Using (B-20) and replacing $\lambda \hat{W}(t)$ by $W(t)$ [*cf.* (A-3)], we finally obtain:

$$\mathscr{P}_{if}(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi} t'} W_{fi}(t')\, dt' \right|^2 \qquad \text{(B-24)}$$

Consider the function $\tilde{W}_{fi}(t')$, which is zero for $t' < 0$ and $t' > t$, and equal to $W_{fi}(t')$ for $0 \leqslant t' \leqslant t$ (*cf.* fig. 1). $\tilde{W}_{fi}(t')$ is the matrix element of the perturbation "seen" by the system between the time $t = 0$ and the measurement time t, when we try to determine if the system is in the state $| \varphi_f \rangle$. Result (B-24) shows that $\mathscr{P}_{if}(t)$ is proportional to the square of the modulus of the Fourier transform of the perturbation actually "seen", $\tilde{W}_{fi}(t')$. This Fourier transform is evaluated at an angular frequency equal to the Bohr angular frequency associated with the transition under consideration.

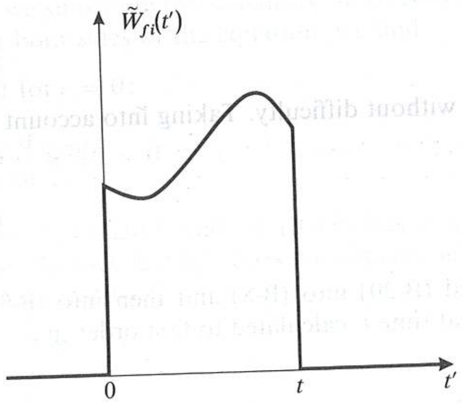

FIGURE 1

The variation of the function $\tilde{W}_{fi}(t')$ with respect to t'. $\tilde{W}_{fi}(t')$ coincides with $W_{fi}(t')$ in the interval $0 \leqslant t' \leqslant t$, and goes to zero outside this interval. It is the Fourier transform of $\tilde{W}_{fi}(t')$ that enters into the transition probability $\mathscr{P}_{if}(t)$ to lowest order.

Note also that the transition probability $\mathscr{P}_{if}(t)$ is zero to first order if the matrix element $W_{fi}(t)$ is zero for all t.

COMMENT:

We have not discussed the validity conditions of the approximation to first order in λ. Comparison of (B-11) with (B-19) shows that this approximation simply amounts to replacing, on the right-hand side of (B-11), the coefficients $b_k(t)$ by their values $b_k(0)$ at time $t = 0$. It is therefore clear that, so long as t remains small enough for $b_k(0)$ not to differ very much from $b_k(t)$, the approximation remains valid. On the other hand, when t becomes large, there is no reason why the corrections of order 2, 3, etc. in λ should be negligible.

C. AN IMPORTANT SPECIAL CASE: A SINUSOIDAL OR CONSTANT PERTURBATION

1. Application of the general equations

Now assume that $W(t)$ has one of the two simple forms:

$$\hat{W}(t) = \hat{W} \sin \omega t \qquad \text{(C-1-a)}$$

$$\hat{W}(t) = \hat{W} \cos \omega t \qquad \text{(C-1-b)}$$

where $\hat{W}$ is a time-independent observable and ω, a constant angular frequency. Such a situation is often encountered in physics. For example, in complements A_{XIII} and B_{XIII}, we consider the perturbation of a physical system by an electromagnetic wave of angular frequency ω; $\mathscr{P}_{if}(t)$ then represents the probability, induced by the incident monochromatic radiation, of a transition between the initial state $| \varphi_i \rangle$ and the final state $| \varphi_f \rangle$.

With the particular form (C-1-a) of $\hat{W}(t)$, the matrix elements $\hat{W}_{fi}(t)$ take on the form:

$$\hat{W}_{fi}(t) = \hat{W}_{fi} \sin \omega t = \frac{\hat{W}_{fi}}{2i} (e^{i\omega t} - e^{-i\omega t}) \qquad \text{(C-2)}$$

where $\hat{W}_{fi}$ is a time-independent complex number. Let us now calculate the state vector of the system to first order in λ. If we substitute (C-2) into general formula (B-20), we obtain:

$$b_n^{(1)}(t) = -\frac{\hat{W}_{ni}}{2\hbar} \int_0^t [e^{i(\omega_{ni} + \omega)t'} - e^{i(\omega_{ni} - \omega)t'}]\, dt' \qquad \text{(C-3)}$$

The integral which appears on the right-hand side of this relation can easily be calculated and yields:

$$b_n^{(1)}(t) = \frac{\hat{W}_{ni}}{2i\hbar} \left[\frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} - \frac{1 - e^{i(\omega_{ni} - \omega)t}}{\omega_{ni} - \omega} \right] \qquad \text{(C-4)}$$

Therefore, in the special case we are treating, general equation (B-24) becomes:

$$\mathscr{P}_{if}(t; \omega) = \lambda^2 \, |b_f^{(1)}(t)|^2 = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2 \qquad \text{(C-5-a)}$$

(we have added the variable ω in the probability $\mathscr{P}_{if}$, since the latter depends on the frequency of the perturbation).

If we choose the special form (C-1-b) for $\hat{W}(t)$ instead of (C-1-a), a calculation analogous to the preceding one yields:

$$\mathscr{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} + \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2 \qquad \text{(C-5-b)}$$

$\hat{W} \cos \omega t$ becomes time-independent if we choose $\omega = 0$. The transition probability $\mathscr{P}_{if}(t)$ induced by a constant perturbation W can therefore be obtained by replacing ω by 0 in (C-5-b):

$$\mathscr{P}_{if}(t) = \frac{|W_{fi}|^2}{\hbar^2 \omega_{fi}^2} |1 - e^{i\omega_{fi}t}|^2 = \frac{|W_{fi}|^2}{\hbar^2} F(t, \omega_{fi}) \quad \text{(C-6)}$$

with:

$$F(t, \omega_{fi}) = \left[\frac{\sin (\omega_{fi}t/2)}{\omega_{fi}/2} \right]^2 \quad \text{(C-7)}$$

In order to study the physical content of equations (C-5) and (C-6), we shall first consider the case in which $| \varphi_i \rangle$ and $| \varphi_f \rangle$ are two discrete levels (§ 2), and then the one in which $| \varphi_f \rangle$ belongs to a continuum of final states (§ 3). In the first case, $\mathscr{P}_{if}(t; \omega)$ [or $\mathscr{P}_{if}(t)$] really represents a transition probability which can be measured, while, in the second case, we are actually dealing with a probability density (the truly measurable quantities then involve a summation over a set of final states). From a physical point of view, there is a distinct difference between these two cases. We shall see in complements C_{XIII} and D_{XIII} that, over a sufficiently long time interval, the system oscillates between the states $| \varphi_i \rangle$ and $| \varphi_f \rangle$ in the first case, while it leaves the state $| \varphi_i \rangle$ irreversibly in the second case.

In §2, in order to concentrate on the resonance phenomenon, we shall choose a sinusoidal perturbation, but the results obtained can easily be transposed to the case of a constant perturbation. Inversely, we shall use this latter case for the discussion of §3.

2. Sinusoidal perturbation which couples two discrete states: the resonance phenomenon

a. RESONANT NATURE OF THE TRANSITION PROBABILITY

When the time t is fixed, the transition probability $\mathscr{P}_{if}(t; \omega)$ is a function only of the variable ω. We shall see that this function has a maximum for:

$$\omega \simeq \omega_{fi} \quad \text{(C-8-a)}$$

or:

$$\omega \simeq -\omega_{fi} \quad \text{(C-8-b)}$$

A resonance phenomenon therefore occurs when the angular frequency of the perturbation coincides with the Bohr angular frequency associated with the pair of states $| \varphi_i \rangle$ and $| \varphi_f \rangle$. If we agree to choose $\omega \geqslant 0$, relations (C-8) give the resonance conditions corresponding respectively to the cases $\omega_{fi} > 0$ and $\omega_{fi} < 0$.

In the first case (*cf.* fig. 2-a), the system goes from the lower energy level E_i to the higher level E_f by the resonant absorption of an energy quantum $\hbar\omega$. In the second case (*cf.* fig. 2-b), the resonant perturbation stimulates the passage of the system

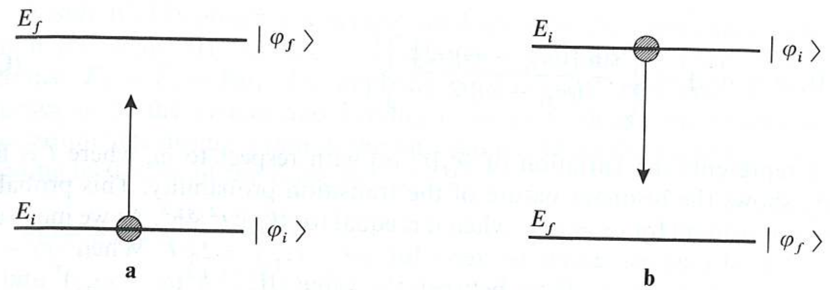

FIGURE 2

The relative disposition of the energies E_i and E_f associated with the states $| \varphi_i \rangle$ and $| \varphi_f \rangle$. If $E_i < E_f$ (fig. a), the $| \varphi_i \rangle \longrightarrow | \varphi_f \rangle$ transition occurs through absorption of an energy quantum $\hbar\omega$. If, on the other hand, $E_i > E_f$ (fig. b), the $| \varphi_i \rangle \longrightarrow | \varphi_f \rangle$ transition occurs through induced emission of an energy quantum $\hbar\omega$.

from the higher level E_i to the lower level E_f (accompanied by the induced emission of an energy quantum $\hbar\omega$). Throughout this section, we shall assume that ω_{fi} is positive (the situation of figure 2-a). The case in which ω_{fi} is negative could be treated analogously.

To reveal the resonant nature of the transition probability, we note that expressions (C-5-a) and (C-5-b) for $\mathscr{P}_{if}(t; \omega)$ involve the square of the modulus of a sum of two complex terms. The first of these terms is proportional to:

$$A_+ = \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} = -i\, e^{i(\omega_{fi} + \omega)t/2} \frac{\sin [(\omega_{fi} + \omega)t/2]}{(\omega_{fi} + \omega)/2} \quad \text{(C-9-a)}$$

and the second one, to:

$$A_- = \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} = -i\, e^{i(\omega_{fi} - \omega)t/2} \frac{\sin [(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \quad \text{(C-9-b)}$$

The denominator of the A_- term goes to zero for $\omega = \omega_{fi}$, and that of the A_+ term, for $\omega = -\omega_{fi}$. Consequently, for ω close to ω_{fi}, we expect only the A_- term to be important; this is why it is called the "resonant term", while the A_+ term is called the "anti-resonant term" (A_+ would become resonant if, for negative ω_{fi}, ω were close to $-\omega_{fi}$).

Let us then consider the case in which:

$$|\omega - \omega_{fi}| \ll |\omega_{fi}| \quad \text{(C-10)}$$

neglecting the anti-resonant term A_+ (the validity of this approximation will be discussed in § c below). Taking (C-9-b) into account, we then obtain:

$$\mathscr{P}_{if}(t;\omega) = \frac{|W_{fi}|^2}{4\hbar^2} F(t, \omega - \omega_{fi}) \tag{C-11}$$

with:

$$F(t, \omega - \omega_{fi}) = \left\{ \frac{\sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right\}^2 \tag{C-12}$$

Figure 3 represents the variation of $\mathscr{P}_{if}(t;\omega)$ with respect to ω, where t is fixed. It clearly shows the resonant nature of the transition probability. This probability presents a maximum for $\omega = \omega_{fi}$, when it is equal to $|W_{fi}|^2 t^2/4\hbar^2$. As we move away from ω_{fi}, it decreases, going to zero for $|\omega - \omega_{fi}| = 2\pi/t$. When $|\omega - \omega_{fi}|$ continues to increase, it oscillates between the value $|W_{fi}|^2/\hbar^2(\omega - \omega_{fi})^2$ and zero ("diffraction pattern").

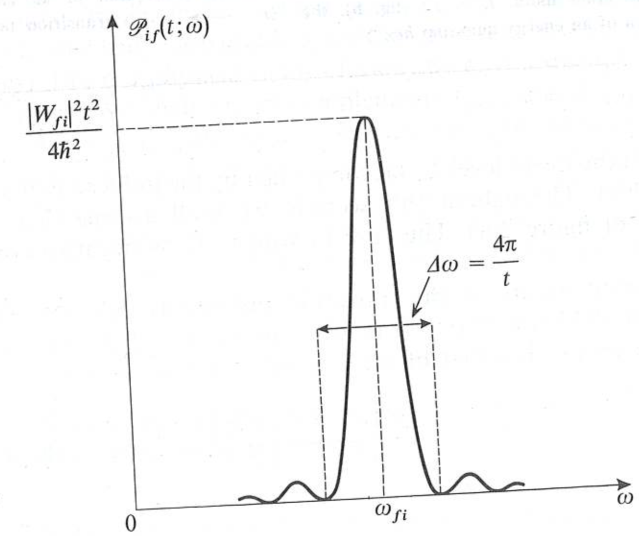

FIGURE 3

Variation, with respect to ω, of the first-order transition probability $\mathscr{P}_{if}(t;\omega)$ associated with a sinusoidal perturbation of angular frequency ω; t is fixed. When $\omega \simeq \omega_{fi}$, a resonance appears whose intensity is proportional to t^2 and whose width is inversely proportional to t.

b. THE RESONANCE WIDTH AND THE TIME-ENERGY UNCERTAINTY RELATION

The resonance width $\Delta\omega$ can be approximately defined as the distance between the first two zeros of $\mathscr{P}_{if}(t;\omega)$ about $\omega = \omega_{fi}$. It is inside this interval that the transition probability takes on its largest values [the first secondary

maximum of $\mathscr{P}_{if}$, attained when $(\omega - \omega_{fi})t/2 = 3\pi/2$, is equal to $|W_{fi}|^2 t^2/9\pi^2\hbar^2$, that is, less than 5 % of the transition probability at resonance]. We then have:

$$\Delta\omega \simeq \frac{4\pi}{t} \tag{C-13}$$

The larger the time t, the smaller this width.

Result (C-13) presents a certain analogy with the time-energy uncertainty relation (*cf.* chap. III, §D-2-e). Assume that we want to measure the energy difference $E_f - E_i = \hbar\omega_{fi}$ by applying a sinusoidal perturbation of angular frequency ω to the system and varying ω so as to detect the resonance. If the perturbation acts during a time t, the uncertainty ΔE on the value $E_f - E_i$ will be, according to (C-13), of the order of:

$$\Delta E = \hbar\,\Delta\omega \simeq \frac{\hbar}{t} \tag{C-14}$$

Therefore, the product $t\Delta E$ cannot be smaller than $\hbar$. This recalls the time-energy uncertainty relation, although t here is not a time interval characteristic of the free evolution of the system, but is externally imposed.

c. VALIDITY OF THE PERTURBATION TREATMENT

Now let us examine the limits of validity of the calculations leading to result (C-11). We shall first discuss the resonant approximation, which consists of neglecting the anti-resonant term A_+, and then the first-order approximation in the perturbation expansion of the state vector.

α. Discussion of the resonant approximation

Using the hypothesis $\omega \simeq \omega_{fi}$, we have neglected A_+ relative to A_-. We shall therefore compare the moduli of A_+ and A_-.

The shape of the function $|A_-(\omega)|^2$ is shown in figure 3. Since $|A_+(\omega)|^2 = |A_-(-\omega)|^2$, $|A_+(\omega)|^2$ can be obtained by plotting the curve which is symmetric with respect to the preceding one relative to the vertical axis $\omega = 0$. If these two curves, of width $\Delta\omega$, are centered at points whose separation is much larger than $\Delta\omega$, it is clear that, in the neighborhood of $\omega = \omega_{fi}$, the modulus of A_+ is negligible compared to that of A_-. The resonant approximation is therefore justified on the condition* that:

$$2|\omega_{fi}| \gg \Delta\omega \tag{C-15}$$

that is, using (C-13):

$$t \gg \frac{1}{|\omega_{fi}|} \simeq \frac{1}{\omega} \tag{C-16}$$

Result (C-11) is therefore valid only if the sinusoidal perturbation acts during a time t which is large compared to $1/\omega$. The physical meaning of such a condition

* Note that if condition (C-15) is not satisfied, the resonant and anti-resonant terms interfere: it is not correct to simply add $|A_+|^2$ and $|A_-|^2$.

is clear: during the interval $[0, t]$, the perturbation must perform numerous oscillations to appear to the system as a sinusoidal perturbation. If, on the other hand, t were small compared to $1/\omega$, the perturbation would not have the time to oscillate and would be equivalent to a perturbation varying linearly in time [in the case (C-1-a)] or constant [in the case (C-1-b)].

COMMENT:

For a constant perturbation, condition (C-16) can never be satisfied, since ω is zero. However, it is not difficult to adapt the calculations of § b above to this case. We have already obtained [in (C-6)] the transition probability $\mathcal{P}_{if}(t)$ for a constant perturbation by directly setting $\omega = 0$ in (C-5-b). Note that the two terms A_+ and A_- are then equal, which shows that if (C-16) is not satisfied, the anti-resonant term is not negligible.

The variation of the probability $\mathcal{P}_{if}(t)$ with respect to the energy difference $\hbar\omega_{fi}$ (with the time t fixed) is shown in figure 4. This probability is maximal when $\omega_{fi} = 0$, which corresponds to what we found in §b above: if its angular frequency is zero, the perturbation is resonant when $\omega_{fi} = 0$ (degenerate levels). More generally, the considerations of § b concerning the features of the resonance can be transposed to this case.

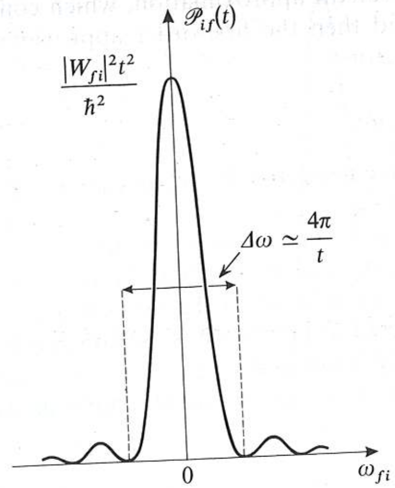

FIGURE 4

Variation of the transition probability $\mathcal{P}_{if}(t)$ associated with a constant perturbation with respect to $\omega_{fi} = (E_f - E_i)/\hbar$, for fixed t. A resonance appears, centered about $\omega_{fi} = 0$ (conservation of energy), with the same width as the resonance of figure 3, but an intensity four times greater (because of the constructive interference of the resonant and anti-resonant terms, which, for a constant perturbation, are equal).

β. *Limits of the first-order calculation*

We have already noted (*cf.* comment at the end of §B-3-b) that the first-order approximation can cease to be valid when the time t becomes too large. This can indeed be seen from expression (C-11), which, at resonance, can be written:

$$\mathcal{P}_{if}(t\,;\omega = \omega_{fi}) = \frac{|W_{fi}|^2}{4\hbar^2}\, t^2 \qquad \text{(C-17)}$$

This function becomes infinite when $t \longrightarrow \infty$, which is absurd, since a probability can never be greater than 1.

In practice, for the first-order approximation to be valid at resonance, the probability in (C-17) must be much smaller than 1, that is*:

$$t \ll \frac{\hbar}{|W_{fi}|} \qquad \text{(C-18)}$$

To show precisely why this inequality is related to the validity of the first-order approximation, it would be necessary to calculate the higher-order corrections from (B-14) and to examine under what conditions they are negligible. We would then see that although inequality (C-18) is necessary, it is not rigorously sufficient. For example, in the terms of second or higher order, there appear matrix elements $\hat{W}_{kn}$ of $\hat{W}$ other than $\hat{W}_{fi}$, on which certain conditions must be imposed for the corresponding corrections to be small.

Note that the problem of calculating the transition probability when t does not satisfy (C-18) is taken up in complement C_{XIII}, in which an approximation of a different type is used (the secular approximation).

3. Coupling with the states of the continuous spectrum

If the energy E_f belongs to a continuous part of the spectrum of H_0, that is, if the final states are labeled by continuous indices, we cannot measure the probability of finding the system in a *well-defined* state $|\,\varphi_f\,\rangle$ at time t. The postulates of chapter III indicate that in this case the quantity $|\langle\,\varphi_f\,|\,\psi(t)\,\rangle|^2$ which we found above (approximately) is a probability density. The physical predictions for a given measurement then involve an integration of this probability density over a certain group of final states (which depends on the measurement to be made). We shall consider what happens to the results of the preceding sections in this case.

a. INTEGRATION OVER A CONTINUUM OF FINAL STATES; DENSITY OF STATES

α. *Example*

To understand how this integration is performed over the final states, we shall first consider a concrete example.

We shall discuss the problem of the scattering of a spinless particle of mass m by a potential $W(\mathbf{r})$ (*cf.* chap. VIII). The state $|\,\psi(t)\,\rangle$ of the particle at time t can

* For this theory to be meaningful, it is obviously necessary for conditions (C-16) and (C-18) to be compatible. That is, we must have:

$$\frac{1}{|\omega_{fi}|} \ll \frac{\hbar}{|W_{fi}|}$$

This inequality means that the energy difference $|E_f - E_i| = \hbar\,|\omega_{fi}|$ is much larger than the matrix element of $W(t)$ between $|\,\varphi_i\,\rangle$ and $|\,\varphi_f\,\rangle$.