CHAPTER I

Transition Amplitudes in Electrodynamics

The goal of this first chapter is to introduce the concept of transition amplitude, which is essential for the quantum description of interactions between atoms and photons.

We begin in Section A by recalling that the transition amplitude associated with a physical process is the evolution-operator matrix element between the initial and final states of the process under study. The calculation of these amplitudes frequently uses perturbation theory and is based on the splitting of the total Hamiltonian H into an unperturbed part H_0 and a coupling V.

We then discuss in Section B the basic ideas of quantum mechanics concerning the time dependence of transition amplitudes. Distinctions are made among several cases according to whether the initial and final states of the process under study belong to the discrete or to the continuous spectrum of H_0. The three complements explore this problem in greater detail. Complement A_I assembles several important results concerning the perturbative calculation of transition amplitudes and physical quantities that can be deduced from these amplitudes (transition rates, cross-sections, etc.). Complement B_I introduces the concept of effective Hamiltonian, which is useful for describing situations where several energy levels of H_0 forming a well-isolated manifold are indirectly coupled through other levels of H_0. Complement C_I presents a very simple model of a discrete state coupled to a continuum, which allows one to exactly calculate the transition amplitudes and to understand the way the discrete state of H_0 can be traced in the eigenstates of H.

In Section C, we apply these ideas to a system of charged particles interacting with the electromagnetic field. Starting with the Hamiltonian H of quantum electrodynamics in the Coulomb gauge, we consider several possible splittings of this Hamiltonian into an unperturbed part H_0 and a coupling V. We emphasize the advantages of the Coulomb gauge, which allows the Coulomb interaction to be included in the particle Hamiltonian, and the bound states of charged particles, such as atoms, molecules, or ions to be considered as "unperturbed". We also introduce diagrammatic representations of interaction processes that allow the evolution of the global system to be simply visualized. These are the interaction processes (absorption, emission, scattering, etc.) that we will review in Chapter II.

A—PROBABILITY AMPLITUDE ASSOCIATED WITH A PHYSICAL PROCESS

The idea of probability amplitude plays a central role in the quantum description of the time evolution of a physical process. The system under study is prepared at an instant t_i in a given state $|\psi_i\rangle$. The probability amplitude of finding it, at another instant t_f, in the state $|\psi_f\rangle$ is given, in the Schrödinger representation, by

$$\langle\psi_f|U(t_f,t_i)|\psi_i\rangle, \tag{A.1}$$

where $U(t_f,t_i)$ is the evolution operator between t_i and t_f. The main advantage of these amplitudes (A.1) is that they can be multiplied: the amplitude for going from $|\psi_1\rangle$ to $|\psi_2\rangle$ between t_1 and t_2, and then from $|\psi_2\rangle$ to $|\psi_3\rangle$ between t_2 and t_3 is given by the product

$$\langle\psi_3|U(t_3,t_2)|\psi_2\rangle\langle\psi_2|U(t_2,t_1)|\psi_1\rangle. \tag{A.2}$$

Another interesting property of the amplitudes (A.1) is that they interfere. If the system is not observed at an intermediate instant t_2, the amplitudes associated with all the possible intermediate states must be summed over. It is in fact well known that

$$\langle\psi_3|U(t_3,t_1)|\psi_1\rangle = \sum_n \langle\psi_3|U(t_3,t_2)|\varphi_n\rangle\langle\varphi_n|U(t_2,t_1)|\psi_1\rangle \tag{A.3}$$

where the $\{|\varphi_n\rangle\}$ form an orthonormal basis of states.

The calculation of the amplitude (A.1) assumes, of course, that we already know how to determine $|\psi_i\rangle$ and $|\psi_f\rangle$. Generally the initial state and the final state are characterized by well-defined values of some physical variables. Thus we must be able to calculate the eigenvalues and eigenstates of the observables that represent these physical variables. We must also know the evolution operator $U(t_f,t_i)$ which is determined by diagonalizing the Hamiltonian H of the system. However, in most cases, and particularly in electrodynamics, we do not know how to exactly calculate the eigenstates and eigenvalues of H. It is thus necessary to resort to approximation methods.

The perturbative calculation of amplitudes (A.1) depends in general on the splitting of the Hamiltonian H into an "unperturbed" part H_0, for which the eigenstates $|\varphi_n\rangle$ and eigenvalues E_n are known, and a perturba

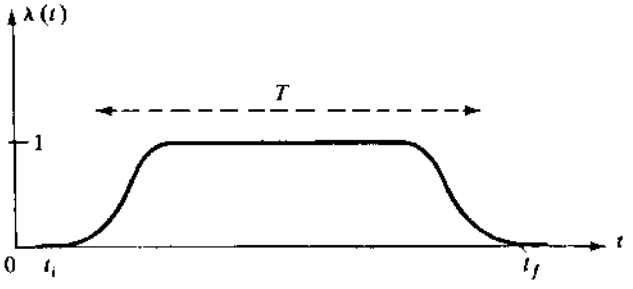


Figure 1. Temporal variation of the parameter $\lambda(t)$ allowing the perturbation V to be adiabatically switched on and switched off. This simulates a collision of duration T.

tion $V = H - H_0$:

$$H = H_0 + V. \tag{A.4}$$

Since any state $|\psi_i\rangle$ or $|\psi_f\rangle$ may always be expanded on the basis $|\varphi_n\rangle$ of eigenstates of H_0, the amplitudes (A.1) can be expressed as a function of the quantities

$$\langle\varphi_p|U(t_f, t_i)|\varphi_n\rangle, \tag{A.5}$$

which represent the transition amplitudes induced by the perturbation V between unperturbed states. In this chapter, we will concern ourselves with these transition amplitudes and with their calculation in the form of a perturbative expansion in powers of V.

When the problem under study can be stated in terms of collisions, it is quite convenient to adiabatically "switch on" and "switch off" the perturbation V by formally multiplying V by a parameter $\lambda(t)$, whose time variations are represented in Figure 1. In this way we can "simulate" the collision of two wave packets, which initially ($t \leq t_i$) do not interact because they are too distant from each other, and then, after the collision ($t_f \leq t$), are again separated and no longer interact. The limit of the expression (A.5), when the duration T of the collision (see Figure 1) tends to infinity, is simply an element of the scattering matrix S. (The evolution operator U must then be taken in interaction representation with respect to H_0 to eliminate the free evolution exponentials in t_i and in t_f due to H_0; see Complement A_1, §1).

B—TIME DEPENDENCE OF TRANSITION AMPLITUDES

To give some idea of the type of physical information that may be extracted from the preceding transition amplitudes, we are going to distinguish among different cases, depending on whether the initial and final states $|\varphi_i\rangle$ and $|\varphi_f\rangle$ of the process belong to the discrete or to the continuous spectrum of the unperturbed Hamiltonian H_0. For each of these cases, we review the time dependence that quantum mechanics predicts for the matrix elements of the evolution operator, and we show how it is possible to connect the transition amplitudes to measurable physical quantities such as level shifts, lifetimes, cross sections, etc. Such general ideas will be useful for analyzing the physical processes to be reviewed in Chapter II.

1. Coupling between Discrete Isolated States

We begin by considering the case in which the unperturbed Hamiltonian H_0 has one or several discrete eigenstates that are well isolated from all other eigenstates of H_0.

One particularly simple case is that of a single discrete state $|\varphi_1\rangle$, well isolated, having unperturbed energy E_1. Let us now consider the amplitude

$$\tilde{U}_{11}(T) = \langle \varphi_1 | \tilde{U}(T) | \varphi_1 \rangle \tag{B.1.a}$$

where

$$\tilde{U}(T) = e^{iH_0T/2\hbar} U(T)\, e^{iH_0T/2\hbar} \tag{B.1.b}$$

is the evolution operator between $t_i = -T/2$ and $t_f = +T/2$ in the interaction representation with respect to H_0 (see Complement A_1, §1). $\tilde{U}_{11}(T)$ represents the probability amplitude that the system, prepared in state $|\varphi_1\rangle$ at t_i, is still there a time T later. By inserting on the right or on the left of $U(T) = \exp(-iHT/2\hbar)$ the closure relation on the eigenstates of H, a superposition of exponentials of T appears, one of which has a clearly preponderant weight (zero order in V):

$$\tilde{U}_{11}(T) \simeq |\langle \varphi_1 | \psi_1 \rangle|^2\, e^{-i\delta E_1 T/\hbar}. \tag{B.2}$$

In (B.2), $|\psi_1\rangle$ is the eigenstate of H that approaches $|\varphi_1\rangle$ when V tends to zero, and δE_1 is the shift of state $|\varphi_1\rangle$ due to the coupling V, given by the

well-known perturbative expansion:

$$\delta E_1 = \langle \varphi_1 | V | \varphi_1 \rangle + \sum_{n \neq 1} \frac{\langle \varphi_1 | V | \varphi_n \rangle \langle \varphi_n | V | \varphi_1 \rangle}{E_1 - E_n} + \cdots . \qquad \text{(B.3)}$$

The study of the amplitude (B.1.a) allows the level shifts to be calculated. Note that, in the expansion of the amplitude (B.2), it is sufficient to know the term linear in T to obtain δE_1. We will encounter situations of this type in the study of the radiative shift of atomic states caused by the virtual emission and reabsorption of a photon.

Another interesting case is the one in which H_0 has two discrete states, $|\varphi_1\rangle$ and $|\varphi_2\rangle$, well isolated from the others, having the same unperturbed energy $E_1 = E_2$. Consider the amplitude

$$\tilde{U}_{21}(T) = \langle \varphi_2 | \tilde{U}(T) | \varphi_1 \rangle \qquad \text{(B.4)}$$

which allows us to calculate the probability

$$P_{21}(T) = |\tilde{U}_{21}(T)|^2 \qquad \text{(B.5)}$$

that the system, initially in the state $|\varphi_1\rangle$, passes after a time T to the state $|\varphi_2\rangle$. It is well known in quantum mechanics (the two-level problem) that $P_{21}(T)$ has an oscillating character. The frequency of this reversible oscillation of the system between $|\varphi_2\rangle$ and $|\varphi_1\rangle$, called the "Rabi nutation frequency", is proportional to the coupling introduced by V between $|\varphi_1\rangle$ and $|\varphi_2\rangle$, either directly (if $\langle \varphi_2 | V | \varphi_1 \rangle$ is nonzero), or indirectly (if $\langle \varphi_2 | V | \varphi_1 \rangle$ is zero) via other levels far from $|\varphi_1\rangle$ and $|\varphi_2\rangle$ (see Complement B_1). Such situations occur, for example, when an atomic system interacts with an intense monochromatic wave (see Complement A_{VI}).

If several discrete eigenstates of H_0 that are close to each other form a group sufficiently well isolated from all the other levels of H_0, then the transition amplitudes between two levels of the group are superpositions of Rabi oscillations with different amplitudes and frequencies. At the limit where the number of coupled states becomes extremely large, the interferences between these different Rabi oscillations eventually give an irreversible character to the evolution of the system. This is what we will study now by considering couplings involving a continuum of eigenstates of H_0.

2. Resonant Coupling between a Discrete Level and a Continuum

In this paragraph we assume that a discrete state $|\varphi_i\rangle$, having energy E_i, is coupled by V to a continuum $|\varphi_f\rangle$ of eigenstates of H_0 (the energy E_f of $|\varphi_f\rangle$ varies continuously).

The calculation of the transition amplitude $\langle \varphi_f | \tilde{U}(T) | \varphi_i \rangle$ is well-known in quantum mechanics. At the lowest order in V, that is, first order, we find (see Complement A_I, §2-b)

$$\tilde{U}_{fi}(T) = \langle \varphi_f | \tilde{U}(T) | \varphi_i \rangle \simeq \delta_{fi} - 2\pi i \delta^{(T)}(E_f - E_i) V_{fi} + \cdots \quad \text{(B.6)}$$

where $V_{fi} = \langle \varphi_f | V | \varphi_i \rangle$ is the matrix element of V between $\langle \varphi_f |$ and $| \varphi_i \rangle$ and where $\delta^{(T)}(E_f - E_i)$ is a delta function of width $\hbar/T$ that expresses the conservation of the unperturbed energy to within $\hbar/T$ (uncertainty related to the interaction duration T). In fact, $\delta(T)(E_f - E_i)$ is the Fourier transform of the product of an exponential with frequency $(E_f - E_i)/\hbar$ and a square function of width T. To obtain the transition probability from $| \varphi_i \rangle$ to $| \varphi_f \rangle$, we must take the square of the modulus of (B.6). Because states $| \varphi_i \rangle$ and $| \varphi_f \rangle$ are assumed to be different, the first term of (B.6), δ_{fi}, is zero. In addition, the square of $\delta^{(T)}$ is proportional to $T\delta^{(T)}$ [see Complement A_I, Equation (49)]. The probability of transition from $| \varphi_i \rangle$ to $| \varphi_f \rangle$ is thus proportional to the duration of the interaction, which allows us to define a transition rate equal to

$$w_{fi} = \frac{1}{T} |\tilde{U}_{fi}(T)|^2 \simeq \frac{2\pi}{\hbar} |V_{fi}|^2 \delta^{(T)}(E_f - E_i). \quad \text{(B.7)}$$

In fact, the final state $| \varphi_f \rangle$, which belongs to a continuous spectrum, is not normalizable. The quantity that does have a physical meaning is the transition rate toward a group of final states. For example, the sum of (B.7) over all the states $| \varphi_f \rangle$ gives the transition rate Γ of the discrete state $| \varphi_i \rangle$ to any state of the continuum:

$$\begin{aligned} \Gamma &= \sum_f w_{fi} = \frac{2\pi}{\hbar} \sum_f |V_{fi}|^2 \delta^{(T)}(E_f - E_i) \\ &= \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_f = E_i). \end{aligned} \quad \text{(B.8)}$$

In the second line of (B.8), it is assumed that $|V_{fi}|^2$ depends only on E_i and ρ is the density of final states evaluated at $E_f = E_i$ (Fermi's golden rule).

Another interesting quantity is the probability $|\tilde{U}_{ii}(T)|^2$ that the system will remain in the discrete state $| \varphi_i \rangle$ after a time interval T. The preceding perturbative calculation gives (conservation of the norm):

$$|\tilde{U}_{ii}(T)|^2 = 1 - \sum_f |\tilde{U}_{fi}(T)|^2 \simeq 1 - \Gamma T. \quad \text{(B.9)}$$

The probability of finding the system in state $|\varphi_i\rangle$ thus decreases proportionally to Γ. In fact, a nonperturbative calculation of the amplitude $\tilde{U}_{ii}(T)$, to which we will return in Chapter III, is possible (*). It gives

$$\tilde{U}_{ii}(T) = e^{-\Gamma T/2} e^{-i\delta E_i T/\hbar} \tag{B.10}$$

which shows that the discrete state decays exponentially over time with a "lifetime":

$$\tau = \frac{1}{\Gamma}. \tag{B.11}$$

The probability $|\tilde{U}_{ii}(T)|^2$ decays indeed as $\exp(-\Gamma T) = \exp(-T/\tau)$. A shift δE_i of the discrete state also appears as a result of its coupling with the continuum. The expression for δE_i is

$$\delta E_i = \mathscr{P} \sum_f \frac{|V_{fi}|^2}{E_i - E_f} \tag{B.12}$$

where $\mathscr{P}$ denotes the principal part. Thus it is clear that the study of transition amplitudes involving a discrete state and a continuum gives access to important physical quantities, such as lifetimes or level shifts. In Chapter II we will discuss an important example of this type of situation, the spontaneous emission of radiation by a discrete excited atomic state.

Remark

The exponential decay of $|\tilde{U}_{ii}(T)|^2$ is a simple example of irreversible evolution resulting from the superposition of an extremely large number of Rabi oscillations having different frequencies (see end of preceding subsection). It is important, however, to note that such a result holds only if the continuum to which the discrete state $|\varphi_i\rangle$ is coupled is extremely flat, more precisely, if the quantity $|V_{fi}|^2\rho(E_f)$ varies extremely slowly with E_f. If the continuum has structures responsible for rapid variations in $|V_{fi}|^2\rho(E_f)$, damped oscillations may persist in $|\tilde{U}_{ii}(T)|^2$ (see Complement C_{III}).

3. Couplings inside a Continuum or between Continua

It remains for us to consider the case in which both the initial state $|\varphi_i\rangle$ and the final state $|\varphi_f\rangle$ of the physical process being studied belong to the same continuum or to two different continua of eigenstates of H_0. Situa-

(*) A simple model of a discrete state coupled to a continuum is also analyzed in Complement C_I. It allows the exponential decay described by expression (B.10) to be simply obtained.

tions of this type are frequently encountered in the study of the scattering of photons by atoms. In this case, the state $|\varphi_i\rangle$ ($|\varphi_f\rangle$) represents the atom in a given energy level in the presence of an incident (scattered) photon. Because the energy of incident and scattered photons may vary in a continuous fashion, $|\varphi_i\rangle$ and $|\varphi_f\rangle$ do indeed belong to a continuum.

For sufficiently large T, the transition amplitude $\tilde{U}_{fi}(T)$ is just an element of the S matrix. The quantum calculation of $\tilde{U}_{fi}(T)$ gives (see Complements A_I and B_{III}):

$$\tilde{U}_{fi}(T) = \delta_{fi} - 2\pi i \delta^{(T)}(E_f - E_i)\mathscr{T}_{fi} \tag{B.13}$$

where $\delta^{(T)}$ is a delta function of width $\hbar/T$, and where $\mathscr{T}_{fi}$ is the transition matrix which can be expanded in powers of V (Born expansion) as

$$\mathscr{T}_{fi} = \langle\varphi_f|V|\varphi_i\rangle + \langle\varphi_f|V\frac{1}{E_i - H_0 + i\eta}V|\varphi_i\rangle + \\ + \langle\varphi_f|V\frac{1}{E_i - H_0 + i\eta}V\frac{1}{E_i - H_0 + i\eta}V|\varphi_i\rangle + \cdots \tag{B.14}$$

η being an infinitely small and positive quantity.

Remark

If the Born expansion does not converge, then expression (B.14) becomes meaningless. This occurs, for instance, when H_0 has a discrete eigenstate $|\varphi_k\rangle$ whose energy E_k coincides with that of the initial $|\varphi_i\rangle$ and final $|\varphi_f\rangle$ states ("resonant scattering" case). However, a compact expression of the transition matrix $\mathscr{T}_{fi}$ can be determined (see complement B_{III}, §1.b):

$$\mathscr{T}_{fi} = \langle\varphi_f|V|\varphi_i\rangle + \langle\varphi_f|V\frac{1}{E_i - H + i\eta}V|\varphi_i\rangle \tag{B.15}$$

where it is H instead of H_0 that appears in the denominator of the second term. We can verify that the formal expansion of the expression (B.15) actually results in the expansion (B.14). Indeed, the identity

$$\frac{1}{A} = \frac{1}{B} + \frac{1}{B}(B - A)\frac{1}{A} \tag{B.16}$$

applied to $A = E_i - H + i\eta$, $B = E_i - H_0 + i\eta$ gives

$$\frac{1}{E_i - H + i\eta} = \frac{1}{E_i - H_0 + i\eta} + \frac{1}{E_i - H_0 + i\eta} V \frac{1}{E_i - H + i\eta}. \quad \text{(B.17)}$$

The iteration of (B.17), when substituted into the second term of (B.15), gives (B.14).

As in subsection B.2, if $|\varphi_f\rangle \neq |\varphi_i\rangle$, the calculation of the transition probability $|\varphi_i\rangle \to |\varphi_f\rangle$ causes the square of the $\delta^{(T)}$ function, which is proportional to $T\delta^{(T)}$, to appear. It is thus possible to define a transition rate

$$w_{fi} = \frac{1}{T}|\tilde{U}_{fi}(T)|^2 = \frac{2\pi}{\hbar}|\mathscr{T}_{fi}|^2 \delta^{(T)}(E_f - E_i). \quad \text{(B.18)}$$

Since the final state $|\varphi_f\rangle$ is not normalizable, only the sum of w_{fi} over a group of final states has a physical meaning. This summation causes the density of final states $\rho(E_f = E_i)$ to appear. Finally, the initial state $|\varphi_i\rangle$ is also nonnormalizable because it belongs to a continuum. However, an incident flux can be associated with such a state $|\varphi_i\rangle$, and it is well known that the ratio of the transition rate from state $|\varphi_i\rangle$ toward a group of final states and the incident flux associated with $|\varphi_i\rangle$ is simply a *scattering cross-section*. We can thus see how it is possible to derive a measurable physical quantity, such as a cross-section, from the transition amplitudes $\tilde{U}_{fi}(T)$ between two states belonging to two continua. In the following, we will give several examples of scattering processes (Rayleigh, Raman, and Compton scattering, photoionization, bremsstrahlung, etc.).

Remark

Expression (B.18) appears as a generalized Fermi golden rule, where the coupling $\mathscr{T}_{fi}$ between $|\varphi_i\rangle$ and $|\varphi_f\rangle$ contains all the orders in V. However, it should be emphasized that expression (B.13), and expression (B.18), which results from it, are valid at all orders in V only if $|\varphi_i\rangle$ and $|\varphi_f\rangle$ both belong to a continuum. In addition, the exact expression (B.15) for $\mathscr{T}_{fi}$ must be used if intermediate resonant states exist. In the case where either one of the two states $|\varphi_i\rangle$ or $|\varphi_f\rangle$ is discrete, the difference between $\tilde{U}_{fi}(T)$ and δ_{fi} is proportional to $\delta^{(T)}(E_f - E_i)$ only at the lowest order in V.

C—APPLICATION TO ELECTRODYNAMICS

1. Coulomb Gauge Hamiltonian

We will now consider the electrodynamics case. The system under study consists of an ensemble of charged particles α, having charge q_α and mass m_α, interacting with an electromagnetic field. Let $\mathbf{r}_\alpha$ and $\mathbf{p}_\alpha = (\hbar/i)\nabla_\alpha$ be the position and momentum of the particle α, and $\mathbf{A}(\mathbf{r})$ be the potential vector of the field which, in the Coulomb gauge, is transverse ($\mathbf{A} = \mathbf{A}_\perp$). The Hamiltonian that describes the dynamics of this system is written, in the Coulomb gauge (see Appendix, §3),

$$H = \sum_\alpha \frac{1}{2m_\alpha}\left[\mathbf{p}_\alpha - q_\alpha \mathbf{A}(\mathbf{r}_\alpha)\right]^2 - \sum_\alpha \frac{g_\alpha q_\alpha}{2m_\alpha}\mathbf{S}_\alpha \cdot \mathbf{B}(\mathbf{r}_\alpha) + V_{\text{Coul}} + H_R. \tag{C.1}$$

The first term of (C.1) represents the kinetic energies of the particles, since the velocity $\dot{\mathbf{r}}_\alpha$ of the particle α is

$$\dot{\mathbf{r}}_\alpha = \frac{1}{i\hbar}[\mathbf{r}_\alpha, H] = \frac{\partial H}{\partial \mathbf{p}_\alpha} = \frac{1}{m_\alpha}\left[\mathbf{p}_\alpha - q_\alpha \mathbf{A}(\mathbf{r}_\alpha)\right]. \tag{C.2}$$

The second term of (C.1) represents the interaction of the spin magnetic moments of the particles ($\mathbf{S}_\alpha$ is the spin of the particle α; g_α is its Landé factor) with the magnetic field $\mathbf{B}$ of the radiation field evaluated at the points where the particles are located. The third term, V_{Coul}, is the Coulomb energy of the system of particles. It is the sum of the Coulomb interaction energies between pairs of particles (α, β) and of the Coulomb self-energies $\varepsilon^\alpha_{\text{Coul}}$ of each particle

$$V_{\text{Coul}} = \sum_{\alpha \neq \beta} \frac{q_\alpha q_\beta}{8\pi\varepsilon_0}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \sum_\alpha \varepsilon^\alpha_{\text{Coul}}. \tag{C.3}$$

$\varepsilon^\alpha_{\text{Coul}}$ is a constant given by formula (43) in the Appendix. Finally, the last term H_R is the energy of the transverse field (electric $\mathbf{E}_\perp$ and magnetic $\mathbf{B}$):

$$H_R = \frac{\varepsilon_0}{2}\int d^3r\left[\mathbf{E}_\perp^2(\mathbf{r}) + c^2\mathbf{B}^2(\mathbf{r})\right] \tag{C.4.a}$$

which can also be expressed simply as function of the annihilation and

creation operators a_j and a_j^+ of a photon in the normal vibrational "mode" j of the field (identified by the wave vector $\mathbf{k}_j$, the polarization $\boldsymbol{\varepsilon}_j$, and the frequency $\omega_j = ck_j$)

$$H_R = \sum_j \hbar\omega_j \left(a_j^+ a_j + \tfrac{1}{2}\right). \tag{C.4.b}$$

Each mode j is thus associated with a one-dimensional harmonic oscillator. The eigenstate $|n_j\rangle$ of such an oscillator (with $n_j = 0, 1, 2 \ldots$) represents a state in which the mode j contains n_j photons having energy $\hbar\omega_j$, momentum $\hbar\mathbf{k}_j$ and polarization $\boldsymbol{\varepsilon}_j$. Finally, recall that the different transverse fields $\mathbf{E}_\perp$ and $\mathbf{B}$, as well as $\mathbf{A}$, can be expressed as a linear combination of operators a_j and a_j^+ (see expressions (29), (30), and (28) in the Appendix).

For what follows, it is useful to rewrite the Hamiltonian H in the form

$$H = \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + H_R + V_{\text{Coul}} + H_{I1} + H_{I2} + H_{I1}^S \tag{C.5.a}$$

with

$$H_{I1} = -\sum_\alpha \frac{q_\alpha}{m_\alpha} \mathbf{p}_\alpha \cdot \mathbf{A}(\mathbf{r}_\alpha) \tag{C.5.b}$$

$$H_{I1}^S = -\sum_\alpha g_\alpha \frac{q_\alpha}{2m_\alpha} \mathbf{S}_\alpha \cdot \mathbf{B}(\mathbf{r}_\alpha) \tag{C.5.c}$$

$$H_{I2} = \sum_\alpha \frac{q_\alpha^2}{2m_\alpha} \left[\mathbf{A}(\mathbf{r}_\alpha)\right]^2. \tag{C.5.d}$$

The splitting of H into $H_0 + V$ may be achieved in several ways. We will now discuss two that lead to different types of perturbative expansions for the transition amplitudes.

2. Expansion in Powers of the Charges q_α

A first possibility consists of gathering in H_0 all the terms independent of q_α:

$$H_0 = \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + H_R. \tag{C.6.a}$$

The charges q_α thus appear as coupling parameters characterizing the strength of the perturbation:

$$V = V_{\text{Coul}} + H_{I1} + H_{I1}^S + H_{I2}. \tag{C.6.b}$$

The eigenstates of H_0 thus simply represent the free particles (eigenstates of $\mathbf{p}_\alpha^2/2m_\alpha$) in the presence of transverse photons (eigenstates of H_R). No bound state of the particles can appear in H_0, because no coupling, either direct or indirect, can exist between the particles.

All terms contained in V— the Coulomb interaction as well as the interaction between the particles and the transverse field—will then be treated in a perturbative fashion. The physics problems that can be studied simply with such an approach are thus essentially particle-particle or particle-photon scattering problems (Coulomb scattering, Compton scattering, bremsstrahlung emission, etc.).

3. Expansion in Powers of the Interaction with the Transverse Field

The second splitting of H that we will consider here consists of collecting in H_0 all the terms that depend either on the dynamical variables of the particles, or on the dynamical variables of the transverse field, but not on both at the same time:

$$H_0 = H_P + H_R \tag{C.7.a}$$

where

$$H_P = \sum_\alpha \frac{\mathbf{p}_\alpha^2}{2m_\alpha} + V_{\text{Coul}} \tag{C.7.b}$$

is a particle Hamiltonian. The perturbation V thus contains all terms containing both the particle operators and transverse field operators:

$$V = H_{I1} + H_{I1}^S + H_{I2}. \tag{C.7.c}$$

The perturbative expansion in powers of V is thus an expansion in powers of the interaction between the particles and the transverse field.

Since the Coulomb interaction V_{Coul} is included in the particle Hamiltonian, such a Hamiltonian can now describe bound states. In fact, the eigenstates of H_P are characterized by two types of quantum numbers: on the one hand, the *external* quantum numbers, describing the motion of the center of mass of the group of particles, and on the other hand, the

internal quantum numbers, describing the excitation state of the system of particles in the center-of-mass reference frame. For example, if the particles under study form an atom or a molecule, the internal quantum numbers indicate the energy levels of this atom or this molecule. The eigenstates of H_0 thus describe situations in which systems of particles, such as atoms, molecules, ions, etc. in well-defined internal states and with a well-defined global momentum, are in the presence of a certain number of transverse photons characterized by well-defined energy, momentum, and polarization.

The perturbative treatment of V then allows us to describe the processes of absorption or emission of photons by such systems of particles. Further on we will give a diagrammatic representation of the transition amplitudes induced by V that allow these different processes to be visualized.

Remark

When the system of particles consists of several distinct systems $A, B, \ldots$ (atoms, molecules, ions, electrons, etc.) well separated from each other, it may be advantageous to retain in H_0 only the Coulomb energies inside each system, V_{Coul}^{AA}, V_{Coul}^{BB}, and to include in the interaction Hamiltonian V the Coulomb interaction energy between different systems, $V_{\text{Coul}}^{AB} \ldots$. The eigenstates of H_0 thus represent situations in which the different systems $A, B, \ldots$ are in well-defined external and internal states, without mutual interactions, and in the presence of a certain number of photons.

4. Advantages of Including the Coulomb Interaction in the Particle Hamiltonian

The first advantage of the splitting (C.7) as compared to (C.6) is that it allows us to consider states where charged particles are bound by the Coulomb interaction (atoms, molecules, ions, etc.) as unperturbed states. Such states can indeed exist before the switching on and survive after the switching off of V. (See Figure 1.) With the other splitting (C.6), no bound state could exist in the absence of V (*). Atoms, molecules, ions, etc. would dissociate into nuclei and electrons before the switching on and after the switching off of V, and it would be much more difficult to describe the emission, absorption, or scattering of photons by such systems.

(*) Of course, we ignore here any interactions other than electromagnetic ones, such as, for example, strong interactions responsible for the cohesion of nuclei.

The second advantage of the splitting (C.7) is that V_{Coul} is, in the nonrelativistic domain, much more important than the interaction with the transverse field. It is thus natural to start with the eigenstates of H_0 and deal with the effect of interactions with the transverse field as a perturbation.

Remarks

(i) The elimination of the scalar potential and the longitudinal vector potential causes the Coulomb interaction to appear as a purely particle term in the Coulomb gauge representation. In another gauge, for example, in the Lorentz gauge, the Coulomb interaction appears only in a second-order treatment of the interaction between particles and scalar and longitudinal potentials (*). The advantages of the splitting (C.7) that we just discussed are thus closely connected to the choice of the Coulomb gauge.

(ii) Such advantages also exist in other formulations of quantum electrodynamics equivalent to Coulomb gauge electrodynamics, such as, for example, the one leading to the electric dipole Hamiltonian (see Appendix, §5). The new Hamiltonian H', which is the unitary transform of $H = H_0 + V$, may also be written in the form $H' = H_0 + V'$, where H_0 has the same expression as in (C.7) and contains in particular the Coulomb interaction.

5. Diagrammatic Representation of Transition Amplitudes

Let us use, for example, the splitting (C.7). The perturbative expansion of the evolution operator causes the transition amplitudes to appear as products of matrix elements of V between eigenstates of H_0 and of free evolution exponentials between two interactions, these products being summed over all times and over all intermediate states (see Complement A_I, §2.a):

$$\begin{aligned}\langle \varphi_f | U(t_f, t_i) | \varphi_i \rangle = {} & \delta_{fi}\, e^{-iE_i(t_f - t_i)/\hbar} + \\ & + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{t_f \geq \tau_n \cdots \tau_2 \geq \tau_1 \geq t_i} d\tau_n \cdots d\tau_2\, d\tau_1 \times \\ & \times \sum_{\varphi_{n-1} \cdots \varphi_1} e^{iE_f(t_f - \tau_n)/\hbar} \langle \varphi_f | V | \varphi_{n-1} \rangle e^{-iE_{n-1}(\tau_n - \tau_{n-1})/\hbar} \cdots \\ & \cdots \langle \varphi_2 | V | \varphi_1 \rangle e^{-iE_1(\tau_2 - \tau_1)/\hbar} \langle \varphi_1 | V | \varphi_i \rangle e^{-iE_i(\tau_1 - t_i)/\hbar}. \end{aligned} \tag{C.8}$$

In what follows, it will be convenient to use diagrammatic representations

(*) See, for example, Complement B_V of *Photons and Atoms—Introduction to Quantum Electrodynamics*.

of these products, because such representations allow one to visualize the physical processes involved in the transition amplitude.

The free propagation of particles will be represented by straight lines, while that of photons will be represented by wavy lines. Next to each line will be quantum numbers indicating the corresponding free state ($a, b, \ldots$ for the state of particles, wave vector $\mathbf{k}$, and polarization ϵ for photons). Each of these lines has associated with it exponential factors of the type $\exp[-iE(\tau_k - \tau_l)/\hbar]$, describing the free evolution of the state of energy E between times τ_k and τ_l associated with the ends of the line (these times are not explicitly shown on the diagram to keep it as simple as possible). Each diagram is read going from bottom to top (following the time course of the process). The lines for particles and for photons coming from the bottom correspond to the free state in the ket $|\varphi_i\rangle$ of the matrix element; the lines for particles and for photons going toward the top correspond to the free state in the bra $\langle\varphi_f|$. The matrix elements of V are represented by the points at which these lines intersect (vertex), with the matrix element being taken between the state described by the lines which arrive at the vertex and that described by those which leave from it. A photon line arriving and disappearing at this point (Figure 2*a*) corresponds to the annihilation of a photon (a term of H_{I1} and H_{I1}^S). A photon line leaving from this point (Figure 2*b*) corresponds to the creation of a photon ($a^\dagger$ term of H_{I1} and H_{I1}^S). The two-photon terms of H_{I2} corre-

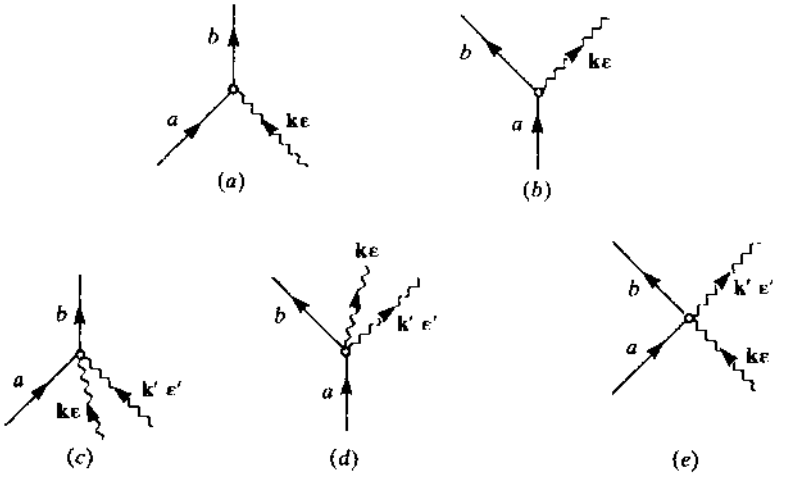


Figure 2. Different types of vertex corresponding to different matrix elements of V.

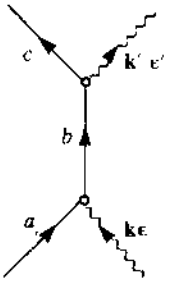


Figure 3. Diagrammatic representation of transition amplitude (C.9).

spond to the three Figures 2*c* (a^2 term annihilating two photons), 2*d* (a^{+2} term creating two photons), and 2*e* (aa^+ or a^+a terms creating one photon while annihilating another).

In many processes, there is more than one interaction between atoms and fields. The corresponding diagram thus contains several vertices and several lines associated with the free propagation between interactions. It symbolizes the product of all the quantities (matrix elements of V, free evolution exponentials) represented in this way. For example, the diagram in Figure 3 symbolizes the quantity

$$\begin{aligned} &\exp\left[-i(E_c + \hbar\omega')(t_f - \tau_2)/\hbar\right]\langle c; \mathbf{k}'\boldsymbol{\varepsilon}'|V|b; 0\rangle \times \\ &\quad \times \exp\left[-iE_b(\tau_2 - \tau_1)/\hbar\right]\langle b; 0|V|a; \mathbf{k}\boldsymbol{\varepsilon}\rangle \times \\ &\quad \times \exp\left[-i(E_a + \hbar\omega)(\tau_1 - t_i)/\hbar\right] \end{aligned} \tag{C.9}$$

and represents the amplitude that the system of particles, initially in state a, absorbs at instant τ_1 an incident photon $\mathbf{k}\boldsymbol{\varepsilon}$ and passes into state b, then finishes at instant τ_2 in state c by emitting a photon $\mathbf{k}'\boldsymbol{\varepsilon}'$. Other types of diagrams will be introduced later on in this book.

Remark

In other formulations of quantum electrodynamics equivalent to Coulomb gauge electrodynamics, the interaction Hamiltonian V' may have matrix elements that are more simple than V. For example, in the electric dipole point of view (see Appendix, §5), the interaction Hamiltonian (of the form $-q\mathbf{E}_\perp \cdot \mathbf{r}$) contains only one-photon terms that are linear in a and a^+. There are no more two-photon terms such as those coming from $\mathbf{A}^2$ and resulting in matrix elements of the same type as those represented in Figures 2*c*, 2*d*, and 2*e*. This results in a great simplification in the higher order terms of the perturbative expansion of the transition amplitudes.

General References

For the importance of transition amplitudes, see Feynman, Volume III, Chapters 3 and 7, Cohen-Tannoudji, Diu, and Laloë, Chapter III, Section E; Levy-Leblond and Balibar, Chapters 4 and 5.

The perturbative calculation of transition amplitudes may be found in many quantum mechanics books. See, for example, Messiah, Chapter XVII; Cohen-Tannoudji, Diu, and Laloë, Chapter XIII; Merzbacher, Chapter XVIII; Schiff, Chapters 8 and 9; Feynman and Hibbs, Chapter VI. References concerning transition amplitudes between two continua (collision problems) will be given in Chapter III.

For Coulomb gauge electrodynamics, see the Appendix and the references therein.

COMPLEMENT A_I

PERTURBATIVE CALCULATION OF TRANSITION AMPLITUDES—SOME USEFUL RELATIONS

In Chapter I, without presenting any formal proofs, we used several results concerning transition amplitudes. The goal of this complement is to sketch a brief derivation of these results and to gather several useful relations to which we will continue to refer throughout this book.

We will begin (§1) by introducing the interaction representation and by emphasizing its advantages. We will then (§2) proceed to the perturbative calculation of transition amplitudes and to the determination of the lowest-order terms (order 0, 1, 2) in the expansion of these amplitudes in powers of the coupling V. Finally, we will study (§3) the transition probability from an initial state toward a final state by distinguishing several cases according to the discrete or continuous nature of the energy spectrum.

1. Interaction Representation

As in Chapter I, the Hamiltonian H of the system under study is split into

$$H = H_0 + V. \tag{1}$$

The unperturbed Hamiltonian H_0 is assumed to be time independent. The coupling V may or may not depend on time [for example, if V is multiplied by the parameter $\lambda(t)$, whose temporal variations are shown in Figure 1 of the chapter].

Going from the usual Schrödinger representation to the interaction representation with respect to H_0 is achieved by applying the unitary transformation

$$T(t) = e^{iH_0(t-t_0)/\hbar} \tag{2}$$

to the vectors $|\psi(t)\rangle$ and operators A of the Schrödinger representation, t_0 being a reference instant that we take as the origin of time ($t_0 = 0$). If

$|\tilde{\psi}(t)\rangle$ and $\tilde{A}(t)$ represent the vectors and operators in the new representation, then we have

$$|\tilde{\psi}(t)\rangle = e^{iH_0t/\hbar}|\psi(t)\rangle \tag{3.a}$$

$$\tilde{A}(t) = e^{iH_0t/\hbar} A e^{-iH_0t/\hbar}. \tag{3.b}$$

If V were zero, the interaction representation would be identical to the Heisenberg representation, and $|\tilde{\psi}(t)\rangle$ would remain fixed over time. It follows that, in the general case where V is nonzero, $|\tilde{\psi}(t)\rangle$ evolves only as a result of the presence of the coupling V. To see this more precisely, let us determine the evolution equation of $|\tilde{\psi}(t)\rangle$ by applying $i\hbar d/dt$ to (3.a) and by using the Schrödinger equation for $i\hbar d|\psi(t)\rangle/dt$. We get

$$\begin{aligned} i\hbar\frac{d}{dt}|\tilde{\psi}(t)\rangle &= -H_0|\tilde{\psi}(t)\rangle + e^{iH_0t/\hbar}(H_0 + V)|\psi(t)\rangle \\ &= \tilde{V}(t)|\tilde{\psi}(t)\rangle \end{aligned} \tag{4}$$

where

$$\tilde{V}(t) = e^{iH_0t/\hbar} V e^{-iH_0t/\hbar}. \tag{5}$$

Equation (4) clearly shows that the rate of variation of $|\tilde{\psi}(t)\rangle$ is at least first order in V. In particular, in the study of a collision process, where the coupling V can be switched off in the remote past and the far future (see Figure 1 in Chapter I), the state vector does not evolve in the interaction representation before the collision begins and after it ends. This allows us to understand how the matrix elements of the evolution operator $\tilde{U}(t_f, t_i)$ in interaction representation have a well-defined limit when t_f and t_i tend, respectively, to $+\infty$ and $-\infty$ (scattering matrix). It is useful also for what follows to determine the relation that exists between $\tilde{U}(t_f, t_i)$ and the evolution operator $U(t_f, t_i)$ in the Schrödinger representation. The equation

$$|\psi(t_f)\rangle = U(t_f, t_i)|\psi(t_i)\rangle \tag{6}$$

gives, taking in account (3.a)

$$|\tilde{\psi}(t_f)\rangle = \tilde{U}(t_f, t_i)|\tilde{\psi}(t_i)\rangle \tag{7}$$

with

$$\tilde{U}(t_f, t_i) = e^{iH_0 t_f/\hbar}\, U(t_f, t_i) e^{-iH_0 t_i/\hbar}. \tag{8}$$

2. Perturbative Expansion of Transition Amplitudes

a) Perturbative Expansion of the Evolution Operator

The evolution operator $U(t_f, t_i)$ of the Schrödinger representation is defined by (6), and satisfies the initial condition

$$U(t_i, t_i) = \mathbb{1}. \tag{9}$$

Taking into account the Schrödinger equation satisfied by $|\psi(t_f)\rangle$, Equation (6) is equivalent to the integral equation

$$U(t_f, t_i) = U_0(t_f, t_i) + \frac{1}{i\hbar}\int_{t_i}^{t_f} dt\, U_0(t_f, t) V U(t, t_i) \tag{10}$$

where

$$U_0(t_f, t_i) = e^{-iH_0(t_f - t_i)/\hbar} \tag{11}$$

is the unperturbed evolution operator associated with H_0. To prove this equivalence, it is sufficient to verify that the operator U defined by (10) actually satisfies (9) and the evolution equation

$$i\hbar \frac{d}{dt_f} U(t_f, t_i) = (H_0 + V) U(t_f, t_i). \tag{12}$$

By successive iterations, Equation (10) thus leads to the well-known perturbative expansion of the evolution operator

$$U(t_f, t_i) = U_0(t_f, t_i) + \sum_{n=1}^{\infty} U^{(n)}(t_f, t_i) \tag{13.a}$$

with

$$U^{(n)}(t_f, t_i) = \left(\frac{1}{i\hbar}\right)^n \int_{t_f \geq \tau_n \cdots \tau_2 \geq \tau_1 \geq t_i} d\tau_n \cdots d\tau_2\, d\tau_1 \times$$
$$\times e^{-iH_0(t_f - \tau_n)/\hbar} V \cdots V e^{-iH_0(\tau_2 - \tau_1)/\hbar} V e^{-iH_0(\tau_1 - t_i)/\hbar}. \tag{13.b}$$

The structure of the term (13.b) is that of a product of $(n+1)$ unperturbed evolution operators separated by n interaction operators V. By taking the matrix elements of (13.b) between the eigenstates $\langle\varphi_f|$ and $|\varphi_i\rangle$ of H_0 and by inserting $(n-1)$ times the closure relation on the eigenstates of H_0, between two successive V operators, formula (C.8) of the chapter is obtained.

Equation (8) finally allows us to obtain the perturbative expansion of the evolution operator in the interaction representation

$$\tilde{U}(t_f, t_i) = \mathbb{1} + \sum_{n=1}^{\infty} \tilde{U}^{(n)}(t_f, t_i) \tag{14.a}$$

$$\tilde{U}^{(n)}(t_f, t_i) = \left(\frac{1}{i\hbar}\right)^n \int_{t_f \geq \tau_n \cdots \tau_2 \geq \tau_1 \geq t_i} \mathrm{d}\tau_n \cdots \mathrm{d}\tau_2\, \mathrm{d}\tau_1 \tilde{V}(\tau_n) \cdots \tilde{V}(\tau_2)\tilde{V}(\tau_1). \tag{14.b}$$

Comparison of (14.b) and (13.b) demonstrates that using the interaction representation eliminates the free evolution exponentials $\exp(-iH_0 t_f/\hbar)$ and $\exp(iH_0 t_i/\hbar)$ relative to the initial and final times. Let $\mathscr{S}_{fi}$ be the matrix element of $\tilde{U}(t_f, t_i)$ between the eigenstates $\langle\varphi_f|$ and $|\varphi_i\rangle$ of H_0

$$\mathscr{S}_{fi} = \langle\varphi_f|\tilde{U}(t_f, t_i)|\varphi_i\rangle. \tag{15}$$

The perturbative expansion (14) thus yields

$$\mathscr{S}_{fi} = \delta_{fi} + \sum_{n=1}^{\infty} \mathscr{S}_{fi}^{(n)} \tag{16.a}$$

$$\mathscr{S}_{fi}^{(n)} = \langle\varphi_f|\tilde{U}^{(n)}(t_f, t_i)|\varphi_i\rangle. \tag{16.b}$$

We will now calculate the first- and second-order terms in V of this perturbative expansion of the transition amplitude $\mathscr{S}_{fi}$.

b) First-Order Transition Amplitude

Using (16.b), (14.b), and (5), we get

$$\mathscr{S}_{fi}^{(1)} = \frac{1}{i\hbar} \int_{t_i}^{t_f} \mathrm{d}\tau_1\, V_{fi}\, \mathrm{e}^{i(E_f - E_i)\tau_1/\hbar} \tag{17}$$

where we have set $V_{fi} = \langle\varphi_f|V|\varphi_i\rangle$. We assume here that V is time

independent and select the origin of time such that

$$t_i = -T/2 \qquad t_f = +T/2 \tag{18}$$

where T is the duration of the interaction. The integral over τ_1 of (17) can thus be calculated and it yields

$$\mathscr{S}_{fi}^{(1)} = -2\pi i V_{fi} \delta^{(T)}(E_f - E_i) \tag{19}$$

where

$$\delta^{(T)}(E_f - E_i) = \frac{1}{2\pi} \int_{-T/2}^{+T/2} \frac{d\tau_1}{\hbar} e^{i(E_f - E_i)\tau_1/\hbar}$$

$$= \frac{1}{\pi} \frac{\sin(E_f - E_i)T/2\hbar}{(E_f - E_i)}. \tag{20}$$

According to the first equality in (20), $\delta^{(T)}(E_f - E_i)$ tends to $\delta(E_f - E_i)$ when $T \to \infty$. In fact, according to the second equality in (20), $\delta^{(T)}(E_f - E_i)$ is a diffraction function, represented in Figure 1. Its maximal amplitude $T/2\pi\hbar$ is obtained for $E_f - E_i = 0$, and its width is on the order of $4\pi\hbar/T$ (distance between the first two zeros on either side of the

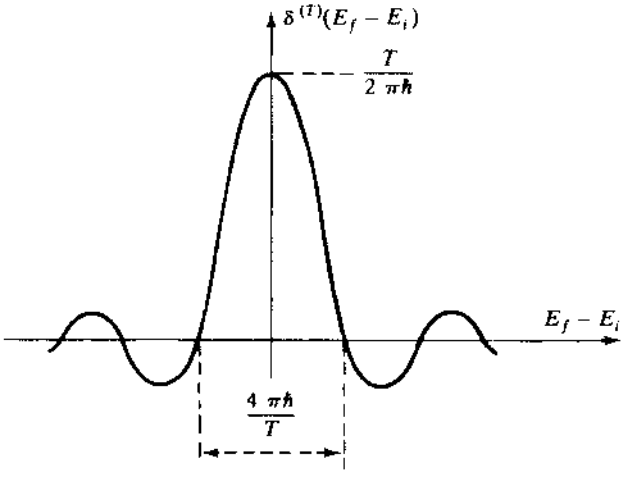


Figure 1. Variations of the function $\delta^{(T)}(E_f - E_i)$ versus $(E_f - E_i)$.

maximum). Its integral equals 1. Hence this function is an approximate delta function expressing the conservation of energy with an uncertainty $\hbar/T$ due to the finite duration of the interaction.

Remark

If V is multiplied by the function $\lambda(t)$ shown in Figure 1 of Chapter I, relation (19) remains valid but $\delta^{(T)}$ is then the Fourier transform of a square function with a width on the order of T, with smooth edges. The function $\delta^{(T)}$ is in this case an apodized diffraction function for which the integral is always equal to 1 and which can still be considered as a delta function of width $\hbar/T$.

c) Second-Order Transition Amplitude

For second order, Equations (16.b), (14.b), and (5) yield

$$\mathscr{S}_{fi}^{(2)} = \left(\frac{1}{i\hbar}\right)^2 \int_{+T/2 \geq \tau_2 \geq \tau_1 \geq -T/2} \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \times \times \sum_k V_{fk} V_{ki}\, \mathrm{e}^{i(E_f - E_k)\tau_2/\hbar}\, \mathrm{e}^{i(E_k - E_i)\tau_1/\hbar}. \tag{21}$$

The sum over the intermediate states $|\varphi_k\rangle$ represents a sum over the eigenstates of H_0. To eliminate the restriction $\tau_2 \geq \tau_1$, the integrand in (21) is multiplied by the Heaviside function $\theta(\tau_2 - \tau_1)$, which is equal to 1 for $\tau_2 > \tau_1$ and equal to 0 for $\tau_2 < \tau_1$. We then use the identity

$$\mathrm{e}^{-iE_k(\tau_2 - \tau_1)/\hbar}\, \theta(\tau_2 - \tau_1) = \lim_{\eta \to 0_+} \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\mathrm{e}^{-iE(\tau_2 - \tau_1)/\hbar}}{E + i\eta - E_k}\, \mathrm{d}E \tag{22}$$

which can be easily checked by calculating the integral of (22) by the method of residues. Equation (21) may thus be rewritten

$$\mathscr{S}_{fi}^{(2)} = \left(\frac{1}{i\hbar}\right)^2 \left(\frac{-1}{2\pi i}\right) \int_{T/2}^{+T/2} \mathrm{d}\tau_2 \int_{T/2}^{+T/2} \mathrm{d}\tau_1 \times \times \int_{-\infty}^{+\infty} \mathrm{d}E\, \mathrm{e}^{i(E_f - E)\tau_2/\hbar}\, \mathrm{e}^{-i(E_i - E)\tau_1/\hbar}\, W_{fi}(E) \tag{23}$$

where

$$W_{fi}(E) = \lim_{\eta \to 0_+} \sum_k \frac{V_{fk} V_{ki}}{E + i\eta - E_k}. \tag{24}$$

From subsection 2-b above, the integrals over τ_2 and τ_1 give, respectively, $2\pi\hbar\delta^{(T)}(E_f - E)$ and $2\pi\hbar\delta^{(T)}(E_i - E)$. These two functions are practically zero as soon as E differs from E_f for the former and from E_i for the latter by more than $\hbar/T$. Their product is thus a function of E which is nonzero if E_f and E_i are equal within $\hbar/T$, and if E also coincides with this common value of E_i and E_f within $\hbar/T$.

To carry out the latter integral over E which remains to be done in (23), we must now compare the width in E of $\delta^{(T)}(E_f - E)\delta^{(T)}(E_i - E)$ which is on the order of $\hbar/T$ about $E_i \simeq E_f$, to the width of the other function $W_{fi}(E)$ which appears in (23). In many cases, which we will describe further on, $W_{fi}(E)$ is a function of E that varies only slightly with E over an interval of width $\hbar/T$. It is thus possible to replace $W_{fi}(E)$ by $W_{fi}(E_i)$ in (23) and to take $W_{fi}(E_i)$ out of the integral, which gives

$$\mathscr{S}_{fi}^{(2)} = -\frac{1}{2\pi i}\frac{4\pi^2\hbar^2}{(i\hbar)^2}\left[\lim_{\eta \to 0_+}\sum_k \frac{V_{fk}V_{ki}}{E_i - E_k + i\eta}\right]\times$$
$$\times\int_{-\infty}^{+\infty} dE\,\delta^{(T)}(E - E_i)\delta^{(T)}(E - E_f). \tag{25}$$

The integral over E of (25) can be easily calculated from the integral form (20) of $\delta(T)$

$$\int_{-\infty}^{+\infty} dE\,\delta^{(T)}(E - E_i)\,\delta^{(T)}(E - E_f) =$$
$$= \frac{1}{4\pi^2\hbar^2}\int_{-\infty}^{+\infty} dE \int_{-T/2}^{T/2} d\tau \int_{-T/2}^{T/2} d\tau'\, e^{i(E - E_f)\tau/\hbar}\, e^{i(E - E_i)\tau'/\hbar}. \tag{26}$$

(Note that there is no restriction on the temporal order of τ and τ'.) The integral over E of (26) gives $2\pi\hbar\delta(\tau + \tau')$, so that (26) reduces to

$$\int_{-\infty}^{+\infty} dE\,\delta^{(T)}(E - E_i)\,\delta^{(T)}(E - E_f)$$
$$= \frac{1}{2\pi\hbar}\int_{-T/2}^{+T/2} d\tau\, e^{i(E_i - E_f)\tau/\hbar} = \delta^{(T)}(E_i - E_f). \tag{27}$$

Finally, by substituting (27) into (25), we obtain

$$\mathscr{S}_{fi}^{(2)} = -2\pi i\left[\lim_{\eta \to 0_+}\sum_k \frac{V_{fk}V_{ki}}{E_i - E_k + i\eta}\right]\delta^{(T)}(E_i - E_f). \tag{28}$$

Let us now specify the cases for which $W_{fi}(E)$ may be indeed considered to be a function of E varying slowly on the scale of $\hbar/T$. Essentially, there must not be any discrete eigenstates $|\varphi_k\rangle$ of H_0 for which the energy E_k is extremely close to E_i and E_f. In such a case, the function $(E - E_k + i\eta)^{-1}$ would vary quite rapidly with E near $E = E_i$, because it diverges for $E = E_k$. By contrast, note that H_0 may have a continuous spectrum E_k near $E_i \simeq E_f$. In this case, the sum over k in (24) becomes actually an integral over E_k. The fraction $1/(E + i\eta - E_k)$ is then expressed as a function of $\delta(E - E_k)$ and $\mathcal{P}[1/(E - E_k)]$ and yields, after integration over E_k, functions of E which have no reason to diverge near $E_i \simeq E_f$. For sufficiently large T, these functions may thus be considered as varying slowly on the scale of $\hbar/T$.

Finally, summarizing the results obtained in this paragraph, we may write

$$\mathcal{S}_{fi} = \delta_{fi} - 2\pi i \delta^{(T)}(E_f - E_i)\left[V_{fi} + \lim_{\eta \to 0,} \sum_k \frac{V_{fk}V_{ki}}{E_i - E_k + i\eta}\right] + 0(V^3). \tag{29}$$

Remarks

(i) If either the initial state $|\varphi_i\rangle$ or the final state $|\varphi_f\rangle$ or both states are discrete, the intermediate state $|\varphi_k\rangle$ may be the same as this discrete state in the sum (24), which leads to a divergence of $W_{fi}(E)$ near E_i or E_f. This may, however, occur only if the diagonal element of V in the discrete state, V_{ii} (or V_{ff}), is nonzero. We can always put these diagonal elements back into H_0 (which amounts to replacing E_i by $E_i + V_{ii}$). It is then possible to use expression (28) for $\mathcal{S}_{fi}^{(2)}$. Nevertheless, for orders higher than 2, it is, in general, impossible to prevent $|\varphi_i\rangle$ (or $|\varphi_f\rangle$) from appearing as an intermediate state.

(ii) In Chapter III, we will introduce methods for calculating transition amplitudes that are more powerful than those discussed in this complement. These methods allow us to sum up all the terms of the perturbation expansion in which one or more discrete states, which appear as intermediate states, might lead to divergences of the transition amplitudes because their energy is extremely close to that of the initial and final states. We will thus obtain nonperturbative expressions for these transition amplitudes that are valid under conditions for which expression (29) is not. The same approach allows us to generalize expression (29) of $\mathcal{S}_{fi}$ for higher orders in the case of a scattering problem where $|\varphi_i\rangle$ and $|\varphi_f\rangle$ both belong to the continuous spectrum of H_0. We obtain in this case

$$\mathcal{S}_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i)\mathcal{T}_{fi} \tag{30}$$

where the transition matrix $\mathscr{T}_{fi}$ is given by expression (B.15) in Chapter 1. When it is valid, the expansion in powers of V of $\mathscr{T}_{fi}$ is the Born expansion, the first two terms of which appear inside the brackets in (29).

3. Transition Probability

a) Calculation of the Transition Probability to a Final State Different from the Initial State

Assume that $|\varphi_f\rangle$ is different from $|\varphi_i\rangle$. The first term, δ_{fi}, of (29) is thus zero. The transition probability $\mathscr{P}_{fi}(T)$ from $|\varphi_i\rangle$ to $|\varphi_f\rangle$ at the end of time T is

$$\mathscr{P}_{fi}(T) = |\mathscr{T}_{fi}|^2 = 4\pi^2\left[\delta^{(T)}(E_i - E_f)\right]^2 \times \times \left| V_{fi} + \lim_{\eta \to 0_+} \sum_k \frac{V_{fk}V_{ki}}{E_i - E_k + i\eta} \right|^2 + \cdots . \quad (31)$$

From (20), the function

$$\left[\delta^{(T)}(E_f - E_i)\right]^2 = \frac{1}{\pi^2} \frac{\sin^2(E_f - E_i)T/2\hbar}{(E_f - E_i)^2} \quad (32)$$

is the square of a diffraction function. For $E_f = E_i$, $[\delta^{(T)}(E_f - E_i)]^2$ reaches its maximum value, $T^2/4\pi^2\hbar^2$. The distance between the first two zeros of this function on either side of its maximum is, as for $\delta^{(T)}$, equal to $4\pi\hbar/T$ and gives some idea of its width. Later on, we will need the integral over E_f of this function, which is on the order of $(T^2/4\pi^2\hbar^2) \times (4\pi\hbar/T)$, that is, on the order of $T/\pi\hbar$. In fact, from (27), we obtain

$$\int_{-\infty}^{+\infty} dE_f \left[\delta^{(T)}(E_f - E_i)\right]^2 = \frac{T}{2\pi\hbar}. \quad (33)$$

b) Transition Probability between Two Discrete States. Lowest-Order Calculation

Let us begin by assuming that $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are two discrete eigenstates of H_0, having energies E_i and E_f that are close to each other and far from all other eigenstates of H_0. To lowest order in V, the transition probability from $|\varphi_i\rangle$ to $|\varphi_f\rangle$ is written, using (31) and (32)

$$\mathscr{P}_{fi}(T) = \frac{4|V_{fi}|^2}{(E_f - E_i)^2} \sin^2(E_f - E_i)T/2\hbar. \quad (34)$$

This relation is, of course, valid only if T is sufficiently small so that the perturbative treatment of V is justified. It is interesting to compare it with the exact formula obtained in the simple case where $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are the only eigenstates of H_0, and where as a consequence the exact diagonalization of $H_0 + V$ is possible (*):

$$\mathscr{P}_{fi}(T) = \frac{4|V_{fi}|^2}{(E_f - E_i)^2 + 4|V_{fi}|^2} \sin^2\left[\frac{T}{2\hbar}\sqrt{(E_f - E_i)^2 + 4|V_{fi}|^2}\right]. \quad (35)$$

Expressions (34) and (35) are identical to lowest order in V_{fi}. In particular, for $E_f = E_i$, Equation (34) gives

$$\mathscr{P}_{fi}(T) = |V_{fi}|^2 T^2/\hbar^2 \quad (36)$$

which is the first term in the expansion in powers of V_{fi} of the function $\sin^2[|V_{fi}|T/\hbar]$ describing the resonant Rabi nutation between $|\varphi_i\rangle$ and $|\varphi_f\rangle$.

c) Case Where the Final State Belongs to an Energy Continuum. Density of States

When the final state belongs to an energy continuum, $\mathscr{P}_{fi}(T)$ is no longer a transition probability, but rather a *transition probability density*. The quantity which has a physical meaning is thus the probability that the system will reach a group of final states characterized by eigenvalues falling within a certain domain D_f. To be specific, let us first consider two concrete examples which will allow us to introduce the concept of density of states.

α) *Density of States for a Free Massive Particle*

We consider a free particle with mass M. The final states $|\varphi_f\rangle$ are momentum states $|\mathbf{p}\rangle$ satisfying the classical orthonormalization relation

$$\langle \mathbf{p}|\mathbf{p}'\rangle = \delta(\mathbf{p} - \mathbf{p}'). \quad (37)$$

The final state $|\mathbf{p}_f\rangle$ has no physical meaning (its norm is infinite). By contrast, we can consider the probability that in the final state, the momentum of the particle points into the solid angle $\delta\Omega_f$ about the direction of $\mathbf{p}_f$ and its energy is within the interval δE_f about $E_f = p_f^2/2M$.

(*) See, for example, Cohen-Tannoudji, Diu, and Laloë, Chapter IV. §C-3. We also assume here that $V_{ii} = V_{ff} = 0$.

These conditions define a domain D_f in momentum space and the corresponding probability equals

$$\delta\mathscr{P}(\mathbf{p}_f, T) = \int_{\mathbf{p}\in D_f} \mathrm{d}^3p \left|\langle \mathbf{p}|\tilde{U}(T)|\varphi_i\rangle\right|^2. \tag{38}$$

Instead of using p_x, p_y, p_z to characterize the final state $|\mathbf{p}\rangle$, it is also possible to use other variables such as the energy E and the polar angles θ and φ characterizing the direction of $\mathbf{p}$. If $\mathrm{d}\Omega$ is the solid angle corresponding to $\mathrm{d}\theta$ and $\mathrm{d}\varphi$, one has

$$\mathrm{d}^3p = p^2\,\mathrm{d}p\,\mathrm{d}\Omega = \rho(E)\,\mathrm{d}E\,\mathrm{d}\Omega \tag{39}$$

where $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi$ and where

$$\rho(E) = p^2\frac{\mathrm{d}p}{\mathrm{d}E} = p^2\frac{M}{p} = M\sqrt{2\overline{ME}} \tag{40}$$

is by definition the density of final states. Expression (38) is thus written

$$\delta\mathscr{P}(\mathbf{p}_f, T) = \int_{\substack{\Omega\subset\delta\Omega_f \\ E\subset\delta E_f}} \mathrm{d}\Omega\,\mathrm{d}E\,\rho(E)\left|\langle \mathbf{p}|\tilde{U}(T)|\varphi_i\rangle\right|^2. \tag{41}$$

Remark

It is possible to discretize the continuum and to obtain final states of norm 1 by enclosing the particles in a cubic box with sides of length L and by imposing periodic boundary conditions to obtain final states having the same spatial dependence as the states $|\mathbf{p}\rangle$. The sum over the final states included in a domain D_f is thus a true discrete sum. When L tends to infinity, it is convenient to replace this discrete sum by an integral. The density of states $\rho(E)$ is thus defined such that $\rho(E)\,\mathrm{d}E\,\mathrm{d}\Omega$ is the number of discretized states contained in the domain associated with $\mathrm{d}E$ and $\mathrm{d}\Omega$. As a result of the periodic boundary conditions, the possible values of the wave vector $\mathbf{k}$ (which is equal to $\mathbf{p}/\hbar$) form a regular lattice of points in k space with one point per elementary volume $(2\pi/L)^3$. The number of states in d^3k is thus $(L/2\pi)^3k^2\,\mathrm{d}k\,\mathrm{d}\Omega$, which for $\rho(E)$ gives the value

$$\rho(E) = \frac{L^3}{(2\pi)^3}\frac{1}{\hbar^3}M\sqrt{2ME}. \tag{42}$$

The final result for the transition amplitude (41) certainly does not depend on L. To see this, it is sufficient to note that the presence of $\langle \mathbf{p}|$ in the matrix element of the evolution operator implies that the square of the modulus of this matrix element contains a factor $1/L^3$ which compensates for the factor L^3 appearing in the density of states (42).

β) Density of States for a Photon

Another important example of energy continuum is that of one-photon states $|\mathbf{k}\boldsymbol{\varepsilon}\rangle$ satisfying the orthonormalization relation

$$\langle \mathbf{k}'\boldsymbol{\varepsilon}'|\mathbf{k}\boldsymbol{\varepsilon}\rangle = \delta_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}'}\delta(\mathbf{k}-\mathbf{k}'). \tag{43}$$

Recall that the states $|\mathbf{k}\boldsymbol{\varepsilon}\rangle$ result from the action of creation operators $a_{\boldsymbol{\varepsilon}}^{-}(\mathbf{k})$ on the vacuum. It is thus possible to write an equation analogous to (38) where it is also necessary to sum over the polarizations and to replace d^3p by

$$\mathrm{d}^3k = k^2\,\mathrm{d}k\,\mathrm{d}\Omega = \rho(E)\,\mathrm{d}E\,\mathrm{d}\Omega \tag{44}$$

with

$$\rho(E) = k^2\frac{\mathrm{d}k}{\mathrm{d}E} = \frac{E^2}{\hbar^2c^2}\frac{1}{\hbar c} = \frac{E^2}{\hbar^3c^3}. \tag{45}$$

To determine (45), we have used the relation $E = \hbar\omega = \hbar ck$ between the photon energy E and the modulus k of its wave vector (instead of $E = p^2/2M$).

In the case where the radiation is confined in a box of volume L^3, (45) must be replaced by

$$\rho(E) = \frac{L^3}{(2\pi)^3}\frac{E^2}{\hbar^3c^3}. \tag{46}$$

γ) General Case

In the general case, we assume that the final state $|\varphi_f\rangle$, belonging to an energy continuum, is characterized by its energy E and a group of other physical variables designated by β, and we get

$$\delta\mathscr{P}(E_f,\beta_f,T) = \int_{\substack{E\simeq\delta E_f\\ \beta\simeq\delta\beta_f}} \mathrm{d}E\,\mathrm{d}\beta\,\rho(E,\beta)\left|\langle E,\beta|\bar{U}(T)|\varphi_i\rangle\right|^2 \tag{47}$$

for the probability that, starting from the normalized state $|\varphi_i\rangle$, the system will arrive after time T in one of the final states of the domain D_f characterized by δE_f and $\delta\beta_f$. In (47), $\rho(E,\beta)$ is the density of final states which, in the general case, depends on both E and β.

d) Transition Rate toward a Continuum of Final States

In expression (47), $|\langle E,\beta|\bar{U}(T)|\varphi_i\rangle|^2$, is simply the square of the modulus of the transition amplitude $\mathscr{T}_{fi}$ given in (29) with δ_{fi} 0. At the lowest order in V we obtain, by writing $v(E,\beta;\varphi_i)$, the matrix element V_{fi}:

$$\delta\mathscr{P}(E_f,\beta_f,T) \simeq \int_{\substack{E\in\delta E_f\\ \beta\in\delta\beta_f}} \mathrm{d}E\,\mathrm{d}\beta\,\rho(E,\beta)4\pi^2|v(E,\beta;\varphi_i)|^2\left[\delta^{(T)}(E-E_i)\right]^2. \quad (48)$$

In general, $\rho(E,\beta)|v(E,\beta;\varphi_i)|^2$ is a function of E varying with E much more slowly than $[\delta^{(T)}(E-E_i)]^2$ which, for sufficiently large T, has an extremely small width, on the order of $\hbar/T$. If this is the case, we can then replace $[\delta^{(T)}(E-E_i)]^2$ by a "delta function" centered on E_i. Because the integral over E of $[\delta^{(T)}(E-E_i)]^2$ is, according to (33), equal to $T/2\pi\hbar$, we are justified to write (with regard to slowly varying functions of E)

$$\left[\delta^{(T)}(E-E_i)\right]^2 \simeq \frac{T}{2\pi\hbar}\delta^{(T)}(E-E_i). \quad (49)$$

The substitution of (49) into (48) then shows that $\delta\mathscr{P}$ is proportional to the duration T of the interaction, which allows us to define a transition probability *per unit time* $\delta w(E_f,\beta_f)$

$$\delta w(E_f,\beta_f) = \frac{1}{T}\delta\mathscr{P}(E_f,\beta_f,T) = \frac{2\pi}{\hbar}\int_{\substack{E\in\delta E_f\\ \beta\in\delta\beta_f}} \mathrm{d}E\,\mathrm{d}\beta\,\rho(E,\beta)|v(E,\beta;\varphi_i)|^2\delta^{(T)}(E \quad E_i). \quad (50)$$

Assume that the interval δE_f contains E_i and that δE_f is greater than the width $\hbar/T$ of $\delta^{(T)}(E-E_i)$. The integral over E is thus straightforward. If, in addition, $\delta\beta_f$ is sufficiently small so that the integral over β becomes

unnecessary, we finally get

$$\frac{\delta w(E_f, \beta_f)}{\delta \beta_f} = \frac{2\pi}{\hbar} \left| T(E_f = E_i, \beta_f; \varphi_i) \right|^2 \rho(E_f = E_i, \beta_f) \qquad (51)$$

which is simply the Fermi golden rule for the transition probability per unit time and per unit interval $\delta\beta$.

Remark: Sum over Polarizations

Let us return to the photon example. Frequently the squared matrix element of (50) has the form $|\boldsymbol{\varepsilon} \cdot \mathbf{X}_i|^2$, where $\mathbf{X}$ is a vectorial quantity and where $\boldsymbol{\varepsilon}$ is the polarization vector of the photon. If we do not observe the polarization of the emitted photon, then we must, for a given emission direction $\mathbf{k}$, sum over the two states of polarization $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ orthogonal to $\mathbf{k}$ and orthogonal to each other; that is, calculate

$$\sum_{\boldsymbol{\varepsilon} \perp \mathbf{k}} |\boldsymbol{\varepsilon} \cdot \mathbf{X}|^2 = \sum_{i,j=x,y,z} \left(\sum_{\boldsymbol{\varepsilon} \perp \mathbf{k}} \varepsilon_i \varepsilon_j \right) X_i X_j^*. \qquad (52)$$

To evaluate the sum between parentheses in (52), it is sufficient to note that $\boldsymbol{\varepsilon}$, $\boldsymbol{\varepsilon}'$, and $\boldsymbol{\kappa} = \mathbf{k}/\kappa$ form an orthonormal basis for which the closure relation is written

$$\varepsilon_i \varepsilon_j + \varepsilon_i' \varepsilon_j' + \kappa_i \kappa_j = \delta_{ij} \qquad (53)$$

from which we deduce

$$\sum_{\boldsymbol{\varepsilon} \perp \mathbf{k}} \varepsilon_i \varepsilon_j = \varepsilon_i \varepsilon_j + \varepsilon_i' \varepsilon_j' = \delta_{ij} - \kappa_i \kappa_j = \delta_{ij} - \frac{k_i k_j}{k^2} \qquad (54)$$

and consequently

$$\sum_{\boldsymbol{\varepsilon} \perp \mathbf{k}} |\boldsymbol{\varepsilon} \cdot \mathbf{X}|^2 = \mathbf{X} \cdot \mathbf{X}^* - \frac{(\mathbf{k} \cdot \mathbf{X})(\mathbf{k} \cdot \mathbf{X}^*)}{k^2}. \qquad (55)$$

e) Case Where both the Initial and Final States Belong to a Continuum

In this case, the initial state is itself also not physical (because it has an infinite norm). It is nevertheless possible to derive from it a quantity having a physical meaning, such as a particle flux, if $|\varphi_i\rangle$ represents an incident free particle having a well-defined momentum.

Let us calculate such an incident flux for a particle having mass M and for a photon. It is thus particularly convenient to use discretized states in a cube having sides of length L. In the discretized state $|\mathbf{p}_i\rangle$ or $|\mathbf{k}_i\rangle$, having norm 1, the particle density is $1/L^3$ (one particle in a volume L^3) and the velocity equals $\mathbf{p}_i/M = \hbar\mathbf{k}_i/M$ for the particle of mass M, or $c\boldsymbol{\kappa}_i$ for the photon (where $\boldsymbol{\kappa}_i = \mathbf{k}_i/k_i$). From that we deduce that the incident flux $\boldsymbol{\Phi}_i$ equals

$$\boldsymbol{\Phi}_i = \frac{\mathbf{p}_i}{M}\frac{1}{L^3} = \frac{\hbar\mathbf{k}_i}{M}\frac{1}{L^3} \tag{56}$$

for the free particle with mass M and

$$\boldsymbol{\Phi}_i = \frac{c}{L^3}\boldsymbol{\kappa}_i \tag{57}$$

for the photon. Dividing by $|\boldsymbol{\Phi}_i|$ the transition probability per unit time and per unit solid angle yields the differential scattering cross-section from $\mathbf{k}_i$ toward $\mathbf{k}_f$.

Remark

If both $|\varphi_i\rangle$ and $|\varphi_f\rangle$ belong to a continuum, two factors $1/L^3$ appear in the squared matrix element of (51). One factor $1/L^3$ is compensated for by the factor L^3 that appears in the final-state density (see Remark in paragraph 3-c above). The other factor $1/L^3$ compensates for the one appearing in expression (56) or (57) of the flux, when $\delta w/\delta\Omega$ is divided by this flux. It is therefore clear that the scattering cross-section does not depend on L.

General References

Same bibliography as for Chapter 1.

COMPLEMENT B_I

DESCRIPTION OF THE EFFECT OF A PERTURBATION BY AN EFFECTIVE HAMILTONIAN

1. Introduction—Motivation

For many systems, the eigenstates of the Hamiltonian H cannot be exactly determined. In contrast, those of an approximate Hamiltonian H_0 are sometimes known. Thus, in the case of electrodynamics, we saw in Section C of the chapter that the Hamiltonian is diagonalizable in the absence of coupling between the particles and the field. In this case, perturbation theory can be used to determine the eigenstates of H, by taking as a perturbation the difference between H and H_0.

In this complement, we will consider the case of a Hamiltonian H_0 having energy levels $E_{i\alpha}$ which are grouped into manifolds $\mathscr{E}_\alpha^0, \mathscr{E}_\beta^0, \ldots$ that are well separated from each other. The subscript i denotes the different levels $|i, \alpha\rangle$ of the same manifold, and P_α is the projector over the manifold $\mathscr{E}_\alpha^0$:

$$H_0|i, \alpha\rangle = E_{i\alpha}|i, \alpha\rangle \tag{1}$$

$$P_\alpha = \sum_i |i, \alpha\rangle\langle i, \alpha|. \tag{2}$$

To say that the manifolds are well separated signifies that the spectrum of H_0 has the shape indicated in Figure 1. More precisely, we assume

$$|E_{i\alpha} - E_{j\alpha}| \ll |E_{i\alpha} - E_{j\beta}| \qquad \text{with } \alpha \neq \beta. \tag{3}$$

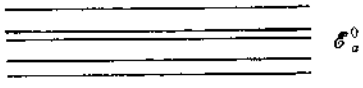
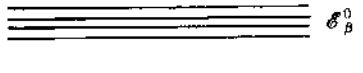


Figure 1. Manifolds $\mathscr{E}_\alpha^0, \mathscr{E}_\beta^0, \ldots$ of the Hamiltonian H_0.



In physical terms, the quantum number i characterizes the degrees of freedom for which the Bohr frequencies $(E_{i\alpha} - E_{j\alpha})/\hbar$ (intervals between levels of a same manifold) are small. In contrast, the index α is a quantum number relative to quantities for which the Bohr frequencies $(E_{i\alpha} - E_{j\beta})/\hbar$ (intervals between two different manifolds) are much larger. Thus, the existence of well-separated manifolds reveals the presence within the system of two types of degrees of freedom: fast degrees of freedom characterized by Greek indices such as α, and slow degrees of freedom characterized by Roman subscripts such as i.

Situations of this type are encountered in many physics problems, especially in the study of interactions between matter and radiation. Let us consider, for example, the system made up, on the one hand, of an electron in a external static potential and, on the other hand, of a mode $\mathbf{k}\varepsilon$ of the radiation field with frequency ω. In the absence of interaction between the electron and the radiation, the energy levels of the overall system are designated by the quantum numbers i of the electron in the external potential and the number $\alpha = N$ of photons in the mode. If the frequency ω of the mode under consideration is extremely large as compared to the frequencies $(E_i - E_j)/\hbar$ characterizing the movement of the electron in the external potential, the situation is analogous to that in Figure 1. The manifold $\mathscr{E}_\alpha^0 = \mathscr{E}_N^0$ thus consists of the energy levels of the electron in the external potential in the presence of N photons and the other manifolds corresponding to a number $N' \neq N$ of photons are at a distance $(N' - N)\hbar\omega$.

To obtain the total Hamiltonian H, let us now add to H_0 the perturbation or the coupling which we write in the form λV, where λ is a dimensionless parameter:

$$H = H_0 + \lambda V. \tag{4}$$

The operator V has matrix elements inside a manifold as well as between two different manifolds. For example, for the system mentioned above, the interaction between the electron and the mode $\mathbf{k}\varepsilon$ couples the manifold $\mathscr{E}_N^0$ to manifolds $\mathscr{E}_{N+1}^0$ (and $\mathscr{E}_{N-1}^0$), the corresponding physical processes being the emission (and absorption) of a photon $\mathbf{k}\varepsilon$ by the electron. If λ is sufficiently small, more precisely, if

$$|\langle i, \alpha|\lambda V|j, \beta\rangle| \ll |E_{i\alpha} - E_{j\beta}| \qquad (\beta \neq \alpha) \tag{5}$$

the energy levels of the Hamiltonian H are clustered, as are those of H_0,

in manifolds $\mathscr{E}_\alpha, \mathscr{E}_\beta, \ldots$ well separated from each other, the levels of $\mathscr{E}_\alpha$ tending to those of $\mathscr{E}_\alpha^0$ when $\lambda \to 0$.

The physical effects of the coupling λV are of two types. On the one hand, the wave functions are modified. In particular, the wave functions of the manifold $\mathscr{E}_\alpha^0$ are "contaminated" by the wave functions of other manifolds $\mathscr{E}_\beta^0$ with $\beta \neq \alpha$. On the other hand, the energies are modified. In particular, the slow Bohr frequencies (within one manifold) are changed. Let us now study in more detail these two types of effect in the case of the physical example introduced above. As a result of the contamination of the states of $\mathscr{E}_N^0$ by those of $\mathscr{E}_{N\pm1}^0$, N is no longer a good quantum number, and the electron observables, which commute with the photon number operator, may thus have nonzero matrix elements between perturbed states of $\mathscr{E}_N$ and perturbed states of $\mathscr{E}_{N\pm1}$. Physically, rapid components at frequency ω appear in the electron motion, which, in fact, correspond to the vibration of the electron in the electric field of mode $\mathbf{k}\varepsilon$. In addition, the nonresonant coupling between $\mathscr{E}_N^0$ and $\mathscr{E}_{N\pm1}^0$ shifts the states of $\mathscr{E}_N^0$ to second order in λV. Physically, the virtual emission and reabsorption (or virtual absorption and reemission) of one photon by the electron changes the slow electron motion in the external potential.

In this complement, we are essentially interested in the modification made to the slow motion by the coupling λV and not to the contamination of wave functions. Our goal is to attempt to construct a Hamiltonian acting only within each manifold $\mathscr{E}_\alpha^0$ such that its eigenvalues in $\mathscr{E}_\alpha^0$ are identical to those of H in $\mathscr{E}_\alpha$. Such a Hamiltonian, called the effective Hamiltonian, acts only on the slow degrees of freedom because its matrix elements between $\langle i, \alpha|$ and $|j, \beta\rangle$ are zero if $\alpha \neq \beta$. Because it correctly describes the slow motion, it incorporates the effect on the slow degrees of freedom of the coupling of the latter with the fast degrees of freedom. In the case of the physical system described above, the effective Hamiltonian is a *purely electronic* Hamiltonian which describes the perturbed slow motion of the electron by means of corrective electron terms: correction to the kinetic energy of the electron (due to the fact that its inertia is modified by the virtual photon cloud which surrounds it) and correction to the potential energy (due to the fact that the electron vibrating in the field of the mode ω averages the static external potential over the extent of its vibrational mode) (*). Other important physical examples may be given, e.g., the *effective magnetic interaction* between two electrons associated with the virtual emission of a transverse photon by an electron and the

(*) Such an effective Hamiltonian is derived in P. Avan, C. Cohen-Tannoudji, J. Dupont-Roc, and C. Fabre, *J. Physique*, 37, 993 (1976).

reabsorption of this photon by the other electron (see Chapter II, Section F).

We will show in this complement how an effective Hamiltonian can be constructed by means of a unitary transformation applied to the total Hamiltonian H (*). The principle of the method is described in Section 2. We will then determine (§3) the unitary transformation and the expression of the effective Hamiltonian. Finally, we will examine (§4) the case in which the system under study is an ensemble of two subsystems whose interaction is described by the coupling λV. We will demonstrate in particular how it is possible to obtain an operator expression for the effective Hamiltonian which involves only observables of the system that evolve with slow frequencies.

2. Principle of the Method

Thus we are seeking an effective Hamiltonian H' having the following properties:

a) H' is Hermitian

b) H' has the same eigenvalues as H, with the same degeneracy

c) H' has no matrix elements between *unperturbed* manifolds $\mathscr{E}_\alpha^0, \mathscr{E}_\beta^0, \ldots$

Properties a) and b) result in the fact that there is a unitary transformation

$$T = e^{iS} \tag{6}$$

$$S = S^+ \tag{7}$$

which allows us to go from H to H'

$$H' = THT^+. \tag{8}$$

Property c) is expressed by the equation

$$P_\alpha H' P_\beta = 0 \qquad \text{for } \alpha \neq \beta. \tag{9}$$

(*) A review of the different ways of formally constructing effective Hamiltonians may be found in D. J. Klein, *J. Chem. Phys.*, **61**, 786 (1974). A more recent reference explicitly gives the terms of the effective Hamiltonian up to the fifth order: J. Shavitt and L. T. Redmon, *J. Chem. Phys.*, **73**, 5711 (1980).

The matrix representing H' in the unperturbed initial basis $|i, \alpha\rangle$ is block diagonal. Each block is relative to a manifold $\mathscr{E}_\alpha^0$ and represents an effective Hamiltonian H_{eff}^α which describes the perturbed levels of this manifold

$$H' = \sum_\alpha P_\alpha H_{\text{eff}}^\alpha. \tag{10}$$

Equations (8) and (9) are not sufficient to entirely determine the transformation T. In fact, if T is a solution, we can construct an infinite number of other solutions of the form UT, where U is an arbitrary unitary transformation acting only inside manifolds $\mathscr{E}_\alpha^0$. One way to remove this uncertainty is to impose on S the condition that it does not have matrix elements inside each manifold:

$$P_\alpha S P_\alpha = 0 \qquad \text{for any } \alpha. \tag{11}$$

To explicitly calculate S, it is convenient to write it in the form of an expansion in powers of λ

$$S = \lambda S_1 + \lambda^2 S_2 + \cdots + \lambda^n S_n + \cdots. \tag{12}$$

It is obvious that the zero-order term is zero, because H_0 is itself diagonal in the basis $\{|i, \alpha\rangle\}$. Equation (8) can then be expanded in the form

$$H' = H - [iS, H] + \frac{1}{2!}[iS, [iS, H]] + \frac{1}{3!}[iS, [iS, [iS, H]]] + \cdots. \tag{13}$$

By substituting S from expression (12), we obtain an expansion of the effective Hamiltonian.

$$H' = H_0 + \lambda H_1' + \lambda^2 H_2' + \cdots + \lambda^n H_n' + \cdots. \tag{14}$$

Each term H_n' can be expressed as a function of S_n, of H_0 and of V. Conditions (9) and (11), applied step by step, determine S_n, and consequently H'.

It is helpful to write the effective Hamiltonian H' thus determined in the form

$$H' = H_0 + W \tag{15}$$

where

$$W = \lambda H_1' + \lambda^2 H_2' + \cdots + \lambda^p H_p' + \cdots . \tag{16}$$

W is called the "level-shift" operator. According to Property b) of H', W produces exactly the same effect over the energy levels of H_0 as the perturbation λV. In contrast, according to Property c), it has the advantage of acting only inside manifolds. If we seek only new energies in the manifold $\mathscr{E}_\alpha$, it is much simpler to use W than to use λV, which couples $\mathscr{E}_\alpha^0$ to all other manifolds.

3. Determination of the Effective Hamiltonian

a) Iterative Calculation of S

Let us order the expression (13) for H' in increasing powers of λ, after having replaced S by its expansion (12) and H by its expression (4). Thus

$$\begin{aligned} H' = H_0 &+ [i\lambda S_1, H_0] + \lambda V + \\ &+ [i\lambda^2 S_2, H_0] + [i\lambda S_1, \lambda V] + \frac{1}{2}[i\lambda S_1, [i\lambda S_1, H_0]] + \\ &\vdots \\ &+ [i\lambda^n S_n, H_0] + [i\lambda^{n-1} S_{n-1}, \lambda V] + \\ &+ \frac{1}{2}[i\lambda^{n-1} S_{n-1}, [i\lambda S_1, H_0]] + \\ &+ \frac{1}{2}[i\lambda S_1, [i\lambda^{n-1} S_{n-1}, H_0]] + \cdots + \\ &+ \frac{1}{n!}[i\lambda S_1, [i\lambda S_1, \cdots [i\lambda S_1, H_0] \cdots]] + \\ &\vdots . \end{aligned} \tag{17}$$

The last term of (17) contains n stacked commutators.

Let us first consider first-order terms in λ:

$$\lambda H_1' = [i\lambda S_1, H_0] + \lambda V \tag{18}$$

and write that the matrix element of H_1' between two different manifolds

is zero. We obtain the equation

$$\langle i, \alpha | i\lambda S_1 | j, \beta \rangle (E_{j\beta} - E_{i\alpha}) + \langle i, \alpha | \lambda V | j, \beta \rangle = 0 \qquad (19)$$

which determines the matrix elements of S_1 between two different manifolds, since the other elements are zero according to (11).

$$\langle i, \alpha | i\lambda S_1 | j, \beta \rangle = \frac{\langle i, \alpha | \lambda V | j, \beta \rangle}{E_{i\alpha} - E_{i\beta}}, \qquad \text{for } \alpha \neq \beta \qquad (20.a)$$

$$\langle i, \alpha | i\lambda S_1 | j, \alpha \rangle = 0. \qquad (20.b)$$

Let us now consider the nth-order term, $\lambda^n H'_n$. It involves all the operators S_p, p ranging from 1 to n. The fact that all matrix elements of $\lambda^n H'_n$ between two different manifolds α and β are zero allows us to express the matrix elements of $\lambda^n S_n$ between these same manifolds as a function of those of the operators S_p of lower order than n. Indeed, $\lambda^n S_n$ appears only in a single term, that of the commutator with H_0. We thus obtain an equation of the type

$$\langle i, \alpha | i\lambda^n S_n | j, \beta \rangle (E_{j\beta} - E_{i\alpha}) =$$

$$\mathscr{F}(\lambda V; \lambda S_1, \ldots, \lambda^{n-1} S_{n-1}) \qquad \text{for } \alpha \neq \beta \qquad (21.a)$$

additionally with

$$\langle i, \alpha | i\lambda^n S_n | j, \alpha \rangle = 0 \qquad (21.b)$$

Step by step, S is thus entirely determined.

b) Expression of the Second-Order Effective Hamiltonian

Note first of all that the expression for the nth-order effective Hamiltonian does not involve $\lambda^n S_n$. In fact, we have previously seen that, in the expression for the nth-order term of (17), S_n is involved only in the simple commutator with H_0. Because H_0 is diagonal with regard to α and since S_n is nondiagonal, such a commutator is nondiagonal and thus does not contribute to the expression of H' within each manifold. Hence, to determine the effective Hamiltonian up to order 2, it is thus sufficient to know λS_1, which is given by (20.a). The matrix elements of H' within the

manifold α are written

$$\langle i|H^{\alpha}_{\text{eff}}|j\rangle = \langle i,\alpha|H'|j,\alpha\rangle = \\ = \langle i,\alpha|H_0 + \lambda V + [i\lambda S_1, \lambda V] + \tfrac{1}{2}[i\lambda S_1,[i\lambda S_1, H_0]] + \cdots |j,\alpha\rangle. \tag{22}$$

Let us show that the last term of (22) is identical, except for one factor, to the next to last term. In fact, $[i\lambda S_1, H_0]$ is purely nondiagonal, and according to (19), its matrix elements are opposite to those of λV between different manifolds. Let us call λV^{nd} the nondiagonal part (which connects the different manifolds) of λV. Hence we have

$$[i\lambda S_1, H_0] + \lambda V^{\text{nd}} = 0 \tag{23}$$

and the last term of (22) is reduced to $-[i\lambda S_1, \lambda V^{\text{nd}}]/2$. The next-to-last term also involves only the nondiagonal part of λV, so that the product by λS_1 yields a diagonal term. Hence, up to second order, H^{α}_{eff} is reduced to

$$H^{\alpha}_{\text{eff}} = H_0 P_\alpha + P_\alpha \lambda V P_\alpha + \tfrac{1}{2} P_\alpha [i\lambda S_1, \lambda V] P_\alpha + \cdots. \tag{24}$$

Similar simplifications occur in all orders.

Let us now explicitly calculate the matrix elements of the last term of (24) by using the matrix elements (20.a) of λS_1:

$$\begin{aligned}\langle i,\alpha|[i\lambda S_1, \lambda V]|j,\alpha\rangle &= \sum_{k,\gamma\neq\alpha} \langle i,\alpha|i\lambda S_1|k,\gamma\rangle\langle k\gamma|\lambda V|j,\alpha\rangle - \\ &\quad - \langle i,\alpha|\lambda V|k,\gamma\rangle\langle k,\gamma|i\lambda S_1|j,\alpha\rangle \\ &= \sum_{k,\gamma\neq\alpha} \langle i,\alpha|\lambda V|k,\gamma\rangle\langle k,\gamma|\lambda V|j,\alpha\rangle \times \\ &\quad \times \left[\frac{1}{E_{i\alpha} - E_{k\gamma}} + \frac{1}{E_{j\alpha} - E_{k\gamma}}\right].\end{aligned} \tag{25}$$

We finally get, for $\langle i|H^{\alpha}_{\text{eff}}|j\rangle$ up to second order in λ:

$$\begin{aligned}\langle i|H^{\alpha}_{\text{eff}}|j\rangle &= E_{i\alpha}\delta_{ij} + \langle i,\alpha|\lambda V|j,\alpha\rangle + \\ &\quad + \frac{1}{2}\sum_{k,\gamma\neq\alpha} \langle i,\alpha|\lambda V|k,\gamma\rangle\langle k,\gamma|\lambda V|j,\alpha\rangle \times \\ &\quad \times \left[\frac{1}{E_{i\alpha} - E_{k\gamma}} + \frac{1}{E_{j\alpha} - E_{k\gamma}}\right] + \cdots.\end{aligned} \tag{26}$$

The first term of (26) represents the unperturbed energy of levels of $\mathscr{E}_\alpha^0$, the second term represents the *direct* coupling between the levels i and j of $\mathscr{E}_\alpha^0$, and the third term represents the *indirect* coupling between these two levels through all the levels $k\gamma$ of other manifolds $\mathscr{E}_\gamma^0$. This last term has the structure of a second-order perturbation term, that is, a product of two matrix elements of λV divided by an unperturbed energy denominator (the two energies $E_{i\alpha}$ and $E_{j\alpha}$ of the two levels of $\mathscr{E}_\alpha^0$ appearing symmetrically if they are different).

c) Higher-Order Terms

We have seen how, step by step, the higher-order terms may be explicitly calculated. In fact, at least from a formal point of view, the expression for the effective Hamiltonian may also be given in compact algebraic forms. These two types of expressions may be found in the references quoted at the beginning of this complement.

4. Case of Two Interacting Systems

We will now consider the case of two systems $\mathscr{A}$ and $\mathscr{R}$, with respective Hamiltonians H_A and H_R, that interact by means of a Hamiltonian λV. The spacings between energy levels of $\mathscr{R}$ are assumed to be large as compared to those of $\mathscr{A}$. This is shown by the following equations:

$$H_0 = H_A + H_R \tag{27}$$

$$H_A|i\rangle = E_i|i\rangle \tag{28}$$

$$H_R|\alpha\rangle = E_\alpha|\alpha\rangle \tag{29}$$

$$|E_i - E_j| \ll |E_\alpha - E_\beta|, \qquad \alpha \neq \beta. \tag{30}$$

We assume that the coupling between the two systems is written in the form

$$\lambda V = \lambda \sum_\mu A_\mu R_\mu \tag{31}$$

where the operators A_μ (resp. R_μ) are relative to the subsystem $\mathscr{A}$ (resp. $\mathscr{R}$). Finally, we assume A_μ and R_μ to be purely *nondiagonal* in the bases $\{|i\rangle\}$ and $\{|\alpha\rangle\}$.

To determine H_{eff}^α, let us replace $E_{i\alpha}$ by $E_i - E_\alpha$, in (26), and λV by its expression (31). Because R_μ is nondiagonal in α, the second term of (26)

is zero. Hence we get

$$\langle i|H^{\alpha}_{\mathrm{eff}}|j\rangle = E_{\alpha} + E_i\delta_{ij} + \\ + \frac{1}{2}\sum_{\mu\mu'}\sum_{k,\gamma\neq\alpha}\big(\langle\alpha|\lambda R_{\mu}|\gamma\rangle\langle\gamma|\lambda R_{\mu'}|\alpha\rangle\big)\big(\langle i|A_{\mu}|k\rangle\langle k|A_{\mu'}|j\rangle\big)\times \\ \times\left[\frac{1}{E_{\alpha}-E_{\gamma}+E_i-E_k}+\frac{1}{E_{\alpha}-E_{\gamma}+E_i-E_k}\right]. \tag{32}$$

By using the inequality (30), we can expand the fractions appearing in (32)

$$\frac{1}{E_{\alpha}-E_{\gamma}+E_i-E_k}=\frac{1}{E_{\alpha}-E_{\gamma}}-\frac{E_i-E_k}{(E_{\alpha}-E_{\gamma})^2}+\cdots \tag{33}$$

and the equivalent by replacing i by j. The second order term becomes

$$\sum_{\mu\mu'}\left(\sum_{\gamma\neq\alpha}\langle\alpha|\lambda R_{\mu}|\gamma\rangle\frac{1}{E_{\alpha}-E_{\gamma}}\langle\gamma|\lambda R_{\mu'}|\alpha\rangle\right)\times \\ \times\left(\sum_{k}\langle i|A_{\mu}|k\rangle\langle k|A_{\mu'}|j\rangle\right)+ \\ -\sum_{\mu\mu'}\left(\sum_{\gamma\neq\alpha}\frac{\langle\alpha|\lambda R_{\mu}|\gamma\rangle\langle\gamma|\lambda R_{\mu'}|\alpha\rangle}{(E_{\alpha}-E_{\gamma})^2}\right)\times \\ \times\left(\sum_{k}\langle i|A_{\mu}|k\rangle\langle k|A_{\mu'}|j\rangle\left(\frac{E_k-E_i+E_k-E_j}{2}\right)\right). \tag{34}$$

Note that the sum over γ may be extended to the case $\gamma=\alpha$, because the corresponding terms $\langle\alpha|R_{\mu}|\alpha\rangle$ are zero. The closure relations over states $|\gamma\rangle$ on one hand, and over $|k\rangle$ on the other hand thus allow us to rewrite these two terms in operator forms. Actually

$$\sum_{k}\langle i|A_{\mu}|k\rangle\langle k|A_{\mu'}|j\rangle(E_k-E_i+E_k-E_j) \\ =\langle i|\big[A_{\mu},H_A\big]A_{\mu'}-A_{\mu}\big[A_{\mu'},H_A\big]|j\rangle. \tag{35}$$

Finally, the effective Hamiltonian may be written in operator form:

$$H^{\alpha}_{\text{eff}} = E_{\alpha}\mathbb{1}_{\mathscr{A}} + H_A + \sum_{\mu\mu'} \langle\alpha|\lambda R_{\mu} \frac{1}{E_{\alpha} - H_R} \lambda R_{\mu'}|\alpha\rangle A_{\mu} A_{\mu'} +$$

$$+ \frac{1}{2} \sum_{\mu\mu'} \langle\alpha|\lambda R_{\mu} \frac{1}{(E_{\alpha} - H_R)^2} \lambda R_{\mu'}|\alpha\rangle \big([A_{\mu}, H_A] A_{\mu'} - A_{\mu} [A_{\mu'}, H_A] \big)$$

$$+ \cdots . \tag{36}$$

Hence it does indeed appear as a sum of operators relative to $\mathscr{A}$, with coefficients that are the average value in the state $|\alpha\rangle$ of operators relative to $\mathscr{R}$. The first two terms represent the free evolution in the manifold $\mathscr{E}^0_{\alpha}$. The third term describes the effect of virtual transitions to other manifolds. The last term of (36) is a correction to the third term which takes into account the fact that a virtual transition to the manifold β is not infinitely short but rather lasts a time which is on the order of $\hbar/|E_{\alpha} - E_{\beta}|$. The operators A_{μ} and $A_{\mu'}$ have the time to evolve when acted upon by H_A during this period. This is expressed by the last term of (36).

COMPLEMENT C_1

DISCRETE LEVEL COUPLED TO A BROAD CONTINUUM: A SIMPLE MODEL

Many interaction processes between atoms and photons may be analyzed in terms of a discrete level coupled to a continuum. Such an analysis can provide good insights into these processes, but it often requires a detailed knowledge of the essential characteristics of the new eigenstates resulting from the coupling between the discrete state and the continuum. Hence we consider it important to devote a complement to the analysis of this problem. The results obtained will allow us to clarify several of the discussions in Chapter II.

Rather than considering the most general situation, we prefer to limit ourselves in the majority of this complement to a sufficiently simple model so that formalism will not be a major obstacle. This model cannot, of course, include all the details of the phenomena, but it will allow us to point out and to explain their essential features.

We begin (§1) by describing the model and the simplifying assumptions, which consist of taking a continuum extending from $-\infty$ to $+\infty$ on the energy axis and a coupling with the discrete state independent of the energy. "Seen" from the discrete state, the continuum appears in this case to be completely "flat" and structureless. It is then possible, after "discretization" of the continuum, to perform an exact calculation of the eigenstates and eigenvalues of the total Hamiltonian. The essential result is that the contamination of the new eigenstates by the discrete state is significant only in an interval centered on the energy of the discrete state, the width of this interval being on the order of $\hbar\Gamma$, where Γ is the transition rate of the discrete state to the continuum calculated by using the Fermi golden rule (§2). We then demonstrate (§3) how this "dissolution" of the discrete state, over an interval of width $\hbar\Gamma$ in the new continuum, allows us to quantitatively understand several important physical phenomena, such as the exponential decay of the discrete state, the excitation of this discrete state starting from another state of the system, the resonant scattering through this discrete state, and Fano profiles. The last subsection (§4) provides some indications concerning the way eigenstates of the new continuum may be calculated in more general situations (nonflat continuum) and without discretization of the continuum.

1. Description of the Model (*)

a) The Discrete State and the Continuum

Let us consider a Hamiltonian H_0 which has as eigenstates a discrete state $|\varphi\rangle$ and a continuum of states $|E, \beta\rangle$. For the state $|E, \beta\rangle$, E denotes the eigenvalue associated with H_0 (unperturbed energy) and β denotes other quantum numbers allowing one to distinguish $|E, \beta\rangle$ among orthogonal states having the same energy E.

Assume that the discrete state $|\varphi\rangle$ is coupled to the continuum $|E, \beta\rangle$ by a coupling Hamiltonian V. It is always possible to change the basis within each subspace of energy E of the continuum in order to single out the linear combination of states $|E, \beta\rangle$ which is coupled to $|\varphi\rangle$, and which is denoted by $|E\rangle$, among all other orthogonal linear combinations which are not coupled to $|\varphi\rangle$. We use v_E to denote the matrix element $\langle E|V|\varphi\rangle$. Knowing eigenvalues and eigenvectors of the total Hamiltonian allows us to determine the dynamics of the system. It is thus appropriate to diagonalize the total Hamiltonian in the base $\{|\varphi\rangle, |E\rangle \cdots\}$ (**). We begin by introducing some simplifications which will allow us to reduce the calculations as much as possible while retaining the essential physical results.

b) Discretization of the Continuum

First we discretize the continuum. Such a step was presented for the electromagnetic field in the chapter, with the introduction of a fictitious box with periodic boundary conditions. If the dimension L of the box is large compared to all other characteristic lengths of the problem, the physical results will not depend on the volume L^3 and will be obtained at the limit $1/L^3 \to 0$.

We thus proceed similarly and replace the states of the continuum $|E\rangle$ by discrete states $|k\rangle$ spaced by δ in energy. The density of states is thus $1/\delta$. The matrix element $\langle k|V|\varphi\rangle$ is designated v_k. The physical results are obtained at the limit $\delta \to 0$.

(*) Such a model was introduced by U. Fano, *Nuovo Cimento*, **12**, 156 (1935).

(**) We assume that V has no matrix elements within the continuum. Then the linear combinations of states $|E, \beta\rangle$, of the same energy E, which are not coupled to the discrete state $|\varphi\rangle$ remain eigenstates of the total Hamiltonian, with the eigenvalue E. If $\langle E, \beta|V|E', \beta'\rangle$ was different from zero, a prediagonalization of the Hamiltonian inside the continuum would result in the previous situation.

The application of Fermi's golden rule for a system initially in state $|\varphi\rangle$ leads to a transition rate Γ to the continuum equal to

$$\Gamma = \frac{2\pi}{\hbar} v^2 \frac{1}{\delta} \tag{1}$$

where v is the matrix element (assumed to be real) of V between $|\varphi\rangle$ and the state $|k\rangle$ of the same energy as $|\varphi\rangle$. Relation (1) clearly implies that, at the limit $\delta \to 0$, v^2/δ must remain constant and equal to $\hbar\Gamma/2\pi$.

c) Simplifying Assumptions

First we assume that the discretized continuum extends from $-\infty$ to $+\infty$ with equidistant levels separated by the quantity δ. The unperturbed energy of the level $|k\rangle$ is thus

$$\langle k|H_0|k\rangle = E_k = k\delta \tag{2.a}$$

where k is any integer (positive, negative, or zero). In what follows, the energy E_φ of the discrete level is taken as the origin of energies ($E_\varphi = 0$) and thus coincides with the energy of the level $k = 0$ of the quasi-continuum.

$$\langle \varphi|H_0|\varphi\rangle = E_\varphi = 0. \tag{2.b}$$

For the coupling, we assume that all the matrix elements of V between the level $|\varphi\rangle$ and the states $|k\rangle$ are equal and real

$$v_k = \langle k|V|\varphi\rangle = \langle \varphi|V|k\rangle = v. \tag{2.c}$$

Finally, all the other matrix elements of V are assumed to be zero.

$$\langle \varphi|V|\varphi\rangle = \langle k|V|k'\rangle = 0. \tag{2.d}$$

2. Stationary States of the System. Traces of the Discrete State in the New Continuum

a) The Eigenvalue Equation

Let E_μ and $|\psi_\mu\rangle$ be the eigenvalues and eigenvectors of the total Hamiltonian $H = H_0 + V$.

$$H|\psi_\mu\rangle = E_\mu|\psi_\mu\rangle. \tag{3}$$

Let us project Equation (3) respectively onto $\langle k|$ and $\langle \varphi|$. Using the assumptions made concerning H_0 and V [see relations (2)], we get

$$E_k\langle k|\psi_\mu\rangle + v\langle \varphi|\psi_\mu\rangle = E_\mu\langle k|\psi_\mu\rangle \tag{4.a}$$

$$\sum_k v\langle k|\psi_\mu\rangle = E_\mu\langle \varphi|\psi_\mu\rangle. \tag{4.b}$$

Equation (4.a) gives (*):

$$\langle k|\psi_\mu\rangle = v\frac{\langle \varphi|\psi_\mu\rangle}{E_\mu - E_k}. \tag{5}$$

This expression, when substituted into (4.b), yields the eigenvalue equation

$$\sum_k \frac{v^2}{E_\mu - E_k} = E_\mu. \tag{6}$$

In addition, by using (5) and the normalization condition

$$\sum_k \left|\langle k|\psi_\mu\rangle\right|^2 + \left|\langle \varphi|\psi_\mu\rangle\right|^2 = 1 \tag{7}$$

we find for the components of $|\psi_\mu\rangle$ on $|\varphi\rangle$ and $|k\rangle$ (with an appropriate choice of phase):

$$\langle \varphi|\psi_\mu\rangle = \frac{1}{\left[1 + \Sigma_{k'}\left(\frac{v}{E_\mu - E_{k'}}\right)^2\right]^{1/2}} \tag{8.a}$$

$$\langle k|\psi_\mu\rangle \quad \frac{v/(E_\mu - E_k)}{\left[1 + \Sigma_{k'}\left(\frac{v}{E_\mu - E_{k'}}\right)^2\right]^{1/2}}. \tag{8.b}$$

Let us return to the eigenvalue equation (6). It involves a series of the form $\Sigma_k(z-k)^{-1}$ with $z = E_\mu/\delta$. Similarly, the sum $\Sigma_k(z-k)^{-2}$ appears in the components (8.a) and (8.b) of the eigenvectors. It is possible

(*) We will see further on that $E_\mu \quad E_k$ is always nonzero.

to show that (*)

$$\sum_k (z-k)^{-2} = \frac{\pi^2}{\sin^2 \pi z}. \tag{9}$$

By integration, we obtain

$$\sum_k (z-k)^{-1} = \frac{\pi}{\tan \pi z}. \tag{10}$$

It follows that the eigenvalue equation (6) takes the simpler form

$$\frac{\pi v^2}{\delta \tan(\pi E_\mu/\delta)} = E_\mu \tag{11}$$

that we will transform, by using (1), into

$$\frac{1}{\tan(\pi E_\mu/\delta)} = \frac{2E_\mu}{\hbar\Gamma}. \tag{12}$$

Finally, we introduce the angle defined by

$$\varphi_\mu = \tan^{-1} \frac{\hbar\Gamma}{2E_\mu} \tag{13.a}$$

which allows us to write the solution of (12) in the form

$$\frac{E_\mu}{\delta} = m + \frac{\varphi_\mu}{\pi} \tag{13.b}$$

where m is an integer (≥ 0 or ≤ 0). Since φ_μ is (by definition of the $\tan^{-1}$ function) between $-\pi/2$ and $\pi/2$, φ_μ/π is the difference between E_μ/δ and the integer closest to E_μ/δ. We will use this angle φ_μ later on.

b) Graphic Determination of the New Eigenvalues

To determine the eigenvalues of the total Hamiltonian, we must solve Equation (12); that is, find the intersections of the line $y = ax$ with the curve $y = 1/\tan bx$ (a and b being respectively equal to $2/\hbar\Gamma$ and π/δ). This may be done graphically (see Figure 1).

(*) See, for example, Cartan (Chapter V).

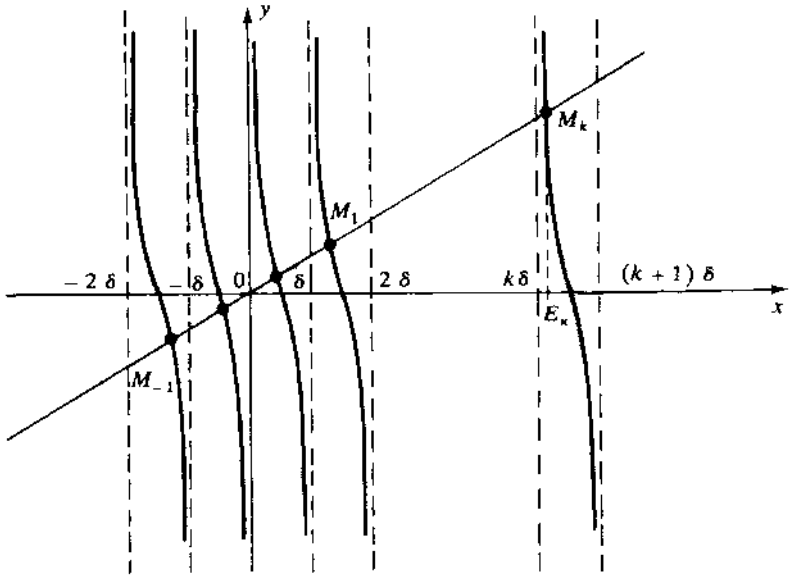


Figure 1. Graphic determination of the eigenvalues of H. The abscissa of each point of intersection between the line $y = 2x/\hbar\Gamma$ and the curve $y = 1/\tan(\pi x/\delta)$ is an eigenvalue of the total Hamiltonian. Let M_k be the point of intersection whose abscissa is between $k\delta$ and $(k+1)\delta$ (the abscissa of M_{-k} being between $-(k+1)\delta$ and $-k\delta$). The associated eigenvalue is denoted E_κ (Greek index corresponding to the Roman index k).

An eigenvalue $E_{\pm\kappa}$ is associated with each intersection M_k between the line $y = ax$ and the curve $y = 1/\tan bx$ (the unperturbed levels are indicated by a Roman index and the perturbed levels by corresponding Greek index). It is clear from Figure 1 that the new eigenvalues $E_{\pm\kappa}$ are interspersed between the old ones ($E_k < E_\kappa < E_{k+1}$ and $E_{-(k+1)} < E_{-\kappa} < E_{-k}$). The eigenstates of H thus form a quasi-continuum for which the density of states is extremely close to $1/\delta$ (there is one eigenstate per interval of energy δ).

We also note in Figure 1 that, for sufficiently large values of k, the abscissa of point M_k differs very little from $k\delta$, so that, to a first approximation, we have $E_\kappa = E_k$. This relation is satisfied when, at the point of intersection, the curve is sufficiently close to its asymptote. According to (12), this occurs when

$$E_\kappa \gg \hbar\Gamma. \tag{14}$$

The presence of the discrete level thus significantly modifies the eigenvalues and eigenvectors of the quasi-continuum only over an energy interval on the order of $\hbar\Gamma$ around the energy of the discrete level.

c) Probability Density of the Discrete State in the New Continuum

In the presence of the coupling V, the discrete state $|\varphi\rangle$ is found diluted in the different states $\{|\psi_\mu\rangle\}$ of the quasi-continuum of H, the component of $|\varphi\rangle$ in the state $|\psi_\mu\rangle$ being given by the square of the expression (8.a). To transform the denominator of this expression, we use (9). We get

$$1 + v^2 \sum_k \left(\frac{1}{E_\mu - E_k} \right)^2 = 1 + \frac{v^2}{\delta^2} \sum_k \left(\frac{E_\mu}{\delta} - k \right)^2$$

$$= 1 + \frac{\pi^2 v^2}{\delta^2} \left(1 + \left(\tan \pi \frac{E_\mu}{\delta} \right)^{-2} \right) \qquad (15)$$

that is, using (11) and (1)

$$1 + v^2 \sum_k \left(\frac{1}{E_\mu - E_k} \right)^2 = 1 + \frac{\pi^2 v^2}{\delta^2} + \frac{E_\mu^2}{v^2} = \frac{1}{v^2} \left[v^2 + \left(\frac{\hbar\Gamma}{2} \right)^2 + E_\mu^2 \right] \qquad (16)$$

which finally yields

$$\langle \varphi | \psi_\mu \rangle = \frac{v}{\left[v^2 + \left(\frac{\hbar\Gamma}{2} \right)^2 + E_\mu^2 \right]^{1/2}}. \qquad (17)$$

Let us consider an interval $[E, E + \mathrm{d}E]$ with $\mathrm{d}E$ large compared to δ, but small compared to $\hbar\Gamma$. The probability $\mathrm{d}N_\varphi$ of finding the discrete state $|\varphi\rangle$ in this interval equals

$$\mathrm{d}N_\varphi = \sum_{E < E_\mu < E + \mathrm{d}E} |\langle \varphi | \psi_\mu \rangle|^2 \simeq \frac{\mathrm{d}E}{\delta} |\langle \varphi | \psi_\mu \rangle|^2 \qquad (18)$$

which yields, taking into account (17) and (1),

$$\frac{dN_\varphi}{dE} = \frac{v^2/\delta}{v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E^2} = \frac{\hbar\Gamma/2\pi}{v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E^2}. \tag{19}$$

At the limit $\delta \to 0$, v^2 tends to 0 and expression (19) becomes

$$\frac{dN_\varphi}{dE} = \frac{\hbar\Gamma/2\pi}{\left(\frac{\hbar\Gamma}{2}\right)^2 + E^2} \tag{20}$$

which is a Lorentzian curve of width $\hbar\Gamma$, centered on $E = E_\varphi = 0$ and having an integral over E equal to 1.

Such a result demonstrates that, after coupling, the discrete level $|\varphi\rangle$ is spread over an interval of width $\hbar\Gamma$ in the new continuum. In other words, only the levels of the new continuum located in an interval on the order of $\hbar\Gamma$ about E_φ retain the memory of the level $|\varphi\rangle$ in their wave function.

3. A Few Applications of This Simple Model

The results obtained above concerning the new continuum of states $\{|\psi_\mu\rangle\}$ and the density dN_φ/dE characterizing the traces of the discrete state $|\varphi\rangle$ in this new continuum are helpful for a quantitative treatment of several problems. We review now some of them.

a) Decay of the Discrete Level (*)

Let us first attempt to calculate the probability that the system, initially prepared (at $t = 0$) in the discrete state $|\varphi\rangle$, still remains in the same state an instant t later. Let us use the relation (17) and expand $|\varphi\rangle$ on the basis of eigenstates $|\psi_\mu\rangle$ of the Hamiltonian. We get

$$|\psi(0)\rangle = |\varphi\rangle = \sum_\mu \frac{v}{\left[v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E_\mu^2\right]^{1/2}} |\psi_\mu\rangle. \tag{21}$$

(*) This problem may also be treated by using the Weisskopf-Wigner method. See, for example Cohen-Tannoudji, Diu, and Laloë, Complement D_{XIII}.

At time t, this state $|\psi(t)\rangle$ becomes

$$|\psi(t)\rangle = \sum_{\mu} \frac{v\, e^{-iE_\mu t/\hbar}}{\left[v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E_\mu^2\right]^{1/2}} |\psi_\mu\rangle \tag{22}$$

and the probability amplitude of finding the system in the state $|\varphi\rangle$ is, according to (21) and (22), equal to

$$\langle\varphi|\psi(t)\rangle = \sum_{\mu} \frac{v^2\, e^{-iE_\mu t/\hbar}}{v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E_\mu^2} \tag{23}$$

which we may rewrite by replacing v^2 by $(\hbar\Gamma/2\pi)\delta$:

$$\langle\varphi|\psi(t)\rangle = \delta \sum_{\mu} \frac{(\hbar\Gamma/2\pi) e^{-iE_\mu t/\hbar}}{v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E_\mu^2}. \tag{24}$$

At the limit $\delta \to 0$, the sum $\delta\sum_\mu f(E_\mu)$ tends to an integral $\int dE\, f(E)$, so that

$$\langle\varphi|\psi(t)\rangle = \int_{-\infty}^{+\infty} \frac{\hbar\Gamma}{2\pi} \frac{e^{-iEt/\hbar}}{\left(\frac{\hbar\Gamma}{2}\right)^2 + E^2}\, dE. \tag{25}$$

This integral is calculated by the method of residues and reduces to

$$\langle\varphi|\psi(t)\rangle = e^{-\Gamma|t|/2}. \tag{26}$$

The probability of finding the system at the instant t in the level $|\varphi\rangle$ is thus

$$|\langle\varphi|\psi(t)\rangle|^2 = e^{-\Gamma|t|}. \tag{27}$$

It decays exponentially with a time constant Γ^{-1}.

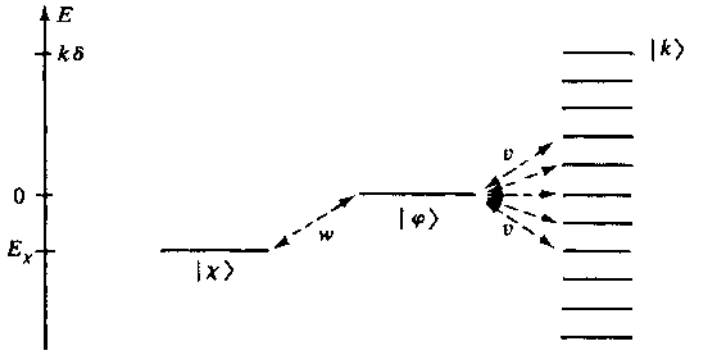


Figure 2. Energy-level scheme considered in this paragraph. The arrows represent the coupling between the levels.

b) Excitation of the System in the Discrete Level from Another State

Let us now assume that the system under study has another discrete level $|\chi\rangle$, with unperturbed energy E_χ, orthogonal to the discrete state $|\varphi\rangle$ and to the quasi-continuum of states $\{|k\rangle\}$. This level $|\chi\rangle$ is coupled directly only to the state $|\varphi\rangle$ by a coupling Hamiltonian W.

$$\langle\varphi|W|\chi\rangle = w \tag{28.a}$$

$$\langle k|W|\chi\rangle = 0. \tag{28.b}$$

All the other matrix elements of W are assumed to be zero.

We show in this section that, if w is sufficiently small, the system, initially in state $|\chi\rangle$, leaves this state with a well-defined rate. In other words, as a consequence of its coupling with a discrete level $|\varphi\rangle$, which is itself coupled to a continuum, the level $|\chi\rangle$ acquires a finite lifetime.

We have shown previously (§2) that the coupling of $|\varphi\rangle$ with the states $|k\rangle$ gives rise to a new quasi-continuum of states $|\psi_\mu\rangle$. Let us now calculate $\langle\psi_\mu|W|\chi\rangle$. Because W couples $|\chi\rangle$ only to $|\varphi\rangle$, we have

$$\langle\psi_\mu|W|\chi\rangle = \langle\psi_\mu|\varphi\rangle\langle\varphi|W|\chi\rangle = \langle\psi_\mu|\varphi\rangle w. \tag{29}$$

It thus appears that W couples the level $|\chi\rangle$ to the quasi-continuum of states $\{|\psi_\mu\rangle\}$. If the coupling w remains small, the probability per unit

time that the system leaves the state $|\chi\rangle$ is given by Fermi's golden rule:

$$\Gamma_{\chi} = \frac{2\pi}{\hbar} |\langle \psi_{\mu} | W | \chi \rangle|^2 \frac{1}{\delta} . \tag{30}$$

(The density of states $\{|\psi_{\mu}\rangle\}$, for $E_{\mu} = E_{\chi}$, is equal to $1/\delta$.) By using (29) and (17), we find at the limit $\delta \to 0$:

$$\Gamma_{\chi} = w^2 \frac{\Gamma}{\left(\frac{\hbar\Gamma}{2}\right)^2 + E_{\chi}^2} . \tag{31}$$

In the particular case where $|\chi\rangle$ and $|\varphi\rangle$ have the same energy ($E_{\chi} = E_{\varphi} = 0$), expression (31) becomes

$$\Gamma_{\chi} = \frac{4w^2}{\hbar^2 \Gamma} . \tag{32}$$

Hence, a discrete state $|\chi\rangle$ coupled to another discrete state $|\varphi\rangle$ which is unstable will itself decay irreversibly, with a rate Γ_{χ} given by (32).

Remarks

(i) The treatment presented above is valid only for sufficiently small w. More precisely the coupling w must be smaller than the width $\hbar\Gamma$ of the interval over which $|\langle \psi_{\mu} | W | \chi \rangle|^2$ is significant, or equivalently, the width of the interval of the new continuum $\{|\psi_{\mu}\rangle\}$ in which the probability that $|\varphi\rangle$ is present is important. Such a result may also be understood by comparing the period of the Rabi oscillation between $|\chi\rangle$ and $|\varphi\rangle$, which is on the order of $\hbar/w$, and the lifetime of the system in the level $|\varphi\rangle$, which is on the order of Γ^{-1}. If this lifetime is shorter than the period of the Rabi oscillation, a system initially in the state $|\chi\rangle$ will evolve irreversibly to the continuum because, once it has passed through $|\varphi\rangle$, it will immediately decay in the continuum $\{|k\rangle\}$ and will have an extremely low probability of returning to $|\chi\rangle$. Note that the condition $w \ll \hbar\Gamma$ implies that $\Gamma_{\chi} \ll \Gamma$. The lifetime associated with the level $|\chi\rangle$ is much longer than that associated with the level $|\varphi\rangle$.

(ii) The level $|\chi\rangle$ introduced above may itself be part of the continuum $\{|k\rangle\}$ (this is in particular the case for the absorption of a photon between the ground state a and a discrete excited state b of an atom, a problem that we will consider in subsection B-4 of Chapter II). To apply the preceding treatment, we must remove the state $|\chi\rangle$ from the continuum. Clearly, if δ is sufficiently small, the new continuum resulting from the coupling between the discrete state $|\varphi\rangle$ and the continuum of states $\{|k\rangle\}$ from which we have subtracted $|\chi\rangle$

will be sufficiently close to the continuum $\{|\psi_\mu\rangle\}$ studied above, so that all the preceding results remain valid.

c) Resonant Scattering through a Discrete Level

Let us now consider two levels $|\chi_i\rangle$ and $|\chi_j\rangle$ having the same energy E_χ. For example, in the problem of the resonant scattering of a photon by an atom, $|\chi_i\rangle$ and $|\chi_j\rangle$ are states which represent the atom in the ground state in the presence of the incident or scattered photon, respectively (see §C-3 of Chapter II). These two levels $|\chi_i\rangle$ and $|\chi_j\rangle$ are coupled to $|\varphi\rangle$ by a coupling term W ($\langle\varphi|W|\chi_i\rangle = w_i$ and $\langle\varphi|W|\chi_j\rangle = w_j$). On the other hand, we assume that $|\chi_i\rangle$ and $|\chi_j\rangle$ are neither coupled to each other ($\langle\chi_i|W|\chi_j\rangle = 0$) nor to the levels of the quasi-continuum $\{|k\rangle\}$ ($\langle k|W|\chi_i\rangle = 0$). We will study the scattering from $|\chi_i\rangle$ to $|\chi_j\rangle$ and show that, even if $E_\chi = E_\varphi$, the scattering amplitude does not diverge. This result is, of course, related to the fact that the discrete level $|\varphi\rangle$ is spread by the coupling V in the quasi-continuum of states $\{|\psi_\mu\rangle\}$.

First, we recall how the scattering amplitude diverges when the coupling between the discrete state $|\varphi\rangle$ and the continuum $\{|k\rangle\}$ is not taken into consideration. To lowest order in V, the transition matrix element is written

$$\mathcal{T}_{ji} \simeq \lim_{\eta \to 0_+} \langle\chi_j|W\frac{1}{E_\chi - H_0 + i\eta}W|\chi_i\rangle \tag{33}$$

that is, again

$$\mathcal{T}_{ji} \simeq \lim_{\eta \to 0_+} \frac{\langle\chi_j|W|\varphi\rangle\langle\varphi|W|\chi_i\rangle}{E_\chi - E_\varphi + i\eta} \tag{34}$$

an expression that diverges if $E_\chi = E_\varphi$.

The coupling between $|\varphi\rangle$ and $|k\rangle$ appears only to higher orders in V. In fact it is possible to write the transition matrix element to all orders in V. It is sufficient to replace H_0 by $H = H_0 + V$ in (33) [see expression (B.15) in this chapter]. Because W couples $|\chi_i\rangle$ and $|\chi_j\rangle$ only to $|\varphi\rangle$, we get

$$\mathcal{T}_{ji} \simeq \lim_{\eta \to 0_+} \langle\chi_j|W|\varphi\rangle\langle\varphi|\frac{1}{E_\chi - H + i\eta}|\varphi\rangle\langle\varphi|W|\chi_i\rangle. \tag{35}$$

Let us now introduce the closure relation over the eigenstates $|\psi_\mu\rangle$ of H in the central matrix element of (35). The density of the state $|\varphi\rangle$ in the

new continuum then appears explicitly, and expression (35) becomes, taking (17) and (1) into consideration,

$$\mathscr{T}_{ji} = \lim_{\eta \to 0_+} w_j^* w_i \delta \sum_{\mu} \frac{\hbar\Gamma/2\pi}{(E_\chi - E_\mu + i\eta)\left(E_\mu^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 - v^2\right)}. \quad (36)$$

In the limit $\delta \to 0$, this sum tends to the following integral:

$$\mathscr{T}_{ji} = w_j^* w_i \lim_{\eta \to 0_+} \int_{-\infty}^{+\infty} \mathrm{d}E \, \frac{\hbar\Gamma/2\pi}{(E_\chi - E + i\eta)\left(E^2 + \left(\frac{\hbar\Gamma}{2}\right)^2\right)} \quad (37)$$

which may be calculated by the residue method and gives

$$\mathscr{T}_{ji} = w_j^* w_i \frac{1}{E_\chi + i\hbar(\Gamma/2)}. \quad (38)$$

The scattering amplitude thus does not diverge any more when $E_\chi = E_\varphi = 0$. Note that everything happens as if, in the lowest-order expression, the energy of the discrete level $|\varphi\rangle$ had been replaced by a complex energy $E_\varphi - i\hbar\Gamma/2 = -i\hbar\Gamma/2$. While remaining finite, the transition matrix element thus varies in a resonant fashion when E_χ is swept over an interval of width $\hbar\Gamma$ about $E_\varphi = 0$.

d) Fano Profiles

We come back to the case where the system has another state $|\chi\rangle$ coupled to $|\varphi\rangle$ by a coupling term $W(\langle\varphi|W|\chi\rangle = w)$, but we now assume that $|\chi\rangle$ is also directly coupled by W to the states $\{|k\rangle\}$ of the quasi-continuum. We also make a simplifying assumption concerning the matrix elements $\langle k|W|\chi\rangle$ which are assumed to be independent of $|k\rangle$ $(\langle k|W|\chi\rangle = w')$. What is the probability that a level $|\psi_\mu\rangle$ will be excited from $|\chi\rangle$? This probability is proportional to the square of the matrix element $\langle\psi_\mu|W|\chi\rangle$ which may be calculated from (17) and (5):

$$\langle\psi_\mu|W|\chi\rangle = \frac{\langle\varphi|W|\chi\rangle v + \Sigma_k \langle k|W|\chi\rangle v^2/(E_\mu - E_k)}{\left[v^2 + \left(\frac{\hbar\Gamma}{2}\right)^2 + E_\mu^2\right]^{1/2}} \quad (39)$$

an expression which is written, taking (6) into consideration,

$$\langle \psi_\mu | W | \chi \rangle = \frac{wv + w' E_\mu}{\left[v^2 + \left(\frac{\hbar \Gamma}{2} \right)^2 + E_\mu^2 \right]^{1/2}}. \tag{40}$$

When the energy of the state E_μ varies, the two terms of the numerator of the right-hand side of (40) add up or subtract depending on the respective signs of E_μ and of vw/w'. Hence the lineshape (probability of excitation as a function of E_μ) is generally asymmetric.

Relation (40) is frequently rewritten as a function of the reduced variables

$$\varepsilon_\mu = \frac{E_\mu}{\hbar \Gamma / 2} \tag{41}$$

$$q = \frac{\delta}{\pi v} \frac{w}{w'} \tag{42}$$

ε_μ is the energy in units of $\hbar \Gamma / 2$. The parameter q defined in (42) characterizes the ratio between the coupling to the discrete state $|\varphi\rangle$ and the coupling to the quasi-continuum $\{|k\rangle\}$. Let us also introduce the parameter ξ

$$\xi = \frac{4v^2}{\hbar^2 \Gamma^2} = \frac{2}{\pi} \frac{\delta}{\hbar \Gamma}. \tag{43}$$

ξ^{-1} represents the number of levels of the discretized continuum within the natural width ($\xi \to 0$ when $\delta \to 0$). By using these definitions, we obtain from (40)

$$\frac{\left| \langle \psi_\mu | W | \chi \rangle \right|^2}{w'^2} \propto \frac{|q + \varepsilon_\mu|^2}{1 + \varepsilon_\mu^2 + \xi}. \tag{44}$$

In Figure 3 we have represented several possible excitation profiles obtained for different values of q. They are called Fano profiles (*). Note

(*) Such profiles are encountered in several physical situations, for example in photoionization near an autoionizing state.

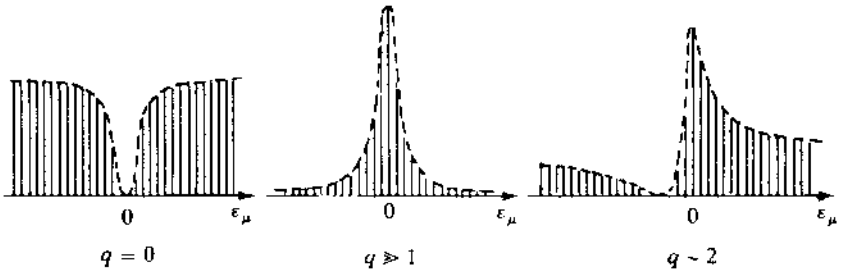


Figure 3. Fano profiles obtained for different values of q. The intensity of the transitions to the states $|\psi_\mu\rangle$ of the quasi-continuum is represented by solid lines. The dashed line corresponding to the envelope of these intensities allows us to visualize the profile of excitation at the continuous limit ($\delta \to 0$). Note that except for the limiting situations $q = 0$ and $q \gg 1$, the profiles are asymmetric.

that the situation $q \gg 1$ (case where the coupling between $|\chi\rangle$ and $|\varphi\rangle$ is much larger than the coupling between $|\chi\rangle$ and $|k\rangle$) corresponds to the situation considered in subsection 3-b of this complement.

Remark

In all the situations considered previously, the limit $\delta \to 0$ did not pose any problem. This is not always the case, and certain precautions must be taken when the problem under study (*) involves quantities such as $\langle k|\psi_\mu\rangle$ [relation (8.b)] in which the factor $1/(E_\mu - E_k)$ appears. Actually, in the discrete case $(E_\mu - E_k)$ never vanishes (see Figure 1), and thus division by $(E_\mu - E_k)$ presents no difficulties. This is what we did, for example, to deduce (5) from (4.a). By contrast, more precautions must be taken in determining the limit of $1/(E_\mu - E_k)$. In order to determine such a limit considered as a distribution, we reexpress $(E_\mu - E_k)^{-1}$ as a function of the angle φ_μ defined by Equation (13.a) and of the integer m closest to E_μ/δ (see Figure 1). By using Equation (13.b) and the fact that $E_k = k\delta$, we obtain

$$\frac{1}{E_\mu - E_k} = \frac{1}{\left(m - k + \dfrac{\varphi_\mu}{\pi}\right)\delta}. \tag{45}$$

(*) This is the case, for example, when one studies the energy distribution of the final states resulting from the disintegration of the discrete state.

Let us rewrite (45) as the sum of an odd function of $(m-k)$ and an even function.

$$\frac{1}{E_\mu - E_k} = \frac{(m-k)\delta}{(m-k)^2\delta^2 - (\varphi_\mu\delta/\pi)^2} - \frac{\varphi_\mu\delta/\pi}{(m-k)^2\delta^2 - (\varphi_\mu\delta/\pi)^2}. \quad (46)$$

Since φ_μ/π is, in modulus, less than $\frac{1}{2}$, $\varphi_\mu\delta/\pi$ tends to zero when δ tends to zero. The first term of the right-hand side of (46) is odd in $(m-k)\delta$, and hence tends, when $\delta \to 0$, to $\mathscr{P}(1/(E'-E))$, where E' and E are associated, respectively, with E_μ and E_k and $\mathscr{P}$ denotes the principal part. Let us now analyze the second term. It has significant values only for m close to k. In particular, for $E_m = E_k$, its value is equal to $\pi/(\varphi_\mu\delta)$ and thus tends to infinity when $\delta \to 0$. When $E_m \neq E_k$, this term has the opposite sign but its value remains on the order of $1/\delta$ for small $(m-k)$. Its width in E_k is of the order of δ. The second term of (46) thus tends to a distribution localized in $E_m = E_k$ when $\delta \to 0$. Let us now calculate the sum.

$$-\delta\sum_k \frac{\varphi_\mu\delta/\pi}{(m-k)^2\delta^2 - (\varphi_\mu\delta/\pi)^2} = \sum_p \frac{\varphi_\mu/\pi}{(\varphi_\mu/\pi)^2 - p^2}. \quad (47)$$

The sum of this series is known (*) to be $\pi/\tan\varphi_\mu$; that is, again according to (13.a),

$$\frac{2\pi}{\hbar\Gamma}E_\mu. \quad (48)$$

It follows that the limit $\delta \to 0$ of the second term of (46) is

$$(2\pi/\hbar\Gamma)E\delta(E-E').$$

Finally,

$$\lim_{\delta\to 0}\frac{1}{E_\mu - E_k} = \mathscr{P}\left(\frac{1}{E'-E}\right) + \frac{2\pi}{\hbar\Gamma}E\delta(E-E'). \quad (49)$$

4. Generalization to More Realistic Continua. Diagonalization of the Hamiltonian without Discretization

We return in this last subsection to the problem of a discrete state $|\varphi\rangle$ coupled to a continuum of states $\{|E\rangle\}$, to directly study (without discretizing the continuum) the eigenstates $|\psi(E)\rangle$ of the total Hamiltonian. In contrast to the situation in subsections 2 and 3, we will not make any

(*) See for example, Cartan, corrected exercise 25, p. 226.

restrictive assumptions on the continuum and on its coupling with the state $|\varphi\rangle$. In particular, the matrix element $\langle E|V|\varphi\rangle = v(E)$ is now an arbitrary function of E. The orthonormalization relation between states of the continuum is

$$\langle E'|E\rangle = \delta(E - E') \tag{50}$$

and the matrix elements of the Hamiltonian H_0 and of the coupling V are

$$\langle \varphi|H_0|\varphi\rangle = E_\varphi \tag{51.a}$$

$$\langle E|H_0|E'\rangle = E\delta(E - E') \tag{51.b}$$

$$\langle E|V|\varphi\rangle = v(E) \tag{51.c}$$

$$\langle E'|V|E\rangle = \langle \varphi|V|\varphi\rangle \quad 0 \tag{51.d}$$

Let $|\psi(E')\rangle$ be an eigenstate of H_0 with eigenvalue E'

$$H|\psi(E')\rangle = E'|\psi(E')\rangle. \tag{52}$$

To find the expansion of $|\psi(E')\rangle$ over the unperturbed states $|\varphi\rangle$ and $|E\rangle$, we proceed as in subsection 2-a and first project (52) onto $|\varphi\rangle$, then onto $|E\rangle$. We thus obtain the equations

$$E_\varphi\langle\varphi|\psi(E')\rangle + \int \mathrm{d}E\, v(E)^*\langle E|\psi(E')\rangle = E'\langle\varphi|\psi(E')\rangle \tag{53.a}$$

$$E\langle E|\psi(E')\rangle + v(E)\langle\varphi|\psi(E')\rangle = E'\langle E|\psi(E')\rangle. \tag{53.b}$$

Equation (53.b) is transformed to

$$(E' - E)\langle E|\psi(E')\rangle = v(E)\langle\varphi|\psi(E')\rangle. \tag{54}$$

Distribution, theory allows the general solution of (54) to be written in the form

$$\langle E|\psi(E')\rangle = \left[\mathscr{P}\frac{1}{E' - E} + z(E')\delta(E - E')\right]v(E)\langle\varphi|\psi(E')\rangle \tag{55}$$

where $z(E')$ is an arbitrary function of E'. To determine this function $z(E')$, we substitute (55) into (53.a), and we obtain

$$E_\varphi + \mathscr{P}\int \mathrm{d}E\, \frac{|v(E)|^2}{E' - E} + z(E')|v(E')|^2 = E' \tag{56}$$

that is

$$E_\varphi + \hbar\Delta(E') + \frac{1}{\pi}\hbar\frac{\Gamma(E')}{2}z(E') = E' \tag{57}$$

with

$$\Gamma(E') = \frac{2\pi}{\hbar}|v(E')|^2 \tag{58.a}$$

$$\Delta(E') = \frac{1}{\hbar}\mathscr{P}\int \mathrm{d}E\,\frac{|v(E)|^2}{E'-E} = \frac{1}{2\pi}\mathscr{P}\int \mathrm{d}E\,\frac{\Gamma(E)}{E'-E}. \tag{58.b}$$

From this we deduce

$$z(E') = 2\pi\frac{E' - E_\varphi - \hbar\Delta(E')}{\hbar\Gamma(E')}. \tag{59}$$

Equations (55) and (59) allow us to find the new eigenvectors to within a normalization coefficient, which is determined by the equation

$$\langle\psi(E')|\psi(E)\rangle = \delta(E'-E). \tag{60}$$

We do not give here the calculation of this normalization coefficient, but we will simply quote the result (*):

$$|\psi(E')\rangle = \frac{1}{\left\{\left[E' - E_\varphi - \hbar\Delta(E')\right]^2 + \left[\hbar\Gamma(E')/2\right]^2\right\}^{1/2}} \times\left\{v(E')\left[|\varphi\rangle + \mathscr{P}\int \mathrm{d}E\,\frac{V(E)}{E'-E}|E\rangle\right] + \left[E' - E_\varphi - \hbar\Delta(E')\right]|E'\rangle\right\}. \tag{61}$$

No restrictive assumption having been made on the variation of the coupling $v(E)$ with E, the vectors thus obtained may be applied to the study of many problems.

(*) See U. Fano, *Phys. Rev.*, **124**, 1866 (1961).