IRREVERSIBLE RELAXATION†‡

We want to study the relaxation of an initially prepared state. We will show that first-order perturbation theory for transfer to a continuum leads to irreversible transfer—an exponential decay—when you include the depletion of the initial state.

The Golden Rule gives the probability of transfer to a continuum (for a constant perturbation):

$$\bar{w}_{k'\ell} = \frac{\partial P_{k'\ell}}{\partial t} = \frac{2\pi}{\hbar} |V_{k'\ell}|^2 \rho(E_k = E_{\ell})$$

$$\bar{P}_{k'\ell} = \bar{w}_{k'\ell} (t - t_0)$$

$$\bar{P}_{k'\ell} = 1 - \bar{P}_{k'\ell}$$

The probability of being observed in $|k\rangle$ varies linearly in time. This will clearly only work for short times, which is no surprise since we said for first-order P.T. $b_k(t) \approx b_k(0)$.

What long-time behavior do we expect?

A time-independent rate is also expected for exponential relaxation. In fact, for exponential relaxation out of a state $|\ell\rangle$, the short time behavior looks just like the first order result:

$$\bar{P}_{\ell\ell}(t) = \bar{P}_{\ell\ell}(0) \exp(-\bar{w}_{\ell\ell} t)$$

$$= 1 - \bar{w}_{\ell\ell} t + \cdots$$

So we might believe that $\bar{w}_{k'\ell}$ represents the tangent to the relaxation behavior at $t = 0$.

$$\bar{w}_{k'\ell} = \left. \frac{\partial P_{k'\ell}}{\partial t} \right|_{t_0}$$

The problem is we don’t account for depletion of initial state.

† Cohen-Tannoudji, et al. p. 1344; Merzbacher, p. 510.
From an exact solution to the two-level problem, we saw that probability oscillates sinusoidally between the two states with a frequency given by the coupling:

\[ \Omega_R = \sqrt{\Delta^2 + \Omega_R^2} \]

But we don’t have a two-state system. Rather, we are relaxing to a continuum. We might imagine that coupling to a continuous distribution of states may in fact lead to exponential relaxation, if destructive interferences exist between oscillations at many frequencies representing exchange of amplitude between the initial state and continuum states.

**COUPLING TO CONTINUUM**

When we look at the long-time probability amplitude of the initial state (including depletion and feedback), we will find that we get exponential decay. The decay of the initial state is irreversible because there is feedback with a distribution of destructively interfering phases.

Let’s look at transitions to a continuum of states \( \{ \ell\} \) from an initial state \( |\ell\rangle \)—under constant perturbation. These form a complete set; so for \( H(t) = H_0 + V(t) \) with \( H_0 |n\rangle = E_n |n\rangle \), we have

\[
1 = \sum_n |n\rangle \langle n| = |\ell\rangle \langle \ell| + \sum_k |k\rangle \langle k|_{\text{initial}} + \sum_k |k\rangle \langle k|_{\text{continuum}}
\]

We want a more accurate description of:

\[
b_k(t) = \langle k | U_f(t, t_0) | \ell\rangle
\]
The exact solution to $U_I$ was:

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} d\tau \ V_I(\tau) U_I(\tau, t_0)$$

For first-order P.T., we set this to 1. Here we keep as is...

$$b_k(t) = \langle k | \epsilon \rangle - \frac{i}{\hbar} \int_{t_0}^{t} d\tau \ \langle k | V_I(\tau) U_I(\tau, t_0) | \epsilon \rangle$$

\[\uparrow \text{insert} \sum_n |n\rangle \langle n|\]

$$= \delta_{k\epsilon} - \frac{i}{\hbar} \sum_n \int_{t_0}^{t} d\tau \ e^{i\omega_n \tau} \ V_{kn} b_n(\tau)$$

Here $V_{kn}$ is not a function of time

or in its differential form:

$$ih \frac{\partial b_k}{\partial t} = \sum_n e^{i\omega_n t} \ V_{kn} b_n(t) \quad (1)$$

These exact forms allow for feedback. This is the general form, where the amplitudes $b_k$ depend on all other states.

For transitions into the continuum, let’s assume that transitions in the continuum only occur from initial state: $\langle k | V | k' \rangle = 0$. Moreover $\langle \epsilon | V | k \rangle = \langle \epsilon | V | k' \rangle = \text{constant}$. So we can remove summation, and express the complex amplitude of a continuum state as

$$b_k = -\frac{i}{\hbar} V_{k\ell} \int_{t_0}^{t} d\tau \ e^{i\omega_k \tau} b_\ell(\tau) \quad (2)$$

We want to calculate the rate of leaving $|\ell\rangle$, including feeding from continuum back into initial state. From (1):

$$ih \frac{\partial}{\partial t} b_\ell = \sum_{k \neq \ell} e^{i\omega_k t} \ V_{k\ell} b_k + V_{\ell\ell} b_\ell$$

\[\uparrow \text{sum over continuum}\]

feedback into $|\ell\rangle$
Substitute (2) into (3), and setting \( t_0 = 0 \):

\[
\frac{\partial b_{\ell}}{\partial t} = -\frac{1}{\hbar^2} \sum_{k \neq \ell} |V_{k\ell}|^2 \int_0^t b_{k}(\tau) e^{i\omega_k (\tau-t)} \, d\tau - \frac{i}{\hbar} V_{\ell\ell} b_{\ell}(t)
\]

This is an integro-differential equation: the time-development of \( b_{\ell} \) depends on entire history of the system. Note we have two time variables:

\[
\tau: |\ell\rangle \rightarrow |k\rangle \\
t: |k\rangle \rightarrow |\ell\rangle
\]

Assumption: \( b_{\ell} \) varies slowly relative to \( \omega_{k\ell} \), so we can remove it from integral. This is effectively a weak coupling statement: \( \hbar \omega_{k\ell} \gg V_{k\ell} \). (remember that \( b \) is in the interaction picture and it doesn’t oscillate at \( \omega_{k\ell} \).

\[
\frac{\partial b_{\ell}}{\partial t} = b_{\ell} \left[ -\frac{1}{\hbar^2} \sum_{k \neq \ell} |V_{k\ell}|^2 \int_0^t e^{i\omega_k (\tau-t)} \, d\tau - \frac{i}{\hbar} V_{\ell\ell} \right]
\]

Now, we want the long time behavior: \( t \gg \frac{1}{\omega_{k\ell}} \), so we want to investigate the limit \( t \rightarrow \infty \).

Focus on integral. Defining \( t' = \tau - t \) \( \, dt' = d\tau \)

\[
\int_0^t e^{i\omega_k (\tau-t)} \, d\tau = \int_0^t e^{i\omega_k \tau} \, dt'
\]

Note on integral: \( \lim_{T \rightarrow \infty} \int_0^T e^{i\omega \tau} \, d\tau = \pi \delta(\omega) \) (purely oscillatory / not well behaved)

Instead integrate \( \int_0^\infty e^{i(\omega+\epsilon)\tau} \, d\tau \) take \( \epsilon \rightarrow 0 \)

\[
\lim_{\epsilon \rightarrow 0^+} \frac{1}{i\omega + \epsilon} = \frac{\epsilon}{\omega^2 + \epsilon^2} + i \frac{\omega}{\omega^2 + \epsilon^2} \Rightarrow +\pi \delta(\omega) - i\frac{\omega}{\omega}
\]

Cauchy Principle Part: \( \mathbb{P}_\perp \frac{1}{x} = \begin{cases} 
\frac{1}{x} & x \neq 0 \\
0 & x = 0
\end{cases} \)
\[
\frac{\partial b_\ell}{\partial t} = b_\ell \left[ -\frac{\pi}{\hbar^2} \sum_{k \neq \ell} |V_{k\ell}|^2 \delta(\omega_{k\ell}) - \frac{i}{\hbar} \left( V_{\ell\ell} + \sum_{k \neq \ell} \frac{|V_{k\ell}|^2}{E_k - E_\ell} \right) \right]
\]

Term 1 is just the Golden Rule rate! Here we have replaced the sum over continuum states by an integral

\[
\sum_{k \neq \ell} \frac{\delta(\omega_{k\ell})}{\hbar} \Rightarrow \rho(E_k = E_\ell) \quad \bar{w}_{k\ell} = \int dE_k \rho(E_k) \left[ \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \right]
\]

Term 2 is just the correction of the energy of \(E_\ell\) from second-order time-independent perturbation theory, \(\Delta E_\ell\).

\[
\Delta E_\ell = \langle \ell | V | \ell \rangle + \sum_{k \neq \ell} \frac{|\langle k | V | \ell \rangle|^2}{E_k - E_\ell}
\]

So, we have

\[
\frac{\partial b_\ell}{\partial t} = b_\ell \left( -\frac{\bar{w}_{k\ell}}{2} - \frac{i}{\hbar} \Delta E_\ell \right)
\]

with \(b_\ell(0) = 1\),

\[
b_\ell(t) = \exp \left( -\frac{\bar{w}_{k\ell} t}{2} - \frac{i}{\hbar} \Delta E_\ell t \right)
\]

Exponential decay! Irreversible relaxation from coupling to the continuum.

Switching back to Schrödinger Picture, \(c_\ell = b_\ell e^{-i\omega_\ell t}\)

\[
c_\ell(t) = \exp \left[ -\left( \frac{\bar{w}_{k\ell}}{2} + i \frac{E_\ell + \Delta E_\ell}{\hbar} \right) t \right]
\]
We expect solutions to the T.D.S.E. to be complex and oscillatory:

\[ c_\ell = \exp[\tilde{\Omega}t] \]

\[
\text{Im}[\tilde{\Omega}] = \frac{\bar{w}_{k\ell}}{2} \quad \text{dissipative}
\]

\[
\text{Re}[\tilde{\Omega}] = \frac{-E'_\ell}{\hbar} \quad \text{dispersive}
\]

\[
P_\ell = |c_\ell|^2 = \exp[-\bar{w}_{k\ell}t]
\]

Probability decays exponentially from initial state.
Fermi’s Golden Rule rate tells you about long times!

What is the probability of appearing in \( |k\rangle \)? Using eqn.

\[
b_k(t) = -\frac{i}{\hbar} \int_0^t V_{k\ell} e^{i\bar{w}_{k\ell} \tau} b_\ell(\tau) \, d\tau
\]

\[
b_k(t) = V_{k\ell} \frac{1 - \exp\left(-\frac{\bar{w}_{k\ell}}{2} t - \frac{i}{\hbar} (E'_\ell - E_k) t\right)}{E_k - E'_\ell + i\hbar \bar{w}_{k\ell} / 2} = V_{k\ell} \frac{1 - c_\ell(t)}{E_k - E'_\ell + i\hbar \bar{w}_{k\ell} / 2}
\]

For long times \( (t \to \infty) \)

\[
P_{k\ell} = \frac{|V_{k\ell}|^2}{(E_k - E'_\ell)^2 + \Gamma^2 / 4}
\]

\[ \Gamma \equiv \bar{w}_{k\ell} \cdot \hbar \]