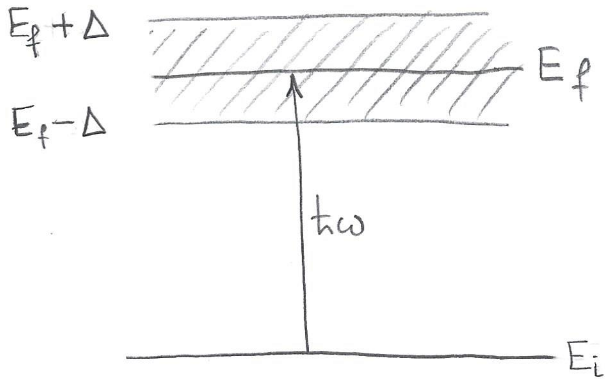
Fermi's golden rule



In many problems of practical interest the final states lie in a band of energies. For example, this situation takes place when an atom gets ionized and we deal with scattering states of the electron that comprise a continuum.

If the density of final states is $g(E_f)$ then the number of energy states in the interval $[E_f, E_f + dE_f]$ is

$$dN = g(E_f)\,dE_f$$

The probability that a transition occurs to a state in the band of width 2Δ centered at E_f is

$$\overline{P_{if}} = \int_{E_f-\Delta}^{E_f+\Delta} P_{if}\, g(E_f')\, dE_f'$$

If we use the expression for P_{if} in the case of a harmonic perturbation (obtained in a previos lecture), namely

$$P_{if} = \frac{|\mathcal{H}'_{fi}|^2}{\hbar^2(\omega_{fi}-\omega)^2}\sin^2\left[\frac{(\omega_{fi}-\omega)t}{2}\right]$$

we get the following

$$\overline{P_{if}} = \int_{E_f-\Delta}^{E_f+\Delta} dE_f'\, g(E_f')\, \frac{|\mathcal{H}'_{fi}|^2}{\hbar^2}\, \frac{\sin^2\beta}{4\frac{\beta^2}{t^2}}$$

where $\beta = \frac{1}{2}(\omega_{fi}-\omega)t = \frac{1}{2}\left(\frac{E_f - E_i}{\hbar} - \omega\right)t$

and $\mathcal{H}'_{fi} = \langle \psi_f | \mathcal{H}'(\vec{r}) | \psi_i \rangle$ is the transition matrix element

For fixed values of E_i, t, and ω we have $dE_f' = \frac{2\hbar\, d\beta}{t}$

and

$$\overline{P}_{if} = \frac{t}{2\hbar} \int_{-\delta}^{+\delta} g(E_f') \, |\mathcal{H}_{fi}'|^2 \, \frac{\sin^2\beta}{\beta^2} \, d\beta$$

Here 2δ is the corresponding spread in β values. Because of the rapid decay of $\frac{\sin^2\beta}{\beta^2}$ we can replace the integration interval from $[-\delta, \delta]$ to $[-\infty, +\infty]$. Moreover, if we assume that g and $\mathcal{H}_{fi}'$ are slowly varying known functions, we can take them outside the integral:

$$\overline{P}_{if} = \frac{t}{2\hbar} g(E_f) \, |\mathcal{H}_{fi}'|^2 \cdot \underbrace{\int_{-\infty}^{+\infty} \frac{\sin^2\beta}{\beta^2} \, d\beta}_{\pi} = \frac{\pi t}{2\hbar} g(E_f) \, |\mathcal{H}_{fi}'|^2 \qquad (*)$$

It should be noted that the form of the harmonic perturbation we used to obtain P_{if} in a previous lecture was $\mathcal{H}(\bar{r}) \sin\omega t$. Most textbooks tend to use $2\mathcal{H} \sin\omega t$ or $\mathcal{H}(e^{i\omega t} + e^{-i\omega t})$ instead. This results in an additional factor of 4 in the expression for $\overline{P}_{if}$:

$$\overline{P}_{if} = \frac{2t\pi}{\hbar} g(E_f) \, |\mathcal{H}_{fi}'|^2$$

In formula $(*)$ this factor is essentially hidden in $|\mathcal{H}_{fi}'|$.

The transition probability rate is easily obtained by taking a derivative of $\overline{P}_{if}$

$$\overline{W}_{if} = \frac{2\pi}{\hbar} g(E_f) \, |\mathcal{H}_{fi}'|^2$$

One might worry that in the long time litim we may find that the probability of transition is diverging. So how can we justify the use of the perturbation theory? For a transition with $\omega_{fi} \neq \omega$ the long time limit is reached when $t \gg \frac{1}{\omega_{fi} - \omega}$ — a value that can still be very short compared to the mean transition time, which depends on the transition matrix element

Alternative way to derive the golden rule

If we assume that $H'(\vec{r},t) = e^{\varepsilon t} \mathcal{H}'(\vec{r})\, e^{-i\omega t}$, where ε is small, H' is turned on gradually and we are looking at times much smaller than $\frac{1}{\varepsilon}$. If $t_0 = -\infty$ then

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} \langle f|\mathcal{H}'|i\rangle\, e^{i(\omega_{fi}-\omega-i\varepsilon)t'}\, dt' =$$

$$= -\frac{1}{\hbar} \frac{e^{i(\omega_{fi}-\omega-i\varepsilon)t}}{\omega_{fi}-\omega-i\varepsilon} \langle f|\mathcal{H}'|i\rangle$$

$$|c_f^{(1)}|^2 = \frac{1}{\hbar^2} \frac{e^{2\varepsilon t}}{(\omega_{fi}-\omega)^2+\varepsilon^2} |\mathcal{H}'_{fi}|^2$$

$$W_{fi} = \lim_{\varepsilon\to 0} \frac{d}{dt} \frac{1}{\hbar^2} \frac{e^{2\varepsilon t}}{(\omega_{fi}-\omega)^2+\varepsilon^2} |\mathcal{H}'_{fi}|^2 = \frac{2|\mathcal{H}'_{fi}|^2}{\hbar^2} \underbrace{\lim_{\varepsilon\to 0} \frac{\varepsilon}{(\omega_{fi}-\omega)^2+\varepsilon^2}}_{\pi\cdot\delta(\omega_{fi}-\omega)} =$$

$$= \frac{2\pi|\mathcal{H}'_{fi}|^2}{\hbar^2} \delta(\omega_{fi}-\omega) = \frac{2\pi|\mathcal{H}'_{fi}|^2}{\hbar} \delta(E_f-E_i-\hbar\omega)$$

This last formula should be understood is such a way that it requires an integral over a band of energy, i.e. it is only applicable if there is a continuum of final energies:

$$\overline{W_{fi}} = \int W_{fi}\, dE_f' = \int \frac{2\pi|\mathcal{H}'_{fi}|^2}{\hbar} \delta(E_f'-E_i-\hbar\omega)\, g(E_f')\, dE_f'$$

$$= \frac{2\pi|\mathcal{H}'_{fi}|^2}{\hbar} g(E_i+\hbar\omega) = \frac{2\pi}{\hbar} |\mathcal{H}'_{fi}|^2 g(E_f)$$

Second order transitions

Although the first order perturbation theory is often sufficient to obtain meaningful values of the transition probabilities, sometimes the transition matrix element $\langle f|\mathcal{H}'|i\rangle$ happens to be identically zero due to the symmetry (e.g. selection rules). At the same time other transition matrix elements may not necessarily be zeros. In such an event the transition may be accomplished via an indirect route. We can estimate the transition probabilities by turning to the second order of the perturbation theory:

$$c_f^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m{}' \int_{t_0}^{t} dt'\, H'_{fm}(t')\, e^{i\omega_{fm}t'} \int_{t_0}^{t'} dt''\, H'_{mi}(t'')\, e^{i\omega_{mi}t''}$$

Let us suppose that a harmonic perturbation is gradually switched on (ε is small):

$$H'(\vec{r},t) = e^{\varepsilon t}\,\mathcal{H}'(\vec{r})\,e^{-i\omega t}$$

and $t_0 = -\infty$, then

$$c_f^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m{}' \mathcal{H}'_{fm}\mathcal{H}'_{mi} \int_{-\infty}^{t} dt'\, e^{i(\omega_{fm}-\omega-i\varepsilon)t'} \int_{-\infty}^{t'} dt''\, e^{i(\omega_{mi}-\omega-i\varepsilon)t''} =$$

$$= -\frac{1}{\hbar^2}\sum_m{}' \mathcal{H}'_{fm}\mathcal{H}'_{mi}\left(\frac{-i}{\omega_{mi}-\omega-i\varepsilon}\right) \int_{-\infty}^{t} dt'\, e^{i(\overbrace{\omega_{fm}+\omega_{mi}}^{\omega_{fi}}-2\omega-2i\varepsilon)t'} =$$

$$= \frac{1}{\hbar^2}\sum_m \mathcal{H}'_{fm}\mathcal{H}'_{mi}\,\frac{1}{\omega_{mi}-\omega-i\varepsilon}\,\frac{e^{i(\omega_{fi}-2\omega-2i\varepsilon)t}}{\omega_{fi}-2\omega-2i\varepsilon} =$$

$$= \frac{1}{\hbar^2}\,\frac{e^{i(\omega_{fi}-2\omega)t}\,e^{2\varepsilon t}}{\omega_{fi}-2\omega-2i\varepsilon}\sum_m{}' \frac{\mathcal{H}'_{fm}\mathcal{H}'_{mi}}{\omega_{mi}-\omega-i\varepsilon}$$

$$|C_f^{(2)}|^2 = \frac{1}{\hbar^4}\,\frac{e^{4\varepsilon t}}{(\omega_{fi}-2\omega)^2+(2\varepsilon)^2}\left|\sum_m{}' \frac{\mathcal{H}'_{fm}\mathcal{H}'_{mi}}{\omega_{mi}-\omega-i\varepsilon}\right|^2$$

$$W_{fi}^{(2)} = \lim_{\varepsilon\to 0}\frac{d}{dt}|C_f^{(2)}|^2 = \lim_{\varepsilon\to 0}\frac{2}{\hbar^4}\underbrace{\frac{2\varepsilon}{(\omega_{fi}-2\omega)^2+(2\varepsilon)^2}}_{\pi\,\delta(\omega_{fi}-2\omega)}\left|\sum_m{}' \frac{\mathcal{H}'_{fm}\mathcal{H}'_{mi}}{\omega_{mi}-\omega-i\varepsilon}\right|^2 =$$

$$= \frac{2\pi}{\hbar^4}\left|\sum_m{}' \frac{\mathcal{H}'_{fm}\mathcal{H}'_{mi}}{\omega_{mi}-\omega-i\varepsilon}\right|^2 \delta(\omega_{fi}-2\omega)$$

This is a transition in which the system gains energy $2\hbar\omega$ from the harmonic perturbation, i.e. two "photons" are absorbed, first taking the system into the intermediate energy $\hbar\omega_m$ (which is short-lived and therefore not well defined in energy) and then to the final energy $\hbar\omega_f$. There is no energy conservation requirement for the intermediate (virtual) transition. The energy is conserved between the initial and final states, however.