4 Time-dependent perturbations

In the introductory lecture course on quantum mechanics, we have developed perturbation theory for stationary, i.e. time-independent, problems. A number of important problems, however, involve time-dependent perturbations, such as interacting atoms with light, thereby inducing absorption and emission processes.

4.1 Dyson series

Let us consider systems defined by

$$H(t) = H_0 + V(t) . \tag{4.1}$$

where we assume that H_0 defines a known (soluble) stationary system and $V(t)$ parametrizes a time-dependent perturbation. The exact solution would be provided by the solution to the Schrödinger equation

$$i\hbar \frac{d}{dt} |\Psi, t\rangle = H(t) |\Psi, t\rangle . \tag{4.2}$$

Here, we have chosen the Schrödinger picture where the states evolve in time.

Time-dependent perturbation theory is best formulated in the interaction (or Dirac) picture.

Schematically, the interaction picture arises from the Schrödinger picture by "undoing" the free evolution of the states,

$$|\psi_I, t\rangle = e^{\frac{i}{\hbar}(t-t_0)H_0} |\psi, t\rangle \tag{4.3}$$

with an arbitrary reference time t_0, and evolving the operators with the "free" Hamiltonian,

$$V_I = e^{\frac{i}{\hbar}(t-t_0)H_0} V e^{-\frac{i}{\hbar}(t-t_0)H_0} \tag{4.4}$$

Let us derive the evolution equation for the states in the interaction picture

$$i\hbar \partial_t |\psi_I, t\rangle \overset{(4.3)}{=} e^{\frac{i}{\hbar}(t-t_0)H_0} \left(-H_0 + i\hbar\partial_t\right) |\psi, t\rangle$$

$$\overset{\substack{(4.2)\\(4.1)}}{=} e^{\frac{i}{\hbar}(t-t_0)H_0} \left(-H_0 + H_0 + V\right) |\psi, t\rangle$$

$$= e^{\frac{i}{\hbar}(t-t_0)H_0} V e^{-\frac{i}{\hbar}(t-t_0)H_0} e^{\frac{i}{\hbar}(t-t_0)H_0} |\psi, t\rangle$$

$$= V_I |\psi_I, t\rangle \tag{4.5}$$

The generator of the time-evolution of the interaction-picture states thus is only

the time-dependent interaction part of the Hamiltonian.

In the following, let us assume the perturbation is only switched on during a time interval in between t_i and t_f,

$$V(t) = 0 \qquad \text{for} \quad t \notin [t_i, t_f] \tag{4.6}$$

At very early times, the wave function $|\Psi_I, t\rangle$ is therefore time independent. Starting from a time $t_0 < t_i$, the time evolution is generated by the time evolution in the interaction picture

$$|\Psi_I, t\rangle = U_I(t, t_0)\, |\Psi_I, t_0\rangle \tag{4.7}$$

U_I is unitary and satisfies the standard properties of time evolution operators,

$$U_I^+(t, t_0)\, U_I(t, t_0) = \mathbb{1} \quad , \; U(t_0, t_0) = \mathbb{1}$$

$$\text{and} \quad U_I(t, t_0) = U(t, t_1)\, U(t_1, t_0) \; . \tag{4.8}$$

The corresponding Schrödinger equation for U_I is obviously

$$i\hbar\,\partial_t U_I(t,t_0) = V_I(t)\,U_I(t,t_0). \tag{4.9}$$

It can also be formulated in an integral form using (4.8) as an initial condition:

$$U_I(t,t_0) = \mathbb{1} + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t_1)\,U_I(t_1,t_0)\,dt_1 \tag{4.10}$$

This equation can be iterated, using

$U_I^{(0)}(t,t_0) = \mathbb{1}$ as zeroth-order approximation (which is exact for $t < t_i$). To higher orders, we find

$$U_I^{(1)}(t,t_0) = \mathbb{1} + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t_1)\,dt_1 \tag{4.11}$$

$$U_I^{(2)}(t,t_0) = \mathbb{1} + \frac{1}{i\hbar}\int_{t_0}^{t} V_I(t_1)dt_1 + \left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2\; V_I(t_1)\,V_I(t_2) \tag{4.12}$$

Higher orders can easily be generated in the same fashion. The result can be summarized into

a simple though comparatively formal expression. In order to motivate this expression, let us take a close look at the second-order term:

$$\int_{t_0}^{t} dt_1\, V_I(t_1) \int_{t_0}^{t_1} dt_2\, V_I(t_2) \tag{4.13}$$

$$= \frac{1}{2} \int_{t_0}^{t} dt_1\, V_I(t_1) \int_{t_0}^{t_1} dt_2\, V_I(t_2)$$

$$+ \frac{1}{2} \int_{t_0}^{t} dt_2 V_I(t_2) \int_{t_0}^{t_2} dt_1 V_I(t_1)$$

substitute $(t_1 \leftrightarrow t_2)$ →

$$= \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \Big(\theta(t_1 - t_2)\, V_I(t_1) V_I(t_2) + \theta(t_2 - t_1)\, V_I(t_2) V_I(t_1) \Big)$$

$$=: \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2\, T\big(V_I(t_1)\, V_I(t_2)\big)$$

$$= T\left(\frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2\, V_I(t_1)\, V_I(t_2) \right) \tag{4.14}$$

where we have introduced the time-ordered operator product

$$T\big(A_1(t_1)\, A_2(t_2)\big) = \theta(t_1 - t_2)\, A_1(t_1) A_2(t_2) - \theta(t_2 - t_1) \cdot A_2(t_2) A_1(t_1) \tag{4.15}$$

Time-ordering means the operators at later times are placed to the left of operators at earlier times. This concept generalizes to higher-order products of operators. For $t_n \geq t_{n-1} \geq \dots \geq t_2 \geq t_1$, we get for example

$$T\left(V_I(t_1)\, V_I(t_2) \dots V_I(t_n)\right) = V_I(t_n)\, V_I(t_{n-1}) \dots V_I(t_1) . \tag{4.14}$$

Also the argument leading to (4.14) generalizes to higher orders,

$$\int_{t_0}^{t} dt_1\, V_I(t_1) \int_{t_0}^{t_1} dt_2\, V_I(t_2) \dots \int_{t_0}^{t_{n-1}} dt_n\, V_I(t_n) = \frac{1}{n!}\, T \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \dots \int_{t_0}^{t} dt_n \left(V_I(t_1) \dots V_I(t_n)\right) \tag{4.15}$$

Such that the iteration of $U_I(t,t_0)$ to infinite order yields

$$U(t,t_0) = \lim_{n\to\infty} U^{(n)}(t,t_0) = \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n\, V_I(t_1) \dots V_I(t_n)$$

$$= T \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \frac{1}{n!} \left(\int_{t_0}^{t} dt'\, V_I(t')\right)^n \tag{4.16}$$

This can formally be written as

$$U_I(t,t_0) = T \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t')\right) \qquad (4.17)$$

(4.17) should be viewed as a simple notation for Dyson's series representation (4.16) of the time-evolution operator. It plays an essential role in time-dependent perturbation theory (this section) as well as in scattering theory (next section). For instance, the asymptotic limit of U

$$S := \lim_{\substack{t_0 \to -\infty \\ t \to \infty}} U_I(t,t_0) \qquad (4.18)$$

(if it exists) (and if $S^\dagger S = S S^\dagger = \mathbb{1}$) defines the so called scattering matrix which maps asymptotic states of the distant past to those in the distant future,

$$|\Psi_{OUT}\rangle = S\,|\Psi_{IN}\rangle \tag{4.19}$$

$$\text{where} \quad |\Psi_{IN}\rangle = |\Psi_I, t_0 \to -\infty\rangle$$
$$|\Psi_{OUT}\rangle = |\Psi_I, t \to \infty\rangle \tag{4.20}$$

4.2 First-order transitions and Fermi's golden rule

As a first example, let us study the transition probability and rate for an initial state

$$|\Psi_{I,n}, t_0\rangle = |n\rangle \quad \text{at early times} \quad t_0 < t_i$$

to a final state $|m\rangle$, $m \neq n$, at later times mediated by a time-dependent perturbation.

To first-order in the Dyson series, the transition amplitude is given by

$$A_{n\to m}(t) = \langle m, t | \Psi_{I,n}(t)\rangle$$

$$= \underbrace{\langle m|n\rangle}_{=0 \text{ for } m\neq n} + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 \langle m|V_I(t_1)|n\rangle \tag{4.21}$$

$$\Rightarrow A_{n\to m}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 \langle m| e^{\frac{i}{\hbar}(t_1-t_0)H_0} V(t_1) e^{-\frac{i}{\hbar}(t_1-t_0)H_0} |n\rangle \tag{4.22}$$

Using that $H_0|n\rangle = E_n|n\rangle$, we get

$$A_{n\to m}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 \underbrace{e^{i\frac{E_{mn}}{\hbar}(t_1-t_0)}}_{=: e^{i\omega_{mn}(t_1-t_0)}} V_{mn}(t_1) \tag{4.23}$$

where we have introduced

$$E_{mn} = E_m - E_n = \hbar\omega_{mn} \qquad \text{and} \qquad V_{mn}(t) = \langle m|V(t)|n\rangle \tag{4.24}$$

for the energy differences and the matrix elements of the perturbation operator. We finally obtain for the transition probability at time (t) (starting from time t_0):

$$P_{n\to m}(t) = |\langle m|\psi_{I,n}(t)\rangle|^2 = \left|\frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, e^{i\omega_{mn}t_1} V_{mn}(t_1)\right|^2 \tag{4.25}$$

which contains the Fourier transform of the matrix element.

Let us study this transition probability in two different limits: for a suddenly or adiabatically switched on perturbation. Surprisingly, we will find the same answer in both cases

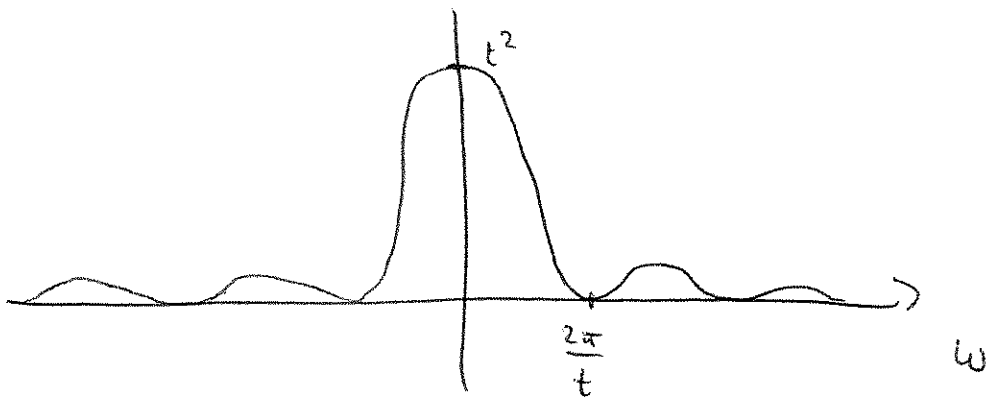
4.2.1 Sudden perturbation

Let $V(t) = \Theta(t)\, V$ with $V = \text{const.}$, i.e. the perturbation is suddenly switched on at $t = 0$. From (4.25), we read off the transition probability,

$$P_{n\to m}(t) = \left| \frac{1}{i\hbar} \int_0^t e^{i\omega_{mn} t'} V_{mn} \right|^2 = \frac{4}{\hbar^2} \frac{\sin^2(\frac{1}{2}\omega_{mn} t)}{\omega_{mn}^2} |V_{mn}|^2 \tag{4.26}$$

The time dependence is encoded in the factor

$$f_t(\omega) = \frac{4 \sin^2 \frac{1}{2}\omega t}{\omega^2} \tag{4.27}$$



For small times or small frequencies, $\omega t \ll 1$, this factor behaves like

$$f_t(\omega) \simeq t^2 + \mathcal{O}((\omega t)^2) \qquad (4.28)$$

As a function of ω, there is a strong peak at $\omega = 0$.

Hence, for large times, only those transitions with $\omega \simeq 0$, i.e. $E_m \approx E_n$, are allowed, more precisely

$$t\,|E_m - E_n| \ll 2\pi\hbar \qquad (4.29)$$

This implies that those transitions are favored for sudden perturbations for which the energy is conserved up to $\frac{2\pi\hbar}{t}$.

As a function of t, $P_{n\to m}(t)$ oscillates if $\omega_{mn} > 0$ (i.e. for a discrete spectrum). The recurrence time is $t \sim \frac{2\pi}{\omega_{mn}}$.

For identical initial and final energies, $\omega_{mn} = 0$, the transition probability increases $\sim t^2$.

If $P_{n\to m}$ becomes large than 1 for some t, this signals the break-down of perturbation theory.

If the system is exposed to a perturbation for a very long time, i.e., $t\to\infty$, we observe that

$$\lim_{t\to\infty}\frac{f_t(\omega)}{t}=\lim_{t\to\infty}\frac{4\sin^2\left(\frac{\omega}{2}t\right)}{\omega^2 t}\to 2\pi\,\delta(\omega). \qquad (4.30)$$

This restricts possible transitions to those between degenerate energy levels,

$$P_{n\to m}=\frac{2\pi t}{\hbar^2}|V_{mn}|^2\,\delta(\omega_{mn})=\frac{2\pi t}{\hbar}|V_{mn}|^2\delta(E_{mn}), \qquad (4.31)$$

with the δ function implementing energy conservation.

From this, we can drive the transition rate,

$$\Gamma_{n\to m}(t)=\frac{d}{dt}P_{n\to m}=\frac{2\pi}{\hbar}\delta(E_{mn})|V_{mn}|^2 \qquad (4.32)$$

Fermi's golden rule (Fermi 1950) (Wentzel 1927)

(NB: from a formal viewpoint, it is important to perform the discussion on the level of the probability ~~amplitude~~ instead of the amplitude. Going back to (4.23) in the limit $t_0 \to -\infty$ and $t \to \infty$, we would have found that $A_{n\to m} = \frac{2\pi}{\hbar} V_{mn}\, \delta(\omega_{mn})$.

The square of the amplitude would then have involved a square of a δ function

$$P_{n\to m} \stackrel{?}{\propto} |\delta(\omega_{mn})|^2$$

From the proper treatment given above, we observe that one δ function remains, and the other corresponds to the "time volume", "$\delta(\omega) \sim t|_{t\to\infty}$".

This rather sloppy way of dealing with squares of δ function may be used as a simple mnemotic for the result of a clean analysis involving finite time switches.)

For quantitative analyses, Fermi's golden rule is quantitatively very successful. This is somewhat surprising:

- it cannot be applied directly to discrete spectra, where the probabilities oscillate. Hence, (4.32) shouldn't be applied for too long times (though it has been derived in the long-time limit.

- for degenerate states $E_{mm} = 0$, we have observed above that perturbation theory breaks down for too long times when the probability increases with t^2. Again: (4.32) has been derived in the long-time limit....

We conclude that the golden rule is applicable in a subtle intermediate parameter range (which in most cases is the physically relevant range), where t is sufficiently large, but not too large to invalidate perturbation theory. Also the final state should be in a part of the

Spectrum which is continuous, or where the energy levels are sufficiently dense, in order to avoid the problem of recurrences. Quantitatively, a typical level distance δE should satisfy

$$\delta E \cdot t \ll 2\pi\hbar . \qquad (4.33)$$

Let us finally consider the transition of a state $|m\rangle$ to <u>any</u> state $|k\rangle$ in the (spectral) vicinity of $|m\rangle$:

$$\sum_k P_{m\to k} = \sum_k |V_{km}|^2 \underbrace{\frac{4\sin^2 \frac{E_{km} t}{2\hbar}}{E_{km}^2}}_{f(E_{km})} , \qquad (4.34)$$

where we sum over all these "neighboring" states $|k\rangle$, say lying in an interval $\frac{2\pi\hbar}{t}$ near E_m.

Let us assume that all V_{km}'s are similar, $V_{km} \sim V_{mm}$ and that the spectra is so dense that the sum can be approximated by an integral,

$$\sum_k f(E_{km}) \sim \int dE\, g(E)\, f(E) \qquad (4.35)$$

where $g(E)$ is the spectral density. In the discrete case, $g(E)$ is a δ comb,

$$g(E) = \sum_n \delta(E - E_n) , \tag{4.36}$$

and we get back the discrete RHS of (4.35). However, the RHS can also be applied if the spectrum is continuous (and the spectral density a continuous function).

Using again that $f(E)$ approaches a δ function for long times, we find for the transition rate

$$\Gamma_{n\to m} = \dot{P}_{n\to m} = \frac{2\pi}{\hbar} |\langle m|V|n\rangle|^2 g(E_n) \tag{4.37}$$

where g measures the density of states near the final state energy level.

4.2.2 Adiabatic Perturbation

Let us now consider the opposite extreme case, where the perturbation is switched on very slowly (adiabatically). As a specific model, we consider

$$V(t,x) = e^{\eta t} V(x), \quad \eta > 0, \tag{4.38}$$

finally taking the limit $\eta \to 0$.
Upon insertion into the first-order formula (4.23), we obtain for the amplitude,

$$A_{n\to m}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} dt_1 \, e^{\eta t_1} e^{i\omega_{mn}(t_1 - t_0)} V_{mn} \tag{4.39}$$

Since the perturbation vanishes exponentially for $t_1 \to -\infty$, we replace the lower integral boundary by $-\infty$.
Up to an irrelevant phase, this yields

$$A_{n\to m}(t) = \frac{e^{(\eta + i\omega_{mn})t}}{i\eta - \omega_{mn}} \frac{V_{mn}}{\hbar}. \tag{4.40}$$

For the transition probability, this implies

$$P_{n\to m} = \frac{e^{2\eta t}}{\omega_{mn}^2 + \eta^2} \frac{|V_{mn}|^2}{\hbar^2}. \tag{4.41}$$

This is a bell-shaped curve as a function of the frequency ω_{mn}. The most-likely energy difference between initial and final state thus lies within the width set by η. For small η, we obtain the rate

$$\Gamma_{n\to m} = \dot{P}_{n\to m} \sim \frac{2\eta}{\omega_{mn}^2 + \eta^2} \frac{|V_{mn}|^2}{\hbar^2} . \qquad (4.42)$$

In the limit $\eta \to 0$, we again discover a δ function since

$$\lim_{\eta\to 0} \frac{2\eta}{\omega^2+\eta^2} \to 2\pi\,\delta(\omega) . \qquad (4.43)$$

Hence, even in the (opposite) adiabatic limit, we rediscover Fermi's golden rule

$$\Gamma_{n\to m} = \frac{2\pi}{\hbar^2} |V_{mn}|^2 \,\delta(\omega_{mn}) , \qquad (4.44)$$

which agrees with (4.32).

This exemplifies that the golden rule for the rate is rather robust against modifications of

how perturbations are switched on.

4.2.3 Example: electric excitation of a hydrogen atom

A hydrogen atom in the ground state is put into an electric field which is switched on and off according to

$$\vec{E}(t) = \vec{E}_0 \, e^{-t^2/\tau^2} . \tag{4.45}$$

Let us compute the probability to find the atom in an excited state, say with quantum numbers $n=2$, $l=1$, $m=0$, after a long time $t \gg \tau$. The electric field (4.45) can be parameterized by the potential

$$V = e E_0 z \, e^{-t^2/\tau^2} \tag{4.46}$$

Since $\vec{E}(t)$ becomes exponentially small at large times, and t should be much bigger than τ, $t \gg \tau$, we set the integral boundaries in the amplitude

to $\pm\infty$:

$$A_{|100\rangle \to |210\rangle} = \frac{eE_0}{i\hbar} \langle 210|z|100\rangle \int_{-\infty}^{\infty} dt_1 \, e^{i(\omega_{210}-\omega_{100})t_1} \cdot e^{-t_1^2/\tau^2}$$

$$= \frac{eE_0}{i\hbar} \langle 210|z|100\rangle \, \tau\sqrt{\pi} \, e^{-\omega^2\tau^2/4}, \qquad (4.47)$$

where the integral can be done by completing the square, and $\omega = \omega_{210} - \omega_{100}$ denotes the frequency of the photon being emitted in the transition $|210\rangle \to |100\rangle$. The resulting probability is

$$P_{|100\rangle - |210\rangle} = \pi \left(\frac{eE_0\tau}{\hbar}\right)^2 |\langle 210|z|100\rangle|^2 \, e^{-\omega^2\tau^2/2} \qquad (4.48)$$

For large τ, i.e. for very "slow" perturbations, the transition probability vanishes exponentially. The atom then has enough time to (adiabatically) adjust to the perturbed levels without actually

performing a transition to a different level.

4.2.4 Periodic perturbations

As another rather important example, let us study periodic perturbations of a system defined by H_0. We consider a hermitean perturbation operator with harmonic time dependence

$$V(\omega,t) = e^{\eta t}\left(e^{-i\omega t}V(\vec{x}) + e^{i\omega t}V^{\dagger}(\vec{x})\right). \tag{4.49}$$

Here, we included an adiabatic switch for the perturbation $\sim e^{\eta t}$. Using

$$\langle m|V^{\dagger}|n\rangle = \langle n|V|m\rangle^{*}$$

$$\Rightarrow (V^{\dagger})_{mn} = V^{*}_{nm}, \tag{4.50}$$

the transition amplitude to first order reads

$$A_{n\to m}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} dt_1\, e^{\eta t_1} e^{i\omega_{mn}t_1}\left(e^{-i\omega t_1}V_{mn} + e^{i\omega t_1}V^{*}_{nm}\right) \tag{4.51}$$

Replacing t_0 by $-\infty$ due to adiabaticity leads us to

$$A_{n\to m}(\omega,t) = \frac{1}{\hbar}\left(\frac{e^{-i\omega t} V_{mn}}{\omega_{nm}+\omega+i\eta} + \frac{e^{i\omega t} V_{nm}^{*}}{\omega_{nm}-\omega+i\eta} \right) e^{\eta t + i\omega_{nm} t} \qquad (4.52)$$

The rate follows straightforwardly from squaring (4.52) and taking the time derivative,

$$\Gamma_{n\to m}(\omega,t) = \frac{1}{\hbar^2} e^{2\eta t}\left(\frac{2\eta}{(\omega_{nm}+\omega)^2+\eta^2} |V_{mn}|^2 + \frac{2\eta}{(\omega_{nm}-\omega)^2+\eta^2} |V_{nm}|^2 \right)$$

$$+ \frac{2}{\hbar^2} e^{2\eta t}\left(\frac{(\eta - i\omega) e^{-2i\omega t}}{\omega_{nm}^2 + (\omega+i\eta)^2} V_{mn} V_{nm} + \frac{(\eta+i\omega) e^{2i\omega t}}{\omega_{nm}^2+(\omega-i\eta)^2} V_{mn}^{*} V_{nm}^{*} \right) \qquad (4.53)$$

The terms in the last line are interference terms arising from the two time dependencies $e^{-i\omega t}, e^{i\omega t}$. Averaging over a few periods, these oscillatory terms drop out. The first line reduces by means of the adiabatic limit, where

$$\frac{2\eta}{(\omega_{nm}+\omega)^2+\eta^2} \xrightarrow{\eta\to 0} 2\pi\,\delta(\omega_{nm}+\omega), \qquad (4.54)$$

to

$$\overline{\Gamma}_{n\to m}(\omega) = \frac{2\pi}{\hbar^2}\left(\delta(\omega_{nm}-\omega)|V_{nm}|^2 + \delta(\omega_{nm}+\omega)|V_{mn}|^2 \right) \qquad (4.55)$$

($\overline{\Gamma}$: averaging)

For the case $|V_{mn}| = |V_{nm}|$ and after summing (or integrating) over dense final states, we obtain

$$\sum_m \overline{F}_{n\to m}(\omega) = \frac{2\pi}{\hbar} |V_{nm}|^2 \left(\delta(E_n + \hbar\omega) + \delta(E_m - \hbar\omega) \right) \tag{4.56}$$

This is Fermi's golden rule for the special case of periodic perturbations. It has an obvious interpretation:

if $E_m > E_n$ and if $\omega > 0$, the second term in (4.55) vanishes, as the argument of the δ function is never zero. The transition is very likely, if $\omega \simeq \omega_{nm}$ for finite t and $\hbar\omega = E_{mn}$ for $t \to \infty$. Is H_0 for instance an atomic Hamiltonian, and $V(\vec{x}, t)$ a (model for) an electromagnetic wave, then the first term in (4.55) describes an absorption of a quantum of energy (a photon) $\hbar\omega$.

In turn, if $E_n > E_m$ and $\omega > 0$ the second term ↑ describes induced emission of

↑ in (4.55)

a photon by an atom stimulated by an external electromagnetic wave.

A further process, spontaneous emission, cannot be explained within non-relativistic quantum mechanics. Roughly speaking, spontaneous emission is "stimulated" by the fluctuations of the radiation field (and thus requires an understanding of the quantized radiation field).

4.3 Second-order transitions

If $\langle m|V(t)|n\rangle$ vanishes for all times, e.g. due to selection rules, first-order perturbation theory predicts that the transition probability is zero. This might be nothing but an artefact of 1st-order perturbation theory as can be investigated by taking a closer look at the 2nd order:

$$\langle m|\psi_{I\,m}(t)\rangle = \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \langle m|V_I(t_1)V_I(t_2)|n\rangle \qquad (4.57)$$

where we have assumed that $m \neq n$ and that the first order indeed vanishes. Using

$$V_I(t) = e^{\frac{i}{\hbar} t H_0} V(t) e^{-i \frac{t}{\hbar} H_0}$$ and inserting a complete set of states $\mathbb{1} = \sum_k |k\rangle\langle k|$, we find

$$\langle m | U_{I,n}(t) \rangle = \frac{1}{(i\hbar)^2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \sum_k e^{i\omega_{mk} t_1} \langle m|V(t_1)|k\rangle \langle k|V(t_2)|n\rangle \cdot e^{i\omega_{kn} t_2} \tag{4.58}$$

Assuming again adiabaticity of the perturbation and repeating the steps following (4.38), we obtain for the amplitude

$$A_{n\to m}(t) = -\frac{1}{\hbar^2} e^{i\omega_{mn} t} \frac{e^{2\eta t}}{\omega_{mn} + 2i\eta} \sum_k \frac{V_{mk} V_{kn}}{\omega_{nk} + i\eta} \tag{4.59}$$

Squaring and taking the time-derivative, we obtain the rate (using again the limit $\eta \to 0$),

$$\Gamma_{n\to m}(t) = \frac{2\pi}{\hbar^4} \left| \sum_k \frac{V_{mk} V_{kn}}{\omega_{nk} + i\eta} \right|^2_{\eta\to 0} \delta(\omega_{nm}) , \tag{4.60}$$

which is the 2nd-order version of Fermi's golden rule (provided that the first order vanishes).

The interpretation is obvious: instead of doing a transition from n to m directly, the system first goes through an intermediate "virtual" state $|k\rangle$. As this virtual state is not observed (and the energy not measured), there is no need for absolute energy conservation – also due to the uncertainty relation $\Delta t \, \Delta E \geq \hbar$. As the intermediate state is not detected, one has to sum over all possible intermediate states on the amplitude level. The probability or the rate thus contains also interference terms of different paths (in state space).