**Second-Order Time-Dependent Perturbation Theory**

Let us consider the extension of time-dependent perturbation theory to second order in the interaction $H_1(t)$. The starting point is the set of differential equations

$$i\hbar \frac{da_n^{(j+1)}(t)}{dt} = \sum_m \langle n|H_1(t)|m\rangle e^{i\omega_{nm}t} a_m^{(j)}(t), \quad j = 0, 1, 2, \ldots \tag{1}$$

If we assume that the system starts at time $t = t_0$ in an unperturbed stationary state $|i\rangle$, then for any $t \geq t_0$,

$$a_n^{(0)}(t) = \delta_{n,i}, \tag{2}$$

$$a_n^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^{t} dt' \langle n|H_1(t')|i\rangle e^{i\omega_{ni}t'}, \tag{3}$$

$$a_n^{(2)}(t) = -\frac{i}{\hbar} \sum_m \int_{t_0}^{t} dt' \langle n|H_1(t')|m\rangle e^{i\omega_{nm}t'} a_m^{(1)}(t'). \tag{4}$$

We will study the behavior of $a_n^{(2)}(t)$ for three different time dependences of $H_1(t)$.

**Sudden perturbation.** Suppose that the perturbation turns on suddenly at time $t = t_0 = 0$, and is constant thereafter:

$$H_1(t) = \tilde{H}\theta(t), \tag{5}$$

where $\tilde{H}$ contains no time dependence. One can prove by integrating the Schrödinger equation that, unless $H(t)$ contains a delta function $\delta(t)$, $|\psi(t = 0^+)\rangle = |\psi(t = 0^-)\rangle$, i.e., an instantaneous change in $H$ produces no instantaneous change in $|\psi\rangle$.

In this case, Eqs. (2)–(4) can be used to study the transient effects of the abrupt change in the Hamiltonian. Introducing the shorthand $\tilde{H}_{nm} = \langle n|\tilde{H}|m\rangle$,

$$a_n^{(1)}(t) = \tilde{H}_{ni} \frac{1 - e^{i\omega_{ni}t}}{\hbar\omega_{ni}} \xrightarrow{\omega_{ni}=0} -i\tilde{H}_{ni}\, t/\hbar, \tag{6}$$

$$a_n^{(2)}(t) = \sum_{m|\omega_{mi}\neq 0} \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2\omega_{mi}} \left( \frac{1 - e^{i\omega_{nm}t}}{\omega_{nm}} - \frac{1 - e^{i\omega_{ni}t}}{\omega_{ni}} \right) + \sum_{m|\omega_{mi}=0} \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2\omega_{ni}} \left( \frac{1 - e^{i\omega_{ni}t}}{\omega_{ni}} + ite^{i\omega_{ni}t} \right). \tag{7}$$

Care must be taken in Eq. (7) when any of the frequency denominators vanishes. For instance, if $\omega_{ni} = 0$, the second summand must be replaced by $-\frac{1}{2}\tilde{H}_{nm}\tilde{H}_{mi}\,(t/\hbar)^2$.

Equation (7) shows that $a_n^{(2)}(t)$ can be nonzero even if $\tilde{H}_{ni} = 0$ and $a_n^{(1)}(t) = 0$; the system can "get from $|i\rangle$ to $|n\rangle$" (i.e., acquire a nonzero amplitude $a_n$) through a pair of "virtual" (energy non-conserving) transitions—the first from $|i\rangle$ to an intermediate state $|m\rangle$, the second from $|m\rangle$ to $|n\rangle$. In the limit $t \to \infty$, the transition rate from $|i\rangle$ to $|n\rangle$ can be nonzero due to the vanishing of any frequency denominator in Eq. (7). If

$\omega_{ni} = 0$, the combination of virtual transitions conserves energy overall. If $\omega_{mi} = 0$ or $\omega_{nm} = 0$ but $\omega_{ni} \neq 0$, a virtual transition is combined with a "real" (energy-conserving) transition, such that energy is not conserved overall.

Even more complicated transitions, involving multiple intermediate states, are possible at higher orders in $H_1$.

One can repeat the above for the sudden turn-on of a harmonic perturbation. Although $a_n^{(2)}(t)$ contains many more terms, virtual transitions again feature.

**Adiabatic perturbation.** Now suppose instead that a perturbation turns on very slowly, starting at $t = t_0 = -\infty$, according to

$$H_1(t) = \tilde{H} e^{\eta t}, \tag{8}$$

where $\tilde{H}$ is again time-independent, and the turn-on rate $\eta$ is a small, positive real number. In this case,

$$a_n^{(1)}(t) = -\frac{i}{\hbar}\tilde{H}_{ni}\int_{-\infty}^{t} dt'\; e^{i(\omega_{ni}-i\eta)t'} = -\tilde{H}_{ni}\frac{e^{i(\omega_{ni}-i\eta)t}}{\hbar(\omega_{ni}-i\eta)}, \tag{9}$$

and

$$\begin{aligned} a_n^{(2)}(t) &= \frac{i}{\hbar}\sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar(\omega_{mi}-i\eta)}\int_{-\infty}^{t} dt'\; e^{i(\omega_{ni}-2i\eta)t'} \\ &= \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2(\omega_{ni}-2i\eta)(\omega_{mi}-i\eta)} e^{i(\omega_{ni}-2i\eta)t}. \end{aligned} \tag{10}$$

This implies that

$$|\psi(t)\rangle = e^{-i\varepsilon_i t/\hbar}\sum_n \left(\delta_{n,i} - \frac{\tilde{H}_{ni}e^{\eta t}}{\hbar(\omega_{ni}-i\eta)} + \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}e^{2\eta t}}{\hbar^2(\omega_{ni}-2i\eta)(\omega_{mi}-i\eta)}\right)|n\rangle + \ldots \tag{11}$$

Here and below, the terms "..." are of third order or higher in $H_1$.

Within *time-independent* perturbation theory, the effect of a perturbation $H_1 = \tilde{H} \equiv H_1(t=0)$ is to convert the stationary state $|n\rangle$ into

$$|\psi_n\rangle = |n\rangle + \sum_{m\neq n}\left(-\frac{\tilde{H}_{mn}}{\hbar\omega_{mn}} - \frac{\tilde{H}_{mn}\tilde{H}_{nn}}{\hbar^2\omega_{mn}^2} + \sum_{k\neq n}\frac{\tilde{H}_{mk}\tilde{H}_{kn}}{\hbar^2\omega_{mn}\omega_{kn}}\right)|m\rangle + \ldots \tag{12}$$

Thus, for any $n \neq i$,

$$\begin{aligned} \langle\psi_n|\psi(0)\rangle &= -\frac{\tilde{H}_{ni}}{\hbar(\omega_{ni}-i\eta)} + \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2(\omega_{ni}-2i\eta)(\omega_{mi}-i\eta)} - \frac{\tilde{H}^*_{in}}{\hbar\omega_{in}} \\ &\quad + \sum_{m\neq n}\frac{\tilde{H}^*_{mn}\tilde{H}_{mi}}{\hbar^2\omega_{mn}(\omega_{mi}-i\eta)} - \frac{\tilde{H}^*_{in}\tilde{H}_{nn}}{\hbar^2\omega_{in}^2} + \sum_{m\neq n}\frac{\tilde{H}^*_{im}\tilde{H}^*_{mi}}{\hbar^2\omega_{in}\omega_{mn}} + \ldots \end{aligned} \tag{13}$$

With a little bit of algebra, one can show that in the adiabatic limit, described by an infinitesimal turn-on rate $\eta \to 0^+$, the first- and second-order terms on the right-hand-side of Eq. (13) all cancel, implying that (up to possible third-order corrections)

$$|\langle\psi_i|\psi(t)\rangle|^2 = 1. \tag{14}$$

Equation (14) turns out to be an *exact* result, which leads to ...

*The adiabatic theorem:* Up to an overall phase, any eigenstate $|n(H_0)\rangle$ of an initial Hamiltonian $H_0$ evolves smoothly under an adiabatic perturbation into the corresponding eigenstate $|n(H)\rangle$ of the Hamiltonian $H(t) = H_0 + H_1(t)$.

**Constant perturbation and level decay.** The limit $\eta \to 0^+$ of the slow onset describes a perturbation that is constant in time. This type of perturbation might describe the effect of some background interaction which has been left out of the Hamiltonian $H_0$. (An example is the effect of gravity on the hydrogen atom.)

Let us examine the effect of such a background interaction on the initial state $|i\rangle$. Specializing Eqs. (2), (9), and (10) to the case $n = i$ (keeping $\eta$ finite for now),

$$a_i(t) = 1 - \frac{i}{\hbar}\tilde{H}_{ii}\frac{e^{\eta t}}{\eta} + \frac{i}{\hbar^2}\sum_m \frac{|\tilde{H}_{mi}|^2}{\omega_{mi} - i\eta}\frac{e^{2\eta t}}{2\eta} + \dots \tag{15}$$

Hence

$$\frac{da_i(t)}{dt} = -\frac{i}{\hbar}\tilde{H}_{ii}e^{\eta t} + \frac{i}{\hbar^2}\sum_m \frac{|\tilde{H}_{mi}|^2}{\omega_{mi} - i\eta}e^{2\eta t} + \dots \tag{16}$$

and

$$\frac{1}{a_i(t)}\frac{da_i(t)}{dt} = -\frac{i}{\hbar}\tilde{H}_{ii}e^{\eta t} + \frac{i}{\hbar^2}\sum_m \frac{|\tilde{H}_{mi}|^2}{\omega_{mi} - i\eta}e^{2\eta t} + \left(\frac{i}{\hbar}\tilde{H}_{ii}\frac{e^{\eta t}}{\eta}\right)\left(-\frac{i}{\hbar}\tilde{H}_{ii}e^{\eta t}\right) + \dots \tag{17}$$

or

$$\frac{d\ln a_i(t)}{dt} = -\frac{i}{\hbar}\tilde{H}_{ii}e^{\eta t} + \frac{i}{\hbar^2}\sum_{m\neq i} \frac{|\tilde{H}_{mi}|^2}{\omega_{mi} - i\eta}e^{2\eta t} + \dots \tag{18}$$

Now let us take the constant-perturbation limit $\eta \to 0^+$. Recalling that

$$\lim_{\eta\to 0^+} \frac{1}{\omega \pm i\eta} = P\left(\frac{1}{\omega}\right) \mp i\pi\delta(\omega), \tag{19}$$

where $P$ is the Cauchy principal part, we find

$$\frac{d\ln a_i(t)}{dt} = -i\Sigma_i/\hbar. \tag{20}$$

Here,

$$\Sigma_i = \tilde{H}_{ii} - P\sum_{m\neq i}\frac{|\tilde{H}_{mi}|^2}{\varepsilon_m - \varepsilon_i} - i\pi\sum_{m\neq i}|\tilde{H}_{mi}|^2\delta(\varepsilon_m - \varepsilon_i) \equiv \Delta E_i - i\hbar/2\tau_i \tag{21}$$

is the (time-independent) *self-energy*, which has a real part

$$\Delta E_i = \mathrm{Re}\,\Sigma_i = \tilde{H}_{ii} - P\sum_{m\neq i}\frac{|\tilde{H}_{mi}|^2}{\varepsilon_m - \varepsilon_i}, \tag{22}$$

and an imaginary part

$$-\frac{\hbar}{2\tau_i} = \pi\sum_{m\neq i}|\tilde{H}_{mi}|^2\delta(\varepsilon_m - \varepsilon_i). \tag{23}$$

Equation (20) implies that

$$a_i(t) = a_i(0)e^{-i\Sigma_i t/\hbar},$$

or

$$c_i(t) = \langle i|\psi(t)\rangle = c_i(0)\, e^{-i(\varepsilon_i+\Delta E_i)t/\hbar}\, e^{-t/2\tau_i}. \tag{24}$$

The real part of $\Sigma_i$ shifts the effective eigenenergy entering the phase evolution of $c_i(t)$ from $\varepsilon_i$ to $\varepsilon_i + \Delta E_i$. The imaginary part of $\Sigma_i$ affects the magnitude of $c_i(t)$, causing the occupation probability to decay as

$$|c_i(t)|^2 = |c_i(0)|^2 e^{-t/\tau_i}. \tag{25}$$

Note, from Eq. (21), that the decay rate (inverse lifetime)

$$\tau_i^{-1} = \frac{2\pi}{\hbar}\sum_{m\neq i} |\tilde{H}_{mi}|^2 \delta(\varepsilon_m - \varepsilon_i) \tag{26}$$

is just the total Golden-rule scattering rate out of state $i$.

It is also of interest to replace the time-independent $\tilde{H}$ in Eq. (8) by $\tilde{H}e^{-i\omega t} + \tilde{H}^\dagger e^{i\omega t}$. Within the rotating-wave approximation, the results of this section still hold with $\omega_{mi} \to \omega_{mi} \pm \omega$ and $\varepsilon_m - \varepsilon_i \to \varepsilon_m - \varepsilon_i \pm \hbar\omega$.

**Spectral broadening due to a background perturbation.** Suppose that we regard the constant perturbation $H_1$ from the previous section as a background perturbation, and consider the effect of another perturbation $H_2(t)$ applied only for $t > 0$. For simplicity, let us assume that $H_2(t)$ has no time dependence for $t > 0$, i.e.,

$$H_2(t) = \hat{H}\theta(t), \tag{27}$$

and consider transitions from an initial state $|i\rangle$ to a stable final state $|f\rangle$. Writing $a_i^{(0)}(t) = \exp(-i\Sigma_i t/\hbar)$ to account for the background perturbation $H_1$, we can find the transition amplitude due to $H_2$:

$$a_f^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt' \langle f|H_2(t')|i\rangle e^{i(\omega_{fi}-\Sigma_i/\hbar)t'} = \langle f|\hat{H}|i\rangle\, \frac{1 - e^{i(\omega_{fi}-\Sigma_i/\hbar)t}}{\hbar\omega_{fi} - \Sigma_i}. \tag{28}$$

Comparing the corresponding transition probability,

$$|a_f^{(1)}(t)|^2 = |\langle f|\hat{H}|i\rangle|^2\, \frac{1 - 2e^{-t/2\tau_i}\cos\left[(\varepsilon_f - \varepsilon_i - \Delta E_i)t/\hbar\right] + e^{-t/\tau_i}}{(\varepsilon_f - \varepsilon_i - \Delta E_i)^2 + (\hbar/2\tau_i)^2} \tag{29}$$

$$\xrightarrow{t\gg\tau_i} \frac{|\langle f|\hat{H}|i\rangle|^2}{(\varepsilon_f - \varepsilon_i - \Delta E_i)^2 + (\hbar/2\tau_i)^2}, \tag{30}$$

with the result obtained for $H_1 = 0$,

$$|a_f^{(1)}(t)|^2 = |\langle f|\hat{H}|i\rangle|^2 \left[\frac{\sin(\omega_{fi}t/2)}{\hbar\omega_{fi}/2}\right]^2 \xrightarrow{t\to\infty} \frac{2\pi t}{\hbar}|\langle f|\hat{H}|i\rangle|^2 \delta(\varepsilon_f - \varepsilon_i), \tag{31}$$

reveals two consequences of the background perturbation: (1) The transition probability saturates at long times, instead of increasing linearly. (2) The distribution of accessible final-state energies broadens from a delta function $\delta(\varepsilon_f - \varepsilon_i)$ into a Lorentzian

$$P(\varepsilon_f) = \frac{1}{\pi}\frac{\hbar/2\tau_i}{(\varepsilon_f - \varepsilon_i - \Delta E_i)^2 + (\hbar/2\tau_i)^2}. \tag{32}$$