}{2T_p} - i\frac{\Delta E'}{\hbar}\right)\sigma_{eg}B_g}_{\text{absorption}} \qquad \underbrace{-\left(\frac{1}{2T_p} - i\frac{\Delta E'}{\hbar}\right)B_e\sigma_{eg}}_{\text{stimulated emission}}\,. \tag{5.30c}$$

We have added the Zeeman terms $(-i/\hbar)[H_Z, \sigma]$, assuming that the Zeeman splittings Ω_e and Ω_g in e and g are small compared to the spectral width Δ of the incident light so that $1/2T_p$ and $\Delta E'$ do not depend on Ω_e and Ω_g.

5.2.3. Explicit form of the master equation in some particular cases

(i) Two-level atom. We take $B_e = B_g = |(\hat{\varepsilon}_0 \cdot \hat{r}_{eg})|^2 = 1$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_e = -\Gamma\sigma_e - \frac{1}{T_\mathrm{p}}(\sigma_e - \sigma_g)\,,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_g = \Gamma\sigma_e - \frac{1}{T_\mathrm{p}}(\sigma_g - \sigma_e)\,,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{eg} = -i\left(\omega_0 - \frac{2\Delta E'}{\hbar}\right)\sigma_{eg} - \left(\tfrac{1}{2}\Gamma + \frac{1}{T_\mathrm{p}}\right)\sigma_{eg}\,. \tag{5.31}$$

In terms of $\langle \boldsymbol{S}\rangle$, (5.31) may be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle S_z\rangle = -\Gamma(\langle S_z\rangle + \tfrac{1}{2}) - \frac{2}{T_\mathrm{p}}\langle S_z\rangle\,,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle S_\pm\rangle = -\left(\tfrac{1}{2}\Gamma + \frac{1}{T_\mathrm{p}}\right)\langle S_\pm\rangle \pm i\left(\omega_0 - \frac{2\Delta E'}{\hbar}\right)\langle S_\pm\rangle\,. \tag{5.32}$$

(ii) $J_g = 0 \leftrightarrow J_e = 1$ transition with a σ polarization ($\hat{\boldsymbol{\varepsilon}}_0 = \boldsymbol{e}_x$). We will suppose that $\Delta E' = 0$ and we will put $1/T_\mathrm{p} = \gamma$. We get for the elements of σ_e and σ_g (see eqs. (5.6)),

free evolution	spontaneous emission	absorption	stimulated emission
$\dot{\sigma}_{++} =$	$-\Gamma\sigma_{++}$	$+\gamma\sigma_{00}$	$-\frac{1}{2}\gamma(\sigma_{++}+\sigma_{++}-\sigma_{-+}-\sigma_{+-})$,
$\dot{\sigma}_{--} =$	$-\Gamma\sigma_{--}$	$+\gamma\sigma_{00}$	$-\frac{1}{2}\gamma(\sigma_{--}+\sigma_{--}-\sigma_{-+}-\sigma_{+-})$,
$\dot{\sigma}_{-+} = 2i\omega_e\sigma_{-+}$	$-\Gamma\sigma_{-+}$	$-\gamma\sigma_{00}$	$+\frac{1}{2}\gamma(\sigma_{++}+\sigma_{--}-2\sigma_{-+})$,
$\dot{\sigma}_{00} =$	$+\Gamma(\sigma_{++}+\sigma_{--})$	$-2\gamma\sigma_{00}$	$+\gamma(\sigma_{++}+\sigma_{--}-\sigma_{-+}-\sigma_{+-})$.

(5.33)

We do not write the evolution of optical coherences. ω_e is the Zeeman splitting in e.

(iii) $J_g = \frac{1}{2} \leftrightarrow J_e = \frac{1}{2}$ transition. We would now like to give an idea of what happens when Zeeman coherences exist in both levels e and g, and, for that purpose, we take the simplest possible example of such a situation, the case of a transition $J_g = \frac{1}{2} \leftrightarrow J_e = \frac{1}{2}$.

We restrict ourselves to a broad-line excitation. The light beam is supposed to be σ^+ polarized and to propagate along $0z$, the magnetic field being applied along $0x$. The relaxation of the ground state (which was absent in the previous

case as $J_g = 0$) is supposed to be produced by the leakage of atoms from the cell through a small hole (the probability per unit time of escaping from the cell is $1/T$). A balance is provided by an entering flux of n_0 atoms per unit time, all in the ground state and completely unpolarized. If the collisions with the inner walls of the cell are not disorienting, the relaxation time is simply T.

As in the previous example, we suppose $\Delta E' = 0$ and we put $1/T_p = \gamma$. We do not write the evolution of optical coherences. ω_e and ω_g are the Zeeman splittings in e and g.

For the spontaneous emission terms, we use eqs. (4.114).

$$
\begin{aligned}
&\text{relaxation} && \text{Larmor precession} \\
\dot{\sigma}^e_{++} &= -\sigma^e_{++}/T && +\tfrac{1}{2} i\omega_e(\sigma^e_{+-} - \sigma^e_{-+}) \\
& && -\Gamma\sigma^e_{++} && +\tfrac{2}{3}\gamma\sigma^g_{--} && -\tfrac{2}{3}\gamma\sigma^e_{++}, \\
\dot{\sigma}^e_{--} &= -\sigma^e_{--}/T && -\tfrac{1}{2} i\omega_e(\sigma^e_{+-} - \sigma^e_{-+}) \\
& && -\Gamma\sigma^e_{--}, \\
\dot{\sigma}^e_{-+} &= -\sigma^e_{-+}/T && -\tfrac{1}{2} i\omega_e(\sigma^e_{++} - \sigma^e_{--}) \\
& && -\Gamma\sigma^e_{-+} && && -\tfrac{1}{3}\gamma\sigma^e_{-+}, \\
\dot{\sigma}^g_{++} &= \tfrac{1}{2} n_0 - \sigma^g_{++}/T && +\tfrac{1}{2} i\omega_g(\sigma^g_{+-} - \sigma^g_{-+}) \\
& && +\tfrac{1}{3}\Gamma\sigma^e_{++} + \tfrac{2}{3}\Gamma\sigma^e, \\
\dot{\sigma}^g_{--} &= \tfrac{1}{2} n_0 - \sigma^g_{--}/T && -\tfrac{1}{2} i\omega_g(\sigma^g_{+-} - \sigma^g_{-+}) \\
& && +\tfrac{1}{3}\Gamma\sigma^e_{--} + \tfrac{2}{3}\Gamma\sigma^e_{++} && -\tfrac{2}{3}\gamma\sigma^g_{--} && +\tfrac{2}{3}\gamma\sigma^e_{++}, \\
\dot{\sigma}^g_{-+} &= -\sigma^g_{-+}/T && -\tfrac{1}{2} i\omega_g(\sigma^g_{++} - \sigma^g_{--}) \\
& && -\tfrac{1}{3}\Gamma\sigma^e_{-+} && -\tfrac{1}{3}\gamma\sigma^g_{-+}. && && (5.34) \\
& && \text{spontaneous emission} && \text{absorption} && \text{stimulated emission}
\end{aligned}
$$

5.2.4. Physical discussion

(i) Rate equations. Let us discuss the third and fourth term of each equa-

tion (5.30) (written on the second line of each equation). The third term of eqs. (5.30a) and (5.30b) couples $\dot{\sigma}_e$ to σ_g and $\dot{\sigma}_g$ to σ_g. It describes the effect of *absorption processes* which take atoms from g and transfer them to e. The fourth term of these equations couples $\dot{\sigma}_e$ to σ_e and $\dot{\sigma}_g$ to σ_e. It describes the effect of *stimulated emission processes* which take atoms from e and transfer them to g. These processes also affect σ_{eg} (third term and fourth term of (5.30c)).

Eqs. (5.30) are *rate equations.* They do not couple σ_e and σ_g to optical coherences σ_{eg}. This important difference with the generalized Bloch equations derived in subsect. 5.1 for a monochromatic excitation will be discussed later on.

(ii) Physical interpretation of $1/T_p$ and $\Delta E'$. $1/T_p$ is the probability per unit time of an absorption or stimulated emission process, and is proportional to the incident light intensity at frequency ω_0 (see (5.24)). $\Delta E'$ describes the *light shifts* produced by the light irradiation. For example, for a two-level atom, the last equation (5.31) shows that the atomic frequency is changed from ω_0 to $\omega_0 - 2\Delta E'/\hbar$ in presence of the light irradiation. $\Delta E'$ is $\neq 0$ even for a non-resonant irradiation (see (5.24)). This shows that $\Delta E'$ is due to virtual absorptions and reemissions (or stimulated emissions and reabsorptions) of photons by the atom. (For a detailed discussion of light shifts and optical pumping, see refs. [9,10,28,29].)

(iii) Angular aspect. As the atom interacts with a light beam having a definite polarization and a definite direction of propagation, absorption and stimulated emission processes do not have the spherical symmetry of spontaneous emission (which is due to the interaction of atoms with a spherically symmetric set of empty modes).

Let us compare for example the second and the fourth columns of eqs. (5.33). One sees on the last equation that spontaneous emission does not couple $\dot{\sigma}_{00}$ to the Zeeman coherence σ_{+-}. This is due to the fact that σ_{00} and σ_{+-} do not have the same transformation properties in a rotation around $0Z$ so that they cannot be coupled by a spherically symmetric process. But such a coupling exists for stimulated emission and is at the origin of "saturated resonances" which will be discussed in the next section.

More generally, the effect of absorption inside the g multiplicity and the effect of stimulated emission inside the e multiplicity are described by the two hermitian operators B_g and B_e given by (5.28) and (5.25). In general, B_e and B_g are not scalar. The eigenvectors $|g_i\rangle$ of B_g, corresponding to eigenvalues r_i, are the sublevels of g which have a well defined light broadening r_i/T_p and a well defined light shift $r_i \Delta E'$. $\Delta E' B_g$ can be considered as an effective Hamiltonian describing the light shifts induced by the light beam inside the g multi-

plicity. Similar considerations can be developed for B_e and stimulated emission processes.

(iv) Condition of validity of eqs. (5.30). Let us recall (see eq. (5.15)) that the "pumping time" T_p must be much longer than the correlation time $\tau'_C = 1/\Delta$ of the light beam. Using the equation of definition of $1/T_p$ (5.24), and eq. (5.14) which defines the parameter v characterizing the coupling between the atoms and the light beam, one easily finds that

$$\frac{1}{T_p} \sim \frac{v^2}{\hbar^2} \frac{1}{\Delta}, \tag{5.34}$$

so that eq. (5.15) may be written as

$$\frac{v^2}{\hbar^2 \Delta^2} = \frac{v^2 \tau'^2_C}{\hbar^2} \ll 1, \tag{5.35}$$

which means that the effect of the coupling with the light beam during the correlation time τ'_C of this beam is extremely small. This condition is very similar to the one used in sect. 4 for deriving the master equation of a small system coupled to a large reservoir.

In the present case, we can consider that the light beam is a large reservoir, so large that one can consider only a single absorption or stimulated emission process during τ'_C. Eqs. (5.30) describe the effect on σ_e and σ_g of an indefinite number of uncorrelated one-photon processes.

Let us finally note that, according to (5.34),

$$\frac{1}{T_p} \sim \frac{v}{\hbar} \frac{v}{\hbar \Delta} = \frac{v}{\hbar} \frac{v\tau'_C}{\hbar}. \tag{5.36}$$

$1/T_p$ is smaller than $v/\hbar$ by the motional narrowing factor $v\tau'_C/\hbar$.

Remark: Eqs. (5.30) may still be used if $1/T_p$ and $\Delta E'$ are functions of time (excitation by a light pulse) provided that the time characterizing the evolution of $1/T_p$ and $\Delta E'$ is much longer than τ'_C [30].

(v) Existence of two regimes.

$\boxed{\frac{1}{T_p} \ll \Gamma}$ or according to (5.34): $v \ll \hbar\sqrt{\Gamma\Delta}$.

One can drop the stimulated emission terms of eqs. (5.30a) and (5.30b) which are negligible compared to the spontaneous emission ones (note that

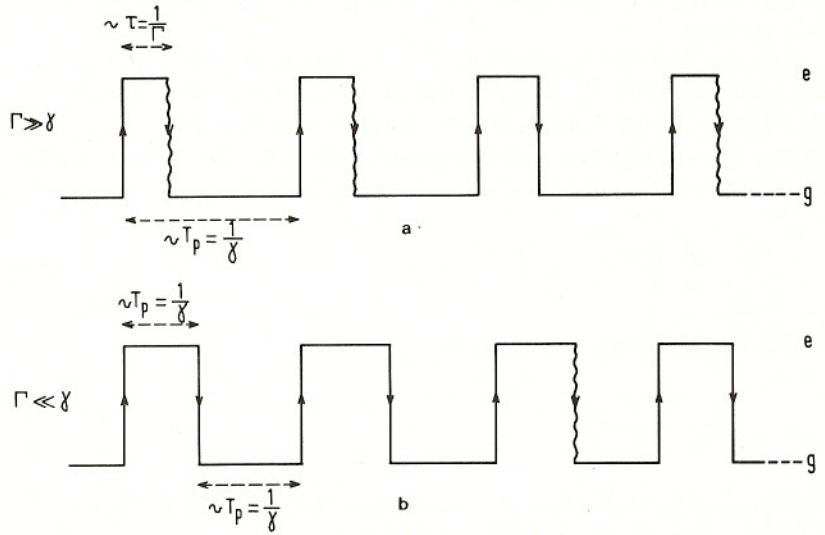

Fig. 31.

we must keep the absorption terms since they involve σ_g which may be much greater than σ_e). We get in this way the usual optical pumping equations which have been first derived for thermal sources

$$\boxed{\Gamma \lesssim \frac{1}{T_p} \ll \frac{1}{\tau_C}} \quad \text{or according to (5.34):} \quad \sqrt{\Gamma \Delta} \lesssim v/\hbar \ll \Delta \,.$$

Suppose now that $1/T_p$ is of the order of Γ, or larger than Γ, the condition of validity (5.15) being maintained. In this case, we must keep the terms contained in the last column of (5.30) which are at the origin of some new effects which are observed in optical pumping experiments performed with intense laser sources [25]. We will discuss some of these effects in the next section.

Figs. 31a and 31b visualize the evolution of the atom in these two regimes. The ascending and descending straight lines represent absorption and stimulated emission processes, the descending wavy lines spontaneous emission processes. The mean time spent by the atom in the ground state is $T_p = 1/\gamma$. The mean time spent in e is $\tau = 1/\Gamma$ when $\Gamma \gg \gamma$ (in this case, the deexcitation of the atom is mainly due to spontaneous emission) or $T_p = 1/\gamma$ when $\Gamma \ll \gamma$ (in this case, the deexcitation is mainly due to stimulated emission).

(vi) Comparison with the monochromatic excitation. The correlation time

of the perturbation is, for a monochromatic excitation, very long and it becomes impossible to neglect the correlations between successive interactions of the atom with the light wave. We cannot consider that the atom undergoes, from time to time and without any phase memory, transitions from g to e or from e to g as this is visualized in fig. 31. For a monochromatic excitation, we have a coherent oscillation between e and g, analogous to the Rabi nutation in magnetic resonance. Furthermore, the optical coherence σ_{eg} becomes significant and oscillates at the same Rabi frequency, in quadrature with the populations of e and g. In the broad line case, σ_{eg} is negligible as the coherence time $\tau'_C = 1/\Delta$ is too short for permitting σ_{eg} to build up appreciably.

At the end of these lectures, we will say a few words on the case $v/\hbar \gg \Delta > \Gamma$ which cannot be described either by Bloch equations like (5.4) or by rate equations like (5.30).

6. Application to the interpretation of some level crossing experiments

6.1. $J_g = 0 \leftrightarrow J_e = 1$ transition

In order to discuss some of the new effects which appear in optical pumping experiments performed with laser sources, we will consider the simplest possible transition $J_g = 0 \leftrightarrow J_e = 1$, and a resonance which does not require the use of any RF field, the Hanle zero-field level crossing resonance. We will suppose that the light beam, propagating along $0z$, is linearly polarized along $0x$, and that a magnetic field $\boldsymbol{B}_0$ is applied along $0z$ (situation considered for eqs. (5.7) and (5.33)).

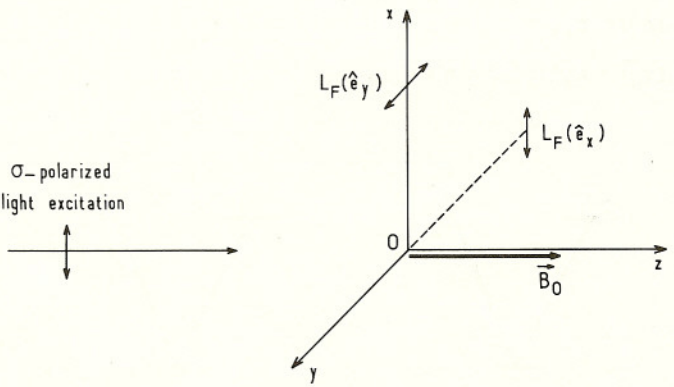

Fig. 32.

6.1.1. Detection signals

One measures the variations with B_0 of several types of fluorescence light:
$L_F(\hat{e}_x)$: Total fluorescence light reemitted along $0y$ with a polarization $\hat{e}_x$;
$L_F(\hat{e}_y)$: Total fluorescence light reemitted along $0x$ with a polarization $\hat{e}_y$;
$L_F(\hat{e}_y) - L_F(\hat{e}_x)$: Difference between these two signals.

According to (3.13) and (3.14), $L_F(\hat{e}_x)$ and $L_F(\hat{e}_y)$ are given by the one-time averages

$$L_F(\hat{e}_x) \simeq \langle D_x^{(+)}(t) D_x^{(-)}(t) \rangle = \mathrm{Tr}\, \sigma_e(t) P_e D_x P_g D_x P_e \,, \tag{6.1}$$

$$L_F(\hat{e}_y) \simeq \langle D_y^{(+)}(t) D_y^{(-)}(t) \rangle = \mathrm{Tr}\, \sigma_e(t) P_e D_y P_g D_y P_e \,. \tag{6.2}$$

The matrix elements of D_x and D_y are given below (up to a multiplicative factor). (To calculate these matrix elements, we use the standard components of $\boldsymbol{D}$

$$D_+ = -\sqrt{\tfrac{1}{2}}(D_x + iD_y) \,, \qquad D_0 = D_z \,, \qquad D_- = \sqrt{\tfrac{1}{2}}(D_x - iD_y) \,,$$

so that

$$D_x = -\sqrt{\tfrac{1}{2}}(D_+ - D_-) \,, \qquad D_y = i\sqrt{\tfrac{1}{2}}(D_+ + D_-) \,,$$

and we apply Wigner-Eckart's theorem.) We get in this way

$$L_F(\hat{e}_x) \sim \sigma_{++} + \sigma_{--} - 2\mathcal{R}e\, \sigma_{-+} \,, \tag{6.3}$$

$$L_F(\hat{e}_y) \sim \sigma_{++} + \sigma_{--} + 2\mathcal{R}e\, \sigma_{-+} \,, \tag{6.4}$$

$$L_F(\hat{e}_y) - L_F(e_x) \sim 2\mathcal{R}e\, \sigma_{-+} \,. \tag{6.5}$$

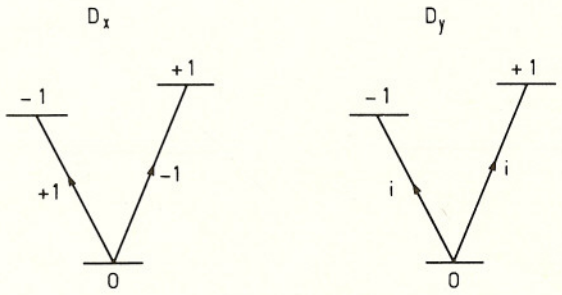

Fig. 33.

We see that the detection signals are sensitive, not only to the populations σ_{++} and σ_{--} of the two Zeeman sublevels of e, but also to the *Zeeman coherence* σ_{-+} between these two sublevels. This is very important for level crossing resonance experiments. In some experiments, where g is not the ground state, but the lower level of a pair of excited levels, the observation of the fluorescence light emitted from g, with for example a π polarization, gives a signal I_π proportional to the population σ_{00} of g

$$I_\pi \sim \sigma_{00} \,. \tag{6.6}$$

(In this case, eqs. (5.7) and (5.33) have to be slightly modified to introduce the rate of preparation of atoms in levels e and g, the spontaneous decay of g, the spontaneous decay of e to levels other than g. But this does not modify the physical results.)

The principle of the calculation is now straightforward. We have to solve eqs. (5.7) or (5.33) according to the type of irradiation which is used (narrow line + atomic beam, or broad line + resonance cell). The steady state solution of these equations gives us a quantitative interpretation for the four signals (6.3)–(6.6).

6.1.2. Broad line excitation (spectral lamp or free running multimode laser)

We will use eqs. (5.33). Let us first briefly recall what the situation is when an ordinary thermal source is used (broad line excitation with $\gamma \ll \Gamma$). Neglecting the terms in the last column of (5.33), we readily get the steady state solution of these equations. To lowest order in γ, this solution is

$$\sigma_{++} = \sigma_{--} = \tfrac{1}{2}(N_0 - \sigma_{00}) = \gamma N_0/\Gamma \,, \tag{6.7}$$

$$\sigma_{-+} = -\frac{\gamma N_0}{\Gamma - 2i\omega_e} \,, \tag{6.8}$$

where $N_0 = \sigma_{++} + \sigma_{--} + \sigma_{00}$ is the total number of atoms (N_0 is a constant of motion, as can be seen by adding the first two equations (5.33) to the last one).

We see that the *Zeeman coherence* σ_{-+} exhibits a resonant behaviour when the Larmor frequency ω_e is varied around 0, by sweeping the magnetic field B_0. This is the origin of the *Hanle zero-field level crossing resonance* appearing on the fluorescence light (for example $L_F(\hat{e}_x)$),

$$L_F(\hat{e}_x) = \frac{2\gamma N_0}{\Gamma}\left(1 + \frac{\Gamma^2}{\Gamma^2 + 4\omega_e^2}\right) \,, \tag{6.9}$$

and which has a Lorentzian shape and a width Γ independent of γ, i.e. of the light intensity. On the other hand, no resonances appear on the populations σ_{++}, σ_{--}, σ_{00} which are independent of ω_e.

What are the modifications which appear when we use a much more intense broad-line source (for example, a free running multimode laser)? We now have to keep the last column of eqs. (5.33). The calculations are a little more difficult, but it remains possible to get analytical expressions for the steady state solution of these equations.

We find for the populations

$$\sigma_{++} = \sigma_{--} = \tfrac{1}{2}(N_0 - \sigma_{00}) = \frac{\gamma N_0}{\Gamma + 3\gamma}\left[1 - S\frac{\Gamma'^2}{\Gamma'^2 + 4\omega_e^2}\right], \tag{6.10}$$

$$S = \frac{\gamma}{\Gamma + 4\gamma}, \qquad \Gamma' = \left[\frac{\Gamma(\Gamma+\gamma)(\Gamma+4\gamma)}{(\Gamma+3\gamma)}\right]^{1/2} \tag{6.11}$$

The populations now exhibit a resonant behaviour near $\omega_e = 0$. The corresponding resonances are called "*saturation resonances*". They have a Lorentzian shape, a contrast S, and a width Γ'.

The saturation resonance appearing on σ_{00} may be interpreted in the following way. A first interaction with the laser (absorption process) removes the atom from the ground state and puts it in a coherent superposition of the -1 and $+1$ sublevels of e (fig. 34a). The combined effect of Larmor precession and spontaneous emission gives rise to the well known resonant behaviour of the Zeeman coherence σ_{-+}. A second interaction with the laser (induced emission process) brings back the atom to the ground state (fig. 34b) and partially confers to the population σ_{00} of this state the resonant behaviour of σ_{-+}. Such a process cannot occur for spontaneous emission which is an isotropic process and which, on the average, does not couple σ_{-+} to σ_{00}.

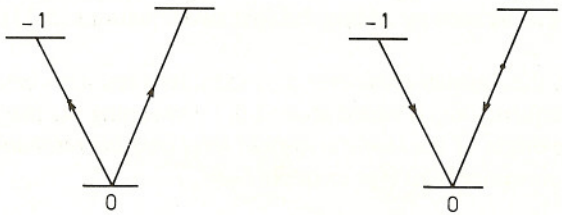

Fig. 34.

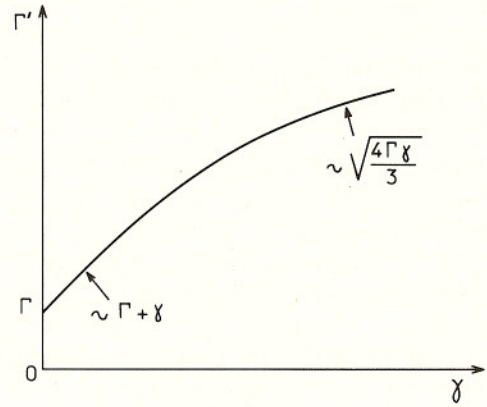

Fig. 35.

Eq. (6.11) gives the variations of Γ' with γ, i.e. with the light intensity (see fig. 35). Γ' is equal to Γ for $\gamma = 0$ and increases linearly with γ for $\gamma \ll \Gamma$. This may be interpreted as a radiative broadening proportional to the laser intensity. For $\gamma \gg \Gamma$, Γ' increases only as $\sqrt{\frac{4}{3}\gamma\Gamma}$, i.e. as the amplitude of the light wave. This shows that some care must be taken when extracting atomic data from experimental results. Plotting the width Γ' of a saturation (or Hanle) resonance as a function of the laser intensity, and extrapolating linearly to zero light intensity, may lead to wrong results if the majority of experimental points do not fall in the linear range of fig. 35.

When $\gamma \gg \Gamma$, i.e. at very high intensities, σ_{++} and σ_{--} tend to $\frac{1}{4}N_0$, σ_{00} to $\frac{1}{2}N_0$. The contrast S of the saturation resonance reaches the limiting value $\frac{1}{4}$.

The steady state solution for σ_{-+} may also be calculated from eqs. (5.33) and included with (6.10) in the expression (6.3) of $L_F(\hat{e}_x)$. We get for $L_F(\hat{e}_x)$,

$$L_F(\hat{e}_x) = \frac{2\gamma N_0}{\Gamma + 3\gamma} + \frac{2\gamma N_0(\Gamma + 2\gamma)}{(\Gamma + 3\gamma)(\Gamma + 4\gamma)} \frac{\Gamma'^2}{\Gamma'^2 + 4\omega_e^2}, \tag{6.12}$$

i.e. the sum of a constant and of a Lorentzian curve having the same width Γ' as the saturation resonance. It follows that the Hanle resonances undergo the same radiative broadening as the saturation resonances. For large values of γ/Γ, the shape of the resonance does not change when γ increases, provided that the scale of the horizontal axis is contracted proportionally to $\sqrt{\gamma}$.

Let us summarize these new results which appear when the light source is a free running multimode laser: saturation resonances observable on the populations of the Zeeman sublevels, radiative broadening of these resonances (and

also of the Hanle resonances), which is not a simple linear function of the laser intensity.

A detailed experimental verification of all the above results has been done on the $2s_2 \leftrightarrow 2p_1$ transition of Ne ($\lambda = 1.52\ \mu m$). See refs. [31,32].

6.1.3. Monochromatic excitation (single mode laser + atomic beam)

We now consider the case of an atomic beam irradiated perpendicularly by a single mode laser. We have therefore to use eqs. (5.7). We suppose that the illuminated portion of the beam is sufficiently long so that each atom reaches a steady state regime when passing through this zone. As before, $\sigma_{++} + \sigma_{--} + \sigma_{00} = N_0$ is a constant of motion and represents the total number of atoms in the illuminated zone. To simplify the discussion, we will suppose that $\omega = \omega_0$, i.e. that the laser frequency ω is tuned at the center of the atomic line (the general case $\omega \neq \omega_0$ is studied in ref. [24]).

The steady state solution of eqs. (5.7) may be found in an analytical form after some simple algebra, and we get for the Hanle signal,

$$L_F(\hat{e}_x) = 16v^2 N_0(\Gamma^2 + 4v^2)/D\,, \tag{6.13}$$

where

$$D = 16\omega_e^4 + (8\Gamma^2 + 16v^2)\omega_e^2 + (\Gamma^2 + 4v^2)(\Gamma^2 + 16v^2)\,. \tag{6.14}$$

The theoretical curves computed from (6.13) (and represented in ref. [24]) exhibit a radiative broadening when the laser intensity, i.e. v^2, increases. The shape is no more Lorentzian and, when ω_e is very large, the signal does not tend to a non-zero value (as is the case for the Hanle resonances obtained with a broad-line excitation – see expression (6.12)). This is due to the fact that, when ω_e increases, the frequencies $\omega_0 \pm \omega_e$ of the two optical lines $0 \leftrightarrow +1$ and $0 \leftrightarrow -1$ are out of resonance with the laser frequency ω.

When $v \to 0$, expression (6.14) takes the simple form

$$L_F = 16v^2 N_0 \frac{\Gamma^2}{(4\omega_e^2 + \Gamma^2)^2}\,. \tag{6.15}$$

We find the square of a Lorentz curve which is easy to understand: a first Lorentz denominator describes, as in the previous case, the decrease of the Zeeman coherence due to the Larmor precession, the second one comes from the Zeeman detuning of the two components of the optical line with respect to the laser frequency.

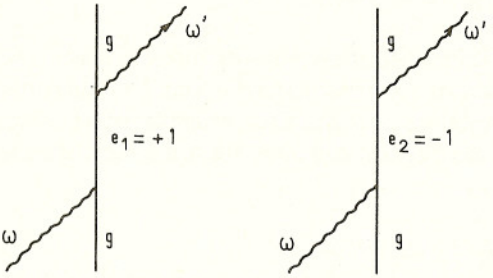

Fig. 36.

Expression (6.15) may also be obtained from the Born amplitude for the resonant scattering (fig. 36) [33]. The initial state corresponds to the atom in the ground state in the presence of an impinging ω photon. The atom can absorb this photon and jump to one of the two excited sublevels ± 1 of energies $\omega_0 \pm \omega_e$, and then fall back to the ground state by emitting the fluorescence photon. As there are two intermediate states for the scattering process, the scattering amplitude A is the sum of two terms which are respectively proportional to $1/(\omega - \omega_0 - \omega_e + \frac{1}{2}i\Gamma)$ and to $1/(\omega - \omega_0 + \omega_e + \frac{1}{2}i\Gamma)$. As we assume $\omega = \omega_0$, we get

$$A = \frac{1}{-\omega_e + \frac{1}{2}i\Gamma} + \frac{1}{\omega_e + \frac{1}{2}i\Gamma} = -\frac{4i\Gamma}{4\omega_e^2 + \Gamma^2}. \tag{6.16}$$

The cross section is proportional to $|A|^2$ and has the same ω_e and Γ dependence as expression (6.15). For $v^2 \gg \Gamma$, the shape of the curve giving L_F does not change any more when v increases, provided that the scale of the horizontal axis is contracted proportionally to v. The variations of the other detection signals: $L_F(\hat{e}_y)$, $L_F(\hat{e}_x) - L_F(\hat{e}_y)$ are studied in ref. [24].

To summarize, we see that the essentially new results obtained in the absence of the Doppler effect (single mode laser and atomic beam) come from the Zeeman detuning of the atomic lines. The zero-field level crossing resonances have more complicated shapes (non-Lorentzian), but they still have a width which is of the order of Γ at low laser intensity and which increases with the laser intensity.

Hanle resonances with a monochromatic excitation have been observed by several experimental groups (see refs. [34–36]). The agreement with the above theoretical predictions seems quite good.

6.2. More complicated situations

In the examples studied above, no structure was existing in level g. There was only one Zeeman coherence in level e, and the Hanle effect was only observable in this level. We now give a few examples of what happens when both levels e and g have a Zeeman structure. We restrict ourselves to a broad line excitation.

6.2.1. $J_g = \frac{1}{2} \leftrightarrow J_e = \frac{1}{2}$ transition

We will use eqs. (5.34) which are the rate equations for the various matrix elements σ^e_{++}, σ^e_{--}, σ^e_{+-} and σ^g_{++}, σ^g_{--}, σ^g_{+-} of σ_e and σ_g. ω_g is the Larmor precession in g. As before, γ is the reciprocal of the pumping time. We note that the absorption and stimulated emission terms are simpler than in (5.33), whereas the Larmor precession terms are a little more complicated. This is due to the choice of the axis of quantization $0z$ which is parallel not to the magnetic field, but to the direction of propagation of the σ^+ polarized laser beam.

In a Hanle experiment performed on a $J = \frac{1}{2}$ level, one detects components of the atomic orientation J perpendicular to the magnetic field $\boldsymbol{B}_0$. As $\boldsymbol{B}_0$ is along $0x$, we are interested here in J^e_z (z component of the orientation of level e), i.e. in $\sigma^e_{++} - \sigma^e_{--}$ (one can for example measure the difference between the σ^+ and σ^- fluorescence light reemitted along $0z$). To study these Hanle signals, we have to find the steady state solution of (5.34). Putting

$$\Gamma_e = \Gamma + \frac{1}{T}, \qquad \Gamma_g = \frac{1}{T},$$

$$\Gamma'_e = \Gamma_e + \tfrac{1}{3}\gamma, \qquad \Gamma'_g = \Gamma_g + \tfrac{1}{3}\gamma, \tag{6.17}$$

we get for $\sigma^e_{++} - \sigma^e_{--}$,

$$\sigma^e_{++} - \sigma^e_{--} = \tfrac{1}{2} n_0 T \frac{\Gamma_e \Gamma'_e}{\omega_e^2 + \Gamma_e \Gamma'_e} \frac{1}{D}, \tag{6.18}$$

where

$$D = 1 + \frac{3\Gamma_e}{2\gamma} + \frac{1}{2}\frac{\Gamma_e \Gamma'_e}{\omega_e^2 + \Gamma_e \Gamma'_e} + \frac{1}{2}\frac{\Gamma_e}{\Gamma_g}\frac{\Gamma_g \Gamma'_g}{\omega_e^2 + \Gamma_g \Gamma'_g}$$

$$+ \frac{1}{3}\frac{\Gamma}{\Gamma_g}\frac{(\omega_e \omega_g - \Gamma'_e \Gamma'_g)\Gamma_e \Gamma_g}{(\omega_e^2 + \Gamma_e \Gamma'_e)(\omega_g^2 + \Gamma_g \Gamma'_g)}. \tag{6.19}$$

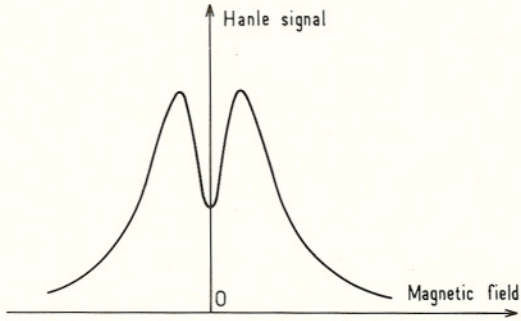

Fig. 37.

Fig. 37 gives an idea of the variations with the magnetic field of the Hanle signal computed from (6.18) and (6.19). (Precise theoretical curves corresponding to different values of the light intensity, i.e. of γ, are given in ref. [23].)

One clearly sees in fig. 37 that the Hanle signal observed on the fluorescence light emitted from e exhibits a structure. The dip observed in the centre of the curve is associated with the Hanle effect of g: at very low intensities, this dip has a width determined by the relaxation time T of the ground state, whereas the broad resonance has a width Γ.

When the light intensity increases, one finds that the widths of both resonances increase. At very high intensities, the two Hanle effects of e and g are completely mixed in a time short compared to $1/\Gamma$ and T, but this mixing does not smooth out the structure apparent in fig. 37: we always get the superposition of two resonances with different widths and opposite signs giving rise to a curve with two maxima.

6.2.2. $J_g = 2 \leftrightarrow J_e = 1$ transition

More complicated structures may be observed if the values of the angular momenta J_e and J_g are higher than $\frac{1}{2}$. For example, in the case of a $J_e = 1 \leftrightarrow J_g = 2$ transition, and for a σ linearly polarized excitation, one can observe Hanle signals with three maxima. As in the previous example, the coupling between the two transverse alignments of e and g (perpendicular to the magnetic field) gives rise to a structure similar to that of fig. 37. But as $J_g > 1$, there is also in the ground state g a "hexadecapole" moment (Hertzian coherence $\sigma^g_{-2,+2}$) which can be induced in this case after two interactions with the laser, one absorption and one induced emission processes (see fig. 38a). A third interaction with the laser (absorption) can couple this hexadecapole mo-

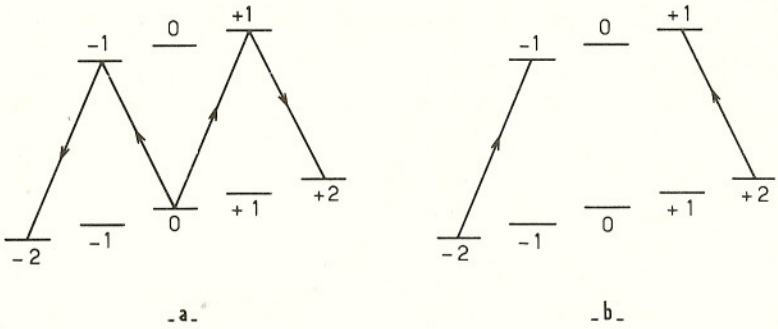

Fig. 38.

ment to the transverse alignment of e ($\sigma^e_{-1,+1}$) (see fig. 38b). As the Hanle resonance associated with $\sigma^g_{-2,+2}$ has a smaller width (the resonant denominator is $\Gamma_g^2 + 16\omega_e^2$), the total result of these various couplings is to give for some values of γ a structure with three maxima. This effect has been observed on the $3s_2 \leftrightarrow 2p_4$ transition of Ne ($\lambda = 6328$ Å) and interpreted quantitatively [25,32,37]. For another manifestation of hexadecapole moment, see also ref. [38].

Optical pumping of molecules also provides several examples of Hanle resonances observed in levels having very high angular momentum [39]. Some efforts have been made to write the optical pumping equations in a basis of quasiclassical states well adapted to the high values of J [40].

To summarize the results of this paragraph, we see that one can observe, on the fluorescence light emitted from e, level crossing resonances having a width much smaller than the natural width of e. This is not related to the broad-line or narrow-line character of the pumping light (as it appears already on the results of the previous paragraph). These narrow resonances must be attributed to the other state g of the optical line which has a longer lifetime or a higher J value.

7. Spectral distribution of the fluorescence light emitted by a two-level atom

After having calculated some one-time averages in order to interpret the various characteristics of level crossing resonances, we now come back to the problem of the spectral distribution of the fluorescence light emitted by a two-level atom which is more difficult as it requires the evaluation of two-time averages.

7.1. Monochromatic excitation

Let us first recall the master equation written in terms of the equivalent fictitious spin $\frac{1}{2}$: Bloch's equations (5.5) for the average value of the spin $\langle \boldsymbol{S} \rangle$:

$$\begin{array}{lccc} \langle \dot{S}_z \rangle = & & -\Gamma(\langle S_z \rangle + \tfrac{1}{2}) & +\tfrac{1}{2} i \omega_1 (\langle S_- \rangle - \langle S_+ \rangle) , \\ \langle \dot{S}_\pm \rangle = & \pm i(\omega_0 - \omega_L)\langle S_\pm \rangle & -\tfrac{1}{2}\Gamma \langle S_\pm \rangle & \mp i \omega_1 \langle S_z \rangle . \\ & \text{free evolution} & \text{spontaneous emission} & \text{coupling with the laser} \end{array} \tag{7.1}$$

According to (3.15) and (3.17), the spectral distribution $\mathcal{I}(\omega)$ of the fluorescence light is given by

$$\mathcal{I}(\omega) \sim \int_0^\theta \mathrm{d}t \int_0^\theta \mathrm{d}t' \langle S_+(t) S_-(t') \rangle \mathrm{e}^{-i(\omega - \omega_L)(t-t')} . \tag{7.2}$$

In (7.2), θ is the measurement time of the detector. In fact, we are limited by the time T during which the atoms radiate: $\theta > T$. T is approximately the time spent by an atom inside the laser beam. Therefore, in (7.2) we can replace θ by T.

7.1.1. "Naive" approach of the problem based on Bloch's equations

Before evaluating the two-time average contained in (7.2), let us first give a naive approach of the problem, strongly suggested by the analogy with a magnetic resonance experiment, but which, in the present case, is incorrect. Then, in trying to understand where the mistake is, we will get some physical insight into the problem [41].

What is the solution of eqs. (7.1) for an atom flying through the laser beam? After a transient regime which starts when the atom enters the laser beam at $t = 0$, and which lasts for a time of the order of $\tau = \Gamma^{-1}$ (damping time of the transient solutions of eqs. (7.1)), $\langle \boldsymbol{S}(t) \rangle$ reaches a stationary value $\langle \boldsymbol{S} \rangle_{\mathrm{st}}$, independent of t, and corresponding to the steady state solution of (7.1). This situation lasts during all the transit time T through the laser beam (remember that $T \gg \tau$). After that, the atom leaves the laser beam at time $t = T$, and $\langle \boldsymbol{S} \rangle$ damps to zero in a short time, of the order of τ. This behaviour is schematically represented in fig. 39.

At this stage, one is very tempted to consider that the light radiated by the atom corresponds to this evolution of $\langle \boldsymbol{S}(t) \rangle$ (we have to return from the ro-

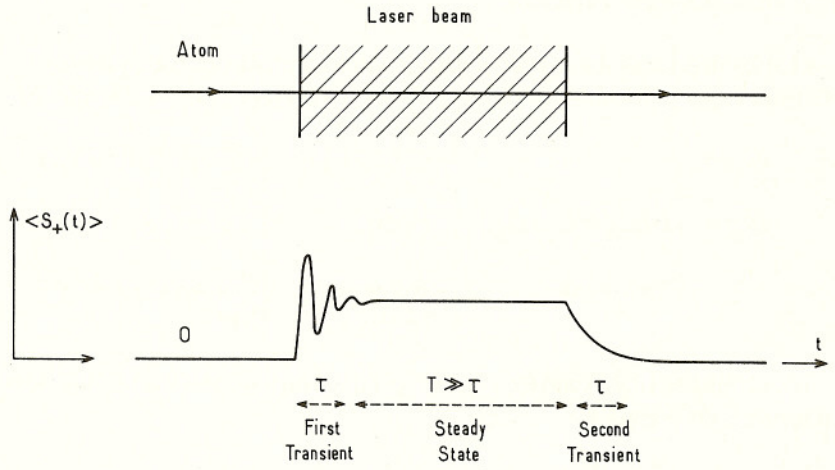

Fig. 39.

tating to the laboratory reference frame) and, consequently, that its spectrum is given by the squared modulus of the FT of $\langle S_+(t)\rangle e^{i\omega_L t}$. If such a conclusion were correct, one would get first an elastic component, at frequency ω_L, representing the contribution of the forced steady state motion $\langle S_+\rangle_{st} e^{i\omega_L t}$ of the dipole moment driven by the laser field and which, as we have seen above, is the main part of the motion of the dipole. Strictly speaking, this elastic component would have a non-zero width $1/T$ (corresponding to the finite transit time T), much smaller however than Γ (as $T \gg \tau$). In addition, one would get a small inelastic component, associated with the two small transient regimes appearing at the two small regions where the atom enters or leaves the laser beam. This suggests that one could suppress these inelastic components just by eliminating the light coming from these two regions, which is wrong as we shall see later on.

7.1.2. What is missing in this approach? Importance of the fluctuations

The method we have just outlined is not correct. A mathematical argument for showing it is that, when we calculate the squared modulus of the FT of $\langle S_+(t)\rangle$, we find an expression analogous to (7.2), but where $\langle S_+(t)S_-(t')\rangle$ is replaced by $\langle S_+(t)\rangle\langle S_-(t')\rangle$, and these two quantities are not equal.

It is perhaps more interesting to try to understand physically where the mistake is. The important point is that the light emitted by the atom is not radiated by its average dipole moment represented by $\langle S_\pm(t)\rangle$, but by its in-

stantaneous dipole moment $S_{\pm}(t)$, and, even though the effect of spontaneous emission on $\langle \boldsymbol{S}(t) \rangle$ may be shown to be correctly described by the damping terms of eqs. (7.1), such a description is incorrect for $\boldsymbol{S}(t)$.

Let us try to visualize the evolution of $\boldsymbol{S}(t)$. We can consider the atom as being constantly "shaken" by the "vacuum fluctuations" of the quantized electromagnetic field [42]. These random fluctuations, which have an extremely short correlation time, have a cumulative effect on the atom in the sense that they damp $\langle \boldsymbol{S}(t) \rangle$, but we must not forget that they make the instantaneous dipole moment $S_{\pm}(t)$ fluctuate permanently around its mean value. The light which comes out is radiated not only by the mean motion of the dipole, but also by its fluctuations around the mean motion.

When we consider the effect of atoms on the incident electromagnetic wave which drives them, i.e. when we study how they absorb or amplify this wave, the average motion $\langle \boldsymbol{S}(t) \rangle$ is very important since it has definite phase relations with the driving field. The fluctuations of $\boldsymbol{S}(t)$ act only as a source of noise and can be ignored in a first step. In the problem we are studying here, we cannot ignore the fluctuations since they play an essential role: we are interested in spontaneous emission, not in absorption or induced emission, and the fluctuations of $S_{\pm}(t)$ cannot be neglected.

7.1.3. Elastic and inelastic parts of the fluorescence spectrum

Let us write

$$S_{\pm}(t) = \langle S_{\pm}(t) \rangle + \delta S_{\pm}(t) , \tag{7.3}$$

where $\delta S_{\pm}(t)$ is the deviation from the average value and obviously satisfies

$$\langle \delta S_{\pm}(t) \rangle = 0 . \tag{7.4}$$

Inserting (7.3) into (7.2), and using (7.4), one immediately gets

$$\langle S_{+}(t) S_{-}(t') \rangle = \langle S_{+}(t) \rangle \langle S_{-}(t') \rangle + \langle \delta S_{+}(t) \delta S_{-}(t') \rangle . \tag{7.5}$$

One clearly sees from (7.5) that, in the spectrum of the fluorescence light, there is an elastic component corresponding to the first term of (7.5) and which is the light radiated by the average motion of the dipole. In addition, we get an inelastic component corresponding to the last term of (7.5) and which is the light radiated by the fluctuations. The spectrum of this inelastic part is determined by the temporal dependence of these fluctuations, i.e. by their dynamics.

Before studying this problem, let us show how it is possible to derive simple expressions for the total intensity radiated elastically and inelastically, I_{el} and I_{inel}. Integrating (7.2) over ω, one gets a $\delta(t-t')$ function which gives, when using (7.5),

$$I_{el} \sim \int_0^T dt |\langle S_+(t)\rangle|^2 ,$$

$$I_{inel} \sim \int_0^T dt \langle \delta S_+(t) \delta S_-(t)\rangle = \int_0^T dt [\langle S_+(t) S_-(t)\rangle - |\langle S_+(t)\rangle|^2]$$

$$= \int_0^T dt [\tfrac{1}{2} + \langle S_z(t)\rangle - |\langle S_+(t)\rangle|^2] . \qquad (7.6)$$

(We have used the relation $S_+ S_- = \boldsymbol{S}^2 - S_z^2 + S_z$ and the identities $\boldsymbol{S}^2 = \frac{3}{4}$, $S_z^2 = \frac{1}{4}$ valid for a spin $\frac{1}{2}$.)

As the two small transient regimes near $t = 0$ and $t = T$ have a very small relative contribution (of the order of τ/T), we can replace in (7.6), $\langle S_+(t)\rangle$ and $\langle S_z(t)\rangle$ by the steady state solution $\langle S_+\rangle_{st}$ and $\langle S_z\rangle_{st}$ of Bloch's equations. We get in this way

$$I_{el} \sim T |\langle S_+\rangle_{st}|^2 ,$$

$$I_{inel} \sim T [\tfrac{1}{2} + \langle S_z\rangle_{st} - |\langle S_+\rangle_{st}|^2] . \qquad (7.7)$$

This clearly shows that I_{el} and I_{inel} are proportional to T and that the inelastic part of the fluorescence is radiated uniformly throughout the whole period of time spent by the atom in the laser beam, and not only at the beginning or at the end of this period, as suggested by the naive approach described above. The calculation of $\langle \boldsymbol{S}\rangle_{st}$ is straightforward and one gets

$$\langle S_x\rangle_{st} = \frac{2\omega_1 \Delta\omega}{\Gamma^2 + 2\omega_1^2 + 4(\Delta\omega)^2} , \qquad \langle S_y\rangle_{st} = \frac{\Gamma\omega_1}{\Gamma^2 + 2\omega_1^2 + 4(\Delta\omega)^2} ,$$

$$\langle S_z\rangle_{st} = -\frac{1}{2} \frac{\Gamma^2 + 4\Delta\omega^2}{\Gamma^2 + 2\omega_1^2 + 4(\Delta\omega)^2} , \quad \text{where } \Delta\omega = \omega_L - \omega_0 . \qquad (7.8)$$

From (7.7) and (7.8), one deduces

$$\frac{I_{\mathrm{el}}}{T} \sim \frac{\omega_1^2[\Gamma^2 + 4(\omega_0 - \omega_L)^2]}{[\Gamma^2 + 4(\omega_0 - \omega_L)^2 + 2\omega_1^2]^2},$$

$$\frac{I_{\mathrm{inel}}}{T} \sim \frac{2\omega_1^4}{[\Gamma^2 + 4(\omega_0 - \omega_L)^2 + 2\omega_1^2]^2}. \tag{7.9}$$

Similar results are derived in ref. [16] where I_{el} and I_{inel} are called coherent and incoherent scattering.

For very low intensities of the light beam ($\omega_1 \ll \Gamma, |\omega_L - \omega_0|$), we see that I_{el} varies as ω_1^2, i.e. as the light intensity I, whereas I_{inel} varies as ω_1^4, i.e. as I^2 (see fig. 40). Most of the light is scattered elastically and we can define a cross section for such a process which is well described by fig. 2. I_{inel} is much smaller and can be considered as due to non-linear scattering processes of the type shown in fig. 7.

For very high intensities ($\omega_1 \gg \Gamma, |\omega_L - \omega_0|$), we see on the contrary that I_{el} tends to 0 (fig. 40). This is due to the fact that the atomic transition is completely saturated: the two populations are equalized ($\langle S_z \rangle_{\mathrm{st}} = 0$) and the dipole moment is reduced to 0 ($\langle S_{\pm} \rangle_{\mathrm{st}} = 0$). On the other hand, I_{inel} is very large and independent of the light intensity I (this appears clearly in the bracket of the last equation (7.7) which reduces to $\frac{1}{2}$ as $\langle S_z \rangle_{\mathrm{st}} = \langle S_+ \rangle_{\mathrm{st}} = 0$). This means that the atom spends half of its time in e and cannot therefore

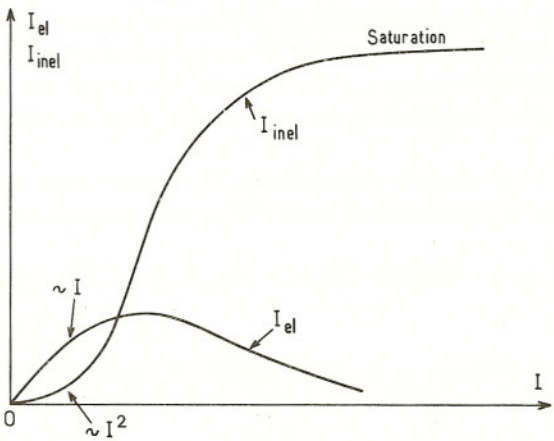

Fig. 40.

emit more than $\frac{1}{2}T/\tau$ photons. Increasing the incident light intensity cannot change this number.

One therefore concludes that inelastic scattering, which is due to the fluctuations of S_+, is predominant in strong resonant fields. If we ignore these fluctuations, we miss all the physics. One can finally try to understand why these fluctuations are so effective at high intensities ($I_{\text{inel}} \gg I_{\text{el}}$) whereas they have little influence at low intensities ($I_{\text{inel}} \ll I_{\text{el}}$). I think this is due to the fact that the greater the probability to find an atom in the excited state e is, the more sensitive is this atom to the vacuum fluctuations. Some components of the vacuum fluctuations are resonant for the atom in e as they can induce it to emit spontaneously a photon whereas they can only produce a level shift of g. At low intensities, most of the atoms are in g and are not very sensitive to the vacuum fluctuations whereas at high intensities half of the atoms are in e and fluctuate appreciably.

7.1.4. How to study the dynamics of the fluctuations? Quantum regression theorem

Let us now discuss the temporal dependence of $\langle \delta S_+(t) \delta S_-(t') \rangle$. Considering the physical discussion given above, it seems that a good idea would be to try to write down an equation of motion for $\boldsymbol{S}(t)$ (and not for $\langle \boldsymbol{S}(t) \rangle$) including the random character of the force exerted by vacuum fluctuations. These fluctuations have a cumulative effect on $\boldsymbol{S}(t)$ which can be described by damping terms analogous to those appearing in (7.1). In addition, $\boldsymbol{S}(t)$ fluctuates around its mean value in a way which can be considered as resulting from the action of a random "*Langevin force*" $\boldsymbol{F}(t)$, having an extremely short correlation time and a zero average value [43]. It is clear that some relations must exist between the damping coefficients Γ and the statistical properties of $\boldsymbol{F}(t)$ (relations between dissipation and fluctuations) but we will not consider this problem here since, hereafter, we will only use the ultra short memory character of $\boldsymbol{F}(t)$.

So, we will write the following equations of motion (which can be derived from the Heisenberg equations of motion after some manipulations):

$$\frac{\mathrm{d}}{\mathrm{d}t} S_z(t) = -\tfrac{1}{2} i\omega_1 S_+(t) - \Gamma S_z(t) + \tfrac{1}{2} i\omega_1 S_-(t) - \tfrac{1}{2}\Gamma + F_z(t) ,$$

$$\frac{\mathrm{d}}{\mathrm{d}t} S_\pm(t) = [\pm i(\omega_0 - \omega_L) - \tfrac{1}{2}\Gamma] S_\pm(t) \mp i\omega_1 S_z(t) + F_\pm(t) , \qquad (7.10)$$

with

$$\langle F_z \rangle = \langle F_\pm \rangle = 0 ,$$

$$\langle F_i(t) F_j(t') \rangle = 0 , \quad \text{if } |t - t'| \gtrsim \tau_C . \tag{7.11}$$

When averaged, (7.10) reduces to Bloch's equations (7.1) since $\langle \boldsymbol{F} \rangle = 0$.

Subtracting (7.1) from (7.10), one gets the equations of motion for $\delta \boldsymbol{S} = \boldsymbol{S} - \langle \boldsymbol{S} \rangle$ which look like eq. (7.10) except for the inhomogeneous term $-\frac{1}{2}\Gamma$ which disappears in the subtraction. We will write these equations in the form

$$\frac{\mathrm{d}}{\mathrm{d}t} \delta S_i(t) = \sum_j \mathcal{B}_{ij} \delta S_j(t) + F_i(t) , \tag{7.12}$$

where $i, j = +, z, -$ and where the $\mathcal{B}_{ij}$ are the coefficients of the homogeneous Bloch equation, forming the following 3×3 matrix:

$$\| \mathcal{B} \| = \begin{array}{c} \\ + \\ z \\ - \end{array} \begin{array}{c} \begin{array}{ccc} + & z & - \end{array} \\ \begin{pmatrix} -(\frac{1}{2}\Gamma + i\Delta\omega) & -i\omega_1 & 0 \\ -\frac{1}{2} i\omega_1 & -\Gamma & \frac{1}{2} i\omega_1 \\ 0 & i\omega_1 & -(\frac{1}{2}\Gamma - i\Delta\omega) \end{pmatrix} \end{array} . \tag{7.13}$$

We have put $\Delta\omega = \omega_L - \omega_0$.

From now, we will suppose that $t > t'$. To calculate the correlation function $\langle \delta S_+(t) \delta S_-(t') \rangle$ when $t < t'$, we will use the following relation:

$$\langle \delta S_+(t) \delta S_-(t') \rangle = (\langle \delta S_+(t') \delta S_-(t) \rangle)^* , \tag{7.14}$$

which is a consequence of the adjoint character of S_+ and S_-: $S_+ = (S_-)^+$.

Consider now the product $\delta S_+(t) \delta S_-(t')$ with $t > t'$, and let us try to understand how it varies with t. When calculating $\mathrm{d}\langle \delta S_+(t) \delta S_-(t') \rangle / \mathrm{d}t$ and using (7.12) for $\mathrm{d}\delta S_+(t)/\mathrm{d}t$, the only difficulty which appears comes from the Langevin term $F_+(t) \delta S_-(t')$, since we have not explicited $F_+(t)$. But we only need to calculate $\mathrm{d}\langle \delta S_+(t) \delta S_-(t') \rangle / \mathrm{d}t$, so that we only need to calculate the average $\langle F_+(t) \delta S_-(t') \rangle$. And it is easy to understand that such an average gives 0 since the motion of the dipole at t', $S_-(t')$ cannot be correlated with the Langevin force $F_+(t)$ at a later time t, as a consequence of the ultra short correlation time of $F_+(t)$. It follows that the rate of the t-variation of the three correlation functions $\langle \delta S_i(t) \delta S_-(t') \rangle$ (with $t > t'$, and $i = +, z, -$) is described by a set of three first order differential equations with the same coefficients

as the ones appearing in the homogeneous Bloch equations giving the rate of variation of $\langle S_i(t)\rangle$. More precisely, we have, for $t > t'$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \delta S_i(t)\delta S_-(t')\rangle = \sum_j \mathcal{B}_{ij}\langle \delta S_j(t)\delta S_-(t')\rangle \,. \tag{7.15}$$

This important result is a particular case of the "*quantum regression theorem*" [44]. In the present case, it means that, when the dipole undergoes a fluctuation and is removed from its steady state, the subsequent evolution and the damping of this fluctuation are the same as the transient behaviour of the mean dipole moment starting from a non-steady state initial condition.

7.1.5. Quantitative calculation of the correlation function

Mathematically, the quantum regression theorem gives the possibility of calculating two time averages once the $\mathcal{B}_{ij}$'s are known (see eqs. (7.15)), i.e. once the master equation giving the evolution of one-time averages is known.

We give in this section two different methods for calculating $\langle \delta S_+(t)\delta S_-(t')\rangle$, and, consequently, the spectral distribution of the inelastic part of the fluorescence spectrum which, according to (7.2), (7.5) and (7.14) is given by

$$\mathcal{I}_{\mathrm{inel}}(\omega) \sim 2\mathcal{R}e \int_0^T \mathrm{d}t \int_0^t \mathrm{d}t' \langle \delta S_+(t)\delta S_-(t')\rangle \mathrm{e}^{-i(\omega-\omega_L)(t-t')} \,. \tag{7.16}$$

The elastic part of the fluorescence light is not strictly speaking a $\delta(\omega-\omega_L)$ function. It has a finite width which is the larger of the two following quantities: width $\Delta\nu$ of the laser, inverse $1/T$ of the transit time of atoms through the laser beam. We have already calculated in § 7.1.3 the ratio between the integrals over ω of the elastic and inelastic parts of the fluorescence spectrum.

(i) First method. Let V_α ($\alpha = 1,2,3$) be the three eigenvectors of the matrix (7.13) corresponding to eigenvalues E_α. As (7.13) is not hermitian, these eigenvalues E_α are not real and may be written as

$$E_\alpha = i\delta_\alpha - \gamma_\alpha \,, \tag{7.17}$$

where δ_α and γ_α are real.

Therefore, we have for $t > t'$

$$V_\alpha(t) = V_\alpha(t')\mathrm{e}^{E_\alpha(t-t')} \,. \tag{7.18}$$

Let us expand $\delta S_+(t)$ on the $V_\alpha(t)$,

$$\delta S_+(t) = \sum_\alpha C_\alpha V_\alpha(t) . \tag{7.19}$$

Inserting (7.19) into the correlation function $\langle \delta S_+(t) \delta S_-(t') \rangle$, using the quantum regression theorem and (7.18) and (7.17), we get

$$\langle \delta S_+(t) \delta S_-(t') \rangle = \sum_\alpha C_\alpha \langle V_\alpha(t') \delta S_-(t') \rangle e^{i\delta_\alpha(t-t')} e^{-\gamma_\alpha(t-t')} , \tag{7.20}$$

so that (7.16) may be rewritten as

$$\mathcal{I}_{\text{inel}}(\omega) \sim 2\mathcal{R}e \int_0^T d(t-t') \int_0^T dt' \sum_\alpha C_\alpha \langle V_\alpha(t') \delta S_-(t') \rangle$$

$$\times e^{-i(\omega-\omega_L-\delta_\alpha)(t-t')} e^{-\gamma_\alpha(t-t')} . \tag{7.21}$$

As γ_α is of the order of $\Gamma = 1/\tau$ (τ is radiative lifetime of e) and as $T \gg \tau$, we can replace the upper limit T of the integral over $t - t'$ by $+\infty$. Neglecting the two small transient regimes near $t = 0$ and $t = T$, we can also in the integral over t' replace $\langle V_\alpha(t') \delta S_-(t') \rangle$ by the steady state value $\langle V_\alpha \delta S_- \rangle_{\text{st}}$, so that we finally have

$$\frac{1}{T} \mathcal{I}_{\text{inel}}(\omega) \sim 2\mathcal{R}e \sum_\alpha C_\alpha \langle V_\alpha \delta S_- \rangle_{\text{st}} \int_0^\infty e^{-[i(\omega-\omega_L-\delta_\alpha)+\gamma_\alpha]\tau} d\tau . \tag{7.22}$$

We get a very simple result: the inelastic spectrum consists of three components having a Lorentzian shape (more precisely, when we take the real part, we find a mixture of absorption and dispersion shapes). Each of these components α has:

a mean position $\omega_L + \delta_\alpha$;

a half-width γ_α;

a weight $C_\alpha \langle V_\alpha \delta S_- \rangle_{\text{st}}$.

(ii) Application. Shape of the inelastic spectrum at resonance ($\Delta\omega = \omega_L - \omega_0 = 0$) and in strong resonant fields ($\omega_1 \gg \Gamma$). Let us come back to eq. (7.12) and change from the three quantities $\delta S_i \{\delta S_x + i\delta S_y, \delta S_z, \delta S_x - i\delta S_y\}$ to the three quantities $\{\delta S_\alpha = \delta S_y + i\delta S_z, \delta S_\beta = \delta S_x, \delta S_\gamma = \delta S_y - i\delta S_z\}$. We find that the matrix $\mathcal{B}$ given in (7.13) transforms into

$$\begin{array}{c} \\ \alpha \\ \beta \\ \gamma \end{array} \begin{array}{c} \begin{array}{ccc} \alpha & \beta & \gamma \end{array} \\ \begin{pmatrix} i\omega_1 - \frac{3}{4}\Gamma & 0 & \frac{1}{4}\Gamma \\ 0 & -\frac{1}{2}\Gamma & 0 \\ \frac{1}{4}\Gamma & 0 & -i\omega_1 - \frac{3}{4}\Gamma \end{pmatrix} \end{array} . \tag{7.23}$$

As $\omega_1 \gg \Gamma$, the two off-diagonal elements of (7.23) are much smaller than the differences between any pair of diagonal elements, and we can, to a very good approximation, consider that (7.23) is diagonal. We know therefore the eigenvectors and eigenvalues of (7.13):

$$\begin{aligned} V_\alpha &= \delta S_y + i\delta S_z , & E_\alpha &= i\omega_1 - \tfrac{3}{4}\Gamma , \\ V_\beta &= \delta S_x , & E_\beta &= -\tfrac{1}{2}\Gamma , \\ V_\gamma &= \delta S_y - i\delta S_z , & E_\gamma &= -i\omega_1 - \tfrac{3}{4}\Gamma . \end{aligned} \tag{7.24}$$

Let us now calculate C_α, C_β, C_γ. From

$$\delta S_x + i\delta S_y = V_\beta + \tfrac{1}{2}i(V_\alpha + V_\gamma) \tag{7.25}$$

we deduce

$$C_\alpha = \tfrac{1}{2}i , \qquad C_\beta = 1 , \qquad C_\gamma = \tfrac{1}{2}i . \tag{7.26}$$

We still have to calculate the $\langle V_\alpha \delta S_- \rangle_{\mathrm{st}}$. As $\omega_1 \gg \Gamma$, we will take for the steady state value of the atomic density matrix the completely depolarized matrix

$$\sigma_{\mathrm{st}} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \tag{7.27}$$

corresponding to a complete saturation of the atomic transition (two equal populations and no dipole moment). Using elementary properties of Pauli matrices, we get

$$\begin{aligned} \langle V_\alpha \delta S_- \rangle_{\mathrm{st}} &= \langle (\delta S_y + i\delta S_z)(\delta S_x - i\delta S_y) \rangle_{\mathrm{st}} \\ &= \langle (S_y + iS_z)(S_x - iS_y) \rangle_{\mathrm{st}} - \underbrace{\langle S_y + iS_z \rangle_{\mathrm{st}} \langle S_x - iS_y \rangle_{\mathrm{st}}}_{= 0 \quad \text{since } \langle \boldsymbol{S} \rangle_{\mathrm{st}} = 0 ,} \end{aligned}$$

$$\tfrac{1}{2}\mathrm{Tr}(S_y + iS_z)(S_x - iS_y) = -\tfrac{1}{2}i\,\mathrm{Tr}\,S_y^2 = -\tfrac{1}{4}i\,, \tag{7.28}$$

and similarly

$$\langle V_\beta \delta S_- \rangle_{\mathrm{st}} = \tfrac{1}{2}\mathrm{Tr}\,S_x(S_x - iS_y) = \tfrac{1}{2}\mathrm{Tr}\,S_x^2 = \tfrac{1}{4}\,, \tag{7.29}$$

$$\langle V_\gamma \delta S_- \rangle_{\mathrm{st}} = \tfrac{1}{2}\mathrm{Tr}(S_y - iS_z)(S_x - iS_y) = -\tfrac{1}{2}i\,\mathrm{Tr}\,S_y^2 = -\tfrac{1}{4}i\,. \tag{7.30}$$

Finally, inserting all these quantities in (7.22), we get

$$\frac{1}{T}\,\mathcal{I}_{\mathrm{inel}}(\omega) = \frac{1}{4}\left[\frac{\frac{3}{4}\Gamma}{(\omega-\omega_{\mathrm{L}}-\omega_1)^2+(\frac{3}{4}\Gamma)^2}\right.$$

$$\left. + 2\,\frac{\frac{1}{2}\Gamma}{(\omega-\omega_{\mathrm{L}})^2+(\frac{1}{2}\Gamma)^2} + \frac{\frac{3}{4}\Gamma}{(\omega-\omega_{\mathrm{L}}+\omega_1)^2+(\frac{3}{4}\Gamma)^2}\right]. \tag{7.31}$$

We find that $\mathcal{I}_{\mathrm{inel}}$ consists of three Lorentz curves (with an absorption shape), centred on $\omega_{\mathrm{L}} + \omega_1$, ω_{L}, $\omega_{\mathrm{L}} - \omega_1$ with half widths $\frac{3}{4}\Gamma$, $\frac{1}{2}\Gamma$, $\frac{3}{4}\Gamma$, respectively (see fig. 41). The total area under the central component is two times larger than the total area under each sideband. As the central component is narrower by a factor $\frac{2}{3}$, its height is three times larger than the one of each sideband.

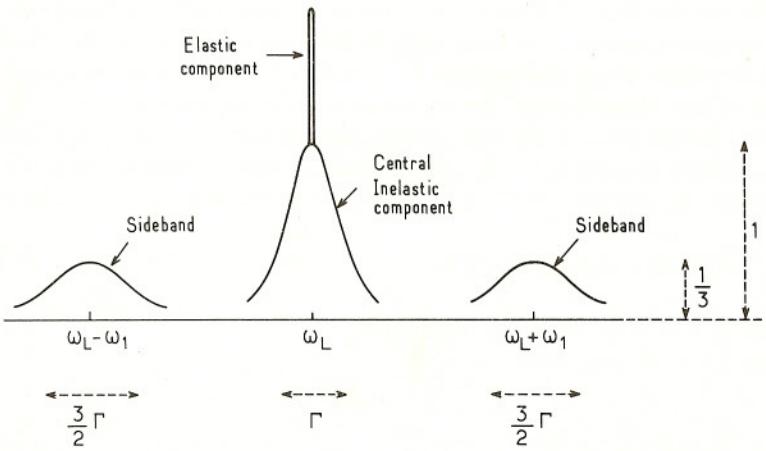

Fig. 41.

We have also represented the elastic component which still exists when ω_1/Γ is not infinite. This elastic component must not be confused with the central component of the inelastic component. It has a much smaller width (which is the width $\Delta\nu$ of the laser or $1/T$). I_{el} is spread over $\Delta\nu$ (or $1/T$) whereas the central component of $\mathcal{I}_{\text{inel}}(\omega)$, corresponding to an intensity $\frac{1}{2}I_{\text{inel}}$, is spread over Γ. It follows that the ratio between the heights of the elastic component and the central inelastic component is of the order of

$$2\frac{I_{\text{el}}}{I_{\text{inel}}}\frac{\Gamma}{\Delta\nu} \quad \text{or} \quad 2\frac{I_{\text{el}}}{I_{\text{inel}}}\Gamma T, \tag{7.32}$$

i.e. much larger than $I_{\text{el}}/I_{\text{inel}}$ which is given by (7.9). We must therefore have $\omega_1 \gg \Gamma$ in order to be allowed to neglect the elastic component.

Such a structure is simple to understand. The two sidebands correspond to the modulation of δS_y due to the transient precession of the fluctuating part of $\boldsymbol{S}$ around $\boldsymbol{B}_1$ at frequency ω_1 (see fig. 9; as we are at resonance, $B_0 = 0$). As the projection of $\boldsymbol{S}$ in the plane $Y0Z$ perpendicular to $\boldsymbol{B}_1$ is alternatively parallel to $0Y$ and $0Z$, and as the two damping coefficients associated to S_z and S_y are respectively Γ and $\frac{1}{2}\Gamma$ (see eqs. (7.1)), one understands why, when $\omega_1 \gg \Gamma$, the damping of the precession around $\boldsymbol{B}_1$ is given by $\frac{1}{2}[\Gamma + \frac{1}{2}\Gamma] = \frac{3}{4}\Gamma$ and this explains the width $\frac{3}{4}\Gamma$ of the two sidebands. The central component is associated with the transient behaviour of δS_x, which is not modulated by the precession around $\boldsymbol{B}_1$ and which has a damping coefficient $\frac{1}{2}\Gamma$. This explains the position and the width of the central component.

We see also that the classical treatment of the laser field, combined with the quantum regression theorem, leads to the same results as a correct quantum treatment taking into account the transfer of coherence between pairs of levels of the "dressed atom" having the same Bohr frequency (§ 4.3.3).

(iii) Second method. We now present a second method which gives directly an analytical expression for $\mathcal{I}_{\text{inel}}(\omega)$ and which does not require the diagonalization of the matrix (7.13). Let us introduce the quantity $\mathcal{J}_{ij}(t, t')$ given by

$$\mathcal{J}_{ij}(t, t') = \langle \delta S_i(t) \delta S_j(t') \rangle \theta(t - t') , \tag{7.33}$$

where $(t - t')$ is the Heaviside function.

As $T \gg \tau$, we can write

$$\mathcal{I}_{\text{inel}}(\omega)/T = 2\mathcal{R}e \int_{-\infty}^{+\infty} \mathrm{d}\tau \, \mathrm{e}^{-i(\omega-\omega_{\text{L}})\tau} \, \mathcal{J}_{+-}(\tau) . \tag{7.34}$$

Note that because of the $\theta(t-t') = \theta(\tau)$ function, the integral over τ can be extended to $-\infty$. It follows that $\mathcal{I}_{\text{inel}}(\omega)$ is proportional to the real part of the FT of $\mathcal{S}_{+-}(\tau)$. If we put

$$g_{+-}(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}\tau\, \mathrm{e}^{-i\omega\tau}\, \mathcal{S}_{+-}(\tau)\,, \tag{7.35a}$$

$$\mathcal{S}_{+-}(\tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}\omega\, \mathrm{e}^{i\omega\tau} g_{+-}(\omega)\,, \tag{7.35b}$$

we get

$$\mathcal{I}_{\text{inel}}(\omega)/T \sim 2\mathcal{R}e\, g_{+-}(\omega - \omega_{\text{L}})\,. \tag{7.36}$$

Let us now take the derivative of (7.33) with respect to t. Using (7.15) and

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta(t-t') = \frac{\mathrm{d}}{\mathrm{d}\tau}\theta(\tau) = \delta(\tau) \tag{7.37}$$

we get

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\mathcal{S}_{i-}(\tau) = \sum_j \mathcal{B}_{ij}\, \mathcal{S}_{j-}(\tau) + \mathcal{S}_{i-}(0)\delta(\tau)\,. \tag{7.38}$$

By this method, we introduce the initial conditions in the differential equation. We have

$$\mathcal{S}_{i-}(0) = \mathcal{R}_{i-} = \langle \delta S_i \delta S_- \rangle_{\text{st}} = \langle S_i S_- \rangle_{\text{st}} - \langle S_i \rangle \langle S_- \rangle_{\text{st}}\,. \tag{7.39}$$

The $\mathcal{R}_{i-}$ can immediately be calculated from the steady state solution (7.8) of Bloch's equation. We find

$$\mathcal{R}_{+-} = \frac{2\omega_1^4}{(\Gamma^2 + 2\omega_1^2 + 4\Delta^2)^2}\,, \qquad \mathcal{R}_{0-} = \frac{-\omega_1^3(2\Delta - i\Gamma)}{(\Gamma^2 + 2\omega_1^2 + 4\Delta^2)^2}\,,$$

$$\mathcal{R}_{--} = \frac{-\omega_1^2(2\Delta - i\Gamma)^2}{(\Gamma^2 + 2\omega_1^2 + 4\Delta^2)^2}\,. \tag{7.40}$$

Let us finally take the Fourier transform of (7.38). Using (7.35a), we get

$$i\omega g_{i-}(\omega) = \sum_j \mathcal{B}_{ij} g_{j-}(\omega) + \mathcal{R}_{i-} \ . \tag{7.41}$$

Eqs. (7.41) are a set of three linear equations between the three unknown quantities $g_{+-}(\omega)$, $g_{0-}(\omega)$, $g_{--}(\omega)$ with inhomogeneous terms given by (7.40). From these equations, we can immediately determine $g_{+-}(\omega)$, which is given by a ratio of two determinants. This analytical expression for $g_{+-}(\omega)$, combined with (7.36), gives $\mathcal{I}_{\text{inel}}(\omega)$ for any values of ω, ω_1/Γ, $\Delta\omega = \omega_L - \omega_0$.

7.1.6. Comparison with other calculations and with experimental results

A lot of theoretical papers have been published on the spectral distribution of resonance fluorescence [1,16,45–56].

The first paper predicting the spectrum represented in fig. 41, with the correct values for the heights and widths of the various components is Mollow's paper [11], which uses a classical description of the laser field and where analytical expressions are also given for the non-resonant case ($\omega_L \neq \omega_0$). Subsequent papers, using a quantum description of the laser field, obtain the same results (see for example refs. [51,55], and also ref. [57] where the problem of the equivalence between classical and quantum descriptions of the laser field is discussed). Other calculations predict different values for the heights and widths of the sidebands of the spectrum represented in fig. 41. I think they are based upon too crude approximations, as the one which neglects the interference between different cascading amplitudes in the dressed atom approach described in § 2.2.3.

Concerning the experimental situation, the first experimental observation of the fluorescence spectrum of an atomic beam irradiated at right angle by a laser beam was published last year by Schuda, Stroud and Hercher [59]. The precision is perhaps not yet sufficient to allow a quantitative comparison between theory and experiment. Similar experiments are being done in other laboratories [35,60]. A three-peak structure has been observed at resonance.

Such an experiment is difficult to perform. A first difficulty is the spatial inhomogeneity of the laser intensity. As the interval travelled by the atom during its radiative lifetime is short compared to the diameter of the laser beam, each part of the illuminated portion of the atomic beam radiates a three-peak spectrum with a splitting ω_1 corresponding to the local amplitude of the laser field. A too large spreading of this amplitude would wash out the structure. We must also not forget the elastic component which is not completely negligible when ω_1 is not very large compared to Γ.

7.2. Broad line excitation with $T_p \gg 1/\Delta$

The spectral distribution of the fluorescence light reemitted by an atomic beam irradiated by an intense broad line spectrum does not seem to have been investigated.

If the pumping time T_p is longer than the correlation time $\tau'_C = 1/\Delta$ of the light wave, we can use the master equation (5.32) and extend the quantum regression theorem to the Langevin equation associated with (5.32). We find immediately

$$\frac{d}{dt}\langle \delta S_+(t)\delta S_-(t')\rangle$$

$$= \left[i\left(\omega_0 - \frac{2\Delta E'}{\hbar}\right) - \left(\tfrac{1}{2}\Gamma + \frac{1}{T_p}\right)\right] \langle \delta S_+(t)\delta S_-(t')\rangle \,. \tag{7.42}$$

At vanishing light intensities, we can neglect $\Delta E'/\hbar$ compared to ω_0 and $1/T_p$ compared to $\frac{1}{2}\Gamma$. We find the result obtained in § 2.1.2 from lowest order QED: a Lorentz curve centred on ω_0 with a half-width $\frac{1}{2}\Gamma$ (see fig. 4).

At higher light intensities, we find that this Lorentz curve is shifted by an amount $-2\Delta E'/\hbar$, and broadened by an amount $1/T_p$, these two quantities $\Delta E'/\hbar$ and $1/T_p$ being proportional to the light intensity.

7.3. What happens with a real non-ideal laser beam?

Let us consider a realistic laser light, having a non-zero spectral width $\Delta\nu$ and a very large intensity. More precisely, we suppose $\sqrt{\overline{\omega_1^2}} \gg \Gamma, \Delta\nu$ where $\sqrt{\overline{\omega_1^2}}$ is the mean Rabi nutation frequency associated with the probability distribution of the amplitude of the laser. As $\sqrt{\overline{\omega_1^2}}\,\tau'_C = \sqrt{\overline{\omega_1^2}}/\Delta\nu$ is not small, the motional narrowing condition is not satisfied and we cannot introduce rate equations like (5.32). When $\Delta\nu \gtrsim \Gamma$, the light wave does not appear monochromatic for the atom and we cannot introduce Bloch's equations like (5.5).

A first important remark is that the knowledge of $\Delta\nu$ is not sufficient for characterizing the light beam. One can imagine different light beams having all the same spectral width $\Delta\nu$, i.e. the same first order correlation function, but completely different microscopic behaviour, corresponding to different higher order correlation functions [14]. One can for example consider a light beam emitted by a laser well above threshold, which has a very well defined amplitude undergoing very small fluctuations, and a phase $\phi(t)$ which, in addition to short time fluctuations, slowly diffuses in the complex plane with a charac-

teristic time $1/\Delta\nu$. At the opposite, we can consider a quasi-monochromatic Gaussian field, or a laser just above threshold, for which both phase and amplitude fluctuate appreciably with the same characteristic time $1/\Delta\nu$.

We have done, in collaboration with Paul Avan, calculations of the fluorescence spectrum corresponding to different models of light beams [58]. The general idea of these calculations is the following. We consider a light wave which has two types of fluctuations: *short-time* fluctuations (for example, erratic motion of the phase) and *long-time* fluctuations (for example, slow phase diffusion or slow amplitude variations). We assume that the correlation time of the short-time fluctuations is sufficiently short to allow a perturbative treatment of these fluctuations. Their effect is therefore analogous to the one of a relaxation process. We treat to all orders the coupling with the slowly varying light wave assuming that the long-time fluctuations are sufficiently slow to be *adiabatically* followed by the atom. Finally, we make statistical averages over the long-time fluctuations. These calculations show that the shape of the spectrum is very sensitive to the microstructure of the light beam. The three-peak structure described above is only maintained when the fluctuations of the amplitude are sufficiently small. The three components are broadened differently in a way which depends not only on the phase diffusion, but also on the short-time fluctuations of this phase $\phi(t)$ (more precisely of $\mathrm{d}\phi/\mathrm{d}t$). When the fluctuations of the amplitudes are too large, only the central component survives, superposed on a broad background having a width of the order of $\sqrt{\overline{\omega_1^2}}$. This is easy to understand: there is a destructive interference of the various Rabi nutations around $\boldsymbol{B}_1$, as a consequence of the too large spreading of the possible values of B_1.

We are also investigating the sensitivity of level crossing signals to the fluctuations of the laser beam. The only calculations which have been performed up to now (see sect. 5) suppose either a pure coherent field or a very broad line excitation ($\Delta\nu \gg \Gamma, \sqrt{\overline{\omega_1^2}}$) so that, within the correlation time of the light wave, at most one interaction between the atom and the light can occur: in such a case, only the first order correlation function plays a role. It would be interesting to try to fill the gap between these two extreme situations.

7.4. Intensity and photon correlations

Instead of looking at the spectrum $\mathcal{I}(\omega)$ of the fluorescence light, one could try to measure the intensity correlations of this light, which are characterized by the correlation function

$$\langle I(t')I(t = t' + \tau)\rangle\,, \tag{7.43}$$

$I(t)$ being the current of the photomultiplier.

As the fluorescence light is in general very weak, it is better to use photon correlation techniques, and to measure the probability

$$P(t', t = t' + \tau) \tag{7.44}$$

for detecting one photon at time t' *and* another one at a later time $t = t' + \tau$. In this last paragraph, we try to calculate $P(t', t)$.

$P(t', t)$ is related to higher order correlation functions of the electric field. It is shown in ref. [14], p. 84, that

$$P(t', t) \sim \langle E^{(-)}(t')E^{(-)}(t)E^{(+)}(t)E^{(+)}(t')\rangle . \tag{7.45}$$

We will restrict ourselves to the case where there is at most one atom inside the laser beam at any time, so that the two detected photons are emitted by the same atom (very low densities for the atomic beam). In this case, the positive and negative frequency parts of the scattered electric field are proportional to $S_-(t - r/c)$ and $S_+(t - r/c)$, respectively, so that we have to calculate the correlation function

$$\langle S_+(t')S_+(t)S_-(t)S_-(t')\rangle \tag{7.46}$$

which can also be written as

$$\begin{aligned}&\langle S_+(t')[\tfrac{1}{2} + S_z(t)]S_-(t')\rangle \\ &\quad = \tfrac{1}{2}\langle S_+(t')S_-(t')\rangle + \langle S_+(t')S_z(t)S_-(t')\rangle .\end{aligned} \tag{7.47}$$

(For a spin-$\frac{1}{2}$, $S_+S_- = \frac{1}{2} + S_z$.)

As above, we consider only steady state conditions, so that $\langle S_+(t')S_-(t')\rangle$ does not depend on t' and $\langle S_+(t')S_z(t)S_-(t')\rangle$ only depends on $t - t'$. We will put

$$p = \langle S_+(t')S_-(t')\rangle , \tag{7.48}$$

where p is the steady state probability for finding the atom in its upper state ($S_+S_- = \frac{1}{2} + S_z$ is the projector into this upper state). Finally we have

$$P(t', t) \sim \tfrac{1}{2}p + \langle S_+(t')S_z(t)S_-(t')\rangle . \tag{7.49}$$

For calculating the correlation function appearing in (7.49), we will use a method very similar to the one of § 7.1.4. We start from the Heisenberg equa-

tions of motion (7.10), multiply them at right by $S_-(t')$, at left by $S_+(t')$, and take the average. As the motion of the dipole at time t' cannot be correlated with the Langevin force at a later time t, we get

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle S_+(t')S_i(t)S_-(t')\rangle$$

$$= \sum_j \mathcal{B}_{ij}\langle S_+(t')S_j(t)S_-(t')\rangle + C_i\langle S_+(t')S_-(t')\rangle\,, \tag{7.50}$$

with

$$t > t'\,, \qquad i = z, +, -\,.$$

Here $\mathcal{B}_{ij}$ and C_i are the homogeneous and inhomogeneous coefficients appearing in Bloch's equations (only C_z is different from zero and equal to $-\frac{1}{2}\Gamma$; see first eq. (7.10)).

Using (7.48), and introducing the reduced correlation functions $\Gamma_i(t, t')$ given by

$$\langle S_+(t')S_i(t)S_-(t')\rangle = p\,\Gamma_i(t, t')\,, \tag{7.51}$$

we easily transform (7.50) into

$$\frac{\mathrm{d}}{\mathrm{d}t}\Gamma_i(t, t') = \sum_j \mathcal{B}_{ij}\,\Gamma_j(t, t') + C_i\,. \tag{7.52}$$

We get a very simple result: the t dependence of the three correlation functions $\Gamma_i(t, t')$ is given by Bloch's equations. According to (7.49) and (7.51), the photon correlation signal $p(t, t')$ is given by

$$P(t', t) \sim p\,[\tfrac{1}{2} + \Gamma_z(t, t']\,. \tag{7.53}$$

We have already mentioned that $\frac{1}{2} + S_z$ is the projector into the upper state. As Γ_+, Γ_-, Γ_z satisfy Bloch's equations, $\frac{1}{2} + \Gamma_z(t, t')$ may be interpreted as the probability, computed from Bloch's equations, for finding the atom in its upper state at time t. It remains to find the initial conditions, i.e. the values of the Γ_i for $t = t'$.

For a spin-$\frac{1}{2}$, we have

$$(S_+)^2 = (S_-)^2 = 0\,, \qquad S_+S_zS_- = -\tfrac{1}{2}S_+S_-\,. \tag{7.54}$$

It follows that

$$\langle S_+(t')S_+(t')S_-(t')\rangle = \langle S_+(t')S_-(t')S_-(t')\rangle = 0\,,$$

$$\langle S_+(t')S_z(t')S_-(t')\rangle = -\tfrac{1}{2}\langle S_+(t')S_-(t')\rangle = -\tfrac{1}{2}p\,. \tag{7.55}$$

Consequently, we get from (7.51) and (7.55)

$$\Gamma_+(t=t') = \Gamma_-(t=t') = 0\,, \qquad \Gamma_z(t=t') = -\tfrac{1}{2}\,. \tag{7.56}$$

This result shows that the initial conditions for the Γ_i correspond to an atom in its lower state.

Finally, we have obtained in (7.53) a very simple result: the probability of detecting one photon at time t' and another one at time t is given by a product of two factors: p, which is the probability for detecting one photon, and $\frac{1}{2} + \Gamma_z(t, t')$ which is the probability, computed from Bloch's equation, that the atom, starting from its lower state at time t' is found in its upper state at the later time t. The physical interpretation of this result is clear: the probability of detecting the first photon is p. The detection of this first photon "reduces the wave packet". Immediately after this detection, the atom is certainly in its lower state. Then, it evolves and, in order to be able to emit a second photon, it must be raised in its upper state during the time interval $t - t'$.

Fig. 42 shows for example the variations of $P(t', t)$ with $t - t'$, at resonance ($\omega_L = \omega_0$), and for very high intensities of the laser beam ($\omega_1 \gg \Gamma$). One finds in this case from Bloch's equations that $p = \frac{1}{2}$ and that

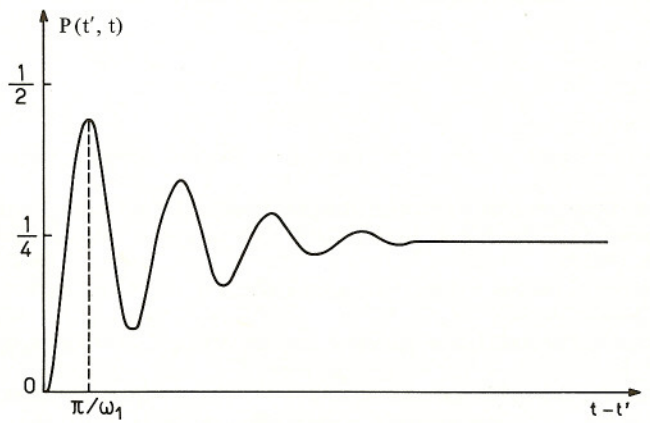

Fig. 42.

$$P(t', t) \sim \tfrac{1}{4}[1 - e^{-3\Gamma t/4} \cos \omega_1 (t - t')] . \tag{7.57}$$

When $t = t', P(t', t) = 0$: at time t', the atom is in its lower state and cannot emit a second photon. $P(t', t)$ is maximum when $t - t' = \pi/\omega_1$. This time interval corresponds to a "π pulse" which transfers the atom from g to e. When $t - t' \gg 1/\Gamma$, the two emission processes are independent and $P(t', t)$ reduces to $p^2 = \frac{1}{4}$.

The very simple interpretation given above raises the following questions: Is it possible to consider such an experiment as a possible test of the postulate of the reduction of the wave packet? What would be the predictions of other quantum theories of measurement (such as "hidden variables")? We just ask these questions here without entering further into these problems.

Let us finally give some orders of magnitude concerning the feasibility of such an experiment. We have mentioned above that each atom remains about 10^{-6} sec in the laser beam. If we want to have at most one atom in the laser beam at any time, one could not send more than 10^6 atoms per second. As each atom emits about 50 photons, this would correspond to a number of emitted photons less than 5×10^7 per second (in 4π solid angle). It does not seem hopeless to make photon correlation experiments with such intensities.

Note added after the course

The suggestion of photon correlation experiments for studying the fluorescence light emitted by atoms irradiated with strong resonant fields has been made independently by Carmichael and Walls (D.F. Walls, private communication; H.J. Carmichael and D.F. Walls, refs. [63,66]).

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