Chapter 8

Perturbation Theory

One of the simplest examples of evaluation of the functional transition amplitudes is their perturbative expansion. Now, we split the action in two

$$S = S_0 + \sigma \tag{8.1}$$

where S_0 is an action whose functional amplitudes we can evaluate exactly, and which gives us a reasonable zero order description of our system, and σ is treated as a small perturbation. Therefore, in the notation of the previous section, we can write the following expansion

$$<\chi|1|\psi>_{S_0+\sigma} = <\chi|e^{\frac{i}{\hbar}\sigma}|\psi>_{S_0} =$$

$$= <\chi|1|\psi>_{S_0} + \frac{i}{\hbar} <\chi|\sigma|\psi>_{S_0} + \frac{1}{2!}\left(\frac{i}{\hbar}\right)^2 <\chi|\sigma^2|\psi>_{S_0} + ... \tag{8.2}$$

We shall work out (8.2) in more detail for the standard case when σ is determined by a perturbative potential $V(x,t)$, and S_0 is that of a "free" motion. Then

$$\sigma = -\int dt\, V(x(t),t) \tag{8.3}$$

where $x(t)$ is the quantal trajectory. Thus the expansion in (8.2) becomes

$$e^{-\frac{i}{\hbar}\int_{t_a}^{t_b} dt V(x(t),t)} = 1 - \frac{i}{\hbar}\int_{t_a}^{t_b} dt\, V(x(t),t) + \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \left[\int_{t_a}^{t_b} V(x(t),t)\right]^2 + \ldots, \tag{8.4}$$

and the perturbative expansion of the propagator,

$$K(b,a) = \int [\mathcal{D}x(t)]\, e^{\frac{i}{\hbar}\int_{t_a}^{t_b} dt\,(\frac{m}{2}\dot{x}^2 - V(x,t))}, \tag{8.5}$$

goes as follows:

$$K(b,a) = K_0(b,a) + K_1(b,a) + K_2(b,a) + ... \tag{8.6}$$

where

$$K_0 = \int [\mathcal{D}x(t)]\, e^{\frac{i}{\hbar}\int_{t_a}^{t_b} dt \frac{m}{2}\dot{x}^2}\,,$$

$$K_1 = -\frac{i}{\hbar}\int [\mathcal{D}\,x(t)]\, e^{\frac{i}{\hbar}\int_{t_a}^{t_b} dt \frac{m}{2}\dot{x}^2} \int_{t_a}^{t_b} ds\, V(x(s),s)\,, \tag{8.7}$$

$$K_2 = \frac{1}{2!}\left(-\frac{i}{\hbar}\right)^2 \int [\mathcal{D}x(t)]\, e^{\frac{i}{\hbar}\int_{t_a}^{t_b} dt \frac{m}{2}\dot{x}^2} \int_{t_a}^{t_b} ds\, V(x(s),s) \int_{t_a}^{t_b} ds'\, V(x(s'),s')\,.$$

etc.

In order to exhibit the structure of consecutive terms of the expansion (8.6) let us analyze the first order contribution and exchange the order of integration: first let us do the sum over trajectories with s fixed and then integrate over ds

$$K_1(b,a) = -\frac{i}{\hbar}\int_{t_a}^{t_b} ds \int [\mathcal{D}x(t)]\, e^{\frac{i}{\hbar}\int_{t_a}^{t_b} dt \frac{m}{2}\dot{x}^2}\, V(x(s),s)\,. \tag{8.8}$$

For the quantal trajectory $x(s)$ we choose $t_a < s = t_c < t_b$ and then a corresponding (arbitrary) x_c. So, we have free propagation from (x_a, t_a) to (x_c, t_c), then the scattering takes place with the amplitude $-\frac{i}{\hbar}V dx_c dt_c$ and then free propagation continues from (x_c, t_c) to (x_b, t_b). In the end we have to integrate over $dx_c dt_c$:

$$K_1(b,a) = -\frac{i}{\hbar}\int_{t_a}^{t_b}\int_{-\infty}^{+\infty} K_0(b,c)\, V(c)\, K_0(c,a)\, dx_c dt_c\,. \tag{8.9}$$

Following analogous steps we can see that $K_2(b,a)$ is composed of two scatterings at some intermediate space-time points d and c and free propagation in between:

$$K_2(b,a) = \left(-\frac{i}{\hbar}\right)^2 \int\int K_0(b,c)\, V(c)\, K_0(c,d)\, V(d)\, K_0(d,a)\, d\tau_c d\tau_d \tag{8.10}$$

where $d\tau = dxdt$. Note that the time sequence $t_c > t_d$ is kept by the propagators K_0, because they are defined to be such that

$$K_0(b,a) = 0 \qquad \text{for} \qquad t_b < t_a\,. \tag{8.11}$$

Note that in (8.7) there is a factor $1/2$ which disappeared in (8.10). This is the consequence of (8.11). Indeed, we can write

$$\int_{t_a}^{t_b} ds\, V(x(s),s) \int_{t_a}^{t_b} ds' V(x(s'),s') =$$

$$= \int_{t_a}^{t_b} ds\, V(x(s),s) \int_{s}^{t_b} ds'\, V(x(s'),s') + \int_{t_a}^{t_b} ds\, V(x(s),s) \int_{t_a}^{s} ds'\, V(x(s'),s')\,.$$

The integrand of the l.h.s. is symmetric in s and s', therefore, each of the two terms on the r.h.s. equals

$$\tfrac{1}{2}\int_{t_a}^{t_b} ds\, V(x(s),s)\int_{t_a}^{t_b} ds'\, V(x(s'),s')\ .$$

But only the second of them, because of (8.11), contributes to $K_2(b,a)$. So, we can keep in (8.10) the integration over the whole available space-time and the factor $\frac{1}{2}$ disappears because of the causal behavior of $K_0(b,a)$.

In fact similar things happen at all orders of our perturbative expansion (8.6). The $1/n!$ factors which appear in the expansion (8.4) disappear when we write down each $K_n(b,a)$ in terms of $n+1$ K_0' s.

Note that the expansion (8.6) leads to an integral equation for $K(b,a)$. Indeed, we can write

$$\begin{aligned} K(b,a) \;=\; & K_0(b,a) \;-\; \frac{i}{\hbar}\int K_0(b,c)\,V(c)\,K_0(c,a)\,d\tau_c \\ & + \left(-\frac{i}{\hbar}\right)^2 \int\int K_0(b,c)\,V(c)\,K_0(c,d)\,V(d)\,K_0(d,a)\,d\tau_c d\tau_d \;+\; ... \\ =\; & K_0(b,a) \;-\; \frac{i}{\hbar}\int K_0(b,c)\,V(c)\,d\tau_c \Big[K_0(c,a) \\ & - \frac{i}{\hbar}\int K_0(c,d)\,V(d)\,K_0(d,a)\,d\tau_d \;+\; ... \Big]\,. \end{aligned} \tag{8.12}$$

The expression in the square brackets equals $K(c,a)$, thus the integral equation follows

$$K(b,a) \;=\; K_0(b,a) \;-\; \frac{i}{\hbar}\int K_0(b,c)\,V(c)\,K(c,a)\,d\tau_c\,. \tag{8.13}$$

Note that (8.13) results in an integral equation for the wave functions. Indeed, $K(b,a)$ tells us how to evolve a wave function in time and space:

$$\psi(b) = \int K(b,a) f(a)\,dx_a \tag{8.14}$$

where $f(a)$ is the wave function at the space-time point a. Inserting (8.13) (or the perturbative expansion of $K(b,a)$ into (8.14)) we get

$$\psi(b) = \phi(b) - \frac{i}{\hbar}\int K_0(b,c)\,V(c)\,\psi(c)\,d\tau_c \tag{8.15}$$

where

$$\phi(b) = \int K_0(b,a) f(a)\,dx_a\,. \tag{8.16}$$

These integral equations can serve to generate multiple scattering corrections both to propagators and wave functions.

Note that in the perturbative expansion (8.6) $K_0(b,a)$ does not have to represent propagation of a free particle: it can be any propagator whose analytic structure is known. This is illustrated on the example which follows.

8.1 Stationary state perturbation theory

Now we shall work out in detail the case in which we have the exact solutions for the energy eigenfunctions ϕ_n and their eigenvalues E_n, thus the zero order propagation is not that of the free motion. The zero order propagator is now:

$$K_0(2,1) = \sum_n \phi_n(x_2)\phi_n^*(x_1)\, e^{-\frac{i}{\hbar}E_n(t_2-t_1)}\,, \qquad t_2 > t_1\,. \tag{8.17}$$

Writing down the perturbative expansion (8.6) with $K_0(2,1)$ given by (8.17), we have from (8.9)

$$\begin{aligned} K(2,1) \;=\; & \sum_n \phi_n(x_2)\phi_n^*(x_1)\, e^{-\frac{i}{\hbar}E_n(t_2-t_1)} \\ & -\frac{i}{\hbar}\sum_n\sum_m \int \phi_m(x_2)\phi_m^*(x_3)\, e^{-\frac{i}{\hbar}E_m(t_2-t_3)}\, V(x_3,t_3) \\ & \times \phi_n(x_3)\phi_n^*(x_1)\, e^{-\frac{i}{\hbar}E_n(t_3-t_1)}\, dx_3 dt_3 + \ldots\,. \end{aligned} \tag{8.18}$$

We see that in each term of the expansion (8.14) the factor $\phi_m(x_2)\phi_n^*(x_1)$ appears, hence we can write

$$K(2,1) \;=\; \sum_n\sum_m \lambda_{mn}(t_2,t_1)\,\phi_m(x_2)\phi_n^*(x_1)\,. \tag{8.19}$$

Clearly, $\lambda_{mn}(t_2,t_1)$ is the transition amplitude from the stationary state n to the stationary state m in time t_2-t_1, caused by the perturbation $V(x,t)$:

$$\lambda_{mn}(t_2,t_1) = \int \phi_m^*(x_2)\, K(x_2,t_2;x_1,t_1)\,\phi_n(x_1)\, dx_2 dx_1\,. \tag{8.20}$$

Note that when $V=0$ all amplitudes $\lambda_{m\neq n}=0$.

Expanding $\lambda_{mn}(t_2,t_1)$ in a perturbation series with increasing powers of V, we obtain

$$\lambda_{mn}(t_2,t_1) \;=\; \delta_{mn}e^{-\frac{i}{\hbar}E_n(t_2-t_1)} \;+\; \lambda_{mn}^{(1)}(t_2,t_1) \;+\; \lambda_{mn}^{(2)}(t_2,t_1) \;+\; \ldots \tag{8.21}$$

where the first term on the r.h.s. is $\lambda_{mn}^{(0)}(t_2,t_1)$. From the perturbative expansion of $K(b,a)$, we find from (8.9)

$$\lambda_{mn}^{(1)}(t_2,t_1) \;=\; -\frac{i}{\hbar}\, e^{-\frac{i}{\hbar}E_m t_2} e^{+\frac{i}{\hbar}E_n t_1} \int_{t_1}^{t_2} dt_3\, V_{mn}(t_3)\, e^{\frac{i}{\hbar}(E_m-E_n)t_3}\,, \tag{8.22}$$

and from (8.10)

$$\begin{aligned} \lambda_{mn}^{(2)}(t_2,t_1) \;=\; & \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_m t_2}\, e^{+\frac{i}{\hbar}E_n t_1} \sum_k \int_{t_1}^{t_2} dt_4\, e^{\frac{i}{\hbar}t_4(E_m-E_k)}\, V_{mk}(t_4) \\ & \times \left[\int_{t_1}^{t_4} dt_3\, e^{\frac{i}{\hbar}t_3(E_k-E_n)}\, V_{kn}(t_3)\right], \end{aligned} \tag{8.23}$$

etc., where

$$V_{mn}(t) \;=\; \int dx\, \phi_m^*(x)\, V(x,t)\, \phi_n(x)\,. \tag{8.24}$$

Clearly, this perturbation theory is applicable to the systems whose zero order description is in terms of a time independent Hamiltonian. The perturbative interaction V however, may assume various time dependencies.

Note that the integral equation for $K(b,a)$ implies the following integral equation for λ_{mn}:

$$\lambda_{mn}(t_2,t_1) = \delta_{mn} E^{-\frac{i}{\hbar}E_n(t_2-t_1)} \;-\; \frac{i}{\hbar}\int_{t_1}^{t_2} dt_3\, e^{-\frac{i}{\hbar}E_m(t_2-t_3)} \sum_k V_{mk}(t_3)\, \lambda_{kn}(t_3,t_1)\,. \tag{8.25}$$

Differentiating both sides of this integral equation with respect to t_2 we obtain a differential equation for λ_{mn}:

$$\frac{d}{dt_2}\lambda_{mn}(t_2,t_1) = -\frac{i}{\hbar}\sum_k V_{mk}(t_2)\, \lambda_{kn}(t_2,t_1) - \frac{i}{\hbar}E_m\, \lambda_{mn}(t_2,t_1)\,. \tag{8.26}$$

Let us discuss now the first order transition amplitude in more detail. Let

$$V(x,t) = V(x) \quad \text{for} \quad t>0 \qquad \text{and} \qquad 0 \quad \text{otherwise}\,.$$

From (8.22) we get for the probability of transition $n \to m$ in time T:

$$P(n\to m) \;=\; |\lambda_{mn}^{(1)}|^2 \;=\; |V_{mn}|^2\, \frac{4\sin^2\left[\frac{(E_m-E_n)T}{2\hbar}\right]}{(E_m-E_n)^2}\,. \tag{8.27}$$

For large T , $P(n\to m)$ is a strongly fluctuating function of $E_m - E_n = \Delta E$. It reaches its maximum $(T/\hbar)^2$ at $\Delta E = 0$. The total probability of transition (to any final energy) is

$$\int_{-\infty}^{+\infty} dE_m\, \rho(E_m) P(n\to m) \;=\; \rho(E_n)\, |V_{mn}|^2\, \frac{2\pi}{\hbar} T \;=\; \Gamma\, T \tag{8.28}$$

where $\rho(E_m)$ is the density of the final states, and where we employed conservation of energy in the transition $n \to m$.

This leads to a few comments. Firstly, the large T limit is reasonable because the time involved in any realistic detection is much longer than any "atomic scales" of our quantal system. But then the transitions $\Delta E = 0$ dominate, and we are dealing with processes which conserve the energy. Secondly, the total transition probability is proportional to T, hence it is useful to introduce the concept of the *transition rate* Γ of the process in question (compare (8.29)). This transition rate is therefore given directly through the well defined quantities

$$\Gamma \;=\; \frac{2\pi}{\hbar}|V_{mn}|^2 \rho(E_n)\,. \tag{8.29}$$

It is the famous "golden rule" of Fermi. Note that since

$$\lim_{T\to\infty} \frac{4\sin^2\left[\frac{(E_m-E_n)T}{2\hbar}\right]}{(E_m-E_n)^2} \;=\; \frac{2\pi}{\hbar} T\,\delta(E_m-E_n)\,, \tag{8.30}$$

we can introduce a *differential transition rate*

$$\Gamma(n\to m) \;=\; \frac{2\pi}{\hbar}|V_{mn}|^2\,\delta(E_m-E_n)\,. \tag{8.31}$$

Indeed,

$$\Gamma \;=\; \int dE_m\,\rho(E_m)\,\Gamma(n\to m) \;=\; \frac{2\pi}{\hbar}|V_{mn}|^2\,\rho(E_n)\,. \tag{8.32}$$

The fact that the probability becomes infinite for very large T is an artifact of the first approximation which is valid, after all, only when V is very small and the probability is also very small (in other words: to have internal consistency we have to take T large, but *not too large*). As it will be argued below the higher orders may remedy these shortcomings. The fluctuations of P with ΔE, on the other hand, stem from the sudden switch-on of the interaction V at $t=0$. They are of no physical consequence.

Before discussing all these limitations, let us mention still another one. When we set $E_n = E_m$ in (8.27) we obtain

$$P(n\to m) \;=\; |V_{mn}|^2\,\frac{T^2}{\hbar^2}\,. \tag{8.33}$$

Therefore, for two degenerate states the *rate* concept does not make sense. Let us, however, consider a simple model of a degenerate system which can be solved exactly with the help of the set of differential equations (8.26).

Take a two level system whose two eigenenergies are the same, $E_1 = E_2 = E$. As it turns out we can find an exact solution for its four amplitudes:

$$\begin{aligned}
|\lambda_{11}|^2 = |\lambda_{22}|^2 &= \cos^2\left(|V_{12}|\frac{T}{\hbar}\right)\\
|\lambda_{12}|^2 = |\lambda_{21}|^2 &= \sin^2\left(|V_{12}|\frac{T}{\hbar}\right)\,.
\end{aligned} \tag{8.34}$$

These results can be obtained from (8.26):

$$\begin{aligned}
\frac{d\lambda_{11}}{dt} &= -\frac{i}{\hbar}E\,\lambda_{11} - \frac{i}{\hbar}(V_{11}\lambda_{11}+V_{12}\lambda_{21})\\
\frac{d\lambda_{12}}{dt} &= -\frac{i}{\hbar}E\,\lambda_{12} - \frac{i}{\hbar}(V_{11}\lambda_{12}+V_{12}\lambda_{22})\\
\frac{d\lambda_{21}}{dt} &= -\frac{i}{\hbar}E\,\lambda_{21} - \frac{i}{\hbar}(V_{21}\lambda_{11}+V_{22}\lambda_{21})\\
\frac{d\lambda_{22}}{dt} &= -\frac{i}{\hbar}E\,\lambda_{22} - \frac{i}{\hbar}(V_{21}\lambda_{12}+V_{22}\lambda_{22})\,.
\end{aligned} \tag{8.35}$$

We simplify these equations setting $V_{12} = V_{21} = v$ and $V_{11} = V_{22} = 0$ (taking $V_{11} = V_{22} \neq 0$ would merely renormalize the energy, whereas $V_{11} \neq V_{22}$ would remove the degeneracy). The symmetry of the problem tells us to take $\lambda_{22} = \lambda_{11}$ and $\lambda_{12} = \lambda_{21}$. Finally, we obtain:

$$\begin{aligned} \frac{d\lambda_{11}}{dt} &= -\frac{i}{\hbar}(E\,\lambda_{11} + v\lambda_{12}) \\ \frac{d\lambda_{12}}{dt} &= -\frac{i}{\hbar}(E\,\lambda_{12} + v\lambda_{11})\,. \end{aligned} \tag{8.36}$$

Substituting

$$\lambda_{11} = e^{-\frac{i}{\hbar}Et}\,f(t)\,, \qquad \lambda_{12} = e^{-\frac{i}{\hbar}Et}\,g(t)\,,$$

with the initial conditions $f(0) = 1$ and $g(0) = 0$, we find

$$f(t) = \cos\left(\frac{|v|}{\hbar}t\right)\,, \qquad g(t) = -i\sin\left(\frac{|v|}{\hbar}t\right)\,. \tag{8.37}$$

Thus, indeed, we obtain (8.34). So, our system oscillates between the two states, and the first order perturbation gives the correct answer for $|v|T \ll \hbar$, which is $|\lambda_{12}|^2 = |v|^2T^2/\hbar^2$.

The moral of all this is that we should use the first order perturbation with clear understanding of its limitations. Let us suppose, for instance, that the final states form a fairly dense but discrete set of states. We get the following limitations on T. The energy conservation demands that the width of the group of the final states Δ_m be bigger than the distance of the first zero of $P(n \to m)$, i.e. $2\pi\hbar/T$ (compare (8.27)). This gives a lower limit on T:

$$T > \frac{2\pi\hbar}{\Delta_m}\,.$$

On the other hand the distance between the final states δ_m must be less than $2\pi\hbar/T$. This gives the upper limit for T:

$$T < \frac{2\pi\hbar}{\delta_m}\,.$$

Clearly, the *golden formula* works when

$$\Delta_m \gg \delta_m\,. \tag{8.38}$$