

IRREVERSIBLE RELAXATION[†]

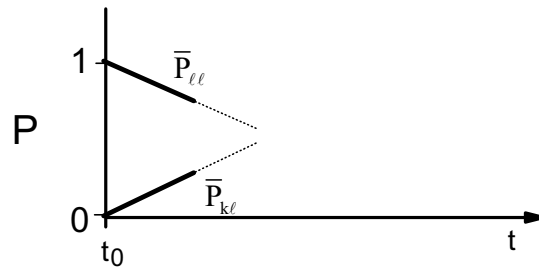
We want to study the relaxation of an initially prepared state. We will show that first-order perturbation theory for transfer to a continuum leads to irreversible transfer—an exponential decay—when you include the depletion of the initial state.

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

$$\bar{w}_{k\ell} = \frac{\partial \bar{P}_{k\ell}}{\partial t} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \rho(E_k = E_\ell)$$

$$\bar{P}_{k\ell} = \bar{w}_{k\ell} (t - t_0)$$

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



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. $b_k(t) \approx b_k(0)$.

So $\bar{w}_{k\ell}$ represents the tangent to the relaxation behavior at $t = 0$.

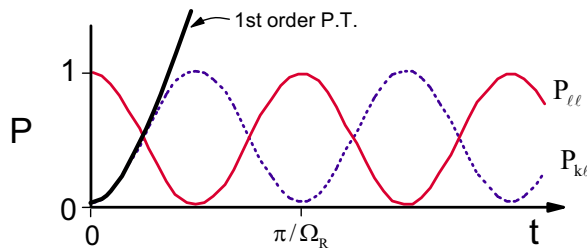
$$\bar{w}_{k\ell} = \left. \frac{\partial \bar{P}_{k\ell}}{\partial t} \right|_{t_0}$$

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

What long-time behavior do we expect?

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:

[†] Cohen-Tannoudji, et al. p. 1344; Merzbacher, p. 510.



$$\Omega_R = \frac{\sqrt{\Delta^2 + V_{k\ell}^2}}{\hbar}$$

But we don't have a two-state system. Rather, we are relaxing to a continuum.

Fermi's Golden Rule says we have a time-independent rate, $\bar{w}_{k\ell}$. Statistically, for relaxation from an initial state, including depletion of the initial state, a constant rate implies exponential decay:

$$P_{\ell\ell}(t + dt) = P_{\ell\ell}(t)[1 - \bar{w}_{k\ell} dt]$$

$$\frac{\partial P_{\ell\ell}}{\partial t} = \frac{P_{\ell\ell}(t + dt) - P_{\ell\ell}(t)}{dt} = -P_{\ell\ell}(t) \bar{w}_{k\ell}$$

$$P_{\ell\ell}(t) = \exp[-\bar{w}_{k\ell} t]$$

$$P_{\ell\ell}(0) = 1$$

You get exponential decay with some big assumptions:

Irreversible decay: the system never returns to its initial state—no feedback as in two-level system

History independent of initial state: whether or not the initial state is occupied does not influence future development

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 $\{|k\rangle\}$ from an initial state $|\ell\rangle$ —under constant perturbation.

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

We want a more accurate description of:

$$b_k(t) = \langle k | U_I(t, t_0) | \ell \rangle$$

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...

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

↑ insert $\sum_n |n\rangle\langle n|$

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

Here V_{kn} is not a function of time

or in its differential form:

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

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: $\langle k | V | k' \rangle = 0$.

So we can remove summation, and express the complex amplitude of a continuum state as

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

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

$$i\hbar \frac{\partial}{\partial t} b_\ell = \sum_{k \neq \ell} e^{i\omega_k t} V_{\ell k} b_k + V_{\ell \ell} b_\ell \quad (3)$$

Substitute (2) into (3), and setting $t_0 = 0$:

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

This is an integro-differential equation: the time-development of b_ℓ 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_ℓ varies slowly relative to $\omega_{k\ell}$, so we can remove it from integral.

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

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 $t' = \tau - t$ $dt' = d\tau$

$$\int_0^t e^{i\omega_{k\ell}(\tau-t)} d\tau = \int_0^t e^{i\omega_{k\ell}t'} dt'$$

Note on integral: $\lim_{T \rightarrow \infty} \int_0^T e^{+i\omega t'} dt'$ (purely oscillatory / not well behaved)

Instead integrate $\int_0^\infty e^{(i\omega + \epsilon)t'} dt'$ take $\epsilon \rightarrow 0$

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

Cauchy Principle Part: $\mathbb{P} \frac{1}{x} = \begin{cases} \frac{1}{x} & x \neq 0 \\ 0 & x = 0 \end{cases}$

$$\frac{\partial b_\ell}{\partial t} = b_\ell \left[\underbrace{-\frac{\pi}{\hbar^2} \sum_{k \neq \ell} |V_{k\ell}|^2 \delta(\omega_{k\ell})}_{\text{term 1}} - \frac{i}{\hbar} \left(V_{\ell\ell} + \underbrace{\mathbb{P} \sum_{k \neq \ell} \frac{|V_{k\ell}|^2}{E_k - E_\ell}}_{\text{term 2}} \right) \right]$$

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

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

Term 2 is just the correction of the energy of E_ℓ from second-order time-independent perturbation theory, ΔE_ℓ .

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

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, $c_\ell = b_\ell e^{-i\omega_\ell t}$

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

We expect solutions to the T.D.S.E. to be complex and oscillatory:

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

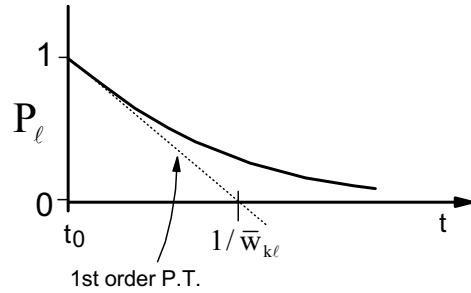
$$\text{Im}[\tilde{\Omega}] = \frac{\bar{w}_{k\ell}}{2} \quad \text{dissipative}$$

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

$E'_\ell \equiv E_\ell + \Delta E$

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

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. 2:

$$b_k(t) = -\frac{i}{\hbar} \int_0^t V_{k\ell} e^{i\omega_{k\ell}\tau} b_\ell(\tau) d\tau$$

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

↖
Final state resonant with shifted initial states.

For long times ($t \rightarrow \infty$)

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

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

