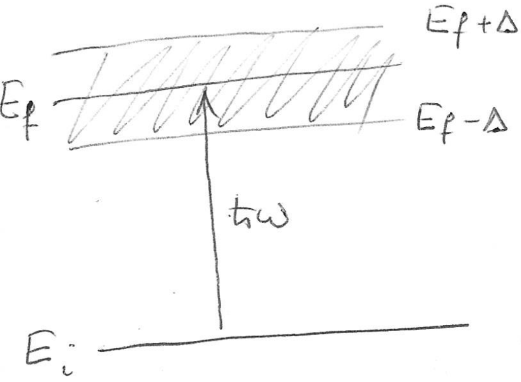
Fermi's golden rule

In many problems of practical interest, the final excited states lie in a band of energies. This takes place, for example, for ionization of free-particle scattering states that compise a continuum. If the density of final states is $g(E_f)$ then the number of energy states in the interval $[E_f, E_f+\Delta E_f]$ is



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

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

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

By inserting the expression we obtained in the last lecture for P_{if} (under harmonic perturbation) $\left(P_{if} = \frac{|H'_{fi}|^2}{\hbar^2(\omega_{fi}-\omega)^2} \sin^2\left[\frac{(\omega_{fi}-\omega)t}{2}\right] \right)$ the we get following

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

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

$$2\beta\hbar = (E_f - E_i - \hbar\omega)t$$

For fixed E_i, t, and ω

$$dE_f' = \frac{2\hbar\, d\beta}{t}$$

and

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

where 2δ is the corresponding spread in β values

Because of 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

$$\int_{-\infty}^{+\infty} \frac{\sin^2\beta}{\beta^2}\, d\beta = \pi$$

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

It should be noted that our harmonic perturbation (see previous lecture) was of the form $\mathcal{H}(r)\cos\omega t$. Most textbooks tend to use $2\mathcal{H}\cos\omega t$ or $\mathcal{H}(r)\left(e^{i\omega t} + e^{-i\omega t}\right)$ instead. If we change $\cos\omega t \to 2\cos\omega t$ we will get a factor of 4 in our expression for $\overline{P}_{if}$

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

Then the related transition probability rate is

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

This formula is often called the Fermi golden rule

One might worry that, in the long time limit, 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 matrix element

Second order transitions

Although the first order perturbation theory is often sufficient to describe the transition probabilities, sometimes first order matrix element $\langle f | \mathcal{H}' | i \rangle$ is identically zero due to symmetry (e.g. selection rules), but other matrix elements are non-zero. In such cases, the transition may be accomplished by an inderect route. We can estimate the transition probabilities by turning to the second order of perturbation theory

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

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

$$H'(t) = e^{\varepsilon t} \mathcal{H}(\bar{r}) e^{-i\omega t} \quad \text{and} \quad t_0 \to -\infty$$

then

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

This yields

$$c_f^{(2)}(t) = -\frac{1}{\hbar^2} e^{i(\omega_{fi}-2\omega)t} \frac{e^{2\varepsilon t}}{\omega_{fi}-2\omega-2i\varepsilon} \sum_m \frac{\langle f|\mathcal{H}'|m\rangle \langle m|\mathcal{H}'|i\rangle}{\omega_m-\omega_i-\omega-i\varepsilon}$$

Then the transition rate is

$$\frac{d}{dt}|c_n^{(2)}|^2 = \frac{2\pi}{\hbar^4} \left| \sum_m \frac{\langle f|\mathcal{H}'|m\rangle \langle m|\mathcal{H}'|i\rangle}{\omega_m-\omega_i-\omega-i\varepsilon} \right|^2 \delta(\omega_{fi}-2\omega)$$

where we used the identity

$$\lim_{\varepsilon\to 0} \frac{2\varepsilon}{(\omega_{fi}-\omega)^2+\varepsilon^2} \to 2\pi\,\delta(\omega_{fi}-\omega)$$

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

Alternative derivation of the golden rule

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

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

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

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

$$W_{fi} = \frac{d}{dt} |c_f^{(1)}|^2 = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}' | i \rangle|^2\, \delta(\omega_{fi} - \omega)$$