Two-state approximation in the adiabatic and sudden-perturbation limits

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(Received 6 March 1978)

The properties of the two-state approximation are considered from the point of view of atomic collision theory in the limit of large and small values of a characteristic collision time T. For large T (the adiabatic limit) asymptotically exact expressions are obtained for the elastic-scattering phase shifts and for the nonadiabatic transition probability due to the pseudocrossing of terms. This approximation is carried out under fairly general assumptions about the Hamiltonian, enabling us to consider such processes as transitions between Σ-Π terms caused by rotation of an internuclear axis. Such general problems of the adiabatic approximation as the applicability of adiabatic perturbation theory, the introduction of a dynamical basis, and the properties of the electronic wave functions in the pseudocrossing region are discussed. For small T (the sudden-peturbation limit) the evolution operator to zeroth and first order in T is calculated. We introduce a general and unambiguous definition of an adiabatic basis as a basis of eigenvectors of the evolution matrix to zeroth order in T.

I. INTRODUCTION

The nonstationary two-level problem presents a very useful model for the investigation of collisions of heavy atomic particles and is widely used in other applications of quantum mechanics. A vast literature is devoted to this problem (see, e.g., Nikitin[1] and references therein). Specific forms of the time dependence of the Hamiltonian have been considered, as well as general problems of theory, including various approximate methods. The latter may be subdivided into those constructed in a mathematically rigorous manner, such as expansions in certain small parameters describing the interaction, and those of a semiempirical or interpolative character. There are also numerical computations for specific Hamiltonians.

The present work is devoted to a systematic exposition of the first approach for the case in which the expansion parameter is associated with the characteristic time T of the change in the Hamiltonian. If T^{-1} is small, we have the adiabatic case; if $T \to 0$ we have the limit of a suddenly switched-on perturbation. (These two limits are in close analogy with the quasiclassical approximation and perturbation theory.) Despite the fact that a considerable number of articles have been devoted to these physically extremely important situations (especially the adiabatic one), as far as we know there have been no reports of work in which the indicated approach is developed in a systematic and sufficiently general form. Moreover, such a treatment is of interest from the point of view of getting concrete results of a mathematically rigorous character which can be used, for example, to check numerical computations or to construct and check various approximations; at a fundamental level it is significant that, as indicated by general considerations, there exist cases which are not described by the conventional models, the most widely used being the Landau-Zener model. Such an alternative situation is realized, for example, in the problem of transitions between Σ-Π terms crossing in a united atom. This is considered in detail in a separate paper.[2] Problems of this sort have made it necessary to generalize the existing theory.

Other fundamental results connected with the approach used here include the possibility of obtaining qualitative physical conclusions, as well as the possibility of introducing certain new and useful concepts and of sharpening or generalizing others that are widely used in the literature but which are not rigorously and uniquely defined.

As already noted above, the literature on the two-level problem and its applications is substantial, and we have not attempted to review it here. We merely refer to the review[1] and monograph[3] of Nikitin and to certain later works in which the bibliography has been extended.[4-6]

The starting point of the present work is the Schrödinger equation for the nonstationary two-level problem in an adiabatic basis

$$\begin{aligned} \frac{d}{dt} Z_1 &= W(t) \exp\left(i \int_0^t \Delta E(t')\, dt'\right) Z_2, \\ \frac{d}{dt} Z_2 &= -W(t) \exp\left(-i \int_0^t \Delta E(t')\, dt'\right) Z_1, \end{aligned} \tag{1}$$

with the initial condition $Z_1 \to 1$ and $Z_2 \to 0$ for $t \to -\infty$. Here, $\Delta E(t)$ is the splitting of the adiabatic energy levels (terms), and $W(t)$ is the matrix element for the interaction of adiabatic states. A basis of adiabatic states has the obvious advantage

that it permits an unambiguous definition as a basis of eigenvectors of the instantaneous Hamiltonian of the system $H(t)$ at the given fixed time t. The equations for any two-level system can, of course, be brought to the form (1) in an arbitrary basis (although the quantities ΔE and W will then have another meaning). The special feature of an adiabatic basis is revealed if we introduce the characteristic time T for change in the Hamiltonian H; we may then consider that H depends only on the variable $\tau = t/T$. The splitting of the adiabatic terms ΔE also depends only on τ, while the interaction W takes the form

$$W = T^{-1} w(\tau) .$$

We assume that for $t \to \pm\infty$ the Hamiltonian has definite limits, and the problem consists in finding the transition probabilities between the two corresponding adiabatic states.

We note that equations similar to (1) also arise in the stationary two-level problem (corresponding to the quantum description of the motion of the nuclei in atomic collisions) when it is treated in the quasiclassical approximation (see, e.g., Refs. 4 and 5).

Section II of the present paper is devoted to the adiabatic case and Sec. III to the sudden-perturbation limit. Section IV contains some concluding remarks.

II. ADIABATIC APPROXIMATION

In the region of small collision velocities of the atoms v, analytic expressions can be obtained for the quantities of interest by asymptotic methods. This is important because for small v ($v \equiv T^{-1}$) the coefficients (and, hence, the functions Z_1 and Z_2) in Eq. (1) oscillate rapidly, and the numerical solution of these equations by computer becomes a complicated problem.

In the adiabatic limit, the time dependence of the functions $Z_1(t)$ and $Z_2(t)$ is obtained quite easily; however, the transition probability is not so easily obtained. The situation is completely analogous to the well-known problem of over-barrier reflection in the quasiclassical approximation, where it is comparatively easy to calculate the wave function for each point in much the same way, but the reflection coefficient is obtained only in the framework of the considerably more complicated étalon-equation method.[7]

Let us look first at the calculation of the functions $Z_1(t)$ and $Z_2(t)$. For slow variation in the Hamiltonian, the population of the initial state $|Z_1(t)|^2$ is always close to unity.[8] Since neither the modulus nor the phase of $Z_1(t)$ changes significantly during the course of a collision, the rapidly changing phase factor in Eq. (1) must be attributed to variation in the function $Z_2(t)$. Introducing the new notation

$$P = Z_1, \quad Q = Z_2 \exp\left(i \int_0^t \Delta E(t')\, dt' \right), \tag{2}$$

we obtain equations with smoothly varying coefficients

$$\frac{dP}{dt} = WQ ; \quad \frac{dQ}{dt} = i\Delta E Q - WP . \tag{3}$$

In the system of equations (3), we introduce explicitly the small parameter v ($\tau = vt$):

$$v \frac{dP}{d\tau} = WQ , \tag{4a}$$

$$v \frac{dQ}{d\tau} = i\Delta E Q - WP . \tag{4b}$$

As noted above, in the zeroth approximations we must set $P(\tau) = 1$. Since the small parameter v stands before the τ-derivative in Eq. (4b), in the first approximation this term should be dropped; hence for $Q(\tau)$ we obtain

$$Q^{(1)}(\tau) = -i \frac{W}{\Delta E} = -iv \frac{w(\tau)}{\Delta E(\tau)} . \tag{5}$$

The correction for $P(\tau)$ is obtained from Eq. (4a) by using the approximation (5) for $Q(\tau)$;

$$P^{(1)}(\tau) = -iv \int_{-\infty}^{\tau} \frac{w^2(\tau')}{\Delta E(\tau')}\, d\tau' . \tag{6}$$

Further iteration of the system of equations (4a) and (4b) yields an expansion of the functions P and Q in powers of v,

$$P = 1 + \sum_{n=1}^{\infty} P^{(n)}(\tau) v^n , \quad Q = \sum_{n=1}^{\infty} Q^{(n)}(\tau) v^n ,$$

where the functions $P^{(n)}$ and $Q^{(n)}$ are calculated from the recursion relations

$$P^{(n)} = \int_{-\infty}^{\tau} w(\tau') Q^{(n)}(\tau')\, d\tau' ,$$

$$Q^{(n)}(\tau) = \frac{1}{i\Delta E(\tau)} \left(\frac{d}{d\tau} Q^{(n-1)} + w P^{(n-1)} \right) .$$

The normalization in the nth approximation is fulfilled to terms of higher order.

Returning to the behavior of the functions Z_1 and Z_2, we find in the first approximation the following result:

$$Z_1(\tau) = 1 - iv \int_{-\infty}^{\tau} \frac{w^2(\tau')}{\Delta E(\tau')}\, d\tau' + o(v) , \tag{7a}$$

$$Z_2(\tau) = \exp\left(-i \int_0^t \Delta E(t')\, dt' \right) \times \left(-iv \frac{w(\tau)}{\Delta E(\tau)} + o(v) \right) . \tag{7b}$$

The power-law dependence of P and Q on v has a simple physical interpretation. The quantity $|P(\tau)|^2$. is the probability of remaining in the initial state when the interaction between states is suddenly switched on at the moment $t=\tau/v$, and the transition probability is given here by the quantity $|Q(\tau)|^2$. On the other hand, it is well known that sudden switching on of the interaction leads to a power-law dependence of the transition probabilities on the parameters of the problem. The power-law form of the expansion of P and Q is a reflection of this fact.

If the interaction always varies adiabatically and analytically then this approach does not enable us to obtain the transition probability since $Q^{(n)}(\tau) \to 0$, for $\tau \to +\infty$ and for all n. We note, however, that although this approach does not enable us to find the transition probability, it does not follow that we obtain no information concerning the final results of the collision. Thus, if in Eq. (7a) we let $\tau \to +\infty$, we obtain the elastic scattering phase shift ϕ in the first channel to first order,

$$\phi = -v\int_{-\infty}^{+\infty} \frac{w^2(\tau)}{\Delta E(\tau)}\,d\tau\,, \quad \varphi = \arg Z_1(\infty)\,. \tag{8}$$

The analogous result for the second channel differs by a sign.

The iterative expansion constructed above is nothing more than the result of systematic diagonalization of the right-hand side of the system of Eqs. (1). We may write the two-level system in the form

$$iv\frac{d}{d\tau}\vec{Z} = \hat{H}_n\vec{Z}\,, \quad \hat{H}_n = \begin{pmatrix} E_n & W_n \\ W_n^* & -E_n \end{pmatrix}, \tag{9}$$

where $\hat{H}_0$ is the Hamiltonian in the diabatic basis. The transition from approximation n to approximation $n+1$ consists in writing the system (9) in a basis of eigenvectors of the matrix $\hat{H}_n$: $\hat{H}_n\vec{X}_n = \lambda_n\vec{X}_n$. After simple manipulations in the new basis, a system of equations (9) is obtained, where the matrix elements of the operator $\hat{H}_{n+1}$ are connected with those of the operator $\hat{H}_n$ in the following manner:

$$E_{n+1} = (E_n^2 + |W_n|^2)^{1/2}, \tag{10}$$

$$W_{n+1} = -iv\frac{E_n^2}{2E_{n+1}^2}\frac{d}{d\tau}\left(\frac{|W_n|}{E_n}\right). \tag{11}$$

The components of the eigenvector $\vec{X}_n$ are calculated in the initial basis in which Eq. (1) is written. They correspond exactly to the expansion of the solutions of Eqs. (3) to nth order. This is seen immediately from the fact, following from (11), that $W_n \sim v^n$. The diagonal matrix element E_n, which for $n=0$ is a diabatic term and for $n=1$ is an adiabatic term, could naturally be called (for $n>1$) a dynamical (or velocity-dependent) term of nth order. The notation of a dynamical term was introduced earlier[9] in connection with the problem of mixing of hydrogenlike levels in collisions of atoms with charged particles. In that case it turned out to be quite useful. Here, dynamical terms arise naturally in an arbitrary two-level system. An interesting and universal feature of dynamical terms is the fact that the distance between them increases with the growth of n [this follows directly from Eq. (10)], the terms being maximally repelled in the pseudocrossing region. The phase shift ϕ, Eq. (8), which is a correction to the adiabatic phase shift $-\int_0^t \Delta E(t')\,dt'$, is associated with just this effective separation of the terms. The effect of this correction on the interference oscillations of the excitation cross sections is discussed by Ostrovskii and Kharchenko.[10]

Since the completion of our work, some additional references have come to our attention. The transformation (2) and the further expansion in powers of v was used by Lebeda and Thorson[11] to speed up the numerical integration of the system of differential operators in the adiabatic domain. A representation for the stationary (quantum) multilevel problem, analogous to the representation of dynamical terms, has been suggested recently by Klar and Fano,[12] who called it the post-adiabatic representation.

Let us return now to the calculation of the transition probability. We shall follow Solov'ev[13] here (the more general problem of transitions with the simultaneous pseudocrossing of an arbitrary number of terms was considered in Refs. 14 and 15).

When v is small, the transition probability is also small; the main contribution comes from the region of closest approach of the terms (the pseudocrossing region). The adiabatic perturbation theory, in which the function Z_1 is taken everywhere equal to unity, and which at first glance seems natural for such a situation, gives an invalid result.[16] We discuss below some reasons for the nonvalidity of the adiabatic perturbation theory. The asymptotically exact value of the transition probability for small v is obtained by the étalon-equation method. This method is explained in detail, e.g., in the monograph of Heading[7] (see also Nikitin[3] and Landau and Liftshitz[17]). For our purposes it is more convenient to use a somewhat different approach, which in essence is identical with the étalon-equation method.

The exact transition probability amplitude F is given by the expression

$$F=-\int_{-\infty}^{+\infty} W(t)\exp\left(-i\int_0^t \Delta E(t')\,dt'\right) \times Z_1(t)\,dt\,. \tag{12}$$

For small v the exponential in (12) oscillates rapidly, and the transition amplitude is calculated in a straightforward manner by deforming the integration contour, and using the method of steepest descent. The saddle points $t_c=\tau_c/v$ are determined by the equation $\Delta E(\tau_c)=0$ and are the same as the crossing points of the terms. Thus, to obtain the transition amplitude it is necessary to calculate Z_1 only in a small neighborhood of the crossing point of terms.

We consider first the pseudocrossing of terms, i.e., the case when Im $t_c\neq 0$. In the neighborhood of point τ_c let

$$\Delta E(\tau)=\alpha(\tau-\tau_c)^\nu+o[(\tau-\tau_c)^\nu]\,,\quad \alpha=\text{const}\,. \tag{13}$$

With the Hamiltonian

$$\hat H(\tau)=\begin{pmatrix} H_{11}(\tau) & H_{12}(\tau)\\ H_{12}(\tau) & H_{22}(\tau)\end{pmatrix}$$

describing the interaction between diabatic states of a quasimolecule $f_1(q,\tau)$ and $f_2(q,\tau)$ (q is the collection of electron coordinates), the difference of terms $\Delta E(\tau)$ and the matrix element $w(\tau)$ are expressed in terms of $H_{ik}(\tau)$ as follows[3] ($\Delta H=H_{11}-H_{22}$):

$$\Delta E(\tau)=(\Delta H^2+4H_{12}^2)^{1/2}, \tag{14}$$

$$w(\tau)=\Delta E^{-2}\left(H_{12}\frac{d}{d\tau}\Delta H-\Delta H\frac{d}{d\tau}H_{12}\right) +\int f_1(q,\tau)\frac{\partial f_2(q,\tau)}{\partial\tau}\,dq\,. \tag{15}$$

For complex τ, the electronic Hamiltonian is no longer self-adjoint, and in the general case when eigenvalues coincide it is not reducible to diagonal form, but rather to the Jordan normal form, i.e., $H_{12}(\tau_c)\neq 0$. Taking this situation into account and using Eq. (13), we see it is not difficult to obtain

$$w(\tau)=\frac{i\nu}{2(\tau-\tau_c)}+o\left(\frac{1}{\tau-\tau_c}\right). \tag{16}$$

To calculate the function Z_1 to first order in the neighborhood of point τ_c, it suffices to retain only the pole in Eq. (16). Then, introducing the new variable

$$x=-\frac{i\alpha(\tau-\tau_c)^{\nu+1}}{v(\nu+1)}\,,$$

we can write the system of equations (1) as follows:

$$x\frac{dA}{dx}=\gamma e^{-x}B\,,\quad x\frac{dB}{dx}=\gamma e^{x}A\,, \tag{17}$$

where $\gamma=\nu/2(1+\nu)$, $A=Z_1$, $B=iZ_2\exp[i\int_0^{t_c}\Delta E(t)\,dt]$. The solution to the system (17) is expressed in terms of confluent hypergeometric functions

$$A=C_1\frac{\Gamma(1+\gamma)}{\Gamma(1+2\gamma)}x^\gamma F(\gamma,1+2\gamma,-x) +C_2\frac{\Gamma(1-\gamma)}{\Gamma(1-2\gamma)}x^{-\gamma}F(-\gamma,1-2\gamma,-x)\,. \tag{18}$$

The asymptotic behavior of the solution to (17) is reached for $v\to 0$ with fixed difference $\tau-\tau_c$. Choosing the coefficients C_1 and C_2 such that the initial condition $Z_1\to 1$ for $t\to-\infty$ is satisfied, and substituting the solution obtained into Eq. (12), we obtain, with the method of steepest descent,

$$|F|=2\sin\pi\gamma\left|\exp\left(-i\int_0^{t_c}\Delta E(t)\,dt\right)\right|\,. \tag{19}$$

The above considerations enable us to see clearly the reasons for the nonvalidity of adiabatic perturbation theory; namely, in this theory $Z_1=1$ is substituted into Eq. (12), while in fact the presence of the pole in $w(\tau)$ [see (16)] leads to a drastic change in Z_1 in the neighborhood of the saddle point [see (18)].

Let us look more closely at the reasons for the occurrence of a pole in the matrix element $w(\tau)$. As noted above, for complex τ the exact electronic Hamiltonian is no longer self-adjoint, and, consequently, it is reducible when the eigenvalues coincide to the Jordan normal form, which has only one eigenvector, i.e., the electronic wave functions corresponding to these terms are identical,

$$\Psi_1(q,\tau_c)=\Psi_2(q,\tau_c)\,, \tag{20}$$

(in the particular case of $\nu=\frac{1}{2}$ this relation was obtained in Ref. 17). We note that this condition does not enable us to use the standard degenerate perturbation theory in the neighborhood of τ_c. Condition (20) implies one more feature of the behavior of the wave functions at the point τ_c. Let us choose the electronic wave functions $\phi_1(q,\tau)$ and $\phi_2(q,\tau)$, corresponding to the terms $E_1(\tau)$ and $E_2(\tau)$, to be normalized in some way with respect to the asymptotic behavior in coordinate space. Then,

$$\Psi_1(q,\tau)=\phi_1(q,\tau)\Big/\left(\int\phi_1^2(q,\tau)\,dq\right)^{1/2},$$
$$\Psi_2(q,\tau)=\phi_2(q,\tau)\Big/\left(\int\phi_2^2(q,\tau)\,dq\right)^{1/2}.$$

The wave functions $\Psi_1(q,\tau)$ and $\Psi_2(q,\tau)$ satisfy the orthonormality condition

$$\int\Psi_1^2(q,\tau)\,dq=\int\Psi_2^2(q,\tau)\,dq=1\,, \tag{21}$$

$$\int \Psi_1(q,\tau)\Psi_2(q,\tau)\,dq = 0\,. \tag{22}$$

The normalization is taken on the real axis without complex conjugation (this can always be done), and hence can be continued into the complex τ plane. At the point τ_c, Eq. (20) is satisfied, and at first glance the condition (21) contradicts the condition (22). This contradiction is removed by the condition

$$\int \phi_1^2(q,\tau_c)\,dq = \int \phi_2^2(q,\tau_c)\,dq = 0\,, \tag{23}$$

which implies that the normalizing coefficient in the wave functions $\Psi_1(q,\tau)$ and $\Psi_2(q,\tau)$ goes to infinity at the point τ_c. This explains the occurrence of the pole in the matrix element $w(\tau)$ at τ_c.

It is not difficult to convince oneself by direct calculations that conditions (20) and (23) are satisfied for the problem of a particle in the field of two zero-range potentials.[13] If we turn to the problem of transitions due to rotation of an internuclear axis between terms crossing in a united atom with orbital angular momentum l and represent the electronic wave function in the form

$$\Psi = f_l(r)Y_{lm}(\theta,\phi)\,,$$

then in the pseudocrossing region the basic time-dependence is contained in the spherical functions, since these are functions with angular momentum projection m on the internuclear axis, the direction of which changes. The continuation of the spherical functions into the complex domain of angles leads to conditions (20) and (23) for the value of the angles corresponding to the point τ_c.

In the transition amplitude calculated with adiabatic perturbation theory only the factor $2\pi\gamma$ before the exponential differs from the exact result [the exact value of this factor is $2\sin\pi\gamma$, see (19)]. Thus, there arises a certain formal parameter γ characterizing the applicability of adiabatic perturbation theory. For small γ the adiabatic-perturbation result goes over to the exact result. In general however, the range of variation of γ is restricted to $0<\gamma<\frac{1}{2}$. For the most interesting cases—the Landau-Zener model and the problem of Σ-Π transitions with rotation of the internuclear axis[2]—γ equals, respectively, $\frac{1}{6}$ and $\frac{1}{4}$. For these cases the exact value of the factor before the exponential is 1 and $\sqrt{2}$, respectively, and the adiabatic-perturbation value is $\frac{1}{3}\pi \simeq 1.05$ and $\frac{1}{2}\pi \simeq 1.57$; i.e., the discrepancy here is not large.

The case in which the terms cross at real τ_c is simpler. Here there are no anomalous effects reflected in the conditions (20) and (23), the matrix element has no pole, and, as a result, the adiabatic perturbation theory gives the exact result in the limit of small v. For the transition probability in this case we obtain

$$|F|^2 = 2\pi v^3 w^2(\tau_c)\left(\frac{d\Delta E(\tau)}{d\tau}\bigg|_{\tau=\tau_c}\right)^{-1}. \tag{24}$$

(The exponential has been dropped here, because it has a modulus of unity.)

III. SUDDEN-PERTURBATION APPROXIMATION

In this section, we consider the limiting case opposite to the adiabatic case—the case of small interaction time T (i.e., of large velocities or small Massey parameters). This limit can be called the diabatic or nonadiabatic limit. We shall principally use the term "sudden-perturbation limit," the justification for which will be discussed in detail below.

In real physical systems a decrease in the interaction time T ultimately leads to a violation of the two-state approximation caused by the possibility of transitions to other states. Here, we consider the case in which T is still sufficiently large compared with the inverse frequency of transition to the remaining adiabatic terms that these transitions can be ignored.

In the equations of the two-state approximation (1) we introduce the new variable φ (cf. Refs. 4 and 5)

$$\varphi(t) = \int_{-\infty}^{t} W(t')\,dt'\,, \qquad \frac{d}{d\varphi}Z_1 = \exp\left(i\int_{\tilde{\varphi}}^{\varphi}\frac{\Delta E}{W}\,d\varphi'\right)Z_2\,, \tag{25}$$

$$\frac{d}{d\varphi}Z_2 = -\exp\left(-i\int_{\tilde{\varphi}}^{\varphi}\frac{\Delta E}{W}\,d\varphi'\right)Z_1\,, \qquad \tilde{\varphi} = \int_{-\infty}^{0} W(t')\,dt'\,. \tag{26}$$

The variable φ varies within finite limits from 0 to some φ_0,

$$\varphi_0 = \int_{-\infty}^{+\infty} W(t')\,dt'\,, \tag{27}$$

where φ_0 is independent of T. In the problem of transitions caused by rotation of the internuclear axis, φ is interpreted as the angle of rotation of the internuclear axis.

Bearing in mind that in the zeroth approximation for $T\to 0$ the exponential in (26) can be replaced by unity, we represent these equations in the form

$$\frac{d}{d\varphi}\vec{Z}=\hat{H}\vec{Z},\quad \hat{H}=\hat{H}^{(0)}+\hat{V},\quad \hat{H}^{(0)}=\begin{pmatrix}0&1\\-1&0\end{pmatrix},\quad \vec{Z}=\begin{pmatrix}Z_1\\Z_2\end{pmatrix},$$

$$\hat{V}(\varphi)=\begin{bmatrix}0 & \exp\left(i\int_{\tilde{\varphi}}^{\varphi}\frac{\Delta E}{W}\,d\varphi'\right)-1\\ 1-\exp\left(-i\int_{\tilde{\varphi}}^{\varphi}\frac{\Delta E}{W}\,d\varphi'\right) & 0\end{bmatrix}, \tag{28}$$

where $\hat{V}(\varphi)$ plays the role of a perturbation. Introducing the time-evolution matrix $S(t',t)$ for the initial system (1)

$$\vec{Z}(t')=\hat{S}(t',t)\vec{Z}(t), \tag{29}$$

we obtain in the zeroth approximation

$$\hat{S}^{(0)}(t,-\infty)=\begin{pmatrix}\cos\varphi(t) & \sin\varphi(t)\\ -\sin\varphi(t) & \cos\varphi(t)\end{pmatrix}. \tag{30}$$

This result can be considered to be a consequence of the action on the system of the sudden perturbation. Indeed, formally extending the domain of variability of φ from $-\infty$ to $+\infty$, we may assume that for $\varphi<0$ and $\varphi>\varphi_0$ there results a degenerate two-level system, in which transitions are absent,

$$\hat{H}^{(0)}=0,\quad \varphi<0,\quad \varphi>\varphi_0. \tag{31}$$

In the interval $0<\varphi<\varphi_0$ the perturbation is suddenly switched on with the constant Hamiltonian $H^{(0)}$, which leads to a mixing of states, where the result of its action is determined only by the magnitude of φ_0, i.e., by the integral of the interaction $W(t)$. In particular, in the important Landau-Zener case it is easy to find directly from (27) that $\varphi_0=\frac{1}{2}\pi$, i.e., the system remains in these states that are customarily called diabatic. In the more general exponential model of Nikitin $\varphi_0=\pi-\frac{1}{2}\theta$, where the model parameter θ is introduced in accordance with Nikitin.[1,3]

To define the concept of diabatic terms in the general case is difficult (cf. Refs. 18 and 19), and they are usually introduced on the basis of qualitative considerations specific to each problem. However, (as already noted in Sec. I) an adiabatic basis can always be introduced uniquely. Taking into account the simple results obtained above, we can suggest a universal and unambiguous definition of a diabatic basis in terms of states of the adiabatic basis. We introduce the diabatic states such that for $t\to-\infty$ they coincide with the adiabatic states, and for finite t they coincide with the columns of the matrix $\hat{S}^{(0)}(t,-\infty)$ (we emphasize that for $t\to+\infty$ the adiabatic and diabatic bases no longer coincide. Then, for small interaction times T, the picture of the evolution of the system in time is as follows: The wave function is not able to change, a fact which corresponds to its invariability in the diabatic basis. The change in the Hamiltonian can be considered to be fast (sudden). To get the transition amplitude between adiabatic states, we must expand the invariant wave function in the new adiabatic basis, which changes as a result of the change in the Hamiltonian; this leads to Eq. (30).

Let us turn now to the calculation of the correction to the zeroth approximation. We have, to first order in the perturbation $\hat{V}$,

$$\hat{S}(t,t')=\hat{S}^{(0)}(t,t')+\hat{S}^{(1)}(t,t'), \tag{32}$$

$$\hat{S}^{(1)}(t,-\infty)=\hat{S}^{(0)}(t,-\infty)\times\int_{-\infty}^{t}dt'\,[\hat{S}^{(0)}(t',-\infty)]^{-1}\times\hat{V}(t')W(t')\hat{S}^{(0)}(t',-\infty). \tag{33}$$

In calculating the last integral in low order with respect to $T\to 0$, we should replace $\hat{V}(t)$ by the first term of the corresponding expansion $\hat{V}^{(0)}(t)$

$$\hat{V}^{(0)}(t)=\begin{pmatrix}0 & i\int_{-\infty}^{t}\Delta E(t')\,dt'\\ i\int_{-\infty}^{t}\Delta E(t')\,dt' & 0\end{pmatrix}. \tag{34}$$

Considering also that $W\sim T^{-1}$ for $T\to 0$ (see Sec. I), we find that, for small T, $\hat{S}^{(1)}(\infty,-\infty)$ goes as T.

However, for those cases in which $\Delta E(t)$ grows sufficiently fast for $t\to\infty$, the integral (33), on substitution of $\hat{V}^{(0)}(t)$ for $\hat{V}(t)$, becomes divergent at the upper and lower limits, and the quantity $\hat{S}^{(1)}(\infty,-\infty)$ takes on a different order of smallness in T. This is precisely what happens in the Landau-Zener model, as well as in the model describing Σ-Π transitions.

In order to investigate this case under sufficiently general assumptions, we assume a power-law behavior at large $|t|$ for the splitting $\Delta E(t)$ and the

matrix element of the nonadiabatic coupling $W(t)$

$$W(t)\sim T^{-1}c\,|t/T|^{-\lambda},\quad \Delta E(t)\sim b\,|t/T|^{\mu},\quad |t|\to\infty, \tag{35}$$

with some constant coefficients c and b. For $T\to 0$ the asymptotic behavior of the integral (33) for $\hat{S}^{(1)}(\infty,-\infty)$ is determined basically by the large $|t|$ and can be written explicitly

$$\hat{S}^{(1)}(\infty,-\infty) = dT^{\zeta}\begin{pmatrix} \exp(-\frac{1}{2}i\pi\zeta)\sin\varphi_0, & -\cos(\frac{1}{2}\pi\zeta)\cos\varphi_0 \\ \cos(\frac{1}{2}\pi\zeta)\cos\varphi_0, & \exp(\frac{1}{2}i\pi\zeta)\sin\varphi_0 \end{pmatrix},$$

$$d=-\Gamma(-\zeta)\frac{c}{1+\mu}\left(\frac{b}{1+\mu}\right)^{\zeta},\quad \zeta=\frac{\lambda-1}{\mu+1}. \tag{36}$$

The latter expression is valid for $\lambda-\mu<2$, while for $\lambda-\mu>2$ we must use the expansion of $V(t)$ described above. In the intermediate case $\lambda-\mu=2$, the integral in question can also turn out to be convergent, depending on the subsequent terms in the expansion of ΔE for $|t|\to\infty$. By direct calculation we may verify the unitarity of the matrix $\hat{S}^{(0)}+\hat{S}^{(1)}$ to terms linear in T^{ζ}, inclusive.

We give here the same results in the form of the first terms of the expansion of the nonadiabatic transition probability and elastic scattering phase shift in the sudden-perturbation approximation,

$$|F|^2=|\sin\varphi_0+dT^{\zeta}\cos(\tfrac{1}{2}\pi\zeta)\cos\varphi_0|^2, \tag{37}$$

$$-\phi=\begin{cases} dT^{\zeta}\sin(\frac{1}{2}\pi\zeta)tg\varphi_0, & \cos\varphi_0>0, \\ \dfrac{\pi\zeta}{2}, & \cos\varphi_0=0, \\ \pi+dT^{\zeta}\sin(\frac{1}{2}\pi\zeta)tg\varphi_0, & \cos\varphi_0<0. \end{cases} \tag{38}$$

As an illustration, we consider once again two important examples. The splitting of adiabatic terms at large $|t|$ is linear in the Landau-Zener model ($\mu=1$) and quadratic in the problem of the rotation of the internuclear axis ($\mu=2$). The interaction $W(t)$ in both cases[20] falls off quadratically with time ($\lambda=2$). Thus, in the Landau-Zener model the correction to the zeroth approximation is of order $T^{1/2}$, while in the problem of rotation of the axis it is of order $T^{1/3}$. We remark also that if for $\lambda=2$ a term goes to finite limits for large $|t|$ ($\mu=0$), we are dealing with just the case discussed above, in which the next term in the asymptotic expansion of $\Delta E(t)$ is important.

We have shown that the order of $\hat{S}^{(1)}$ for $T\to 0$ depends heavily on the behavior of the terms for $|t|\to\infty$. Since the terms of the real problem can have not only a power-law behavior, we must find the range of time t that gives the main contribution to the integral (33) for $\hat{S}^{(1)}(\infty,-\infty)$. A simple estimate for $\lambda-\mu<2$ yields

$$|t_{cr}|\sim(\lambda/b)^{1/(1+\mu)}T^{\mu/(1+\mu)}.$$

The run of ΔE and W for $t\sim t_{cr}$ determines the behavior of $\hat{S}^{(1)}$. We note that the magnitude of t_{cr} is determined principally by the splitting of the adiabatic terms, $\Delta E(t)$.

It is possible to note a certain analogy between the sudden-switching limit considered here and the work of Golubkov, Dalidchik, and Ivanov,[21] where it is shown that for a Hamiltonian of sufficiently general form with sudden switching on and off of a perturbation constant in time the expansion of the transition amplitudes also contains nonintegral powers of the interaction time T.

IV. CONCLUSIONS

In conclusion, we will discuss briefly the importance of the limitations assumed in the present work. A number of results of this article are of a general nature and are immediately extended to multilevel systems. This generalizability pertains especially to the definition given here of nth-order dynamical terms and diabatic terms, as well as to the methods of calculating the elastic scattering phase shift in the adiabatic approximation. However, the analysis of the other problems is considerably complicated when the two-state approximation is dropped. In the adiabatic limit there appears the possibility of direct crossing of several terms. Physically, this is realized, for example, for terms undergoing transition to a state of the united atom with $l\geq 2$. Later, in the example of $l=2$ we propose to examine the difficulties arising here, which are essentially connected with the specifics of the multilevel problem.[15] Another case of the simultaneous crossing of several terms was considered in the work of one of the authors.[14]

One more important problem not touched upon in the present article is the problem of finding the next terms in the expansion of the transition matrix in the adiabatic limit and in the sudden-perturbation limit. We note only that even the determination of the order of these terms in the small parameter T or T^{-1} is generally a nontrivial problem, especially in the adiabatic case.

ACKNOWLEDGMENTS

The authors are grateful to D. W. Norcross and S. Geltman for their comments on the manuscript. Part of this work was done while one of us (Yu. N. D.) was a Visiting Fellow at the Joint Institute for Laboratory Astrophysics, Boulder, Colorado. The help and hospitality of JILA personnel are gratefully acknowledged.

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