PART I

SEMI-CLASSICAL DESCRIPTION OF MATTER–LIGHT INTERACTION

1 The evolution of interacting quantum systems

In this work we shall study the interaction of matter and light. In so doing we shall rely heavily on the description of such processes provided by quantum mechanics. This appears on a number of levels: firstly, a *quantum description of matter* is indispensable if one wants to understand *on the microscopic scale* the different kinds of interaction processes that can occur. Secondly, a *quantum description of light* often turns out to be useful, sometimes necessary, to better understand these processes. We shall study phenomena such as spontaneous emission, which can only be properly treated by a theory taking into account the quantum nature of both light and matter.

In the following chapters we shall address, amongst others, the following question: 'given an atom prepared at a given time in a particular state and subjected from this time onwards to electromagnetic radiation, what is the state of the atom and radiation at any later moment in time?' In order to be able to answer this question it will be necessary for us to know how to calculate the evolution of a quantum system in a small number of typical situations. These methods we shall demonstrate in the first chapter.

The evolution of the coupled atom–light system depends on the temporal dependence of the applied light field, which could, for example, be applied from a given moment and thereafter remain unchanged in intensity, or, perhaps, be appreciable only for a finite period of time (pulsed excitation). We shall see that the nature of the evolution depends also on the *structure of the energy spectrum* of the system considered, whether it is describable by a set of *discrete levels* well separated in energy, or by a *continuum*.

This chapter starts with a brief reminder of some elementary results of quantum mechanics (Section 1.1). In the following section we demonstrate the use of a perturbative method to calculate the probability of the transition of a quantum state from a given initial to a given final state under the influence of an interaction. Finally in Section 1.3 we shall study the case in which the initial state is coupled to a very large number of closely spaced energy levels (we speak of a *quasi-continuum* of states). We derive an important result for the transition probability, known as *Fermi's golden rule*. Finally, in the conclusion we discuss the different regimes of temporal evolution that can be obtained.

This chapter is rounded off by two *complements*. Complement 1A outlines a simple model which enables us to understand the transition between the two limiting situations of Sections 1.2 (two discrete coupled levels) and 1.3 (a discrete level coupled to a continuum). Complement 1B addresses the situation where a quantum system is interacting with a random perturbation, whose frequency spectrum is broad (broadband excitation). In that case, one finds a transition probability as in Section 1.3.

1.1 Review of some elementary results of quantum mechanics

We start by recalling some important results relating to a quantum system described by a Hamiltonian $\hat{H}_0$ independent of time.[1] We designate by $|n\rangle$ and E_n the eigenstates and eigenenergies of $\hat{H}_0$. Suppose at time $t = 0$ the system is in the most general state:

$$|\psi(0)\rangle = \sum_n \gamma_n |n\rangle . \tag{1.1}$$

Using the Schrödinger equation,[2] one can show that the system is found at a later time in the state:

$$|\psi(t)\rangle = \sum_n \gamma_n e^{-iE_n t/\hbar} |n\rangle . \tag{1.2}$$

The probability of finding the system in the state $|\varphi\rangle$ is then

$$P_\varphi(t) = |\langle\varphi|\,\psi(t)\rangle|^2 \tag{1.3}$$

and the probability that the system has made a transition from state $|\psi(0)\rangle$ to the state $|\varphi\rangle$ between times 0 and t is therefore

$$P_{\psi(0)\to\varphi}(t) = |\langle\varphi|\,\psi(t)\rangle|^2 . \tag{1.4}$$

In particular, if the system is initially prepared in the eigenstate $|n\rangle$ of $\hat{H}_0$, it is given at any later time t by the state vector

$$|\psi(t)\rangle = e^{-iE_n t/\hbar} |n\rangle . \tag{1.5}$$

The probability of finding it later in a state $|m\rangle$ of $\hat{H}_0$ with $m \neq n$ is then zero:

$$P_{n\to m}(t) = |\langle m|\,\psi(t)\rangle|^2 = 0. \tag{1.6}$$

For example, the electron of an atom of hydrogen initially in the state $|n, l, m\rangle$ would remain indefinitely in this state if the atom were not coupled to the exterior environment. In practice it undergoes transitions to different levels under the effect of *exterior interactions* of various origins: collisions with ions, atoms or electrons, oscillating electromagnetic fields etc. The coupling with the quantized electromagnetic field is also responsible for spontaneous transitions between an excited and lower energy levels accompanied by the emission of a photon. This is the process of *spontaneous emission* that we shall treat in Chapter 6.

In these different examples the evolution of the system is driven by a *time-dependent* Hamiltonian, this time dependence being sinusoidal in the case of an electromagnetic field, impulsive in the case of a collision. In general, the state vector describing the system cannot be calculated *exactly* for all time. We show in the next section, however, that one can obtain an exact expression for transition probabilities in the form of a series expansion.

[1] In this work we shall distinguish the operators of quantum theory by a hat, e.g. $\hat{H}$.
[2] See CDL, § III.D.2.

A problem that is formally similar, that we shall also treat, is that in which the total Hamiltonian $\hat{H}_0 + \hat{W}$ is independent of time, but in which the system is prepared in an eigenstate of $\hat{H}_0$ and detected at a later instant, t', in another eigenstate of $\hat{H}_0$. The corresponding transition probabilities will be calculated using a similar series method since, as we shall demonstrate, this problem is mathematically identical to the case in which the coupling $\hat{W}$ is applied transiently in the interval of time between $t = 0$ and $t = t'$.

1.2 Transition between discrete levels induced by a time-dependent perturbation

1.2.1 Presentation of the problem

We consider a system described by a Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t). \tag{1.7}$$

$\hat{H}_0$ is independent of time, its eigenstates and eigenvalues being denoted by $|n\rangle$ and E_n:

$$\hat{H}_0 |n\rangle = E_n |n\rangle . \tag{1.8}$$

$\hat{H}_1(t)$ is an interaction term of which the matrix elements between the eigenstates of $\hat{H}_0$ are assumed small compared to the energy differences between these eigenstates, $\langle n|\hat{H}_0|m\rangle \ll |E_n - E_m|$. At this stage the time dependence of $\hat{H}_1(t)$ is left arbitrary, it could for example be constant for a finite interval of time and zero outside this interval.

The coupling $\hat{H}_1(t)$ will be capable of inducing transitions between different eigenstates of $\hat{H}_0$. Here we propose to calculate the corresponding transition probabilities $P_{n\to m}(t)$ supposing, for simplicity, that the levels are non-degenerate in energy. More general treatments can be found in standard texts on quantum mechanics.[3]

1.2.2 Examples

Before studying the mathematical development, we present two examples of physical systems well described by the model we propose to adopt. These will be of use to us later to provide a physical illustration of the results obtained.

Interaction of an atom with a classical electromagnetic field

Consider an atom[4] described by the atomic Hamiltonian $\hat{H}_0$ and which interacts with an incident classical electromagnetic wave of which the electric field at the position of the (stationary) atom is

[3] See, for example, CDL, Chapter XIII.
[4] More precisely, we consider for simplicity a one-electron atom such as hydrogen.

$$\mathbf{E}(t) = \mathbf{E}\cos(\omega t + \varphi). \tag{1.9}$$

We shall see in Chapter 2 that the interaction of the atom with the field can, to a good approximation, be written in terms of an *electric dipole* coupling:

$$\hat{H}_1(t) = -\hat{\mathbf{D}} \cdot \mathbf{E}(t), \tag{1.10}$$

where $\hat{\mathbf{D}}$ is the electric dipole of the atom,

$$\hat{\mathbf{D}} = q\hat{\mathbf{r}}. \tag{1.11}$$

Here q is the electronic charge and $\mathbf{r}$ the radius vector between the atomic nucleus and its valence electron.

Under the action of $\hat{H}_1(t)$ the electron, initially in the eigenstate $|n, l, m\rangle$ of $\hat{H}_0$, will be able to undergo transitions to other states $|n', l', m'\rangle$. If the energy of the latter state is higher than that of the former the energy necessary to excite the atom is taken from the electromagnetic field (this is *absorption*), if it is lower there is a transfer of energy from the atom to the field (this is *stimulated emission*). We shall come back to these processes and their consequences in Chapter 2.

Collision processes

We consider a stationary atom A, of which the internal energy levels are the eigenstates of a Hamiltonian, $\hat{H}_0$ and suppose that another particle B passes in the neighbourhood of A (Figure 1.1).

$\hat{V}$ is the interaction potential between the collider B and the atom A; it depends on the distance R between B and A. For atom A this interaction is represented by an operator acting in the space of states of A. Its matrix elements between those states are a function of R and tend to zero as R becomes very large. Since R varies in time, *the interaction Hamiltonian itself also depends on time*. If before the collision, when the atoms are far apart, atom A is in the state $|n\rangle$, there is the possibility that after the collision it will be found in a different state $|m\rangle$. If the energies of the initial and final states are the same, the collision is described as *elastic*, otherwise it is termed *inelastic*. This type of collision-induced transition is responsible, for example, for the excitation of atoms in a discharge lamp (a neon lamp, for example) or, as we shall see in Chapter 3, in certain kinds of laser.

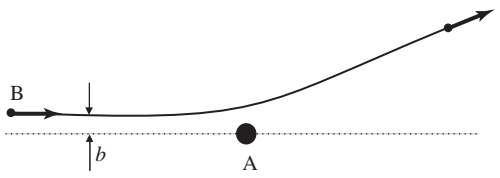

Figure 1.1 Collisional interaction between a particle B and an atom A. The distance of closest approach, b, is called the impact parameter. The interaction depends only on the R = AB distance, hence $\hat{V}(t) = \hat{V}(|\mathbf{R}(t)|)$.

1.2.3 Perturbation series expansion of the system wavefunction

The evolution of atom A is determined by solving the Schrödinger equation using the Hamiltonian of Equation (1.7). To this end we are going, in the following, to employ a method of approximate solution based on perturbation theory, which is valid provided the matrix elements of $\hat{H}_1(t)$ are small compared to those of $\hat{H}_0$.[5] In order to be able to identify the successive orders of the perturbation expansion more easily we rewrite $\hat{H}_1(t)$ in the form

$$\hat{H}_1(t) = \lambda \hat{H}'_1(t), \tag{1.12}$$

where $\hat{H}'_1(t)$ has matrix elements of the same order of magnitude as those of $\hat{H}_0$ and where λ is a real, dimensionless parameter much smaller than unity, which characterizes the relative strength of the interaction $\hat{H}_1(t)$. In the first of our two examples, λ is proportional to the amplitude of the incident electric field, in the second it is a function of the impact parameter b. In each case it will be possible to find experimental conditions in which the approximation $\lambda \ll 1$ is valid (weak electric field, large impact parameter).

The Schrödinger equation for the system is

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left(\hat{H}_0 + \lambda \hat{H}'_1(t)\right) |\psi(t)\rangle . \tag{1.13}$$

Expanding $|\psi(t)\rangle$ in the basis of eigenstates of $\hat{H}_0$ we get

$$|\psi(t)\rangle = \sum_n \gamma_n(t)\, e^{-iE_n t/\hbar} |n\rangle . \tag{1.14}$$

Here we have written the coefficient of the ket $|n\rangle$ as a product of terms $\gamma_n(t)$ and $\exp(-iE_n t/\hbar)$. This separation permits us to take into account the free evolution of the system under the influence of $\hat{H}_0$ alone, since if $\hat{H}_1(t)$ is zero the $\gamma_n(t)$ are *constant* by virtue of Equation (1.2). This will facilitate later developments.

Next, we project Equation (1.13) on an eigenstate $|k\rangle$ of $\hat{H}_0$:

$$\begin{aligned} i\hbar \frac{d}{dt} \langle k|\psi(t)\rangle &= \langle k|\hat{H}_0|\psi(t)\rangle + \lambda \langle k|\hat{H}'_1|\psi(t)\rangle \\ &= E_k \langle k|\psi(t)\rangle + \lambda \sum_n \langle k|\hat{H}'_1(t)|n\rangle \langle n|\psi(t)\rangle, \end{aligned} \tag{1.15}$$

where we have used the *closure relation*: $\sum_n |n\rangle\langle n| = \hat{1}$.

Using expression (1.14) for $|\psi(t)\rangle$, we rewrite (1.15) in the form:

$$\begin{aligned} \left[E_k \gamma_k(t) + i\hbar \frac{d}{dt}\gamma_k(t)\right] e^{-iE_k t/\hbar} &= E_k \gamma_k(t)\, e^{-iE_k t/\hbar} \\ &\quad + \lambda \sum_n \langle k|\hat{H}'_1(t)|n\rangle\, \gamma_n(t)\, e^{-iE_n t/\hbar}. \end{aligned} \tag{1.16}$$

[5] More precisely, in the basis $\{|n\rangle\}$ of the eigenstates of $\hat{H}_0$, the off-diagonal matrix elements $|\langle n|\hat{H}_1|m\rangle|$ must be small compared to the corresponding energy separations $|E_n - E_m|$.

The terms proportional to E_k in the right and left-hand sides simplify to give

$$i\hbar \frac{d}{dt}\gamma_k(t) = \lambda \sum_n \langle k|\, \hat{H}'_1(t)\, |n\rangle\, e^{i(E_k - E_n)t/\hbar}\, \gamma_n(t), \tag{1.17}$$

which is a (possibly infinite) system of differential equations. This system is *exact*, no approximations having been made thus far.

The coefficients $\gamma_k(t)$ depend on λ. Perturbation theory consists of developing $\gamma_k(t)$ as a power series in λ (which, we recall is much smaller than unity):

$$\gamma_k(t) = \gamma_k^{(0)}(t) + \lambda\gamma_k^{(1)}(t) + \lambda^2\gamma_k^{(2)}(t) + \ldots \tag{1.18}$$

In substituting this series in (1.17) we can collect together terms of the same order in λ. In this way we obtain:

- to order 0

$$i\hbar \frac{d}{dt}\gamma_k^{(0)}(t) = 0; \tag{1.19}$$

- to order 1

$$i\hbar \frac{d}{dt}\gamma_k^{(1)}(t) = \sum_n \langle k|\, \hat{H}'_1(t)\, |n\rangle\, e^{i(E_k - E_n)t/\hbar}\, \gamma_n^{(0)}(t); \tag{1.20}$$

- to order r

$$i\hbar \frac{d}{dt}\gamma_k^{(r)}(t) = \sum_n \langle k|\, \hat{H}'_1(t)\, |n\rangle\, e^{i(E_k - E_n)t/\hbar}\, \gamma_n^{(r-1)}(t). \tag{1.21}$$

This system of equations can be solved *iteratively*. In fact the zeroth-order terms are already known: they are *constants determined by the initial state of the system*. On substituting these terms in (1.20) the terms of order one, $\gamma_k^{(1)}(t)$, can be found. These then lead to an expression for $\gamma_k^{(2)}(t)$, and so on. Thus it is possible, in principle, to determine successively all the terms in the expansion (1.18).

1.2.4 First-order theory

Transition probability

Suppose that at initial time t_0, the system is prepared in an eigenstate $|i\rangle$ of $\hat{H}_0$. It follows that all $\gamma_k(t_0)$ are zero except for $\gamma_i(t_0)$ which is equal to one. The solution of (1.19) is then:

$$\gamma_k^{(0)}(t) = \delta_{ki}. \tag{1.22}$$

We now consider the possibility of transitions to level $|k\rangle$ different from the initial state ($k \neq i$). Substituting the result (1.22) into (1.20) and integrating over time we find, for $\gamma_k^{(1)}$

$$\gamma_k^{(1)}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt'\, \langle k|\, \hat{H}'_1(t')\, |i\rangle\, e^{i(E_k - E_i)t'/\hbar}. \tag{1.23}$$

The probability amplitude for finding the system in the state $|k\rangle$ at time t is, according to (1.14) and (1.18), equal to (within a phase factor)

$$\gamma_k^{(0)}(t) + \lambda\gamma_k^{(1)}(t) + \ldots \tag{1.24}$$

For a state $|k\rangle$ different from $|i\rangle$ the zeroth-order term is zero. From this we deduce, also using (1.23), that the amplitude for the transition $|i\rangle$ to $|k\rangle$ to first order and to within a phase factor is

$$S_{ki} = \lambda\gamma_k^{(1)}(t) = \frac{1}{\mathrm{i}\hbar}\int_{t_0}^{t} \mathrm{d}t' \langle k|\hat{H}_1(t')|i\rangle \mathrm{e}^{\mathrm{i}(E_k - E_i)t'/\hbar}, \tag{1.25}$$

since, according to (1.12), $\lambda\hat{H}_1'(t')$ is equal to $\hat{H}_1(t')$. The probability of finding the system in the state $|k\rangle$ is given by the square modulus of (1.25), that is

$$P_{i\to k} = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} \mathrm{d}t' \langle k|\hat{H}_1(t')|i\rangle \mathrm{e}^{\mathrm{i}(E_k - E_i)t'/\hbar}\right|^2. \tag{1.26}$$

The formulae (1.25) and (1.26) are the important results of first-order, time-dependent perturbation theory. We shall use these in what follows. Notice, however, that this perturbative approach is only valid if

$$P_{i\to k} \ll 1, \tag{1.27}$$

that is, effectively, that the interaction Hamiltonian $\hat{H}_1$ induces only small effects in first order so that the full perturbation expansion of (1.18), which includes also the effects of higher-order terms, will converge rapidly. Condition (1.27) is in fact a *necessary* condition, but not sufficient that first-order perturbation theory can be accurately applied.

Example of a collisional process: qualitative study of the accessible energy range

In the following, we shall show that the properties of the *Fourier transform* applied to Equation (1.26) enable us to predict the range of energy over which atomic energy levels can be excited during a collision.

Suppose, for simplicity, that the interaction term $\hat{H}_1(t)$ is of the form:

$$\hat{H}_1(t) = \hat{W} f(t), \tag{1.28}$$

where $\hat{W}$ is an operator acting on atomic variables and $f(t)$ is a real function of time which tends to zero when $t \to \pm\infty$ and attains its maximum value at $t = 0$ (see Figure 1.2). We suppose that before the collision ($t_0 = -\infty$) the system is in a state $|i\rangle$. The amplitude for finding it in a state $|k\rangle$ after the collision ($t_0 = +\infty$) is

$$S_{ki} = \frac{W_{ki}}{\mathrm{i}\hbar}\int_{-\infty}^{+\infty} \mathrm{d}t\, f(t)\, \mathrm{e}^{\mathrm{i}(E_k - E_i)t/\hbar}, \tag{1.29}$$

where W_{ki} is the matrix element $W_{ki} = \langle k\,|\hat{W}|\,i\rangle$.

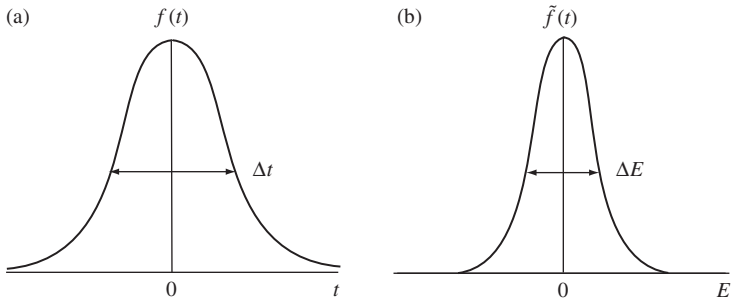

Figure 1.2 **The Fourier transform of the function $f(t)$, centred on the time origin and of width Δt (a) is a function of energy centred on $E = 0$ of width $\Delta E \approx \hbar/\Delta t$ (b).**

Introducing the Fourier transform, $\tilde{f}(E)$ of the function $f(t)$:

$$\tilde{f}(E) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \mathrm{d}t\, f(t)\, \mathrm{e}^{\mathrm{i}Et/\hbar}, \tag{1.30}$$

we obtain the following expression for the transition probability $P_{i\to k}$,

$$P_{i\to k} = \frac{2\pi}{\hbar} |W_{ki}|^2 \left|\tilde{f}(E_k - E_i)\right|^2, \tag{1.31}$$

which depends on the value of $\tilde{f}(E)$ taken at $E = E_k - E_i$.

We now make use of a well-known property of Fourier transforms (Figure 1.2): if the width of the function $f(t)$ is Δt then that of its Fourier transform is of the order of $\hbar/\Delta t$. The expression (1.31) then shows that if the collisional interaction is of duration Δt, the energy levels for which

$$|E_k - E_i| < \frac{\hbar}{\Delta t} \tag{1.32}$$

will have a significant probability of being populated.

Consider the case of a collision in which the interaction is a decreasing function of the distance between the collision partners (see Figure 1.1). The collision duration is of the order of b/v, where b is the impact parameter and v is the relative velocity of the particles. The inequality (1.32) implies that only the states $|k\rangle$ such that

$$|E_k - E_i| \leq \frac{\hbar v}{b} \tag{1.33}$$

will be appreciably populated as a result of the collision.

Comment Formula (1.33) shows that for an impact parameter of the order of 10 nm a collision with an atom of speed 10^7 m.s^{-1} is necessary to excite a ground state hydrogen atom to its first excited state (an energy transfer of about 10 eV). This is a very large velocity associated with a kinetic energy of the order of 1 MeV, very large compared to the excitation energy of the atom. To excite a hydrogen atom with lower energy particles one must consider impact parameters of the order of a Bohr radius. For this type of 'close' collision the matrix elements of $\hat{H}_1$ are not small compared to the energy differences $E_n - E_m$, and the hypothesis of a perturbative interaction is no longer valid.

Case of a constant perturbation suddenly 'switched on'

It often arises that a system is suddenly at $t = 0$ made to interact with a perturbation $\hat{W}$ which has a constant value at all later times.[6] In this section we are going to determine the transition probabilities in first-order perturbation theory for this important situation, a result which will be of use in the remainder of this chapter.

If at time $t = 0$, the system is in the eigenstate $|i\rangle$ of $\hat{H}_0$, the amplitude for finding it in the state $|k\rangle$ at a time T may be calculated from (1.25) thus:

$$S_{ki}(T) = \frac{W_{ki}}{\mathrm{i}\hbar} \frac{\mathrm{e}^{\mathrm{i}(E_k - E_i)T/\hbar} - 1}{\mathrm{i}(E_k - E_i)/\hbar}. \tag{1.34}$$

Hence we deduce the transition probability $P_{i\to k}(T)$:

$$P_{i\to k}(T) = \frac{|W_{ki}|^2}{\hbar^2} g_T(E_k - E_i), \tag{1.35}$$

where

$$g_T(E) = \frac{\sin^2(ET/2\hbar)}{(ET/2\hbar)^2} T^2 \tag{1.36}$$

is the function shown in Figure 1.3.

The important characteristics of this function are the following:

- it has its maximum value of T^2 at $E = 0$;
- its width is of order $2\pi\hbar/T$;
- its area is proportional to T, or more precisely:[7]

$$\int_{-\infty}^{+\infty} \mathrm{d}E\, g_T(E) = 2\pi\hbar T. \tag{1.37}$$

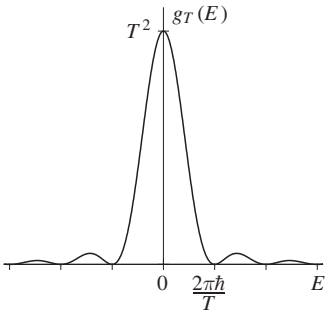

Figure 1.3 Form of the function $g_T(E) = (T\sin(ET/2\hbar)/(ET/2\hbar))^2$. Its value at $E = 0$ is T^2 and the first zeros are at $E = \pm 2\pi\hbar/T$.

[6] As we pointed out in the introduction, this calculation applies equally to the case of a Hamiltonian $\hat{H}_0 + \hat{W}$ independent of time, but when the system is prepared and subsequently detected in an eigenstate of $\hat{H}_0$.

[7] Its value is half the product of its height and of the distance between the two first zeros, as though the function g_T were triangular.