Fermi's golden rule

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Fermi's golden rule [2] is a simple expression for the transition probabilities between states of a quantum system, which are subjected to a perturbation. It is used for a large variety of physical systems covering, e.g., nuclear reactions, optical transitions, or scattering of electrons in solids.

1 Main results

We consider a quantum system described by an Hamiltonian $\hat{H}_0$ with known eigenstates $|c^0\rangle$, i.e.

$$\hat{H}_0|c^0\rangle = E_c^0|c^0\rangle$$

Now we raise the question, how a small extra term $\hat{V}(t)$ (called *perturbation*) affects the system. In contrast to $\hat{H}_0$, the perturbation can be time-dependent, but it may also be constant, i.e. $\hat{V}(t) = \hat{V}$. Examples for perturbations are an additional electric field $\mathcal{F}$ with $\hat{V} = e\mathcal{F}\hat{z}$, or the presence of an electromagnetic wave with frequency ω, coupling to the electron via $\hat{V}(t) \propto \cos(\omega t)$ (this example is treated explicitly in Section 4). Thus we have the Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \tag{1}$$

In contrast to the stationary perturbation theory, where approximations for the eigenstates of the perturbed Hamiltonian are evaluated, *we consider here the time dependence* $|\Psi(t)\rangle$ *of a system, which is prepared in the state* $|\Psi(0)\rangle = |a^0\rangle$ *at* $t = 0$. Of particular interest is the probability $P_b(t)$ to find the system in another eigenstate $|b^0\rangle$ of $\hat{H}_0$ at a later time t, which can be evaluated via

$$P_b(t) = |\langle b^0|\Psi(t)\rangle|^2 \quad \text{for} \quad |\Psi(0)\rangle = |a^0\rangle \tag{2}$$

Without the perturbation (i.e. $\hat{V} = 0$), the eigenstate $|a^0\rangle$ provides the trivial time dependence $|\Psi(t)\rangle = \mathrm{e}^{-\mathrm{i}E_a^0 t/\hbar}|a^0\rangle$. Thus $P_b(t) = 0$ for $b \neq a$ and $P_a(t) = 1$ and the system stays in state $|a^0\rangle$ forever. However, for a finite perturbation $\hat{V}(t)$, the state $|a^0\rangle$ is no longer an eigenstate of the full Hamiltonian (1) and the time dependent solution of the Schrödinger equation provides admixtures to the different states $|b^0\rangle$.

The central result is that for weak perturbations and long times, the transition probability $P_b(t)$ raises linear in time as $P_b(t) = \Gamma_{a\to b} \times t$ for $b \neq a$. This *transition rate* $\Gamma_{a\to b}$ from state a to state b is given by:

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[2] The concept was developed by P.A.M. Dirac, Proc. Royal Soc. Lond. A Mat. **114**, 243 (1927). E. Fermi later coined the name golden rule, as he heavily used it for nuclear reactions.

Fermi's golden rule:
For a *time-independent perturbation potential* $\hat{V}$ the *transition rate* from state a to state b is given by

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}|\langle b^0|\hat{V}|a^0\rangle|^2\delta(E_b^0 - E_a^0) \tag{3}$$

Thus transitions are only possible if the initial and final state have the same energy.
For a *periodic perturbation potential* $\hat{V}(t) = \hat{F}\mathrm{e}^{-\mathrm{i}\omega t} + \hat{F}^\dagger\mathrm{e}^{\mathrm{i}\omega t}$ with frequency ω one obtains

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}|\langle b^0|\hat{F}|a^0\rangle|^2\delta(E_b^0 - E_a^0 - \hbar\omega) + \frac{2\pi}{\hbar}|\langle b^0|\hat{F}^\dagger|a^0\rangle|^2\delta(E_b^0 - E_a^0 + \hbar\omega)\,. \tag{4}$$

In this case transitions are only possible if the energy of the final state is $\hbar\omega$ higher/lower than the energy of the initial state, This corresponds to the *absorption/emission* of the *energy quantum* $\hbar\omega$ from/to the oscillating field, respectively.

This will be proven in the subsequent section 2. Note that the delta-function appearing in Fermi's golden rule requires an integral over one of the arguments to be of any meaning. Thus Fermi's golden rule is only applicable if there is either a continuum of final states or a continuum of frequencies ω to integrate over. Otherwise no linear time dependence $P_b(t) = \Gamma_{a\to b}t$ is recovered. E.g., for the case of two-level system in a strong monochromatic laser field one observes an oscillatory behavior $P_b(t) \propto \sin^2(\Omega_R t/2)$, called Rabi oscillation (which is not further discussed here).

2 Time-dependent perturbation theory

Using the completeness of the eigenstates of $\hat{H}_0$ an arbitrary quantum state can be written as

$$|\Psi(t)\rangle = \sum_c g_c(t)\mathrm{e}^{-\mathrm{i}E_c^0 t/\hbar}|c^0\rangle \tag{5}$$

where the phase factor $\mathrm{e}^{-\mathrm{i}E_c^0 t/\hbar}$ has been introduced for convenience[3]. This state has to satisfy the Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\,.$$

For the full Hamiltonian (1) the term $\hat{H}_0$ cancels with the time-derivatives of the factors $\mathrm{e}^{-\mathrm{i}E_c^0 t/\hbar}$ resulting in

$$\sum_c \mathrm{i}\hbar\mathrm{e}^{-\mathrm{i}E_c^0 t/\hbar}\frac{\partial g_c(t)}{\partial t}|c^0\rangle = \sum_c g_c(t)\mathrm{e}^{-\mathrm{i}E_c^0 t/\hbar}\hat{V}(t)|c^0\rangle\,. \tag{6}$$

Multiplying by $\langle b^0|\mathrm{e}^{\mathrm{i}E_b^0 t/\hbar}$ from the left provides

$$\mathrm{i}\hbar\frac{\partial g_b(t)}{\partial t} = \sum_c \mathrm{e}^{\mathrm{i}(E_b^0 - E_c^0)t/\hbar}\langle b^0|\hat{V}(t)|c^0\rangle g_c(t)$$

or after integration

$$g_b(t) = g_b(0) + \frac{1}{\mathrm{i}\hbar}\int_0^t \mathrm{d}t' \sum_c \mathrm{e}^{\mathrm{i}(E_b^0 - E_c^0)t'/\hbar}\langle b^0|\hat{V}(t')|c^0\rangle g_c(t')\,. \tag{7}$$

[3]The generalization of this ad-hoc approach is the interaction representation

With the initial condition, that the system is in state $|a^0\rangle$ at time $t=0$, we have $g_c(0)=0$ for $c\neq a$ and $g_a(0)=1$. Thus Eq. (7) provides $g_c(t)=\delta_{c,a}+\mathcal{O}(V)$. Inserting this into $g_c(t')$ on the left hand side of Eq. (7) we find.

$$g_b(t)=\frac{1}{\mathrm{i}\hbar}\int_0^t \mathrm{d}t' \mathrm{e}^{\mathrm{i}(E_b^0-E_a^0)t'/\hbar}\langle b^0|\hat{V}(t')|a^0\rangle+\mathcal{O}(V^2)\quad\text{for}\quad b\neq a \tag{8}$$

The t'-integral is easily solvable for fictitious perturbations of the form

$$\hat{V}(t)=\hat{F}\mathrm{e}^{-\mathrm{i}\omega t}$$

resulting in the transition-probability

$$P_b(t)=|\langle b^0|\Psi(t)\rangle|^2=|g_b(t)|^2=|\langle b^0|\hat{F}|a^0\rangle|^2 D_t\left(E_b^0-E_a^0-\hbar\omega\right)\quad\text{for}\quad b\neq a \tag{9}$$

with the auxiliary function

$$D_t(\Delta E)=\left|\frac{1}{\hbar}\int_0^t \mathrm{d}t' \mathrm{e}^{\mathrm{i}\Delta E t'/\hbar}\right|^2=\left|\frac{\mathrm{e}^{\mathrm{i}\Delta E t/\hbar}-1}{\mathrm{i}\Delta E}\right|^2=\left|\mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t/\hbar}\frac{\mathrm{e}^{\mathrm{i}\frac{\Delta E}{2}t/\hbar}-\mathrm{e}^{-\mathrm{i}\frac{\Delta E}{2}t/\hbar}}{\mathrm{i}\Delta E}\right|^2=\frac{4\sin^2\left(\frac{\Delta E}{2}t/\hbar\right)}{\Delta E^2} \tag{10}$$

Figure 1 shows that $D_t(\Delta E)$ has large values only for $-2\pi\hbar/t<\Delta E<2\pi\hbar/t$, where the maximum $D_t(0)=t^2/\hbar^2$ increases rapidly with time. Furthermore a glance to a table of integrals[4] gives $\int_{-\infty}^{\infty}\mathrm{d}x D_t(x)=2\pi t/\hbar$. Thus we define the function

$$\delta_t(\Delta E)=\frac{\hbar}{2\pi t}D_t\left(\Delta E\right)$$

which is a representation of the δ-function in the limit $t\to\infty$. Now we consider two typical cases:

(i) Setting $\omega=0$, i.e. considering a constant potential $\hat{V}(t)=\hat{V}$, we obtain from Eq. (9)

$$\Gamma_{a\to b}(t)=\frac{P_{a\to b}(t)}{t}=\frac{2\pi}{\hbar}|\langle b^0|\hat{V}|a^0\rangle|^2\delta_t(E_b^0-E_a^0) \tag{11}$$

(ii) Now we consider periodic perturbation potentials. Being a part of the Hamiltonian, $\hat{V}(t)$ is a Hermitian operator, The most general form of a Hermitian operator containing a single frequency component ω is

$$\hat{V}(t)=\hat{F}\mathrm{e}^{-\mathrm{i}\omega t}+\hat{F}^\dagger\mathrm{e}^{\mathrm{i}\omega t}$$

Treating both terms separately (which is possible for $t\gg\omega/2\pi$, where the δ_t functions do not overlap) we obtain

$$\Gamma_{a\to b}(t)=\frac{2\pi}{\hbar}|\langle b^0|\hat{F}|a^0\rangle|^2\delta_t(E_b^0-E_a^0-\hbar\omega)+\frac{2\pi}{\hbar}|\langle b^0|\hat{F}^\dagger|a^0\rangle|^2\delta_t(E_b^0-E_a^0+\hbar\omega)\,. \tag{12}$$

In both cases the function $\delta_t(\Delta E)$ can be replaced by a δ-function, resulting in Eqs. (3,4), if the following conditions are met:

- There is an integration over a continuum of final states $|b^0\rangle$ or frequencies ω, as the δ-function is only properly defined together with an integral over its argument.
- The observation time t is sufficiently long, so that the matrix element $|\langle b^0|\hat{V}|a^0\rangle|$ (or $|\langle b^0|\hat{F}_\omega|a^0\rangle|$) is approximately constant within the energy range $|E_b^0-E_a^0\pm\hbar\omega|\lesssim 2\pi\hbar/t$ of the allowed final states b (or frequencies ω).
- The perturbation $\hat{V}$ is sufficiently weak, so that the probability to reach any possible state $\sum_{b\neq a}P_b(t)=\sum_{b\neq a}\Gamma_{a\to b}t$ does not reach unity within the observation time.

[4]Eq. (3.741(3)) in D. Zwillinger: *Table of Integrals, Series and Products* (Academic Press, Waltham 2015)

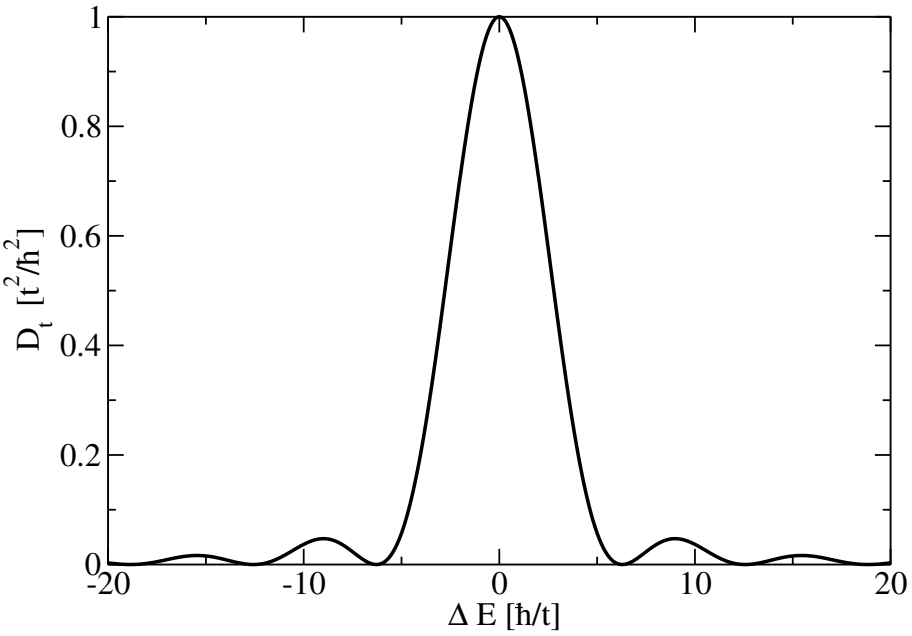

Figure 1: The function $D_t(\Delta E)$ from Eq. (10). As $\hbar = 0.66 eV/fs$ the energy scale is 0.66 meV for $t = 1$ ps (semiconductors), 0.66 eV for $t = 1$ fs (molecules), and 0.66 MeV for $t = 10^{-21}$ s (high energy physics).

3 Example: β-decay of the neutron

Nuclei are eigenstates of the strong interaction but not necessarily eigenstates of the weak interaction, which causes transitions between different nuclei. For the β-decay of the neutron the following many-particle states are of relevance:

- A neutron (in rest):
  State $|a^0\rangle$ with energy $E_a^0 = m_n c^2$
- A proton (almost in rest) + free electron with wave vector $\mathbf{k}_e$ + free antineutrino with wave vector $\mathbf{k}_\nu$:
  State $|b^0\rangle = |\mathbf{k}_e, \mathbf{k}_\nu\rangle$ with energy

  $$E_b^0 = m_p c^2 + \sqrt{m_e^2 c^4 + \hbar^2 c^2 k_e^2} + \sqrt{m_\nu^2 c^4 + \hbar^2 c^2 k_\nu^2}$$

  where we take into account a possible finite mass m_ν of the neutrinos.[5]

In addition we assume that the matrix element $|\langle \mathbf{k}_e, \mathbf{k}_\nu | \hat{V}_{\text{weak interaction}} | a^0 \rangle|^2 = g^2$ is constant. (This is a point-interaction, as assumed by Enrico Fermi 1934.) In a typically experiment, the momentum $\mathbf{p}_e = \hbar \mathbf{k}_e$ of the final electron is measured. Thus, we want to evaluate the transition rate to a final state $\mathbf{k}_e$ with arbitrary $\mathbf{k}_\nu$

$$\Gamma_{a\to \mathbf{k}_e} = \int \underbrace{\mathrm{d}^3 k_\nu}_{4\pi k_\nu^2 \mathrm{d}k_\nu} \frac{2\pi}{\hbar} g^2 \delta \left(\underbrace{(m_p - m_n)c^2 + \sqrt{m_e^2 c^4 + \mathbf{p}_e^2 c^2}}_{=-A(\mathbf{p}_e)} + \sqrt{m_\nu^2 c^4 + \hbar^2 c^2 k_\nu^2} \right)$$

[5] As indicated by Neutrino oscillations. Nobel price 2002 to R. Davis, M. Koshiba, and R. Giacconi, `http://nobelprize.org/nobel_prizes/physics/laureates/2002/phyadv02.pdf`)

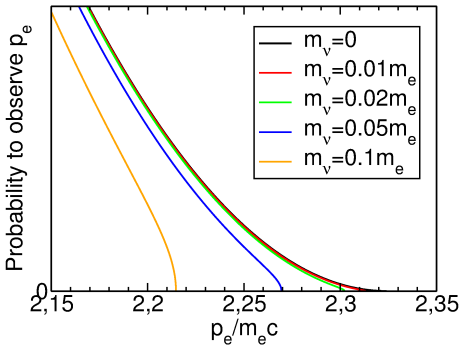

Figure 2: Probability (in arbitrary units) to find a specific momentum $\mathbf{p}_e$ of the electron after the neutron decay assuming different masses of the antineutrino.

Now, we use the relation

$$\int_a^b \mathrm{d}x\, g(x)\delta(f(x)) = \sum_i \frac{g(x_i)}{|f'(x_i)|}$$

where the x_i satisfy $f(x_i) = 0$ within the interval $a < x_i < b$. and define the step function by $\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$. After a few lines of algebra we find:

$$\Gamma_{a\to\mathbf{k}_e} = \frac{8\pi^2 g^2}{\hbar^4 c^3} A(\mathbf{p}_e)\sqrt{A(\mathbf{p}_e)^2 - m_\nu^2 c^4}\,\Theta(A(\mathbf{p}_e) - m_\nu c^2)$$

which shows a characteristic momentum dependence for small A (i.e. close to the maximum electron momentum), as displayed in Fig. 2. Fitting to experimental data provides a rather small upper limit for the neutrino mass, currently $2\mathrm{eV}/c^2$ from the β-decay of Tritium[6]. (Note that for such small energies the kinetic energy of the final nucleus becomes relevant, which was neglected for simplicity here.)

4 Example: Radiation transitions

Consider a hydrogen atom with the Hamilton operator

$$\hat{H}_0 = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|}$$

where the eigenstates are given by $|a^0\rangle = |n, l, m, m_s\rangle$ with principal quantum number n, and the quantum numbers for total angular momentum l, its projection to the z axis m_l, as well as spin projection m_s. An electromagnetic wave (light) with frequency ω can be described by the electromagnetic potentials (in Coulomb gauge $\mathrm{div}\mathbf{A} = 0$)

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{\omega}\mathbf{E}_0(\omega)\cos(\mathbf{k}(\omega)\cdot\mathbf{r} - \omega t) \quad \text{and} \quad \varphi(\mathbf{r}, t) = 0$$

The Hamilton-Operator reads (here $e > 0$ is the elementary charge).

$$\begin{aligned}\hat{H} =& \frac{[\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r}, t)]^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|} + g_e\frac{e}{2m_e}\hat{\mathbf{S}}\cdot\mathbf{B}(\mathbf{r}, t)\\ =& \hat{H}_0 + \frac{e}{m_e\omega}\mathbf{E}_0(\omega)\cdot\hat{\mathbf{p}}\frac{1}{2}\left(\mathrm{e}^{\mathrm{i}(\mathbf{k}(\omega)\cdot\mathbf{r}-\omega t)} + \mathrm{e}^{-\mathrm{i}(\mathbf{k}(\omega)\cdot\mathbf{r}-\omega t)}\right)\\ &+ g_e\frac{e}{2m_e}\hat{\mathbf{S}}\cdot\left[\mathbf{k}(\omega)\times\mathbf{E}_0(\omega)\frac{\mathrm{i}}{2\omega}\left(\mathrm{e}^{\mathrm{i}(\mathbf{k}(\omega)\cdot\mathbf{r}-\omega t)} - \mathrm{e}^{-\mathrm{i}(\mathbf{k}(\omega)\cdot\mathbf{r}-\omega t)}\right)\right] + \mathcal{O}(E_0^2)\end{aligned}$$

For visible light we have $k = 2\pi/\lambda \sim 2\pi/600\mathrm{nm}$. In contrast the atomic size is of the order $\sim a_B = 0.0529$ nm, and atomic momenta are of the order $\hbar/a_B$. Thus terms with kr (in the exponent) as well as the spin-term ($Sk \sim \hbar 2\pi/600\mathrm{nm} \ll p$) are negligible in a first approximation.

The transition rate between two atomic levels a and b is given by Eq. (12)

$$\Gamma_{a\to b}(t) = \frac{2\pi}{\hbar}\left|\frac{e}{2m_e\omega}\langle b^0|\mathbf{E}_0(\omega)\cdot\hat{\mathbf{p}}|a^0\rangle\right|^2 \left[\delta_t(E_b^0 - E_a^0 - \hbar\omega) + \delta_t(E_b^0 - E_a^0 + \hbar\omega)\right]$$

[6] according to the Particle Data Group, W-M Yao et al., J. Phys. G: Nucl. Part. Phys. **33** 1 (2006)

Thus, the radiation field is exchanging energy in portions of $\hbar\omega$ (*photons*) with the atom. Accordingly the processes are called absorption and emission of a photon by the atoms.

The size of the transition rate is given by the matrix element, which for $|a^0\rangle = |n,l,m,m_s\rangle$ and $|b^0\rangle = |n',l',m',m_s'\rangle$ is given by

$$\langle b^0|\hat{\mathbf{p}}|a^0\rangle = \langle n',l',m',m_s'|m_e\frac{\mathrm{i}}{\hbar}[\hat{H}_0,\hat{\mathbf{r}}]|n,l,m,m_s\rangle = m_e\frac{\mathrm{i}}{\hbar}(E^0_{n'l'}-E^0_{nl})\underbrace{\langle n',l',m',m_s'|\hat{\mathbf{r}}|n,l,m,m_s\rangle}_{=-\frac{1}{e}\mathbf{d}_{ba}}$$

Using the properties of the spherical harmonics, one finds that the *dipole matrix element* $\mathbf{d}_{ba} = 0$ vanishes unless $l' = l \pm 1$, $m_s' = m_s$ and $m' =\in \{m-1, m, m+1\}$.

For an atom interacting with electromagnetic radiation of frequency ω the transition rate reads

$$\Gamma_{a\to b} = \frac{2\pi}{\hbar}\left|\frac{\mathbf{E}_0\cdot\mathbf{d}_{ba}}{2}\right|^2\left[\delta_t(E^0_b-E^0_a-\hbar\omega)+\delta_t(E^0_b-E^0_a+\hbar\omega)\right].$$

between the atomic levels a and b in dipole approximation ($e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ and $\hbar k \ll p$). The possible processes are the **induced absorption** and the **induced emission** of a photon. Both processes exhibit the same rate. The *selection rules* are $\Delta l = \pm 1$, $\Delta m = 0, \pm 1$ and $\Delta m_s = 0$.

Remarks: Taking into account the **quantization** of the electromagnetic field we have $\hat{F}^\dagger \neq \hat{F}$ and the transition rates differ for emission and absorption. This can be described by the additional **spontaneous emission**, which is also possible if the electromagnetic field is in its ground state (the vacuum fluctuations of the field constitute the perturbation potential).

If one takes into account higher order terms $e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \approx 1+\mathrm{i}\mathbf{k}\cdot\mathbf{r}$, one obtains the electrical quadrupole and magnetic dipole transitions. The latter also include the spin-term in Eq. (4). In both cases one obtains different selection rules than for dipole approximation but the rates are several orders of magnitude smaller because of the reduced matrix elements.