§6.5. Transition Probability for General Cases: Time-Dependent Perturbation Theory

(1). Time-Dependent Perturbation Theory

The approximation method is valid under the condition of

$$\hat{H}'(t) \ll \hat{H}_0 \qquad (49).$$

Thus, the $\hat{H}'$ can be treated as a perturbation to $\hat{H}_0$ states.

We write $C_n(t)$ in the expansion of many orders of approximations:

$$C_n(t) = C_n^{(0)}(t) + C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots \qquad (50).$$

The initial conditions for solving the Schrödinger equation is that

at $t=0$, $|\psi(0)\rangle \equiv |\psi(t=0)\rangle = |\Phi_i(t=0)\rangle = |\phi_i\rangle$. (51)

From Eq. (6), we have:

$$C_f(t=0) = \langle \Phi_f(t=0) | \psi(0)\rangle = \langle \Phi_f | \Phi_i \rangle = \delta_{fi} \qquad (52)$$

Substitute Eq. (50) into the Schrödinger Eq. (13), we obtain

$$i\hbar \frac{dC_f^{(0)}(t)}{dt} + i\hbar \frac{dC_f^{(1)}(t)}{dt} + i\hbar \frac{dC_f^{(2)}(t)}{dt} + \cdots$$

$$= \sum_n C_n^{(0)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} + \sum_n C_n^{(1)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} + \sum_n C_n^{(2)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} + \cdots \qquad (53)$$

We then set equal the terms of same order approximation on both sides of the equation (53). Note: Since $\hat{H}' \ll \hat{H}_0$, H'_{fn} is already a first order approximation. Considering $C_n^{(0)}(t)$ is the zeroeth-order approximation of the coefficient $C_n(t)$, the first term on the right side of Eq. (53) is already a first order approximation. Therefore, there is no zeroeth-order term on the right side of Eq. (53). So we have:

$$\begin{cases} i\hbar \dfrac{dC_f^{(0)}(t)}{dt} = 0 & (54) \\ i\hbar \dfrac{dC_f^{(1)}(t)}{dt} = \sum_n C_n^{(0)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} & (55) \\ i\hbar \dfrac{dC_f^{(2)}(t)}{dt} = \sum_n C_n^{(1)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} & (56) \\ \cdots\cdots \end{cases}$$

From Eq. (54), we get $C_f^{(0)}(t) = \text{Constant}$ (57)

From the initial condition Eq. (51), $C_f(t=0) = \delta_{fi}$

Since $\hat{H}'(t=0) = 0$, we have $C_f^{(r)}(t=0) = 0$, $(r \geq 1)$

$$\begin{cases} C_f^{(0)}(t=0) = \delta_{fi}. \end{cases}$$

Considering Eq. (57), we have

$$\begin{cases} C_f^{(0)}(t) = C_f^{(0)}(t=0) = \delta_{fi} & (58). \\ C_n^{(0)}(t) = \delta_{ni} \end{cases}$$

Substitute Eq.(58) into Eq.(55), we have

$$i\hbar \frac{d C_f^{(1)}(t)}{dt} = e^{i\omega_{fi} t} \; H'_{fi}(t) \qquad (59).$$

The equation can be integrated to give

$$C_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi} t'} \; H'_{fi}(t)\, dt' \qquad (60).$$

Since the final state $|\Phi_f\rangle$ is different from the initial state $|\Phi_i\rangle$, from Eq.(58), we have $C_f^{(0)}(t) = 0$. (61).

Therefore, by taking the first order approximation, we get

$$C_f(t) = C_f^{(0)}(t) + C_f^{(1)}(t)$$

$$= \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi} t'} \; H'_{fi}(t')\, dt' \qquad (62).$$

From our discussion above about the transition probability and Eq.(8), the transition probability from $|\Phi_i\rangle$ to $|\Phi_f\rangle$ under $\hat{H}'(t)$ perturbation is given by

$$P_{if}(t) = |C_f(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi} t'} \; H'_{fi}(t')\, dt' \right|^2 . \qquad (63).$$

In spectroscopy, we usually use a term called transition rate, which is defined as the transition probability in unit time, i.e.,

$$W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{d}{dt} |C_f(t)|^2 \qquad (64)$$

$$= \frac{1}{\hbar^2} \frac{d}{dt} \left| \int_0^t e^{i\omega_{fi} t'} \; H'_{fi}(t')\, dt' \right|^2 .$$

Note: from the point of view of time-dependent perturbation theory, after integrating Eq. (60) to obtain $C_f^{(1)}(t)$, $C_f^{(1)}(t)$ can be substituted into the 2nd order equation (56) to derive $C_f^{(2)}(t)$. This procedure can go on to higher order approximations $C_f^{(r)}(t)$.

Then $C_f(t) = \sum_r C_f^{(r)}(t)$, (65)

so the transition probability $P_{if}(t) = |C_f(t)|^2$.

transition rate: $W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{d |C_f(t)|^2}{dt}$

The time-dependent perturbation theory, like Eqs. (63) and (64), gives the general equation for transition probability. We need to derive the matrix element $H'_{fi} \equiv \langle \varphi_f | \hat{H}' | \varphi_i \rangle$, which depends on ① the perturbation $\hat{H}'$ and ② the eigenstates $|\varphi_f\rangle$ and $|\varphi_i\rangle$.

(2) For radiation absorption and transition, we care about the periodic perturbation (i.e., sinusoidal perturbation like EM waves):

$$\hat{H}' = \hat{F} \cos \omega t = \frac{\hat{F}}{2} (e^{i\omega t} + e^{-i\omega t}) \qquad (66)$$

where W is a time-independent operator, and ω is a constant angular frequency of the EM wave. Substitute Eq. (66) into Eq. (62):

$$C_f(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi} t'} H'_{fi}(t') \, dt'$$

$$= \frac{F_{fi}}{2i\hbar} \int_0^t e^{i\omega_{fi} t'} \left(e^{i\omega t'} + e^{-i\omega t'} \right) dt' \qquad (67)$$

$$= \frac{F_{fi}}{2i\hbar} \int_0^t \left[e^{i(\omega_{fi} + \omega) t'} + e^{i(\omega_{fi} - \omega) t'} \right] dt'$$

$$= -\frac{F_{fi}}{2\hbar} \left[\frac{e^{i(\omega_{fi} + \omega) t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi} - \omega) t} - 1}{\omega_{fi} - \omega} \right]$$

Therefore, under the sinusoidal perturbation, the transition probability is given by

$$P_{if}(t) = |C_f(t)|^2 = \frac{|F_{fi}|^2}{4\hbar^2} \left| \frac{e^{i(\omega_{fi} + \omega) t} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi} - \omega) t} - 1}{\omega_{fi} - \omega} \right|^2 \qquad (68)$$

$$\boxed{F_{fi} = \langle \varphi_f | \hat{F} | \varphi_i \rangle}$$

Eq. (68) reveals the resonance nature of the transition probability:

Case 1: When $\omega \approx \omega_{fi}$, the 2nd term on the right side of Eq. (68) is much larger than the first term:

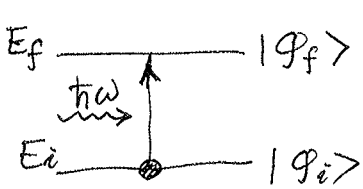
$$A_- = \frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega} = i e^{i(\omega_{fi}-\omega)t/2} \frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2} \quad (69)$$

Case 2: When $\omega \approx -\omega_{fi}$, the first term becomes dominant

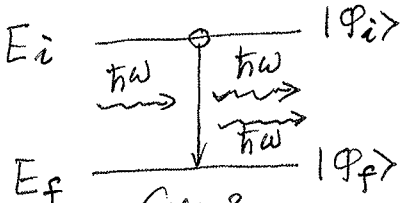
$$A_+ = \frac{e^{i(\omega_{fi}+\omega)t}-1}{2} = i e^{i(\omega_{fi}+\omega)t/2} \frac{\sin[(\omega_{fi}+\omega)t/2]}{(\omega_{fi}+\omega)/2} \quad (70).$$

Let us choose $\omega \geq 0$ all the time, then

Case 1, $\omega_{fi} \approx \omega > 0$, means $E_f > E_i$, i.e., the atom absorbs a photon and makes a transition from the lower level $|\varphi_i\rangle$ to the higher level $|\varphi_f\rangle$



Case 1



Case 2

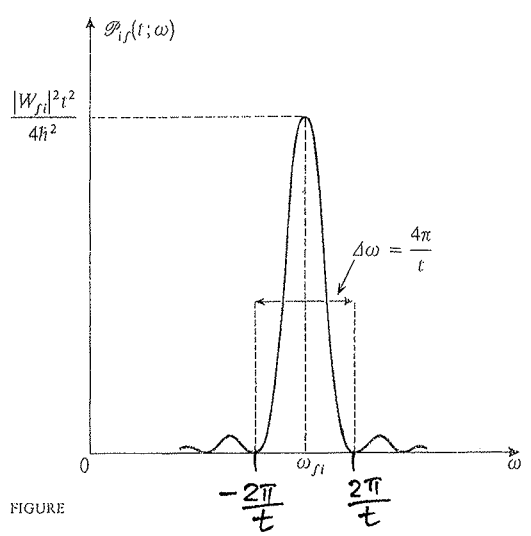
Case 2, $\omega_{fi} \approx -\omega < 0$, means $E_f < E_i$, i.e., the atom goes from the higher level $|\varphi_i\rangle$ to the lower level $|\varphi_f\rangle$ by stimulatedly emitting a photon.

When ω is far away from $\pm\omega_{fi}$, the transition probability is very small. Thus, the transitions we care about are a resonance phenomenon.

Therefore, when $\omega \approx \omega_{fi}$, we only take A_- term, and when $\omega \approx -\omega_{fi}$, we only take A_+ term. Thus, the transition probability is given by

$$P_{if}(t) = \frac{|F_{fi}|^2}{4\hbar^2} \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2}, \qquad (71)$$

where "+" for $\omega \approx -\omega_{fi}$ (emission) and "−" for $\omega \approx \omega_{fi}$ (absorption).



FIGURE

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.

An example for $\omega \approx \omega_{fi}$ (absorption) case is shown in above figure for fixed time t. This clearly shows the resonant nature of the transition probability: The probability reaches the maximum when $\omega = \omega_{fi}$. As we move away from ω_{fi}, the transition probability decreases, going to zero for $|\omega - \omega_{fi}| = 2\pi/t$. When $|\omega - \omega_{fi}|$ continues to increase, the probability oscillates between a much smaller value $\frac{|W_{fi}|^2}{\hbar^2(\omega-\omega_{fi})^2}$ and zero.

(3) The resonance width $\Delta\omega$ can be approximately defined as the distance between the two zeros of $P_{if}(t)$ about $\omega = \omega_{fi}$.

$$\Delta\omega \approx \frac{4\pi}{t} \qquad (72)$$

$\Rightarrow$ The larger the time t, the smaller this width.

Eq. (72) presents a certain analogy with the time-energy uncertainty relation. 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 of the order of

$$\Delta E = \hbar\Delta\omega \approx \frac{\hbar}{t} 4\pi .$$

$\therefore \Delta E \cdot t > \hbar$. This recalls the time-energy uncertainty relation: $\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$.

Note: here, the t is the time of measurements. Since the measurement time t is not infinite, it will cause uncertainty of the energy level E_f. When no perturbation presents, due to the spontaneous emission A_{21}, the lifetime — the time interval of the free evolution of the atom — i finite, the energy level E_f (higher than ground state) has uncertainty: $\Delta E_f \cdot \tau \geq \frac{\hbar}{2}$. (73)

Thus, the spontaneously emitted spectral lines have certain width for resonance $\Delta\omega = \frac{\Delta E_f}{\hbar} \geq \frac{1}{2\tau}$, which also results in the natural linewidth for absorption.

Note: Above approximation is valid under the condition:

$$\Delta\omega = |\omega - \omega_{fi}| \ll 2\omega_{fi}$$

Thus, $\Delta t = t \gg \frac{1}{\omega_{fi}} \simeq \frac{1}{\omega}$ is required condition.

(4) When t is large enough ($t \to \infty$), Eq.(71) takes the limit of

$$\lim_{t\to\infty} \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = \pi t\, \delta[(\omega_{fi} \pm \omega)/2] \qquad (74)$$

Recall $\delta(ax) = \frac{1}{a}\delta(x)$, (75)

then Eq.(74) becomes: $\lim_{t\to\infty} \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = 2\pi t\, \delta(\omega_{fi} \pm \omega)$ (76)

From Eq.(71),

$$\therefore\ P_{if}(t) = \frac{\pi t}{2\hbar^2} |F_{fi}|^2 \delta(\omega_{fi} \pm \omega) \qquad (77)$$

The transition rate:

$$W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{\pi}{2\hbar^2} |F_{fi}|^2 \delta(\omega_{fi} \pm \omega)$$

$$= \frac{\pi}{2\hbar} |F_{fi}|^2 \delta(E_f - E_i \pm \hbar\omega) \qquad (78)$$

Note: $\delta(ax) = \frac{1}{a}\delta(x)$, $\therefore\ \delta\left(\frac{E_f - E_i}{\hbar} \pm \omega\right) = \hbar\, \delta(E_f - E_i \pm \hbar\omega)$

This further exhibits the resonance feature of radiation absorption and emission.

(5) Limits of the first-order calculation:

The first-order approximation can cease to be valid when the time becomes too large. This can be seen from two examples:

① From Eq.(71), at resonance $\omega = \pm\omega_{fi}$, the transition probability

$$P_{if}(t) = \frac{|F_{fi}|^2}{4\hbar^2} t^2 \qquad (79)$$

Note: $\frac{\sin^2 x}{x^2} = 1$ when $x = 0$, $\therefore\ \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = t^2$ @ $\omega = \pm\omega_{fi}$

② From Eq. (77), at resonance $\omega = \pm\omega_{fi}$,

$$P_{if}(t) = \frac{\pi t}{2\hbar^2}|F_{fi}|^2 \qquad (80)$$

Both Eq. (79) and Eq. (80) become infinite when $t \to \infty$, 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 Eqs. (79) or (80) must be much smaller than 1, i.e.,

$$t \ll \frac{\hbar}{|F_{fi}|} \qquad (81)$$

Indeed, for this theory to be meaningful, it is necessary to have another condition to be matched:

$$t \gg \frac{1}{|\omega_{fi}|} \qquad (82)$$

Thus, for the 1st-order approximation to be valid, the conditions below must be matched:

$$\frac{1}{|\omega_{fi}|} \ll t \ll \frac{\hbar}{|F_{fi}|} \qquad (83).$$

i.e., $$\frac{1}{\hbar|\omega_{fi}|} = \frac{1}{|E_f - E_i|} \ll \frac{1}{|F_{fi}|} \qquad (84)$$

The energy difference $|E_f - E_i| = \hbar|\omega_{fi}|$ must be much larger than the matrix element $|F_{fi}|$.

To show precisely why the inequality Eq. (81) and Eq. (82) is related to the validity of the first-order approximation, it would be necessary to calculate the higher-order correction and to examine under what conditions they are negligible. It turns the inequality Eq. (81) is a necessary condition, but not rigorously sufficient.

The problem of calculating the transition probability when t does not satisfy Eq. (81) can be found in the complement C_{XIII} in the book "Quantum Mechanics" Volume Two by Claude Cohen-Tannoudji (Nobel Laureat), in which an approximation of a different method is used — the secular approximation. Of course, higher-order perturbation theory can also be used.

(6) Non-monochromatic Radiation Field Excitation:

Above we only consider monochromatic waves. When the radiation has certain linewidth (bandwidth), i.e., not a single sinusoidal wave anymore, we can take Fourier transform on the radiation field:

$$\hat{H}'(t) = \int_{-\infty}^{+\infty} \hat{H}'(\omega)\, e^{-i\omega t}\, d\omega, \qquad (85)$$

where $\hat{H}'(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \hat{H}'(t)\, e^{i\omega t}\, dt.$

is the amplitude of monochromatic wave with angular frequency ω in the Fourier transform of $\hat{H}'(t)$.

Thus, the matrix element $\hat{H}'_{fi}(t) \equiv \langle \varphi_f | \hat{H}'(t) | \varphi_i \rangle$ is given by

$$H'_{fi}(t) = \int_{-\infty}^{+\infty} H'_{fi}(\omega)\, e^{-i\omega t}\, d\omega. \qquad (86)$$

$$\therefore C_f(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'}\cdot H'_{fi}(t')\,dt'$$

$$= \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'}dt' \int_{-\infty}^{+\infty} H'_{fi}(\omega)e^{-i\omega t}\,d\omega$$

$$= \frac{1}{i\hbar}\int_{-\infty}^{+\infty} d\omega\, H'_{fi}(\omega)\, 2\pi\,\delta(\omega_{fi}-\omega)$$

$$= \frac{2\pi}{i\hbar} H'_{fi}(\omega_{fi}) \qquad (87)$$

$$\therefore P_{if}(t) = |C_f(t)|^2 = \frac{4\pi^2}{\hbar^2}\left|H'_{fi}(\omega_{fi})\right|^2 \qquad (88)$$

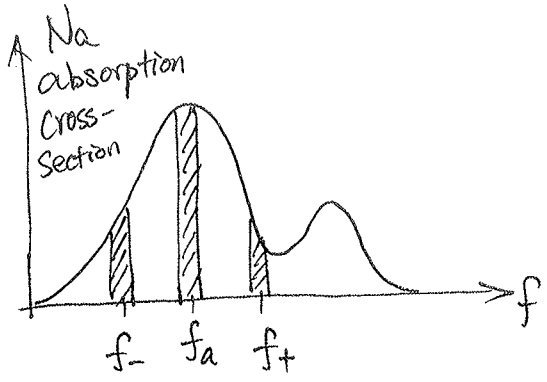
Therefore, the transition probability is proportional to the matrix element $|H'_{fi}(\omega_{fi})|^2$, $\hat{H}'_{fi}(t)$'s component at angular frequency ω_{fi}. This makes lots of sense, because for a broad-band excitation, the useful energy is only the energy at the frequency of Bohr frequency ω_{fi}. Energy at other frequencies is useless.

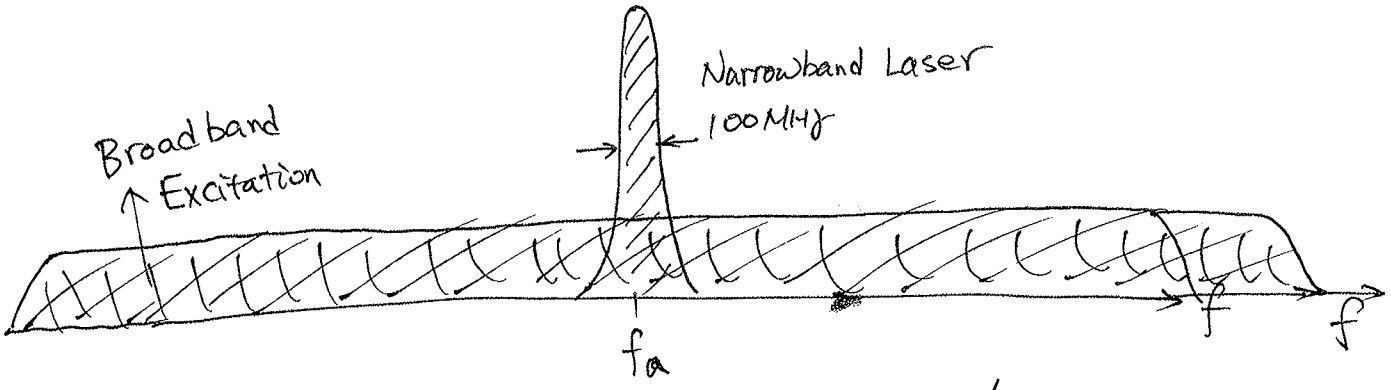
Example: in Na lidar application, we want ~100MHz narrow-band laser light @ 3 frequencies. The available power is ~ 1.5 W. Now somebody can produce 10W power @ 589nm but with 5 GHz linewidth. The useful power is

about $\frac{100\,MHz}{5\,GHz} \times 10W = \frac{1}{50}\times 10W = 0.2W$

For 100 MHz laser @ 3-freq, useful power $\frac{1.5W}{3} = 0.5W$.

—The narrowband is better!!!





Why do we want to waste energy/power at the frequencies where we can't have resonance?

— Narrowband Laser is better!!!