§6.3. Transition Probabilities : Statement of the Problem

Above we introduce the Einstein A and B coefficients phenomenologically to describe the absorption and emission phenomena. However, to quantitatively describe the transition phenomena, we must understand this transition concept from QM frame-work. What is transition probability in QM ?

(1) Transition is a change of state of an atom with time, i.e., the atom (regarded as a QM system) changes its state from one eigenstate to another.
— The eigenstates and eigenvalues of Hamiltonian operator are solved by solving the energy eigenvalue equation, i.e., the time-independent Schrödinger equation.
— The evolution of state with time is described by the time-dependent Schrödinger equation. Therefore, the transition problem should be solved in the frame work of QM Schrödinger equation.

(2) Without radiation field, the atom is usually in one of its energy eigenstates. Transition involves changing the atomic state from one eigenstate to another — essentially the atomic state becomes a superposition of eigenstates. Thus, the atom has certain probability to be in another eigenstate.

Let us keep the above two points in mind and solve the time-dependent Schrödinger equation to derive transition probability.

Consider a physical system with Hamiltonian $\hat{H}_0$. The eigenvalues and eigenstates of $\hat{H}_0$ are denoted by E_n and $|\varphi_n\rangle$:

$$\hat{H}_0 |\varphi_n\rangle = E_n |\varphi_n\rangle \qquad (1)$$

Assume that $\hat{H}_0$ is <u>not</u> explicitly time-dependent. Thus, its eigenstates are stationary states given by

$$|\Phi_n(t)\rangle = |\varphi_n\rangle e^{-iE_n t/\hbar} \qquad (2)$$

which satisfies the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\Phi_n(t)\rangle = \hat{H}_0 |\Phi_n(t)\rangle. \qquad (3)$$

The solution of stationary states is obtained as the following:

Since $\hat{H}_0$ is not explicitly dependent on time, we can use separation of variables and write $|\Phi_n(t)\rangle = T(t)|\varphi_n\rangle$, where $T(t)$ is a time factor and $|\varphi_n\rangle$ does not depend on t.

Substitute $|\Phi_n(t)\rangle = T(t)|\varphi_n\rangle$ into the Schrödinger equation:

$$i\hbar \frac{dT(t)}{dt} |\varphi_n\rangle = T(t)\hat{H}_0 |\varphi_n\rangle = T(t) E_n |\varphi_n\rangle$$

$$\Rightarrow i\hbar \frac{dT(t)}{dt} = T(t) E_n$$

$$\Rightarrow T(t) = T_0 e^{-iE_n t/\hbar}$$

$$\therefore |\Phi_n(t)\rangle = T_0 |\varphi_n\rangle e^{-iE_n t/\hbar}$$

Since at $t=0$, $|\Phi(t=0)\rangle = |\varphi_n\rangle$, $\Rightarrow T_0 = 1$

$$\therefore |\Phi_n(t)\rangle = |\varphi_n\rangle e^{-iE_n t/\hbar}$$

At $t=0$, a perturbation is applied to the system. The Hamiltonian operator of the system then becomes:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t) \qquad (4)$$

Before the perturbation is added, the system is assumed to be initially in the stationary state $|\Phi_i\rangle$, an eigenstate of $\hat{H}_0$ with eigenvalue E_i. Starting at $t=0$ when the perturbation is applied, the system evolves:

① The state $|\Phi_i\rangle$ is no longer (in general) an eigenstate of the perturbed Hamiltonian $\hat{H}(t)$.

② The state evolves to be the superposition of several eigenstates of $\hat{H}_0$. So there will be probability $P_{if}(t)$ of finding the system in another eigenstate $|\Phi_f\rangle$ of $\hat{H}_0$ at time t.

In other words, the perturbation causes the system to make transitions between the stationary states of the unperturbed system:

$$|\Phi_i\rangle \longrightarrow |\Phi_f\rangle.$$

The evolution of state $|\psi(t)\rangle$ with time is determined by the Schrödinger equation: $i\hbar \frac{d|\psi(t)\rangle}{dt} = \hat{H}(t)|\psi(t)\rangle \qquad (5)$.

Since the stationary states of $\hat{H}_0$ form an orthonormal, complete basis, the state $|\psi(t)\rangle$ can be expanded on this basis:

$$|\psi(t)\rangle = \sum_n C_n(t)|\Phi_n(t)\rangle. \qquad (6)$$

The initial condition of $|\psi(t)\rangle$ is

$$|\psi(t=0)\rangle = |\Phi_i\rangle. \qquad (7)$$

Since $|\psi(t)\rangle$ is a superposition of the stationary states of $\hat{H}_0$, there will be probability to find the system in another stationary state $|\Phi_f\rangle$ which is different from the initial state $|\Phi_i\rangle$.

According to QM, this probability is given by:

$$P_{if}(t) = |\langle \Phi_f | \psi(t) \rangle|^2 = |C_f(t)|^2 \quad (8)$$

$P_{if}(t)$ means the probability of finding the system in the state $|\Phi_f\rangle$ at time t when evolving from the initial state $|\Phi_i\rangle$. Thus, $P_{if}(t)$ is the transition probability of the system from the initial state $|\Phi_i\rangle$ to the final state $|\Phi_f\rangle$ at time t and under Hamiltonian operator $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$.

Therefore, the problem becomes how to solve the Schrödinger equation (5) to derive the coefficient $C_f(t)$. Substitute Eqs. (4) and (6) into Eq. (5):

$$i\hbar \sum_n \left(|\Phi_n(t)\rangle \frac{dC_n(t)}{dt} \right) + i\hbar \sum_n \left(C_n(t) \frac{\partial}{\partial t} |\Phi_n(t)\rangle \right) \quad (9)$$
$$= \sum_n \left(C_n(t) \hat{H}_0 |\Phi_n(t)\rangle \right) + \sum_n \left(C_n(t) \hat{H}'(t) |\Phi_n(t)\rangle \right)$$

Recall Eq. (3): $i\hbar \frac{\partial}{\partial t} |\Phi_n(t)\rangle = \hat{H}_0 |\Phi_n(t)\rangle$, we can cancel the 2nd term on the left with the 1st term on the right of Eq. (9). Thus, we obtain:

$$i\hbar \sum_n \left(|\Phi_n(t)\rangle \frac{dC_n(t)}{dt} \right) = \sum_n \left(C_n(t) \hat{H}'(t) |\Phi_n(t)\rangle \right) \quad (10)$$

Use $\langle \Phi_f(t)| = |\Phi_f(t)\rangle^* = e^{iE_f t/\hbar} \langle \phi_f|$ to time both sides of Eq. (10), we obtain:

$$i\hbar \sum_n \left(\langle \Phi_f | \Phi_n \rangle \frac{d C_n(t)}{dt} \right) = \sum_n \left(C_n(t) \langle \Phi_f | \hat{H}' | \Phi_n(t) \rangle \right) \quad (11)$$

Recall $\langle \Phi_m | \Phi_n \rangle = e^{i(E_m - E_n)t/\hbar} \langle \varphi_m | \varphi_n \rangle = e^{i(E_m - E_n)t/\hbar} \delta_{mn} = \delta_{mn}$ (12)

∴ Eq. (11) becomes:

$$i\hbar \frac{d C_f(t)}{dt} = \sum_n \left(C_n(t) e^{i(E_f - E_n)t/\hbar} \langle \varphi_f | \hat{H}' | \varphi_n \rangle \right)$$

$$= \sum_n \left(C_n(t) e^{i\omega_{fn} t} H'_{fn} \right) \quad (13)$$

where $\omega_{fn} \equiv (E_f - E_n)/\hbar$ (14)

$$H'_{fn} \equiv \langle \varphi_f | \hat{H}' | \varphi_n \rangle \quad (15)$$

Note that from Schrödinger equation (5) to Eq. (13), it is an exact derivation. So Eq. (13) is equivalent to Eq. (5). In other words, Eq. (13) is another form of Schrödinger Equation. To derive the transition probability $P_{if}(t) = |C_f(t)|^2$, we need to solve Eq. (13) to obtain $C_f(t)$.

It is usually difficult to solve Eq. (13) exactly, except a few occasions. ① In our class, we will introduce the exact solution for a special case — a two-level system that we will obtain the Rabi oscillation and Rabi frequency. ② Then we will introduce the time-dependent perturbation theory to solve the equation with approximations for general cases. ③ Armed with these knowledges, we will then go to the full Quantum Treatment of the Radiative Transitions.

§6.4. Semi-Classical Description of Transition Probabilities for 2-level System

① Semiclassical Description:

$\hat{H}_0 = \hat{H}_a$ (the atom is described by QM)

$\vec{E} = \vec{E}_0 \cos(\omega t - kz)$ (the radiation is described by a classical EM wave)

$\hat{H}' = \hat{\vec{p}} \cdot \vec{E} = \hat{\vec{p}} \cdot \vec{E}_0 \cos\omega t$ (the interaction between the atom and the radiation field is the dipole approximation $\hat{\vec{p}} = -e\hat{\vec{r}}$)

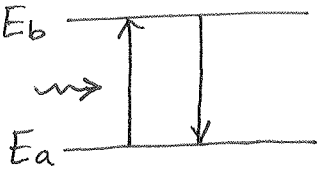
Thus, $\hat{H} = \hat{H}_0 + \hat{H}'$ as the total Hamiltonian operator.

Phenomenologically introduce A_{ki} for the spontaneous emission.

By solving the Schrödinger equation $i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H}(t)|\psi(t)\rangle$ as described above, we can derive Einstein B coefficients B_{12} and B_{21}. But the spontaneous emission A_{21} is added phenomenologically. Only QED, i.e, the Quantization of the radiation field can naturally include the spontaneous emission.

② Weak-Field Approximation for 2-Level System.

Let us consider a 2-level atomic system, with $\hat{H}_0$ eigenstates $|\varphi_a\rangle$ and $|\varphi_b\rangle$ and eigenvalues of energy E_a and E_b. The system state $|\psi(t)\rangle$ can be expressed as the superposition of these two states.



$$|\psi(t)\rangle = a(t)|\varphi_a\rangle e^{-iE_at/\hbar} + b(t)|\varphi_b\rangle e^{-iE_bt/\hbar} \qquad (16)$$

Going through the same process as we did in Section 6.3, we will come to Eq. (13). Thus, for the 2-level system,

the Schrödinger equation Eq.(13) gives us the following equations:

$$\begin{cases} i\hbar \dfrac{da(t)}{dt} = a(t)\, e^{i\omega_{aa}t} \langle \varphi_a | \hat{H}' | \varphi_a \rangle + b(t) e^{i\omega_{ab}t} \langle \varphi_a | \hat{H}' | \varphi_b \rangle \\ i\hbar \dfrac{db(t)}{dt} = a(t) e^{i\omega_{ba}t} \langle \varphi_b | \hat{H}' | \varphi_a \rangle + b(t) e^{i\omega_{bb}t} \langle \varphi_b | \hat{H}' | \varphi_b \rangle \end{cases}$$

Since $\omega_{aa} = (E_a - E_a)/\hbar = 0$, $\omega_{ab} = (E_a - E_b)/\hbar$,

$$\therefore \begin{cases} \dot{a}(t) = -\dfrac{i}{\hbar}\left[a(t)\, H'_{aa} + b(t)\, H'_{ab}\, e^{i(E_a - E_b)t/\hbar} \right] \\ \dot{b}(t) = -\dfrac{i}{\hbar}\left[a(t)\, H'_{ba}\, e^{i(E_b - E_a)t/\hbar} + b(t)\, H'_{bb} \right] \end{cases} \qquad (17)$$

$\because \hat{H}' = \hat{\vec{P}} \cdot \vec{E} = -e\hat{\vec{r}} \cdot \vec{E} = \hat{H}(\hat{\vec{r}})$

$\therefore \langle \varphi_a | \hat{H}' | \varphi_b \rangle = -eE \langle \varphi_a | \hat{\vec{r}} | \varphi_b \rangle$, $\langle \varphi_a | \hat{H}' | \varphi_a \rangle = H'_{aa}$

Since $\hat{\vec{r}}$ has odd parity, $\langle \varphi_a | \hat{\vec{r}} | \varphi_a \rangle = \langle \varphi_b | \hat{\vec{r}} | \varphi_b \rangle = 0$

We define the atomic dipole matrix element:

$$D_{ab} \equiv D_{ba} \equiv -e \langle \varphi_a | \hat{\vec{r}} | \varphi_b \rangle \qquad (18)$$

$$\Omega_{ab} = D_{ab} E_0/\hbar = \Omega_{ba} \text{ is called the Rabi frequency.} \qquad (18b)$$

$$\therefore \begin{cases} \dot{a}(t) = -\dfrac{i}{\hbar} b(t) \cdot E_0 \dfrac{e^{i\omega t} + e^{-i\omega t}}{2} D_{ab}\, e^{i\omega_{ab}t/\hbar} \\ \quad = -\dfrac{i}{2} \Omega_{ab} \cdot b(t) \left[e^{i(\omega_{ab} - \omega)t} + e^{i(\omega_{ab} + \omega)t} \right] \\ \dot{b}(t) = -\dfrac{i}{2} \Omega_{ab} \cdot a(t) \left[e^{-i(\omega_{ab} - \omega)t} + e^{-i(\omega_{ab} + \omega)t} \right] \end{cases} \qquad (19)$$

If decay into other levels is neglected, then the relation

$$|a(t)|^2 + |b(t)|^2 = 1 \qquad (20)$$

must hold at all times t.

Suppose at $t=0$, the atoms are in the lower state E_a,

$$\therefore\ a(0)=1,\quad b(0)=0 \qquad \text{— initial conditions} \qquad (21)$$

Assume the radiation field E_0 is sufficiently small so that for times $t<T=\frac{1}{\Omega_{ab}}$, the population of E_b remains small compared with that of E_a, i.e., $|b(t<T)|^2 \ll 1$. — weak-field approximation (22)

Under this weak-field condition, we can solve Eq.(19) by an iterative procedure starting with $a^{(0)}(t)=1$, $b^{(0)}(t)=0$. This iterative procedure is to put lower order $a^{(n-1)}(t)$ and $b^{(n-1)}(t)$ into the Eq.(19) for the higher order $\dot{a}^{(n)}(t)$ and $\dot{b}^{n}(t)$. In the 1st order appr.

$$\begin{cases} \dot{a}^{(1)}(t) = -\frac{i}{2}\Omega_{ab}\, b^{(0)}(t)\left[e^{i(\omega_{ab}-\omega)t} + e^{i(\omega_{ab}+\omega)t}\right] = 0 \\ \dot{b}^{(1)}(t) = -\frac{i}{2}\Omega_{ab}\, a^{(0)}(t)\left[e^{-i(\omega_{ab}-\omega)t} + e^{-i(\omega_{ab}+\omega)t}\right] \\ \qquad\quad = \frac{i}{2}\Omega_{ab}\left[e^{i(\omega_{ba}-\omega)t} + e^{i(\omega_{ba}+\omega)t}\right] \end{cases} \qquad (23)$$

From initial condition, we obtain the solution to the 1st order approximation:

$$\begin{cases} a(t) = a^{(0)}(t) + a^{(1)}(t) = a^{(0)}(t) = 1 \\ b(t) = b^{(0)}(t) + b^{(1)}(t) = \frac{\Omega_{ab}}{2}\left[\frac{e^{i(\omega_{ba}-\omega)t}}{\omega_{ba}-\omega} + \frac{e^{i(\omega_{ba}+\omega)t}}{\omega_{ba}+\omega}\right] \end{cases} \qquad (24)$$

For the 1st term, noticeable absorption occurs only if ω is close to ω_{ba}, i.e., in the optical frequency range: $|\omega_{ba}-\omega| \ll \omega_{ba}$. The 2nd term $(\omega_{ba}+\omega)$, is small compared to the 1st term, and may be neglected. — Rotating-wave approximation.

In the rotating-wave approximation, the probability $|b(t)|^2$ that finding the system is in the upper level E_b at time t is

$$|b(t)|^2 = \left(\frac{\Omega_{ab}}{2}\right)^2\left[\frac{\sin(\omega_{ba}-\omega)t/2}{(\omega_{ba}-\omega)/2}\right]^2. \qquad (25)$$

Since the initial condition is that all atoms are in the lower level E_a, $|b(t)|^2$ gives the transition probability for the atom to go from E_a to E_b during the time t: $P_{ab}(t) = |b(t)|^2$.

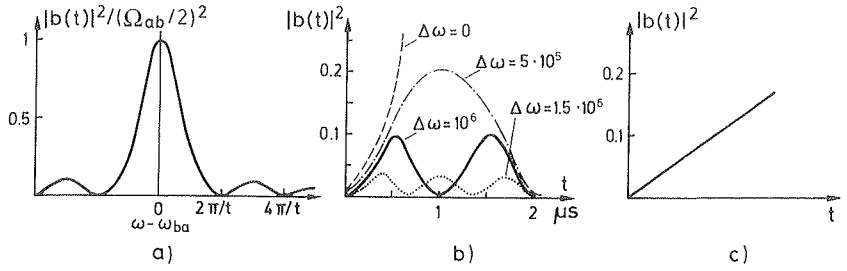


Fig. 2.18. (**a**) Normalized transition probability as a function of the detuning $(\omega-\omega_{ba})$ in the rotating-wave approximation; (**b**) probability of a transition to the upper level as a function of time for different detuning; (**c**) $|b(t)|^2$ under broadband excitation and weak fields

Since $\lim_{x\to 0}\frac{(\sin xt)^2}{x^2}=t^2$, the transition probability at resonance $(\omega\to\omega_{ba})$ is given by $$|b(t)|^2_{\omega=\omega_{ba}}=\left(\frac{\Omega_{ab}}{2}\right)^2 t^2, \qquad (26)$$

which increases proportionally with t^2. Note that the conclusion from above derivation is only valid under the following conditions:

$$|b(t)|^2 \ll 1, \quad \text{i.e., } \Omega_{ab}^2 t^2 \ll 1 \text{ or } t \ll T=\frac{\hbar}{D_{ab}E_0}=\frac{1}{\Omega_{ab}}. \qquad (27)$$

This small-signal approximation only holds if the maximum interaction time T of the field with the atom is restricted to $t \ll T$.

Recall Heisenbergy uncertainty principle, the spectral analysis of a wave with the finite detection time T gives the spectral width $\Delta\omega \approx \frac{1}{T}$. Thus, we cannot assume monochromaticity, but have to take into account the frequency distribution of the interaction term.

③. Transition Probabilities with Broad-Band Excitation.

Let us consider a radiation source with broad bandwidth. Instead of using a single frequence $\vec{E}=\vec{E}_0\cos\omega t$, we introduce the spectral energy density $\rho(\omega)$ within the frequency range of the absorption line for the radiation field. We can generalize Eq. (25) to include the interaction of broadband radiation with our two-level system by integrating Eq. (25) over all frequencies ω of the radiation field. This yields the total transition probability $P_{ab}(t)$