

# s03E05 Time-dependent perturbation theory

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## 1 The interaction picture

Suppose that the Hamiltonian is a sum of two parts

$$H = H_0 + H_1$$

with the first part  $H_0$  having eigenstates  $\psi_i$ , namely  $H_0\psi_i = E_i\psi_i$ . If the initial state is  $\psi_i$ , the transition probability to  $\psi_j$  after a time evolution of length  $t$  is equal to

$$p_{i \rightarrow j} = |\langle \psi_j | e^{-iHt} | \psi_i \rangle|^2$$

and we have  $\sum_j p_{i \rightarrow j} = 1$  due to the completeness of the eigenstates  $\psi_j$ . Notice that the symbol  $\exp -iHt$  should really mean the time-ordered version of it. What we are going to derive in the following will be true in the general case.

We would like to know the effect of  $H_1$  on the transition probability, since if  $H_1$  vanishes then we simply have  $p_{i \rightarrow j} = \delta_{ij}$ . A method called the interaction picture simplifies the calculation somewhat, and at the same time provides us with some new insights. In effect, it does the following:

$$\begin{aligned} p_{i \rightarrow j} &= |\langle \psi_j | e^{-iHt} | \psi_i \rangle|^2 \\ &= |\langle \psi_j | e^{iH_0t} e^{-iHt} | \psi_i \rangle|^2 \end{aligned}$$

where the operator  $\exp(iH_0t)\exp(-iHt)$  satisfies the following differential equation

$$\begin{aligned} d_t e^{iH_0t} e^{-iHt} &= -i e^{iH_0t} H_1 e^{-iHt} \\ &= -i e^{iH_0t} H_1 e^{-iH_0t} e^{iH_0t} e^{-iHt} \\ &\equiv -i H_{1I} e^{iH_0t} e^{-iHt} \end{aligned}$$

The solution is given by the Dyson series

$$e^{iH_0t} e^{-iHt} = 1 - i \int_0^t dt' H_{1I} - \int_0^t dt' \int_0^{t'} dt'' H_{1I} H_{1I} + \dots$$

Therefore, to first order in  $H_1$ , the transition amplitude is equal to

$$\begin{aligned}\langle \psi_j | e^{iH_0 t} e^{-iHt} | \psi_i \rangle &= \delta_{ij} - i \int_0^t dt' \langle \psi_j | H_{1I} | \psi_i \rangle \\ &= \delta_{ij} - i \int_0^t dt' \langle \psi_j | H_1 | \psi_i \rangle e^{-i\omega_{ij} t'}\end{aligned}$$

## 2 A diagrammatic representation

The operator  $\exp(iH_0 t) \exp(-iHt)$  can also be written as

$$e^{iH_0 t} e^{-iHt} = \mathcal{T} \exp \left( -i \int_0^t dt' H_{1I} \right)$$

which may be generalized to

$$U_{21} \equiv U_2 U_{1\dagger} = e^{iH_0 t_2} e^{-iHt_2} e^{-iH_0 t_1} = \mathcal{T} \exp \left( -i \int_{t_1}^{t_2} dt' H_{1I} \right)$$

with the following diagrammatic representation

$$\begin{aligned}1 &\rightsquigarrow 2 \rightsquigarrow 1 \\ 1 &\rightsquigarrow 2 \rightarrow 1 \rightarrow 2 \rightarrow 1 \rightarrow 2 \rightsquigarrow 1 \\ 0 &\rightarrow 1 \rightsquigarrow 2 \rightarrow 0 \rightarrow 2 \rightarrow 0 \rightarrow 2 \rightsquigarrow 1 \rightarrow 0\end{aligned}$$

## 3 Case I: Constant perturbation

Suppose that  $H_1 = V$  is a constant operator, then the transition amplitude above evaluates to

$$\langle \psi_j | e^{iH_0 t} e^{-iHt} | \psi_i \rangle = V_{ji} \frac{e^{-i\omega_{ij} t} - 1}{\omega_{ij}}$$

assuming  $j \neq i$ . The transition probability is

$$p_{i \rightarrow j} = |V_{ji}|^2 \left( \frac{\sin \omega_{ij} t / 2}{\omega_{ij} / 2} \right)^2$$

which takes the form of the familiar "sinc" function. Interestingly, when  $t$  is very large, the transition probability  $p_{i \rightarrow j}$  has the limiting behavior

$$p_{i \rightarrow j} \rightarrow |V_{ji}|^2 2\pi t \delta^1(\omega_{ij})$$

This is a first sign of **Fermi's golden rule**.

However, the result above should only hold for sufficiently small  $t$ , since the expression of the transition probability does not always satisfy  $p_{i \rightarrow j} \leq 1$ . This is also called the **unitarity bound**. For example,

$$\omega_{ij} = 0 \Rightarrow p_{i \rightarrow j} = |V_{ji}|^2 t^2$$

and thus we require that  $t \ll |V_{ji}|^{-1}$ .

## 4 Case II: Monochromatic perturbation

Suppose that  $H_1 = V \exp -i\omega t + V^\dagger \exp i\omega t$ , where  $V$  is a constant operator. This form will come out more naturally later when we discuss Dirac's derivation of the Einstein's coefficients. The transition amplitude is equal to

$$\langle \psi_j | e^{iH_0 t} e^{-iHt} | \psi_i \rangle = V_{ji} \frac{e^{-i\omega_{ij}t} e^{-i\omega t} - 1}{\omega_{ij} + \omega} + V_{ij*} \frac{e^{-i\omega_{ij}t} e^{i\omega t} - 1}{\omega_{ij} - \omega}$$

which, assuming  $j \neq i$ , contains two terms. Thus  $p_{i \rightarrow j}$  will contain four terms.

To make some simplifications, we may focus on the case when  $\omega$  is close to  $\pm\omega_{ij}$ . If for example  $\omega$  is close to  $+\omega_{ij}$ , then the second term dominates, and the transition probability  $p_{i \rightarrow j}$  is approximately equal to

$$p_{i \rightarrow j} \approx |V_{ij}|^2 \left( \frac{\sin \omega_{ij-} t / 2}{\omega_{ij-} / 2} \right)^2$$

where  $\omega_{ij-} \equiv \omega_{ij} - \omega$ .

Although we may not take  $t \rightarrow \infty$ , when the final state lies in a spectrum continuum, it can be justified (see Tong Chen's notes) that we may take  $t$  large, such that

$$\langle \psi_j | e^{iH_0 t} e^{-iHt} | \psi_i \rangle \approx -iV_{ji} 2\pi \delta^1(\omega_{ij} + \omega) - iV_{ij*} 2\pi \delta^1(\omega_{ij} - \omega)$$

which means that

$$p_{i \rightarrow j} \approx |V_{ji}|^2 2\pi t \delta^1(\omega_{ij} + \omega) + |V_{ij}|^2 2\pi t \delta^1(\omega_{ij} - \omega)$$

where the cross terms vanish since  $\omega \neq 0$ . Here we have used one of the delta functions to evaluate the other delta function integral, and obtained  $t$ .

## 5 Einstein's coefficients

The Einstein's coefficients are defined by

$$\begin{aligned} d_t n_1 &= A_{12} n_2 + B_{12} \rho_\omega n_2 - B_{21} \rho_\omega n_1 \\ d_t n_2 &= -d_t n_1 \end{aligned}$$

and Einstein: when  $d_t n_1 = d_t n_2 = 0$ ,

$$\frac{n_2}{n_1} = \frac{B_{21} \rho_\omega}{A_{12} + B_{12} \rho_\omega} = e^{-\beta \omega}$$

## 6 The electromagnetic field is quantized

Consider the following interaction between the atoms and the photons

$$H_1 = V a + V^\dagger a^\dagger$$

which gives us the transition probability

$$\begin{aligned} p_{1,n \rightarrow 2,n-1} &= n_\omega |V_{21}|^2 2\pi t \delta^1(\omega_{21} - \omega) \\ p_{2,n \rightarrow 1,n+1} &= (n_\omega + 1) |V_{21}|^2 2\pi t \delta^1(\omega_{21} - \omega) \end{aligned}$$

and thus the Einstein's coefficients are

$$d_t n_1 \propto -n_\omega |V_{21}|^2 n_1 + (n_\omega + 1) |V_{21}|^2 n_2$$

For phonons, the energy per unit volume is

$$\mathcal{E} = 2 \int \frac{d^3 k}{(2\pi)^3} \frac{\omega}{e^{\beta \omega} - 1} = \int d\omega \frac{\omega^2}{\pi^2} \frac{\omega}{e^{\beta \omega} - 1} = \int d\omega n_\omega \frac{\omega^3}{\pi^2}$$

which gives us the spectral energy density

$$\rho_\omega = n_\omega \frac{\omega^3}{\pi^2}$$

and thus we read

$$\begin{aligned} B_{21} &= B_{12} \\ A_{12} &= B_{12} \frac{\omega^3}{\pi^2} \end{aligned}$$