Time Dependent Perturbation Theory

Adaptation and Solved Examples from
Chapter 7 of Quantum Mechanics for Scientists and Engineers by David A. B. Miller

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Dec 27, 2025

Table of Contents

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Consider the general hamiltonian as a sum of the time-independent hamiltonian and a time-dependent term.

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_o + \hat{\mathcal{H}}_{int}(t). \quad (1)$$

We have the following.

$$\hat{\mathcal{H}}_o |\psi_n\rangle = \hbar\omega_n |\psi_n\rangle. \quad (2)$$

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{\mathcal{H}}|\psi\rangle. \quad (3)$$

Let us express the wavefunction in Eq. (3) as a linear sum in the orthonormal basis $|\psi_n\rangle$ as follows.

$$|\psi\rangle = \sum_n a_n(t)e^{-i\omega_n t}|\psi_n\rangle. \quad (4)$$

From Eq. (1 - 4),

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{\mathcal{H}}_o|\psi\rangle + \hat{\mathcal{H}}_{int}(t)|\psi\rangle,$$

$$i\hbar\frac{\partial}{\partial t}\sum_n a_n(t)e^{-i\omega_n t}|\psi_n\rangle = \hat{\mathcal{H}}_o\sum_n a_n(t)e^{-i\omega_n t}|\psi_n\rangle + \hat{\mathcal{H}}_{int}(t)\sum_n a_n(t)e^{-i\omega_n t}|\psi_n\rangle,$$

$$i\hbar\sum_n \dot{a}_n(t)e^{-i\omega_n t}|\psi_n\rangle + \hbar\omega_n\sum_n a_n(t)e^{-i\omega_n t}|\psi_n\rangle = \sum_n a_n(t)e^{-i\omega_n t}\hat{\mathcal{H}}_o|\psi_n\rangle + \sum_n a_n(t)e^{-i\omega_n t}\hat{\mathcal{H}}_{int}(t)|\psi_n\rangle,$$

$$i\hbar\sum_n \dot{a}_n(t)e^{-i\omega_n t}|\psi_n\rangle = \sum_n a_n(t)e^{-i\omega_n t}\hat{\mathcal{H}}_{int}(t)|\psi_n\rangle.$$

Changing the indices from n to k,

$$i\hbar \sum_k \dot{a}_k(t) e^{-i\omega_k t} |\psi_k\rangle = \sum_k a_k(t) e^{-i\omega_k t} \hat{\mathcal{H}}_{int}(t) |\psi_k\rangle.$$

Multiplying by $\langle \psi_n |$ and using orthonormality of the basis.

$$i\hbar \dot{a}_n(t) e^{-i\omega_n t} = \sum_k a_k(t) e^{-i\omega_k t} \langle \psi_n | \hat{\mathcal{H}}_{int}(t) | \psi_k \rangle. \quad (5)$$

We define the following for convenience..

$$\omega_{nk} \equiv \omega_n - \omega_k. \quad\quad\quad (6)$$

$$H_{nk}(t) = \langle \psi_n | \hat{\mathcal{H}}_{int}(t) | \psi_k \rangle. \quad\quad (7)$$

The Eq. (5) becomes.

$$\dot{a}_n(t) = \frac{1}{i\hbar} \sum_k a_k(t) e^{i\omega_{nk} t} H_{nk}(t). \quad\quad (9)$$

If we replace the interaction hamiltonian $\hat{\mathcal{H}}_{int}(t)$ by $\gamma \hat{\mathcal{H}}_{int}(t)$ then let the corresponding n^{th} coefficient be given as follows. We will use γ for mathematical housekeeping (terms of order γ^k matching). Finally we will replace γ by 1.

$$a_n = a_n^{(0)} + \gamma a_n^{(1)} + \gamma^2 a_n^{(2)} + ... \quad\quad (10)$$

Substituting (10) in (9)

$$\dot{a}_n^{(0)} + \gamma \dot{a}_n^{(1)} + \gamma^2 \dot{a}_n^{(2)} + ... = \frac{1}{i\hbar} \sum_k \left(a_k^{(0)} + \gamma a_k^{(1)} + \gamma^2 a_k^{(2)} + ... \right) e^{i\omega_{nk} t} \gamma H_{nk},$$

$$\dot{a}_n^{(0)} + \gamma \dot{a}_n^{(1)} + \gamma^2 \dot{a}_n^{(2)} + ... = \gamma \frac{1}{i\hbar} \sum_k \left(a_k^{(0)} e^{i\omega_{nk} t} H_{nk} \right) + \gamma^2 \frac{1}{i\hbar} \sum_k \left(a_k^{(1)} e^{i\omega_{nk} t} H_{nk} \right) + ...$$

Comparing the terms of same powers of γ:

$$\dot{a}_n^{(0)} = 0. \quad\quad (11)$$

$$\dot{a}_n^{(1)} = \frac{1}{i\hbar} \sum_k \left(a_k^{(0)} e^{i\omega_{nk} t} H_{nk} \right).$$

$$\dot{a}_n^{(m+1)} = \frac{1}{i\hbar} \sum_k \left(a_k^{(m)} e^{i\omega_{nk} t} H_{nk} \right). \quad\quad (12)$$

We will take,

$$a_n^{(0)}(t) = a_n(0),$$

$$a_n^{(k)}(0) = 0, \; for \; k > 0. \quad\quad (13)$$

From Eq. (10), to first order,

$$a_n(t) \approx a_n(0) + a_n^{(1)}(t). \quad\quad (14)$$

Dipole Perturbation Starting with Ground State

Consider following assumptions:

1. We have a one dimensional potential well for the time-independent hamiltonian. The corresponding eigenfunctions have a definite parity, even or odd around $z = z_0$. This means that the following vanishes whenever $|\psi_n\rangle$ and $|\psi_k\rangle$ share the same parity.

$$\langle \psi_n | (z - z_0) | \psi_k \rangle$$

2. The interaction hamiltonian is a direct coupling (length gauge) for electron. This is because of a spatially uniform but possibly time-varying electric field along the z direction.

$$\hat{\mathcal{H}}_{int}(t) = -q\vec{E}.\hat{d} = eE(t)z. \qquad (15)$$

This implies the following.

$$H_{nk}(t) = \langle \psi_n | \hat{\mathcal{H}}_{int}(t) | \psi_k \rangle = H_{nk}(t) = eE(t)\langle \psi_n | | (z - z_0) | \psi_k \rangle,$$

$$H_{nk}(t) = eE(t)L_z \int_a^b (\xi - \xi_0) \psi_n^*(\xi) \psi_k(\xi) d\xi. \qquad (16)$$

Here, $\xi = z/L_z$ with L_z being some characteristic length of the potential well. Similarly, we define a dimensionless unit of time using a characteristic frequency Ω of the interaction hamiltonian as follows.

$$t = \eta/\Omega. \qquad (17)$$

Let us define electric field in terms of a dimensionless function $f(t)$ as follows.

$$E(t) = E_0 f(t). \qquad (18)$$

Let us also define the following dimensionless quantities.

$$M_{nk} = \int_a^b (\xi - \xi_0) \psi_n^*(\xi) \psi_k(\xi) d\xi. \qquad (19)$$

$$C_{int} = \frac{eE_0 L_z}{\hbar\Omega}. \qquad (20)$$

Thus we can write Eq. (16) as follows.

$$H_{nk}(t) = C_{int} f(t) M_{nk} \hbar\Omega. \qquad (21)$$

We have separated the dimensionless quantities upfront in Eq. (21). Let us reiterate that due to the first assumption above, $M_{nk} = 0$, whenever n^{th} and k^{th} states share the same parity. In particular, $M_{kk} = 0$ for all k.

3. The system is in the ground state ($n = 1$) at time $t = 0$.
   Thus in this case we have,

$$a_n(0) = [1, 0, 0, 0, ...]. \qquad (22)$$

Using the above three assumptions in Eq. (12),

$$\dot{a}_n^{(1)} = \frac{1}{i\hbar}\sum_k \left(a_k^{(0)} e^{i\omega_{nk}t} H_{nk}(t) \right) = \frac{1}{i\hbar} a_1^{(0)} e^{i\omega_{n1}t} H_{n1}(t) = \frac{1}{i\hbar} e^{i\omega_{n1}t} H_{n1}(t).$$

$$\dot{a}_n^{(1)} =- iC_{int} M_{n1} \Omega f(t) e^{i\omega_{n1}t}.$$

$$a_n^{(1)}(t) =- iC_{int} M_{n1} \Omega \int_0^t f(t) e^{i\omega_{n1}t} dt. \qquad (23)$$

Using Eq. (22 - 23) in Eq. (14), we get the following first order result.

$$a_1(t) \approx 1.$$

$$a_n(t) \approx - iC_{int} M_{n1} \Omega \int_0^t f(t) e^{i\omega_{n1}t} dt. \qquad (24)$$

Correspondingly, the probability of finding the electron in the nth state after time t is given as,

$$P_n(t) \approx C_{int}^2 M_{n1}^2 \left| \Omega \int_0^t f(t') e^{i\omega_{n1}t'} dt' \right|^2 = C_{int}^2 M_{n1}^2 g_n(t). \qquad (25)$$

Problem 7.1.1

Given:

$$\hat{\mathcal{H}}_{int}(t) =- q\vec{E}.\hat{d} = eE_o L_z \sin(\tfrac{m\pi t}{\Delta t})\left(z/L_z - 1/2\right) = C_{int} \hbar\Omega \sin(m\Omega t)(\xi - 1/2).$$

$$\omega_n = \frac{\hbar}{2m_{eff}}\left(\frac{n\pi}{L_z}\right)^2.$$

$$|\psi_n\rangle = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right), \ 0 < z < L_z.$$

$$L_z = 10 \ nm,$$
$$\Delta t = 100 \ fs,$$
$$E_0 = 46.4 \ kV/cm,$$
$$m_{eff} = 0.07 \ m_e.$$

We identify:

$$a = 0.$$
$$b = 1.$$
$$\Omega = \frac{\pi}{\Delta t} = 31.42 \ THz \ rad.$$
$$\omega_{21} = 244.8 \ THz \ rad.$$
$$f(t) = \sin(m\Omega t).$$
$$C_{int} = \frac{eE_0 L_z}{\hbar\Omega} = 2.24.$$

From Eq. (19),

$$M_{nk} = \int_0^1 (\xi - 1/2) \sin(n\pi\xi) \sin(k\pi\xi) d\xi.$$

Here are some values of M_{nk} listed in the matrix format where n and k correspond to the row and column number, respectively.

$$\begin{pmatrix}
0 & -\dfrac{8}{9\,\pi^2} & 0 & -\dfrac{16}{225\,\pi^2} & 0 & -\dfrac{24}{1225\,\pi^2} \\[2ex]
-\dfrac{8}{9\,\pi^2} & 0 & -\dfrac{24}{25\,\pi^2} & 0 & -\dfrac{40}{441\,\pi^2} & 0 \\[2ex]
0 & -\dfrac{24}{25\,\pi^2} & 0 & -\dfrac{48}{49\,\pi^2} & 0 & -\dfrac{8}{81\,\pi^2} \\[2ex]
-\dfrac{16}{225\,\pi^2} & 0 & -\dfrac{48}{49\,\pi^2} & 0 & -\dfrac{80}{81\,\pi^2} & 0 \\[2ex]
0 & -\dfrac{40}{441\,\pi^2} & 0 & -\dfrac{80}{81\,\pi^2} & 0 & -\dfrac{120}{121\,\pi^2} \\[2ex]
-\dfrac{24}{1225\,\pi^2} & 0 & -\dfrac{8}{81\,\pi^2} & 0 & -\dfrac{120}{121\,\pi^2} & 0
\end{pmatrix}$$

From Eq. (25),

$$P_2(t) \approx (2.25)^2 \left(\frac{8}{9\pi^2}\right)^2 \left|\Omega \int\limits_0^t \sin(m\Omega t')e^{i\omega_{n1}t'}\,dt'\right|^2 = 0.041 g_n(t).$$
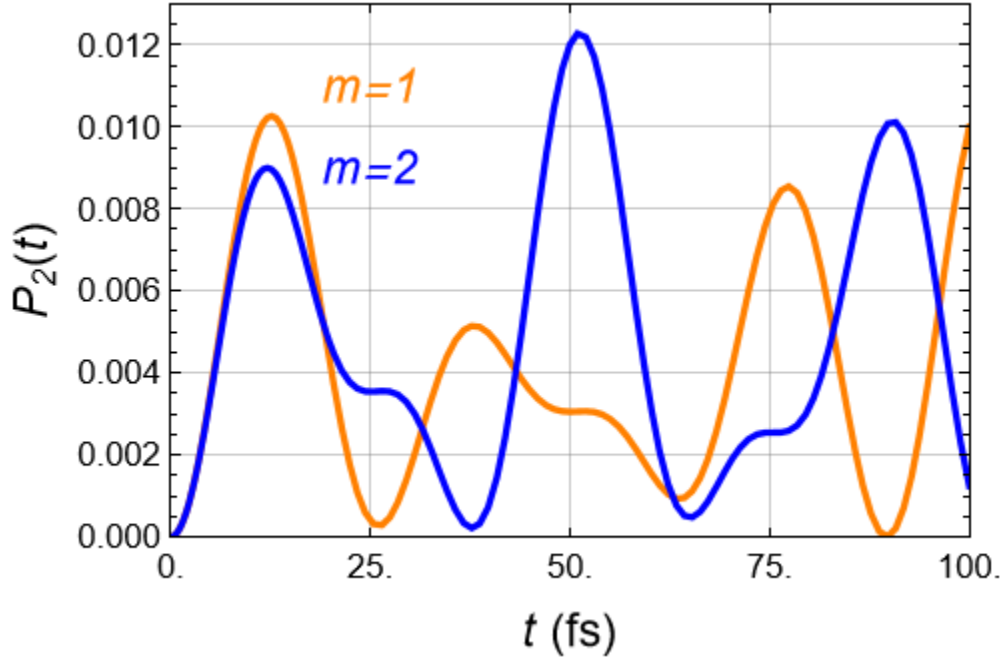
$$g_n(t) = \left|\Omega \int\limits_0^t \sin(m\Omega t')e^{i\omega_{n1}t'}\,dt'\right|^2,$$

$$g_n(t) = \frac{1}{4}\left|\Omega \int\limits_0^t (e^{-im\Omega t'} - e^{im\Omega t'})e^{i\omega_{n1}t'}\,dt'\right|^2,$$

$$g_n(t) = \frac{1}{4}\left|\Omega \int\limits_0^t \left(\left(e^{i\left(\omega_{21}-m\Omega\right)t'} - e^{i\left(\omega_{21}+m\Omega\right)t'}\right)dt'\right|^2,$$

$$g_n(t) = \frac{1}{4}\left|\Omega\left(\frac{e^{i\left(\omega_{21}-m\Omega\right)t}-1}{\left(\omega_{21}-m\Omega\right)} - \frac{e^{i\left(\omega_{21}+m\Omega\right)t}-1}{\left(\omega_{21}+m\Omega\right)}\right)\right|^2.$$

The probability $P_2(t)$ is plotted, for $m = 1$ and $m = 2$, for the time interval 0 to Δt.

Problem 7.1.2

Given:

$$\hat{\mathcal{H}}_{int}(t) = -q\vec{E}\cdot\hat{d} = eE_0L_ze^{-t/\tau}(\xi - 1/2) = C_{int}\hbar\Omega e^{-\Omega t}(\xi - 1/2).$$

$$\omega_n = \frac{\hbar}{2m_{eff}}\left(\frac{n\pi}{L_z}\right)^2.$$

$$|\psi_n\rangle = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right), \quad 0 < z < L_z.$$

$$L_z = 10 \, nm,$$

$$m_{eff} = 0.07 \, m_e.$$

We identify:

$$\Omega = \frac{1}{\tau}.$$

$$\omega_{21} = 244.8 \, THz \, rad.$$

$$f(t) = e^{-\Omega t}.$$

$$C_{int} = \frac{eE_0L_z}{\hbar\Omega}.$$

The matrix elements M_{nk} are the same as before.

From Eq. (25),

$$P_2(t) \approx \left(\frac{eE_0L_z}{\hbar\Omega}\right)^2\left(\frac{8}{9\pi^2}\right)^2\left|\Omega\int_0^t e^{-\Omega t'}e^{i\omega_{n1}t'}dt'\right|^2.$$

Let us substitute,

$$E_{pulse} = AE_0^2\tau.$$

$$P_2(t) \approx \frac{E_{pulse}}{A}\left(\frac{8eL_z}{9\pi^2\hbar}\right)^2 \frac{1}{\tau}\left|\int_0^t e^{-t'/\tau}e^{i\omega_{n1}t'}dt'\right|^2,$$

$$P_2(t) \approx \frac{E_{pulse}}{A}\left(\frac{8eL_z}{9\pi^2\hbar}\right)^2 \frac{1}{\tau}\left|\frac{1}{(i\omega_{n1}-1/\tau)}\left(e^{(i\omega_{n1}-1/\tau)t} - 1\right)\right|^2,$$

$$P_2(t) \approx \frac{E_{pulse}}{A}\left(\frac{8eL_z}{9\pi^2\hbar}\right)^2 \frac{\tau}{1+\omega_{n1}^2\tau^2}\left(e^{(i\omega_{n1}-1/\tau)t} - 1\right)\left(e^{(-i\omega_{n1}-1/\tau)t} - 1\right),$$

$$P_2(t) \approx \frac{E_{pulse}}{A}\left(\frac{8eL_z}{9\pi^2\hbar}\right)^2 \frac{\tau}{1+\omega_{n1}^2\tau^2}\left(1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos\omega_{n1}t\right).$$

As $t \to \infty$,

$$P_2(\infty) \approx \frac{E_{pulse}}{A}\left(\frac{8eL_z}{9\pi^2\hbar}\right)^2 \frac{\tau}{1+\omega_{n1}^2\tau^2}.$$

For maximum transition probability, $\tau = 1/\omega_{21}$.

Finally we write the expression in terms of E_0 again.

$$P_2(t) \approx \left(\frac{8eE_0L_z}{9\pi^2\hbar\omega_{32}}\right)^2 \frac{\omega_{n1}^2\tau^2}{1+\omega_{n1}^2\tau^2}\left(1 + e^{-2t/\tau} - 2e^{-t/\tau}\cos\omega_{n1}t\right).$$

$$P_2(\infty) \approx \left(\frac{8eE_0L_z}{9\pi^2\hbar\omega_{32}}\right)^2 \frac{\omega_{n1}^2\tau^2}{1+\omega_{n1}^2\tau^2}.$$
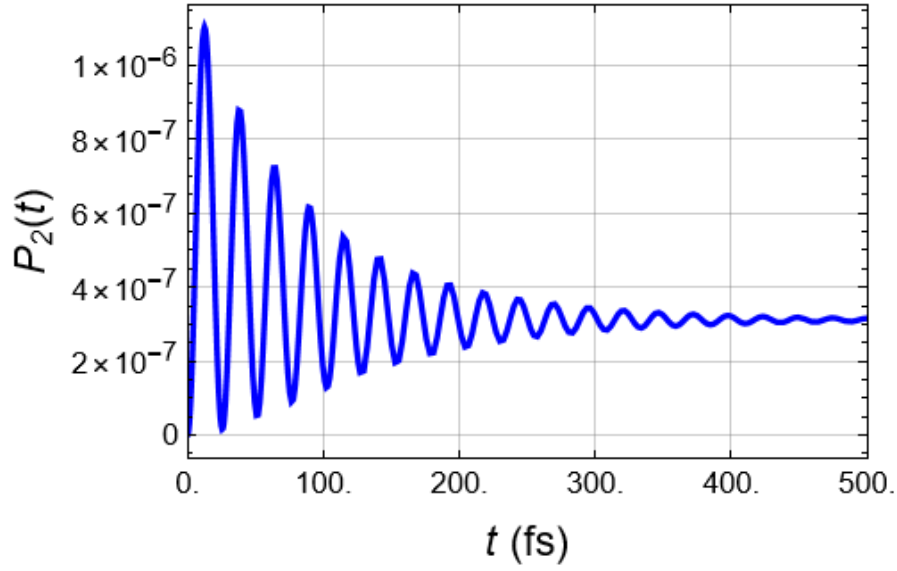
Consider the case for,

$$\tau = 100\ fs.$$
$$E_0 = 1\ kV/cm.$$

$$P_2(\infty) \approx 3.12 \times 10^{-7}.$$
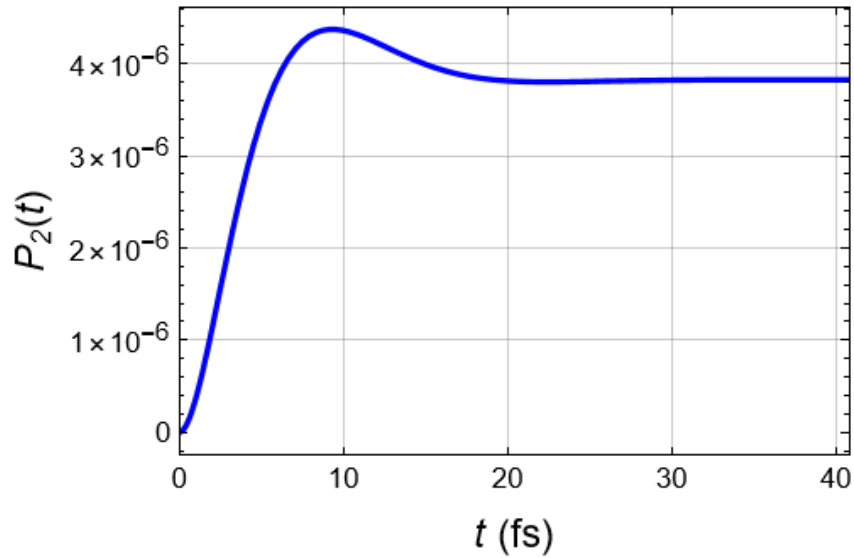
Here is a plot of $P_2(t)$ in this case.

For same energy, but maximal τ,

$$\tau = 1/\omega_{21} = 4.084\,fs.$$

$$E_0 = 1kV/cm\sqrt{\frac{100\,fs}{4.084\,fs}} = 4.95kV/cm.$$

$$P_2(\infty) \approx 3.82 \times 10^{-6}.$$

Here is a plot of $P_2(t)$ in this case.

For 10^{11} electrons in the quantum well. The number of electrons moving to second energy level and hence contributing to the photo current per pulse will be as follows:

$$3.12 \times 10^4 \text{ photo-electrons per pulse for } \tau = 100\,fs.$$

$$3.82 \times 10^5 \text{ photo-electrons per pulse for } \tau = 4.1\,fs \text{ (same energy)}.$$

Simple Oscillating Perturbations

Given:

$$\hat{\mathcal{H}}_{int}(t) = -q\vec{E}.\hat{d} = 2eE_o z \cos(\Omega t) = C_{int} \hbar\Omega \, \xi f(t). \quad (26)$$

Here,

$$f(t) = 2\cos(\Omega t).$$

$$C_{int} = \frac{eE_0 L_z}{\hbar\Omega}.$$

$$M_{nk} = \int_a^b (\xi - \xi_0)\psi_n^*(\xi)\psi_k(\xi)d\xi.$$

$$H_{nk}(t) = C_{int} f(t) M_{nk} \hbar\Omega$$

Starting from the kth state, the probability of transition to the nth state is given as follows.

$$P_{nk}(t) \approx C_{int}^2 M_{nk}^2 \left|\Omega \int_0^t 2\cos(\Omega t')e^{i\omega_{nk}t'}dt'\right|^2,$$

$$P_{nk}(t) \approx C_{int}^2 M_{nk}^2 \left|\Omega \int_0^t \left(e^{i(\omega_{nk}+\Omega)t'} + e^{i(\omega_{nk}-\Omega)t'}\right)dt'\right|^2,$$

$$P_{nk}(t) \approx C_{int}^2 M_{nk}^2 \left|\frac{\Omega}{(\omega_{nk}+\Omega)}\left(e^{i(\omega_{nk}+\Omega)t} - 1\right) + \frac{\Omega}{(\omega_{nk}-\Omega)}\left(e^{i(\omega_{nk}-\Omega)t} - 1\right)\right|^2.$$

Let us define,

$$\omega_{nk+} = \frac{\omega_{nk}+\Omega}{2}, \quad (27a)$$

$$\omega_{nk-} = \frac{\omega_{nk}-\Omega}{2}. \quad (27b)$$

$$P_{nk}(t) \approx C_{int}^2 M_{nk}^2 \left|\frac{\Omega}{\omega_{nk+}}\left(e^{i2\omega_{nk+}t} - 1\right) + \frac{\Omega}{2\omega_{nk-}}\left(e^{i2\omega_{nk-}t} - 1\right)\right|^2.$$

$$P_{nk}(t) \approx \left(C_{int} M_{nk}\Omega t\right)^2 \left|e^{i\omega_{nk+}t}\frac{\sin(\omega_{nk+}t)}{\omega_{nk+}t} + e^{i\omega_{nk-}t}\frac{\sin(\omega_{nk-}t)}{\omega_{nk-}t}\right|^2,$$

$$P_{nk}(t) \approx \left(C_{int}M_{nk}\Omega t\right)^2 \left|e^{i\omega_{nk+}t}sinc(\omega_{nk+}t) + e^{i\omega_{nk-}t}sinc(\omega_{nk-}t)\right|^2,$$

$$P_{nk}(t) \approx \left(C_{int}M_{nk}\Omega t\right)^2 \left(sinc^2(\omega_{nk+}t) + sinc^2(\omega_{nk-}t) + 2\,sinc(\omega_{nk+}t)\,sinc(\omega_{nk-}t)\cos(\Omega t)\right). \quad (28)$$

Consider $\Omega \approx \omega_n - \omega_k$. In this case, $\omega_{nk-} << \omega_{nk+}$. So for time t such that,

$$\omega_{nk-}t << 1 << \omega_{nk+}t$$

$$P_{nk}(t) \approx \left(C_{int}M_{nk}\Omega t\right)^2 sinc^2\left(\frac{\omega_{nk}-\Omega}{2}t\right),$$

If $n > k$, this is the case of absorption, otherwise it is the case of stimulated emission.