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 $t \geq t_0$,

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

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

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

The properties of $a_n^{(2)}(t)$ can best be understood by considering several different time dependences of $H_1(t)$.

Sudden perturbation. Suppose that a 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. In this case, Eqs. (2)–(4) can be used to study the transient effects of the abrupt change in the Hamiltonian. One finds

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

$$\begin{aligned} a_n^{(2)}(t) &= -\frac{i}{\hbar} \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar\omega_{mi}} \int_0^t dt' \left(e^{i\omega_{nm}t'} - e^{i\omega_{ni}t'} \right) \\ &= -\sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2\omega_{mi}} \left(\frac{1 - e^{i\omega_{ni}t}}{\omega_{ni}} - \frac{1 - e^{i\omega_{nm}t}}{\omega_{nm}} \right), \end{aligned} \tag{7}$$

where $\tilde{H}_{nm} = \langle n|\tilde{H}|m\rangle$.

The most notable aspect of Eq. (4) is that $a_n^{(2)}(t)$ can be nonzero even if $\tilde{H}_{ni} = 0$ and, hence, $a_n^{(1)}(t) = 0$. In effect, the system can get from $|i\rangle$ to $|f\rangle$ 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 $|f\rangle$. 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 η 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

$$\begin{aligned} a_n^{(2)}(t) &= \frac{i}{\hbar}\sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar(\omega_{mi}-i\eta)}\int_{-\infty}^{t} dt'\ e^{i(\omega_{ni}-2i\eta)t'} \\ &= \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2(\omega_{ni}-i2\eta)(\omega_{mi}-i\eta)} e^{i(\omega_{ni}-2i\eta)t}. \end{aligned} \tag{10}$$

This implies that

$$|\psi(t)\rangle = e^{-i\varepsilon_i t/\hbar}\sum_n \left(\delta_{n,i} - \frac{\tilde{H}_{ni}e^{\eta t}}{\hbar(\omega_{ni}-i\eta)} + \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}e^{2\eta t}}{\hbar^2(\omega_{ni}-i2\eta)(\omega_{mi}-i\eta)}\right)|n\rangle + \dots \tag{11}$$

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

Within *time-independent* perturbation theory, the effect of $\tilde{H}_1 \equiv H_1(t=0)$ is to convert the stationary state $|n\rangle$ into

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

Thus, for any $n \neq i$,

$$\begin{aligned} \langle\psi_n|\psi(0)\rangle &= -\frac{\tilde{H}_{ni}}{\hbar(\omega_{ni}-i\eta)} + \sum_m \frac{\tilde{H}_{nm}\tilde{H}_{mi}}{\hbar^2(\omega_{ni}-i2\eta)(\omega_{mi}-i\eta)} - \frac{\tilde{H}_{in}^*}{\hbar\omega_{in}} \\ &\quad + \sum_{m\neq n}\frac{\tilde{H}_{mn}^*\tilde{H}_{mi}}{\hbar^2\omega_{mn}(\omega_{mi}-i\eta)} - \frac{\tilde{H}_{in}^*\tilde{H}_{nn}}{\hbar^2\omega_{in}^2} + \sum_{m\neq n}\frac{\tilde{H}_{im}^*\tilde{H}_{mi}^*}{\hbar^2\omega_{in}\omega_{mn}} + \dots \end{aligned} \tag{13}$$

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 η finite for now),

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

Hence

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

and

$$\frac{d\ln a_i(t)}{dt} = \frac{1}{a_i(t)}\frac{da_i(t)}{dt} = -\frac{i}{h}\tilde{H}_{ii}e^{\eta t} + \frac{i}{\hbar^2}\sum_{m\neq i} \frac{|\tilde{H}_{mi}|^2}{\omega_{mi} - i\eta}e^{2\eta t} + \dots \tag{17}$$

Now let us take the limit of a constant perturbation. Recalling that

$$\lim_{\eta\to 0^+}\frac{1}{\omega - i\eta} = P\left(\frac{1}{\omega}\right) + i\pi\delta(\omega), \tag{18}$$

where P is the Cauchy principal part, we find

$$\frac{d\ln a_i(t)}{dt} = -\frac{i}{h}\Sigma_i, \tag{19}$$

where the (time-independent) *self-energy*, or complex energy shift, is

$$\Sigma_i = \tilde{H}_{ii} - P\sum_{m\neq i}\frac{|\tilde{H}_{mi}|^2}{\varepsilon_m - \varepsilon_i} - i\pi\sum_{m\neq i}|\tilde{H}_{mi}|^2\delta(\varepsilon_m - \varepsilon_i). \tag{20}$$

Equation (19) implies that

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

or

$$c_i(t) = \langle i|\psi(t)\rangle = c_i(0)\, e^{-i(\varepsilon_i + \mathrm{Re}\,\Sigma_i)t/\hbar}\, e^{\mathrm{Im}\,\Sigma_i\, t/\hbar}. \tag{21}$$

This in turn means that the occupation probability decays in time according to

$$|c_i(t)|^2 = |c_i(0)|^2 e^{-t/\tau_i}, \tag{22}$$

with a decay rate (inverse lifetime)

$$\tau_i^{-1} = -\frac{2}{\hbar}\mathrm{Im}\,\Sigma_i \geq 0. \tag{23}$$