Decay Width / Exponential Decay

For a Hamiltonian $V = e^{-i\omega t}$

The Fermi Golden Rule tells us

$$R_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Suppose $i$ and $f$ are atomic levels. We do not expect a perfect delta function since we know the excited state of an atom does not live forever. Instead, it suffers from spontaneous decay. This will broaden the line.

Where does this come from?

The full quantum system consists of the atom plus the electromagnetic radiation field, which supports a continuum of levels.

In reality

$|i\rangle = |\text{atom, vacuum}\rangle$ \hspace{1cm} $i$: ground state

$|f\rangle = |\text{atom, vacuum}\rangle$ \hspace{1cm} But this is not an eigenstate of atom + EM Hamiltonian

In fact $|f\rangle$ can decay to

$|\text{atom, vacuum}\rangle \rightarrow |\text{atom, photon}\rangle$

Only when we ignore the emitted photon we can say

$|f\rangle \rightarrow |\text{atom}\rangle$
we can try to see this by using a very crude model to account for this process.

\[
C_f(t) = \frac{1}{\hbar} \int_0^t e^{i(\omega_f - \omega_e)t'} e^{-i\omega_t'} \langle f| \hat{V}| i \rangle \otimes e^{-RC(t-t')}
\]

Modify with exponential decay: because system's decay rate \( \Gamma \) out of state \( f \).

\[
C_f(t) = \frac{1}{\hbar} \langle f| \hat{V}| i \rangle e^{-\frac{\Gamma}{\hbar} t} \left[ e^{-\frac{i(\omega_f - \omega_e)\hbar}{\hbar^2} t} e^{-t(\omega_f - \omega_e) + \Gamma} \right]
\]

\[
|G(0)|^2 \approx |\langle f| \hat{V}| i \rangle|^2 \frac{1}{\hbar^2 (\omega_f - \omega_e)^2 + \Gamma^2}
\]

This does not grow linearly with time. Saturates to a constant but we can deal with this with a simple model again.

Focus only on two levels: \( i \) and \( f \). Let \( \Gamma \) be the transition rate from \( i \rightarrow f \).

\[
\frac{d}{dt} |C_i|^2 = -2\Gamma |C_f|^2 + R |C_i|^2 - R |C_f|^2
\]

\[
\frac{d}{dt} |C_f|^2 = 2\Gamma |C_i|^2 + R |C_f|^2 - R |C_i|^2
\]

Steady state \((2\Gamma + R)|C_f|^2 = R |C_i|^2 \rightarrow |C_f|^2 \sim \frac{1}{R}

\text{then} \quad R < \Gamma
\[ \frac{1}{C_4^{12}} \approx \frac{R}{2\gamma} \]
\[ R = 2\Gamma |C_4^{12}|^2 \]

\[ \Rightarrow \quad \text{R} = \frac{1}{\hbar^2} \frac{<f|V|i>^2}{(\omega_{fi} - \omega)^2 + \hbar^2} \]

Consider \( \Gamma \to 0 \)

\[ \lim_{\Gamma \to 0} \frac{2\Gamma}{\hbar^2 (\omega_{fi} - \omega)^2 + \hbar^2} = \frac{2\pi}{\hbar^2} \delta(\omega_{fi} - \omega) \]

So

\[ \lim_{\Gamma \to 0} \text{R} = \frac{2\Gamma}{\hbar^2} \frac{1}{<f|V|i>^2} \delta(\omega_{fi} - \omega) \]

which recovers the Fermi Golden Rule.

So we conclude that Lorentzian line shape comes from (crude) model of exponential decay of final state.

Can we do a bit better than this?

We will follow the treatment used by Wigner and Weisskopf in 1939.

Idea: first to avoid fast transient oscillations, let's consider the case when the potential is gradually turned on

\[ V(t) = e^t V \quad \text{v: constant} \]

\( n \) small and positive

At the end of the calculation one could set \( n \to 0 \). In this case the potential becomes constant.
This treatment can be easily generalized to the harmonic oscillation perturbation discussed above. In this case all we need to do is to change $E_f$ in the constant potential case by $E_f + \hbar \omega$.

We now assume that the system started in the state $|1\rangle$. We set it as $y$ at $t \to -\infty$ the system started in $|1\rangle$ what we want to compute is $c_i(t)$.

From perturbation theory we get

$$C_{00}(t) = 0 \quad n \neq i$$

$$C_{00}(t) = -\frac{\hbar}{\omega} \lim_{E_0 \to -\infty} \left( e^{-i \omega t} \int_{t_0}^{t} e^{i \omega t' } dt' \right)$$

$$= -\frac{\hbar}{\omega} \frac{e^{-i \omega t}}{m + i \omega \hbar}$$

$$|C_{00}(t)|^2 = \frac{N \hbar \omega^2}{\hbar^2} \frac{e^{2\hbar t}}{\eta^2 + \omega^2 \hbar^2}$$

The rate $\frac{d}{dt} |C_{00}(t)|^2 = \frac{2 N \hbar \omega^2}{\hbar^2} \frac{M \hbar^2}{\eta^2 + \omega^2 \hbar^2}$

Let $\hbar \to 0$ $\eta = \hbar \delta (\omega \hbar) = \hbar \delta (E_n - E_0)$

So $R_{\text{int}} = \frac{2N}{\hbar} \frac{N \hbar \omega^2}{\hbar^2} \delta \left( E_n - E_0 \right)$ Fermi Golden Rule
Now let's try to compute the effect of the perturbation on the initial state:

\[ C_i^{(0)} = 1 \]

\[ C_i^{(1)} = -i \cdot V_{ei} \lim_{\Delta t \to 0} \frac{e^{-i \Delta t}}{\hbar} = -i \cdot V_{ei} \left( \frac{\Delta t}{\hbar} \right) \]

\[ C_i^{(n)} = \left( -i \frac{\Delta t}{\hbar} \right)^n V_{mn} \frac{1}{\hbar} \lim_{\Delta t \to 0} \frac{e^{-i \Delta t}}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]

\[ \left( -i \frac{\Delta t}{\hbar} \right)^n V_{mn} \frac{1}{\hbar} \]

\[ \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]

Therefore up to second order

\[ C_i(t) = 1 - i \cdot V_{ei} \left( \frac{\Delta t}{\hbar} \right) + \left( -i \frac{\Delta t}{\hbar} \right)^2 V_{mn} \frac{1}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]

Looking at the time derivative,

Letting \( \Delta t \to 0 \)

\[ C_i(t) \approx -i V_{ei} \left( \frac{\Delta t}{\hbar} \right) + \left( -i \frac{\Delta t}{\hbar} \right)^2 V_{mn} \frac{1}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]

\[ C_i(t) \approx 1 - i V_{ei} \left( \frac{\Delta t}{\hbar} \right) \]

\[ \approx -i V_{ei} + \left( -i \frac{\Delta t}{\hbar} \right)^2 \frac{V_{mn}^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]

\[ C_i(t) \approx 1 - i V_{ei} \]

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\[ \approx -i V_{ei} \left( \frac{\Delta t}{\hbar} \right) \]

\[ \approx -i V_{ei} \left( \frac{\Delta t}{\hbar} \right) \frac{V_{mn}^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\Delta t}{\hbar} \right)^n \]
Note that this result is correct up to second order in $V$

- Note the right hand side is time independent

If we postulate that

$$ C_i(t) = e^{-i D_i t/\hbar} $$

so that

$$ C_i(t) = \frac{C_i(t)}{\hbar} $$

$$ C_i(0) = 1 $$

This implies that, when we expand

$$ D_i = D_i^{(0)} + D_i^{(1)} + D_i^{(2)} + \cdots $$

That $D_i^{(0)} = 0$, $V$. To zero order $C_i$ is just 1.

$$ D_i^{(1)} = V C_i $$

For $D_i^{(2)}$, recall that

$$ \lim_{n \to 0} \frac{1}{x + in} = \frac{1}{x} - i \pi \delta(x) $$

$$ \text{Re} \left( D_i^{(2)} \right) = \sum_{\text{me}, \text{m}'} \frac{1}{V \text{me}^2} \frac{E_i - E_m}{m' \text{m}'} $$

$$ \text{Im} \left( D_i^{(2)} \right) = \sum_{\text{me}, \text{m}'} \frac{1}{V \text{me}^2} \delta(E_i - E_m) \sum_{\text{m}'} $$
But Im(Δi) has an expression that looks like the termi golden rule. In fact we can identify

\[ \text{Im} \left( \Delta_i \right) = \frac{2\pi}{\hbar} \sum \left| V_{mi} \right|^2 (E_i - E_m) = -2 \frac{\text{Im} (\Delta_i)}{\hbar} \]

If we call \[ \Gamma_i = 2 \text{Im} (\Delta_i) \] then we conclude that the rate at which \[ |i\rangle \] disappears is equal to the rate the population in other states grows.

\[ C_i(t) = e^{-\frac{i\hbar (\text{Re} \Delta_i)t}{\hbar} + \frac{i\hbar \text{Im} (\Delta_i)t}{\hbar}} \]

\[ = e^{-\frac{i\hbar (\text{Re} \Delta_i)t}{\hbar} - \frac{i\hbar \text{Im} (\Delta_i)t}{\hbar}} \]

\[ = e^{-\frac{\Gamma_i t}{\hbar}} \]

\[ |C_i|^2 = e^{-\frac{\Gamma_i t}{\hbar}} \]

of second order

\[ |C_i|^2 = 1 - \frac{\Gamma_i t}{\hbar} \]

\[ |C_i|^2 + \sum |C_{mi}|^2 \approx 1 - \frac{\Gamma_i t}{\hbar} + \frac{\sum \Gamma_{mi} t}{\hbar} = 1 \]

Conservation of probability

The real part of the energy shift is called level shift. The imaginary part, (up to a factor of 2) is called decay width.

Sets the lifetime of state \[ i \]
To understand that better, let's look at the Fourier transform of \( \langle ci(t) \rangle \)

\[
\int \psi(E) e^{i (E_0 + \text{Re}(\Delta) t / \hbar)} e^{-i E t / \hbar} dE = \psi(E)
\]

\[
|f(E)|^2 \frac{1}{\left[ \left( E - (E_0 + \text{Re}(\Delta)) \right)^2 + \Gamma^2/4 \right]}
\]

\( \Gamma \): usual meaning of full width at half maximum