

CHAPTER IV

Radiation Considered as a Reservoir: Master Equation for the Particles

A—INTRODUCTION—OVERVIEW

In this chapter, we focus on the *evolution of the particles* and we derive equations describing such an evolution. A famous example of this approach is the one used by Einstein, who in 1917 introduced equations describing the effect of absorption, stimulated emission, and spontaneous emission processes between levels a and b of an atom immersed in the black-body radiation field (*)

$$\begin{cases} \frac{dN_b}{dt} = -A_{b \rightarrow a} N_b + u(\omega)(B_{a \rightarrow b} N_a - B_{b \rightarrow a} N_b) \\ \frac{dN_a}{dt} = A_{b \rightarrow a} N_b + u(\omega)(B_{b \rightarrow a} N_b - B_{a \rightarrow b} N_a). \end{cases} \quad (\text{A.1})$$

In (A.1) N_a and N_b are the numbers of atoms in states a and b ($E_b > E_a$), $A_{b \rightarrow a}$ is the spontaneous emission rate from b to a , $B_{a \rightarrow b}$ (and $B_{b \rightarrow a}$) are the absorption (and stimulated emission) rates from a to b (and from b to a), and $u(\omega)$ is the energy density of the radiation field at the frequency $\omega = (E_b - E_a)/\hbar$. The purpose of this chapter is to justify and to generalize equations of this type starting from the basic equations of quantum electrodynamics describing the coupled evolution of the particles and the field.

(*) A. Einstein, *Phys. Z.* **18**, 121 (1917).

First note that the particles, forming a subsystem of a larger system, may be described only by a *density operator*. Indeed, even if the global system is in a pure state described by a state vector, the state of the particles is, in general, a *statistical mixture of states*. The density operator σ describing such a mixture is obtained by making a *partial trace* over the variables of the radiation field of the density operator ρ of the global system:

$$\sigma = \text{Tr}_R \rho \quad (\text{A.2.a})$$

i.e., again, in terms of matrix elements

$$\langle a | \sigma | b \rangle = \sigma_{ab} = \sum_{\mu} \langle a, \mu | \rho | b, \mu \rangle = \sum_{\mu} \rho_{a\mu b\mu}. \quad (\text{A.2.b})$$

The Roman subscripts a and b describe the states of the particles, and the Greek subscripts μ describe the states of the radiation field (*). Thus, the state of the atom with two levels a and b introduced above is described by the *density matrix*:

$$\begin{pmatrix} \sigma_{bb} & \sigma_{ba} \\ \sigma_{ab} & \sigma_{aa} \end{pmatrix} \quad (\text{A.3})$$

In addition to the *populations* σ_{bb} and σ_{aa} of the two levels, proportional to the quantities N_b and N_a appearing in (A.1), there are the nondiagonal elements σ_{ab} and σ_{ba} , also called *coherences* between a and b , which are related to certain physical variables, evolving at the frequency $(E_b - E_a)/\hbar$, such as the electric dipole moment of the atom.

Before attempting to derive an evolution equation for σ , it might be useful to draw inspiration from other examples in classical physics where we are concerned with only one part of the global system.

Consider, for example, the *Brownian motion* of a heavy particle immersed in a gas or in a liquid of light particles, with which it undergoes constant collisions. As a result of the difference in mass, a very large number of collisions is required to make the velocity of the heavy particle vary appreciably. How can we describe the motion of the heavy particle? A first possibility is to introduce a *Langevin equation*, where the effect of the fluid on the particle is described by two types of force: a *friction force*, which describes the cumulative effect of the collisions and which damps

(*) It is clear that the information contained in σ is not as complete as the information contained in ρ . In particular, the reduced density operator σ describes neither the radiation field nor the correlations existing between the particles and the radiation field.

the velocity of the particle with a characteristic time T_R ; a *Langevin force*, which describes the fluctuations of the instantaneous force about its average value, and varies with a characteristic time on the order of the collision time τ_c , which is much shorter than T_R . Another possibility is to derive an evolution equation for the statistical distribution function $f(\mathbf{r}, \mathbf{p})$ describing the position and the momentum of the heavy particle. In general, one studies the variation Δf of f over an interval of time Δt that is very short compared with T_R (so that the average velocity of the particle varies slightly during Δt), but very long compared with τ_c (so that many elementary collisions occur during this time interval). The equation giving $\Delta f/\Delta t$ is then simple. It is a *Fokker–Planck* equation, describing how the distribution function shifts and broadens under the influence of the collisions.

We retain from the foregoing example the following general ideas. First, the relevant particle \mathcal{A} interacts with a system \mathcal{R} having a very large number of degrees of freedom (the ensemble of the other particles of the gas or of the liquid). The “heat capacity” of \mathcal{R} is therefore very large, and there is no macroscopic modification of the state of \mathcal{R} under the influence of the coupling with \mathcal{A} . \mathcal{R} can be considered to be a *reservoir*. Then, the evolution equation for \mathcal{A} is simple, if there are *two distinct time scales* in the problem: a very short time τ_c characterizing the fluctuations of the perturbation exerted by \mathcal{R} on \mathcal{A} , and a much longer time T_R characterizing the rate of variation of \mathcal{A} . If we consider only a *coarse-grained rate of variation*, averaged over a time Δt such that $\tau_c \ll \Delta t \ll T_R$, then simple *kinetic equations* can be obtained for the distribution functions of \mathcal{A} .

Is it possible to apply the foregoing ideas to the case where \mathcal{A} is an ensemble of particles (that we assume here to form an atom or a molecule) and \mathcal{R} is the radiation field? First, \mathcal{R} actually has an infinite number of degrees of freedom, corresponding to the infinite number of modes of the electromagnetic field. If \mathcal{A} is an atom (or a small number of atoms), it is legitimate to consider that the state of \mathcal{R} changes only slightly as a result of its coupling with \mathcal{A} . What, then, are the conditions for the appearance of two distinct time scales? The dynamics of the field fluctuations (electric or magnetic) acting on the charged particles are described by the *correlation functions* of these fields. It can be shown (*) that, if the state of the field is the vacuum (which corresponds to the problem of spontaneous emission of photons by \mathcal{A}), these correlation functions $\langle E(t)E(t - \tau) + E(t - \tau)E(t) \rangle$ decrease very rapidly with τ . The correlation time τ_c of

(*) See, for example, *Photons and Atoms—Introduction to Quantum Electrodynamics*, III-C-3 and Complement C_{III}.

these vacuum fluctuations is very short, shorter than the period $2\pi/\omega_0$ of the relevant transition $b \rightarrow a$, which itself is much shorter than the lifetime $1/\Gamma$ of the level b , which characterizes the evolution of the atom. A similar result holds for an atom interacting with an incident wave whose spectral width $\Delta\omega$ is sufficiently large (*) and whose intensity is sufficiently low. Indeed, the correlation time of the incident field is on the order of $\tau_c = \Delta\omega^{-1}$, and the average time T_R after which an absorption or emission process occurs (evolution time for the atom) is inversely proportional to the light intensity I , so that, for appropriate values of $\Delta\omega$ and I , the condition $\tau_c \ll T_R$ is satisfied. This is the case in particular for black-body radiation, or for radiation emitted by ordinary sources (such as discharge lamps), which are neither completely monochromatic nor very intense.

Thus a large number of situations exist in which the radiation field can be considered as a reservoir exerting on the atom a perturbation that varies extremely rapidly on the atomic evolution time scale. In this Chapter, we show how the *master equation* giving the coarse-grained rate of variation of the density operator of \mathcal{A} can be derived simply and in a *perturbative manner* when the coupling V between \mathcal{A} and \mathcal{R} has a weak effect during the correlation time τ_c of the fluctuations of \mathcal{R} . This situation is reminiscent of the weak-collision regime in Brownian motion. The condition expressing that the coupling has a weak effect during τ_c is known as the *motional narrowing* condition for reasons that will become clear later on. We begin (Section B) by deriving the master equation. We then provide a physical interpretation for the coefficients appearing in this equation (Section C), and we discuss the conditions of validity for the approximations used to derive the master equation (Section D). The results derived in these three parts are valid in general for any small system \mathcal{A} coupled to a reservoir \mathcal{R} , provided the condition of motional narrowing is satisfied.

We return in Section E to the problem of a two-level atom coupled to the radiation field and we use the foregoing results to derive the evolution equations for the atomic density matrix under the influence of spontaneous emission, absorption, and stimulated emission processes. We are interested not only in internal degrees of freedom (populations of the two levels a and b and coherence between a and b), but also in the evolution of the external degrees of freedom (velocity of the center of mass) due to momentum exchanges between the atom and the photons.

Three complements continue the discussion of this chapter. Complement A_{IV} shows that the two-time averages appearing in the master

(*) We exclude here the case where the atom interacts with resonant monochromatic radiation (see Chapters V and VI).

equation can be related to two categories of statistical functions, the symmetric correlation functions describing the dynamics of the fluctuations of the observables of \mathcal{A} and \mathcal{R} , and the linear susceptibilities describing the linear response of each system to an external perturbation. These functions can be used to show how the different physical effects described by the master equation can be simply interpreted by considering that the two interacting systems, \mathcal{A} and \mathcal{R} , fluctuate and polarize each other. Complements B_{IV} and C_{IV} illustrate the different ideas introduced in this chapter by using the simple example of a harmonic oscillator coupled to a reservoir of harmonic oscillators. The evolution of the oscillator is studied in the Schrödinger representation (Complement B_{IV}), as well as in the Heisenberg representation (Complement C_{IV}). In particular, we show how the Heisenberg equations for the oscillator can be transformed and put in a form similar to that of the Langevin equation for Brownian motion. Such a calculation demonstrates the close connection that exists between fluctuations and dissipation.

**B—DERIVATION OF THE MASTER EQUATION FOR A
SMALL SYSTEM \mathcal{A} INTERACTING WITH A RESERVOIR \mathcal{R}**

**1. Equation Describing the Evolution of the Small System in the
Interaction Representation**

Let

$$H = H_A + H_R + V \quad (\text{B.1})$$

be the Hamiltonian of the global system $\mathcal{A} + \mathcal{R}$: H_A is the Hamiltonian of \mathcal{A} , H_R is the Hamiltonian of \mathcal{R} , and V is the interaction between \mathcal{A} and \mathcal{R} . The density operator ρ of the global system $\mathcal{A} + \mathcal{R}$ obeys the evolution equation

$$\frac{d}{dt}\rho(t) = \frac{1}{i\hbar}[H, \rho(t)] \quad (\text{B.2})$$

which becomes, in the interaction representation with respect to $H_A + H_R$:

$$\frac{d}{dt}\tilde{\rho}(t) = \frac{1}{i\hbar}[\tilde{V}(t), \tilde{\rho}(t)] \quad (\text{B.3})$$

with

$$\tilde{\rho}(t) = e^{i(H_A+H_R)t/\hbar} \rho(t) e^{-i(H_A+H_R)t/\hbar} \quad (\text{B.4.a})$$

$$\tilde{V}(t) = e^{i(H_A+H_R)t/\hbar} V e^{-i(H_A+H_R)t/\hbar}. \quad (\text{B.4.b})$$

The advantage of the interaction representation is that, if V is sufficiently small, $\tilde{\rho}(t)$ evolves slowly and in particular no longer contains the unperturbed free evolution exponentials.

Integrating Equation (B.3) between t and $t + \Delta t$ yields

$$\tilde{\rho}(t + \Delta t) = \tilde{\rho}(t) + \frac{1}{i\hbar} \int_t^{t+\Delta t} dt' [\tilde{V}(t'), \tilde{\rho}(t')] \quad (\text{B.5})$$

an equation that can be iterated to give

$$\begin{aligned} \Delta\tilde{\rho}(t) &= \frac{1}{i\hbar} \int_t^{t+\Delta t} dt' [\tilde{V}(t'), \tilde{\rho}(t)] + \\ &+ \left(\frac{1}{i\hbar} \right)^2 \int_t^{t+\Delta t} dt' \int_t^{t'} dt'' [\tilde{V}(t'), [\tilde{V}(t''), \tilde{\rho}(t'')]] \end{aligned} \quad (\text{B.6})$$

where we have set

$$\Delta\tilde{\rho}(t) = \tilde{\rho}(t + \Delta t) - \tilde{\rho}(t). \quad (\text{B.7})$$

Here we are interested in the evolution of the small system \mathcal{A} . Equation (A.2.a), which defines the reduced density operator σ of \mathcal{A} from the density operator ρ of $\mathcal{A} + \mathcal{R}$ becomes, in the interaction representation

$$\tilde{\sigma}(t) = \text{Tr}_R \tilde{\rho}(t). \quad (\text{B.8})$$

By taking the trace with respect to \mathcal{R} of Equation (B.6), we obtain

$$\begin{aligned} \Delta\tilde{\sigma}(t) = & \frac{1}{i\hbar} \int_t^{t+\Delta t} dt' \text{Tr}_R [\tilde{V}(t'), \tilde{\rho}(t)] + \\ & + \left(\frac{1}{i\hbar} \right)^2 \int_t^{t+\Delta t} dt' \int_t^{t'} dt'' \text{Tr}_R [\tilde{V}(t'), [\tilde{V}(t''), \tilde{\rho}(t'')]]. \end{aligned} \quad (\text{B.9})$$

Up to this point, no approximation has been introduced and Equation (B.9) is exact. Before going further and introducing some approximations, we must now describe the assumptions concerning the reservoir.

2. Assumptions Concerning the Reservoir

a) STATE OF THE RESERVOIR

Let

$$\tilde{\sigma}_R(t) = \text{Tr}_{\mathcal{A}} \tilde{\rho}(t) \quad (\text{B.10})$$

be the density operator of \mathcal{R} obtained by taking a partial trace over \mathcal{A} of $\tilde{\rho}(t)$. Because \mathcal{R} is a reservoir, the variation of $\tilde{\sigma}_R(t)$ due to the coupling with \mathcal{A} is weak. To a first approximation, $\tilde{\sigma}_R(t)$ may be considered to be constant in the interaction representation (*):

$$\tilde{\sigma}_R(t) \approx \tilde{\sigma}_R(0) = \sigma_R. \quad (\text{B.11})$$

Moreover, we assume that the reservoir is in a stationary state, that is, that σ_R commutes with H_R :

$$[\sigma_R, H_R] = 0. \quad (\text{B.12})$$

In other words, σ_R has no nondiagonal elements between eigenstates of H_R with different eigenvalues and can therefore be considered as a

(*) The coupling V , of course, causes weak correlations to appear between \mathcal{A} and \mathcal{R} that are essential for the evolution of \mathcal{A} (see §D-4).

statistical mixture of eigenstates $|\mu\rangle$ of H_R

$$H_R|\mu\rangle = E_\mu|\mu\rangle \quad (\text{B.13})$$

with weight p_μ

$$\sigma_R = \sum_\mu p_\mu |\mu\rangle\langle\mu|. \quad (\text{B.14})$$

This is the case in particular when \mathcal{R} is in thermodynamic equilibrium at temperature T , the p_μ being then equal to

$$p_\mu = Z^{-1} e^{-E_\mu/k_B T} \quad (\text{B.15.a})$$

$$Z = \sum_\mu e^{-E_\mu/k_B T}. \quad (\text{B.15.b})$$

b) ONE-TIME AND TWO-TIME AVERAGES FOR THE RESERVOIR OBSERVABLES

The interaction V between \mathcal{A} and \mathcal{R} will be taken as a product of an observable A of \mathcal{A} and an observable R of \mathcal{R} .

$$V = -AR \quad (\text{B.16})$$

which gives, in the interaction representation

$$\tilde{V}(t) = -\tilde{A}(t)\tilde{R}(t) \quad (\text{B.17})$$

with

$$\tilde{A}(t) = e^{iH_A t/\hbar} A e^{-iH_A t/\hbar} \quad (\text{B.18.a})$$

$$\tilde{R}(t) = e^{iH_R t/\hbar} R e^{-iH_R t/\hbar} \quad (\text{B.18.b})$$

because the observables of \mathcal{A} commute with those of \mathcal{R} .

Remark

The following calculations may be adapted easily to the more general case where V is a sum of products of operators A_p of \mathcal{A} and R_p of \mathcal{R} , having the form $-\sum_p A_p R_p$.

We assume that the average value of R in the state σ_R of R is zero

$$\text{Tr}[\sigma_R R] = \text{Tr}[\sigma_R \tilde{R}(t)] = 0 \quad (\text{B.19})$$

the first equation following from (B.18.b), (B.12), and the invariance of the

trace of a product in a circular permutation. It follows that, for all t

$$\text{Tr}_R[\sigma_R \tilde{V}(t)] = \tilde{A}(t) \text{Tr}[\sigma_R \tilde{R}(t)] = 0. \quad (\text{B.20})$$

The average value in σ_R of the coupling $\tilde{V}(t)$ is therefore zero. If this were not the case, it would suffice to reinsert $\text{Tr}_R[\sigma_R V]$ into H_A and to take $V - (\text{Tr}_R[\sigma_R V]) \otimes \mathbb{I}_R$ as the new interaction Hamiltonian, \mathbb{I}_R being the unit operator in the state space of \mathcal{R} .

The average value of $\tilde{R}(t)$ in σ_R is a one-time average. We now consider the *two-time average*

$$g(t', t'') = \text{Tr}[\sigma_R \tilde{R}(t') \tilde{R}(t'')] \quad (\text{B.21})$$

equal to the average value in the state σ_R of a product of two observables $\tilde{R}(t')$ and $\tilde{R}(t'')$ taken at two different times t' and t'' . In Complement A_{IV}, we analyze the physical meaning of the function $g(t', t'')$. In particular, we show that the real part of $g(t', t'')$ is a symmetric correlation function describing the *dynamics of the fluctuations of R* in the state σ_R , whereas the imaginary part of $g(t', t'')$ is related to a *linear susceptibility*. By using (B.12), (B.18), and the invariance of the trace of a product in a circular permutation, it is easy to show that $g(t', t'')$ depends only on $\tau = t' - t''$:

$$\begin{aligned} \text{Tr}_R[\sigma_R \tilde{R}(t') \tilde{R}(t'')] &= \text{Tr}_R[\sigma_R e^{iH_R t'/\hbar} R e^{-iH_R(t'-t'')/\hbar} R e^{-iH_R t''/\hbar}] \\ &= \text{Tr}_R[\sigma_R \tilde{R}(\tau) \tilde{R}(0)] = g(\tau). \end{aligned} \quad (\text{B.22})$$

To evaluate $g(\tau)$ more precisely, we substitute expression (B.14) for σ_R into (B.22). This gives

$$\begin{aligned} g(\tau) &= \text{Tr} \sum_{\mu} \left\{ p_{\mu} |\mu\rangle \langle \mu| \tilde{R}(\tau) \tilde{R}(0) \right\} \\ &= \sum_{\mu} p_{\mu} \langle \mu | \tilde{R}(\tau) \tilde{R}(0) | \mu \rangle \\ &= \sum_{\mu} \sum_{\nu} p_{\mu} |R_{\mu\nu}|^2 e^{i\omega_{\mu\nu}\tau} \end{aligned} \quad (\text{B.23})$$

where we have set

$$R_{\mu\nu} = \langle \mu | R | \nu \rangle \quad (\text{B.24})$$

$$\omega_{\mu\nu} = \omega_{\mu} - \omega_{\nu} \quad (\text{B.25.a})$$

$$\omega_{\mu} = E_{\mu}/\hbar. \quad (\text{B.25.b})$$

Because p_μ and $|R_{\mu\nu}|^2$ are real, it is clear from (B.23) that

$$g(-\tau) = g(\tau)^*. \quad (\text{B.26})$$

Expression (B.23) shows that $g(\tau)$ is a superposition of exponentials oscillating at the different Bohr frequencies $\omega_{\mu\nu}$ of \mathcal{R} . Because \mathcal{R} is a reservoir, it has a very dense ensemble of energy levels and, consequently, a quasi-continuous spectrum of Bohr frequencies, so that the exponentials of (B.23) interfere destructively once τ becomes large enough. More precisely, we assume here that the function $g(\tau)$ tends rapidly to zero when τ increases, and we call τ_c the order of magnitude of the width in τ of $g(\tau)$.

Finally, the assumptions made about \mathcal{R} are equivalent to assuming that \mathcal{R} is in a stationary state and exerts on \mathcal{A} a “force” fluctuating about a zero average value with a short correlation time τ_c .

3. Perturbative Calculation of the Coarse-Grained Rate of Variation of the Small System

We now return to the exact equation (B.9), and we derive from it a master equation for $\tilde{\sigma}$ by introducing several approximations which will be discussed later on (Section D).

If V is sufficiently small, and if Δt is sufficiently short compared with the evolution time T_R of $\tilde{\sigma}$, it seems legitimate to neglect the evolution of $\tilde{\rho}$ between t and t'' in the last term of (B.9), which is already second-order in V and to replace $\tilde{\rho}(t'')$ by $\tilde{\rho}(t)$. Such an approximation is equivalent to an iteration of (B.5) in which only terms up to second order in V are retained.

After such an approximation, the right-hand side of (B.9) contains only $\tilde{\rho}(t)$, which can still be written in the form

$$\tilde{\rho}(t) = \text{Tr}_R \tilde{\rho}(t) \otimes \text{Tr}_{\mathcal{A}} \tilde{\rho}(t) + \tilde{\rho}_{\text{correl}}(t) \quad (\text{B.27})$$

where $\tilde{\rho}_{\text{correl}}(t)$, which is equal to the difference between $\tilde{\rho}(t)$ and the product of the reduced density operators of \mathcal{A} and \mathcal{R} , describes the correlations that exist between \mathcal{A} and \mathcal{R} at time t . In what follows, we will neglect the contribution of $\tilde{\rho}_{\text{correl}}$ to $\Delta\tilde{\sigma}(t)$. Later on, in Section D, we will return to the conditions of validity for such an approximation, which assumes in particular that $\tau_c \ll \Delta t$. The general idea is that the initial correlations between \mathcal{A} and \mathcal{R} at time t disappear after a time τ_c and contribute little to the evolution of $\tilde{\sigma}$ over the interval $[t, t + \Delta t]$, which is

much longer than τ_c (*). Such an approximation is thus equivalent to writing, using (B.8), (B.10), and (B.11)

$$\tilde{\rho}(t) \approx \tilde{\sigma}(t) \otimes \sigma_R. \quad (\text{B.28})$$

We have thus introduced two approximations, one based on the condition $\Delta t \ll T_R$, and the other based on the condition $\Delta t \gg \tau_c$, which implies the existence of two very different time scales $T_R \gg \tau_c$:

$$\tau_c \ll \Delta t \ll T_R. \quad (\text{B.29})$$

These two approximations allow Equation (B.9) to be written in a form relating the increase $\Delta\tilde{\sigma}$ of $\tilde{\sigma}$ between t and $t + \Delta t$ to $\tilde{\sigma}(t)$. Indeed, if in (B.9) we replace $\tilde{\rho}(t'')$ and $\tilde{\rho}(t)$ by (B.28) and divide both sides of the equation by Δt , we obtain [the first term of (B.9) is zero, according to (B.20)]

$$\frac{\Delta\tilde{\sigma}}{\Delta t} = -\frac{1}{\hbar^2} \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \int_t^{t'} dt'' \text{Tr}_R [\tilde{V}(t'), [\tilde{V}(t''), \tilde{\sigma}(t) \otimes \sigma_R]]. \quad (\text{B.30})$$

The rate of variation $\Delta\tilde{\sigma}/\Delta t$ is called the “coarse-grained” rate of variation because it can be considered to be the time average of the instantaneous rate $d\tilde{\sigma}/dt$ over an interval Δt . Indeed, $\Delta\tilde{\sigma}/\Delta t$ can be written

$$\frac{\Delta\tilde{\sigma}}{\Delta t} = \frac{\tilde{\sigma}(t + \Delta t) - \tilde{\sigma}(t)}{\Delta t} = \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \frac{d\tilde{\sigma}}{dt'}. \quad (\text{B.31})$$

All the rapid variations of the instantaneous rate occurring on a time scale smaller than Δt are smoothed out in such an average. The fact that $\Delta\tilde{\sigma}/\Delta t$ depends only on the state $\tilde{\sigma}(t)$ of the system \mathcal{A} at time t means that, examined with a time resolution that is not too high, the evolution of \mathcal{A} depends only on the present and not on the past (Markov process).

Because, according to (B.17) and (B.18), $\tilde{V}(t')$ and $\tilde{V}(t'')$ are, like $\tilde{\sigma}(t) \otimes \sigma_R$, products of observables of \mathcal{A} and of \mathcal{R} commuting with each other, the trace over \mathcal{R} of (B.30) concerns only products of the form $\sigma_R \tilde{R}(t') \tilde{R}(t'')$ or $\sigma_R \tilde{R}(t'') \tilde{R}(t')$. Thus it is clear that the integral of (B.30)

(*) New correlations between \mathcal{A} and \mathcal{R} appear between t and $t + \Delta t$, and these are the ones that cause $\tilde{\sigma}$ to evolve.

depends on the reservoir only through the two-time averages $g(\tau)$ or $g(-\tau)$ introduced above, with $\tau = t' - t''$. To take advantage of the fact that $g(\tau)$ decreases very rapidly with τ , it is convenient to change the variables of integration in (B.30), switching from the variables t' and t'' to the variables τ and t' . Figure 1 shows the domain of integration in t' and t'' of (B.30), which is the triangle $0AB$. The lines corresponding to equal values of τ are parallel to the first bisector $0B$, which corresponds to $\tau = 0$. For fixed τ , we can integrate over t' from $t + \tau$ to $t + \Delta t$, then integrate over τ from 0 to Δt , which gives

$$\int_t^{t+\Delta t} dt' \int_t^{t'} dt'' = \int_0^{\Delta t} d\tau \int_{t+\tau}^{t+\Delta t} dt'. \quad (\text{B.32})$$

Because the two-time averages of the reservoir $g(\tau)$ and $g(-\tau)$ are negligible for $\tau \gg \tau_c$, the only region of the integration domain where the integrand is nonzero is a narrow band of width on the order of τ_c , near $0B$ (hatched region of Figure 1). As $\Delta t \gg \tau_c$, a negligible error is made if the upper bound of the integral in τ of (B.32) is extended to $+\infty$ and if the lower bound of the integral over t' is extended to t . Finally, after expanding the double commutator of (B.30), and using (B.17) and (B.22),

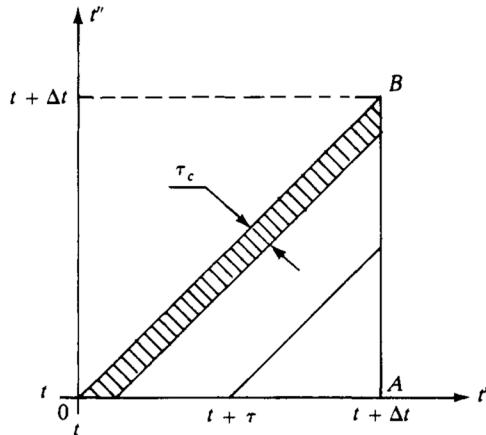


Figure 1. Domain of integration over t' and t'' . As a result of the presence of the two-time averages $g(\tau)$ and $g(-\tau)$ of the reservoir, only a narrow strip of width τ_c near $0B$ contributes (hatched area).

we get

$$\begin{aligned} \frac{\Delta\tilde{\sigma}}{\Delta t} = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \times \\ & \times \left\{ g(\tau) [\tilde{A}(t') \tilde{A}(t' - \tau) \tilde{\sigma}(t) - \tilde{A}(t' - \tau) \tilde{\sigma}(t) \tilde{A}(t')] + \right. \\ & \left. + g(-\tau) [\tilde{\sigma}(t) \tilde{A}(t' - \tau) \tilde{A}(t') - \tilde{A}(t') \tilde{\sigma}(t) \tilde{A}(t' - \tau)] \right\}. \quad (\text{B.33}) \end{aligned}$$

To go further and carry out the integration over t' , we now project the operator Equation (B.33) over a basis of states.

4. Master Equation in the Energy-State Basis

Let $|a\rangle$ be the eigenstates of H_A , having eigenvalues E_a :

$$H_A |a\rangle = E_a |a\rangle. \quad (\text{B.34})$$

Equation (B.33) becomes, in the orthonormal basis $\{|a\rangle\}$

$$\frac{\Delta\tilde{\sigma}_{ab}}{\Delta t} = \sum_{cd} \gamma_{abcd}(t) \tilde{\sigma}_{cd}(t) \quad (\text{B.35})$$

with

$$\begin{aligned} \gamma_{abcd}(t) = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \frac{1}{\Delta t} \int_t^{t+\Delta t} dt' \times \\ & \times \left\{ g(\tau) \left[\delta_{bd} \sum_n \tilde{A}_{an}(t') \tilde{A}_{nc}(t' - \tau) - \tilde{A}_{ac}(t' - \tau) \tilde{A}_{db}(t') \right] + \right. \\ & \left. + g(-\tau) \left[\delta_{ac} \sum_n \tilde{A}_{dn}(t' - \tau) \tilde{A}_{nb}(t') - \tilde{A}_{ac}(t') \tilde{A}_{db}(t' - \tau) \right] \right\}. \quad (\text{B.36}) \end{aligned}$$

The dependence on t' of the integrand of (B.36) can come only from the matrix elements $\tilde{A}_{an}(t')$, $A_{nc}(t' - \tau)$... which vary as $\exp i\omega_{an}t'$, $\exp i\omega_{nc}(t' - \tau)$..., where the ω_{an}, ω_{nc} ... are the Bohr frequencies of \mathcal{A} :

$$\omega_{an} = \omega_a - \omega_n \quad (\text{B.37.a})$$

$$\omega_a = E_a/\hbar \quad \omega_n = E_n/\hbar. \quad (\text{B.37.b})$$

It is then simple to verify that all the terms of (B.36) inside brackets vary as $\exp i(\omega_{ab} - \omega_{cd})t'$. For example, the dependence on t' of the first term

is (taking into account δ_{bd} , it follows that $\omega_b = \omega_d$)

$$\begin{aligned} \exp i(\omega_a - \omega_n + \omega_n - \omega_c)t' &= \exp i(\omega_a - \omega_c)t' = \\ &= \exp i(\omega_a - \omega_b + \omega_d - \omega_c)t' = \exp i(\omega_{ab} - \omega_{cd})t'. \end{aligned} \quad (\text{B.38})$$

The dependence of the second term is

$$\exp i(\omega_a - \omega_c + \omega_d - \omega_b)t' = \exp i(\omega_{ab} - \omega_{cd})t' \quad (\text{B.39})$$

and analogous proofs can be made for the third and fourth terms. It follows that the integral over t' of (B.36) can be calculated easily and gives

$$\frac{1}{\Delta t} \int_t^{t+\Delta t} dt' e^{i(\omega_{ab} - \omega_{cd})t'} = e^{i(\omega_{ab} - \omega_{cd})\Delta t} f[(\omega_{ab} - \omega_{cd})\Delta t] \quad (\text{B.40})$$

where

$$f(x) = e^{ix/2} \frac{\sin(x/2)}{(x/2)}. \quad (\text{B.41})$$

If $|\omega_{ab} - \omega_{cd}| \ll 1/\Delta t$, the value of f in (B.40) is close to 1. By contrast, if $|\omega_{ab} - \omega_{cd}| \gg 1/\Delta t$, it is close to zero. It is thus legitimate to ignore the couplings between $\Delta\tilde{\sigma}_{ab}/\Delta t$ and $\tilde{\sigma}_{cd}$ if $|\omega_{ab} - \omega_{cd}| \gg 1/\Delta t$. Finally, if $|\omega_{ab} - \omega_{cd}| \sim 1/\Delta t$, we will see later on that the condition $T_R \gg \Delta t$ implies that the coupling between $\Delta\tilde{\sigma}_{ab}/\Delta t$ and $\tilde{\sigma}_{cd}$ has a weak effect. We will neglect this effect and retain only the terms coupling $\Delta\tilde{\sigma}_{ab}/\Delta t$ to $\tilde{\sigma}_{cd}$ with $|\omega_{ab} - \omega_{cd}| \ll 1/\Delta t$, terms called *secular* and for which $f = 1$. Finally, with this “secular approximation”, the master equation (B.35) becomes

$$\frac{\Delta\tilde{\sigma}_{ab}}{\Delta t} = \sum_{c,d}^{\text{(sec)}} e^{i(\omega_{ab} - \omega_{cd})t} \mathcal{R}_{abcd} \tilde{\sigma}_{cd}(t) \quad (\text{B.42})$$

where $\sum_{c,d}^{\text{(sec)}}$ indicates that the sum is restricted to states c, d such that $|\omega_{ab} - \omega_{cd}| \ll 1/\Delta t$, and where the \mathcal{R}_{abcd} are coefficients independent of t and Δt and are given by the integral over τ of (B.36).

$$\begin{aligned} \mathcal{R}_{abcd} = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \times \\ & \times \left\{ g(\tau) \left[\delta_{bd} \sum_n A_{an} A_{nc} e^{i\omega_{cn}\tau} - A_{ac} A_{db} e^{i\omega_{ca}\tau} \right] + \right. \\ & \left. + g(-\tau) \left[\delta_{ac} \sum_n A_{dn} A_{nb} e^{i\omega_{nd}\tau} - A_{ac} A_{db} e^{i\omega_{bd}\tau} \right] \right\}. \end{aligned} \quad (\text{B.43})$$

Before calculating the coefficients \mathcal{R}_{abcd} of the master equation and giving them a physical interpretation, we have to switch from the interaction representation to the Schrödinger representation, where the density operator of \mathcal{A} is $\sigma(t)$. From the relation

$$\sigma_{ab}(t) = e^{-i\omega_{ab}t} \tilde{\sigma}_{ab}(t) \quad (\text{B.44})$$

between the matrix elements $\sigma(t)$ and $\tilde{\sigma}(t)$ follows the relation

$$\frac{d\sigma_{ab}(t)}{dt} = -i\omega_{ab}\sigma_{ab}(t) + e^{-i\omega_{ab}t} \frac{d\tilde{\sigma}_{ab}(t)}{dt} \quad (\text{B.45})$$

between the instantaneous rate of variation of σ_{ab} and $\tilde{\sigma}_{ab}$. We approximate the instantaneous rate $d\tilde{\sigma}_{ab}/dt$ appearing in (B.45) by using the coarse-grained rate $\Delta\tilde{\sigma}_{ab}/\Delta t$ calculated in (B.42). We then obtain, by using (B.44)

$$\frac{d}{dt}\sigma_{ab}(t) \approx -i\omega_{ab}\sigma_{ab}(t) + \sum_{c,d}^{(\text{sec})} \mathcal{R}_{abcd}\sigma_{cd}(t). \quad (\text{B.46})$$

The exponential appearing in (B.42) has disappeared. In the Schrödinger representation, the master equation, expanded over the basis of eigenstates of H_A , has the structure of a *linear differential system with time-independent coefficients*.

The first term of the right-hand side of (B.46) describes the free evolution of σ_{ab} , while the second term describes the effect of the interaction with \mathcal{A} . The coefficients \mathcal{R}_{abcd} are thus on the order of $1/T_R$, where T_R is the evolution time of \mathcal{A} . If the matrix elements σ_{ab} and σ_{cd} have sufficiently different eigenfrequencies ω_{ab} and ω_{cd} , that is, if $|\omega_{ab} - \omega_{cd}| \gg 1/T_R$, the coupling \mathcal{R}_{abcd} between them will have very weak effects (in the same way as in quantum mechanics where a coupling V_{ab} between two energy levels E_a and E_b has very weak effects if $|E_a - E_b| \gg V_{ab}$). Because $T_R \gg \Delta t$ [see (B.29)], the condition $|\omega_{ab} - \omega_{cd}| \sim 1/\Delta t$ indeed corresponds to $|\omega_{ab} - \omega_{cd}| \gg 1/T_R$. It is thus legitimate to neglect in (B.42) the coupling between σ_{ab} and σ_{cd} when $|\omega_{ab} - \omega_{cd}|$ is not very small compared with $1/\Delta t$.

C—PHYSICAL CONTENT OF THE MASTER EQUATION

1. Evolution of Populations

The populations σ_{aa} of the energy levels $|a\rangle$ of \mathcal{A} all have the same free evolution frequency ($\omega_{aa} = 0$). The coupling terms that exist among them are thus all secular terms. Moreover, we assume that there is no coherence σ_{cd} with a very low free evolution frequency ($|\omega_{cd}| \ll 1/\Delta t$). Thus the populations are coupled only to populations and Equation (B.46) can be written

$$\frac{d\sigma_{aa}}{dt} = \sum_c \mathcal{R}_{aacc} \sigma_{cc}. \quad (\text{C.1})$$

To calculate \mathcal{R}_{aacc} , we set $b = a$ and $d = c$ in (B.43). First assume that $c \neq a$. The two Kronecker symbols δ_{bd} and δ_{ac} are then zero. The two terms remaining inside the brackets in (B.43) are complex conjugates of each other [see (B.26)] and are regrouped to give

$$\mathcal{R}_{aacc} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau g(\tau) |A_{ac}|^2 e^{i\omega_{ca}\tau}. \quad (\text{C.2})$$

Replacing $g(\tau)$ by its expression (B.23) then gives

$$\mathcal{R}_{aacc} = \frac{1}{\hbar^2} \sum_{a \neq c} p_\mu \sum_\nu \int_{-\infty}^{+\infty} d\tau e^{i(\omega_{\mu\nu} + \omega_{ca})\tau} |A_{ac}|^2 |R_{\nu\mu}|^2. \quad (\text{C.3})$$

The integral over τ is equal to $2\pi\delta(\omega_{\mu\nu} + \omega_{ca})$ and can be rewritten, using (B.25) and (B.37), as $2\pi\hbar\delta(E_\mu + E_c - E_\nu - E_a)$. Also, $|A_{ac}|^2 |R_{\nu\mu}|^2$ is equal, according to (B.16), to $|\langle \nu, a | V | \mu, c \rangle|^2$. Finally, by setting

$$\mathcal{R}_{aacc} = \Gamma_{c \rightarrow a} \quad (\text{C.4})$$

we obtain for $\Gamma_{c \rightarrow a}$

$$\Gamma_{c \rightarrow a} = \frac{2\pi}{\hbar} \sum_\mu p_\mu \sum_\nu |\langle \nu, a | V | \mu, c \rangle|^2 \delta(E_\mu + E_c - E_\nu - E_a). \quad (\text{C.5})$$

The physical interpretation of $\Gamma_{c \rightarrow a}$ is very clear. $\Gamma_{c \rightarrow a}$ is the probability per unit time for the system \mathcal{A} to make a transition from level c to

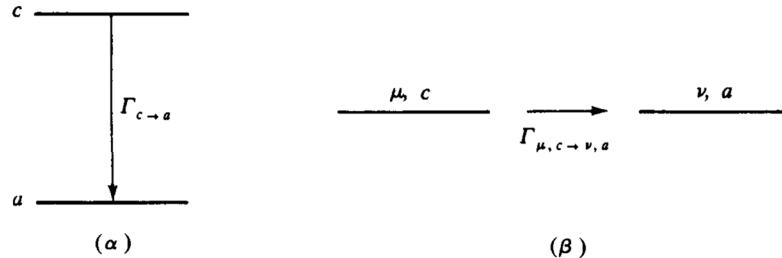


Figure 2. Transition rate between states c and a of \mathcal{A} (α) and states μ, c and ν, a of $\mathcal{A} + \mathcal{R}$ (β). $\Gamma_{c \rightarrow a}$ is obtained from $\Gamma_{\mu, c \rightarrow \nu, a}$ by an average over μ and a sum over ν .

level a as a result of its coupling with \mathcal{R} . Indeed, such a transition corresponds, for the global system $\mathcal{A} + \mathcal{R}$, to a transition $|\mu, c\rangle \rightarrow |\nu, a\rangle$ (Figure 2). Equation (C.5) gives the rate for this transition (in agreement with the Fermi golden rule), *averaged over all the possible initial states μ of the reservoir (weighted by p_μ) and summed over all the final states ν of the reservoir, with the delta function expressing the conservation of energy for the global system $\mathcal{A} + \mathcal{R}$.*

\mathcal{R}_{aaaa} remains to be evaluated. These are now the second and fourth terms inside the brackets of (B.43), which cancel the terms $n = a$ of the first and third sums. The remaining terms $n \neq a$ cause $\Gamma_{a \rightarrow n}$ to appear, and we obtain

$$\mathcal{R}_{aaaa} = - \sum_{n \neq a} \Gamma_{a \rightarrow n}. \quad (\text{C.6})$$

Finally, the master equation for the populations (C.1) is written

$$\frac{d\sigma_{aa}}{dt} = -\sigma_{aa} \sum_{n \neq a} \Gamma_{a \rightarrow n} + \sum_{c \neq a} \sigma_{cc} \Gamma_{c \rightarrow a} \quad (\text{C.7.a})$$

or as

$$\frac{d\sigma_{aa}}{dt} = \sum_{c \neq a} (\sigma_{cc} \Gamma_{c \rightarrow a} - \sigma_{aa} \Gamma_{a \rightarrow c}). \quad (\text{C.7.b})$$

Equation (C.7.a) indicates that the population σ_{aa} of \mathcal{A} decreases as a consequence of the transitions occurring from a to the other levels n , and increases as a result of transitions from other levels c to the level a . The form (C.7.b) exhibits the balance of transfers occurring for each pair of levels c and a and simply yields

$$\sum_a \frac{d}{dt} \sigma_{aa} = 0 \quad (\text{C.8})$$

(conservation of the normalization of σ over time).

Remarks

- (i) Very often, the steady-state solution of equation (C.7.b) corresponds to

$$\sigma_{aa}^{\text{st}} \Gamma_{a \rightarrow c} = \sigma_{cc}^{\text{st}} \Gamma_{c \rightarrow a}. \quad (\text{C.9})$$

Condition (C.9), called the “detailed balance condition”, shows that in the steady state, and for any pair of levels a and c , the number of transitions from a to c compensates for the number of transitions from c to a .

- (ii) If the reservoir \mathcal{R} is in thermodynamic equilibrium at temperature T , that is, if populations p_μ of the levels μ of \mathcal{R} are given by (B.15), it can be shown by using (C.5) (see Exercise 16) that

$$e^{-E_a/k_B T} \Gamma_{a \rightarrow c} = e^{-E_c/k_B T} \Gamma_{c \rightarrow a}. \quad (\text{C.10})$$

Comparing (C.9) with (C.10) then shows that the populations σ_{aa} of \mathcal{A} tend, under the effect of the interaction with \mathcal{R} , to a steady state where they are proportional to $\exp(-E_a/k_B T)$. By interacting with a reservoir in thermodynamic equilibrium, the system \mathcal{A} also reaches thermodynamic equilibrium at the same temperature T .

2. Evolution of Coherences

We now examine the evolution of the nondiagonal elements σ_{ab} of σ , and we first consider the case where the Bohr frequency ω_{ab} associated with the coherence σ_{ab} is nondegenerate, that is, the case where there are no other Bohr frequencies ω_{cd} differing from ω_{ab} by less than $1/\Delta t$. The only secular term is therefore the one coupling the coherence σ_{ab} to itself,

and Equation (B.46) is written

$$\frac{d}{dt}\sigma_{ab} = -i\omega_{ab}\sigma_{ab} + \mathcal{R}_{abab}\sigma_{ab}. \quad (\text{C.11})$$

To calculate \mathcal{R}_{abab} , set $c = a$, $d = b$ in (B.43). This gives

$$\begin{aligned} \mathcal{R}_{abab} = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \left\{ g(\tau) \left[\sum_n |A_{an}|^2 e^{i\omega_{an}\tau} - A_{aa}A_{bb} \right] + \right. \\ & \left. + g(-\tau) \left[\sum_n |A_{bn}|^2 e^{-i\omega_{bn}\tau} - A_{aa}A_{bb} \right] \right\}. \end{aligned} \quad (\text{C.12})$$

We then replace $g(\tau)$ by (B.23), $g(-\tau)$ by $g(\tau)^*$, and evaluate the integrals from $\tau = 0$ to $\tau = \infty$ of the exponentials, leading to the appearance of principal parts and delta functions. We thus obtain

$$\mathcal{R}_{abab} = -\Gamma_{ab} - i\Delta_{ab} \quad (\text{C.13})$$

where Δ_{ab} and Γ_{ab} are real quantities given by

$$\Delta_{ab} = \Delta_a - \Delta_b \quad (\text{C.14})$$

with

$$\Delta_a = \frac{1}{\hbar} \mathcal{P} \sum_\mu p_\mu \sum_\nu \sum_n \frac{|\langle \nu, n | V | \mu, a \rangle|^2}{E_\mu + E_a - E_\nu - E_n} \quad (\text{C.15})$$

and an analogous expression for Δ_b , and where

$$\Gamma_{ab} = \Gamma_{ab}^{\text{nonad.}} + \Gamma_{ab}^{\text{ad.}} \quad (\text{C.16})$$

with

$$\Gamma_{ab}^{\text{nonad.}} = \frac{1}{2} \left(\sum_{n \neq a} \Gamma_{a \rightarrow n} + \sum_{n \neq b} \Gamma_{b \rightarrow n} \right) \quad (\text{C.17})$$

and

$$\begin{aligned} \Gamma_{ab}^{\text{ad.}} = & \frac{2\pi}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} \delta(E_{\mu} - E_{\nu}) \times \\ & \times \left(\frac{1}{2} |\langle \nu, a | V | \mu, a \rangle|^2 + \frac{1}{2} |\langle \mu, b | V | \nu, b \rangle|^2 - \right. \\ & \left. - \text{Re} \langle \mu, a | V | \nu, a \rangle \langle \nu, b | V | \mu, b \rangle \right). \quad (\text{C.18}) \end{aligned}$$

The quantity $\hbar\Delta_{ab}$ represents a *shift*, second order in V , of the frequency ω_{ab} due to the interaction between \mathcal{A} and \mathcal{R} . Indeed, in (C.15), $\hbar\Delta_a$ is the shift of the state $|\mu, a\rangle$ of the global system $\mathcal{A} + \mathcal{R}$, weighted by the probability of occupation p_{μ} of the level μ of the reservoir and summed over μ . Thus $\hbar\Delta_a$ can be considered to be the average energy shift of the state $|a\rangle$ of \mathcal{A} .

The quantity Γ_{ab} represents the *damping* rate of the coherence σ_{ab} due to the interaction between \mathcal{A} and \mathcal{R} . The first contribution to Γ_{ab} , shown in (C.17), comes from nonadiabatic effects, because expression (C.17) is the half sum of the rates with which the system leaves state a or state b . A process removing the system from state a or from state b actually perturbs the oscillation of any physical quantity sensitive to σ_{ab} . The second contribution, shown in (C.18), is called adiabatic because it is due to processes where \mathcal{A} does not change state while interacting with \mathcal{R} , which goes from a state μ to a state ν having the same energy as μ .

Finally, we consider the case where the frequency ω_{ab} is degenerate. As in Equation (B.46), we must take into account the couplings between the coherence σ_{ab} and the other coherences σ_{cd} such that $|\omega_{cd} - \omega_{ab}| \ll 1/\Delta t$. The calculation of \mathcal{R}_{abcd} from (B.43) (with $c \neq a$, $b \neq d$, $|\omega_{ab} - \omega_{cd}| \ll 1/\Delta t$) thus gives

$$\begin{aligned} \mathcal{R}_{abcd} = & \frac{2\pi}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} \langle \nu, a | V | \mu, c \rangle \langle \mu, d | V | \nu, b \rangle \times \\ & \times \delta(E_{\mu} + E_c - E_{\nu} - E_a). \quad (\text{C.19}) \end{aligned}$$

The couplings between different coherences having the same Bohr frequency are important for understanding the shift and the broadening of

transitions of systems having equidistant levels, such as the harmonic oscillator or the dressed atom.

Remark

All the expressions derived in this part that relate physical parameters such as $\Gamma_{b \rightarrow a}$, Δ_a , Γ_{ab}^{ad} , $\Gamma_{ab}^{\text{nonad}}$, \mathcal{R}_{abcd} ... to matrix elements of V remain valid when V , instead of having the form $V = -\mathcal{A}\mathcal{R}$, is generalized as $V = -\sum_p A_p R_p$.

D—DISCUSSION OF THE APPROXIMATIONS

To specify the conditions of validity for the treatment presented in Section B above, we must first evaluate an order of magnitude of the evolution time T_R for the system \mathcal{A} .

1. Order of Magnitude of the Evolution Time for \mathcal{A}

We return to Equation (B.30) and try to evaluate an order of magnitude for the right-hand side. We saw above (end of subsection B-3) that the only part of the domain of integration in Figure 1 that contributes significantly to the integral is a strip of width τ_c near the first bisector OB . On this bisector, $t' = t''$, and the integrand of (B.30) is on the order of $\langle V^2 \rangle_R \tilde{\sigma}(t)$, where

$$\langle V^2 \rangle_R = \text{Tr}_R \tilde{\sigma}_R \tilde{V}(t')^2 = \text{Tr}_R \sigma_R V^2. \quad (\text{D.1})$$

The order of magnitude of the right-hand side of (B.30) is thus obtained by multiplying (D.1) by $1/\hbar^2 \Delta t$ times the area of the cross-hatched portion of Figure 1, which is on the order of $\tau_c \Delta t$

$$\frac{\Delta \tilde{\sigma}}{\Delta t} \sim -\frac{\tau_c}{\hbar^2} \langle V^2 \rangle_R \tilde{\sigma}. \quad (\text{D.2})$$

We denote v^2 the order of magnitude of $\langle V^2 \rangle_R$. The parameter v characterizes the intensity of the coupling between \mathcal{A} and \mathcal{B} . Because the coefficient multiplying $\tilde{\sigma}$ on the right-hand side of (D.2) is on the order of the inverse of the evolution time T_R of \mathcal{A} , we obtain for $1/T_R$ the order of magnitude

$$\frac{1}{T_R} \sim \frac{v^2 \tau_c}{\hbar^2}. \quad (\text{D.3})$$

2. Condition for Having Two Time Scales

Using (D.3), the condition $\tau_c \ll T_R$, on which the entire discussion in Section B above is based, can be written as

$$\frac{v \tau_c}{\hbar} \ll 1. \quad (\text{D.4})$$

Equation (D.4) expresses that the evolution due to the coupling V between \mathcal{A} and \mathcal{R} , characterized by the frequency v/\hbar , has a very weak influence during the correlation time τ_c (a situation similar to the weak-collision regime of Brownian motion where the velocity of the heavy particle changes only slightly during the collision time τ_c).

The parameter v introduced above also characterizes the dispersion of values of V . If the broadening of the spectral lines of \mathcal{A} produced by the coupling with \mathcal{R} were inhomogeneous, the width of the spectral lines would be on the order of v/\hbar . But, from (D.2), the width is approximately $1/T_R$, which is, according to (D.3) and (D.4)

$$\frac{v}{\hbar} \frac{v\tau_c}{\hbar} \ll \frac{v}{\hbar}. \quad (\text{D.5})$$

Thus the fact that the interaction between \mathcal{A} and \mathcal{R} fluctuates rapidly, reduces the inhomogeneous width v/\hbar by a factor $v\tau_c/\hbar \ll 1$, hence the name “motional narrowing” condition given to (D.4).

3. Validity Condition for the Perturbative Expansion

If Equation (B.5) is iterated beyond the second order [while replacing $\tilde{\rho}(t)$ everywhere it appears by (B.28)], we obtain for the second member of (B.30), in addition to the double commutator already there, a triple commutator, a quadruple commutator, etc.

The same procedure as the one followed in subsection D-1 above may be used to evaluate the order of magnitude of the contributions of these terms that are higher order in V . For example, the triple commutator involves the integral over t_1, t_2, t_3 of a product of three operators $\tilde{V}(t_1)\tilde{V}(t_2)\tilde{V}(t_3)$ and of σ_R . Because the three times t_1, t_2, t_3 must be quite close to each other (to within τ_c), the significant volume of integration is on the order of $\tau_c^2 \Delta t$, so that the order of magnitude of the third-order term in V is

$$\frac{v^3}{\hbar^3} \tau_c^2 = \frac{v^2 \tau_c}{\hbar^2} \frac{v \tau_c}{\hbar} \sim \frac{1}{T_R} \frac{v \tau_c}{\hbar}, \quad (\text{D.6})$$

or $v\tau_c/\hbar$ times the second-order term. It thus appears that the small parameter $v\tau_c/\hbar$ also characterizes the perturbation expansion. If condition (D.4) is satisfied, it is legitimate to stop such an expansion at the second order in V .

4. Factorization of the Total Density Operator at Time t

We now examine the approximation consisting of neglecting $\tilde{\rho}_{\text{correl}}(t)$ in (B.27). Assume that the correlations [described by $\tilde{\rho}_{\text{correl}}(t)$] that exist between \mathcal{A} and \mathcal{R} at time t result from interactions that occurred between \mathcal{A} and \mathcal{R} prior to t . This is equivalent to assuming that at a given initial time t_0 , prior to t , \mathcal{A} and \mathcal{R} are not correlated (\mathcal{A} and \mathcal{R} , for example, start to interact at t_0). To lowest order in V , it is necessary to have at least one interaction \tilde{V} prior to t to have $\tilde{\rho}_{\text{correl}}(t) \neq 0$. If we now consider that $\tilde{\rho}_{\text{correl}}(t)$ is nonzero, the contribution to $\Delta\tilde{\sigma}(t)$ of the first-order term in V of (B.9) is no longer zero because it is then no longer possible to use (B.20). Thus, to second order in V , a new contribution to $\Delta\tilde{\sigma}(t)$ appears that results from an interaction prior to t (which creates correlations between \mathcal{A} and \mathcal{R}), and from another interaction in the interval $[t, t + \Delta t]$ (which produces a variation $\Delta\tilde{\sigma}$ of $\tilde{\sigma}$ from these correlations).

The order of magnitude of this contribution that was neglected is

$$\frac{\Delta\tilde{\sigma}}{\Delta t} \sim -\frac{1}{\hbar^2} \frac{1}{\Delta t} \int_{-\infty}^t dt'' \int_t^{t+\Delta t} dt' \langle \tilde{V}(t'') \tilde{V}(t') \rangle_R \tilde{\sigma} \quad (\text{D.7})$$

with t'' varying prior to t , and t' in the interval $[t, t + \Delta t]$. Because $\langle \tilde{V}(t') \tilde{V}(t'') \rangle_R$ is zero once $t' - t'' \gg \tau_c$, the domain of integration is reduced to two intervals of width τ_c on both sides of t , and the order of magnitude of the rate of variation associated with (D.7) is

$$\frac{v^2 \tau_c^2}{\hbar^2 \Delta t} = \frac{v^2 \tau_c}{\hbar^2} \frac{\tau_c}{\Delta t} = \frac{1}{T_R} \frac{\tau_c}{\Delta t}. \quad (\text{D.8})$$

Thus it appears, as we mentioned previously [see discussion before (B.28)], that the contribution of the last term of (B.27) is smaller than that of the first term by a factor $\tau_c/\Delta t$. Because we have taken $\Delta t \gg \tau_c$, it is completely legitimate to neglect such a contribution.

Thus the initial correlations between \mathcal{A} and \mathcal{R} at time t have an effect on the future of $\tilde{\sigma}$ only in the interval $[t, t + \tau_c]$, whereas new correlations are established permanently in the interval $[t, t + \Delta t]$ and cause $\tilde{\sigma}$ to evolve proportionally to Δt .

Remark

It is possible to imagine correlations between \mathcal{A} and \mathcal{R} at time t that can have a spectacular influence on the subsequent evolution of \mathcal{A} . Consider, for example, at time $t_0 = 0$, an atom initially excited in the state $|b\rangle$, with no

incident photon. Radiative decay can occur between 0 and t . Then imagine that at time t , we apply to the state $|\psi(t)\rangle$ of the global system atom + radiation the time-reversal operator K . Because the Schrödinger equation has the time-reversal symmetry, we know that at time $2t$, the atom will have returned to the excited state (more precisely to the state $K|b\rangle$), in the radiation vacuum. It is therefore clear that the state $K|\psi(t)\rangle$ has very specific correlations because the evolution from this state does not at all have the irreversible behavior predicted by the master equation. Thus such an equation cannot always be valid, even if \mathcal{R} is a reservoir. Nonetheless, we should note that correlations of the type contained in the state $K|\psi(t)\rangle$ are very peculiar and extremely difficult to achieve in an experiment. Therefore we exclude all situations of this type from our discussion.

5. Summary

Finally, the treatment presented in Section B is based on the motional narrowing condition (D.4). Under such a condition, two very distinct time scales T_R and τ_c can be defined, and a perturbative calculation can be performed for the variation $\Delta\tilde{\sigma}$ of $\tilde{\sigma}$ in the interval $[t, t + \Delta t]$ with $\tau_c \ll \Delta t \ll T_R$. It is then not necessary to take into account the initial correlations between \mathcal{A} and \mathcal{R} at time t , resulting from interactions between \mathcal{A} and \mathcal{R} prior to t . The fact that the coarse-grained rate of variation $\Delta\sigma/\Delta t$ is given (in the Schrödinger representation) by a differential linear system with constant coefficients implies that the previous approach is valid for all t . The master equation can therefore be used to predict the evolution of $\tilde{\sigma}$ over much longer times, on the order of a few T_R . A remarkable feature of this approach is that a perturbative study of the evolution of the system over a time interval that is short ($\Delta t \ll T_R$), but not too short ($\Delta t \gg \tau_c$), allows its behavior to be predicted over much longer times. In this sense, such an approach is nonperturbative and is similar to the procedure presented in Chapter III where a perturbative calculation of the level-shift operator allows nonperturbative expressions for the transition amplitudes to be obtained.

E—APPLICATION TO A TWO-LEVEL ATOM COUPLED TO THE RADIATION FIELD

In this last part, the foregoing ideas are illustrated using a simple example. We derive and discuss the master equation describing the evolution of the density matrix of an atom with two levels a and b under the effect of spontaneous emission, absorption, and stimulated emission processes. First, the atom is assumed to be infinitely heavy and at rest, which allows us to study the evolution of just the internal degrees of freedom (§1). The translational degrees of freedom of the center of mass are then taken into account, and we will study the evolution of the atomic velocities resulting from momentum exchanges between the atom and the incident radiation field (§2).

1. Evolution of Internal Degrees of Freedom

The atomic electrons are assumed to evolve around a fixed point $\mathbf{0}$. In the electric dipole point of view, the interaction Hamiltonian between the atom and the radiation field is written [see formula (91) in the Appendix]

$$V = -\mathbf{d} \cdot \mathbf{E}_\perp(\mathbf{0}) = -i\mathbf{d} \cdot \sum_i \sqrt{\frac{\hbar\omega_i}{2\epsilon_0 L^3}} \mathbf{\epsilon}_i (a_i - a_i^+) \quad (\text{E.1})$$

where \mathbf{d} is the electric dipole moment and where the field operator is evaluated at the point $\mathbf{0}$.

a) MASTER EQUATION DESCRIBING SPONTANEOUS EMISSION FOR A TWO-LEVEL ATOM

We begin by assuming that the radiation field is in the vacuum state

$$\sigma_R = |0\rangle\langle 0|. \quad (\text{E.2})$$

We previously explained (Section A) why it is legitimate to consider the radiation field in such a state as a reservoir. The state (E.2) indeed satisfies conditions (B.12) and (B.20), taking into account expression (E.1) for V .

The spontaneous emission of a photon from the lower state a cannot conserve the total unperturbed energy. Equation (C.5) thus implies

$$\Gamma_{a \rightarrow b} = 0 \quad (\text{E.3})$$

By contrast, the same equation gives a nonzero result for $\Gamma_{b \rightarrow a}$:

$$\Gamma_{b \rightarrow a} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\epsilon} |\langle a; \mathbf{k}\epsilon | V | b; 0 \rangle|^2 \delta(\hbar\omega - \hbar\omega_{ba}) \quad (\text{E.4.a})$$

which is just the rate Γ for the spontaneous emission of a photon, previously introduced in Chapter II and equal to the inverse of the radiative lifetime τ of level b

$$\Gamma_{b \rightarrow a} = \Gamma = \frac{1}{\tau}. \quad (\text{E.4.b})$$

Equations (C.7) for the populations are thus written here

$$\begin{cases} \frac{d}{dt} \sigma_{bb} = -\Gamma \sigma_{bb} \\ \frac{d}{dt} \sigma_{aa} = +\Gamma \sigma_{bb} \end{cases} \quad (\text{E.5})$$

and have the same form as the Einstein equations (A.1) [with $u(\omega) = 0$].

For the evolution of the nondiagonal element of σ_{ba} , the general results of subsection C-2 give

$$\frac{d}{dt} \sigma_{ba} = -i(\omega_{ba} + \Delta_{ba}) \sigma_{ba} - \frac{\Gamma}{2} \sigma_{ba} \quad (\text{E.6})$$

where $\hbar\Delta_{ba}$ is the difference in radiative shifts of the levels b and a

$$\Delta_{ba} = \Delta_b - \Delta_a \quad (\text{E.7.a})$$

$$\Delta_b = \frac{1}{\hbar} \mathcal{P} \sum_{\mathbf{k}\epsilon} \frac{|\langle a; \mathbf{k}\epsilon | V | b; 0 \rangle|^2}{\hbar\omega_{ba} - \hbar\omega} \quad (\text{E.7.b})$$

$$\Delta_a = \frac{1}{\hbar} \mathcal{P} \sum_{\mathbf{k}\epsilon} \frac{|\langle b; \mathbf{k}\epsilon | V | a; 0 \rangle|^2}{-\hbar\omega_{ba} - \hbar\omega} \quad (\text{E.7.c})$$

and where $\Gamma/2$, which is the half-sum of (E.3) and (E.4.b), is the nonadiabatic contribution to the damping of σ_{ab} [see (C.17)]. The adiabatic contribution (C.18) is zero because V has no diagonal elements in state $|a\rangle$ or state $|b\rangle$ (d is odd and $|a\rangle$ and $|b\rangle$ are assumed to have a well-defined parity).

Remark

We must not forget that the approximation consisting of considering only two atomic levels a and b causes several effects to be lost. First, even if a is the ground state and b is the first excited state, other states more excited than b can decay radiatively to a or b . Moreover, the contribution of other atomic levels c of the atom certainly cannot be ignored in nonresonant processes (virtual emission and reabsorption of a photon) which are the origin of the radiative shifts of a and b .

b) ADDITIONAL TERMS DESCRIBING THE ABSORPTION AND INDUCED EMISSION OF A WEAK BROADBAND RADIATION

We now assume that some photons are initially present. The density operator of the radiation is, according to (B.14), a statistical mixture of eigenstates $|n_1 \cdots n_i \cdots\rangle$ of H_R , representing n_1 photons in the mode $1, \cdots n_i$ photons in the mode $i \cdots$, with a weight $p(n_1 \cdots n_i \cdots)$

$$\sigma_R = \sum_{\{n_i\}} p(n_1 \cdots n_i \cdots) |n_1 \cdots n_i \cdots\rangle \langle n_1 \cdots n_i \cdots|. \quad (\text{E.8})$$

Conditions (B.12) and (B.20) are still satisfied. We explained above (Section A), that if the spectral width of the radiation described by (E.8) is sufficiently broad, and if its intensity is sufficiently low, the condition $\tau_c \ll T_R$ is satisfied, which we assume here.

The transition rate from the lower level a to the higher level b , calculated from (C.5), is no longer zero when (E.2) is replaced by (E.8). We write it as Γ' . It represents the probability per unit time for the absorption of a photon from a and equals

$$\begin{aligned} \Gamma' = \Gamma_{a \rightarrow b} &= \frac{2\pi}{\hbar} \sum_{\{n_i\}} p(n_1 \cdots n_i \cdots) \times \\ &\times \sum_{\{n'_i\}} |\langle b; n'_1 \cdots n'_i \cdots | V | a; n_1 \cdots n_i \cdots \rangle|^2 \delta(E_{\text{final}} - E_{\text{initial}}). \end{aligned} \quad (\text{E.9})$$

Because V is proportional to the field \mathbf{E}_\perp , and \mathbf{E}_\perp is a linear combination of a_i and a_i^+ [see (E.1)], all the n' must be equal to n , except one, n'_i which must equal $n_i \pm 1$. In fact, because $E_b > E_a$, the conservation of energy results in the fact that only $n'_i = n_i - 1$ is possible, so that (E.9) is

rewritten

$$\begin{aligned} \Gamma' = & \frac{2\pi}{\hbar} \sum_{n_1 \cdots n_i \cdots} p(n_1 \cdots n_i \cdots) \times \\ & \times \sum_i |\langle b; n_1 \cdots n_i - 1 \cdots | V | a; n_1 \cdots n_i \cdots \rangle|^2 \delta(\hbar\omega_i - \hbar\omega_{ba}). \end{aligned} \quad (\text{E.10})$$

Because $\langle n_i - 1 | a_i | n_i \rangle = \sqrt{n_i} \langle 0_i | a_i | 1_i \rangle$, Γ' is also equal to

$$\begin{aligned} \Gamma' = & \frac{2\pi}{\hbar} \sum_i \left(\sum_{\{n_i\}} n_i p(n_1 \cdots n_i \cdots) \right) \times \\ & \times |\langle b; 0 | V | a; 1_i \rangle|^2 \delta(\hbar\omega_i - \hbar\omega_{ba}) \end{aligned} \quad (\text{E.11})$$

which causes the average number $\langle n_i \rangle$ of photons in the mode i to appear

$$\langle n_i \rangle = \sum_{\{n_i\}} n_i p(n_1 \cdots n_i \cdots). \quad (\text{E.12})$$

The radiation state thus appears in Γ' only through the average number of photons in each mode. Finally, the function $\delta(\hbar\omega_i - \hbar\omega_{ba})$ expressing the conservation of energy in (E.11) results in the fact that only the average numbers of photons in the resonant modes contribute. Γ' is thus proportional to the average intensity $I(\omega_{ba})$ of the incident radiation at the atomic frequency ω_{ba} .

A similar procedure can be followed for calculating $\Gamma_{b \rightarrow a}$. It is now the matrix elements of a_i^+ between $|b; n_1 \cdots n_i \cdots \rangle$ and $\langle a; n_1 \cdots n_i + 1 \cdots |$ that are involved and (E.11) must be replaced by

$$\Gamma_{b \rightarrow a} = \frac{2\pi}{\hbar} \sum_i (\langle n_i \rangle + 1) |\langle a; 1_i | V | b; 0 \rangle|^2 \delta(\hbar\omega_i - \hbar\omega_{ba}). \quad (\text{E.13})$$

We used the normalization relation for $p(n_1 \cdots n_i \cdots)$. The contribution of the term 1 inside the parentheses $(\langle n_i \rangle + 1)$ in (E.13) gives the previously calculated transition rate Γ associated with the spontaneous emission from b to a . As for the other term $\langle n_i \rangle$, it gives the transition probability Γ' given in (E.11) so that

$$\Gamma_{b \rightarrow a} = \Gamma + \Gamma'. \quad (\text{E.14})$$

Finally, the evolution equations (C.7) for populations become, in the presence of incident radiation,

$$\begin{cases} \frac{d}{dt}\sigma_{bb} = -\Gamma\sigma_{bb} + \Gamma'(\sigma_{aa} - \sigma_{bb}) \\ \frac{d}{dt}\sigma_{aa} = +\Gamma\sigma_{bb} + \Gamma'(\sigma_{bb} - \sigma_{aa}). \end{cases} \quad (\text{E.15})$$

They actually have the general form of the Einstein equations (A.1) because Γ' is proportional to the light intensity at the frequency ω_{ba} and, for an atom with two nondegenerate levels a and b , it can be shown that $B_{a \rightarrow b} = B_{b \rightarrow a}$ in (A.1).

Remarks

(i) Until now, we have made no assumption concerning the angular distribution and the polarization of the incident radiation. If the incident radiation is isotropic and unpolarized, the average number of photons $\langle n_i \rangle$ in a mode i (i.e., a mode $\mathbf{k}_i \epsilon_i$) depends only on the frequency ω_i of this mode and not on $\kappa_i = \mathbf{k}_i/k_i$ and ϵ_i . The sum over i of (E.11) is in fact a sum over $\epsilon_i \perp \mathbf{k}_i$, followed by an angular integral over κ_i and an integral over $k_i = |\mathbf{k}_i|$. If $\langle n_i \rangle$ depends only on ω_i , the sum over ϵ_i and the integral over κ_i are the same in expressions (E.4.a) and (E.11) giving Γ and Γ' . The difference between Γ and Γ' appears only in the integral over ω_i . Because of the function $\delta(\hbar\omega_i - \hbar\omega_{ba})$ appearing in (E.4.a) and (E.11), this difference is simply a multiplying factor $\langle n(\omega_{ba}) \rangle$ for Γ' . For isotropic and unpolarized incident radiation, we have

$$\Gamma' = \Gamma \langle n(\omega_{ba}) \rangle. \quad (\text{E.16})$$

Γ' is thus equal to Γ multiplied by the average number of photons per resonant mode.

(ii) We now assume that the radiation is in thermodynamic equilibrium at temperature T . Such radiation is isotropic and unpolarized so that (E.16) is applicable. Moreover, in this case, we know the value of the probability $p(n_1 n_2 \cdots n_i \cdots)$ [see (B.15)] and, consequently, according to (E.12) the value of $\langle n(\omega_{ba}) \rangle$ which equals (*)

$$\langle n(\omega_{ba}) \rangle = \frac{1}{e^{\hbar\omega_{ba}/k_B T} - 1}. \quad (\text{E.17})$$

(*) See, for example, *Photons and Atoms—Introduction to Quantum Electrodynamics*, Exercise 4 in Complement D_{III}.

We then substitute (E.16) into the first equation (E.15), which gives, in the steady state ($d\sigma_{bb}/dt = 0$)

$$\frac{\sigma_{bb}}{\sigma_{aa}} = \frac{\Gamma'}{\Gamma + \Gamma'} = \frac{\langle n(\omega_{ba}) \rangle}{1 + \langle n(\omega_{ba}) \rangle}. \quad (\text{E.18})$$

It is then sufficient to substitute (E.17) into (E.18) to obtain

$$\frac{\sigma_{bb}}{\sigma_{aa}} = e^{-\hbar\omega_{ba}/k_B T} = e^{-(E_b - E_a)/k_B T}. \quad (\text{E.19})$$

Thus we have derived the Einstein equations from the first principles and showed that they imply that the atom reaches thermodynamic equilibrium.

(iii) The average number of photons per mode for isotropic radiation, $\langle n(\omega) \rangle$, is directly related to the radiation energy density at frequency ω , $u(\omega)$. To show this, we actually express in two different ways the radiation energy density in the frequency interval $[\omega, \omega + d\omega]$. On the one hand, this density is $u(\omega)d\omega$, and on the other hand, it is the average energy per mode $\langle n(\omega) \rangle \hbar\omega$ divided by the volume L^3 , multiplied by the number of modes in the frequency interval $[\omega, \omega + d\omega]$, which, taking into account the two possible polarizations, equals $8\pi k^2 dk/(2\pi/L)^3$. Finally, we have

$$u(\omega) = \frac{\hbar\omega^3 \langle n(\omega) \rangle}{\pi^2 c^3}. \quad (\text{E.20})$$

It remains to examine the new evolution equation for σ_{ba} , which is written

$$\frac{d}{dt}\sigma_{ba} = -i(\omega_{ba} + \Delta_{ba} + \Delta'_{ba})\sigma_{ba} - \frac{1}{2}(\Gamma + 2\Gamma')\sigma_{ba}. \quad (\text{E.21})$$

The new terms, indicated by a prime superscript, describe, on the one hand, an additional damping (in Γ') of σ_{ba} , associated with a shortening of the lifetime of levels a and b as a result of the absorption and stimulated emission processes and, on the other hand, an additional shift Δ'_{ba} of the line $b \leftrightarrow a$

$$\Delta'_{ba} = \Delta'_b - \Delta'_a \quad (\text{E.22})$$

associated with the light shifts of levels a and b produced by the incident

radiation. For example, Δ'_a is given by

$$\begin{aligned} \hbar\Delta'_a = & \mathcal{P} \sum_{n_1 \cdots n_i \cdots} p(n_1 \cdots n_i \cdots) \times \\ & \times \sum_i \frac{|\langle b; n_1 \cdots n_i - 1 \cdots |V|a; n_1 \cdots n_i \cdots \rangle|^2}{\hbar\omega_i - \hbar\omega_{ba}}. \end{aligned} \quad (\text{E.23.a})$$

A calculation analogous to that carried out on (E.10) yields

$$\Delta'_a \sim \mathcal{P} \int \frac{I(\omega) d\omega}{\omega - \omega_{ba}} \quad (\text{E.23.b})$$

and shows that Δ'_a may be significant if the excitation profile $I(\omega)$ is quasi-resonant, while remaining asymmetric with respect to ω_{ba} . We have thus precisely justified the qualitative considerations of subsection E-2 in Chapter II concerning the shift and broadening of the levels of an atom produced by the incident light.

Remarks

- (i) The foregoing discussion can be generalized to the case in which levels a and b each contain several Zeeman sublevels. The master equation can then be used to quantitatively describe the population transfers between Zeeman sublevels of a by absorption-spontaneous emission or absorption-stimulated emission cycles ("optical pumping") as well as the evolution of the various coherences between Zeeman sublevels (*).
- (ii) In (E.23), we considered only processes in which one photon is virtually absorbed from a and then reemitted. Actually, a photon can also be virtually emitted from a , and then reabsorbed, which leads to an expression analogous to (E.23.a), where the quantity appearing in Σ_i is replaced by

$$\frac{|\langle b; n_1 \cdots n_i + 1 \cdots |V|a; n_1 \cdots n_i \cdots \rangle|^2}{-\hbar\omega_i - \hbar\omega_{ba}}. \quad (\text{E.24})$$

The term independent of n_i in (E.24) gives the radiative shift Δ_a of state a [see (E.7.c)]. As for the term proportional to n_i , it gives a contribution similar to (E.23), except for the replacement of $\omega - \omega_{ba}$ by $-\omega - \omega_{ba}$ in the denominator (which demonstrates that this last correction to Δ'_a is very small when the

(*) See, for example, Cohen-Tannoudji.

excitation is quasi-resonant). A more correct expression for Δ'_a is thus

$$\Delta'_a \sim \mathcal{P} \int d\omega I(\omega) \left[\frac{1}{\omega - \omega_{ba}} + \frac{1}{-\omega - \omega_{ba}} \right] = 2\omega_{ba} \mathcal{P} \int \frac{I(\omega) d\omega}{\omega^2 - \omega_{ba}^2}. \quad (\text{E.25})$$

For a real atom, we should also take into account the virtual excitation of all other transitions $a \rightarrow c$ starting from a .

2. Evolution of Atomic Velocities

The goal of this final section is to obtain a master equation describing the evolution of the atomic velocity distribution function due to momentum exchanges between the atom and the radiation field.

The atom is still represented by a two-level system a and b , but we now take into account the motion of its center of mass, with position \mathbf{R} and momentum \mathbf{P} . The eigenfunctions of the Hamiltonian $\mathbf{P}^2/2M$ of the center of mass (where M is the mass of the atom) are plane waves on which periodic boundary conditions are imposed in a cube-shaped box of side L (as for the modes of the radiation field). These eigenfunctions are written

$$\varphi_{\mathbf{p}}(\mathbf{R}) = \frac{1}{\sqrt{L^3}} \exp(i\mathbf{p} \cdot \mathbf{R}/\hbar). \quad (\text{E.26})$$

The atom interacts with a homogeneous isotropic unpolarized radiation field for which the spectral width is sufficiently large and the intensity sufficiently weak so that it is possible to write a master equation for the atom.

We begin (§a) by generalizing equations (E.15) and by deriving equations describing the coupled evolution of internal and translational degrees of freedom. We then show how it is possible, under certain conditions, to eliminate the internal variables and to obtain a Fokker–Planck equation for the atomic velocity distribution function (§b). Finally, we discuss the physical meaning of this equation (§c and §d).

a) TAKING INTO ACCOUNT THE TRANSLATIONAL DEGREES OF FREEDOM IN THE MASTER EQUATION

The atomic density matrix elements are now identified by internal (a or b) and external (\mathbf{p}) quantum numbers. We are interested in the populations $\pi_{b,\mathbf{p}} = \sigma_{b\mathbf{p},b\mathbf{p}}$ and $\pi_{a,\mathbf{p}} = \sigma_{a\mathbf{p},a\mathbf{p}}$ that represent the probability of the atom's being in state b or a with total momentum \mathbf{p} .

In the electric dipole representation (see §5 of the Appendix), the Hamiltonian V_R for the coupling between the atom, assumed to be neutral, and the radiation field is equal to

$$\begin{aligned} V_R &= -\mathbf{d} \cdot \mathbf{E}_\perp(\mathbf{R}) = \\ &= -i\mathbf{d} \cdot \sum_i \sqrt{\frac{\hbar\omega_i}{2\epsilon_0 L^3}} [\epsilon_i a_i e^{i\mathbf{k}_i \cdot \mathbf{R}} - \epsilon_i a_i^+ e^{-i\mathbf{k}_i \cdot \mathbf{R}}] \end{aligned} \quad (\text{E.27})$$

where \mathbf{d} is the electric dipole moment of the atom and where the field operator $\mathbf{E}_\perp(\mathbf{R})$ is evaluated at the center of mass. The equations generalizing (E.15) are thus written

$$\dot{\pi}_{b,p} = \sum_{p'} \Gamma_{ap' \rightarrow bp} \pi_{a,p'} - \sum_{p'} \Gamma_{bp \rightarrow ap} \pi_{b,p} \quad (\text{E.28.a})$$

$$\dot{\pi}_{a,p} = \sum_{p'} \Gamma_{bp' \rightarrow ap} \pi_{b,p'} - \sum_{p'} \Gamma_{ap \rightarrow bp} \pi_{a,p} \quad (\text{E.28.b})$$

where the coefficients $\Gamma_{ap' \rightarrow bp}$ and $\Gamma_{bp' \rightarrow ap}$ are deduced from (C.5) and (E.10). Thus, by setting $\omega_{ba} = \omega_0$, we have

$$\begin{aligned} \Gamma_{ap' \rightarrow bp} &= \frac{2\pi}{\hbar} \sum_{\{n_i\}} p(\{n_i\}) \times \\ &\times \sum_i |\langle b, \mathbf{p}; n_1 \cdots n_i - 1 \cdots | V_R | a, \mathbf{p}'; n_1 \cdots n_i \cdots \rangle|^2 \times \\ &\times \delta \left[\hbar\omega_0 - \hbar\omega_i + \left(\frac{\mathbf{p}^2}{2M} - \frac{\mathbf{p}'^2}{2M} \right) \right]. \end{aligned} \quad (\text{E.29})$$

From (E.27) it is possible to split the matrix element of V_R into a part depending on the center of mass variables and a part depending on the internal variables and radiation field variables. We thus obtain, using the same notation as in subsection E-1:

$$\begin{aligned} \langle b, \mathbf{p}; n_1 \cdots n_i - 1 \cdots | V_R | a, \mathbf{p}'; n_1 \cdots n_i \cdots \rangle &= \\ &= \sqrt{n_i} \langle \mathbf{p} | e^{i\mathbf{k}_i \cdot \mathbf{R}} | \mathbf{p}' \rangle \langle b; 0 | V | a; 1_i \rangle. \end{aligned} \quad (\text{E.30})$$

From Equation (E.26) we get

$$\langle \mathbf{p} | \exp(i\mathbf{k}_i \cdot \mathbf{R}) | \mathbf{p}' \rangle = \delta_{\mathbf{p}-\hbar\mathbf{k}_i, \mathbf{p}'} \quad (\text{E.31})$$

which allows us to rewrite $\Gamma_{a\mathbf{p}' \rightarrow b\mathbf{p}}$ in the form

$$\begin{aligned} \Gamma_{a\mathbf{p}' \rightarrow b\mathbf{p}} &= \frac{2\pi}{\hbar} \sum_i \langle n_i \rangle |\langle b, 0 | V | a, 1_i \rangle|^2 \times \\ &\times \delta_{\mathbf{p}-\hbar\mathbf{k}_i, \mathbf{p}'} \delta(\hbar\omega_0 - \hbar\omega_i + \hbar\xi_D - \hbar\xi_R) \end{aligned} \quad (\text{E.32})$$

where ξ_D and ξ_R are the frequency shifts due, respectively, to the Doppler effect and to the recoil effect

$$\xi_D = \mathbf{k}_i \cdot \mathbf{p}/M \quad (\text{E.33})$$

$$\xi_R = \hbar\mathbf{k}_i^2/2M. \quad (\text{E.34})$$

A similar calculation gives

$$\begin{aligned} \Gamma_{b\mathbf{p}' \rightarrow a\mathbf{p}} &= \frac{2\pi}{\hbar} \sum_i (\langle n_i \rangle + 1) |\langle b, 0 | V | a, 1_i \rangle|^2 \times \\ &\times \delta_{\mathbf{p}+\hbar\mathbf{k}_i, \mathbf{p}'} \delta(\hbar\omega_0 - \hbar\omega_i + \hbar\xi_D + \hbar\xi_R) \end{aligned} \quad (\text{E.35})$$

where ξ_D and ξ_R are still given by (E.33) and (E.34).

Remarks

- (i) By writing Equations (E.28), we have implicitly assumed that the diagonal term $\sigma_{b\mathbf{p}, b\mathbf{p}}$ is not coupled to any nondiagonal term $\sigma_{a\mathbf{p}', a\mathbf{p}''}$. The absence of such couplings does not result from a secular approximation similar to the one in subsection B.4. In fact, \mathbf{p}' and \mathbf{p}'' can have the same modulus and different directions, so that the free evolution frequency of the coherence $\sigma_{a\mathbf{p}', a\mathbf{p}''}$ can be arbitrarily small. Actually, the term coupling $\sigma_{b\mathbf{p}, b\mathbf{p}}$ to $\sigma_{a\mathbf{p}', a\mathbf{p}''}$ is, according to (C.19), equal to

$$\begin{aligned} &\frac{2\pi}{\hbar} \sum_{\{n_i\}} p(\{n_i\}) \sum_i \langle b, \mathbf{p}; n_1 \cdots n_i - 1 \cdots | V_{\mathbf{R}} | a, \mathbf{p}'; n_1 \cdots n_i \cdots \rangle \times \\ &\times \langle a, \mathbf{p}''; n_1 \cdots n_i \cdots | V_{\mathbf{R}} | b, \mathbf{p}; n_1 \cdots n_i - 1 \cdots \rangle \times \\ &\times \delta \left[\hbar\omega_0 - \hbar\omega_i + \left(\frac{\mathbf{p}^2}{2M} - \frac{\mathbf{p}'^2}{2M} \right) \right]. \end{aligned} \quad (\text{E.36})$$

We then separate, in the matrix elements of V_R , the part dependent on the center-of-mass variables as we previously did in (E.30). The first matrix element is proportional to $\delta_{\mathbf{p}-\hbar\mathbf{k}_i, \mathbf{p}'}$ and the second is proportional to $\delta_{\mathbf{p}-\hbar\mathbf{k}_i, \mathbf{p}''}$. It is then clear that we must have $\mathbf{p}' = \mathbf{p}''$. It follows that, for the master equation considered here, there is no coupling between the diagonal and the nondiagonal terms of the density matrix σ .

(ii) A more precise study including the second-order Doppler effect is sometimes necessary. In this case (E.33) must be replaced by

$$\xi_D = \frac{\mathbf{k}_i \cdot \mathbf{p}}{M} - \frac{\omega_0}{2} \frac{\mathbf{p}^2}{M^2 c^2}. \quad (\text{E.37})$$

We now substitute (E.32) and (E.35) into Equations (E.28). The sums over \mathbf{p}' reduce to a single term, because of the delta functions expressing momentum conservation:

$$\begin{aligned} \dot{\pi}_{b, \mathbf{p}} &= \sum_i \frac{2\pi}{\hbar} |\langle b; 0 | V | a; 1_i \rangle|^2 \times \\ &\quad \times \delta(\hbar\omega_0 - \hbar\omega_i + \hbar\xi_D - \hbar\xi_R) \times \\ &\quad \times \{ \langle n_i \rangle \pi_{a, \mathbf{p}-\hbar\mathbf{k}_i} - (\langle n_i \rangle + 1) \pi_{b, \mathbf{p}} \} \end{aligned} \quad (\text{E.38.a})$$

$$\begin{aligned} \dot{\pi}_{a, \mathbf{p}} &= \sum_i \frac{2\pi}{\hbar} |\langle b; 0 | V | a; 1_i \rangle|^2 \times \\ &\quad \times \delta(\hbar\omega_0 - \hbar\omega_i + \hbar\xi_D + \hbar\xi_R) \times \\ &\quad \times \{ (\langle n_i \rangle + 1) \pi_{b, \mathbf{p}+\hbar\mathbf{k}_i} - \langle n_i \rangle \pi_{a, \mathbf{p}} \}. \end{aligned} \quad (\text{E.38.b})$$

To simplify the calculations, we ignore the dependence of $\sum_{\varepsilon_i} |\langle b; 0 | V | a; 1_i \rangle|^2$ with the direction $\boldsymbol{\kappa}_i = \mathbf{k}_i/k_i$ of \mathbf{k}_i , which is equivalent to taking an isotropic radiation pattern (see, however, the remark following). This quantity thus depends only on ω_i [it varies linearly with $\omega_i = ck_i$, according to (E.1)] and can be expressed as a function of Γ

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar} \sum_i |\langle b; 0 | V | a; 1_i \rangle|^2 \delta(\hbar\omega_i - \hbar\omega_0) \\ &= \frac{L^3}{\pi\hbar^2 c^3} \omega_0^3 \sum_{\varepsilon_i} \frac{|\langle b; 0 | V | a; 1_i \rangle|^2}{\omega_i}. \end{aligned} \quad (\text{E.39})$$

By taking the limit $L \rightarrow \infty$ and by calling $\pi_j(\mathbf{p})$ (with $j = a, b$) the

population density of level j in momentum space, we finally obtain for (E.38):

$$\dot{\pi}_b(\mathbf{p}) = \Gamma \int_0^{+\infty} \frac{\omega^3}{\omega_0^3} d\omega \int \frac{d\Omega}{4\pi} \delta(\omega_0 - \omega + \xi_D - \xi_R) \times \\ \times \{ \langle n(\omega) \rangle \pi_a(\mathbf{p} - \hbar\mathbf{k}) - [\langle n(\omega) \rangle + 1] \pi_b(\mathbf{p}) \} \quad (\text{E.40.a})$$

$$\dot{\pi}_a(\mathbf{p}) = \Gamma \int_0^{+\infty} \frac{\omega^3}{\omega_0^3} d\omega \int \frac{d\Omega}{4\pi} \delta(\omega_0 - \omega + \xi_D + \xi_R) \times \\ \times \{ [\langle n(\omega) \rangle + 1] \pi_b(\mathbf{p} - \hbar\mathbf{k}) - \langle n(\omega) \rangle \pi_a(\mathbf{p}) \} \quad (\text{E.40.b})$$

where $d\Omega$ is the elementary solid angle about $\kappa = \mathbf{k}/k$ and where, for each direction κ , the modulus of \mathbf{k} is determined by the argument of the delta function, i.e., by the Doppler and recoil shifts.

The comparison of Equations (E.15) and (E.40) clearly shows what are the new effects connected with the atomic motion. First, when the atom goes from one level to another by absorption or emission of a photon, its momentum increases or decreases by a quantity $\hbar\mathbf{k}$ equal to the momentum of the absorbed or emitted photon. Second, the rates of absorption and stimulated emission involve the average numbers of photons having a frequency which is no longer ω_0 , but is now corrected by the Doppler and recoil shifts.

Remark

If the radiation pattern is not isotropic, it is sufficient to replace $d\Omega/4\pi$ in (E.40) by $I(\kappa)d\Omega/4\pi$, where $I(\kappa)$ is the normalized radiation intensity ($\int d\Omega I(\kappa)/4\pi = 1$), which has the important property of being even [$I(\kappa) = I(-\kappa)$]. The friction coefficient γ and the diffusion coefficient D introduced further on are then tensors and no longer scalars.

b) FOKKER-PLANCK EQUATION FOR THE ATOMIC VELOCITY DISTRIBUTION FUNCTION

The probability density that the momentum of the atom is equal to \mathbf{p} , regardless of its internal state, is given by

$$\pi(\mathbf{p}) = \pi_a(\mathbf{p}) + \pi_b(\mathbf{p}). \quad (\text{E.41})$$

In the electric dipole representation, the momentum \mathbf{p} is identical to $M\mathbf{v}$ [see Equation (78) of the Appendix], so that the function $\pi(\mathbf{p})$ is also the

distribution of atomic velocity \mathbf{v} . We now attempt to derive an evolution equation for $\pi(\mathbf{p})$ from Equations (E.40).

α) The Small Parameters of the Problem

In what follows, we assume that $\hbar\mathbf{k}$ is small compared with the width Δp of the functions $\pi_a(\mathbf{p}), \pi_b(\mathbf{p})$ and that ξ_D and ξ_R are small compared with the width $\Delta\omega$ of the spectral distribution of $\omega^3\langle n(\omega)\rangle$. We thus introduce two small parameters

$$\eta_1 = \frac{\hbar k_0}{\Delta p} \quad (\text{E.42.a})$$

$$\eta_2 = \frac{\xi_D}{\Delta\omega} \sim \frac{k_0 \Delta p}{M \Delta\omega} \quad (\text{E.42.b})$$

from which it is possible to express $\xi_R/\Delta\omega$

$$\frac{\xi_R}{\Delta\omega} \sim \frac{\hbar k_0^2}{2 M \Delta\omega} \sim \eta_1 \eta_2. \quad (\text{E.42.c})$$

The rate of variation $\dot{\pi}(\mathbf{p})$ of $\pi(\mathbf{p})$ is obtained by adding the two equations (E.40). It appears that $\dot{\pi}(\mathbf{p})$ is canceled out if we set $\xi_D = \xi_R = 0$ in the argument of the delta function and $\hbar\mathbf{k} = \mathbf{0}$ in $\pi_a(\mathbf{p} - \hbar\mathbf{k})$ and $\pi_b(\mathbf{p} + \hbar\mathbf{k})$. To order 0, in η_1 and η_2 , we thus have $\dot{\pi}(\mathbf{p}) = 0$.

Remark

The comparison of the second-order Doppler effect $\xi_D^{(2)}$, introduced in (E.37), with $\Delta\omega$ shows that

$$\frac{\xi_D^{(2)}}{\Delta\omega} \sim \left(\frac{k_0 \Delta p}{M \Delta\omega} \right)^2 \frac{\Delta\omega}{\omega_0} \sim \eta_2^2 \frac{\Delta\omega}{\omega_0} \quad (\text{E.43})$$

In situations where $\Delta\omega \leq \omega_0$, the second-order Doppler effect introduces small corrections of order η_2^2 at most.

β) Perturbative Expansion of the Evolution Equation for $\pi(\mathbf{p})$

Because $\dot{\pi}(\mathbf{p})$ is canceled out to order 0 in η_1 and η_2 , it is convenient to expand, on the one hand $\pi_j(\mathbf{p} \pm \hbar\mathbf{k})$ (with $j = a, b$) in powers of $\eta_1 = \hbar k / \Delta p$, and on the other hand, the delta function in powers of ξ_D and ξ_R (which is equivalent after integration over ω to expanding the factor

multiplying the delta function in powers of $\xi_D/\Delta\omega$ and $\xi_R/\Delta\omega$):

$$\pi_j(\mathbf{p} \pm \hbar\mathbf{k}) = \pi_j(\mathbf{p}) \pm \hbar\mathbf{k} \cdot \nabla\pi_j + \frac{1}{2} \sum_{l,m} k_l k_m \frac{\partial^2 \pi_j}{\partial k_l \partial k_m} + \dots \quad (\text{E.44})$$

with $l, m = x, y, z$:

$$\begin{aligned} \delta(\omega_0 - \omega + \xi_D \pm \xi_R) &= \delta(\omega_0 - \omega) + (\xi_D \pm \xi_R)\delta'(\omega_0 - \omega) + \\ &+ \frac{1}{2}(\xi_D \pm \xi_R)^2 \delta''(\omega_0 - \omega) + \dots \end{aligned} \quad (\text{E.45})$$

The expansion (E.45) can be ordered as a function of the small parameters introduced in the preceding paragraph so as to cause the successive appearance of terms of order zero, η_2 , $\eta_1\eta_2$, $\eta_2^2 \dots$, etc.

$$\begin{aligned} \delta(\omega_0 - \omega + \xi_D \pm \xi_R) &= \delta(\omega_0 - \omega) + \\ &+ \xi_D \delta'(\omega_0 - \omega) \pm \xi_R \delta'(\omega_0 - \omega) + \frac{1}{2}\xi_D^2 \delta''(\omega_0 - \omega) + \dots \end{aligned} \quad (\text{E.46})$$

In the equation giving $\dot{\pi}(\mathbf{p})$ obtained by summing the two equations (E.40), the contribution of first-order terms in η_1 or η_2 is zero because of the angular integral

$$\int \frac{d\Omega}{4\pi} k_l = 0 \quad (\text{E.47})$$

(where $l = x, y, z$). The terms in $\eta_1\eta_2$ come either from products of the second terms of developments (E.44) and (E.46) or from the third term of (E.46). By using

$$\int \frac{d\Omega}{4\pi} k_l k_m = \frac{k^2}{3} \delta_{lm} \quad (\text{E.48})$$

we find that the contribution of the terms in $\eta_1\eta_2$ to $\dot{\pi}$ is written

$$\begin{aligned} &- \Gamma \frac{d\langle n(\omega_0) \rangle}{d\omega_0} \frac{\hbar k_0^2}{3M} \nabla \cdot \{ \mathbf{p} [\pi_a(\mathbf{p}) - \pi_b(\mathbf{p})] \} + \\ &+ \Gamma \frac{5\hbar\omega_0}{3Mc^2} \nabla \cdot \{ \mathbf{p} [(\langle n(\omega_0) \rangle + 1)\pi_b(\mathbf{p}) - \langle n(\omega_0) \rangle \pi_a(\mathbf{p})] \}. \end{aligned} \quad (\text{E.49})$$

The terms in η_1^2 come from the second-order terms of the expansion

(E.44) of π_j . Their contribution to $\dot{\pi}$ is equal to

$$\Gamma \frac{\hbar^2 k_0^2}{6} [\langle n(\omega_0) \rangle \Delta\pi(\mathbf{p}) + \Delta\pi_b(\mathbf{p})]. \quad (\text{E.50})$$

Finally, the terms in η_2^2 cancel each other in (E.40.a) and (E.40.b) and disappear from the equation for $\dot{\pi}$.

Thus, up to order 2 in η_1 and η_2 , $\dot{\pi}(\mathbf{p})$ reduces to the sum of (E.49) and (E.50). It clearly appears that $\dot{\pi}(\mathbf{p})$ does not depend only on $\pi(\mathbf{p})$ [and the derivatives of $\pi(\mathbf{p})$ relative to \mathbf{p}]. The presence of $\pi_a(\mathbf{p})$ and $\pi_b(\mathbf{p})$ in (E.49) and (E.50) is a manifestation of the coupling that exists between internal and external variables.

Remark

In the order of perturbation considered here, $\dot{\pi}$ remains equal to the sum of (E.49) and (E.50) even when the second-order Doppler effect is included in ξ_D . This results from the fact that the linear term in ξ_D , obtained by expanding the delta function, disappears from the sum of (E.40.a) and (E.40.b) when we set $\mathbf{k} = \mathbf{0}$ in $\pi_j(\mathbf{p} \pm \hbar\mathbf{k})$.

γ) Adiabatic Elimination of Internal Variables

The fact that $\dot{\pi}(\mathbf{p})$ is smaller than $\dot{\pi}_a(\mathbf{p})$ or $\dot{\pi}_b(\mathbf{p})$ by a factor on the order of $\eta_1\eta_2$ or η_1^2 means that the characteristic evolution time of the external variables is much longer than that of the internal variables. We will use this difference between the two time scales to eliminate the internal variables from the equation giving $\dot{\pi}(\mathbf{p})$.

Because the terms (E.49) and (E.50), whose sum gives $\dot{\pi}(\mathbf{p})$, are already second order in η_1 and η_2 , we can limit ourselves to the order 0 in η_1 and η_2 to study the evolution of the populations $\pi_a(\mathbf{p})$ and $\pi_b(\mathbf{p})$ that appear in these terms. Thus, to order 0 in η_1 and η_2 , Equations (E.40) become

$$\dot{\pi}_b(\mathbf{p}) = \Gamma' \pi_a(\mathbf{p}) - (\Gamma + \Gamma') \pi_b(\mathbf{p}) \quad (\text{E.51.a})$$

$$\dot{\pi}_a(\mathbf{p}) = -\Gamma' \pi_a(\mathbf{p}) + (\Gamma + \Gamma') \pi_b(\mathbf{p}) \quad (\text{E.51.b})$$

where

$$\Gamma' = \Gamma \langle n(\omega_0) \rangle \quad (\text{E.51.c})$$

because the radiation is isotropic [see (E.16)]. Therefore, it follows that, to order 0 in η_1 and η_2 , $\pi_a(\mathbf{p})$ and $\pi_b(\mathbf{p})$ tend with a very short time constant

equal to $1/(\Gamma + 2\Gamma')$, to the values

$$\pi_a(\mathbf{p}) = \frac{\Gamma + \Gamma'}{\Gamma + 2\Gamma'} \pi(\mathbf{p}) = \frac{1 + \langle n(\omega_0) \rangle}{1 + 2\langle n(\omega_0) \rangle} \pi(\mathbf{p}) \quad (\text{E.52.a})$$

$$\pi_b(\mathbf{p}) = \frac{\Gamma'}{\Gamma + 2\Gamma'} \pi(\mathbf{p}) = \frac{n \langle (\omega_0) \rangle}{1 + 2\langle n(\omega_0) \rangle} \pi(\mathbf{p}). \quad (\text{E.52.b})$$

We can therefore consider that $\pi_a(\mathbf{p})$ and $\pi_b(\mathbf{p})$ adapt themselves quasi-instantaneously to the much slower variations of $\pi(\mathbf{p})$ and at each instant take the values given in (E.52). Substituting these equations into (E.49) and (E.50) thus allows us to “adiabatically eliminate” π_a and π_b in favor of π . The contribution of the second line of (E.49) is canceled and we obtain the following equation for $\dot{\pi}$:

$$\frac{\partial}{\partial t} \pi(\mathbf{p}, t) = \gamma \nabla \cdot [\mathbf{p} \pi(\mathbf{p}, t)] + \frac{D}{3} \Delta \pi(\mathbf{p}, t) \quad (\text{E.53})$$

where the coefficients γ and D are given by

$$\gamma = -\frac{\hbar k_0^2}{3M} \Gamma \frac{\Gamma}{\Gamma + 2\Gamma'} \frac{d\langle n(\omega_0) \rangle}{d\omega_0} \quad (\text{E.54})$$

$$D = \hbar^2 k_0^2 \frac{\Gamma'(\Gamma + \Gamma')}{\Gamma + 2\Gamma'}. \quad (\text{E.55})$$

The partial differential equation (E.53) is a Fokker–Planck equation which is very similar to the one encountered in the study of Brownian motion.

c) EVOLUTIONS OF THE MOMENTUM MEAN VALUE AND VARIANCE

To physically interpret the coefficient γ in (E.53), we calculate the rate of variation of the momentum mean value

$$\langle \mathbf{p} \rangle = \int d^3 p \mathbf{p} \pi(\mathbf{p}, t) \quad (\text{E.56})$$

by multiplying both sides of (E.53) by \mathbf{p} and integrating over \mathbf{p} . Integrating the two terms of the right-hand side by parts and assuming that $\pi(\mathbf{p})$ tends

to zero sufficiently rapidly when $|\mathbf{p}| \rightarrow \infty$, we obtain

$$\frac{d}{dt} \langle \mathbf{p} \rangle = -\gamma \langle \mathbf{p} \rangle. \quad (\text{E.57})$$

We assume in what follows that $d\langle n(\omega_0) \rangle / d\omega_0$ is negative, i.e., that the mean number of photons per mode is a decreasing function of ω near ω_0 . The coefficient γ defined in (E.54) is then positive and Equation (E.57) shows that it is the damping rate of the average momentum value (friction coefficient).

The same type of calculation results in

$$\frac{d}{dt} \langle \mathbf{p}^2 \rangle = -2\gamma \langle \mathbf{p}^2 \rangle + 2D \quad (\text{E.58})$$

which shows that the variance σ_p^2 of \mathbf{p}

$$\sigma_p^2 = \langle \mathbf{p}^2 \rangle - \langle \mathbf{p} \rangle^2 \quad (\text{E.59})$$

obeys, taking into account (E.57) and (E.58), the following equation:

$$\frac{d}{dt} \sigma_p^2 = -2\gamma \sigma_p^2 + 2D. \quad (\text{E.60})$$

The coefficient $2D$ thus characterizes the rate of increase of the variance of \mathbf{p} which is also damped at a rate 2γ . The coefficient D is thus a diffusion coefficient for the momentum (see §1-b in Complement C_{IV}).

We now attempt to qualitatively understand why the atomic velocity is damped if $d\langle n(\omega_0) \rangle / d\omega_0$ is negative. To do that, we consider a simplified one-dimensional model where the momenta of the atom and the photons are parallel or antiparallel to Ox . If the atom goes to the right ($v > 0$), the photons that propagate in the opposite direction must have a frequency lower than ω_0 , $\omega_0 - \omega_0 v/c$, in order to interact in a resonant manner with the atom, whereas the photons propagating in the same direction must have a higher frequency, $\omega_0 + \omega_0 v/c$ (Doppler effect). If $d\langle n(\omega_0) \rangle / d\omega_0$ is negative, the atom thus “sees” more resonant photons arriving in the direction opposite to its motion than in the same direction as its motion. The momentum that it will absorb will thus be directed preferentially in the direction opposite to its motion and the atom will be slowed down.

The foregoing reasoning can be made quantitative. Consider the mean momentum gained by an atom of momentum \mathbf{p} in absorption and stimulated emission processes. The atom has a relative probability $\hat{\pi}_a(\mathbf{p}) =$

$\pi_a(\mathbf{p})/\pi(\mathbf{p})$ of being in state a , so that during the time dt , it absorbs $\Gamma \langle n(\omega_0 + \mathbf{k} \cdot \mathbf{v}) \rangle \hat{\pi}_a(\mathbf{p}) dt d\Omega / 4\pi$ photons whose wave vector \mathbf{k} points into the solid angle $d\Omega$. The number of photons emitted through stimulated emission is given by a similar expression where $\hat{\pi}_a$ is replaced by $\hat{\pi}_b$. The rate of variation of the atomic momentum due to these processes is thus, to first order in $\mathbf{k} \cdot \mathbf{v}/\Delta\omega$,

$$\frac{d\mathbf{p}}{dt} = \hbar \mathbf{k} \Gamma \left[\langle n(\omega_0) \rangle + \frac{\mathbf{k} \cdot \mathbf{p}}{M} \frac{d\langle n(\omega_0) \rangle}{d\omega_0} \right] [\hat{\pi}_a(\mathbf{p}) - \hat{\pi}_b(\mathbf{p})] \frac{d\Omega}{4\pi}. \quad (\text{E.61})$$

The angular integration over $\kappa = \mathbf{k}/k$ thus gives, taking into account (E.47) and (E.48),

$$\frac{d\mathbf{p}}{dt} = \frac{\hbar k_0^2}{3M} \frac{d\langle n(\omega_0) \rangle}{d\omega_0} \Gamma [\hat{\pi}_a(\mathbf{p}) - \hat{\pi}_b(\mathbf{p})] \mathbf{p}. \quad (\text{E.62})$$

Spontaneous emission does not contribute to $d\mathbf{p}/dt$ because, in the reference frame of the atom, it occurs with equal probabilities in opposite directions and therefore does not cause the mean velocity of the atom to vary. Finally, by substituting into (E.62) the adiabatic expressions (E.52) for π_a and π_b and by averaging over the initial momentum \mathbf{p} of the atom, we recover equation (E.57) with the expression (E.54) for γ .

To understand the expression (E.55) for the diffusion coefficient D , note that for each elementary process of absorption, stimulated emission or spontaneous emission, the momentum of the atom varies by a quantity whose modulus equals $\hbar k_0$, and whose direction varies randomly from one process to another. In momentum space, the momentum of the atom thus makes a *random walk* with a step $\hbar k_0$. Let dn be the mean total number of elementary processes during dt for an atom of momentum \mathbf{p}

$$dn = [\Gamma' \hat{\pi}_a(\mathbf{p}) + (\Gamma + \Gamma') \hat{\pi}_b(\mathbf{p})] dt. \quad (\text{E.63})$$

According to the well-known properties of a random walk, the increase in \mathbf{p}^2 over a period dt equals

$$d\mathbf{p}^2 = \hbar^2 k_0^2 dn = \hbar^2 k_0^2 [\Gamma' \hat{\pi}_a(\mathbf{p}) + (\Gamma + \Gamma') \hat{\pi}_b(\mathbf{p})] dt. \quad (\text{E.64})$$

It is then sufficient to substitute the adiabatic expressions (E.52) for π_a and π_b into (E.64), and then to average over the initial momentum \mathbf{p} of the atom, to find that \mathbf{p}^2 increases as $2Dt$, where D is given by (E.55).

d) STEADY-STATE DISTRIBUTION. THERMODYNAMIC EQUILIBRIUM

The Fokker–Planck equation (E.53) can be written in the form of a continuity equation

$$\frac{\partial}{\partial t} \pi(\mathbf{p}, t) + \nabla \cdot \mathbf{J}(\mathbf{p}, t) = 0 \quad (\text{E.65})$$

where the “current” $\mathbf{J}(\mathbf{p}, t)$ is given by

$$\mathbf{J}(\mathbf{p}, t) = -\gamma \mathbf{p} \pi(\mathbf{p}, t) - \frac{D}{3} \nabla \pi(\mathbf{p}, t). \quad (\text{E.66})$$

It is then easy to verify that the Fokker–Planck equation has a steady-state solution ($\partial\pi/\partial t = 0$), given by the solution to the equation $\mathbf{J} = \mathbf{0}$, which is written

$$\pi_{\text{st}}(\mathbf{p}) = \mathcal{N} \exp\left[-\frac{3\gamma}{2D} \mathbf{p}^2\right] \quad (\text{E.67})$$

where \mathcal{N} is a normalization constant. In the steady state, the distribution function of momenta or velocities is thus Gaussian.

Finally, we consider the specific case where the radiation field interacting with the atom is in thermodynamic equilibrium. We must then use expression (E.17) for $\langle n(\omega_0) \rangle$. Using (E.16), we obtain for the coefficients γ and D given in (E.54) and (E.55)

$$\gamma = \frac{\Gamma}{6 \sinh(\hbar\omega_0/k_B T)} \frac{\hbar\omega_0}{k_B T} \frac{\hbar\omega_0}{Mc^2} \quad (\text{E.68.a})$$

$$D = \frac{\Gamma}{2 \sinh(\hbar\omega_0/k_B T)} \frac{\hbar^2\omega_0^2}{c^2}. \quad (\text{E.68.b})$$

Substituting (E.68) into (E.67) shows that

$$\pi_{\text{st}}(\mathbf{p}) = \mathcal{N} \exp\left[-\frac{\mathbf{p}^2}{2Mk_B T}\right] \quad (\text{E.69})$$

which is just a thermodynamic equilibrium distribution at temperature T . We thus generalize the results of subsection E-1 above and show that the external degrees of freedom, as well as the internal degrees of freedom,

reach thermodynamic equilibrium when the atoms interact with a radiation field which is itself in thermodynamic equilibrium.

GENERAL REFERENCES

Abragam (Chapter VIII), Louisell (Chapter 6), Cohen-Tannoudji (§4), Agarwal (Chapter 6). Also see the original article by R. K. Wangsness and F. Bloch, *Phys. Rev.*, **89**, 728 (1953).

The discussion of the evolution of atomic velocities in subsection E-2 was derived for the most part from the thesis of J. Dalibard, Université Pierre et Marie Curie, Paris (1986).

COMPLEMENT A_{IV}FLUCTUATIONS AND LINEAR RESPONSE
APPLICATION TO RADIATIVE PROCESSES

We showed in this chapter that, when the radiation field can be considered as a reservoir, the evolution of the density operator of the particles is described by a master equation. In this equation, the reservoir is involved only through a single function $g(\tau)$, which is a two-time average of an observable R of the reservoir.

The purpose of this complement is first to relate the real and imaginary parts of $g(\tau)$ to two statistical functions of the reservoir, a symmetric correlation function and a linear susceptibility function. We show in subsection 1 how these statistical functions can be used to characterize the way the small system is affected by its interaction with the reservoir. From this analysis, it is possible to derive a very general physical interpretation, according to which each of the two-coupled systems, the small system and the reservoir, fluctuates and polarizes the other. More precisely, on the one hand, there are processes in which the small system evolves according to its own dynamics, polarizes the reservoir, which in turn modifies the motion of the system; on the other hand, there are phenomena in which it is the fluctuations of the reservoir that polarize the small system and modify its properties.

We then apply (§2) these general results to the case of an atom interacting with a homogeneous and isotropic radiation field. Black-body radiation and the vacuum field are two examples of this type of situation. We evaluate the statistical functions associated with the atom and with the radiation field, and we interpret the atomic level shifts, as well as the energy exchanges between the atom and the radiation field as resulting from fluctuations of the radiation field and from the radiation reaction.

1. Statistical Functions and Physical Interpretation of the Master Equation

We start with expression (B.22) for the function $g(\tau)$, from which the coefficients (B.43) of the master equation are defined:

$$g(\tau) = T_R [\sigma_R \tilde{R}(\tau) \tilde{R}(0)]. \quad (1)$$

This function $g(\tau)$ is not real, even though R is Hermitian, because, in

general, $\tilde{R}(\tau)$ and $\tilde{R}(0)$ do not commute. To separate the real and imaginary parts of $g(\tau)$, we write

$$g(\tau) = \frac{1}{2} \langle \tilde{R}(\tau)\tilde{R}(0) + \tilde{R}(0)\tilde{R}(\tau) \rangle_R + \frac{i}{2} \langle [\tilde{R}(\tau), \tilde{R}(0)]/i \rangle_R \quad (2)$$

where $\langle \rangle_R$ indicates the average over the reservoir in the state defined by σ_R . The first term in (2) is a symmetric correlation function, and the second is related to a linear susceptibility of the reservoir. We analyze the properties of these two functions before returning to the interpretation of the master equation.

a) SYMMETRIC CORRELATION FUNCTION

Let $C_R(\tau)$ be the symmetric correlation function of the observable R

$$C_R(\tau) = \frac{1}{2} \langle \tilde{R}(\tau)\tilde{R}(0) + \tilde{R}(0)\tilde{R}(\tau) \rangle_R. \quad (3)$$

This function is real and tends to the ordinary correlation function in the classical limit. It gives a physical description of the dynamics of the fluctuations of the observable R in the state σ_R . If R were a random classical function of frequency ω_0 ,

$$R(t) = R_0 \exp[-i(\omega_0 t + \varphi)] + \text{c.c.} \quad (4)$$

and if the amplitude R_0 and the phase φ were independent random variables, φ being uniformly distributed between 0 and 2π , then the correlation function of R would equal

$$C_R(\tau) = \langle R_0^2 \rangle e^{-i\omega_0\tau} + \text{c.c.} \quad (5)$$

The explicit expression for the quantum correlation function defined by (3) is given by the real part of expression (B.23) for $g(\tau)$

$$C_R(\tau) = \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 \cos(\omega_{\mu\nu}\tau). \quad (6)$$

It appears in the form of a sum of expressions of the same type as (5) corresponding to the different Bohr frequencies involved in the motion of R . The function $C_R(\tau)$ is even in τ .

We also use the Fourier transform $\hat{C}_R(\omega)$ of $C_R(\tau)$ defined by

$$C_R(\tau) = \frac{1}{2\pi} \int d\omega \hat{C}_R(\omega) e^{-i\omega\tau} \quad (7)$$

and which equals

$$\hat{C}_R(\omega) = \sum_{\mu} p_{\mu} \sum_{\nu} \pi |R_{\mu\nu}|^2 [\delta(\omega + \omega_{\mu\nu}) + \delta(\omega - \omega_{\mu\nu})]. \quad (8)$$

The function $\hat{C}_R(\omega)$ is also real and even.

Remark

The function $C_R(\tau)$ is the autocorrelation function of the variable R . The correlation function for two different (real) variables R_p and R_q is defined by

$$C_{pq}(\tau) = \frac{1}{2} \langle \tilde{R}_p(0) \tilde{R}_q(\tau) + \tilde{R}_q(\tau) \tilde{R}_p(0) \rangle_R. \quad (9)$$

The previously described properties are generalized as follows:

$$C_{pq}(\tau) = C_{pq}^*(\tau); \quad C_{pq}(\tau) = C_{qp}(-\tau) \quad (10.a)$$

$$\hat{C}_{pq}^*(\omega) = \hat{C}_{pq}(-\omega); \quad \hat{C}_{pq}(\omega) = \hat{C}_{qp}(-\omega). \quad (10.b)$$

b) LINEAR SUSCEPTIBILITY

The symmetric correlation function (3) describes the fluctuations of the observable R of the reservoir. Another statistical function, the linear susceptibility, allows its linear response to an external perturbation to be characterized.

First recall some simple results for a classical damped harmonic oscillator. When such an oscillator is subjected to a periodic force

$$f(t) = F e^{-i\omega t} + \text{c.c.} \quad (11)$$

it has a forced oscillation motion of complex amplitude X :

$$x(t) = X e^{-i\omega t} + \text{c.c.} \quad (12)$$

The amplitude X is proportional to F

$$X = \hat{\chi}(\omega) F. \quad (13)$$

The coefficient of proportionality $\hat{\chi}(\omega)$ is the linear susceptibility of the

oscillator at the frequency ω . This is a function of the parameters characterizing the oscillator. Separation of the real and imaginary parts of $\hat{\chi}(\omega)$

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) + i\hat{\chi}''(\omega) \quad (14)$$

results in the appearance of the components $\hat{\chi}'F$ and $\hat{\chi}''F$ of the motion of x , respectively, in phase and in quadrature with the force $f(t)$. More generally, if $f(t)$ is a sum of oscillating exponentials:

$$f(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} F(\omega) e^{-i\omega t} \quad (15)$$

the response of the oscillator is the sum of the responses associated with each frequency ω :

$$x(t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \hat{\chi}(\omega) F(\omega) e^{-i\omega t}. \quad (16)$$

By inverting the Fourier transform (15) and introducing the Fourier transform of the function $\hat{\chi}(\omega)$

$$\chi(\tau) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \hat{\chi}(\omega) e^{-i\omega\tau} \quad (17)$$

expression (16) is written in the form

$$x(t) = \int_{-\infty}^{+\infty} \chi(t - t') f(t') dt'. \quad (18)$$

We now return to the reservoir \mathcal{R} , which is a quantum system. If it is subjected to a perturbation

$$V(t) = -R\lambda(t) \quad (19)$$

where $\lambda(t)$ is a classical function, its state will become slightly different from the initial steady state σ_R . From perturbation theory, we can determine the motion induced by this perturbation on the mean value of an observable, for example, R , whose mean value in the initial steady state is assumed to be zero for the sake of simplicity. To first order in λ (*), an

(*) See *Photons and Atoms—Introduction to Quantum Electrodynamics*, Exercise 6 in Complement E_{IV}.

expression similar to (18) is obtained for the mean value of R at time t ,

$$\langle R \rangle_t = \int_{-\infty}^{+\infty} \chi_R(\tau) \lambda(t - \tau) d\tau \quad (20)$$

where the linear susceptibility $\chi_R(\tau)$ of the reservoir is given by

$$\chi_R(\tau) = \frac{i}{\hbar} \theta(\tau) \langle [\tilde{R}(0), \tilde{R}(-\tau)] \rangle_R. \quad (21)$$

The mean value is taken as it was previously in the state σ_R of \mathcal{R} and $\theta(\tau)$ equals 1 for $\tau > 0$ and 0 for $\tau < 0$. The comparison of (2) and (21) yields the following relation between $\chi_R(\tau)$ and the imaginary part of $g(\tau)$:

$$\chi_R(\tau) = \frac{2}{\hbar} \theta(\tau) \operatorname{Im} g(-\tau). \quad (22)$$

The explicit expression for $\chi_R(\tau)$ is thus directly deduced from (B.23):

$$\chi_R(\tau) = -\frac{2}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 \theta(\tau) \sin \omega_{\mu\nu} \tau, \quad (23)$$

as well as its Fourier transform, defined as in (7):

$$\hat{\chi}_R(\omega) = \frac{-1}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 \left[\mathcal{P} \frac{1}{\omega_{\mu\nu} + \omega} + \mathcal{P} \frac{1}{\omega_{\mu\nu} - \omega} - i\pi \delta(\omega_{\mu\nu} + \omega) + i\pi \delta(\omega_{\mu\nu} - \omega) \right]. \quad (24)$$

In contrast to $\hat{C}_R(\omega)$, the function $\hat{\chi}_R(\omega)$ is not real, and it is advantageous to separate its real and imaginary parts which characterize the response in phase and in quadrature at the frequency ω :

$$\hat{\chi}_R(\omega) = \hat{\chi}'_R(\omega) + i\hat{\chi}''_R(\omega) \quad (25)$$

$$\hat{\chi}'_R(\omega) = -\frac{1}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 \left[\mathcal{P} \frac{1}{\omega_{\mu\nu} + \omega} + \mathcal{P} \frac{1}{\omega_{\mu\nu} - \omega} \right] \quad (26.a)$$

$$\hat{\chi}''_R(\omega) = \frac{\pi}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 [\delta(\omega_{\mu\nu} + \omega) - \delta(\omega_{\mu\nu} - \omega)]. \quad (26.b)$$

Note that $\hat{\chi}'_R(\omega)$ is even in ω , and that $\hat{\chi}''_R(\omega)$ is odd.

Remark

The generalization to the case of a coupling $V = -\sum_q R_q \lambda_q$ for formulas (20) and (21) is written

$$\langle R_p \rangle_t = \sum_q \int_{-\infty}^{+\infty} \chi_{pq}(\tau) \lambda_q(t - \tau) d\tau \quad (27)$$

$$\chi_{pq}(\tau) = \frac{i}{\hbar} \theta(\tau) \langle [\tilde{R}_p(0), \tilde{R}_q(-\tau)] \rangle_R. \quad (28)$$

If $\hat{\chi}'_{pq}$ and $\hat{\chi}''_{pq}$ are the reactive and dissipative parts defined by separating the principal parts and the delta functions as in (26.a) and (26.b) [these are no longer the real and imaginary parts of $\hat{\chi}_{pq}(\omega)$], their symmetry properties are

$$\hat{\chi}_{pq}(\omega) = \hat{\chi}_{pq}^*(-\omega) \quad (29)$$

$$\hat{\chi}'_{pq}(\omega) = [\hat{\chi}'_{qp}(\omega)]^* \quad \hat{\chi}''_{pq}(\omega) = [\hat{\chi}''_{qp}(\omega)]^*. \quad (30)$$

c) POLARIZATION ENERGY AND DISSIPATION

The linear susceptibility is also involved in the energy exchanges between the system and the external medium near equilibrium. To see this, we return to the example of the classical damped oscillator introduced at the beginning of the preceding subsection and we show that $\hat{\chi}'(\omega)$ and $\hat{\chi}''(\omega)$ appear, respectively, in the expressions giving the polarization energy of the oscillator and the energy dissipated by the damping processes. The results will suggest a physical interpretation for the quantum expressions giving the level shifts of the small system \mathcal{A} , due to its interaction with the reservoir (§1-d), and the energy exchange rates between \mathcal{A} and \mathcal{R} (§1-e).

In the steady-state regime, the work per unit time carried out by the external force (11), averaged over a period T , is equal to:

$$\begin{aligned} \dot{\mathcal{Q}} &= \frac{1}{T} \int_0^T dt f(t) \dot{x}(t) \\ &= \frac{1}{T} \int_0^T dt [-i\omega X e^{-i\omega t} + c.c.] [F e^{-i\omega t} + c.c.] \\ &= (-i\omega X F^* + c.c.) \\ &= \omega \hat{\chi}''(\omega) (2FF^*). \end{aligned} \quad (31)$$

This power is dissipated by the damping process of the oscillator. For this reason $\hat{\chi}''(\omega)$ is called the dissipative part of the susceptibility. It appears clearly in the first line of (31) that only the part f_v of the force $f(t)$ in phase with the velocity \dot{x} contributes to this process.

The other part of the force f_x , in phase with x , does no work in the steady state; it does work only when the oscillation amplitude varies. If this variation is slow, the corresponding work is stored in a reversible form in the oscillator. It is equal to

$$W = \int^t f_x(t') \dot{x}(t') dt'. \quad (32.a)$$

The quasi-stationary part of W equals

$$\bar{W} = \int^t dt' [F_x^* \dot{X} + \text{c.c.}] \quad (32.b)$$

where \dot{X} is the slow variation of the oscillation amplitude and where

$$F_x = \frac{\hat{\chi}'(\omega)}{|\hat{\chi}(\omega)|^2} X \quad (33)$$

is the part of the force in phase with X . In the presence of the driving force, a variation in the oscillation amplitude implies also a variation in the interaction energy

$$W_I = -f(t)x \quad (34)$$

which equals, on average over a period (only f_x contributes),

$$\bar{W}_I = -(F_x^* X + \text{c.c.}) \quad (35)$$

Therefore, in the presence of the driving force, and for slow variations of the parameters, the quantity $U = \bar{W} + \bar{W}_I$ plays the role of potential energy. When Equation (32.b) for \bar{W} is integrated by parts and combined with (35), one finds that the contribution from \bar{W}_I is cancelled and that U

is given by

$$\begin{aligned}
 U &= - \int^t dt' [\dot{F}_x^* X + \text{c.c.}] \\
 &= -\hat{\chi}'(\omega) \int^t dt' [\dot{X}^* X + \text{c.c.}] / |\hat{\chi}(\omega)|^2 \\
 &= -\hat{\chi}'(\omega) |X|^2 / |\hat{\chi}(\omega)|^2 = -\frac{1}{2} \hat{\chi}'(\omega) (2FF^*). \quad (36)
 \end{aligned}$$

U represents the reversible variation of the oscillator energy due to its “polarization” in the presence of the force $f(t)$. It is this reactive part $\hat{\chi}'(\omega)$ of the polarizability that is associated with this physical effect. We will call U the polarization energy, by analogy with the effect of a static electric field on a dielectric medium.

d) PHYSICAL INTERPRETATION OF THE LEVEL SHIFTS

The interaction of the small system \mathcal{A} with the reservoir \mathcal{R} among other effects, gives rise to a shift of the energy levels of \mathcal{A} given by formula (C.15) in the chapter. In this expression, the matrix element $\langle \mu, a | V | \nu, n \rangle$ can be factored into one part relative to \mathcal{A} and another part relative to \mathcal{R} :

$$\begin{aligned}
 \Delta_a &= \frac{1}{\hbar^2} \sum_{\mu} p_{\mu} \sum_{\nu} |\langle \mu | R | \nu \rangle|^2 \times \\
 &\quad \times \left(\sum_n |\langle a | A | n \rangle|^2 \mathcal{P} \frac{1}{\omega_{\mu\nu} + \omega_{an}} \right). \quad (37)
 \end{aligned}$$

To make the statistical functions discussed above appear in this expression, we express the fraction $1/(\omega_{\mu\nu} + \omega_{an})$ as a product of functions relative to each of the two systems, each of these functions having a given parity:

$$\begin{aligned}
 \mathcal{P} \frac{1}{\omega_{\mu\nu} + \omega_{an}} &= \frac{1}{4} \int d\omega \times \\
 &\quad \times \left\{ \left(\mathcal{P} \frac{1}{\omega_{\mu\nu} + \omega} + \mathcal{P} \frac{1}{\omega_{\mu\nu} - \omega} \right) (\delta(\omega + \omega_{an}) + \delta(\omega - \omega_{an})) + \right. \\
 &\quad \left. + \left(\mathcal{P} \frac{1}{\omega_{an} + \omega} + \mathcal{P} \frac{1}{\omega_{an} - \omega} \right) (\delta(\omega + \omega_{\mu\nu}) + \delta(\omega - \omega_{\mu\nu})) \right\}. \quad (38)
 \end{aligned}$$

When (38) is substituted into (37), $\hat{\chi}'_R(\omega)$, $\hat{\chi}'_{Aa}(\omega)$, $\hat{C}_R(\omega)$, and $\hat{C}_{Aa}(\omega)$, appear, where $\hat{C}_{Aa}(\omega)$ and $\hat{\chi}_{Aa}(\omega)$ are the symmetric correlation function and the linear susceptibility of the observable A of the system \mathcal{A} in the state $|a\rangle$, given by expressions analogous to (8) and (24) and where only $p_a = 1$ is nonzero. The shift Δ_a appears in the form of a sum of two terms:

$$\Delta_a = \Delta_a^{\text{fr}} + \Delta_a^{\text{rr}} \quad (39)$$

where

$$\hbar\Delta_a^{\text{fr}} = -\frac{1}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \hat{\chi}'_{Aa}(\omega) \hat{C}_R(\omega) \quad (40)$$

$$\hbar\Delta_a^{\text{rr}} = -\frac{1}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \hat{\chi}'_R(\omega) \hat{C}_{Aa}(\omega). \quad (41)$$

The interpretation of these expressions is simple if they are compared to formula (36): $\hat{C}_R(\omega)d\omega/2\pi$ represents the spectral density defined in (8) for the fluctuations of the observable R of the reservoir in the frequency band $d\omega$. The quantity $-(\frac{1}{2})\hat{\chi}'_{Aa}(\omega)\hat{C}_R(\omega)d\omega/2\pi$ is the polarization energy of the system \mathcal{A} in the state a perturbed by these fluctuations. Therefore, $\hbar\Delta_a^{\text{fr}}$ represents the polarization energy of the small system in the state a induced by the fluctuations of the variable R of the reservoir (the superscript fr indicates fluctuations of the reservoir).

In (41), the roles of \mathcal{A} and \mathcal{R} are reversed. Δ_a^{rr} represents the polarization energy of the reservoir by the small system. The motion of the observable A in the state $|a\rangle$, characterized by \hat{C}_{Aa} , perturbs the equilibrium of the reservoir, and the interaction of A with the polarization thus created in \mathcal{R} , proportional to $\hat{\chi}'_R$, gives rise to the energy shift $\hbar\Delta_a^{\text{rr}}$. This shift therefore represents the effect of the “reservoir reaction” on the small system (which explains the superscript rr). As before, only the reactive part $\hat{\chi}'_R$ of the polarizability of the reservoir contributes to the polarization energy.

e) PHYSICAL INTERPRETATION OF THE ENERGY EXCHANGES

We now consider energy exchanges between the system \mathcal{A} and the reservoir \mathcal{R} . To do this, we start with the rate of variation of the mean atomic energy for the atom initially in the state a :

$$\frac{d}{dt} \langle H_A \rangle_a = \sum_b (E_b - E_a) \Gamma_{a \rightarrow b} \quad (42)$$

where $\Gamma_{a \rightarrow b}$ is the transition rate from a to b , produced by the interaction with the reservoir and given by (C.5).

The replacement of $\Gamma_{a \rightarrow b}$ by its expression (C.5) gives a general explicit expression for $d\langle H_A \rangle_a / dt$:

$$\begin{aligned} \frac{d}{dt} \langle H_A \rangle_a &= \sum_b \hbar \omega_{ba} \left\{ \sum_\mu \frac{2\pi}{\hbar} p_\mu \sum_\nu |\langle \mu | R | \nu \rangle|^2 |\langle a | A | b \rangle|^2 \delta(\hbar \omega_{\mu\nu} + \hbar \omega_{ab}) \right\} \\ &= \frac{2\pi}{\hbar} \sum_\mu p_\mu \sum_\nu |\langle \mu | R | \nu \rangle|^2 \left(\sum_b \omega_{ba} |\langle a | A | b \rangle|^2 \delta(\omega_{\mu\nu} + \omega_{ab}) \right). \end{aligned} \quad (43)$$

We proceed as in subsection 1.d and write

$$\begin{aligned} \omega_{ba} \delta(\omega_{\mu\nu} + \omega_{ab}) &= \frac{1}{4} \int d\omega \omega \times \\ &\times \{ [\delta(\omega_{\mu\nu} + \omega) + \delta(\omega_{\mu\nu} - \omega)] [\delta(\omega + \omega_{ab}) - \delta(\omega - \omega_{ab})] + \\ &+ [\delta(\omega_{\mu\nu} - \omega) - \delta(\omega_{\mu\nu} + \omega)] [\delta(\omega + \omega_{ab}) + \delta(\omega - \omega_{ab})] \}. \end{aligned} \quad (44)$$

When (44) is substituted into (43), the statistical functions for \mathcal{A} and \mathcal{R} appear, and $d\langle H_A \rangle_a / dt$ appears in the form of a sum of two terms

$$\frac{d}{dt} \langle H_A \rangle_a = \dot{\mathcal{Q}}^{\text{fr}} + \dot{\mathcal{Q}}^{\text{rr}} \quad (45)$$

where

$$\dot{\mathcal{Q}}^{\text{fr}} = \int \frac{d\omega}{2\pi} \omega \hat{C}_R(\omega) \hat{\chi}_{Aa}''(\omega) \quad (46.a)$$

$$\dot{\mathcal{Q}}^{\text{rr}} = - \int \frac{d\omega}{2\pi} \omega \hat{\chi}_R''(\omega) \hat{C}_{Aa}(\omega). \quad (46.b)$$

The two terms (46.a) and (46.b) have an especially clear physical meaning when they are compared with expression (31) describing the absorption of energy by a system. The first involves the symmetric correlation function for the reservoir and the linear susceptibility of the atom. It thus describes

the absorption of energy by the small system, when this system is perturbed by the reservoir fluctuations. The second term involves the symmetric correlation function of the small system and the linear susceptibility of the reservoir. It describes the damping by the reservoir of the atomic motion. Because \dot{Q}^{rr} is the energy gained by the atom, $-\dot{Q}^{rr}$ is in fact the energy absorbed by the reservoir, according to the interpretation of expression (31).

2. Applications to Radiative Processes

We now assume that \mathcal{A} is an atom fixed at the origin $\mathbf{0}$ of the coordinate system and that \mathcal{R} is a homogeneous and isotropic broadband radiation field, defined by the probabilities $p(n_1, n_2, \dots, n_i, \dots)$ as in Section E of the chapter. The average number of photons in the mode i , $\langle n_i \rangle$, is defined by (E.12). It depends only on ω_i and is written $\langle n(\omega_i) \rangle$. This average number of photons per mode at the frequency ω_i is related to the energy density of the radiation field by (E.20). For the sake of simplicity, we take a simple model for the atom which consists of a single electron moving in a potential with spherical symmetry about the origin, inside a volume having small dimensions compared with the wavelengths of the incident radiation field. Thus, we can make the long-wavelength approximation for all the modes considered, whose frequency is less than a cutoff frequency ω_M .

Let \mathbf{r} and \mathbf{p} be operators for the position and momentum of the electron, q and m its charge and its mass, and $\mathbf{A}(\mathbf{0})$ the vector potential at $\mathbf{0}$. With the aforementioned approximations, the coupling between the atom and the radiation field is reduced to (*)

$$V = V_x + V_y + V_z \quad (47.a)$$

$$V_x = -\left(\frac{q}{m}p_x\right)A_x(\mathbf{0}). \quad (47.b)$$

The coupling does not have the simple form $V = -AR$, but is instead a sum of such couplings. However, because the system is isotropic, we can easily show that the rate of variation of the density matrix σ_A is the sum of the rates corresponding to V_x, V_y, V_z . Thus, it is sufficient to calculate the statistical functions relative to $R = A_x(\mathbf{0})$ for the field, and $A = qp_x/m$ for the atom and then to sum over x, y, z .

(*) In the long-wavelength approximation, the Hamiltonian H_{I2} does not act on the electron variables.

a) CALCULATION OF THE STATISTICAL FUNCTIONS

We begin with the calculations for the field. Expressions (8) for $\hat{C}_R(\omega)$ and (24) for $\hat{\chi}_R(\omega)$ have the same form:

$$S_{\pm}(\omega) = \sum_{\mu} p_{\mu} \sum_{\nu} |R_{\mu\nu}|^2 f^{\pm}(\omega_{\mu\nu}, \omega) \quad (48)$$

where $f^{\pm}(\omega_{\mu\nu}, \omega)$ is a function of given parity \pm with regard to $\omega_{\mu\nu}$: + for \hat{C} , and - for $\hat{\chi}$. Using a more precise notation for (48), we obtain

$$\begin{aligned} S_{\pm}(\omega) &= \sum_{\{n_i\}} p(n_1, \dots, n_i, \dots) \times \\ &\times \sum_j \left\{ |\langle \dots, n_j, \dots | A_x(\mathbf{0}) | \dots, n_j + 1, \dots \rangle|^2 f^{\pm}(-\omega_j, \omega) + \right. \\ &\left. + |\langle \dots, n_j, \dots | A_x(\mathbf{0}) | \dots, n_j - 1, \dots \rangle|^2 f^{\pm}(\omega_j, \omega) \right\}. \end{aligned} \quad (49)$$

We used the fact that $A_x(\mathbf{0})$ is linear in a_j and a_j^+ , and changes n_j by ± 1 . The matrix elements of (49) equal:

$$|\langle \dots, n_j, \dots | A_x(\mathbf{0}) | \dots, n_j \pm 1, \dots \rangle|^2 = \frac{\hbar}{2\epsilon_0\omega_j L^3} \epsilon_{jx}^2 \left(n_j + \frac{1}{2} \pm \frac{1}{2} \right). \quad (50)$$

The sum over the distributions of photons $\{n_i\}$ weighted by $p(\dots, n_i, \dots)$ causes $\langle n_i \rangle$ to appear, so that

$$\begin{aligned} S_{\pm}(\omega) &= \sum_j \frac{\hbar}{2\epsilon_0\omega_j L^3} \epsilon_{jx}^2 [\langle n_j + 1 \rangle f^{\pm}(-\omega_j, \omega) + \langle n_j \rangle f^{\pm}(\omega_j, \omega)] \\ &= \sum_j \frac{\hbar}{2\epsilon_0\omega_j L^3} \epsilon_{jx}^2 [\pm \langle n_j + 1 \rangle + \langle n_j \rangle] f^{\pm}(\omega_j, \omega). \end{aligned} \quad (51)$$

We replace the discrete sum over the modes by a sum over the polarizations, calculated by using formula (54) from Complement A_I, and an integral over \mathbf{k} (for which the angular part can be calculated explicitly

because $\langle n_j \rangle$ is assumed to depend only on ω_j). This yields

$$S_{\pm}(\omega) = \frac{1}{6\pi^2 \epsilon_0 c^3} \int_0^{\omega_M} d\omega' \hbar \omega' [\pm \langle n(\omega') + 1 \rangle + \langle n(\omega') \rangle] f^{\pm}(\omega', \omega). \quad (52)$$

This result applied successively to \hat{C}_R^{xx} , $\hat{\chi}_R'^{xx}$, $\hat{\chi}_R''^{xx}$ gives

$$\begin{aligned} \hat{C}_R^{xx}(\omega) &= \int_0^{\omega_M} \frac{d\omega'}{3\pi\epsilon_0 c^3} \hbar \omega' \langle n(\omega') + 1/2 \rangle [\delta(\omega' + \omega) + \delta(\omega' - \omega)] \\ &= \frac{1}{3\pi\epsilon_0 c^3} \hbar |\omega| \langle n(|\omega|) + 1/2 \rangle \end{aligned} \quad (53)$$

$$\hat{\chi}_R'^{xx}(\omega) = \frac{1}{6\pi^2 \epsilon_0 c^3} \int_0^{\omega_M} d\omega' \omega' \left[\mathcal{P} \frac{1}{\omega' + \omega} + \mathcal{P} \frac{1}{\omega' - \omega} \right] \quad (54)$$

$$\begin{aligned} \hat{\chi}_R''^{xx}(\omega) &= -\frac{1}{6\pi\epsilon_0 c^3} \int_0^{\omega_M} d\omega' \omega' [\delta(\omega' + \omega) - \delta(\omega' - \omega)] \\ &= \frac{1}{6\pi\epsilon_0 c^3} \omega. \end{aligned} \quad (55)$$

Before commenting on these expressions in the following subsection, we give the expressions $\hat{C}_{Aa}^{xx}(\omega)$ and $\hat{\chi}_{Aa}^{xx}(\omega)$ of the correlation function for the atomic variable qp_x/m , and the corresponding susceptibility, when the atom is in the state $|a\rangle$. The equations equivalent to (8), (26.a), and (26.b) are

$$\hat{C}_{Aa}^{xx}(\omega) = \sum_b \frac{q^2}{m^2} |\langle a | p_x | b \rangle|^2 \pi [\delta(\omega_{ab} + \omega) + \delta(\omega_{ab} - \omega)] \quad (56)$$

$$\hat{\chi}_{Aa}^{xx}(\omega) = \sum_b \frac{-q^2}{\hbar m^2} |\langle a | p_x | b \rangle|^2 \left[\mathcal{P} \frac{1}{\omega_{ab} + \omega} + \mathcal{P} \frac{1}{\omega_{ab} - \omega} \right] \quad (57)$$

$$\hat{\chi}_{Aa}''^{xx}(\omega) = \sum_b \frac{q^2}{\hbar m^2} |\langle a | p_x | b \rangle|^2 \pi [\delta(\omega_{ab} + \omega) - \delta(\omega_{ab} - \omega)]. \quad (58)$$

b) PHYSICAL DISCUSSION

The spectral density of the field fluctuations appears as the sum of two terms:

$$\hat{C}_R^{xx}(\omega) = \frac{1}{3\pi\epsilon_0 c^3} \left[\hbar|\omega| \langle n(|\omega|) \rangle + \frac{1}{2}\hbar|\omega| \right]. \quad (59)$$

The first involves the average number of photons per mode. By using (E.20), it can be put in the form $\pi u(\omega)/3\epsilon_0\omega^2$, thus showing that it is proportional to the energy density of the radiation at the frequency ω , a completely classical quantity. The second term adds 1/2 to $\langle n(\omega) \rangle$ for all the modes. It corresponds to the contribution of vacuum fluctuations, whose zero-point energy equals $\hbar\omega/2$. Therefore, the spectral density of vacuum fluctuations is identical to that of a random isotropic classical electromagnetic field whose frequency distribution corresponds to a half quantum per mode.

The situation is completely different for the susceptibility of the field, which is independent of $\langle n(\omega) \rangle$. This property is related to the linearity of Maxwell equations: The field created by a given source is independent of the existing field. In particular, this results in the fact that the susceptibility of the field is the same for a microscopic source as for a classical macroscopic source. Indeed, (54) and (55) do not contain \hbar . The susceptibility of the field is a classical variable.

Finally, note that, for $\omega > 0$,

$$\hat{C}_R^{xx}(\omega) = 2\hbar \langle n(\omega) + 1/2 \rangle \hat{\chi}_R''^{xx}(\omega). \quad (60)$$

At thermodynamic equilibrium, according to (E.17) we have

$$2\langle n(\omega) + 1/2 \rangle = \left[\tanh \frac{\hbar\omega}{2k_B T} \right]^{-1} \quad (61)$$

and

$$\hat{C}_R^{xx}(\omega) = \hbar \left[\tanh \frac{\hbar\omega}{2k_B T} \right]^{-1} \hat{\chi}_R''^{xx}(\omega). \quad (62)$$

In this particular case, this relation is an expression for the fluctuation-dissipation theorem, relating the spectral density of the fluctuations to the dissipative part of the susceptibility.

c) LEVEL SHIFTS DUE TO THE FLUCTUATIONS OF THE RADIATION FIELD

To calculate the effect on the atomic energy level $|a\rangle$ of the fluctuations of the radiation field, we explicitly calculate expression (40) for the case of the coupling of the atom with the component $A_x(\mathbf{0})$ of the vector potential. By using expressions (57) and (53) for $\hat{\chi}'_{Aa}^{xx}$ and \hat{C}_R^{xx} , we obtain

$$\begin{aligned} \hbar\Delta_{ax}^{\text{fr}} = & -\frac{1}{2}\int \frac{d\omega}{2\pi} \times \\ & \times \left\{ -\frac{1}{\hbar} \sum_b \frac{q^2}{m^2} |\langle a | p_x | b \rangle|^2 \left[\mathcal{P} \frac{1}{\omega_{ab} + \omega} + \mathcal{P} \frac{1}{\omega_{ab} - \omega} \right] \right\} \times \\ & \times \left\{ \frac{1}{3\pi\epsilon_0 c^3} \int_0^{\omega_M} d\omega' \hbar\omega' \langle n(\omega') + 1/2 \rangle [\delta(\omega' + \omega) + \delta(\omega' - \omega)] \right\}. \end{aligned} \quad (63)$$

In the integral over ω , the contributions of $\delta(\omega' + \omega)$ and $\delta(\omega' - \omega)$ are equal, because the rest of the integrand is even in ω . We must then add to (63) analogous contributions coming from $A_y(\mathbf{0})$ and $A_z(\mathbf{0})$, which gives

$$\begin{aligned} \hbar\Delta_a^{\text{fr}} = & \frac{q^2}{6\pi^2\epsilon_0 m^2 c^3} \sum_b |\langle a | p | b \rangle|^2 \times \\ & \times \int_0^{\omega_M} d\omega' \omega' \langle n(\omega') + 1/2 \rangle \left[\mathcal{P} \frac{1}{\omega_{ab} + \omega'} + \mathcal{P} \frac{1}{\omega_{ab} - \omega'} \right]. \end{aligned} \quad (64)$$

The energy-level shift due to the fluctuations of the field appears as the sum of the effect Δ'_a^{fr} of the incident photons, proportional to $\langle n(\omega) \rangle$, and of the effect of the fluctuations of the vacuum Δ_a^{fv} corresponding to the “1/2 per mode” term in (64).

First we expand Δ_a^{fv} . By using the following results

$$\int_0^{\omega_M} \omega' d\omega' \mathcal{P} \frac{1}{\omega' \pm \omega_0} = \omega_M \mp \omega_0 \ln \frac{\omega_M}{\omega_0} + O\left(\frac{\omega_0}{\omega_M}\right) \quad (65.a)$$

$$\int_0^{\omega_M} \omega' d\omega' \left[\mathcal{P} \frac{1}{\omega_0 + \omega'} + \mathcal{P} \frac{1}{\omega_0 - \omega'} \right] = -2\omega_0 \ln \frac{\omega_M}{\omega_0} \quad (65.b)$$

we obtain

$$\hbar\Delta_a^{\text{fv}} = \frac{q^2}{6\pi^2\epsilon_0 m^2 c^3} \sum_b |\langle a | \mathbf{p} | b \rangle|^2 (-\omega_{ab}) \ln \frac{\omega_M}{|\omega_{ab}|}. \quad (66)$$

As shown in Exercise 7, this expression can be transformed into

$$\hbar\Delta_a^{\text{fv}} = \frac{\alpha}{3\pi} \left(\frac{\hbar}{mc} \right)^2 \left(\ln \frac{\omega_M}{cK_a} \right) \langle a | \frac{q^2}{\epsilon_0} \delta(\mathbf{r}) | a \rangle \quad (67)$$

(α = fine structure constant, $\hbar c K_a$ = mean atomic excitation energy). This shift affects only the s states: this is the Lamb shift discussed previously in the treatment of radiative corrections (Chapter II, §E.1.b, Complement B_{II} and Exercise 7). The preceding calculation clearly shows its physical origin: the vacuum fluctuations cause the electron to undergo a vibrational motion during which it averages the Coulomb potential over a distance of approximately $\sqrt{\alpha} \hbar/mc$. The average potential differs from the value of the potential at the average position only inside the source of the Coulomb potential, hence the function $\delta(\mathbf{r})$. Note that the coefficient $\alpha(\hbar/mc)^2$ is proportional to \hbar : the Lamb shift is a quantum effect, just like the vacuum fluctuations that give rise to it. Nevertheless, once the existence of these fluctuations is acknowledged, their effect is the same as the one which would be produced by a random classical field characterized by a spectral density corresponding to an energy $\hbar\omega/2$ per mode.

We return now to the part Δ_a^{fr} of Δ_a^{fr} , proportional to $\langle n(\omega') \rangle$ [see (64)]. It corresponds to the stimulated radiative corrections that we described in subsection E.2 of Chapter II. For the sake of simplicity, assume that $\langle n(\omega') \rangle$ is appreciable only near a frequency ω_L close enough to ω_{ab} so that only a particular level contributes to the sum over all the levels b of (64). The corresponding shift of the level a equals

$$\hbar\Delta_a^{\text{fr}} \approx \frac{q^2}{6\pi^2\epsilon_0 m^2 c^3} |\langle a | \mathbf{p} | b \rangle|^2 \frac{2\omega_{ab}\omega_L}{\omega_{ab}^2 - \omega_L^2} \int d\omega' \langle n(\omega') \rangle. \quad (68)$$

This is the light shift due to the radiation field. Note that this quantity can also be expressed as a function of the mean quadratic value of the electric radiation field. In fact, $\langle n(\omega) \rangle d\omega$ is related to the energy density in the same frequency band $u(\omega) d\omega$ by formula (E.20), and the integral over ω'

of $u(\omega')$ is simply the energy density of the radiation

$$\int d\omega' u(\omega') = \frac{\epsilon_0}{2} \langle E_{\perp}^2 + c^2 B^2 \rangle = \epsilon_0 \langle E_{\perp}^2 \rangle. \quad (69)$$

(For a free and stationary radiation field $\langle E_{\perp}^2 \rangle = c^2 \langle B^2 \rangle$.) Using the relation $\langle a|p|b \rangle = \text{Im } \omega_{ab} \langle a|r|b \rangle$, and the approximation $|\omega_{ab}| \approx \omega_L$, we then have

$$\hbar \Delta_a^{\text{fr}} = \frac{\omega_{ab}}{\hbar(\omega_{ab}^2 - \omega_L^2)} q^2 \frac{|\langle a|r|b \rangle|^2}{3} \langle E_{\perp}^2 \rangle. \quad (70)$$

This expression, which causes the polarization energy of the atom by the electric field to appear, justifies the name “dynamic Stark effect” also given to Δ_a^{fr} .

d) LEVEL SHIFTS DUE TO RADIATION REACTION

Expression (41) for Δ_a^{rr} involves the “susceptibility” χ'_R of the field, which, according to (54), does not depend on $\langle n(\omega) \rangle$. The phenomenon of radiation reaction is therefore independent of the field incident on the atom.

By using expressions (54) for χ'^{xx}_R relative to $A_x(\mathbf{0})$ and (56) for \hat{C}_{Aa}^{xx} relative to p_x , then by summing over the analogous expressions with y and z , we obtain

$$\begin{aligned} \hbar \Delta_a^{\text{rr}} &= -\frac{1}{2} \int \frac{d\omega}{2\pi} \times \\ &\times \left\{ \frac{1}{6\pi^2 \epsilon_0 c^3} \int_0^{\omega_M} d\omega' \omega' \left[\mathcal{P} \frac{1}{\omega' + \omega} + \mathcal{P} \frac{1}{\omega' - \omega} \right] \right\} \times \\ &\times \left\{ \sum_b \frac{q^2}{m^2} |\langle a|p|b \rangle|^2 \pi [\delta(\omega_{ab} + \omega) + \delta(\omega_{ab} - \omega)] \right\} \\ &= -\frac{q^2}{12\pi^2 \epsilon_0 m^2 c^3} \sum_b \int_0^{\omega_M} d\omega' \omega' |\langle a|p|b \rangle|^2 \times \\ &\times \left[\mathcal{P} \frac{1}{\omega' + \omega_{ab}} + \mathcal{P} \frac{1}{\omega' - \omega_{ab}} \right]. \end{aligned} \quad (71)$$

The integral over ω' up to the limit ω_M thus yields, taking into account (65.a):

$$\begin{aligned}\hbar\Delta_a^{\text{rr}} &= \frac{-q^2}{6\pi^2\epsilon_0 m^2 c^3} \sum_b |\langle a | \mathbf{p} | b \rangle|^2 \omega_M \\ &= -\frac{4}{3} \frac{\delta m}{m} \langle a | \frac{\mathbf{p}^2}{2m} | a \rangle\end{aligned}\quad (72)$$

where δm is the correction to the mass of the particle associated with the Coulomb field and given by $\delta mc^2 = \epsilon_{\text{Coul}}$. Hence, the expression (72) is the correction to the kinetic energy of the particle associated with this change in mass. The factor $\frac{4}{3}$ is due to the noncovariant cutoff procedure we used to eliminate the effect of the high-frequency modes. The same factor also appears in classical theory.

Note that ϵ_{Coul} describes the energy associated with the interaction of the particle with its own Coulomb field, in the same way that Δ_a^{rr} describes the effect on the particle of its interaction with its own transverse field. These two effects are the same as those occurring in classical electromagnetism, as demonstrated by the absence of \hbar in the expression for δm . They are independent of the atomic potential and are therefore the same for a free particle. Another consequence of the increase in the mass of the particle is the decrease in its cyclotron frequency in a magnetic field. One can thus qualitatively explain why the Landé factor of the electron is greater than 2 (see Exercises 10 and 12).

e) ENERGY EXCHANGES BETWEEN THE ATOM AND THE RADIATION

We will now consider successively the rates $\dot{\mathcal{Q}}^{\text{fr}}$ and $\dot{\mathcal{Q}}^{\text{rr}}$ associated, respectively, with radiation fluctuations and radiation reaction.

With expressions (46.a), (59), and (58), and after summation of the effects relative to the three components x, y, z , $\dot{\mathcal{Q}}^{\text{fr}}$ is put in the form:

$$\begin{aligned}\dot{\mathcal{Q}}^{\text{fr}} &= \frac{-q^2}{3\pi\epsilon_0\hbar m^2 c^3} \sum_b |\langle a | \mathbf{p} | b \rangle|^2 \times \\ &\quad \times \omega_{ab} \left[\hbar |\omega_{ab}| \langle n(|\omega_{ab}|) \rangle + \frac{1}{2} \hbar |\omega_{ab}| \right].\end{aligned}\quad (73)$$

It is advantageous to write (73) in a form that exhibits the spontaneous emission rate Γ_{ab}^{sp} relative to the transition ab (which occurs of course from the highest level toward the lowest level). By expanding (E.4.a), we

find

$$\Gamma_{ab}^{sp} = \frac{q^2 |\langle a | \mathbf{p} | b \rangle|^2 |\omega_{ab}|}{3\pi\epsilon_0 \hbar m^2 c^3} \quad (74)$$

so that

$$\dot{\mathcal{Q}}^{fr} = \sum_b (E_b - E_a) \Gamma_{ab}^{sp} [\langle n(|\omega_{ab}|) \rangle + \frac{1}{2}] . \quad (75)$$

Just like a random classical perturbation, the fluctuations of the radiation field transfer the population of the state a toward other higher or lower levels b . As in subsection 2-b, the incident radiation field contributes to this process proportionately to $\langle n(|\omega_{ab}|) \rangle$ per mode, and vacuum fluctuations contribute proportionately to $\frac{1}{2}$. Note also that the latter yield a transition rate equal to only half of Γ_{ab}^{sp} .

The quantity $\dot{\mathcal{Q}}^{rr}$ is calculated in the same way from (46.b), (55), and (56). We find:

$$\dot{\mathcal{Q}}^{rr} = \frac{-1}{6\pi\epsilon_0 c^3} \sum_b \frac{q^2}{m^2} |\langle a | \mathbf{p} | b \rangle|^2 \omega_{ab}^2 . \quad (76)$$

This expression can be put into a particularly simple form, because $\langle a | \mathbf{p} | b \rangle \omega_{ab}$ is directly related to the matrix element of the acceleration $\ddot{\mathbf{r}}$ of the electron in the atomic potential:

$$\begin{aligned} \frac{1}{m} \langle a | \mathbf{p} | b \rangle \omega_{ab} &= \frac{1}{m\hbar} \langle a | [H_A, \mathbf{p}] | b \rangle \\ &= -\frac{i}{m} \langle a | \dot{\mathbf{p}} | b \rangle \\ &= -i \langle a | \ddot{\mathbf{r}} | b \rangle . \end{aligned} \quad (77)$$

We can then use the closure relation over b to obtain

$$\dot{\mathcal{Q}}^{rr} = -\frac{2}{3} \frac{q^2}{4\pi\epsilon_0 c^3} \langle a | (\ddot{\mathbf{r}})^2 | a \rangle . \quad (78)$$

The energy lost by the atom per unit time due to the radiation reaction is equal to the average in the state $|a\rangle$ of the power radiated classically by the particle, with this power being proportional to the square of the particle acceleration. $\dot{\mathcal{Q}}^{rr}$ is, moreover, always negative and corresponds to an energy loss, even for the ground state of the atom. Thus, we find here some results that are well known in classical electrodynamics: the Lorentz

damping force, and the fall of the electron onto the nucleus. Of course, it is not possible to consider only the effect of the radiation reaction, because even in the absence of radiation, vacuum fluctuations exist and play a role, as we saw in the preceding paragraph. To compare their respective roles, it is interesting to put (76) in the same form as (75). We obtain

$$\dot{\mathcal{Q}}^{\text{rr}} = \sum_b -|E_b - E_a| \frac{\Gamma_{ab}^{\text{sp}}}{2} \quad (79)$$

whereas

$$\dot{\mathcal{Q}}^{\text{fv}} = \sum_b (E_b - E_a) \frac{\Gamma_{ab}^{\text{sp}}}{2}. \quad (80)$$

If $|a\rangle$ is the ground state, $|E_b - E_a| = (E_a - E_b)$ and $\dot{\mathcal{Q}}^{\text{rr}} + \dot{\mathcal{Q}}^{\text{fv}} = 0$. The atomic ground state is stable, because vacuum fluctuations exactly cancel out the effect of the radiation reaction. The quantized character of the field, of which vacuum fluctuations are a manifestation, is therefore essential for preserving the stability of the ground state of the atom. This result is very general (*): The coupling of a quantized system to a classical dynamic system would lead to incoherences connected in the present case to the fact that the uncertainty relations would be violated for the electron if it were to lose energy from the ground state. If $|a\rangle$ is an excited level, the two energy variation rates cancel out for transitions toward levels b above a (the atom cannot gain energy) and are added together for transitions toward the lower levels b . Thus, we can say that vacuum fluctuations and the radiation reaction contribute equally to the total spontaneous emission transition rate Γ_{ab}^{sp} (**).

REFERENCES

A general discussion of correlation functions and susceptibilities can be found in Martin, Les Houches 1967. See also Landau and Lifchitz, *Statistical Physics*, Chapter XII.

For the particular application considered in this complement, more detailed discussions can be found in J. Dalibard, J. Dupont-Roc, and C. Cohen-Tannoudji, *J. Phys. (Paris)*, **43**, 1617 (1982); **45**, 637 (1984), and in the references therein cited.

(*) I. R. Senitzky *Phys. Rev. Lett.*, **20**, 1062 (1968).

(**) This is why heuristic calculations taking into account only one of these two effects lead to rates which are too small by a factor $\frac{1}{2}$.

COMPLEMENT B_{IV}

MASTER EQUATION FOR A DAMPED HARMONIC OSCILLATOR

1. The Physical System

In Section E of the chapter, we worked out the master equation for a two-level atom interacting with the radiation field. In this complement, we consider the case where the small system \mathcal{A} is a one-dimensional harmonic oscillator of frequency ω_0 whose Hamiltonian is

$$H_{\mathcal{A}} = \hbar\omega_0(b^+b + \frac{1}{2}) \quad (1)$$

where b^+ and b are the creation and annihilation operators of this oscillator. As in the example in Section E, the reservoir \mathcal{R} consists of an infinite number of one-dimensional harmonic oscillators i , of frequency ω_i with creation and annihilation operators a_i^+ and a_i , so that the Hamiltonian H_R for \mathcal{R} is written

$$H_R = \sum_i \hbar\omega_i(a_i^+a_i + \frac{1}{2}). \quad (2)$$

Finally, we take a very simple coupling Hamiltonian between \mathcal{A} and \mathcal{R} of the form

$$V = \sum_i (g_i b^+ a_i + g_i^* b a_i^+) \quad (3)$$

where g_i is the coupling constant between \mathcal{A} and the oscillator i of \mathcal{R} . Each term in (3) describes processes in which \mathcal{A} gains (or loses), one energy quantum $\hbar\omega_0$, whereas one oscillator i of \mathcal{R} loses (or gains) one quantum $\hbar\omega_i$. For the sake of simplicity, we have not included terms of the type ba_i or $b^+a_i^+$ in V because the antiresonant processes to which they give rise cannot contribute to the damping of \mathcal{A} .

Such a model can describe several different physical situations. For example, \mathcal{A} can be a matter harmonic oscillator, i.e., a charge elastically bound to the origin (and constrained to move on one axis, so as to be similar to a one-dimensional oscillator), and the oscillators i of \mathcal{R} can be the different modes of the radiation field. The master equation for \mathcal{A} thus describes how the motion of the elastically-bound charge is damped by the spontaneous emission, absorption and stimulated emission of radiation.

We can also consider \mathcal{A} to be a mode of an electromagnetic cavity, the oscillators i being matter oscillators contained in the walls of the cavity. The master equation for \mathcal{A} then describes the damping of this eigenmode of the cavity due to losses inside the walls.

Aside from its intrinsic interest in connection with the two preceding physical situations, the example discussed in this complement has the great advantage of leading to coupled Heisenberg equations for the operators b and a_i , which are *linear* with respect to these operators. It is then very easy to derive from these equations an evolution equation for b that closely resembles the Langevin equation used to describe Brownian motion in classical theory. This is done in Complement C_{IV}, which also establishes the relationship that exists between fluctuations and dissipation, in classical theory as well as in quantum theory.

To determine the form of the master equation for the harmonic oscillator, it is obvious that we can use the results from Section C of the chapter, and explicitly calculate the coefficients of the master equation in this particular case. Here we take a different approach, and starting from (B.30), directly derive an operator equation for the motion of σ , without making reference to any particular basis (§2). We then use this equation to derive the evolution equations for the populations of the energy levels of H_A , and for the average values of certain observables (§3). Finally, by projecting this equation onto a coherent state basis, we derive the evolution equation for the distribution of quasi-probability $P_N(\beta, \beta^*)$, which has the form of a Fokker–Planck equation (§4).

2. Operator Form of the Master Equation

We rewrite equation (B.30) with the change of variables (B.32) and use the fact that $\tau_c \ll \Delta t$ to extend to $+\infty$ the upper bound of the integral over $\tau = t' - t''$ and extend to t the lower bound of the integral over t' (see discussion at the end of subsection B-3). We then have

$$\begin{aligned} \frac{\Delta\tilde{\sigma}}{\Delta t} &= -\frac{1}{\hbar^2} \frac{1}{\Delta t} \int_0^\infty d(t' - t'') \times \\ &\quad \times \int_t^{t+\Delta t} dt' \text{Tr}_R [\tilde{V}(t'), [\tilde{V}(t''), \tilde{\sigma}(t) \otimes \sigma_R]]. \end{aligned} \quad (4)$$

We write V in the form

$$V = -[b^+ R^{(+)} + b R^{(-)}] \quad (5)$$

where

$$R^{(+)} = - \sum_i g_i a_i \quad R^{(-)} = - \sum_i g_i^* a_i^+. \quad (6)$$

Assume that σ_R is diagonal in the basis $\{|n_1, n_2 \cdots n_i \cdots\rangle\}$ of the eigenstates of H_R [σ_R is still given by formula (E.8)]. Of the two operators $\tilde{V}(t')$ and $\tilde{V}(t'')$ of (4), one must contain a_i , the other containing a_i^+ , so that the trace over R of their product multiplied by σ_R gives a nonzero result in (4). Such a restriction results in only two possibilities, the first consisting of taking $\tilde{V}(t') = -\tilde{b}^+(t')\tilde{R}^{(+)}(t')$ and $\tilde{V}(t'') = -\tilde{b}(t'')\tilde{R}^{(-)}(t'')$, while the second follows from the first by exchanging t' and t'' . Moreover, we can check that the two terms of (4) corresponding to these two possibilities are Hermitian conjugates of each other. In the interaction representation, the operators $\tilde{b}(t), \tilde{a}_i(t) \cdots$ have a very simple time dependence, $\tilde{b}(t) = b e^{-i\omega_0 t}, \tilde{a}_i(t) = a_i e^{-i\omega_i t} \cdots$ as a result of the simplicity of the commutators $[b, H_A], [a_i, H_R] \cdots$.

Finally, by using the invariance of a trace in a circular permutation and the fact that the integrand of (4) depends only on $t' - t''$, we obtain

$$\begin{aligned} \frac{\Delta\tilde{\sigma}}{\Delta t} = & -\frac{1}{\hbar^2} \times \\ & \times \left\{ (b^+ b \tilde{\sigma} - b \tilde{\sigma} b^+) \int_0^\infty \langle \tilde{R}^{(+)}(t') \tilde{R}^{(-)}(t'') \rangle_R e^{i\omega_0(t'-t'')} d(t' - t'') + \right. \\ & + (\tilde{\sigma} b b^+ - b^+ \tilde{\sigma} b) \int_0^\infty \langle \tilde{R}^{(-)}(t'') \tilde{R}^{(+)}(t') \rangle_R e^{i\omega_0(t'-t'')} d(t' - t'') \Big\} \\ & + \text{h.c.} \end{aligned} \quad (7)$$

We now calculate the two-time averages that appear in (7). By using (6) and (E.8), we obtain

$$\begin{aligned} \langle \tilde{R}^{(+)}(t') \tilde{R}^{(-)}(t'') \rangle_R &= \sum_i |g_i|^2 \langle a_i a_i^+ \rangle_R e^{-i\omega_i(t'-t'')} \\ &= \sum_i |g_i|^2 (\langle n_i \rangle + 1) e^{-i\omega_i(t'-t'')} \end{aligned} \quad (8)$$

where $\langle n_i \rangle$ is the average number of excitation quanta of the oscillator i , which is still given by (E.12). An analogous calculation gives

$$\langle \tilde{R}^{(-)}(t'') \tilde{R}^{(+)}(t') \rangle_R = \sum_i |g_i|^2 \langle n_i \rangle e^{-i\omega_i(t'-t'')}. \quad (9)$$

The first integral of (7) thus equals

$$\begin{aligned} & \frac{1}{\hbar^2} \int_0^\infty d\tau \sum_i |g_i|^2 (\langle n_i \rangle + 1) e^{-i(\omega_i - \omega_0)\tau} \\ &= \frac{1}{\hbar^2} \sum_i |g_i|^2 (\langle n_i \rangle + 1) \left[i \mathcal{P} \frac{1}{\omega_0 - \omega_i} + \pi \delta(\omega_0 - \omega_i) \right] \\ &= \frac{\Gamma + \Gamma'}{2} + i(\Delta + \Delta') \end{aligned} \quad (10)$$

where the quantities $\Gamma, \Gamma', \Delta, \Delta'$, which will be interpreted physically later on, are given by

$$\Gamma = \frac{2\pi}{\hbar} \sum_i |g_i|^2 \delta(\hbar\omega_0 - \hbar\omega_i) \quad (11.a)$$

$$\Gamma' = \frac{2\pi}{\hbar} \sum_i |g_i|^2 \langle n_i \rangle \delta(\hbar\omega_0 - \hbar\omega_i) \quad (11.b)$$

$$\hbar\Delta = \mathcal{P} \sum_i \frac{|g_i|^2}{\hbar\omega_0 - \hbar\omega_i} \quad (12.a)$$

$$\hbar\Delta' = \mathcal{P} \sum_i \frac{|g_i|^2 \langle n_i \rangle}{\hbar\omega_0 - \hbar\omega_i}. \quad (12.b)$$

For the second integral of (7) a similar calculation yields

$$\frac{1}{\hbar^2} \int_0^\infty d\tau \sum_i |g_i|^2 \langle n_i \rangle e^{-i(\omega_i - \omega_0)\tau} = \frac{\Gamma'}{2} + i\Delta'. \quad (13)$$

Finally, by substituting (10) and (13) into (7), by using $[b, b^\dagger] = 1$, and by returning to the Schrödinger representation, we obtain the following operator form for the master equation

$$\begin{aligned} \frac{d\sigma}{dt} = & -\frac{\Gamma}{2} [\sigma, b^\dagger b]_+ - \Gamma' [\sigma, b^\dagger b]_+ - \Gamma' \sigma - \\ & - i(\omega_0 + \Delta) [b^\dagger b, \sigma] + \\ & + \Gamma b \sigma b^\dagger + \Gamma' (b^\dagger \sigma b + b \sigma b^\dagger). \end{aligned} \quad (14)$$

In (14), $[A, B]_+$ represents the anticommutator $AB + BA$. Also note the absence of terms involving Δ' .

Remark

As in Section E, some simplifications appear if the average number of quanta $\langle n_i \rangle$ of the oscillator i depends only on the energy of this oscillator, and not on the parameters other than the energy that are used to characterize the oscillators. The same procedure as that leading to (E.16) then yields

$$\Gamma' = \Gamma \langle n(\omega_0) \rangle \quad (15)$$

where $\langle n(\omega_0) \rangle$ is the average number of quanta in the oscillators of the reservoir having the same frequency ω_0 as the oscillator \mathcal{A} . If, moreover, \mathcal{R} is in thermodynamic equilibrium, $\langle n(\omega_0) \rangle$ is equal to $[\exp(\hbar\omega_0/k_B T) - 1]^{-1}$.

3. Master Equation in the Basis of the Eigenstates of H_A

a) EVOLUTION OF THE POPULATIONS

Let σ_{nn} be the population of the energy level $|n\rangle$ of \mathcal{A} . Equation (14) taken in average value in the state $|n\rangle$ gives

$$\begin{aligned} \frac{d}{dt} \sigma_{nn} = & -n\Gamma\sigma_{nn} + (n+1)\Gamma\sigma_{n+1,n+1} + \\ & + (n+1)\Gamma'(\sigma_{n+1,n+1} - \sigma_{nn}) + n\Gamma'(\sigma_{n-1,n-1} - \sigma_{nn}). \end{aligned} \quad (16)$$

The interpretation of Γ and Γ' follows immediately from this equation. If we assume that \mathcal{A} is an atomic oscillator and \mathcal{R} the radiation field, then Γ is associated with the spontaneous emission process, and Γ' with the absorption and stimulated emission processes. More precisely, $n\Gamma$ is the spontaneous emission rate from the level $|n\rangle$ to the lower level $|n-1\rangle$: The level $|n\rangle$ empties by spontaneous emission to the level $|n-1\rangle$ at a rate $n\Gamma$ and is filled from the level $|n+1\rangle$ at a rate $(n+1)\Gamma$ (wavy lines in Figure 1). The factors n and $n+1$ are simply related to the squares of the moduli of the matrix elements of b and b^+ appearing in V [see (3)] between $|n\rangle$ and $|n-1\rangle$ or between $|n+1\rangle$ and $|n\rangle$. Similarly, the absorption processes empty the level $|n\rangle$ toward the level $|n+1\rangle$ at a rate $(n+1)\Gamma'$ and fill it from level $|n-1\rangle$ at a rate $n\Gamma'$ (rising arrows in Figure 1), the stimulated emission processes occurring in the opposite direction at the same rate (falling arrows).

The parameter Δ appearing in (14) is related to “spontaneous” radiative shifts occurring in the absence of any excitation of \mathcal{R} [$\hbar\Delta$ does not depend on $\langle n_i \rangle$ —see (12.a)]. Due to the structure of V , the ground

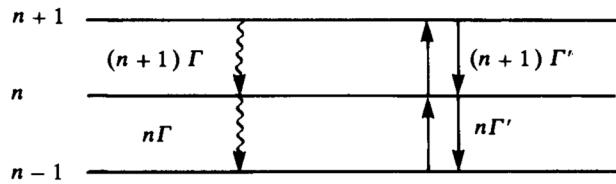


Figure 1. Transfer rate between energy levels of the harmonic oscillator associated with spontaneous emission processes (wavy lines) and absorption and stimulated emission processes (straight lines).

state $|0\rangle$ of the oscillator in the presence of the reservoir in the state $|0_1 0_2 \cdots 0_i\rangle$ is not coupled to any other state. The spontaneous radiative shift $\hbar\Delta_0$ of $|0\rangle$ is therefore zero. By contrast, if the oscillator is in the state $|1\rangle$, the coupling V given in (3) allows transitions in which \mathcal{A} falls from $|1\rangle$ to $|0\rangle$, whereas an oscillator i of \mathcal{R} goes from $|0_i\rangle$ to $|1_i\rangle$. The shift $\hbar\Delta$ is simply the radiative shift associated with such a process (summed over all the oscillators i). The same reasoning can be applied to an oscillator initially in the state $|n\rangle$, which then goes from $|n\rangle$ to $|n-1\rangle$, whereas an oscillator i goes from $|0_i\rangle$ to $|1_i\rangle$. Because $|\langle n-1|b|n\rangle|^2 = n|\langle 0|b|1\rangle|^2$, the spontaneous radiative shift of the state $|n\rangle$ equals $n\hbar\Delta$. Finally, the difference between the shifts $\hbar\Delta_n$ and $\hbar\Delta_{n-1}$ of two adjacent levels is independent of n and equals $\hbar\Delta$, which shows that the perturbed levels of the oscillator remain equidistant with an apparent frequency $\omega_0 + \Delta$, as expressed by the fourth term in (14).

Finally, we consider the last parameter Δ' . Because it depends on the $\langle n_i \rangle$ [see (12.b)], it represents a radiative shift due to the incoming radiation. We calculate such a shift for the level $|1\rangle$. A stimulated emission process causing the oscillator \mathcal{A} to fall from $|1\rangle$ to $|0\rangle$ and an additional quantum $\hbar\omega_i$ to appear in oscillator i shifts level $|1\rangle$ by the quantity $\hbar\Delta'$ given in (12.b). However, we must not forget the absorption processes that result in a jump from $|1\rangle$ to $|2\rangle$ for \mathcal{A} and the disappearance of a quantum $\hbar\omega_i$ for \mathcal{R} . Such a process shifts the level $|1\rangle$ by $-2\hbar\Delta'$, the negative sign resulting from the fact that the energy defect in the intermediate state now equals $\hbar(\omega_i - \omega_0)$, instead of $\hbar(\omega_0 - \omega_i)$ and the factor 2 coming from $|\langle 2|b^+|1\rangle|^2$. Finally, the global shift of the level $|1\rangle$ equals $+\hbar\Delta' - 2\hbar\Delta' = -\hbar\Delta'$. The same results holds for the level $|n\rangle$, which is shifted by $n\hbar\Delta' - (n+1)\hbar\Delta' = -\hbar\Delta'$. Thus, it is clear that the absorption and stimulated emission processes shift all the levels of \mathcal{A} by the same amount and therefore do not change the frequency of the oscillator. This is the reason why Δ' does not appear in (14).

b) EVOLUTION OF A FEW AVERAGE VALUES

First we calculate $d\langle b \rangle / dt$, which allows us to study how the mean position and the mean velocity of \mathcal{A} are damped. Because $\langle b \rangle = \text{Tr}(\sigma b)$

$$\frac{d}{dt} \langle b \rangle = \frac{d}{dt} \text{Tr}(\sigma b) = \text{Tr}\left(\frac{d\sigma}{dt} b\right). \quad (17)$$

We then substitute (14) into the last term of (17). By using the invariance of a trace in a circular permutation and the commutator $[b, b^+] = 1$, we easily obtain

$$\frac{d}{dt} \langle b \rangle = - \left[i(\omega_0 + \Delta) + \frac{\Gamma}{2} \right] \langle b \rangle. \quad (18)$$

Under the influence of the coupling of \mathcal{A} with \mathcal{R} , the oscillation of $\langle b \rangle$ thus undergoes a frequency shift Δ and is damped with a rate $\Gamma/2$.

The result (18) calls for two comments. First, the damping rate of the oscillator does not depend on its initial excitation, contrary to what Figure 1 might suggest, by showing transition rates between levels of \mathcal{A} that increase with the energy of these levels. Second, the damping rate depends only on Γ and not on Γ' . To attempt to understand these two points, we write the evolution equation of the coherence $\sigma_{n+1 n}$ involved in $\langle b \rangle = \sum_n \sqrt{n+1} \sigma_{n+1 n}$. Projecting (14) over $|n+1\rangle$ and $|n\rangle$ yields

$$\begin{aligned} \frac{d}{dt} \sigma_{n+1 n} = & -\frac{1}{2}(2n+1)\Gamma\sigma_{n+1 n} - \\ & -2(n+1)\Gamma'\sigma_{n+1 n} - i(\omega_0 + \Delta)\sigma_{n+1 n} + \\ & + \sqrt{(n+1)(n+2)}(\Gamma + \Gamma')\sigma_{n+2 n+1} + \sqrt{n(n+1)}\Gamma'\sigma_{n n-1}. \end{aligned} \quad (19)$$

The first two terms of (19) essentially describe a destruction of the coherence between $|n+1\rangle$ and $|n\rangle$ due to processes that empty the levels n and $n+1$. The global coefficient of $\sigma_{n+1 n}$ is indeed, according to (C.17), the half-sum of all the transition rates that leave from $|n\rangle$ and $|n+1\rangle$ and which all increase with n . By contrast, the last two terms of (19) describe coherence transfers, supplying $\sigma_{n+1 n}$ from $\sigma_{n+2 n+1}$ by spontaneous and stimulated emission, and from $\sigma_{n n-1}$ by absorption. These transfer terms exist only because the levels of \mathcal{A} are equidistant: the coherences $\sigma_{n+1 n}$, $\sigma_{n+2 n+1}$, and $\sigma_{n n-1}$ evolve at the same frequency (see the end of subsection C-2). These coherence transfers result in the

fact that $\langle b \rangle$ is damped at a rate independent of Γ' and much lower than the coefficient of $\sigma_{n+1,n}$ in (19) (*).

Finally, we calculate the evolution of $\langle b^+b \rangle$

$$\frac{d}{dt} \langle b^+b \rangle = \text{Tr} \left(\frac{d\sigma}{dt} b^+b \right). \quad (20)$$

The same calculation method as that leading to (18) yields

$$\frac{d}{dt} \langle b^+b \rangle = -\Gamma \langle b^+b \rangle + \Gamma'. \quad (21)$$

The spontaneous emission processes thus damp $\langle b^+b \rangle$ with a rate Γ , whereas the absorption and stimulated emission processes give rise to the source term Γ' . In the steady state

$$\langle b^+b \rangle_{\text{st}} = \frac{\Gamma'}{\Gamma}. \quad (22)$$

If the reservoir \mathcal{R} is in thermodynamic equilibrium, we can use (15) to show that

$$\langle b^+b \rangle_{\text{st}} = \langle n(\omega_0) \rangle = \frac{1}{e^{\hbar\omega_0/k_B T} - 1} \quad (23)$$

which is indeed the value corresponding to the oscillator \mathcal{A} at thermodynamic equilibrium.

4. Master Equation in a Coherent State Basis

In classic statistical mechanics, the state of the oscillator \mathcal{A} is defined by a given probability distribution in phase space. In quantum mechanics, the uncertainty relations between x and p prevent us from defining a state corresponding to a point in phase space. We can, however, replace these points by minimum uncertainty states, such as coherent states, and expand σ in the form of a sum of projectors over such states. The evolution equation of the quasi-probability describing the expansion of σ

(*) Such a result derived from the master equation is reminiscent of the result in Exercise 15. The equidistance between the energy levels of the harmonic oscillator gives rise to interferences between the different amplitudes associated with a radiative cascade and results in the fact that the spectral distribution of the emitted radiation is independent of the initial excitation of the oscillator.

over such a basis has the simple form of a Fokker–Planck equation which can be integrated exactly.

a) BRIEF REVIEW OF COHERENT STATES AND THE REPRESENTATION P_N OF THE DENSITY OPERATOR (*)

The coherent states of the oscillator \mathcal{A} are the eigenstates of the annihilation operator b , having eigenvalue β

$$b|\beta\rangle = \beta|\beta\rangle \quad (24.a)$$

$$\langle\beta|b^+ = \beta^*\langle\beta|. \quad (24.b)$$

They can also be written in the form

$$|\beta\rangle = e^{-\beta\beta^*/2} e^{\beta b^+} |0\rangle \quad (25)$$

or equivalently

$$|\beta\rangle = e^{-\beta\beta^*/2} \sum_{n=0}^{\infty} \frac{\beta^n}{\sqrt{n!}} |n\rangle. \quad (26)$$

A representation P_N (also known as a “Glauber representation”) exists for the density operator σ , if it can be written in the form

$$\sigma = \int d^2\beta P_N(\beta, \beta^*) |\beta\rangle\langle\beta| \quad (27)$$

where $d^2\beta = d\operatorname{Re}\beta d\operatorname{Im}\beta$. The advantage of the function $P_N(\beta, \beta^*)$ is that it closely resembles, in certain ways, a classical probability distribution. The hermiticity of σ ($\sigma = \sigma^+$) and its normalization ($\operatorname{Tr} \sigma = 1$) result in the fact that $P_N(\beta, \beta^*)$ is a real and normalized function. Also, it is easy to show that the mean value in the state σ of any function of b and b^+ arranged in the normal order (i.e., with all the b^+ to the left of the b) is thus quite simply expressed as a function of $P_N(\beta, \beta^*)$ (the index N in P_N refers to normal order):

$$\operatorname{Tr} \sigma(b^+)^l (b)^m = \int d^2\beta (\beta^*)^l (\beta)^m P_N(\beta, \beta^*). \quad (28)$$

The function $P_N(\beta, \beta^*)$ can, however, take negative values and relations as simple as (28) are no longer valid for orders other than the normal order. For this reason $P_N(\beta, \beta^*)$ is actually a quasi-probability distribution and not a probability distribution.

(*) For more details, see, for example, *Photons and Atoms—Introduction to Quantum Electrodynamics*, §C-4 in Chapter III and Exercises 5 and 6 of Complement D_{III}.

Remark

Other quasi-probability distributions are also used. For example, the distribution $P_A(\beta, \beta^*)$ gives expressions as simple as (28) for the mean values of products of operators $b''(b^+)^l$ arranged in antinormal order. Likewise, the Wigner distribution $W(\beta_1, \beta_2)$ is adapted to the calculation of mean values of symmetrized products of Hermitian operators $b_1 = (b + b^+)/\sqrt{2}$ and $b_2 = i(b^+ - b)/\sqrt{2}$. It can be shown (*) that P_A and W can be expressed as a function of P_N :

$$P_A(\beta, \beta^*) = \frac{1}{\pi} \int d^2\gamma P_N(\gamma, \gamma^*) \exp(-|\beta - \gamma|^2), \quad (29)$$

$$W(\beta_1, \beta_2) = \frac{2}{\pi} \int d^2\gamma P_N(\gamma, \gamma^*) \exp(-2|\gamma - \beta_1 - i\beta_2|^2). \quad (30)$$

b) EVOLUTION EQUATION FOR $P_N(\beta, \beta^*, t)$

When expression (27) is put into the master Equation (14), terms of the form $b|\beta\rangle\langle\beta|$ and $|\beta\rangle\langle\beta|b^+$ appear, which, according to (24), equal $\beta|\beta\rangle\langle\beta|$ and $\beta^*|\beta\rangle\langle\beta|$, respectively. Other terms, of the form $b^+|\beta\rangle\langle\beta|$ and $|\beta\rangle\langle\beta|b$ also appear, and we now explain how to calculate them. We consider β and β^* to be independent variables (instead of $\text{Re } \beta$ and $\text{Im } \beta$) and take the derivative with respect to β or β^* of the expression

$$|\beta\rangle\langle\beta| = e^{-\beta\beta^*} e^{\beta b^+} |0\rangle\langle 0| e^{\beta^* b} \quad (31)$$

which follows from (25). We then have

$$\begin{cases} \frac{\partial}{\partial\beta} |\beta\rangle\langle\beta| = -\beta^*|\beta\rangle\langle\beta| + b^+|\beta\rangle\langle\beta| \\ \frac{\partial}{\partial\beta^*} |\beta\rangle\langle\beta| = -\beta|\beta\rangle\langle\beta| + |\beta\rangle\langle\beta|b \end{cases} \quad (32)$$

which yields

$$\begin{aligned} b^+|\beta\rangle\langle\beta| &= \left(\beta^* + \frac{\partial}{\partial\beta} \right) |\beta\rangle\langle\beta| \\ |\beta\rangle\langle\beta|b &= \left(\beta + \frac{\partial}{\partial\beta^*} \right) |\beta\rangle\langle\beta|. \end{aligned} \quad (33)$$

(*) See, for example, H. Haken, *Rev. Mod. Phys.* **47**, 67 (1975), in particular page 116, and the references therein cited.

It is possible to transform each of the terms obtained after substituting (27) into (14). Consider, for example, the terms in $b^+ b \sigma$ of (14). They can be written, using (24) and (33)

$$\begin{aligned} b^+ b \sigma &= \int d^2\beta P_N(\beta, \beta^*) b^+ b |\beta\rangle\langle\beta| \\ &= \int d^2\beta P_N(\beta, \beta^*) \beta b^+ |\beta\rangle\langle\beta| \\ &= \int d^2\beta \beta P_N(\beta, \beta^*) \left(\beta^* + \frac{\partial}{\partial\beta} \right) |\beta\rangle\langle\beta|. \end{aligned} \quad (34)$$

Integrating the term in $\partial/\partial\beta$ by parts and assuming that $P_N(\beta, \beta^*)$ vanishes at infinity, we then obtain

$$b^+ b \sigma = \int d^2\beta \left\{ \beta^* \beta P_N(\beta, \beta^*) - \frac{\partial}{\partial\beta} [\beta P_N(\beta, \beta^*)] \right\} |\beta\rangle\langle\beta|. \quad (35)$$

Analogous calculations can be made for all the other terms of (14). By setting the coefficient of $|\beta\rangle\langle\beta|$ equal to zero in the integral over $d^2\beta$, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} P_N(\beta, \beta^*, t) &= \left(\frac{\Gamma}{2} + i\tilde{\omega}_0 \right) \frac{\partial}{\partial\beta} [\beta P_N(\beta, \beta^*, t)] + \\ &\quad + \left(\frac{\Gamma}{2} - i\tilde{\omega}_0 \right) \frac{\partial}{\partial\beta^*} [\beta^* P_N(\beta, \beta^*, t)] + \\ &\quad + \Gamma' \frac{\partial^2}{\partial\beta\partial\beta^*} P_N(\beta, \beta^*, t) \end{aligned} \quad (36)$$

where we have set $\tilde{\omega}_0 = \omega_0 + \Delta$.

c) PHYSICAL DISCUSSION

The first two terms of (36), in $\partial/\partial\beta$ and $\partial/\partial\beta^*$, are drift terms describing how the quasi-probability distribution drifts over time. The last term, in $\partial^2/\partial\beta\partial\beta^*$, is a diffusion term describing the broadening of the distribution.

Equations of the same type as (36) are known as Fokker–Planck equations and are used in a very general way to give an approximate description of the evolution of certain probability distributions [see, for

example, Equation (E.53)]. It should be noted that, for the simple model described here, the Fokker–Planck equation was derived without any approximation from the master equation.

One can check by substitution that the function

$$\frac{1}{\pi \langle n(\omega_0) \rangle (1 - e^{-\Gamma t})} \times \\ \times \exp - \frac{[\beta - \beta_0 e^{-(\Gamma/2 + i\tilde{\omega}_0)t}] [\beta^* - \beta_0^* e^{-(\Gamma/2 - i\tilde{\omega}_0)t}]}{\langle n(\omega_0) \rangle (1 - e^{-\Gamma t})} \quad (37)$$

which reduces to $\delta(\beta - \beta_0)\delta(\beta^* - \beta_0^*)$ for $t = 0$, is a solution of (36) and is therefore the Green's function for this equation. It is a Gaussian centered at a point in the complex plane that executes a spiral motion having angular velocity $\tilde{\omega}_0$ and a radius that decreases exponentially with time. The width of the Gaussian increases with time, from the value 0 for $t = 0$ to the value $\sqrt{\langle n(\omega_0) \rangle}$ for $t = \infty$. For $t \rightarrow \infty$, the expression (37) gives the representation P_N of the equilibrium state

$$P_N^{\text{eq}}(\beta, \beta^*) = \frac{1}{\pi \langle n(\omega_0) \rangle} \exp \left[-\frac{\beta^* \beta}{\langle n(\omega_0) \rangle} \right] \quad (38)$$

$\langle n(\omega_0) \rangle$ being given by (E.17) if the reservoir is in thermodynamic equilibrium.

Remark

Note a remarkable property of $P_N(\beta, \beta^*)$: If $\langle n(\omega_0) \rangle = 0$, i.e., if the reservoir is in the ground state $|0\rangle$, then the Green's function (37) remains a delta function of zero width regardless of t . Such a result expresses that, if a matter oscillator is initially in a coherent state (for which the representation P_N is a delta function), without any incident photons, it continues to remain in a coherent state when it decays by spontaneous emission.

REFERENCES

W. H. Louisell and J. H. Marburger, *IEEE J. Quantum Electron.*, **QE-3**, 348 (1967), and references therein. Louisell, Chapter VI. Glauber, §§8 and 9.

COMPLEMENT C_{IV}

QUANTUM LANGEVIN EQUATIONS FOR A SIMPLE PHYSICAL SYSTEM

The master equation derived in this chapter describes, in the Schrödinger representation, how a small system \mathcal{A} evolves under the influence of its interaction with a large reservoir \mathcal{R} . The purpose of this Complement is to approach the same problem in the *Heisenberg* representation. To simplify the calculations as much as possible, we limit ourselves to the simple model, introduced in Complement B_{IV}, of a harmonic oscillator \mathcal{A} coupled to a reservoir \mathcal{R} of harmonic oscillators. Our purpose is twofold: first, to show that the Heisenberg equations for the observables of \mathcal{A} can be put in a form similar to that of the Langevin equations for classical Brownian motion; then to use these *Heisenberg–Langevin* equations to analyze the relations that exist between *fluctuations and dissipation* and to calculate *correlation functions* for observables of \mathcal{A} .

We begin (§1) by reviewing the essentials of the classical theory of Brownian motion and by analyzing the Langevin equation used to describe such motion. We then derive (§2) the quantum Heisenberg–Langevin equations relative to the simple model of Complement B_{IV} and discuss for these equations the fluctuation-dissipation theorem as well as the quantum regression theorem relative to the correlation functions for \mathcal{A} .

1. Review of the Classical Theory of Brownian Motion

a) LANGEVIN EQUATION

A large particle having mass M and momentum \mathbf{p} is immersed in a homogeneous fluid of lighter particles with which it undergoes continuous collisions that make its motion erratic. The equation introduced by Langevin to phenomenologically describe such motion is written (for a component p of \mathbf{p}):

$$\frac{d}{dt}p(t) = -\gamma p(t) + F(t). \quad (1)$$

The total force acting on the particle is separated into two parts. The first, $-\gamma p(t)$, describes the cumulative effect of collisions, which is to damp the momentum of the particle with a friction coefficient γ . The second is a

fluctuating force $F(t)$, called the Langevin force, which describes the fluctuations of the instantaneous force around its average value. In Equation (1), $F(t)$ is considered to be an external force, independent of $p(t)$, described by a random stationary function of t , satisfying the following properties:

- (i) The average value of $F(t)$ is zero:

$$\overline{F(t)} = 0. \quad (2.a)$$

- (ii) The correlation function for the Langevin force, which describes the dynamics of the fluctuations of $F(t)$, has the form

$$\overline{F(t)F(t')} = 2Dg(t - t') \quad (2.b)$$

where D is a coefficient (that will be interpreted later on) and $g(t - t')$ is an even function of $t - t'$, of width τ_c , whose integral over $t - t'$ equals 1. The properties of parity and of invariance by translation in time of g result from the fact that $\overline{F(t)F(t')}$ is a classical stationary autocorrelation function. The correlation time τ_c of $F(t)$ is on the order of the collision time between the Brownian particle and a particle in the fluid. It is much shorter than the damping time $T_R = \gamma^{-1}$ of $\overline{p(t)}$, because several collisions are necessary to appreciably change the momentum of the heavy particle

$$\tau_c \ll T_R = \gamma^{-1}. \quad (3)$$

With regard to the functions of $t - t'$ varying slowly on the scale of τ_c , $g(t - t')$ thus appears as a delta function, so that the correlation function (2.b) can be approximated by

$$\overline{F(t)F(t')} \simeq 2D\delta(t - t'). \quad (4)$$

b) INTERPRETATION OF THE COEFFICIENT D . CONNECTION BETWEEN FLUCTUATIONS AND DISSIPATION

We now study the evolution of $p(t)$ starting from a well-defined initial value $p(t_0) = p_0$. Integrating (1) gives

$$p(t) = p_0 e^{-\gamma(t-t_0)} + \int_{t_0}^t dt' F(t') e^{-\gamma(t-t')}. \quad (5)$$

Using (2.a), we then obtain for $\overline{p(t)}$

$$\overline{p(t)} = p_0 e^{-\gamma(t-t_0)}. \quad (6)$$

The average momentum therefore is damped with a rate γ . We now calculate the evolution of the variance $\sigma_p^2(t)$ of $p(t)$:

$$\sigma_p^2(t) = \overline{[p(t)]^2} - \overline{[p(t)]}^2 = \overline{[p(t) - \overline{p(t)}]^2}. \quad (7)$$

Using (5) and (6)

$$p(t) - \overline{p(t)} = \int_{t_0}^t dt' F(t') e^{-\gamma(t-t')} \quad (8)$$

so that

$$\sigma_p^2(t) = \int_{t_0}^t dt' \int_{t_0}^t dt'' \overline{F(t') F(t'')} e^{-\gamma(t-t')} e^{-\gamma(t-t'')}. \quad (9)$$

The two exponentials of (9) vary slowly on the scale of τ_c . Using (4) then gives (for $t - t_0 \gg \tau_c$)

$$\sigma_p^2(t) = 2D \int_{t_0}^t dt' e^{-2\gamma(t-t')} = \frac{D}{\gamma} [1 - e^{-2\gamma(t-t_0)}]. \quad (10)$$

Equation (10) shows that $\sigma_p^2(t)$, i.e., the dispersion of the possible values of p , begins by increasing linearly with $t - t_0$:

$$\sigma_p^2(t) \simeq 2D(t - t_0) \quad \text{for } \tau_c \ll t - t_0 \ll \gamma^{-1}. \quad (11)$$

D then appears as a *momentum diffusion coefficient*.

At long times ($t - t_0 \gg \gamma^{-1}$), Equation (10) shows that $\sigma_p^2(t)$ tends to an equilibrium value equal to D/γ , whereas $\overline{p(t)}$ tends to zero according to (6). It follows from (7) that the equilibrium value of $\overline{p^2}$ is

$$\overline{p^2} = \frac{D}{\gamma}. \quad (12)$$

If the fluid is in thermodynamic equilibrium, this equilibrium value must

satisfy

$$\frac{\overline{p^2}}{2M} = \frac{1}{2}k_B T. \quad (13)$$

Substituting (12) into (13) and solving for D then gives the Einstein equation

$$D = Mk_B T \gamma \quad (14)$$

establishing a relationship between the diffusion coefficient D characterizing the *fluctuations* of the Langevin force acting on p and the friction coefficient γ characterizing the *dissipation* force acting on this same variable p . Recall that, according to (11), D also appears as the diffusion coefficient of p .

Remark

Let

$$\delta p(t) = p(t_0 + \delta t) - p(t_0) = p(t_0 + \delta t) - p_0 \quad (15)$$

be the increase of $p(t)$ between t_0 and $t_0 + \delta t$ with $\tau_c \ll \delta t \ll \gamma^{-1}$. Equations (6) and (11) then give

$$\overline{\delta p(t)} = p_0 e^{-\gamma \delta t} - p_0 \approx -p_0 \gamma \delta t \quad (16)$$

$$\overline{[\delta p(t) - \overline{\delta p(t)}]^2} = \overline{[\delta p(t)]^2} - [\overline{\delta p(t)}]^2 = 2D \delta t. \quad (17)$$

Because $[\overline{\delta p(t)}]^2$ varies as $p_0^2 \gamma^2 \delta t^2$ according to (16) and is thus negligible as compared to $D \delta t$, we can write (17) in the form

$$\overline{[\delta p(t)]^2} = 2D \delta t. \quad (18)$$

Equations (16) and (18) give the first- and second-order moments of the increase δp of p over a short time.

c) A FEW CORRELATION FUNCTIONS

We make t_0 tend to $-\infty$ in (5). The random function $p(t)$ has then lost any memory of the initial conditions and can be written at time t' :

$$p(t') = \int_{-\infty}^{t'} dt'' F(t'') e^{-\gamma(t'-t'')}. \quad (19)$$

a) *Correlation between the Momentum and the Langevin Force*

Multiply both sides of (19) by $F(t)$ and take the average value. This gives

$$\overline{p(t')F(t)} = \int_{-\infty}^{t'} dt'' \overline{F(t'')F(t)} e^{-\gamma(t'-t'')} \quad (20)$$

If t is in the future of t' and if $t - t' \gg \tau_c$, we have in (20) $t - t'' \gg \tau_c$ (because $t'' < t'$), so that $\overline{F(t'')F(t)}$ is zero:

$$\overline{p(t')F(t)} = 0 \quad \text{if } t - t' \gg \tau_c. \quad (21)$$

Equation (21) shows that $p(t')$, which depends on the Langevin force in the past of t' , cannot be correlated with the Langevin force $F(t)$ at a time t in the future of t' if $t - t' \gg \tau_c$.

If t is in the past of t' and if $t' - t \gg \tau_c$, we can use (4) and Equation (20) then gives:

$$\overline{p(t')F(t)} = 2D e^{-\gamma(t'-t)} \quad \text{if } t' - t \gg \tau_c. \quad (22)$$

Finally, for t close to t' ($|t - t'| \leq \tau_c$), $\overline{p(t')F(t)}$ varies rapidly between $2D$ and 0 over an interval of width τ_c , and takes a value equal to D for $t = t'$ [this results from Equation (20) written for $t' = t$ and from the fact that $\overline{F(t'')F(t)}$ is even].

All these results are summarized in Figure 1, which shows the variations with t of $\overline{p(t')F(t)}$. The important point, that we will use later on,

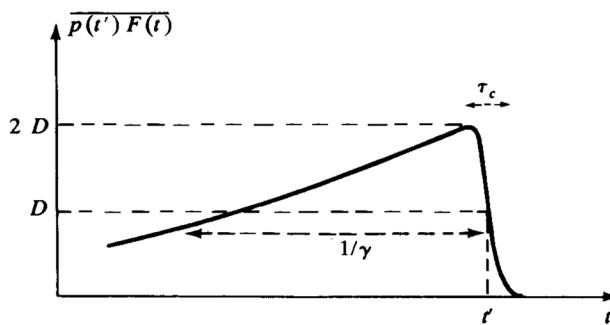


Figure 1. Variations with t of $\overline{p(t')F(t)}$.

is that $p(t')$ is decorrelated from $F(t)$ if $t \geq t'$, except in a small interval of width τ_c near $t = t'$, where $\overline{p(t')F(t)}$ remains finite and on the order of D .

β) Momentum Autocorrelation Function

Multiply both sides of (1) by $p(t')$ and take the average value. This gives

$$\frac{d}{dt} \overline{p(t)p(t')} = -\gamma \overline{p(t)p(t')} + \overline{F(t)p(t')} \quad (23)$$

with the initial condition $\overline{p(t=t')p(t')} = \overline{p^2}$. We will now show that the second term of the right-hand side of (23) can be ignored for $t \geq t'$. Replace t by t'' in (23) and integrate over t'' from t' to t . The contribution of $\overline{F(t'')p(t')}$ to $\overline{p(t)p(t')}$ is equal to $\int_{t'}^t dt'' \overline{F(t'')p(t')}$ and remains bounded by $D\tau_c$ according to Figure 1. Using (3), this contribution is very small compared with $D\gamma^{-1}$, which is simply the initial value $\overline{p^2}$ of $\overline{p(t)p(t')}$ according to (12). One can thus ignore it and consider that, for $t \geq t'$, $\overline{p(t)p(t')}$ obeys

$$t \geq t' \quad \frac{d}{dt} \overline{p(t)p(t')} = -\gamma \overline{p(t)p(t')} \quad (24)$$

It thus appears that $\overline{p(t)p(t')}$ decreases exponentially with $t - t'$ starting from an initial value given by (12). Because $\overline{p(t)p(t')}$ is an autocorrelation function and is thus even in $t - t'$, we finally have

$$\overline{p(t)p(t')} \approx \overline{p^2} e^{-\gamma|t-t'|}. \quad (25)$$

Equation (25) shows that the correlations between $p(t)$ and $\overline{p(t')}$ decrease, i.e., “regress” in the same way as the average value $\overline{p(t)}$, which obeys the equation

$$\frac{d}{dt} \overline{p(t)} = -\gamma \overline{p(t)} \quad (26)$$

analogous to (24).

We could have obtained expression (25) directly from (19) and (4). The advantage of the derivation presented here is that it can be generalized in quantum theory, leading to the “quantum regression” theorem (see §2-g).

Remark

The effect of the correction introduced by the last term in (23) is to round off the sharp point of (25) in $t = t'$ and to make $p(t)p(t')$ start with a horizontal tangent at this point. To derive such a result, we consider the Fourier transforms $\tilde{p}(\omega)$ and $\tilde{F}(\omega)$ of $p(t)$ and $F(t)$. Equation (1) leads to

$$|\tilde{p}(\omega)|^2 = \frac{|\tilde{F}(\omega)|^2}{\gamma^2 + \omega^2}. \quad (27)$$

We can then use the Wiener–Kinchine theorem, which states that the Fourier transforms of $|\tilde{p}(\omega)|^2$ and $|\tilde{F}(\omega)|^2$ are (except for multiplicative coefficients) the autocorrelation functions $\overline{p(t)p(t')}$ and $\overline{F(t)F(t')}$. According to (27), $\overline{p(t)p(t')}$ is thus the convolution product of the Fourier transform of $(\gamma^2 + \omega^2)^{-1}$, i.e., $e^{-\gamma|t-t'|}$, by the Fourier transform of $|\tilde{F}(\omega)|^2$, i.e., $g(t-t')$. Because the width τ_c of $g(t-t')$ is much smaller than that, γ^{-1} , of $\exp(-\gamma|t-t'|)$, we again find that $\overline{p(t)p(t')}$ is nearly equal to $\exp(-\gamma|t-t'|)$, apart from small corrections in τ_c/T_R which round off the sharp point at $t = t'$ over an interval of width τ_c .

2. Heisenberg–Langevin Equations for a Damped Harmonic Oscillator

We now return to the model, introduced in Complement B_{IV}, of a harmonic oscillator \mathcal{A} (of frequency ω_0 , with creation and annihilation operators b^+ and b) coupled to a reservoir of oscillators i (of frequency ω_i , with creation and annihilation operators a_i^+ and a_i). The total Hamiltonian H can be expressed as

$$\begin{aligned} H &= H_A + H_R + V \\ &= \hbar\omega_0 \left(b^+ b + \frac{1}{2} \right) + \sum_i \hbar\omega_i (a_i^+ a_i + \frac{1}{2}) + \sum_i (g_i b^+ a_i + g_i^* b a_i^+) \end{aligned} \quad (28)$$

where g_i is a coupling constant.

a) COUPLED HEISENBERG EQUATIONS

The Heisenberg equation for $b(t)$ is written

$$i\hbar \frac{d}{dt} b(t) = [b(t), H] = \hbar\omega_0 b(t) + \sum_i g_i a_i(t). \quad (29)$$

It depends on the operators $a_i(t)$ of the reservoir whose evolution equation has a similar form:

$$i\hbar \frac{d}{dt} a_i(t) = [a_i(t), H] = \hbar \omega_i a_i(t) + g_i^* b(t). \quad (30)$$

The evolutions of the annihilation operators $b(t)$ and $a_i(t)$ are thus coupled to each other by the linear equations (29) and (30). Note that the simplicity of these equations results from the bilinear form in b or b^+ and a_i or a_i^+ that we have chosen for the interaction V and from the fact that the commutators $[b, b^+]$ and $[a_i, a_i^+]$ simply equal 1. In Complement A_V we will consider the case where the oscillator \mathcal{A} is replaced by a two-level system. The last term of the equation analogous to (29) is then nonlinear because, in this case, it depends not only on the $a_i(t)$, but also on the operators of \mathcal{A} .

It will be convenient for what follows to set:

$$b(t) = \hat{b}(t) e^{-i\omega_0 t} \quad (31.a)$$

$$a_i(t) = \hat{a}_i(t) e^{-i\omega_i t} \quad (31.b)$$

so that \hat{b} and \hat{a}_i evolve only under the influence of V . Equations (29) and (30) then become

$$i\hbar \frac{d}{dt} \hat{b}(t) = \sum_i g_i \hat{a}_i(t) e^{i(\omega_0 - \omega_i)t} \quad (32)$$

$$i\hbar \frac{d}{dt} \hat{a}_i(t) = g_i^* \hat{b}(t) e^{i(\omega_i - \omega_0)t}. \quad (33)$$

b) THE QUANTUM LANGEVIN EQUATION AND QUANTUM LANGEVIN FORCES

We integrate Equation (33) to get

$$\hat{a}_i(t) = \hat{a}_i(t_0) - \frac{i}{\hbar} g_i^* \int_{t_0}^t dt' \hat{b}(t') e^{i(\omega_i - \omega_0)t'} \quad (34)$$

and insert the result obtained into (32). This gives

$$\frac{d}{dt} \hat{b}(t) = - \int_0^{t-t_0} d\tau \kappa(\tau) \hat{b}(t-\tau) + \hat{F}(t) \quad (35)$$

where

$$\kappa(\tau) = \frac{1}{\hbar^2} \sum_i |g_i|^2 e^{i(\omega_0 - \omega_i)\tau} \quad (36)$$

$$\hat{F}(t) = -\frac{i}{\hbar} \sum_i g_i \hat{a}_i(t_0) e^{i(\omega_0 - \omega_i)t}. \quad (37)$$

First consider the function $\kappa(\tau)$ given in (36). Since \mathcal{R} is a reservoir, the frequencies ω_i of the oscillators cover a very wide range. Besides, $|g_i|^2$ generally varies slowly with ω_i . It follows that the set of oscillating exponentials of (36) interfere destructively when τ increases starting from 0, so that $\kappa(\tau)$ becomes negligible as soon as $\tau \gg \tau_c$, where τ_c is the correlation time of the reservoir. In addition, $\hat{b}(t - \tau)$ varies much more slowly with τ , over a time scale $T_R \gg \tau_c$, where T_R is the damping time of \mathcal{A} . We can then neglect the variation with τ of $\hat{b}(t - \tau)$ as compared to that of $\kappa(\tau)$ in the integral of (35), and replace $\hat{b}(t - \tau)$ by $\hat{b}(t)$ which may then be removed from the integral. Assuming $t - t_0 \gg \tau_c$, we get in this way

$$\begin{aligned} \int_0^\infty \kappa(\tau) d\tau &= \frac{1}{\hbar^2} \lim_{\eta \rightarrow 0_+} \sum_i |g_i|^2 \int_0^\infty e^{i(\omega_0 - \omega_i + i\eta)\tau} d\tau \\ &= \frac{1}{\hbar^2} \sum_i |g_i|^2 \left\{ \pi \delta(\omega_0 - \omega_i) + i \mathcal{P} \frac{1}{\omega_0 - \omega_i} \right\} \\ &= \frac{\Gamma}{2} + i\Delta \end{aligned} \quad (38)$$

where Γ and $i\Delta$ are the parameters that were introduced in expressions (11.a) and (12.a) in Complement B_{IV} and which describe respectively the spontaneous emission rate and the spontaneous radiative shift of the oscillator. Equation (35) can then be rewritten:

$$\frac{d}{dt} \hat{b}(t) = -\left(\frac{\Gamma}{2} + i\Delta\right) \hat{b}(t) + \hat{F}(t). \quad (39)$$

To show that Equation (39) can be considered as a Langevin equation, we must now study the properties of the operator $\hat{F}(t)$. According to (37), $\hat{F}(t)$ is an operator of the reservoir. At the initial time t_0 , where both the Schrödinger and Heisenberg representations coincide, we assume that the density operator of the global system is factored in the form $\sigma_A \otimes \sigma_R$

where σ_R is given by the statistical mixture of the states $|n_1 n_2 \cdots n_i \cdots\rangle$ with weights $p(n_1 n_2 \cdots n_i \cdots)$ [see formula (E.8)]. Because $a_i(t_0)$ has no diagonal elements in the state $|n_i\rangle$, it follows that

$$\langle \hat{F}(t) \rangle = \text{Tr } \sigma_A \sigma_R F(t) = 0. \quad (40)$$

The average value of Equation (39) gives

$$\frac{d}{dt} \langle \hat{b}(t) \rangle = -\left(\frac{\Gamma}{2} + i\Delta\right) \langle \hat{b}(t) \rangle \quad (41)$$

which coincides with Equation (18) of Complement B_{IV} [when we return from $\hat{b}(t)$ to $b(t)$ by using (31.a)]. We now calculate the correlation functions of $\hat{F}(t)$ and $\hat{F}^+(t)$. Because only products such as $a_i^+(t_0)a_i(t_0)$ and $a_i(t_0)a_i^+(t_0)$ have nonzero average values (respectively equal to $\langle n_i \rangle$ and $\langle n_i \rangle + 1$) in the state (E.8) of the reservoir, we get

$$\langle \hat{F}(t') \hat{F}(t) \rangle = \langle \hat{F}^+(t') \hat{F}^+(t) \rangle = 0 \quad (42)$$

$$\langle \hat{F}^+(t') \hat{F}(t) \rangle = \sum_i \frac{1}{\hbar^2} |g_i|^2 \langle n_i \rangle e^{i(\omega_0 - \omega_i)(t-t')} \quad (43)$$

$$\langle \hat{F}(t) \hat{F}^+(t') \rangle = \sum_i \frac{1}{\hbar^2} |g_i|^2 (\langle n_i \rangle + 1) e^{i(\omega_0 - \omega_i)(t-t')}. \quad (44)$$

As above, the oscillating exponentials appearing in (43) and (44) interfere destructively as soon as $|t - t'| \gg \tau_c$. The two-time averages (43) and (44) are thus very narrow functions of $\tau = t - t'$. We call $2D_N$ and $2D_A$ the integrals over τ of these functions between $-\infty$ and $+\infty$:

$$2D_N = \int_{-\infty}^{+\infty} d\tau \langle \hat{F}^+(t - \tau) \hat{F}(t) \rangle \quad (45)$$

$$2D_A = \int_{-\infty}^{+\infty} d\tau \langle \hat{F}(t) \hat{F}^+(t - \tau) \rangle \quad (46)$$

(the subscripts N and A indicate the normal or antinormal order of \hat{F}^+ and \hat{F}). Using (43), (44), and formulas (11.a) and (11.b) from Complement

B_{IV}, these integrals equal

$$2D_N = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau \sum_i |g_i|^2 \langle n_i \rangle e^{i(\omega_0 - \omega_i)\tau} = \Gamma' \quad (47)$$

$$2D_A = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\tau \sum_i |g_i|^2 (\langle n_i \rangle + 1) e^{i(\omega_0 - \omega_i)\tau} = \Gamma' + \Gamma. \quad (48)$$

We can thus rewrite (43) and (44) in the form

$$\langle \hat{F}^+(t) \hat{F}(t') \rangle = 2D_N g_N(t - t') \quad (49)$$

$$\langle \hat{F}(t) \hat{F}^+(t') \rangle = 2D_A g_A(t - t') \quad (50)$$

where $g_N(\tau)$ and $g_A(\tau)$ are two normalized functions of τ , of width τ_c (*).

Finally, if we assume that $\langle n_i \rangle$ depends only on ω_i , we can use relation (15) from Complement B_{IV}, with $\Gamma' = \Gamma \langle n(\omega_0) \rangle$ [where $\langle n(\omega_0) \rangle$ is the average number of quanta of the reservoir modes having the same frequency ω_0 as \mathcal{A}], to rewrite (47) and (48) in the form

$$2D_N = \Gamma \langle n(\omega_0) \rangle \quad (51)$$

$$2D_A = \Gamma (1 + \langle n(\omega_0) \rangle). \quad (52)$$

The operators \hat{F} and \hat{F}^+ can therefore be considered to be Langevin forces fluctuating very rapidly around a zero average value. However, it should be noted that these operators do not commute with each other, as shown by the difference between (51) and (52).

c) CONNECTION BETWEEN FLUCTUATIONS AND DISSIPATION

Equations (51) and (52) establish a quantitative relationship between the fluctuations of \hat{F} and \hat{F}^+ , characterized by D_N and D_A , and the damping Γ characterizing the dissipation associated with the motions of b and b^+ . If the reservoir is in thermodynamic equilibrium, $\langle n(\omega_0) \rangle$ is equal to $[\exp(\hbar\omega_0/k_B T) - 1]^{-1}$ and expression (51), for example, becomes

$$2D_N = \frac{\Gamma}{e^{\hbar\omega_0/k_B T} - 1}, \quad (53)$$

(*) Functions g_N and g_A do not have a well-defined parity in τ . With regard to the functions of τ varying over time scales $T_R \gg \tau_c$, they can be considered to be a sum of functions $\delta, \delta', \delta'' \dots$. At the lowest order in τ_c/T_R , they can be replaced by a $\delta(\tau)$ function.

an equation that can be considered as an expression for a quantum fluctuation-dissipation theorem. In contrast to what we did in subsection 1-b above, relation (53) is derived from Heisenberg equations of motion rather than from a phenomenological equation. It is also valid whatever the relative values of $\hbar\omega_0$ and $k_B T$. In particular, if $\hbar\omega_0 \ll k_B T$, Equation (53) becomes

$$2D_N = \frac{\Gamma k_B T}{\hbar\omega_0} \quad (54)$$

and, as in (14), establishes a relationship between D and $\Gamma k_B T$.

The relation (53) between D_N and Γ was derived from (51), i.e., from the explicit calculation of the two-time average $\langle \hat{F}^+(t - \tau)\hat{F}(t) \rangle$ of the Langevin forces appearing in expression (45) for $2D_N$. It is also possible to relate the coefficient D_N to the rate of increase of the “crossed” variance of b^+ and b defined as

$$\mathcal{V}_N(t) = \langle \hat{b}^+(t)\hat{b}(t) \rangle - \langle \hat{b}^+(t) \rangle \langle \hat{b}(t) \rangle \quad (55)$$

with the coefficient D_A being related to the rate of increase of the variance

$$\mathcal{V}_A(t) = \langle \hat{b}(t)\hat{b}^+(t) \rangle - \langle \hat{b}(t) \rangle \langle \hat{b}^+(t) \rangle \quad (56)$$

corresponding to the antinormal order of b and b^+ . Such a result, which will be derived in subsection 2-e below, in a certain sense generalizes the relation (11) demonstrated above for the classical Langevin equation, and shows that the rate of increase of the variance of p is proportional to D .

Before calculating $d\mathcal{V}_N/dt$ and $d\mathcal{V}_A/dt$, we begin by deriving some useful results concerning the two-time averages $\langle \hat{F}^+(t)b(t') \rangle$ or $\langle \hat{b}^+(t')\hat{F}(t) \rangle$.

d) MIXED TWO-TIME AVERAGES INVOLVING LANGEVIN FORCES AND OPERATORS OF \mathcal{A}

We integrate Equation (39) between t_0 and t'

$$\hat{b}(t') = \hat{b}(t_0) e^{-(\Gamma/2 + i\Delta)(t' - t_0)} + \int_{t_0}^{t'} dt'' F(t'') e^{-(\Gamma/2 + i\Delta)(t' - t'')} \quad (57)$$

For $t_0 \rightarrow -\infty$, the first term of (57) is negligible and we then obtain, by

multiplying both sides of (57) by $\hat{F}^+(t)$:

$$\langle \hat{F}^+(t)\hat{b}(t') \rangle = \int_{t_0}^{t'} dt'' \langle \hat{F}^+(t)\hat{F}(t'') \rangle e^{-(\Gamma/2+i\Delta)(t'-t'')}. \quad (58)$$

The same reasoning as that used in subsection 1-c- α then gives, for the variations of $\langle \hat{F}^+(t)\hat{b}(t') \rangle$ with t , results analogous to those shown in Figure 1. For $t > t'$, $\hat{F}^+(t)$ is not correlated with $\hat{b}(t')$, except in an interval of width τ_c near $t = t'$. When t increases and crosses the value t' , $\langle \hat{F}^+(t)\hat{b}(t') \rangle$ goes from the value $2D_N$ to 0 over an interval of width τ_c . In particular, the value for $t = t'$ is given by

$$\begin{aligned} \langle \hat{F}^+(t)\hat{b}(t) \rangle &= \int_{t_0}^t dt'' \langle \hat{F}^+(t)\hat{F}(t'') \rangle e^{-(\Gamma/2+i\Delta)(t-t'')} \\ &\simeq \int_{t_0}^t dt'' \langle \hat{F}^+(t)\hat{F}(t'') \rangle \end{aligned} \quad (59)$$

because $\langle \hat{F}^+(t)\hat{F}(t'') \rangle$ varies much more rapidly with $t - t''$ than the exponential. In the same way, we find

$$\langle \hat{b}^+(t)\hat{F}(t) \rangle \simeq \int_{t_0}^t dt'' \langle \hat{F}^+(t'')\hat{F}(t) \rangle. \quad (60)$$

The change of variable $\tau = t - t''$ and the stationary character of the two-time averages of \hat{F}^+ and \hat{F} allow us to recombine (59) and (60) in the form

$$\langle \hat{b}^+(t)\hat{F}(t) \rangle + \langle \hat{F}^+(t)\hat{b}(t) \rangle = \int_{-(t-t_0)}^{+(t-t_0)} d\tau \langle \hat{F}^+(t-\tau)\hat{F}(t) \rangle = 2D_N. \quad (61)$$

We used (45) and assumed that $t - t_0 \gg \tau_c$.

e) RATE OF VARIATION OF THE VARIANCES \mathcal{V}_N AND \mathcal{V}_A

The evolution of the average value $\langle \hat{b}(t) \rangle$ was determined by the relaxation Equation (41). The evolution Equation (39) of the operator itself results in the appearance of the same rate of variation, which we call

the “drift” term, written $\mathcal{D}(\hat{b}(t))$:

$$\mathcal{D}(\hat{b}(t)) = -\left(\frac{\Gamma}{2} + i\Delta\right)\hat{b}(t). \quad (62)$$

The rate of variation of $\hat{b}(t)$ is then simply the sum of the drift term and the Langevin force

$$\frac{d}{dt}\hat{b}(t) = \mathcal{D}(\hat{b}(t)) + F(t). \quad (63)$$

Similarly

$$\frac{d}{dt}\hat{b}^+(t) = \mathcal{D}(\hat{b}^+(t)) + F^+(t) \quad (64)$$

with

$$\mathcal{D}(\hat{b}^+(t)) = \left(-\frac{\Gamma}{2} + i\Delta\right)\hat{b}^+(t). \quad (65)$$

We now consider the rate of variation of the operators $\hat{b}^+\hat{b}$ and $\hat{b}\hat{b}^+$ appearing in the variances \mathcal{V}_N and \mathcal{V}_A defined in (55) and (56). For $\hat{b}^+\hat{b}$, we first obtain

$$\begin{aligned} \frac{d}{dt}(\hat{b}^+(t)\hat{b}(t)) &= \left(\frac{d}{dt}\hat{b}^+(t)\right)\hat{b}(t) + \hat{b}^+(t)\left(\frac{d}{dt}\hat{b}(t)\right) = \\ &= \mathcal{D}(\hat{b}^+(t))\hat{b}(t) + \hat{b}^+(t)\mathcal{D}(\hat{b}(t)) + \hat{F}^+(t)\hat{b}(t) + \hat{b}^+(t)\hat{F}(t). \end{aligned} \quad (66)$$

Taking the average value of both sides of (66) and using (61) (*), we get

$$\frac{d}{dt}\langle\hat{b}^+(t)\hat{b}(t)\rangle = \langle\mathcal{D}(\hat{b}^+(t))\hat{b}(t)\rangle + \langle\hat{b}^+(t)\mathcal{D}(\hat{b}(t))\rangle + 2D_N \quad (67)$$

(*) The fact that the last two terms of (66) have, according to (61), a nonzero average value prevents us from considering their sum to be a Langevin force in the equation of motion of the operator $\hat{b}^+(t)\hat{b}(t)$.

i.e., also, using (62) and (65):

$$\frac{d}{dt} \langle \hat{b}^+(t) \hat{b}(t) \rangle = -\Gamma \langle \hat{b}^+(t) \hat{b}(t) \rangle + 2D_N. \quad (68)$$

According to (63) and (64), we have

$$\begin{aligned} \frac{d}{dt} \langle \hat{b}^+(t) \rangle \langle \hat{b}(t) \rangle &= \langle \mathcal{D}(\hat{b}^+(t)) \rangle \langle \hat{b}(t) \rangle + \langle \hat{b}(t) \rangle \langle \mathcal{D}(\hat{b}^+(t)) \rangle \\ &= -\Gamma \langle \hat{b}^+(t) \rangle \langle \hat{b}(t) \rangle \end{aligned} \quad (69)$$

so that, by subtraction, Equations (68) and (69) yield, using (55)

$$\frac{d}{dt} \mathcal{V}_N(t) = -\Gamma \mathcal{V}_N(t) + 2D_N. \quad (70)$$

Similar calculations yield

$$\frac{d}{dt} \langle \hat{b}(t) \hat{b}^+(t) \rangle = -\Gamma \langle \hat{b}(t) \hat{b}^+(t) \rangle + 2D_A \quad (71)$$

and consequently

$$\frac{d}{dt} \mathcal{V}_A(t) = -\Gamma \mathcal{V}_A(t) + 2D_A \quad (72)$$

The variances thus tend to increase linearly with t under the influence of the Langevin forces, whose effect is represented by the constant terms $2D_N$ and $2D_A$ of (70) and (72). These terms can thus indeed be considered as diffusion coefficients. The damping Γ limits this diffusion motion and the equilibrium values of (70) and (72) again give the relations among the coefficients D , Γ , and the temperature [see (53)].

Remark

The fact that D_N and D_A are different results from the quantum nature of $F(t)$ and $F^+(t)$ and is essential for preserving the commutation relation between b and b^+ . By subtracting (68) from (71), we find that a necessary condition for

$\langle [\hat{b}(t), \hat{b}^+(t)] \rangle$ remaining equal to 1 is that

$$D_A - D_N = \frac{\Gamma}{2} \quad (73)$$

a condition that is indeed satisfied by (47) and (48).

f) GENERALIZATION OF EINSTEIN'S RELATION

We return to Equation (67). Because the operator $\hat{b}^+(t)\hat{b}(t)$ is an operator of the small system \mathcal{A} , we can associate with it a drift velocity $\mathcal{D}(\hat{b}^+\hat{b})$ whose average value is by definition the rate of variation of $\langle b^+b \rangle$.

$$\frac{d}{dt} \langle \hat{b}^+(t)\hat{b}(t) \rangle = \langle \mathcal{D}(\hat{b}^+(t)b(t)) \rangle \quad (74)$$

In principle the master equation for \mathcal{A} allows us to calculate $d\langle \hat{b}^+\hat{b} \rangle / dt$ and thus to derive $\mathcal{D}(\hat{b}^+\hat{b})$ from it. Indeed, Equation (21) of Complement B_{IV} gives

$$\mathcal{D}(\hat{b}^+(t)\hat{b}(t)) = -\Gamma\hat{b}^+(t)\hat{b}(t) + \Gamma'. \quad (75)$$

Equation (74) allows us to rewrite (67) in the form

$$2D_N = \langle \mathcal{D}(\hat{b}^+\hat{b}) - \mathcal{D}(\hat{b}^+)\hat{b} - \hat{b}^+\mathcal{D}(\hat{b}) \rangle \quad (76)$$

all the operators of the right-hand side of (76) being taken at the same time t . Equation (76) can be considered to be a generalization of the Einstein relation (14) between D and Γ . It expresses the diffusion coefficient D_N relative to $\hat{b}^+\hat{b}$ as a function of the drift velocities that describe the damping of $\hat{b}^+\hat{b}$, \hat{b}^+ , and \hat{b} and which can all be calculated starting from the master equation.

It is also clear from (76) that the diffusion coefficient D_N is associated only with the *non-Hamiltonian* part of the drift velocities. If we indeed had, for any operator G_A of \mathcal{A}

$$\mathcal{D}(G_A) = \frac{i}{\hbar} [H, G_A], \quad (77)$$

then $2D_N$ would be zero because

$$[H, \hat{b}^+ \hat{b}] - [H, \hat{b}^+] \hat{b} - \hat{b}^+ [H, \hat{b}] = 0. \quad (78)$$

It is for this reason that the radiative shifts of the levels of \mathcal{A} , which can be described by an effective Hamiltonian, do not appear in the expression for diffusion coefficients.

In the particular case under consideration here, it is sufficient to substitute (75), (62), and (65) into (76) to immediately obtain expression (47) for D_N .

**g) CALCULATION OF TWO-TIME AVERAGES FOR OPERATORS OF \mathcal{A} .
QUANTUM REGRESSION THEOREM**

We take the Hermitian conjugate of Equation (39), multiply both sides on the right by $b(t')$ and take the average value. This gives

$$\frac{d}{dt} \langle \hat{b}^+(t) \hat{b}(t') \rangle = - \left(\frac{\Gamma}{2} - i\Delta \right) \langle \hat{b}^+(t) \hat{b}(t') \rangle + \langle \hat{F}^+(t) \hat{b}(t') \rangle. \quad (79)$$

Assume that $t \geq t'$. According to what we saw in subsection 2-d concerning the two-time averages $\langle \hat{F}^+(t) \hat{b}(t') \rangle$, the last term of (79) is zero except in a small interval of width τ_c , near $t = t'$, where it is on the order of D_N . It is thus totally legitimate to neglect such a term for $t \gg t'$, the error made on $\langle \hat{b}^+(t) \hat{b}(t') \rangle$ being on the order of $D_N \tau_c$, i.e., according to (51), on the order of $\Gamma' \tau_c \ll 1$. The two-time averages $\langle \hat{b}^+(t) \hat{b}(t') \rangle$ can therefore, to a very good approximation, be considered as obeying the equation

$$t \geq t' \quad \frac{d}{dt} \langle \hat{b}^+(t) \hat{b}(t') \rangle = - \left(\frac{\Gamma}{2} - i\Delta \right) \langle \hat{b}^+(t) \hat{b}(t') \rangle \quad (80)$$

exactly analogous to the Hermitian conjugate of Equation (41):

$$t \geq t' \quad \frac{d}{dt} \langle \hat{b}^+(t) \rangle = - \left(\frac{\Gamma}{2} - i\Delta \right) \langle \hat{b}^+(t) \rangle \quad (81)$$

giving the evolution of the one-time averages.

The foregoing result constitutes the quantum regression theorem which allows us to calculate the evolution of two-time averages using equations having the same structure as those giving the evolution of one-time averages, which are themselves obtained from the master equation.

Finally, using the simple model of an oscillator coupled to a reservoir of oscillators, we were able to extend most of the results obtained from the Langevin description of Brownian motion to a quantum system. We will see in Complement A_V that it is also possible to generalize these results to the case of a two-level atom coupled to a reservoir of oscillators (in this case, the modes of the radiation field), and to thus obtain the Bloch–Langevin equations. Such a generalization is nontrivial because a two-level atom is nonlinear, which causes nonlinear terms to appear in the coupled evolution equations, and makes the manipulation of these equations more difficult than in the linear case studied here.

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