Energy shifts and line widths

So far we have considered how the states other than $|i\rangle$ get populated. How about $c_i(t)$?

Evolution of the initial state

We consider the case where the initial and final states are the same. We switch the interaction on slowly:

$$V(t) = e^{\eta t} V \quad \text{where } \eta \approx \epsilon > 0.$$

Here $\eta \to 0$ at the end.

We suppose that in the far past, $t = -\infty$, the system has been in the state $|i\rangle$.

Check

If $n \neq i$, then the perturbation theory gives

$$\begin{aligned} c_n^{(0)}(t) &= 0 \\ c_n^{(1)}(t) &= -\frac{i}{\hbar} V_{ni} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'} e^{i\omega_{ni} t'}\, dt' \\ &= -\frac{i}{\hbar} V_{ni} \frac{e^{\eta t + i\omega_{ni} t}}{\eta + i\omega_{ni}}. \end{aligned}$$

Up to the lowest non vanishing order the transition probability is

$$|c_n(t)|^2 \approx \frac{|V_{ni}|^2}{\hbar^2} \left(\frac{e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right)$$

and the transition rate correspondingly

$$\frac{d}{dt}|c_n(t)|^2 \approx \frac{2|V_{ni}|^2}{\hbar^2} \left(\frac{\eta e^{2\eta t}}{\eta^2 + \omega_{ni}^2} \right).$$

Now

$$\lim_{\eta \to 0} \frac{\eta}{\eta^2 + \omega_{ni}^2} = \pi \delta(\omega_{ni}) = \pi \hbar \delta(E_n - E_i),$$

so in the limit $\eta \to 0$ we get the Fermi golden rule

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

This is equivalent with our previous result.

Let now $n = i$. We get

$$\begin{aligned} c_i^{(0)} &= 1 \\ c_i^{(1)} &= -\frac{i}{\hbar} V_{ii} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{\eta t'}\, dt' = -\frac{i}{\hbar \eta} V_{ii} e^{\eta t} \end{aligned}$$

$$
\begin{aligned}
c_i^{(2)} &= \left(-\frac{i}{\hbar}\right)^2 \sum_m |V_{mi}|^2 \\
&\quad \times \lim_{t_0\to-\infty} \int_{t_0}^{t} dt'\, e^{i\omega_{im}t'+\eta t'} \int_{t_0}^{t'} dt'' e^{i\omega_{mi}t''+\eta t''} \\
&= \left(-\frac{i}{\hbar}\right)^2 \sum_m |V_{mi}|^2 \\
&\quad \times \lim_{t_0\to-\infty} \int_{t_0}^{t} dt'\, e^{i\omega_{im}t'+\eta t'} \frac{e^{i\omega_{mi}t'+\eta t'}}{i(\omega_{mi}-i\eta)} \\
&= \left(-\frac{i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} \\
&\quad + \left(-\frac{i}{\hbar}\right) \sum_{m\neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}.
\end{aligned}
$$

Thus, up to the second order the coefficient c_i is

$$
\begin{aligned}
c_i(t) &\approx 1 - \frac{i}{\hbar\eta} V_{ii} e^{\eta t} + \left(-\frac{i}{\hbar}\right)^2 |V_{ii}|^2 \frac{e^{2\eta t}}{2\eta^2} \\
&\quad + \left(-\frac{i}{\hbar}\right) \sum_{m\neq i} \frac{|V_{mi}|^2 e^{2\eta t}}{2\eta(E_i - E_m + i\hbar\eta)}.
\end{aligned}
$$

For the logarithmic time derivative of the coefficient c_i up to the second order in the perturbation V we get

$$
\begin{aligned}
\frac{\dot{c}_i}{c_i} &\approx -\frac{i}{\hbar} \frac{V_{ii} - \dfrac{i}{\hbar}\dfrac{|V_{ii}|^2}{\eta} + \displaystyle\sum_{m\neq i} \frac{|V_{mi}|^2}{(E_i - E_m + i\hbar\eta)}}{1 - \dfrac{i}{\hbar}\dfrac{V_{ii}}{\eta}} \\
&\approx \frac{-i}{\hbar} V_{ii} + \left(\frac{-i}{\hbar}\right) \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta},
\end{aligned}
$$

where we have already set $e^{\eta t} \to 1$.
Note We cannot set in the denominator $\eta = 0$, because the states E_m can form nearly a continuum in the vicinity of E_i.
The logarithmic derivative is thus time independent, i.e. of form

$$
\frac{\dot{c}_i(t)}{c_i(t)} = -\frac{i}{\hbar}\Delta_i.
$$

The solution satisfying the initial condition $c_i(0) = 1$ is

$$
c_i(t) = e^{-i\Delta_i t/\hbar}.
$$

Note Δ_i is not necessarily real.
We interprete this so that the state $|i\rangle$ evolves gradually like

$$|i\rangle \longrightarrow c_i(t)|i\rangle = e^{-i\Delta_i t/\hbar}|i\rangle.$$

In the Schrödinger picture the latter contains also a phase factor, or

$$e^{-i\Delta_i t/\hbar}|i\rangle \mapsto e^{-i\Delta_i t/\hbar - iE_i t/\hbar}|i\rangle.$$

Due to the perturbation the energy levels shift like

$$E_i \longrightarrow E_i + \Delta_i.$$

We expand now Δ_i as the power series in the perturbation:

$$\Delta_i = \Delta_i^{(1)} + \Delta_i^{(2)} + \cdots.$$

Comparing with our previous expression

$$\Delta_i = V_{ii} + \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta},$$

we see that in the first order we have

$$\Delta_i^{(1)} = V_{ii}.$$

This is equivalent with the time independent perturbation theory.
Because the energies E_m for almost a continuum we can in the second order term

$$\sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m + i\hbar\eta}$$

replace the summation with the integration. To handle the limit $\eta \to 0$ we recall from the function theory that

$$\lim_{\epsilon\to 0+} \int_{-\infty}^{\infty} \frac{f(z)}{z + i\epsilon} dz = \wp \int_{-\infty}^{\infty} \frac{f(z)}{z} dz - i\pi f(0),$$

where $\wp$ stands for the principal value integral. A common shorthand notation for this is

$$\lim_{\epsilon\to 0} \frac{1}{x + i\epsilon} = \wp \frac{1}{x} - i\pi\delta(x).$$

Thus we get

$$\begin{aligned}
\mathrm{Re}(\Delta_i^{(2)}) &= \wp \sum_{m\neq i} \frac{|V_{mi}|^2}{E_i - E_m} \\
\mathrm{Im}(\Delta_i^{(2)}) &= -\pi \sum_{m\neq i} |V_{mi}|^2 \delta(E_i - E_m).
\end{aligned}$$

The right hand side of the latter equation is familiar from the Fermi golden rule, so we can write

$$\sum_{m\neq i} w_{i\to m} = \frac{2\pi}{\hbar}\sum_{m\neq i}|V_{mi}|^2\delta(E_i - E_m) = -\frac{2}{\hbar}\mathrm{Im}\left[\Delta_i^{(2)}\right].$$

The coefficient $c_i(t)$ can be written with the help of the energy shift as

$$c_i(t) = e^{-(i/\hbar)[\mathrm{Re}(\Delta_i)t]+(1/\hbar)[\mathrm{Im}(\Delta_i)t]}.$$

We define

$$\frac{\Gamma_i}{\hbar} \equiv -\frac{2}{\hbar}\mathrm{Im}(\Delta_i).$$

Then

$$|c_i(t)|^2 = e^{2\mathrm{Im}(\Delta_i)t/\hbar} = e^{-\Gamma_i t/\hbar}.$$

Thus the quantity Γ_i tells us at which rate the state $|i\rangle$ disappears. The quantity

$$\tau_i = \frac{\hbar}{\Gamma_i}$$

is thus the average life time of the state $|i\rangle$.
In the Schrödinger picture the time evolution is

$$c_i(t)e^{-iE_i t/\hbar} = \frac{\hbar}{2\pi}\int f(E)e^{-iEt/\hbar}dE,$$

where the energy spectrum

$$f(E) = \int e^{-i[E_i+\mathrm{Re}(\Delta_i)]t/\hbar - \Gamma_i t/2\hbar}e^{iEt/\hbar}\,dt$$

is the Fourier transform of the coefficient $c_i(t)e^{-iE_i t/\hbar}$. Now

$$|f(E)|^2 \propto \frac{1}{\{E-[E_i+\mathrm{Re}(\Delta_i)]\}^2 + \Gamma_i^2/4},$$

so Γ_i —or excluding the factor -2, the imaginary part of the energy shift— is the width of the decay line and the real part of the energy shift what is usually called the energy shift.
In the case of harmonic perturbations we can repeat the same derivation provided that we substitute

$$E_m - E_i \mapsto E_m - E_i \pm \hbar\omega.$$