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 ψ_i, namely $H_0\psi_i = E_i\psi_i$. If the initial state is ψ_i, the transition probability to ψ_j after a time evolution of length t is equal to

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

and we have $\sum_j p_{i\to j} = 1$ due to the completeness of the eigenstates ψ_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 $p_{i\to j} = \delta_{ij}$. 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:

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

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

$$\begin{aligned} d_t e^{iH_0t}e^{-iHt} &= -ie^{iH_0t}H_1e^{-iHt} \\ &= -ie^{iH_0t}H_1e^{-iH_0t}e^{iH_0t}e^{-iHt} \\ &\equiv -iH_{1I}e^{iH_0t}e^{-iHt} \end{aligned}$$

The solution is given by the Dyson series

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

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

$$\begin{aligned}\langle\psi_j|e^{iH_0t}e^{-iHt}|\psi_i\rangle &= \delta_{ij} - i\int_0^t dt'\,\langle\psi_j|H_{1I}|\psi_i\rangle \\ &= \delta_{ij} - i\int_0^t dt'\,e^{-i\omega_{ij}t'}\langle\psi_j|H_1|\psi_i\rangle\end{aligned}$$

2 A diagrammatic representation

The operator $\exp(iH_0t)\exp(-iHt)$ can also be written as

$$e^{iH_0t}e^{-iHt} = \mathcal{T}\exp\left(-i\int_0^t dt'\,H_{1I}\right)$$

which may be generalized to

$$U_{21} \equiv U_2 U_{1\dagger} = e^{iH_0t_2}e^{-iHt_{21}}e^{-iH_0t_1} = \mathcal{T}\exp\left(-i\int_{t_1}^{t_2} dt'\,H_{1I}\right)$$

with the following diagrammatic representation

$$\begin{gathered}1 \rightsquigarrow 2 \rightsquigarrow 1 \\ 1 \rightsquigarrow 2 \rightarrow 1 \rightarrow 2 \rightarrow 1 \rightarrow 2 \rightsquigarrow 1 \\ 0 \rightarrow 1 \rightsquigarrow 2 \rightarrow 0 \rightarrow 2 \rightarrow 0 \rightarrow 2 \rightsquigarrow 1 \rightarrow 0\end{gathered}$$

3 Case I: Constant perturbation

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

$$\langle\psi_j|e^{iH_0t}e^{-iHt}|\psi_i\rangle = V_{ji}\,\frac{e^{-i\omega_{ij}t}-1}{\omega_{ij}}$$

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

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

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

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

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 $p_{i\to j} \le 1$. This is also called the **unitarity bound**. For example,

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

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 solution to 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 $p_{i\to j}$ will contain four terms.

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

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

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

Although we may not take $t \to \infty$, 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

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

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

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

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

$$p_{1,n\to 2,n-1} = n_\omega |V_{21}|^2 2\pi t \delta^1(\omega_{21} - \omega)$$
$$p_{2,n\to 1,n+1} = (n_\omega + 1)|V_{21*}|^2 2\pi t \delta^1(\omega_{21} - \omega)$$

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

$$B_{21} = B_{12}$$
$$A_{12} = B_{12} \frac{\omega^3}{\pi^2}$$