Today we will consider the special and important case of a sinusoidal oscillation (sec. XIII C, p. 1291-1297 in Cohen-Tannoudji) and apply it to the example of the interaction of an atom with an electromagnetic field (complement XIII A, p. 1304-1315 in Cohen-Tannoudji).

Assume that the time-dependent perturbation is given by

$$\hat{W}(t) = \hat{W} \sin \omega t.$$ 

$\hat{W}$ is time-independent. Then

$$\hat{W}_{fi}(t) = \langle \varphi_f | \hat{W} \sin \omega t | \varphi_i \rangle$$

$$= \langle \varphi_f | \hat{W} | \varphi_i \rangle \sin \omega t$$

$$= \hat{W}_{fi} \sin \omega t$$

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

where $\hat{W}_{fi} \equiv \langle \varphi_f | \hat{W} | \varphi_i \rangle$ is independent of time and has dimensions of energy.
Substitute this expression for $\hat{W}_{fi}(t)$ into the relation for $b^{(1)}_n(t)$

$$b^{(1)}_n(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} \hat{W}_{ni}(t') dt'$$

which we derived last lecture.

$$b^{(1)}_n(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} \frac{\hat{W}_{ni}}{2i} \left( e^{i\omega t'} - e^{-i\omega t'} \right) dt'$$

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

$$= -\frac{\hat{W}_{ni}}{2\hbar} \left[ \frac{e^{i(\omega_{ni}+\omega)t}}{i(\omega_{ni} + \omega)} - \frac{e^{i(\omega_{ni}-\omega)t}}{i(\omega_{ni} - \omega)} \right]_0^t$$

$$= \frac{\hat{W}_{ni}}{2i\hbar} \left[ \frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni} + \omega} - \frac{1 - e^{i(\omega_{ni}-\omega)t}}{\omega_{ni} - \omega} \right]$$
Therefore the time-dependent transition probability becomes

\[ P_{if}(t; \omega) = \lambda^2 |b_f^{(1)}(t)|^2 \]

\[ = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi}+\omega)t}}{\omega_{fi} + \omega} - \frac{1 - e^{i(\omega_{fi}-\omega)t}}{\omega_{fi} - \omega} \right|^2. \]

Now, \( \omega_{fi} \equiv \frac{E_f - E_i}{\hbar} \). \( \omega_{fi} \) can be positive or negative, depending on whether \( E_f > E_i \) or \( E_f < E_i \).

\[ \omega_{fi} > 0 \]
\[ E_f > E_i \]

Absorption of a photon with energy \( \hbar \omega_{fi} \)

\[ E_i \quad \hbar \omega_{fi} \quad E_f \]
\[ \varphi_i \]

\[ \varphi_f \]

\[ \omega_{fi} < 0 \]
\[ E_f < E_i \]

Emission of a photon with energy \( -\hbar \omega_{fi} \)

\[ E_i \quad \hbar \omega_{fi} \quad E_f \]
\[ \varphi_i \]

\[ \varphi_f \]
Write $P_{if}(t; \omega)$ as

$$P_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} |A_+ + A_-|^2$$

where

$$A_+ = \frac{1 - e^{i(\omega_f + \omega)t}}{\omega_f + \omega}$$

Use $e^{i\theta} - e^{-i\theta} = 2i \sin \theta$. Then

$$A_+ = -ie^{i(\omega_f + \omega)t/2} \frac{\sin [(\omega_f + \omega)t/2]}{(\omega_f + \omega)/2}.$$

and similarly

$$A_- = \frac{1 - e^{i(\omega_f - \omega)t}}{\omega_f - \omega}$$

$$A_- = +ie^{i(\omega_f - \omega)t/2} \frac{\sin [(\omega_f - \omega)t/2]}{(\omega_f - \omega)/2}.$$
The denominator of the $A_-$ term goes to zero for $\omega = \omega_{fi}$ and that of the $A_+$ term for $\omega = -\omega_{fi}$. Let us assume that $\omega_{fi} = \frac{E_f - E_i}{\hbar} > 0$ (i.e., absorption). We will later consider $\omega_{fi} < 0$ (emission).

For $\omega$ close to $\omega_{fi} > 0$, we expect only the $A_-$ term to be important since the denominator $(\omega_{fi} - \omega) \to 0$.

$A_-$ is then called the resonant term and $A_+$ the anti-resonant term.
In particular, if $|\omega - \omega_{fi}| \ll |\omega_{fi}|$ then

$$P_{if}(t; \omega) \approx \frac{|W_{fi}|^2}{4\hbar^2} |A_-|^2$$

$$= \frac{|W_{fi}|^2}{4\hbar^2} \left( \sin \left[ \frac{(\omega_{fi} - \omega)t}{2} \right] \frac{(\omega_{fi} - \omega)/2}{(\omega_{fi} - \omega)/2} \right)^2.$$

(since $|\omega + \omega_{fi}| \sim |\omega_{fi}| \gg |\omega - \omega_{fi}|$)

Recall that

$$\lim_{x \to 0} \frac{\sin x}{x} = 1.$$

Use this to evaluate $P_{if}$ at $\omega = \omega_{fi}$.

$$P_{if}(t; \omega_{fi}) = \frac{|W_{fi}|^2}{4\hbar^2} t^2 \left( \sin \left[ \frac{(\omega_{fi} - \omega)t}{2} \right] \right)^2 \bigg|_{\omega=\omega_{fi}}$$

Note that I took out a factor of $t^2$ so that the argument of the sine function is identical to the denominator.
Also, \( P_{if} = 0 \) when \( \frac{(\omega_{fi} - \omega)t}{2} = n\pi, \quad n = \pm 1, \pm 2, \pm 3, \ldots \)

Thus, the first zeros are \( \pm \frac{2\pi}{t} \) above and below \( \omega = \omega_{fi} \).

The first secondary maximum of \( P_{if} \), attained when

\[
\frac{(\omega_{fi} - \omega)t}{2} = \frac{3\pi}{2},
\]

is equal to

\[
\frac{|\hat{W}_{fi}|^2 t^2}{9\pi^2 \hbar^2},
\]

which is less than 5% of the transition probability at the peak.
From the above, we can plot $P_{if}$, for fixed $t$.

\[ P_{\text{max}}(t) = \frac{|W_{fi}|^2 t^2}{4\hbar^2} \]

\[ \sim 0.05 P_{\text{max}}(t) \]

A resonance phenomenon.
Note that for small time $t$, the peak is low and broad; as $t$ increases, the resonance becomes higher and narrower.

Note that there’s a time-energy uncertainty principle here. Assume we want to measure the energy difference $E_f - E_i = \hbar \omega_{fi}$ by applying a sinusoidal perturbation of frequency $\omega$ to the system and varying $\omega$ so as to detect the resonance. If the perturbation acts during a time $t$, the uncertainty $\Delta E$ on the value $E_f - E_i$ will be of order

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

Thus, the product $\Delta E \Delta t \approx 4\pi \hbar$, consistent with the time-energy uncertainty relation

$$\Delta E \Delta t \geq \frac{\hbar}{2}.$$  

(eq. 3.70 in Griffith)
This result, $\Delta Et \approx 4\pi \hbar$, has a direct effect in atomic clocks, where the “clock” is the frequency of electromagnetic radiation absorbed by the atom at resonance. You can see that to get a precise measurement of $\omega_{fi}$, you must measure the resonance absorption over a long period. This is at the heart of the challenges of atomic clocks, which I hope someone will choose as their presentation project.
Note that if we fix \( \omega \) (instead of \( t \)) and ask how \( P_{if}(t; \omega) \) varies with time, we get a sinusoidal oscillation for \( \omega \neq \omega_{fi} \), with a period that depends on \( \omega_{fi} - \omega \).

As \( \omega \to \omega_{fi} \), the period of oscillation gets very long.

For \( \omega = \omega_{fi} \),

\[
P_{if} = \frac{|\hat{W}_{fi}|^2}{4\hbar^2} t^2.
\]
Limits of the approximation

1. We already noted in the last lecture that the first-order approximation can cease to be valid when $t$ becomes too large. For the sinusoidal perturbation, the transition probability at resonance is

$$P_{if}(t; \omega = \omega_{fi}) = \frac{|\hat{W}_{fi}|^2}{4\hbar^2} t^2,$$

which becomes $\infty$ as $t \to \infty$!

But a probability can never be greater than 1. In practice then, for the first-order approximation to be valid, the probability $P_{if}(t; \omega_{fi})$ must be much smaller than 1; that is

$$t \ll \frac{\hbar}{|W_{fi}|}.$$
2. In the expression

\[ P_{i\bar{f}}(t; \omega) = \frac{|\hat{W}_{fi}|^2}{4\hbar^2} |A_+ + A_-|^2 , \]

we ignored the “anti-resonant” term \(|A_+|^2\) (and the cross terms \(A_+ A_-^* + A_-^* A_+)\).

Since

\[ |A_\pm|^2 = \left\{ \frac{\sin \left[ (\omega_{fi} \pm \omega)t/2 \right]}{(\omega_{fi} \pm \omega)/2} \right\}^2 , \]

\[ |A_+ (\omega)|^2 = |A_- (-\omega)|^2 . \]
If these two curves, each of width $\Delta \omega = \frac{4\pi}{t}$, are centered at points whose separation $2|\omega_{fi}|$ 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 $A_-$. Therefore, the resonant approximation is valid if

$$2|\omega_{fi}| \gg \Delta \omega = \frac{4\pi}{t}, \quad \text{or} \quad t \gg \frac{1}{|\omega_{fi}|}.$$
In the neighborhood of $\omega_{fi}$, $\omega_{fi} \approx \omega$. Therefore, the condition is $t \gg \frac{1}{\omega}$; i.e., our results are valid if the sinusoidal perturbation acts during a time $t$ that is large compared to $\frac{1}{\omega}$.

In other words, during the interval $[0, t]$, the perturbation must perform many oscillations to appear to the system as a sinusoidal perturbation.

If we now combine the restrictions of (1) and (2), we have $t$ bounded from above and below:

$$\frac{1}{\omega} \ll t \ll \frac{\hbar}{|W_{fi}|}.$$
Stimulated emission of radiation:

Now let’s consider the case when

\[ E_f < E_i \quad \Rightarrow \quad \omega_{fi} = \frac{E_f - E_i}{\hbar} < 0. \]

Since

\[ |A_{\pm}|^2 = \left\{ \frac{\sin [(\omega_{fi} \pm \omega)t/2]}{(\omega_{fi} \pm \omega)/2} \right\}^2, \]

\[ |A_+(\omega)|^2 = |A_-(-\omega)|^2, \]

if \( \omega_{fi} < 0 \) the anti-resonant term \( |A_+|^2 \) will dominate in \( P_{if} \) because of the factor \( (\omega_{fi} + \omega) \) in the denominator, particularly for \( \omega \) near \( -\omega_{fi} \). (Note that \( -\omega_{fi} \) is a positive number.)
Thus, the probability of making a transition from a higher energy state to a lower energy state has exactly the same behavior as the probability of making a transition from a lower energy state to a higher energy state, in the presence of a sinusoidal perturbation. Therefore, an external field will stimulate transitions down at the same rate as facilitating transitions upward!