> The old idea of a static landscape, like a single musical chord sounded forever, must be abandoned, for such a landscape never existed, except in our imagination.
>
> *D.B. Botkin, "Discordant Harmonies"*

1
Nonstationary Perturbations

1.1
Transition Probability

In a closed system with the time-independent Hamiltonian $\hat{H}^\circ$ and corresponding spectrum E_n of stationary states $|n\rangle$,

$$\hat{H}^\circ|n\rangle = E_n|n\rangle \,, \tag{1.1}$$

in general, any non-stationary wave packet

$$|\Psi(t)\rangle = \sum_n a_n(t)|n\rangle \tag{1.2}$$

evolves in such a way that only the *relative phases* of the components change with time (*quantum beats*). The probability amplitude of finding the system in the n^{th} stationary state is

$$a_n(t) = a_n(0)e^{-(i/\hbar)E_n t} \,, \tag{1.3}$$

and the probabilities

$$w_n(t) = |a_n(t)|^2 = |a_n(0)|^2 \tag{1.4}$$

do not depend on time. Mean energy of the system is preserved as well,

$$\langle E\rangle = \sum_n E_n w_n \,. \tag{1.5}$$

The evolution changes if a *time-dependent perturbation* $\hat{H}'(t)$ is applied to the system. The Hamiltonian of the system,

$$\hat{H} = \hat{H}^\circ + \hat{H}'(t) \,, \tag{1.6}$$

is still the *evolution operator*,

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left[\hat{H}^\circ + \hat{H}'(t)\right]|\Psi(t)\rangle \,, \tag{1.7}$$

though no longer corresponds to conserved energy. The instantaneous state vector $|\Psi(t)\rangle$, as earlier, can be presented by a superposition (1.2) of unperturbed stationary states. The amplitudes $a_n(t)$ physically correspond to the measurement with

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the aid of the *sudden* switching off of the perturbation $\hat{H}'(t)$. As will be discussed in more detail below, at a sudden perturbation (recall Vol. 1 Problem 3.3), the wave function does not have time for changing and its value captured at this moment serves as an initial state for further unperturbed evolution governed again by the time-independent Hamiltonian – then w_n no longer change and can be measured.

With $\hat{H}'$ depending on time, the evolution of the wave function is not reduced to phase dynamics. The absolute probabilities w_n are now changing with time, and this can be revealed by experiments that switch off the perturbation at different moments. Even if at time t_0, the wave function $|\Psi(t_0)\rangle$ did not contain certain components $|n\rangle$, they can appear at later moments. This means that a non-stationary perturbation might be responsible for *quantum transitions* into states different from the initial one. If the transition probabilities are small, $\ll 1$, the perturbation can be called weak, and one can develop a special form of *non-stationary perturbation theory*. We need to stress that we speak of transition probabilities between stationary unperturbed states.

1.2 Perturbative Solution

To find an approximate solution of the time-dependent equation (1.7), it is convenient to use the superposition (1.2) with the redefined amplitudes $a_n(t)$ where the unperturbed exponential time dependence (1.3) is already included explicitly,

$$|\Psi(t)\rangle = \sum_n a_n(t) e^{-(i/\hbar)E_n t} |n\rangle \ . \tag{1.8}$$

The remaining time dependence of the amplitudes $a_n(t)$ is associated only with the perturbation $\hat{H}'(t)$. The transition from the old amplitudes in (1.2) to the new ones in (1.8) is called the transformation to the *interaction picture*; in mathematics, this is a method of *variation of constants*.

Using the ansatz (1.8) in the Schrödinger equation (1.7) and the definition (1.1) of stationary states, we obtain the set of coupled differential equations for new amplitudes $a_m(t)$ whose time dependence is caused only by perturbation $\hat{H}'(t)$,

$$i\hbar \dot{a}_m = \sum_n H'_{mn}(t) a_n(t) e^{i\omega_{mn}t} \ , \quad \omega_{mn} = \frac{E_m - E_n}{\hbar} \ , \tag{1.9}$$

where the matrix elements $H'_{mn}(t)$ of the perturbation $\hat{H}'(t)$ are taken between the *time-independent* basis vectors. The set (1.9) is still equivalent to the full Schrödinger equation. By transforming to the set of *integral* equations, we also incorporate the initial conditions $a_m(t_0)$,

$$a_m(t) = a_m(t_0) + \frac{1}{i\hbar} \int_{t_0}^{t} dt' \sum_n H'_{mn}(t') a_n(t') e^{i\omega_{mn}t'} \ . \tag{1.10}$$

The further approximations vary depending on specific physical conditions related to the strength and character of the perturbation.

Let the perturbation act during a *finite* time interval. At remote time in the past, $t_0 \to -\infty$, the system was in one of the stationary unperturbed states. We call this state *initial* denoting as $|i\rangle$ and assuming that it does belong to the discrete spectrum, $a_n(-\infty) = \delta_{ni}$. In the perturbative regime, the transition probabilities are small. Thus, $a_i(t)$ stays close to one, while $|a_{n\neq i}| \ll 1$ for emerging new components. For $m \neq i$, in (1.9) we only leave the large amplitude $a_i \approx 1$ in the right-hand side and approximately obtain:

$$i\hbar \dot{a}_m \approx H'_{mi}(t) a_i(t) e^{i\omega_{mi}t} \approx H'_{mi}(t) e^{i\omega_{mi}t} \,. \tag{1.11}$$

Thus, the probability amplitude of finding the system in the *final* state $|f\rangle$, also in the discrete spectrum, is equal to

$$a_f(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' \, H'_{fi}(t') e^{i\omega_{fi}t'} \,, \tag{1.12}$$

and the *transition probability* $i \to f$ is given by

$$w_{fi}(t) = |a_f(t)|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{t} dt' \, H'_{fi}(t') e^{i\omega_{fi}t'} \right|^2 \,. \tag{1.13}$$

Therefore, we justify the previously used notion of the matrix element H_{fi} as related to the *transition amplitude*. In the language of *virtual* states, the transition can "happen" at any time $t' < t$, where the phase jump occurs to a different state. In the end, we need to account for the interference of all transitions which took place at different times t'. Since we supposed that in the limit of $t \to \infty$ the perturbation ceases to act, the total transition probability,

$$w_{fi} = |a_f(t \to \infty)|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} dt' \, H'_{fi}(t') e^{i\omega_{fi}t'} \right|^2 \,, \tag{1.14}$$

is determined by the Fourier harmonic of the perturbation for the *frequency equal to the transition frequency* ω_{fi}. One can say that, in the infinitely long limit, energy has to be exactly conserved, and this is ensured by the transfer of the precise amount of energy $E_f - E_i$ from (or to) the source of the external field. The approximation (1.11) is justified if the higher order corrections are small.

Problem 1.1

A finite pulse of spatially uniform electric field

$$\mathcal{E}(t) = \mathcal{E}_0 e^{-t^2/\tau^2} \tag{1.15}$$

is applied to a charged particle placed in the harmonic oscillator potential of frequency ω. In the approximation of weak field, find the probability of excitation of the particle from the ground state to one of the excited oscillator states after the pulse. Establish the condition of validity of perturbation theory. Consider the cases

of short and long pulse duration τ as compared to the period of oscillations (for the same total momentum of the pulse). Consider the oscillations along the field line.

Solution The perturbation operator is

$$\hat{H}'(t) = -e\mathcal{E}(t)\hat{x} = -e\mathcal{E}(t)\sqrt{\frac{\hbar}{2m\omega}}\,(\hat{a} + \hat{a}^{\dagger})\,. \tag{1.16}$$

In the lowest order of perturbation theory, only the transition to the first excited state, $n = 0 \to n = 1$, is possible by action of the creation operator $\hat{a}^{\dagger}$. The transition probability (1.14) for the pulse of the field $\mathcal{E}(t) = \mathcal{E}_0 f(t)$ is given by

$$w_{10} = \frac{1}{\hbar^2}(e\mathcal{E}_0)^2\,\frac{\hbar}{2m\omega}\left|\int_{-\infty}^{\infty} dt\; f(t)e^{i\omega t}\right|^2\,. \tag{1.17}$$

For the Gaussian pulse (1.15),

$$w_{10} = \frac{\pi e^2\mathcal{E}_0^2\tau^2}{2m\hbar\omega}\,e^{-\omega^2\tau^2/2}\,. \tag{1.18}$$

The total momentum transfer by the pulse is

$$P = \int_{-\infty}^{\infty} dt\; e\mathcal{E}(t) = \sqrt{\pi}\,e\mathcal{E}_0\tau\,. \tag{1.19}$$

We can compare the pulses of the same total power, though with different duration,

$$w_{10} = \frac{P^2}{2m\hbar\omega}\,e^{-\omega^2\tau^2/2}\,. \tag{1.20}$$

The mean energy transferred to the oscillator can be found as

$$\Delta E = \hbar\omega\, w_{10} = \frac{P^2}{2m}\,e^{-\omega^2\tau^2/2}\,. \tag{1.21}$$

For any duration, the perturbative approach is valid if $\Delta E \ll \hbar\omega$. The short pulse (the duration τ is much smaller than the oscillation period, $\omega\tau \ll 1$) transfers the whole energy $P^2/2m$, whereas a long pulse, $\omega\tau \gg 1$, is ineffective, the energy transfer is exponentially small, and the oscillator stays in its ground state. The physical basis lies in the fast oscillating character of the motion; the action of the field is compensated during different parts of the period. This is a general rule that slow changing (*adiabatic*) perturbations fail to excite the system. Instead, the system remains in its original state with the wave function adiabatically adjusting to the slowly changing perturbation and coming back after the perturbation is switched off. Later, we will consider the adiabatic case in more detail.

1.3 Formal Series

If we are interested in the transition $i \to f$, where the direct matrix element H'_{fi} is small or just vanishes, we need to check the next order of perturbation theory. The exact set of integral equations (1.10) can be *iterated*,

$$a_m(t) = a_m(t_0) + \frac{1}{i\hbar}\int_{t_0}^{t} dt_1 \sum_n H'_{mn}(t_1) e^{i\omega_{mn}t_1} a_n(t_0) + \left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \sum_{ns} H'_{mn}(t_1) H'_{ns}(t_2) e^{i\omega_{mn}t_1 + i\omega_{ns}t_2} a_s(t_2) \,. \tag{1.22}$$

Again, by using the initial condition at $t_0 \to -\infty$, $a_n(-\infty) = \delta_{ni}$, and leaving in the iterated (third) term of (1.22) the main contribution $s = i$, we find the transition amplitude $i \to f \neq i$ in the second order,

$$a_f(t) \approx a_f^{(1)}(t) + a_f^{(2)}(t) \,, \tag{1.23}$$

where $a_f^{(1)}$ is given by (1.12), while

$$a_f^{(2)}(t) = \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_n H'_{fn}(t_1) H'_{ni}(t_2) e^{i\omega_{fn}t_1 + i\omega_{ni}t_2} \,. \tag{1.24}$$

Including the second order terms, we see that, apart from the direct transition $i \to f$, a *two-step* process is possible through *intermediate* or *virtual* states (recall Vol. 1 Section 5.10), $i \to n \to f$. The transition probability is still $w_{fi} = |a_f(t)|^2$, though now it contains the interference of one-step and all two-step paths. Again, the result is valid only if the higher order terms can be neglected.

Each operator of perturbation $\hat{H}'$ is accompanied by the corresponding time-dependent phase. This is related to the previously mentioned *interaction picture*. Namely, the operator of unperturbed unitary time evolution

$$\hat{U}^\circ(t) = \exp[-(i/\hbar)\hat{H}^\circ t] \tag{1.25}$$

is included in the wave functions, as in (1.2) and (1.3). Correspondingly, to keep physical amplitudes intact, we transform the operators, $\hat{H}' \Rightarrow \breve{H}$,

$$\breve{H}'_{mn}(t) = \langle m| \left(\hat{U}^\circ(t)\right)^{-1} \hat{H}'(t)\, \hat{U}^\circ(t) |n\rangle = H'_{mn}(t) e^{i\omega_{mn}t} \,. \tag{1.26}$$

The interaction picture is intermediate between the Schrödinger and Heisenberg pictures. Here, the operators $\breve{O}$ keep their *unperturbed time dependence* as would be the case in the Heisenberg picture in the absence of perturbation; the time dependence induced by the perturbation $\hat{H}'$ is still in the wave functions.

Let us now consider the structure of the second iteration (1.24). As seen from Figure 1.1, the integration region is a part of (t_2, t_1)-plane bounded from above by the diagonal $t_1 = t_2$. We first integrate, at fixed $t_1 < t$, along the vertical line $-\infty < t_2 < t_1$, and then over all possible values of t_1 from $-\infty$ to t. If we change the order of integration, the same area will be covered by $\int_{-\infty}^{t} dt_2 \int_{t_2}^{t} dt_1$, and we can add two expressions, thus dividing the result by two. However, in the second form, we can also rename the variables $t_2 \leftrightarrow t_1$ so that the result can be presented as

$$a_f^{(2)}(t) = \frac{1}{2}\left(\frac{1}{i\hbar}\right)^2 \times \left\{ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \Big(\check{H}'(t_1)\check{H}'(t_2) \Big)_{fi} + \int_{-\infty}^{t} dt_1 \int_{t_1}^{t} dt_2 \Big(\check{H}'(t_2)\check{H}'(t_1) \Big)_{fi} \right\} . \tag{1.27}$$

Here, we integrate (with the factor of 1/2) over the entire plane up to time t, though in both regions, $t_1 < t_2$ and $t_1 > t_2$. The two operators $\check{H}'$ are *chronologically ordered* with the latest operator on the left-hand side. We introduce the symbol Υ of the chronological product of the operators and write down the result as

$$a_f^{(2)}(t) = \frac{1}{2}\left(\frac{1}{i\hbar}\right)^2 \Upsilon \left\{ \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \Big(\check{H}'(t_1)\check{H}'(t_2) \Big)_{fi} \right\} . \tag{1.28}$$

We can continue the iterations in the same way. The result can be written as an infinite series,

$$a_f(t) = \sum_{n=1} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{t} dt_1 \ldots \int_{-\infty}^{t_{n-1}} dt_n \Big(\check{H}'(t_1) \ldots \check{H}'(t_n) \Big)_{fi} . \tag{1.29}$$

In the n^{th} term, the transition proceeds through $n-1$ intermediate states, and every operator $\check{H}'$ is taken in the interaction picture. The operators $\check{H}'(t)$ taken at different times generally do not commute, and their sequence in the series (1.29) is fixed by the chronological ordering, – time grows from the right to the left. We

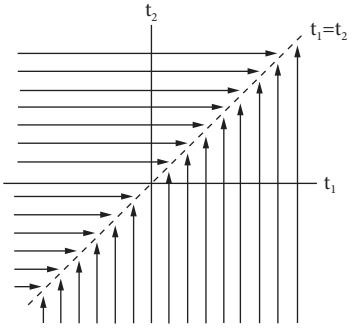

Figure 1.1 Structure of the second approximation leading to chronological ordering.

can explore all possible $n!$ permutations of the integration times, and, analogously to the case of $a_f^{(2)}$, relabeling of the operators keeps the chronological order everywhere. We can also extend the result for $f = i$ by adding the zero order term $1_{fi} = \delta_{fi}$. This leads to the series very much resembling the exponential, but with time ordering in each term,

$$a_f(t) = \delta_{fi} + \sum_{n=1} \frac{1}{n!} \left(\frac{1}{i\hbar}\right)^n \Upsilon \left\{ \int_{-\infty}^{t} dt_1 \dots \int_{-\infty}^{t} dt_n \Big(\breve{H}'(t_1) \dots \breve{H}'(t_n) \Big)_{fi} \right\} . \tag{1.30}$$

Usually, this is denoted by the Υ*-exponent*,

$$a_f(t) = \Upsilon \left\{ \exp\left[-(i/\hbar) \int_{-\infty}^{t} dt' \breve{H}'(t') \right] \right\}_{fi} . \tag{1.31}$$

This symbolic expression can be useful for general derivations, though usually it does not help in specific calculations when the series has to be treated approximately and truncated at some step.

1.4 Adiabatic Perturbations

If the perturbation $\hat{H}'(t)$ is a smooth function of time, for example, changing considerably only during a long time interval $\sim \tau$, its Fourier expansion can have appreciable components only for small frequencies $\omega \leq \omega_0 = 1/\tau$. Then, the transitions with larger frequencies, $\omega_{fi} \geq \omega_0$, are suppressed. We have already seen this in Problem 1.1 in the limit $\omega\tau > 1$. Such slowly changing perturbations are called *adiabatic*. More precisely, for an adiabatic perturbation with respect to a transition $i \to f$, the change of energy during the period, $\delta t \sim 1/\omega_{fi}$, must be small compared to the transition energy $E_f - E_i = \hbar\omega_{fi}$:

$$\delta H \sim \frac{\delta H'}{\delta t}\, \delta t \sim \frac{dH'_{fi}}{dt} \frac{1}{\omega_{fi}} \ll \hbar\omega_{fi} . \tag{1.32}$$

Already a simple estimate shows that under the condition (1.32), the transition probability is small. Let, for example, the perturbation $\hat{H}'$ be smoothly switched on starting at $t = 0$ and switched off at time $\bar{t}$. For $t > \bar{t}$, the transitions are over and the full transition probability is

$$w_{fi} = \frac{1}{\hbar^2} \left| \int_0^{\bar{t}} dt\, H'_{fi}(t) e^{i\omega_{fi}t} \right|^2 . \tag{1.33}$$

By integrating by parts, we can write

$$w_{fi} = \frac{1}{\hbar^2} \left| \left[\frac{e^{i\omega_{fi}t}}{i\omega_{fi}} H'_{fi}(t) \right]_0^{\bar{t}} - \frac{1}{i\omega_{fi}} \int_0^{\bar{t}} dt\, e^{i\omega_{fi}t} \frac{dH'_{fi}(t)}{dt} \right|^2 , \tag{1.34}$$

or, because of the boundary conditions for $\hat{H}'(t)$,

$$w_{fi} = \frac{1}{\hbar^2 \omega_{fi}^2} \left| \int_0^{\bar{t}} dt\, e^{i\omega_{fi}t} \frac{d H'_{fi}(t)}{dt} \right|^2 . \tag{1.35}$$

Assuming the smooth behavior of the derivative $\dot{H}'_{fi}$, we take its squared maximum absolute value out of the integral and calculate the remaining integral,

$$w_{fi} \leq \frac{4 \sin^2(\omega_{fi} t/2)}{\hbar^2 \omega_{fi}^4} \left| \overline{\frac{d H'_{fi}}{dt}} \right|^2 . \tag{1.36}$$

The upper limit for the transition probability is proportional to the square of the small adiabaticity parameter $\dot{H}'_{fi}/(\hbar\omega_{fi}^2)$, which is in agreement with the estimate (1.32).

We see that in the case of a perturbation adiabatically turned on and off, the real transitions are quite weak. Inside the interval $0 < t < \bar{t}$, the transition probability can be noticeable owing to the contribution of the upper limit in the integrated term of (1.34). This means that the state vector $|\Psi(t)\rangle$ differs from the initial one $|i\rangle$ during this interval. If we would switch off the perturbation instantly at some moment inside the interval and expand the function $|\Psi(t)\rangle$ over unperturbed stationary states $|f\rangle$, we would find significant probabilities for transitions $i \to f$. These probabilities would be mainly caused by the sharp removal of the perturbation. In the adiabatic regime, the state vector $|\Psi(t)\rangle$ smoothly changes, accommodating to the slowly evolving perturbation. In the long process, the wave function may change significantly. However, at $t > \bar{t}$, the system will, most probably, return to the original state.

1.5 Adiabatic Perturbation Theory

In our estimate (1.36), we have seen that, although we started with standard perturbation theory, the actual smallness was not ensured by the weakness of the perturbation, but rather by its slow change. It is possible to develop a special variant of perturbation theory where the perturbation $\hat{H}'(t)$ is not required to be weak. Instead, the only small parameter will be the *rate of change* of the perturbation, in the sense of the inequality (1.32). During a long time interval, such slow change of the state vector can end in its large resulting change.

In *adiabatic perturbation theory*, it makes no sense to break up the Hamiltonian as in (1.6). We simply suppose that the Hamiltonian contains some parameters $X_i(t)$ which are given as smooth functions of time, $\hat{H}(t) = \hat{H}(X(t))$. We already know that the state vector will adjust itself to the evolution of $X(t)$. In this smooth adjustment, the evolving ground state of the system will remain ground, the first excited will stay first excited and so on. The adiabatic level dynamics as a function of X reminds a laminar flow without any turbulence (as an example, one can take

the realistic spectrum of nuclear levels at strong mixing, Vol. 1, Figure 19.1). The smaller $dX/dt \equiv \dot{X}$, the higher the accuracy of this character of flow.

At a fixed value of X, we find a set of stationary states $|n; X\rangle$ of the Hamiltonian $\hat{H}(X)$,

$$\hat{H}(X)|n; X\rangle = E_n(X)|n; X\rangle \ . \tag{1.37}$$

The set of instantaneous states $|n; X\rangle$ can be used as a *traveling adiabatic basis* instead of the fixed basis used in (1.8). The usual phase $-E_n t/\hbar$ should now be substituted by the full *dynamical phase* accumulated during the process,

$$\varphi_n(t) = -\frac{1}{\hbar}\int_{-\infty}^{t} dt' \ E_n(X(t')) \ . \tag{1.38}$$

This is similar to the spatial phase $\int k\,dx$ of the semiclassical wave function in a smoothly changing potential.

At each given moment, the traveling basis (1.37) is complete, and we can look for the solution of the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(X(t))|\Psi(t)\rangle \tag{1.39}$$

in the form of the expansion over instantaneous functions $|n; X(t)\rangle$,

$$|\Psi(t)\rangle = \sum_n a_n(t)e^{i\varphi_n(t)}|n; X(t)\rangle \ . \tag{1.40}$$

In the extreme adiabatic limit, the wave function would simply follow the change of $X(t)$ along a given energy term in the parameter space. In reality, at finite velocity $\dot{X}$ of motion in this space, *transitions* between the adiabatic terms described by the residual time dependence of the amplitudes $a_n(t)$ in (1.40) could still occur. The time derivative of the function (1.40) equals

$$\frac{\partial}{\partial t}|\Psi\rangle = \sum_n e^{i\varphi_n(t)}\left[\dot{a}_n - \frac{i}{\hbar}E_n(X(t))a_n + a_n\dot{X}\frac{\partial}{\partial X}\right]|n; X(t)\rangle \ , \tag{1.41}$$

while

$$\hat{H}(t)|\Psi\rangle = \sum_n e^{i\varphi_n(t)}a_n E_n(X(t))|n; X(t)\rangle \ . \tag{1.42}$$

At fixed t and $X = X(t)$, the states $|n; X(t)\rangle$ are orthonormal. Therefore, the projection onto $\langle m; X(t)|$ gives, for each m,

$$\dot{a}_m + \dot{X}\sum_n B_{mn}(t)a_n e^{i[\varphi_n(t)-\varphi_m(t)]} = 0 \ , \tag{1.43}$$

where the role of perturbation inducing transitions is played by the matrix elements of the gradient with respect to the parameters,

$$B_{mn}(t) = \langle m; X(t)|\frac{\partial}{\partial X}|n; X(t)\rangle \ . \tag{1.44}$$

The set of equations (1.43) is still exact. The amplitudes a_n in the traveling basis only change due to the change $\dot{X}$ of the parameters. If we had in the remote past, $t \to -\infty$, the set of the coefficients $a_n^\circ \equiv a_n(-\infty)$, and the evolution is adiabatic, we would expect the amplitudes a_m to stay approximately constant, although the basis states themselves can change significantly. *Adiabatic perturbation theory* uses the expansion over $\dot{X}$,

$$a_m = a_m^\circ + a_m^{(1)}(t) + \dots \tag{1.45}$$

In the first order, we obtain from (1.43)

$$\dot{a}_m^{(1)} = -\dot{X} \sum_n B_{mn}(t) a_n^\circ e^{i[\varphi_n(t) - \varphi_m(t)]} . \tag{1.46}$$

The integral over time provides the solution in the first order,

$$a_m^{(1)}(t) = -\int_{-\infty}^{t} dt' \sum_n B_{mn}(t') \dot{X}(t') e^{i[\varphi_n(t') - \varphi_m(t')]} a_n^\circ . \tag{1.47}$$

Being interested in transition probabilities, let us consider a certain initial state, $a_n^\circ = \delta_{ni}$. With the help of Vol. 1 Equation 19.36, we obtain from (1.47) for the final state $f \neq i$:

$$a_f^{(1)}(t) = -\int_{-\infty}^{t} dt' \, \frac{\langle f; X(t') | \frac{\partial \hat{H}}{\partial X} | i; X(t') \rangle}{E_i(X(t')) - E_f(X(t'))} \, \dot{X}(t') e^{i[\varphi_i(t') - \varphi_f(t')]} . \tag{1.48}$$

This result is reminiscent of usual stationary perturbation theory. It is also a straightforward task to construct higher adiabatic approximations.

1.6 Nonadiabatic Transitions

The adiabatic approximation in the form (1.48) breaks down near the points of *level crossing*. The close approach of different adiabatic energy terms $E(t)$ makes the transition amplitude to grow. Then, in analogy to standard perturbation theory for close levels, the lowest order approximation is insufficient, and it is necessary to diagonalize the Hamiltonian within this subset and find correct linear combinations. The generic result can already be seen in the case of two close levels.

Consider a typical situation when two adiabatic energy terms, $|k, t\rangle$ and $|k', t\rangle$, of a system cross each other at a time moment that can be taken as $t = 0$, Figure 1.2. Without any interaction capable of mixing those states (or for the case of different symmetry that forbids the mixing), we would have the *diabatic* terms $\epsilon_k(t)$ and $\epsilon_{k'}(t)$ shown by dashed lines. If there is a mixing matrix element $H_{k'k} \equiv V$, the *adiabatic* levels *1* and *2* repel each other, and instead of diabatic crossing, we get adiabatic *pseudocrossing*, solid lines in Figure 1.2, when the mixing matrix element determines the instantaneous level spacing (see Vol. 1 Equation 10.39).

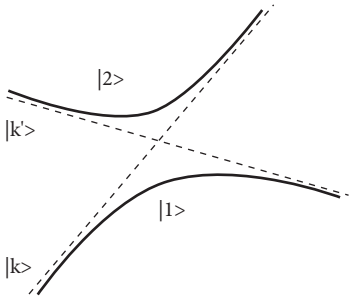

Figure 1.2 Diabatic and adiabatic terms.

Let us start with the lower state $\epsilon_k(t)$ in the remote past, $t \to -\infty$. For a slow change of levels $\epsilon(t)$ and weak interaction $V(t)$, the *adiabatic evolution* will proceed along the term *1* when the wave function is gradually transformed from $|k, -\infty\rangle$ to $|k', \infty\rangle$. The system will always stay in the lower energy state, while the upper term *2* will remain empty. Contrary to that, in the *diabatic regime* of fast passage, the system will go along the unperturbed term $|k, t\rangle$. In general, the process is characterized by the *transition probability P* from *1* to *2* which is, in fact, the probability of preserving the state $|k\rangle$. This probability goes to zero in the adiabatic limit and to one in the opposite case of fast passage.

The two-state system is described by the time-dependent Hamiltonian

$$\hat{H}(t) = \begin{pmatrix} \epsilon_k(t) & V^*(t) \\ V(t) & \epsilon_{k'}(t) \end{pmatrix} . \tag{1.49}$$

Assuming a weak interaction, the considerable transition probability exists only in the vicinity of the crossing point $t = 0$. Here, the main time dependence can be written down as

$$\epsilon_{k,k'}(t) \approx u_{k,k'} t \ , \quad V(t) \approx V(0) \equiv V \tag{1.50}$$

(linear behavior of the diabatic terms approaching their crossing, $u_k > u_{k'}$). The perturbation theory is not valid at the crossing point. However, as in the semiclassical approximation, we can try "going around" the dangerous point to find the transition probability of jumping over the energy gap between the terms *1* and *2*, similarly to matching two semiclassical solutions on different sides of the turning point in coordinate space.

At large $|t|$, when the level spacing $|(u_k - u_{k'})t|$ is large compared to the mixing matrix element $|V|$, we can use normal stationary perturbation theory. Then, the adiabatic terms behave as

$$E_k(t) = u_k t + \frac{|V|^2}{(u_k - u_{k'})t} + \dots \ , \tag{1.51}$$

where the omitted items have more energy denominators with higher powers of t. The expansion (1.51) determines the adiabatic phase (1.38),

$$\varphi_k(t) = -\frac{u_k t^2}{2\hbar} - \frac{|V|^2}{\hbar(u_k - u_{k'})} \ln t + \dots \tag{1.52}$$

The terms not written explicitly do not grow at large t. Now, we act as we did in the semiclassics (see Vol. 1 Sections 15.9–15.12) by extending the solution to complex values of t. We assume that we can go in the complex t plane around the crossing point $t = 0$ along the arch of radius T that is large enough to allow us to neglect residual items, but at the same time, small enough to keep the expansion (1.50) valid.

On the large arch $t = T\exp(i\alpha)$, we need to connect the remote future, $\alpha = 0$, to the remote past, $\alpha = \pm\pi$, where the sign depends on the sense of rotation along the circular contour. At large T, the main term, $\propto T^2$, in the phase (1.52) behaves as

$$i\varphi_k \Rightarrow \frac{u_k T^2}{2\hbar}(-i)e^{2i\alpha} = \frac{u_k T^2}{2\hbar}\left[-i\cos(2\alpha) + \sin(2\alpha)\right]. \tag{1.53}$$

When we approach the real axis at $\alpha \to \pm\pi$, the real part of (1.53) acquires the large exponential factor when $\sin(2\alpha) > 0$; therefore, we need to move along the upper arch. At the end point, we have $t = T\exp(i\pi)$, and the logarithmic part of the phase (1.52) gives $\ln t = \ln T + i\pi$. As a result, the real gain in the amplitude becomes

$$A = e^{(i\pi)(-i/\hbar)|V|^2/(u_k - u_{k'})} = e^{\pi|V|^2/[\hbar(u_k - u_{k'})]}. \tag{1.54}$$

The amplitude of the wave started at large negative t at the low state $|k\rangle$ is greater than the amplitude of *the same state* at large positive t by a factor A (since $u_k > u_{k'}$). Thus, the probability of the diabatic transition across the energy gap between two adiabatic levels is given by

$$P = \frac{1}{A^2} = e^{-2\pi|V|^2/[\hbar(u_k - u_{k'})]}. \tag{1.55}$$

The probability of remaining on the adiabatic trajectory is $1 - P$.

Here, we followed the approach of [1] to derive the *Landau–Zener transition probability* [2, 3]. At very small velocities, $\hbar\Delta u \ll |V|^2$, we return to the extreme adiabatic regime, $P \to 0$. However, this small probability cannot be derived by routine perturbation theory – the result has a *non-analytic* dependence on $(u_k - u_{k'})$. For fast passage, $\hbar\Delta u \gg |V|^2$, the probability of the transition is close to one. This result has a broad area of applicability, from molecular collisions with electron transitions between different energy terms to nuclear reactions. It can also be generalized [1, 4] for multiple crossings approximated by a sequence of pairwise transitions.

1.7 Geometric Phase

Let us assume that the external parameters $\boldsymbol{X} \equiv \{X_i(t)\}$ change with time extremely slowly and, after completing a trajectory in parameter space, return to their original values. In this adiabatic process, the real transitions to other states are negligible and the wave function $|\Psi\rangle$ also returns to its starting point. However, quantum dynamics may add a *geometric phase* to the wave function (*M. Berry* [5]) that should not be confused with a normal dynamical quantum phase (1.38).

If we start at $t = 0$ with a stationary state $|n; \boldsymbol{X}(0)\rangle$, the solution of the Schrödinger equation (1.39) for further adiabatic evolution can be presented in the form of a single term $|n; \boldsymbol{X}(t)\rangle$ in the superposition (1.40), but with the unknown extra phase $\beta_n(t)$,

$$|\Psi(t)\rangle = e^{i\varphi_n(t)} e^{i\beta_n(t)} |n; \boldsymbol{X}(t)\rangle \ . \tag{1.56}$$

As in the derivation of (1.43), we project out the component along the instantaneous vector $|n; \boldsymbol{X}(t)\rangle$ and come to the equation for the new phase,

$$-i\dot{\beta}_n(t) = \sum_i \langle n; \boldsymbol{X}(t)| \frac{\partial}{\partial X_i} |n; \boldsymbol{X}(t)\rangle \dot{X}_i(t) \ , \tag{1.57}$$

or, by introducing the formal gradient vector $\nabla_{\boldsymbol{X}}$ in the parameter space,

$$-i\dot{\beta}_n(t) = \langle n; \boldsymbol{X}(t)| \nabla_{\boldsymbol{X}} |n; \boldsymbol{X}(t)\rangle \cdot \dot{\boldsymbol{X}}(t) \ . \tag{1.58}$$

After a very slow and long journey, we close the contour $\mathcal{C}$ and return to the starting point in parameter space. The full acquired phase β_n is then given by the integral over the closed loop,

$$\beta_n = i \oint dt \, \langle n; \boldsymbol{X}(t)| \nabla_{\boldsymbol{X}} |n; \boldsymbol{X}(t)\rangle \cdot \dot{\boldsymbol{X}}(t) = i \oint_{\mathcal{C}} d\boldsymbol{X} \cdot \langle n; \boldsymbol{X}| \nabla_{\boldsymbol{X}} |n; \boldsymbol{X}\rangle \ . \tag{1.59}$$

Here, the time characteristics of an arbitrary slow process disappeared and the resulting expression has a geometric meaning with the value generally depending on the contour $\mathcal{C}$. Since the states $|n; \boldsymbol{X}\rangle$ are assumed to be normalized at all values of parameters,

$$\langle n; \boldsymbol{X}| n; \boldsymbol{X}\rangle = 1 \ , \tag{1.60}$$

we see that

$$\langle \nabla_{\boldsymbol{X}} (n; \boldsymbol{X})| n; \boldsymbol{X}\rangle \equiv \langle n; \boldsymbol{X}| \nabla_{\boldsymbol{X}} |(n; \boldsymbol{X})\rangle^* = -\langle n; \boldsymbol{X}| \nabla_{\boldsymbol{X}} |n; \boldsymbol{X}\rangle \ . \tag{1.61}$$

Whence, the integrand in (1.59) is imaginary, and the phase β_n is real,

$$\beta_n(\mathcal{C}) = -\,\mathrm{Im} \oint_{\mathcal{C}} d\boldsymbol{X} \cdot \langle n; \boldsymbol{X}| \nabla_{\boldsymbol{X}} |n; \boldsymbol{X}\rangle \ . \tag{1.62}$$

Problem 1.2

Show that the phase β_n is invariant with respect to the choice of the *intrinsic phase* $\alpha(\boldsymbol{X})$ of the state vectors $|n;\boldsymbol{X}\rangle$ which are assumed to be single-valued, $|n;\boldsymbol{X}\rangle \Rightarrow \exp(i\,\alpha(\boldsymbol{X}))|n;\boldsymbol{X}\rangle$, an analog of a gauge transformation.

Solution Use the normalization (1.60) and the fact that the integral over a closed contour of the gradient of a single-valued function vanishes.

In *one-dimensional* parameter space, the contour is traversed back and forth and the geometric phase vanishes. Following [5], we consider the case of a three-dimensional parameter space where the standard vector calculus will help transforming the result. A loop integral (1.62) gives the circulation of the vector $\langle n|\nabla|n\rangle$ where the argument $\boldsymbol{X}$ is omitted. The circulation can be converted into a flux integral of the curl of this vector through a surface $\mathcal{S}$ in the parameter space built on the contour $\mathcal{C}$,

$$\beta_n(\mathcal{C}) = -\,\mathrm{Im}\int_{\mathcal{S}} d\boldsymbol{\mathcal{S}}\cdot \mathrm{curl}\,\langle n|\nabla|n\rangle = -\,\mathrm{Im}\int d\mathcal{S}_i\epsilon_{ijk}\nabla_j\langle n|\nabla_k|n\rangle\ . \quad (1.63)$$

The symmetric in derivatives term $\sim \nabla_j\nabla_k|n\rangle$ vanishes so that

$$\beta_n(\mathcal{C}) = -\,\mathrm{Im}\int d\mathcal{S}_i\epsilon_{ijk}\langle\nabla_j n|\nabla_k n\rangle \equiv -\mathrm{Im}\int d\boldsymbol{\mathcal{S}}\cdot\langle\nabla n|\times|\nabla n\rangle\ . \quad (1.64)$$

Another form of this result comes out if we recall the identity (see Vol. 1 Equation 19.36) for an *off-diagonal* matrix element of the parametric gradient. If we use a complete set of states $|n';\boldsymbol{X}\rangle$ in between the gradients in (1.64), the diagonal contribution $n' = n$ vanishes due to (1.61), and we obtain the *geometric phase* as the flux,

$$\beta_n(\mathcal{C}) = -\int d\boldsymbol{\mathcal{S}}\cdot\boldsymbol{V}_n(\boldsymbol{X})\ , \quad (1.65)$$

of the *Berry vector*,

$$\boldsymbol{V}_n(\boldsymbol{X}) = \mathrm{Im}\sum_{n'\neq n}\frac{\langle n:\boldsymbol{X}|\nabla_{\boldsymbol{X}}\hat{H}|n';\boldsymbol{X}\rangle\times\langle n';\boldsymbol{X}|\nabla_{\boldsymbol{X}}\hat{H}|n;\boldsymbol{X}\rangle}{[E_{n'}(\boldsymbol{X})-E_n(\boldsymbol{X})]^2}\ . \quad (1.66)$$

Again, following [5], we can consider an example of a particle with spin $\boldsymbol{s}$ in the static magnetic field $\boldsymbol{\mathcal{B}}$ described by the standard Hamiltonian

$$\hat{H}(\boldsymbol{\mathcal{B}}) = -g\hbar(\hat{\boldsymbol{s}}\cdot\boldsymbol{\mathcal{B}})\ . \quad (1.67)$$

The components of $\boldsymbol{\mathcal{B}}$ are our parameters $\boldsymbol{X}$, while the traveling state $|n\rangle$ is now labeled as $|m\rangle$ by its spin projection $s_z = m$ on the slowly changing field direction determined by the unit vector $\boldsymbol{b} = \boldsymbol{\mathcal{B}}/\mathcal{B}$ and energy $E_m = -g\hbar m\mathcal{B}$.

Problem 1.3

Calculate the Berry vector $\boldsymbol{V}_m(\boldsymbol{\mathcal{B}})$ (1.66) for this example.

Solution The Berry vector is given by

$$\boldsymbol{V}_m(\boldsymbol{\mathcal{B}}) = \mathrm{Im} \sum_{m' \neq m} \frac{\langle m|\boldsymbol{s}|m'\rangle \times \langle m'|\boldsymbol{s}|m\rangle}{\mathcal{B}^2(m'-m)^2} \,, \tag{1.68}$$

where the traveling state $|m\rangle$ as well as the intermediate states $|m'\rangle$ are taken at the field $\boldsymbol{\mathcal{B}}$. By choosing z as the field axis in calculating (1.68) and using the matrix elements of the angular momentum, we get the Berry vector along the same axis (naturally, this is the only direction that is singled out). Indeed, the transverse components $V_{x,y}$ vanish since they would require one of the matrix elements in the numerator to be that of s_z that does not have off-diagonal matrix elements. For the z-component, we have

$$V_z = \mathrm{Im} \sum_{m'} \frac{(s_x)_{mm'}(s_y)_{m'm} - (s_y)_{mm'}(s_x)_{m'm}}{\mathcal{B}^2(m-m')^2} \,, \tag{1.69}$$

and since here $m - m' = \pm 1$, we can use the completeness of intermediate states to obtain

$$V_z = \frac{1}{\mathcal{B}^2}\,\mathrm{Im} \sum_{m'} [(s_x)_{mm'}(s_y)_{m'm} - (s_y)_{mm'}(s_x)_{m'm}] = \frac{1}{\mathcal{B}^2}\,\mathrm{Im}\,[\hat{s}_x, \hat{s}_y]_{mm} = \frac{m}{\mathcal{B}^2} \,. \tag{1.70}$$

Thus,

$$\boldsymbol{V}_m(\boldsymbol{\mathcal{B}}) = \frac{m}{\mathcal{B}^2}\,\boldsymbol{b} = \frac{m}{\mathcal{B}^3}\,\boldsymbol{\mathcal{B}} = -m\nabla_{\mathcal{B}}\,\frac{1}{\mathcal{B}} \,. \tag{1.71}$$

The result (1.71) shows that the vector Berry field in this case is that of the "charge" m located at the origin of the magnetic parameter space–*monopole* originated by the *point of degeneracy* of the energy levels. By the *Gauss theorem*, the Berry phase (1.65) is then equal to

$$\beta_m(\mathcal{C}) = -m\,\Omega\,(\mathcal{C}) \,, \tag{1.72}$$

where $\Omega\,(\mathcal{C})$ is the solid angle subtended by the contour $\mathcal{C}$ (looking from the origin). This result is valid for both integer and half-integer spins s. For spin 1/2, the whole rotation through an angle 2π in the plane produces $\Omega = 2\pi$, and the spinor wave function changes by $\exp(i\beta_{\pm 1/2}) = -1$, in agreement with the properties of the $\mathcal{SU}(2)$ group, see Vol. 1 Section 20.1.

The result of the last example does not depend on the spin magnitude and, therefore, on the degree of degeneracy of states without magnetic field. In general, singularities related to level crossings at some parameter values (*exceptional points*)

are the sources of the geometric phase. This can be seen in an example of a two level crossing. The effective Hamiltonian of this pair of levels, compare (1.49), can be always written in terms of the Pauli matrices as proportional to $(\boldsymbol{\sigma} \cdot \boldsymbol{X})$, and the coefficients $\boldsymbol{X}$ are the relevant parameters (the unit matrix does not make any mixing). Then, we return to the magnetic field example with spin $s = 1/2$ and the Berry vector (1.71),

$$V_{\pm 1/2} = \mp \frac{1}{2} \frac{\boldsymbol{X}}{|\boldsymbol{X}|^3} \,. \tag{1.73}$$

The geometric phase is still given by the solid angle (1.72).

1.8 Sudden Perturbations

This case is opposite to the adiabatic one. Here, the perturbation changes so fast that its characteristic time τ is short compared to the period of the transition, $\tau \ll 1/\omega_{fi}$. Long ago, we discussed the case of an instant change of the potential, $\tau \to 0$, with the example of Vol. 1 Problem 3.3. Many Fourier-components are now available for the transitions.

Let the perturbation $\hat{H}'(t)$ suddenly be switched on at $t = 0$ and adiabatically quenched at $t \to \infty$. If the perturbation is weak, we can apply the general result (1.14) and, acting similarly to (1.35), express the transition probability as

$$w_{fi} = \frac{1}{\hbar^2 \omega_{fi}^2} \left| \int_{-\infty}^{\infty} dt \, e^{i\omega_{fi} t} \, \frac{d H'_{fi}(t)}{dt} \right|^2 \,. \tag{1.74}$$

In this case, the time derivative of $H'_{fi}(t)$ is not small only in a short time interval τ near $t = 0$. Since $\exp(i\omega_{fi} t)$ does not noticeably change during this interval, we can set this exponent equal to one. The remaining integral gives the full jump of the matrix element equal to H'_{fi} (the perturbation was absent before $t = 0$), and, whence,

$$w_{fi} = \frac{1}{\hbar^2 \omega_{fi}^2} \, |H'_{fi}|^2 \,. \tag{1.75}$$

Again, this resembles the result (Vol. 1 Equation 19.16) of stationary perturbation theory; indeed, after $t = 0$, the weak perturbation does not effectively induce transitions.

In a more general case, when there is no restriction on the strength of perturbations and the only approximation is related to the *rate* of the switching (small τ), we can develop a specific *theory of sudden perturbations*. Let the Hamiltonian change from $\hat{H}$ to $\hat{H}_1$ during a short interval from $t = 0$ to $t = \tau$ being time-independent outside of this interval. Then, it is convenient to use as the working basis the complete set $|n\rangle$ of stationary functions of the *new* Hamiltonian,

$$\hat{H}_1 |n\rangle = E_n |n\rangle \,. \tag{1.76}$$

We are looking for the solution at $t > 0$ as a superposition (1.8) of the eigenstates (1.76). By taking into account that in the short interval $0 < t < \tau$ the actual Hamiltonian differs from $\hat{H}_1$, we define the perturbation $\hat{H}'$ by

$$\hat{H} = \hat{H}' + \hat{H}_1 \,. \tag{1.77}$$

By integrating over time equations (1.9), we obtain for the amplitudes the analog of the set (1.10),

$$a_m(t) = a_m(0) - \frac{i}{\hbar} \sum_n \int_0^\tau dt' \, H'_{mn}(t') e^{i\omega_{mn}t'} a_n(t') \,. \tag{1.78}$$

Since $\exp(i\omega_{mn}t') \approx 1$ for $0 < t' < \tau$,

$$a_{mn}(t) \approx a_m(0) - \frac{i}{\hbar} \sum_n \int_0^\tau dt' \, H'_{mn}(t') a_n(t') \,. \tag{1.79}$$

The result (1.79) simplifies further if, apart from the condition $\omega_{mn}\tau \ll 1$, another inequality,

$$\frac{H'_{mn}\tau}{\hbar} \ll 1 \tag{1.80}$$

is fulfilled (for weak perturbations, $H'_{mn} \ll \hbar\omega_{mn}$, this follows from the first condition). If so, the integral term in (1.79) is small, and we can use the first iteration. In the zeroth order,

$$a^\circ_m(t) = a_m(0) \,. \tag{1.81}$$

This is the same as in our "naive" approach used for Vol. 1 Problem 3.3: the initial state vector is a superposition of new stationary states,

$$|\Psi(0)\rangle = \sum_m a_m(0)|m\rangle \,, \quad a_m(0) = \langle m|\Psi(0)\rangle \,, \tag{1.82}$$

and the transition probability $|\Psi(0)\rangle \to |f\rangle$ is given by

$$w_{f0} = |\langle f|\Psi(0)\rangle|^2 \,. \tag{1.83}$$

With perturbation suddenly switched on, the state vector $|\Psi(0)\rangle$ does not have time for changing and serves as an initial wave packet for the further evolution governed by $\hat{H}_1$. For finding the transition probabilities, it is sufficient to know the weights of various new stationary states in the initial superposition, that is, expand $|\Psi(0)\rangle$ over eigenfunctions of $\hat{H}_1$. After $t = \tau$, these components simply acquire their normal phases evolving independently.

Problem 1.4

For the case of a weak perturbation, derive the result (1.75) from conventional time-dependent perturbation theory.

By iterating the starting solution (1.81) in the integral term (1.78), we find the first order correction due to the finite switching time,

$$a_m^{(1)}(t) = a_m(0) - \frac{i}{\hbar}\sum_n a_n(0)\int_0^t dt'\, H'_{mn}(t') \,. \tag{1.84}$$

Using the meaning (1.82) of the amplitudes $a_n(0)$ and the completeness of the set (1.76), we come to

$$\begin{aligned} a_m^{(1)}(t) &= \langle m|\Psi(0)\rangle - \frac{i}{\hbar}\sum_n \int_0^t dt'\, H'_{mn}(t')\langle n|\Psi(0)\rangle \\ &= \langle m|\Psi(0)\rangle - \frac{i}{\hbar}\int_0^t dt'\,\langle m|\hat{H}'(t')|\Psi(0)\rangle \,. \end{aligned} \tag{1.85}$$

The transition probability in this approximation is

$$w_{f,0}^{(1)} = \left|\langle f|\Psi(0)\rangle - \frac{i}{\hbar}\int_0^\tau dt'\,\langle f|\hat{H}'(t')|\Psi(0)\rangle\right|^2 \,. \tag{1.86}$$

Problem 1.5

A weak external field applied to a system in the initial state $|i\rangle$ depends on time as

$$\hat{H}'(t) = g(t)\hat{A}\,, \quad g(t) = \frac{1}{1+e^{t/\tau}} \,. \tag{1.87}$$

Find the transition probabilities into final states $|f\rangle$ and trace the limits of sudden and adiabatic perturbations.

Solution According to perturbation theory, the transition probability is given by

$$w_{fi} = \frac{|A_{fi}|^2}{\hbar^2}\left|\int_{-\infty}^{\infty} dt\, e^{i\omega_{fi}t} g(t)\right|^2 \,. \tag{1.88}$$

To calculate the Fourier components, we can close the contour by an arc of a large radius in the upper part of the complex plane, $\mathrm{Im}(t) > 0$; the contribution of the arc vanishes (we assume $\omega_{fi} > 0$). The poles of $g(t)$ inside the contour are along the positive part of the imaginary axis, $t_n = i\pi\tau(2n+1)$, where $n = 0, 1, \ldots$ The denominator at these points gives $-(t-t_n)/\tau$, while the corresponding residues are $\exp[-\omega_{fi}\pi\tau(2n+1)]$. The sum is the geometric series that can be expressed through the hyperbolic sine,

$$w_{fi} = \frac{|A_{fi}|^2}{\hbar^2}\left|\frac{\pi\tau}{\sinh(\pi\omega_{fi}\tau)}\right|^2 \,. \tag{1.89}$$

The perturbation $g(t)$ changes from one in the past, $t \to -\infty$, to zero in the future, $t \to \infty$ (a smoothed step). For a very smooth change that takes many periods, the result is exponentially small,

$$w_{fi} \approx \frac{|A_{fi}|^2}{\hbar^2} 4\pi^2 \tau^2 e^{-2\pi\omega_{fi}\tau} , \quad \omega_{fi}\tau \gg 1 , \tag{1.90}$$

a typical adiabatic result. For a very steep change, we obtain the limit independent of the exact value of (small) τ,

$$w_{fi} \approx \frac{|A_{fi}|^2}{\hbar^2 \omega_{fi}^2} , \quad \omega_{fi}\tau \ll 1 , \tag{1.91}$$

in agreement with the sudden approximation (1.75). Looking at the remote Fourier components (large transition frequencies), we can see general mathematical properties: when the integrand does not have singularities on the real axis, this limiting tail is exponentially small, (1.90). At $\tau \to 0$, the singularities are piled up near the real axis, and the asymptotic behavior only has the power law fall-off (1.91). One can also note that the function $g(t)$ describes the particle distribution over energy levels in the Fermi gas when t corresponds to energy with the origin of the scale at the Fermi surface and τ is temperature T. The poles on the imaginary axis correspond to the so-called *Matsubara frequencies* $\omega_n = \pi T(2n + 1)$ which play an important role in statistical physics of Fermi-systems.

1.9 Shake-Off Processes

A typical situation, when one can speak of a sudden perturbation of an atom, occurs in the case of an abrupt influence of an external agent onto the atomic nucleus. It can be, for example, β-decay with the sudden change of the nuclear composition (neutron $\leftrightarrow$ proton) and emission of the positron (or electron) and neutrino (or antineutrino).

A similar process occurs when the system undergoes a fast push from an energetic external particle or electromagnetic field, and the interaction time is so short that we can assume that the Hamiltonian of the constituents, electrons in an atom or nucleons in a nucleus, changes suddenly. For the new Hamiltonian, the previous state becomes non-stationary, including in principle, the components (1.76) corresponding to the continuum. This means that an abrupt action onto the nucleus can lead to the ionization of the atom: roughly speaking, the nucleus receives a push, whereas the electrons (or loosely bound nucleons) do not catch up. In such cases, we speak of *shake-off* processes.

Let the nucleus suddenly obtain a momentum $\boldsymbol{Q}$, its wave function $\Psi_N(\boldsymbol{R})$ is multiplied by the factor $\exp[(i/\hbar)(\boldsymbol{Q} \cdot \boldsymbol{R})]$. This follows from considering the shift operator in momentum space, $\hat{K}(\boldsymbol{Q})$. In full analogy with the displacement opera-

tor $\hat{D}(\boldsymbol{a})$ in coordinate space, see Vol. 1 Section 4.5, the operator $\hat{K}(\boldsymbol{Q})$ should act in momentum space as

$$\hat{K}(\boldsymbol{Q})\Phi(\boldsymbol{p}) = \Phi(\boldsymbol{p} - \boldsymbol{Q}) \,. \tag{1.92}$$

Such an operator is

$$\hat{K}(\boldsymbol{Q}) = e^{(i/\hbar)(\boldsymbol{Q}\cdot\hat{\boldsymbol{R}})} \,, \tag{1.93}$$

and in the coordinate representation the wave function $\Psi_N(\boldsymbol{R})$ of the nucleus is simply multiplied by $e^{(i/\hbar)(\boldsymbol{Q}\cdot\boldsymbol{R})}$.

The stationary wave functions of the electrons in the new situation would be their normal atomic functions moving together with the nucleus. If the acquired velocity of the nucleus of mass M is $\boldsymbol{V} = \boldsymbol{Q}/M$, an electron of mass m will get the same velocity $\boldsymbol{v} = \boldsymbol{V}$ if its gain of momentum is $\boldsymbol{q} = m\boldsymbol{V} = (m/M)\boldsymbol{Q}$. This corresponds to the new stationary functions,

$$\Psi_n(\{\boldsymbol{r}_a\}) \to \Psi_n(\{\boldsymbol{r}_a\})e^{(i/\hbar)\boldsymbol{q}\cdot\sum_a \boldsymbol{r}_a} \,. \tag{1.94}$$

Instead, at this moment, we still have an old electron wave function, let's say Ψ_0 for the ground state that did not have time to change. The probability for the electrons to turn out in the excited state $|f\rangle$ after this impact is determined by the overlap (1.83) of the modified function Ψ_f, (1.82), with the original ground state wave function,

$$w_{f0} = \left|\langle e^{(i/\hbar)\boldsymbol{q}\cdot\sum_a \boldsymbol{r}_a}\Psi_f|\Psi_0\rangle\right|^2 = \left|\langle\Psi_f|e^{-(i/\hbar)\boldsymbol{q}\cdot\sum_a \boldsymbol{r}_a}|\Psi_0\rangle\right|^2 \,. \tag{1.95}$$

In particular, the *survival probability* for the atom to stay in its ground state is

$$w_{00} = \left|\langle\Psi_0|e^{-(i/\hbar)\boldsymbol{q}\cdot\sum_a \boldsymbol{r}_a}|\Psi_0\rangle\right|^2 \,. \tag{1.96}$$

The total probability of all other processes (excitation to various bound states and ionization) is $1 - w_{00}$. The whole consideration is valid if the pulse time $\tau \ll R_{\text{at}}/V$, that is, the distance $V\tau$ traversed by the nucleus during the time of perturbation is small compared with the atomic size R_{at}. The quantity (1.96) is the so-called *atomic form-factor*; it will reappear in Section 3.3.

Problem 1.6

Find the average amount of energy transferred to the electrons in the process when the nucleus acquired the velocity $\boldsymbol{V}$.

Solution The obvious answer is given by the energy-weighted *sum rule* (see Vol. 1 Equation 7.146),

$$\overline{E} = \sum_f (E_f - E_0)w_{f0} = \frac{q^2 N}{2m} = \frac{mV^2}{2} N \,, \tag{1.97}$$

where N is the number of electrons.

Problem 1.7

Find the total probability of excitation and ionization of the hydrogen atom (initially in the ground state) in the process when the proton acquired a velocity V as a result of a very short pulse.

Solution Equation (1.96) gives for the ground state of the hydrogen atom

$$w_{\text{exc}} = 1 - w_{00} = 1 - \frac{1}{[1 + (\hbar V/2e^2)^2]^4} \,. \tag{1.98}$$

Here, the velocity $V = Q/M$ enters in the ratio to a typical atomic velocity (see Vol. 1 Equation 1.30). At $V \ll v_{\text{at}}$, the atom will remain in the ground state; if $V \gg v_{\text{at}}$, the probability of excitation is close to one.