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

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

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

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

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

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

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:

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

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

$$a_n^{(1)}(t) = \tilde{H}_n \frac{1 - e^{i\omega_{nt}}}{\hbar \omega_n}, \quad (6)$$

$$a_n^{(2)}(t) = -\frac{i}{\hbar} \sum_m \tilde{H}_{nm}\tilde{H}_m \int_{t_0}^{t} dt' \left( e^{i\omega_{nm} t'} - e^{i\omega_{nt'} t'} \right)$$

$$= -\sum_m \tilde{H}_{nm}\tilde{H}_m \frac{(1 - e^{i\omega_{nt}})}{\hbar \omega_n} \frac{(1 - e^{i\omega_{nm} t})}{\omega_{nm}}, \quad (7)$$

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 $\tilde{H}_n = 0$ 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

\[
H_1(t) = \tilde{H} e^{i\eta t},
\]

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

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

and

\[
a_n^{(2)}(t) = \frac{i}{\hbar} \sum_m \frac{\tilde{H}_{nm} \tilde{H}_{mi}}{\hbar(\omega_{mi} - i\eta)} \int_{-\infty}^{t} dt' e^{i(\omega_{ni} - 2i\eta)t'}
= \sum_m \frac{\tilde{H}_{nm} \tilde{H}_{mi}}{\hbar^2(\omega_{ni} - i2\eta)(\omega_{mi} - i\eta)} e^{i(\omega_{ni} - 2i\eta)t}.
\]

This implies that

\[
|\psi(t)\rangle = e^{-i\varepsilon t/\hbar} \sum_n \left( \delta_{n,i} - \frac{\tilde{H}_{ni} e^{i\eta t}}{\hbar(\omega_{ni} - i\eta)} + \sum_m \frac{\tilde{H}_{nm} \tilde{H}_{mi} e^{2i\eta t}}{\hbar^2(\omega_{ni} - i2\eta)(\omega_{mi} - i\eta)} \right) |n\rangle + \ldots
\]

Here and below, the terms “...” are of third order or higher in \( H_1 \).

Within time-independent perturbation theory, the effect of \( H_1 \equiv H_1(t = 0) \) is to convert the stationary state \( |n\rangle \) into

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

Thus, for any \( n \neq i \),

\[
\langle \psi_n | \psi(0) \rangle = -\frac{\tilde{H}_{ni}}{\hbar(\omega_{ni} - i\eta)} + \sum_m \frac{\tilde{H}_{nm} \tilde{H}_{mi}}{\hbar^2(\omega_{ni} - i2\eta)(\omega_{mi} - i\eta)} - \frac{\tilde{H}_{in}^*}{\hbar \omega_{in}}
+ \sum_{m \neq n} \frac{\tilde{H}_{mn}^* \tilde{H}_{mi}}{\hbar^2 \omega_{mn}(\omega_{ni} - i\eta)} - \frac{\tilde{H}_{in}^* \tilde{H}_{nn}}{\hbar^2 \omega_{in}^2} + \sum_{m \neq n} \frac{\tilde{H}_{im}^* \tilde{H}_{mi}}{\hbar^2 \omega_{in} \omega_{mn}} + \ldots
\]

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)

\[
|\langle \psi_i | \psi(t) \rangle|^2 = 1.
\]

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),

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

Hence

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

and

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

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

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

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

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

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

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

Equation (19) implies that

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

or

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

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

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

with a decay rate (inverse lifetime)

$$\tau_i^{-1} = -\frac{2}{\hbar} \text{Im} \Sigma_i \geq 0.$$  

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