10.4: Transition Rates from Correlation Functions

We have already seen that the rates obtained from first-order perturbation theory are related to the Fourier transform of the time-dependent external potential evaluated at the energy gap between the initial and final state. Here we will show that the rate of leaving an initially prepared state, typically expressed by Fermi's Golden Rule through a resonance condition in the frequency domain, can be expressed in the time-domain picture in terms of a time-correlation function for the interaction of the initial state with others. The state-to-state form of Fermi's Golden Rule is

$$w_{k\ell} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \tag{10.4.1}$$

We will look specifically at the case of a system at thermal equilibrium in which the initially populated states ℓ are coupled to all states k. Time-correlation functions are expressions that apply to systems at thermal equilibrium, so we will thermally average this expression.

$$\overline{w}_{k\ell} = \frac{2\pi}{\hbar} \sum_{k,\ell} p_\ell |V_{k\ell}|^2 \delta(E_k - E_\ell) \tag{10.4.2}$$

where $p_\ell = e^{-\beta E_\ell}/Z$ and Z is the partition function. The energy conservation statement expressed in terms of E or ω can be converted to the time domain using the definition of the delta function

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{i\omega t} \tag{10.4.3}$$

giving

$$\overline{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell |V_{k\ell}| \int_{-\infty}^{+\infty} dt e^{i(E_k - E_l)t/h} \tag{10.4.4}$$

Writing the matrix elements explicitly and recognizing that in the interaction picture,

$$e^{-iH_0 t/h} |\ell\rangle = e^{-iE_l t/h} |\ell\rangle, \tag{10.4.5}$$

we have

$$\overline{w}_{k\ell} = \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt\, e^{i(E_k - E_\ell)t/\hbar} \langle \ell | V | k \rangle \langle k | V | \ell \rangle \tag{10.4.6}$$

$$= \frac{1}{\hbar^2} \sum_{k,\ell} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V | k \rangle \left\langle k \left| e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar} \right| \ell \right\rangle \tag{10.4.7}$$

Then, since $\sum_k |k\rangle\langle k| = 1$,

$$\overline{w}_{mn} = \frac{1}{\hbar^2} \sum_{\ell = m,n} p_\ell \int_{-\infty}^{+\infty} dt \langle \ell | V_I(0) V_I(t) | \ell \rangle \tag{10.4.8}$$

$$= \overline{w}_{mn} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_I(t) V_I(0) \rangle \tag{10.4.9}$$

As before

$$V_I(t) = e^{iH_0 t/h} V e^{-iH_0 t/\hbar} \tag{10.4.10}$$

The final expression in Equation 10.4.9 indicates that integrating over a correlation function for the time-dependent interaction of the initial state with its surroundings gives the relaxation or transfer rate. This is a general expression. Although the derivation emphasized specific eigenstates, Equation 10.4.9 shows that with a knowledge of a time-dependent interaction potential of any sort, we can calculate transition rates from the time-correlation function for that potential.

The same approach can be taken using the rates of transition in an equilibrium system induced by a harmonic perturbation

$$\overline{w}_{k\ell} = \frac{\pi}{2\hbar^2} \sum_{\ell,k} p_\ell |V_{k\ell}|^2 \left[\delta\left(\omega_{k\ell} - \omega\right) + \delta\left(\omega_{k\ell} + \omega\right)\right] \tag{10.4.11}$$

resulting in a similar expression for the transition rate in terms of a interaction potential time-correlation function

$$\overline{w}_{k\ell} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \left\langle V_I(0) V_I(t) \right\rangle \tag{10.4.12}$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \left\langle V_I(t) V_I(0) \right\rangle \tag{10.4.13}$$

We will look at this closer in the following section. Note that here the transfer rate is expressed in terms of a Fourier transform over a correlation function for the time-dependent interaction potential. Although Equation 10.4.9 is not written as a Fourier transform, it can in practice be evaluated by a Fourier transformation and evaluating its value at zero frequency.

Readings on time-correlation functions

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