Time-dependent perturbation theory

Majority of the time-dependent QM problems do not have neat analytic solution like the 2 level problem treated before.
Thus, we need to lean on approximate perturbative methods so that the time-evolution of the system, that is $c_n(t)$:s, are expanded as

$$c_n(t) = c_n^{(0)} + c_n^{(1)} + c_n^{(2)} + ...$$

Like in the time-independent case, we will proceed iteratively in solving the

$$i\hbar \frac{d}{dt} c_n(t) = \sum_m V_{nm} e^{i\omega_{nm} t} c_m(t),$$

i.e. from $c_n^{(i)}$ we will get $c_n^{(i+1)}$ and so on.
In the interaction picture the time evolution operator is determined by the equation

$$|\alpha, t_0; t\rangle_I = \mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I.$$

Since the time evolution of the state vectors is governed by the equation

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I &= V_I|\alpha, t_0; t\rangle_I \\ &= V_I \mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I, \end{aligned}$$

we see that

$$i\hbar \frac{\partial \mathcal{U}_{\mathcal{I}}(t, t_0)}{\partial t}|\alpha, t_0; t_0\rangle_I = V_I \mathcal{U}_I(t, t_0)|\alpha, t_0; t_0\rangle_I.$$

The interaction picture time evolution operator satisfies thus the equation

$$i\hbar \frac{d}{dt} \mathcal{U}_I(t, t_0) = V_I(t) \mathcal{U}_I(t, t_0).$$

As the initial condition we have obviously

$$\mathcal{U}_I(t, t_0)\big|_{t=t_0} = 1.$$

Integration gives

$$\mathcal{U}_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t') \mathcal{U}_I(t', t_0)\, dt'.$$

By iteration we end up with Dyson's series

$$\begin{aligned} &\mathcal{U}_I(t, t_0) \\ &\quad = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(t') \left[1 - \frac{i}{\hbar} \int_{t_0}^{t'} V_I(t'') \mathcal{U}_I(t'')\, dt'' \right] dt' \\ &\quad = 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt'\, V_I(t') \end{aligned}$$

$$
\begin{aligned}
&+\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, V_I(t')V_I(t'') \\
&+\cdots+\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \cdots \\
&\times \int_{t_0}^{t^{(n-1)}} dt^{(n)} V_I(t')V_I(t'')\cdots V_I(t^{(n)}) \\
&+\cdots .
\end{aligned}
$$

Let us suppose again that we have solved the problem

$$H_0|n\rangle = E_n|n\rangle$$

completely. Let the initial state of the system be $|i\rangle$ at the moment $t = t_0 = 0$, i.e.

$$|\alpha, t_0 = 0; t = 0\rangle_I = |i\rangle.$$

At the moment t this has evolved to the state

$$
\begin{aligned}
|i, t_0 = 0; t\rangle_I &= \mathcal{U}_I(t,0)|i\rangle \\
&= \sum_n |n\rangle\langle n|\mathcal{U}_I(t,0)|i\rangle.
\end{aligned}
$$

Here

$$\langle n|\mathcal{U}_I(t,0)|i\rangle = c_n(t)$$

is the same as the superposition coefficient we used before.
From the relation binding the interaction and Schrödinger picture state vectors we get

$$
\begin{aligned}
|\alpha, t_0; t\rangle_I &= e^{iH_0t/\hbar}|\alpha, t_0; t\rangle_S \\
&= e^{iH_0t/\hbar}\mathcal{U}(t,t_0)|\alpha, t_0; t_0\rangle_S \\
&= e^{iH_0t/\hbar}\mathcal{U}(t,t_0)e^{-iH_0t_0/\hbar}|\alpha, t_0; t_0\rangle_I,
\end{aligned}
$$

so the time evolution operators of these pictures are obtained with the help of the formula

$$\mathcal{U}_I(t,t_0) = e^{iH_0t/\hbar}\mathcal{U}(t,t_0)e^{-iH_0t_0/\hbar}.$$

The matrix elements of the operator $\mathcal{U}_I(t,t_0)$ can now be calculated from the relation

$$\langle n|\mathcal{U}_I(t,t_0)|i\rangle = e^{i(E_nt-E_it_0)/\hbar}\langle n|\mathcal{U}(t,t_0)|i\rangle.$$

We see that

- the matrix element $\langle n|\mathcal{U}_I(t,t_0)|i\rangle$ is not quite the transition amplitude $\langle n|\mathcal{U}(t,t_0)|i\rangle$,
- the transition probabilities satisfy

$$|\langle n|\mathcal{U}_I(t,t_0)|i\rangle|^2 = |\langle n|\mathcal{U}(t,t_0)|i\rangle|^2.$$

Note If the states $|a'\rangle$ and $|b'\rangle$ are not eigenstates of H_0, i.e. $[H_0, A] \neq 0$ and/or $[H_0, B] \neq 0$, then

$$|\langle b'|\mathcal{U}_I(t,t_0)|a'\rangle|^2 \neq |\langle b'|\mathcal{U}(t,t_0)|a'\rangle|^2.$$

In this case the matrix elements are evaluated by expanding the states $|a'\rangle$ and $|b'\rangle$ in the base $\{|n\rangle\}$ formed by the eigenstates of H_0.
Let us suppose now that at the moment $t = t_0$ the system is in the eigenstate $|i\rangle$ of H_0. This state vector can always be multiplied by an arbitrary phase factor, so the Schrödinger picture state vector $|i, t_0; t_0\rangle_S$ can be chosen as

$$|i, t_0; t_0\rangle_S = e^{-iE_i t_0/\hbar}|i\rangle.$$

Then in the interaction picture we have

$$|i, t_0; t_0\rangle_I = |i\rangle.$$

At the moment t this has evolved to the state

$$|i, t_0; t\rangle_I = \mathcal{U}_I(t,t_0)|i\rangle$$

which on the other hand reads

$$|i, t_0; t\rangle_I = \sum_n c_n(t)|n\rangle,$$

so

$$c_n(t) = \langle n|\mathcal{U}_I(t,t_0)|i\rangle,$$

as we already noted.
Now

1. substitute the Dyson series into this
2. expand the coefficient as a power series of the perturbation
$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots,$$
3. equalize the terms $c_n^{(k)}$ with the perturbation terms of the order k,
4. denote
$$e^{i(E_n - E_i)t/\hbar} = e^{i\omega_{ni}t}.$$

We get

$$\begin{aligned}
c_n^{(0)}(t) &= \delta_{ni} \\
c_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t} \langle n|V_I(t')|i\rangle\, dt' \\
&= -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'} V_{ni}(t')\, dt' \\
c_n^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t'} V_{nm}(t') \\
&\quad \times e^{i\omega_{mi}t''} V_{mi}(t'').
\end{aligned}$$

The probability for the transition from the state $|i\rangle$ to the state $|n\rangle$ can be written as

$$\Pr(i \to n) = |c_n(t)|^2 = |c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots|^2.$$

Constant perturbation, Fermi's golden rule

Consider the constant perturbation

$$V(t) = \begin{cases} 0, & \text{when } t < 0 \\ V \quad \text{(time independent)} & \text{when } t \geq 0. \end{cases}$$

switched on at the moment $t = 0$. At the moment $t = 0$ let the system be in the pure state $|i\rangle$. Now

$$\begin{aligned} c_n^{(0)} &= c_n^{(0)}(0) = \delta_{in} \\ c_n^{(1)} &= -\frac{i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni}t'}\, dt' \\ &= \frac{V_{ni}}{E_n - E_i}(1 - e^{i\omega_{ni}t}). \end{aligned}$$

The transition probability to the state $|n\rangle$ is thus

$$\begin{aligned} |c_n^{(1)}|^2 &= \frac{|V_{ni}|^2}{|E_n - E_i|^2}(2 - 2\cos\omega_{ni}t) \\ &= \frac{4|V_{ni}|^2}{|E_n - E_i|^2} \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right], \end{aligned}$$

i.e. dependent both on the matrix elements V_{ni} and the energy difference $E_n - E_i$.

The quantity

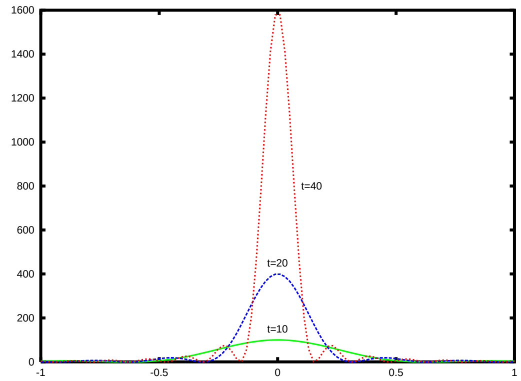
$$\omega \equiv \frac{E_n - E_i}{\hbar}$$

is almost continuous because usually the E_n states form almost a continuum. The transition probability is now

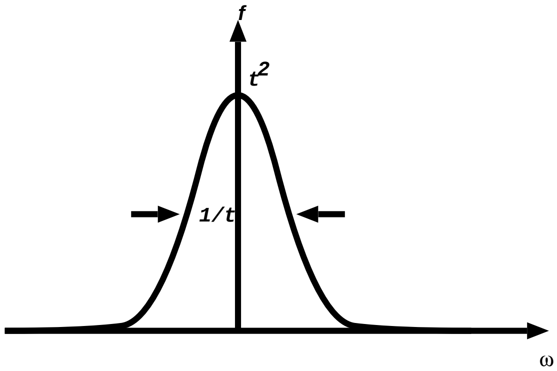
$$|c_n^{(1)}|^2 = \frac{|V_{ni}|^2}{\hbar^2} f(\omega),$$

where

$$f(\omega) = \frac{4\sin^2 \omega t/2}{\omega^2}.$$



above $f(\omega)$ with fixed t=time the perturbation has been switched on, minima appear with $\omega = k \times 2\pi/t$



When t is large then $|c_n(t)|^2 \neq 0$ only if

$$t \approx \frac{2\pi}{\omega} = \frac{2\pi\hbar}{|E_n - E_i|}.$$

If now Δt is the time the perturbation has been on then transitions are possible only if

$$\Delta t \Delta E \approx \hbar.$$

Note If the energy is conserved exactly, i.e.

$$E_n = E_i,$$

then

$$|c_n^{(1)}(t)|^2 = \frac{1}{\hbar^2}|V_{ni}|^2 t^2.$$

The transition probability is proportional to the square of the on-time of the perturbation (and not linearly proportional to the time).
In general we are interested in transitions in which the initial state $|i\rangle$ is fixed but the final state $|n\rangle$ can be any state satisfying the energy conservation rule

$$E_n \approx E_i$$

The total probability for such a transition is now

$$
\begin{aligned}
&\Pr(i \to f) \\
&\quad = \sum_{\substack{n \\ E_n \approx E_i}} |c_n^{(1)}(t)|^2 \\
&\quad = \int dE_n\, \rho(E_n) |c_n^{(1)}|^2 \\
&\quad = 4 \int \sin^2 \left[\frac{(E_n - E_i)t}{2\hbar} \right] \frac{|V_{ni}|^2}{|E_n - E_i|^2} \rho(E_n)\, dE_n .
\end{aligned}
$$

Here $\rho(E)$ is the density of states, i.e.

$$\rho(E)dE = \text{the number of states between} (E, E + dE).$$

Because

$$\lim_{y\to\infty} \frac{1}{\pi} \frac{\sin^2 xy}{yx^2} = \delta(x),$$

we get

$$
\begin{aligned}
\lim_{t\to\infty} \frac{1}{(E_n - E_i)^2} \sin^2 \frac{E_n - E_i}{2\hbar} t &= \frac{\pi t}{4\hbar^2} \delta\left(\frac{E_n - E_i}{2\hbar} \right) \\
&= \frac{\pi t}{2\hbar} \delta(E_n - E_i).
\end{aligned}
$$

The transition probability is thus

$$\lim_{t\to\infty} \Pr(i \to f) = \left(\frac{2\pi}{\hbar} \right) \overline{|V_{ni}|^2} \rho(E_n) t \Big|_{E_n \approx E_i},$$

where $\overline{|V_{ni}|^2}$ is the average of the term $|V_{ni}|^2$.
Note The total transition probability depends linearly on time t.
The transition rate w is defined to be the transition probability per unit time.
We end up with the Fermi golden rule

$$
\begin{aligned}
w_{i\to f} &= \frac{d}{dt} \left(\sum_n |c_n^{(1)}(t)|^2 \right) \\
&= \left(\frac{2\pi}{\hbar} \right) \overline{|V_{ni}|^2} \rho(E_n) \Big|_{E_n \approx E_i} .
\end{aligned}
$$

Quite often this is also written as

$$w_{i\to n} = \left(\frac{2\pi}{\hbar} \right) |V_{ni}|^2 \delta(E_n - E_i),$$

but then one implicitely assumes that it will be integrated in the expression $\int dE_n\, \rho(E_n) w_{i\to n} \cdots$.

Note Some care should be taken when considering $\overline{|V_{ni}|^2}$. The average is over sufficiently nearby states $|n\rangle, |i\rangle$, so that both energies and momenta, for instance, can be considered constant.

Second order corrections
In the second order we got

$$\begin{aligned} c_n^{(2)}(t) &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t'} V_{nm}(t') \\ &\quad \times e^{i\omega_{mi}t''} V_{mi}(t''), \end{aligned}$$

so in the case of the potential

$$V(t) = \begin{cases} 0, & \text{when } t < 0 \\ V \quad \text{(time independent)} & \text{when } t \geq 0. \end{cases}$$

we have

$$\begin{aligned} c_n^{(2)} &= \left(-\frac{i}{\hbar}\right)^2 \sum_m V_{nm}V_{mi} \int_0^t dt'\, e^{i\omega_{nm}t'} \int_0^{t'} dt''\, e^{i\omega_{mi}t''} \\ &= \frac{i}{\hbar} \sum_m \frac{V_{nm}V_{mi}}{E_m - E_i} \int_0^t (e^{i\omega_{ni}t'} - e^{i\omega_{nm}t'}) dt'. \end{aligned}$$

Above

- the term $e^{i\omega_{ni}t'}$ is same as in the coefficient $c_n^{(1)}$, so it contributes only if $E_n \approx E_i$ when $t \to \infty$.
- if E_m in the term $e^{i\omega_{nm}t'}$ differs from E_n and at the same time from E_i it oscillates rapidly and contributes nothing.

So we can write

$$w_{i\to f} = \frac{2\pi}{\hbar} \overline{\left| V_{ni} + \sum_m \frac{V_{nm}V_{mi}}{E_i - E_m} \right|^2} \rho(E_n) \Bigg|_{E_n \approx E_i}.$$

In the second order the term $V_{nm}V_{mi}$ can be thougth to describe *virtual transitions*

$$|i\rangle \longrightarrow |m\rangle \longrightarrow |n\rangle$$

in which both transitions $i \to m$ and $m \to n$ can violate energy conservation while $i \to n$ conserves energy.

Harmonic perturbations
Consider sinusoidal time-dependent potential

$$V(t) = \mathcal{V}e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t},$$

which is again assumed to be switched on at the moment $t = 0$. When $t < 0$, the system is supposed to be in the state $|i\rangle$. The first order term is now

$$\begin{aligned} c_n^{(1)} &= -\frac{i}{\hbar}\int_0^t \left(\mathcal{V}_{ni}e^{i\omega t'} + \mathcal{V}_{ni}^\dagger e^{-i\omega t'}\right) e^{i\omega_{ni}t'}\,dt' \\ &= \frac{1}{\hbar}\left[\frac{1-e^{i(\omega+\omega_{ni})t}}{\omega+\omega_{ni}}\mathcal{V}_{ni} + \frac{1-e^{i(\omega-\omega_{ni})t}}{-\omega+\omega_{ni}}\mathcal{V}_{ni}^\dagger\right]. \end{aligned}$$

This is of the same form as in the case of our earlier step potential, provided that we substitute

$$\omega_{ni} = \frac{E_n - E_i}{\hbar} \longrightarrow \omega_{ni} \pm \omega.$$

Note $\mathcal{V}_{ni}^\dagger \equiv (\mathcal{V}^\dagger)_{ni}$
When $t \to \infty$, $|c_n^{(1)}|^2$ is thus non zero only if

$$\begin{aligned} \omega_{ni} + \omega \approx 0 \quad &\text{or} \quad E_n \approx E_i - \hbar\omega \\ \omega_{ni} - \omega \approx 0 \quad &\text{or} \quad E_n \approx E_i + \hbar\omega. \end{aligned}$$

Obviously, if the first term is important the second one does not contribute and vice versa. The energy of a quantum mechanical system is not conserved in these transitions but the "external" potential either gives (*absorption*) or takes (*stimulated emission*) energy to/from the system. Analogically to the constant potential the transition rate will be

$$w_{i\to n} = \frac{2\pi}{\hbar}|\mathcal{V}_{ni}|^2\delta(E_n - E_i \pm \hbar\omega).$$

Note $|\mathcal{V}_{ni}|^2 = |\mathcal{V}_{in}^\dagger|^2$ which describes *detailed balancing* between absobtion and emission. Otherwise stated

$$\frac{\text{emission } i \to \{n\}}{\rho_n} = \frac{\text{absobtion } n \to \{i\}}{\rho_i}$$