3. IRREVERSIBLE RELAXATION[1]

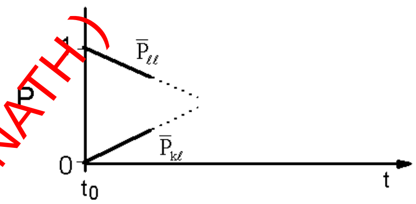
It may not seem clear how irreversible behavior arises from the deterministic TDSE, although this is a hallmark of all chemical systems. To show how this comes about, we will describe the relaxation of an initially prepared state as a result of coupling to a continuum. We will show that first-order perturbation 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 as:

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

$$\overline{P}_{k\ell} = \overline{w}_{k\ell}\left(t - t_0\right) \tag{3.1}$$

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



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:

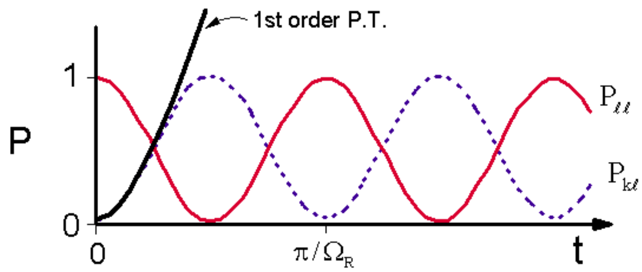
$$\begin{aligned} \overline{P}_{\ell\ell}(t) &= \overline{P}_{\ell\ell}(0)\exp\left(-\overline{w}_{k\ell} t\right) \\ &= 1 - \overline{w}_{k\ell} t + \cdots \end{aligned} \tag{3.2}$$

So we might believe that $\overline{w}_{k\ell}$ represents the tangent to the relaxation behavior at $t = 0$.

$$\overline{w}_{k\ell} = \left.\frac{\partial \overline{P}_{k\ell}}{\partial t}\right|_{t_0} \tag{3.3}$$

The problem we had previously was we don't account for depletion of initial state.

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:



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

But we don't have a two-state system. Rather, we are relaxing to a continuum. 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 intital 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 $\{|k\rangle\}$ from an initial state $|\ell\rangle$ under constant perturbation. These form a complete set; so for $H(t) = H_0 + V(t)$ with $H_0|n\rangle = E_n|n\rangle$.

$$1 = \sum_n |n\rangle\langle n| = \underbrace{|\ell\rangle\langle\ell|}_{\text{initial}} + \underbrace{\sum_k |k\rangle\langle k|}_{\text{continuum}} \tag{3.4}$$

As we go on, you will see that we can identify $|\ell\rangle$ with the "system" and $\{|k\rangle\}$ with the "bath" when we partition $H_0 = H_S + H_B$. We want a more accurate description of the occupation of the initial and continuum states, for which we will use the interaction picture expansion coefficients

$$b_k(t) = \langle k | U_I(t,t_0) | \ell \rangle \tag{3.5}$$

The exact solution to U_I was:

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\, V_I(\tau)\,\underline{U_I(\tau,t_0)} \tag{3.6}$$

For first-order perturbation theory, we set the final term in this equation $U_I(\tau,t_0)\rightarrow 1$. Here we keep it as is.

$$b_k(t) = \langle k|\ell\rangle - \tfrac{i}{\hbar}\int_{t_0}^{t} d\tau \,\langle k|V_I(\tau)\,U_I(\tau,t_0)|\ell\rangle \tag{3.7}$$

Inserting the projection operator $\sum_n |n\rangle\langle n| = 1$, and recognizing $k \neq l$,

$$b_k(t) = -\frac{i}{\hbar}\sum_n \int_{t_0}^{t} d\tau \; e^{i\omega_{kn}\tau}\, V_{kn}\, b_n(\tau) \tag{3.8}$$

Note, here V_{kn} is not a function of time. Equation (3.8) expresses the occupation of state k in terms of the full history of the system from $t_0 \rightarrow t$ with amplitude flowing back and forth between the states n. Equation (3.8) is just the integral form of the coupled differential equations, that we used before:

$$i\hbar\frac{\partial b_k}{\partial t} = \sum_n e^{i\omega_{kn}t}\, V_{kn}\, b_n(t) \tag{3.9}$$

These exact forms allow for feedback between all the states, in which the amplitudes b_k depend on all other states.

Now let's make some simplifying assumptions. For transitions into the continuum, let's <u>assume</u> that transitions in the continuum only occur from the initial state. That is, there are no interactions between the states of the continuum: $\langle k|V|k'\rangle = 0$. This can be rationalized by thinking of this problem as a discrete set of states interacting with a continuum of normal modes. Moreover we will assume that the coupling of the initial to continuum states is a constant for all states k: $\langle \ell|V|k\rangle = \langle \ell|V|k'\rangle = \text{constant}$.

So since you only feed from $|\ell\rangle$ into $|k\rangle$, we can remove the summation in (3.8) and express the complex amplitude of a state within the continuum as

$$b_k = -\tfrac{i}{\hbar}V_{k\ell}\int_{t_0}^{t} d\tau \; e^{i\omega_{k\ell}\tau}\; b_\ell(\tau) \tag{3.10}$$

We want to calculate the rate of leaving $|\ell\rangle$, including feeding from continuum back into initial state. From eq. (3.9) we can separate terms involving the continuum and the initial state:

$$i\hbar \frac{\partial}{\partial t} b_\ell = \sum_{k \neq \ell} e^{i\omega_{\ell k} t} V_{\ell k}\, b_k + V_{\ell\ell}\, b_\ell \tag{3.11}$$

Now substituting (3.10) into (3.11), and setting $t_0 = 0$:

$$\frac{\partial b_\ell}{\partial t} = -\frac{1}{\hbar^2} \sum_{k \neq \ell} \left| V_{k\ell} \right|^2 \int_0^t b_\ell(\tau)\, e^{i\omega_{k\ell}(\tau - t)}\, d\tau - \frac{i}{\hbar} V_{\ell\ell}\, b_\ell(t) \tag{3.12}$$

This is an integro-differential equation that describes how the time-development of b_ℓ depends on entire history of the system. Note we have two time variables for the two propagation routes:

$$\begin{aligned} \tau &: \ |\ell\rangle \rightarrow |k\rangle \\ t &: \ |k\rangle \rightarrow |\ell\rangle \end{aligned} \tag{3.13}$$

The next assumption is that b_ℓ varies slowly relative to $\omega_{k\ell}$, so we can remove it from integral. This is effectively a weak coupling statement: $\hbar\omega_{k\ell} >> V_{k\ell}$. b is a function of time, but since it is in the interaction picture it evolves slowly compared to the $\omega_{k\ell}$ oscillations in the integral.

$$\frac{\partial b_\ell}{\partial t} = b_\ell \left[-\frac{1}{\hbar^2} \sum_{k \neq \ell} \left| V_{k\ell} \right|^2 \int_0^t e^{i\omega_{k\ell}(\tau - t)}\, d\tau - \frac{i}{\hbar} V_{\ell\ell} \right] \tag{3.14}$$

Now, we want the long time evolution of b, for times $t >> \frac{1}{\omega_{k\ell}}$, we will investigate the integration limit $t \rightarrow \infty$.

Complex integration of (3.14): Defining $t' = \tau - t \quad dt' = d\tau$

$$\int_0^t e^{i\omega_{k\ell}(\tau - t)}\, d\tau = \int_0^t e^{i\omega_{k\ell} t'} dt' \tag{3.15}$$

The integral $\lim_{T \rightarrow \infty} \int_0^T e^{+i\omega t'} dt'$ is purely oscillatory and not well behaved. The strategy to solve this is to integrate:

$$\lim_{\varepsilon\to 0^+}\int_0^\infty e^{(i\omega+\varepsilon)t'}\,dt' = \lim_{\varepsilon\to 0^+}\frac{1}{i\omega+\varepsilon}$$
$$= \lim_{\varepsilon\to 0^+}\left(\frac{\varepsilon}{\omega^2+\varepsilon^2}+i\frac{\omega}{\omega^2+\varepsilon^2}\right) \tag{3.16}$$
$$\Rightarrow \quad +\pi\delta(\omega) - i\mathbb{P}\frac{1}{\omega}$$

In the final term we have used the Cauchy Principle Part:

$$\mathbb{P}\left(\frac{1}{x}\right) = \begin{cases} \frac{1}{x} & x \neq 0 \\ 0 & x = 0 \end{cases} \tag{3.17}$$

This leads to

$$\frac{\partial b_\ell}{\partial t} = b_\ell\left[\underbrace{-\frac{\pi}{\hbar^2}\sum_{k\neq\ell}\left|V_{k\ell}\right|^2\delta\left(\omega_{k\ell}\right)}_{term\,1}\underbrace{-\frac{i}{\hbar}\left(V_{\ell\ell}+\mathbb{P}\sum_{k\neq\ell}\frac{\left|V_{k\ell}\right|^2}{E_k-E_\ell}\right)}_{term\,2}\right] \tag{3.18}$$

Term 1 is just the Golden Rule rate, written explicitly as a sum over continuum states instead of an integral

$$\sum_{k\neq\ell}\frac{\delta\left(\omega_{k\ell}\right)}{\hbar} \Rightarrow \rho\left(E_k = E_\ell\right) \tag{3.19}$$

$$\overline{w}_{k\ell} = \int dE_k\;\rho\left(E_k\right)\left[\frac{2\pi}{\hbar}\left|V_{k\ell}\right|^2\delta\left(E_k - E_\ell\right)\right] \tag{3.20}$$

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

$$\Delta E_\ell = \langle \ell | V | \ell \rangle + \sum_{k\neq\ell}\frac{\left|\langle k | V | \ell \rangle\right|^2}{E_k - E_\ell} \tag{3.21}$$

So, the time evolution of b_ℓ is governed by a simple first-order differential equation

$$\frac{\partial b_\ell}{\partial t} = b_\ell\left(-\frac{\overline{w}_{k\ell}}{2} - \tfrac{i}{\hbar}\Delta E_\ell\right) \tag{3.22}$$

Which can be solved with $b_\ell(0)=1$ to give

$$b_\ell(t)=\exp\left(-\frac{\overline{w}_{k\ell}t}{2}-\tfrac{i}{\hbar}\Delta E_\ell\, t\right) \tag{3.23}$$

We see that one has exponential decay of amplitude of b_ℓ! This is a manner of irreversible relaxation from coupling to the continuum.

Switching back to Schrödinger Picture, $c_\ell = b_\ell e^{-i\omega_\ell t}$, we find

$$c_\ell(t)=\exp\left[-\left(\frac{\overline{w}_{k\ell}}{2}+i\frac{E'_\ell}{\hbar}\right)t\right] \tag{3.24}$$

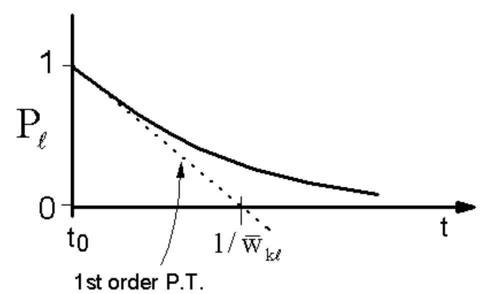
with the corrected energy

$$E'_\ell \equiv E_\ell + \Delta E \tag{3.25}$$

and

$$P_\ell = \left|c_\ell\right|^2 = \exp\left[-\overline{w}_{k\ell}\, t\right]. \tag{3.26}$$

The solutions to the TDSE are expected to be complex and oscillatory. What we see here is a real dissipative component and an imaginary dispersive component. The probability decays exponentially from initial state. Fermi's Golden Rule rate tells you about long times!



Now, what is the probability of appearing in any of the states $|k\rangle$? Using eqn.(3.10):

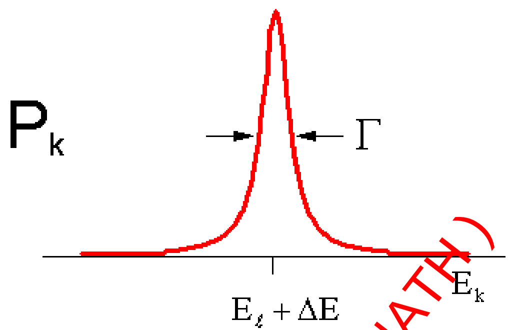
$$\begin{aligned} b_k(t) &= -\frac{i}{\hbar}\int_0^t V_{k\ell}\, e^{i\omega_{k\ell}\tau}\, b_\ell(\tau)\, d\tau \\ &= V_{k\ell}\, \frac{1-\exp\left(-\frac{\overline{w}_{k\ell}}{2}t-\tfrac{i}{\hbar}\left(E'_\ell - E_k\right)t\right)}{E_k - E'_\ell + i\hbar\overline{w}_{k\ell}/2} \\ &= V_{k\ell}\, \frac{1-c_\ell(t)}{E_k - E'_\ell + i\hbar\overline{w}_{k\ell}/2} \end{aligned} \tag{3.27}$$

If we investigate the long time limit $(t\to\infty)$ we find

$$P_{k\ell} = \frac{\left|V_{k\ell}\right|^2}{\left(E_k - E'_\ell\right)^2 + \Gamma^2/4} \tag{3.28}$$

with $$\Gamma \equiv \overline{w}_{k\ell} \cdot \hbar \qquad (3.29)$$

The probability distribution for occupying states within the continuum is described by a Lorentzian distribution with a width given by the relaxation rate. Note that the final states with maximum probability of being occupied is centered at the corrected energy of the initial state E'_ℓ .



Readings

1. Cohen-Tannoudji, C., Diu, B. & Laloë, F. *Quantum Mechanics* (Wiley-Interscience, Paris, 1977) p. 1344; Merzbacher, E. *Quantum Mechanics*, 3rd ed. (Wiley, New York, 1998), p. 510.
2. Nitzan, A. *Chemical Dynamics in Condensed Phases* (Oxford University Press, New York, 2006), p. 305.