Some notes on second order, time-dependent perturbation theory. Equation numbers \( \mathcal{G} \) refer to the notes on time-dep. pert. theory (Notes 32, as of Spring 2012).

The Dyson series and the expansion of the transition amplitude is explained in the Notes. Assume \( \mathcal{H}_i \) is independent of \( t \), and follow the notation of those Notes. The first order transition amplitude (Eq. (27a)) is

\[
\mathcal{C}_n^{(1)}(t) = (-i) \int_0^t dt' \langle n | \mathcal{H}_i (t') | i \rangle \\
= (-i) \int_0^t dt' e^{i \Omega_{ni} t'} \langle n | \mathcal{H}_i | i \rangle \\
= (-i) \left( \frac{e^{i \Omega_{ni} t} - 1}{i \Omega_{ni}} \right) \langle n | \mathcal{H}_i | i \rangle \\
= (-2i) e^{i \Omega_{ni} t/2} \frac{\sin \Omega_{ni} t/2}{\Omega_{ni}} \langle n | \mathcal{H}_i | i \rangle.
\]

Now we do something similar with the second order term, Eq. (27b).

\[
\mathcal{C}_n^{(2)}(t) = (-i)^2 \int_0^t dt' \int_0^{t'} dt'' \langle n | \mathcal{H}_i (t') \mathcal{H}_i (t'') | i \rangle.
\]

One often visualizes this amplitude by saying that the system begins in state \( |i\rangle \), it interacts with the perturbation at time \( t'' \), then it interacts again with the perturbation at time \( t' \), ending up in state \( |n\rangle \) at time \( t \). Notice that the times satisfy

\[0 \leq t'' \leq t' \leq t\]

under the integral.
We insert a resolution of the identity between the two factors of $H_{12}$ and then switch to the Schrödinger picture to give

$$C_n^{(3)}(t) = (-i)^2 \int_0^t \int_0^{t'} dt'' \sum_k \langle n | H_{12}(t') | k \rangle \langle k | H_{12}(t'') | i \rangle$$

$$= (-i)^2 \int_0^t dt' \int_0^{t'} dt'' \sum_k e^{i \omega_{ki} t'} e^{i \omega_{ki} t''} \langle n | H_1 | k \rangle \langle k | H_{12} | i \rangle$$

(where $\omega_{nk} = E_n - E_k$, $\omega_{ki} = E_k - E_i$)

The states $|k\rangle$ are called "intermediate states". Now do the $t''$ integral:

$$C_n^{(\infty)}(t) = (-i)^2 \int_0^t dt' \sum_k e^{i \omega_{ki} t'} \left(\frac{e^{i \omega_{ki} t'} - 1}{i \omega_{ki}}\right) \langle n | H_1 | k \rangle \langle k | H_{12} | i \rangle$$

$$= (-i)^2 \int_0^t dt' \sum_k \left(\frac{e^{i \omega_{ni} t'} - e^{i \omega_{ki} t'}}{i \omega_{ki}}\right) \langle n | H_1 | k \rangle \langle k | H_{12} | i \rangle \rightarrow T_1 + T_2$$

There are two major terms, call them $T_1$ and $T_2$.

$$T_1 = (-i)^2 \int_0^t dt' \sum_k \frac{e^{i \omega_{ni} t'}}{i \omega_{ki}} \langle n | H_1 | k \rangle \langle k | H_{12} | i \rangle$$

$$= (-i)^2 \sum_k \left[\frac{e^{i \omega_{ki} t'} - 1}{(i \omega_{ki})} \right] \frac{1}{(i \omega_{ki})} \langle n | H_1 | k \rangle \langle k | H_{12} | i \rangle$$

$\rightarrow$ this factor is indep. of $k$ and can be taken out of the sum. In fact, it is the same time-dependent factor which,
when squared, leads to a transition rate (a probability proportional to \( t \)) and conservation of energy, in the limit \( t \to \infty \). The relevant relations are

\[
\frac{e^{i\omega t} - 1}{i\omega} = 2e^{i\omega t/2} \frac{\sin \omega t/2}{\omega} \quad \sqrt{\text{makes \ product}} \\
\left| e^{i\omega t/2} \frac{\sin \omega t/2}{\omega} \right|^2 = \frac{\sin^2 \omega t/2}{\omega^2} = \frac{\pi}{2} + \Delta_t(\omega),
\]

\[
\lim_{t \to \infty} \Delta_t(\omega) = \delta(\omega).
\]

The second term is

\[
T_2 = (-i)^2 \int_0^t dt' \sum_k - \frac{e^{i\omega k t'}}{i\omega} \langle n | H_1 | k \rangle \langle k | H_1 | i \rangle
\]

\[
= -(-i)^2 \sum_k \left( e^{i\omega k t} \frac{e^{i\omega k t} - 1}{i\omega k} \right) \frac{1}{i\omega k} \langle n | H_1 | k \rangle \langle k | H_1 | i \rangle.
\]

Here the \( t \)-dependent factor cannot be taken out of the sum, and the square of \( T_2 \) does not give something proportional to time, so when we divide by \( t \) to get a transition rate and take the limit \( t \to \infty \), this term goes to 0. The same is true of the cross terms \( T_1T_2^* \) and \( T_1^*T_2 \). Thus if we are interested in computing a transition rate, the term \( T_2 \) can be dropped.
Thus adding $C_n^{(1)}$ and the first term of $C_n^{(2)}$, we get an effective transition amplitude through 2nd order, with a common time-dependent factor,

$$C_{\text{eff}}^n(t) = (-2i) e^{i \omega n t / 2} \frac{\sin \omega n t / 2}{\omega n i} M,$$

where

$$M = \langle n | H_1 | i \rangle + \sum_k \frac{\langle n | H_1 | k \rangle \langle k | H_1 | i \rangle}{E_i - E_k},$$

and thus for the probability,

$$P_{\text{eff}}^n(t) = 4 \frac{\sin^2 \omega n t / 2}{\omega n^2} |M|^2$$

$$= 2\pi t \Delta_t(\omega n) |M|^2.$$

The simple conclusion is that to go to 2nd order, we need to include the second term in the boxed equation above, and otherwise everything else (transition rates, cross sections, etc.) are the same as in 1st order time-dependent perturbation theory.