# Siegert-state expansion for nonstationary systems. III. Generalized Born-Fock equations and adiabatic approximation for transitions to the continuum

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This paper presents a further development of the Siegert-state expansion approach [O. I. Tolstikhin, Phys. Rev. A **73**, 062705 (2006)]. Here, we switch to the adiabatic representation. We introduce the adiabatic Siegert states and derive the generalized Born-Fock equations describing the time evolution of coefficients in the expansion of the solution to the time-dependent Schrödinger equation in their terms. By constructing the asymptotic solution to these equations, we develop an adiabatic approximation for transitions to the continuum. The leading-order asymptotic formulas for the spectra of ejected particles in the underbarrier (when the initial state remains bound during all the evolution) and overbarrier (when the initial state is temporarily promoted to the continuum) cases are obtained. These formulas are uniform in the momentum of ejected particles and thus give a complete solution to the problem in the adiabatic approximation. Their relation to previous studies of nonadiabatic transitions to the continuum is discussed. The results are illustrated by calculations for a model describing the dissociation of a diatomic molecule by an electric field pulse.

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## I. INTRODUCTION

Considering a nonstationary problem with the Hamiltonian $H(t)=H+V(t)$, where $H$ describes a stationary atomic system and $V(t)$ represents an external field or some deformation of the atomic potential, it is natural to seek the solution to the time-dependent Schrödinger equation (TDSE) in the form of an expansion in terms of the eigenfunctions of $H$. Such an approach, first used by Dirac [1] for developing nonstationary perturbation theory, is a prototype for many close-coupling methods. Expansions in terms of the eigenfunctions of $H$ or any other time-independent basis are called a *diabatic* representation. Born and Fock [2] introduced the *adiabatic* representation in which the momentary eigenfunctions of the full Hamiltonian $H(t)$ are used as a basis in the expansion. Diabatic bases are simpler in implementation and more convenient for the numerical solution, while the adiabatic basis is singled out by its role in the asymptotic solution of the problem in adiabatic approximation. Both representations are widely used in atomic physics.

Seeking the solution as an expansion in a basis eliminates spatial variables from the TDSE, reducing the original partial differential equation to a set of coupled ordinary differential equations in time. Mathematically, this is perfectly justified provided that the basis is complete. Computationally, the resulting coupled equations are much easier to solve and the whole scheme is indeed very efficient as long as one can find a good *discrete* basis which ensures fast convergence. This is the case if the system has only discrete spectrum. However, the continuous spectrum is known to cause much difficulties and cannot be incorporated into the standard scheme without making some essential approximations.

A solution to this problem was proposed in the first paper of the series [3]. The idea is to use Siegert states (SSs) instead of the usual set of bound and scattering states as a basis in the expansion. SSs are also eigenfunctions of the Hamiltonian, but satisfy different boundary conditions: they have only one type of waves, incoming or outgoing, in the asymptotic region. Such an eigenvalue problem, first formulated by Siegert for $s$-wave scattering in a spherically symmetric finite-range potential [4], has a purely discrete spectrum. The set of SSs possesses certain orthogonality and completeness properties which qualify it as a basis suitable for expanding the solution to the TDSE. The use of this basis enables one to treat the continuum with no approximation and on an equal footing with the discrete spectrum. The coupled equations in this case are pseudodifferential, and hence nonlocal in time, which is the price for incorporating the continuum. They can be transformed into coupled Volterra equations which are almost as easy to solve as ordinary differential equations. The mathematical formulation and numerical implementation of this approach are based on the theory of Siegert pseudostates [5–10]. Its computational efficiency was demonstrated by calculations for several model laser-atom interaction problems in the second paper of the series [11] and more recently in [12].

The formulation of [3] employed a diabatic SS basis. In the present paper we switch to the adiabatic representation. Our goal is to develop an adiabatic approximation for transitions to the continuum. The theory of nonadiabatic transitions in the discrete spectrum was pioneered by Born and Fock [2] who obtained the first definite, albeit negative, result known as the adiabatic theorem. An estimate of the probability of a nonadiabatic transition between discrete states was first given by Landau [13], but only some 30 years later Dykhne [14] derived the leading-order asymptotic formula for this quantity. Simultaneously, two basic exactly solvable models were found by Zener [16] and Rosen and Zener [17]. Independently, Stueckelberg [15] developed a semiclassical approximation for the solution to a related but more complex problem of nonadiabatic transitions in the stationary case. These early studies have attracted a new wave of interest and were reexamined in the 1970s [18,19], which resulted in numerous applications of asymptotic methods in atomic physics; see [20–24] and the collection of recent reviews in [25]. In general, it can be said that the mechanisms of nonadia-

 

batic transitions between discrete states in many physical situations are well understood.

On the contrary, transitions from a discrete state to the continuous spectrum have been much less studied. Chaplik [26,27] attempted to extend the work of Dykhne [14] in this direction, but succeeded in obtaining the spectrum of ejected particles only in the deeply underbarrier case and up to an unknown constant factor. Following [14], the derivation in [26,27] was based on the Born-Fock (BF) equations [2]. These equations are convenient for treating nonadiabatic transitions between discrete states [14], but become intractable in the presence of a continuum, which explains the technical difficulties encountered in [26]. Demkov [28] considered overbarrier transitions to the continuum in the zero-range potential (ZRP) model. Devdariani [29] has extended this analysis to the underbarrier case and developed a uniform approximation for the intermediate regime; see also [30] and references therein. Later, to overcome the difficulties associated with the BF equations, Solov'ev [31] developed what is currently known as the advanced adiabatic approach [32] and obtained a general formula for the spectrum of ejected particles in adiabatic approximation. References [26–29,31] are major previous contributions to the subject of the present paper; their results are discussed in more detail below. Without attempting to review all the literature, we mention an important exactly solvable model found by Demkov and Osherov [33] which allows for the inclusion of the continuous spectrum.

In this paper, we attack the theory of nonadiabatic transitions to the continuum from a different standpoint and with different means provided by the SS expansion approach [3]. More specifically, we develop the adiabatic approximation for the problem considered in [3]. The paper is organized as follows. In Sec. II, we formulate the TDSE in a matrix form suitable for the expansion in terms of SSs. In Sec. III, we introduce the adiabatic SSs and derive the generalized Born-Fock (GBF) equations describing the time evolution of the coefficients in the expansion of the solution to the TDSE in their terms. These equations provide a basis for developing the adiabatic approximation in the present approach. From analysis of the singularities of the coupling terms in the GBF equations one can identify three mechanisms of nonadiabatic transitions. Here, we consider only transitions via turning points—a mechanism which is specific for transitions to the continuum. In Secs. IV and V, asymptotic solutions to the GBF equations and formulas for the spectra of ejected particles in underbarrier and overbarrier cases are obtained. In Sec. VI, these results are compared with the results of previous approaches. In Sec. VII, they are illustrated by calculations of the dissociation of a model diatomic molecule by an electric field pulse. Section VIII concludes the paper.

## II. BASIC EQUATIONS

### A. Formulation of the problem

We consider a nonstationary system described by the TDSE (a system of units in which $\hbar=m=1$ and all the quantities involved in the analysis are dimensionless is used throughout the paper)

$$\left[i\frac{\partial}{\partial t}-H(\tau)\right]\psi(r,t)=0, \tag{1}$$

where

$$H(\tau)=-\frac{1}{2}\frac{\partial^2}{\partial r^2}+V(r,\tau). \tag{2}$$

Here $\tau$ is the "slow" time variable,

$$\tau=\epsilon t, \tag{3}$$

and $\epsilon$ is the adiabatic parameter. The adiabatic regime we are interested in corresponds to a slow variation of $V(r,\tau)$ as a function of $t$ and hence small values of $\epsilon$. We assume that for any $\tau$ the potential $V(r,\tau)$ has a finite range,

$$V(r,\tau)|_{r\geq a}=0, \tag{4}$$

or decays sufficiently rapidly as $r$ grows, so that cutting off its tail beyond $r=a$ does not produce any appreciable effect on the observables. In addition, we assume that $V(r,\tau)$ becomes independent of time and is given by the same function in the remote past and future:

$$V(r,\tau)|_{\tau\to\pm\infty}=V(r). \tag{5}$$

The latter assumption is not essential for the present approach, but simplifies the analysis. It is convenient to introduce an unperturbed stationary system with the Hamiltonian

$$H=-\frac{1}{2}\frac{\partial^2}{\partial r^2}+V(r), \tag{6}$$

and present $H(\tau)$ and $V(r,\tau)$ in the form

$$H(\tau)=H+U(r,\tau),\quad V(r,\tau)=V(r)+U(r,\tau), \tag{7}$$

where $U(r,\tau)$ describes the interaction with an external field. Note that both the time-independent $V(r)$ and time-dependent $U(r,\tau)$ parts of the total potential $V(r,\tau)$ vanish beyond $r=a$, and $U(r,\tau)$ vanishes as $\tau\to\pm\infty$. Let $H$ have a bound state defined by

$$(H-E_0)\phi_0(r)=0, \tag{8a}$$

$$\phi_0(0)=\phi_0(\infty)=0, \tag{8b}$$

$$\int_0^\infty \phi_0^2(r)dr=1. \tag{8c}$$

Equation (1) will be considered in the domain $0\leq r<\infty$, $-\infty<t<\infty$, with the boundary condition

$$\psi(0,t)=0 \tag{9}$$

and initial condition

$$\psi(r,t)|_{t\to-\infty}=e^{-iE_0t}\phi_0(r). \tag{10}$$

Physical observables are defined by the coefficients in the expansion of $\psi(r,t)$ in terms of the bound and scattering eigenstates of $H$ after the action of the external field $U(r,t)$ is over. In this paper we consider only transitions to the continuous spectrum. The momentum distribution of ejected par-

ticles is given by [see Eqs. (80) and (85) in [3]]

$$P(k) = k^2 \left| \int_{-\infty}^{\infty} \psi(a,t) e^{iEt} dt \right|^2, \tag{11}$$

and the total probability of transitions to the continuum is

$$P_c = \int_0^{\infty} P(k) \frac{dk}{2\pi}. \tag{12}$$

Our goal is to find the asymptotic solution to this problem for $\epsilon \to 0$.

### B. Matrix form of the time-dependent Schrödinger equation

Let us introduce the function and derivative value operators at $r=a$,

$$\mathcal{F} = \delta(r-a), \quad \mathcal{D} = \delta(r-a)\frac{d}{dr}, \tag{13}$$

and the Hermitized Hamiltonian

$$\tilde{H}(\tau) = H(\tau) + \frac{1}{2}\mathcal{D}. \tag{14}$$

Following [3], we introduce a pseudodifferential operator $\hat{\lambda}_t$ whose action on a function

$$f(t) = \int_{-\infty}^{\infty} f(E) e^{-iEt} \frac{dE}{2\pi} \tag{15}$$

is defined by

$$\hat{\lambda}_t f(t) = \int_{-\infty}^{\infty} ikf(E) e^{-iEt} \frac{dE}{2\pi}. \tag{16}$$

In this paper, $E$ and $k$ always denote energy and momentum related to each other by

$$E = \frac{1}{2}k^2, \quad k = \sqrt{2E}, \tag{17}$$

where the branch of the square-root function for which $\mathrm{Im}\, k > 0$ on the physical sheet of $E$ is meant and it is understood that the integration path in Eqs. (15) and (16) lies on the physical sheet infinitesimally above the real axis. For a more detailed discussion of the operator $\hat{\lambda}_t$ see [3] and Appendix A.

Taking into account Eq. (4), the solution to Eqs. (1), (9), and (10) satisfies the outgoing-wave boundary condition [3,34]

$$\mathcal{D}\psi(r,t) = \mathcal{F}\hat{\lambda}_t \psi(r,t). \tag{18}$$

Using this relation, one can rewrite Eq. (1) in a matrix form [3]

$$\left[ \hat{\lambda}_t - \begin{pmatrix} 0 & 1 \\ -2\tilde{H}(\tau) & \mathcal{F} \end{pmatrix} \right] \begin{pmatrix} \psi(r,t) \\ \tilde{\psi}(r,t) \end{pmatrix} = 0. \tag{19}$$

The first equation in this system, $\tilde{\psi}(r,t) = \hat{\lambda}_t \psi(r,t)$, expresses $\tilde{\psi}(r,t)$ in terms of $\psi(r,t)$. However, it is convenient to treat $\tilde{\psi}(r,t)$ as an independent unknown function. Such an extension of the original Hilbert space enables one to decouple nontrivial dynamics in the inner region $0 \le r \le a$ from free-space propagation in the outer region $r \ge a$. In other words, in the approach based on Eq. (19) instead of Eq. (1) only the inner region is to be considered, while the outer region is dealt with analytically. Note that Eq. (19) is equivalent to Eq. (1) only for solutions satisfying the outgoing-wave boundary condition (18).

## III. GENERALIZED BORN-FOCK EQUATIONS

### A. Adiabatic Siegert basis

The adiabatic Siegert states (ASSs) are defined by the momentary Hamiltonian $H(\tau)$. They are the solutions to the Siegert eigenvalue problem [4]

$$[H(\tau) - E(\tau)]\phi(r;\tau) = 0, \tag{20a}$$

$$\phi(0;\tau) = 0, \tag{20b}$$

$$\left[ \frac{d}{dr} - ik(\tau) \right] \phi(r;\tau) \Big|_{r=a} = 0. \tag{20c}$$

The ASS momentum and energy eigenvalues and eigenfunctions depend on $\tau$ as a parameter and will be denoted by $k_n(\tau)$, $E_n(\tau) = k_n^2(\tau)/2$, and $\phi_n(r;\tau)$. In terms of operators (13), the outgoing-wave boundary condition (20c) reads $\mathcal{D}\phi_n(r;\tau) = ik_n(\tau)\mathcal{F}\phi_n(r;\tau)$. Introducing a new function $\tilde{\phi}_n(r,\tau) = ik_n(\tau)\phi_n(r;\tau)$, one can rewrite Eqs. (20a)–(20c) in a matrix form [3,6]

$$\left[ \begin{pmatrix} 0 & 1 \\ -2\tilde{H}(\tau) & \mathcal{F} \end{pmatrix} - ik_n(\tau) \right] \begin{pmatrix} \phi_n(r;\tau) \\ \tilde{\phi}_n(r;\tau) \end{pmatrix} = 0. \tag{21}$$

For any $\tau$, the two-component solutions to this equation are orthogonal with respect to the inner product [3,6]

$$\int_0^a (\phi_n(r;\tau)\tilde{\phi}_n(r;\tau)) \begin{pmatrix} -\mathcal{F} & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \phi_m(r;\tau) \\ \tilde{\phi}_m(r;\tau) \end{pmatrix} dr = 2ik_n(\tau)\delta_{nm} \tag{22}$$

and satisfy the completeness relation [3,6]

$$\sum_n \frac{1}{2ik_n(\tau)} \begin{pmatrix} \phi_n(r;\tau) \\ \tilde{\phi}_n(r;\tau) \end{pmatrix} (\phi_n(r';\tau)\tilde{\phi}_n(r';\tau)) = \delta(r-r') \begin{pmatrix} 0 & 1 \\ 1 & \mathcal{F} \end{pmatrix}. \tag{23}$$

It is useful to establish a relation between the present approach and the formulation of [3]. In [3], we employed diabatic Siegert states (DSSs) which are the solutions to the Siegert eigenvalue problem (20a)–(20c) with $H(\tau)$ substituted by the stationary Hamiltonian $H$. The corresponding momentum and energy eigenvalues and eigenfunctions will be denoted by $k_n$, $E_n = k_n^2/2$, $\phi_n(r)$, and $\tilde{\phi}_n(r) = ik_n\phi_n(r)$. They satisfy orthogonality and completeness relations similar to Eqs. (22) and (23). The ASSs can be expanded in terms of the DSSs:

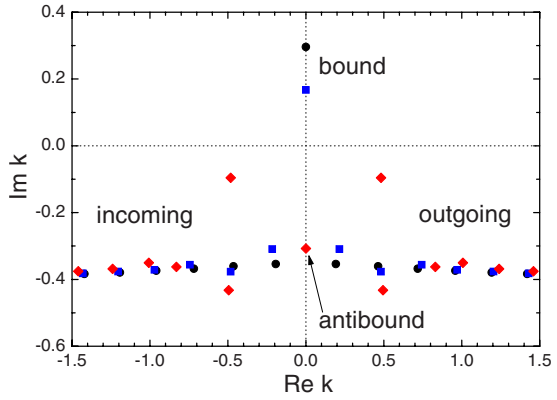


FIG. 1. (Color online) Circles: DSS momentum eigenvalues for the model described in Sec. VII A. Squares (diamonds): ASS momentum eigenvalues for the same model at the maximum of the electric field pulse for $F_0=0.05$ ($F_0=0.2$), which corresponds to the underbarrier (overbarrier) case. In all cases, the eigenvalue representing the initial state lies on the imaginary axis.

$$\begin{pmatrix} \phi_n(r;\tau) \\ \tilde{\phi}_n(r;\tau) \end{pmatrix} = \sum_m T_{nm}(\tau) \begin{pmatrix} \phi_m(r) \\ \tilde{\phi}_m(r) \end{pmatrix}. \tag{24}$$

The transformation matrix is given by

$$T_{nm}(\tau) = \frac{1}{2ik_m} \int_0^a (\phi_m(r)\tilde{\phi}_m(r)) \begin{pmatrix} -\mathcal{F} & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \phi_n(r;\tau) \\ \tilde{\phi}_n(r;\tau) \end{pmatrix} dr. \tag{25}$$

The inverse transformation is defined by the inverse matrix

$$T^{-1}_{nm}(\tau) = \frac{k_n T_{mn}(\tau)}{k_m(\tau)}. \tag{26}$$

Substituting the expansion (24) into Eq. (21) one obtains

$$\sum_l [k_m^2 \delta_{ml} + U_{ml}(\tau)] T_{nl}(\tau) = k_n(\tau) k_m T_{nm}(\tau), \tag{27}$$

where

$$U_{nm}(\tau) = \int_0^a \phi_n(r) U(r,\tau) \phi_m(r) dr. \tag{28}$$

This algebraic eigenvalue problem provides an alternative way to construct ASSs.

The DSSs can be divided into four groups according to the position of $k_n$ in complex plane [3,6] (see Fig. 1): bound (Re $k_n=0$, Im $k_n>0$), antibound (Re $k_n=0$, Im $k_n<0$), outgoing (Re $k_n>0$, Im $k_n<0$), and incoming (Re $k_n<0$, Im $k_n<0$). The DSS representing the initial bound state in Eq. (10) will be indicated by $n=0$. For real $\tau$, the ASSs can also be divided into four similar groups (see Fig. 1), but the number of states in each group may now depend on $\tau$. Taking into account that $U_{nm}(\tau \to \pm\infty)=0$, one can see from Eq. (27) that each ASS converges to one of the DSSs as $\tau \to \pm\infty$. We assume that $T_{nm}(\tau \to -\infty)=\delta_{nm}$, which establishes a one-to-one correspondence between the two sets. This in particular means that the bound state in the initial condition (10) is represented by the ASS with $n=0$. We shall need to consider the solutions to Eq. (21) also for complex $\tau$. To define them, we assume that the potential $V(r,\tau)$ is an analytic function of $\tau$. Then the functions $k_n(\tau)$ and $\phi_n(r;\tau)$, which seem to be independent on the real axis of $\tau$, emerge as different branches of multivalued analytic functions—the eigenvalue $k(\tau)$ and eigenfunction $\phi(r;\tau)$ of Eqs. (20a)–(20c). The Riemann surface of the adiabatic momentum eigenvalue $k(\tau)$ generalizes a similar analytic construction—the Riemann surface of the adiabatic energy eigenvalue—arising in studies of nonadiabatic transitions in the discrete spectrum [21] by incorporating the continuum which is represented by the sheets corresponding to antibound, incoming, and outgoing ASSs.

### B. Siegert-state expansion: Adiabatic representation

The solution to Eq. (19) in the inner region can be sought in the form [3]

$$\begin{pmatrix} \psi(r,t) \\ \tilde{\psi}(r,t) \end{pmatrix} = \sum_n a_n(t) \begin{pmatrix} \phi_n(r;\tau) \\ \tilde{\phi}_n(r;\tau) \end{pmatrix}, \quad 0 \le r \le a. \tag{29}$$

Substituting this into Eq. (19) and using Eq. (22), one obtains coupled equations defining the coefficients $a_n(t)$:

$$\sum_m \hat{\lambda}_{t,nm} a_m(t) - ik_n(\tau) a_n(t) = 0, \tag{30a}$$

$$a_n(t)|_{t\to-\infty} = \delta_{n0} e^{-iE_0 t}, \tag{30b}$$

where the matrix operator $\hat{\lambda}_{t,nm}$ is defined by

$$\hat{\lambda}_{t,nm} = \frac{1}{2ik_n(\tau)} \int_0^a (\phi_n(r;\tau) \;\; \tilde{\phi}_n(r;\tau)) \times \begin{pmatrix} -\mathcal{F} & 1 \\ 1 & 0 \end{pmatrix} \hat{\lambda}_t \begin{pmatrix} \phi_m(r;\tau) \\ \tilde{\phi}_m(r;\tau) \end{pmatrix} dr, \tag{31}$$

and it is understood that $\hat{\lambda}_t$ acts on everything to its right. Equations (30a) describe time evolution of the coefficients in the expansion of the solution to the TDSE (1) in terms of eigenfunctions of the momentary Hamiltonian $H(\tau)$. This feature is in common with the original BF approach [2]. However, Siegert states instead of the usual set of bound and scattering states are used as a basis in the expansion, which results in a purely discrete set of coupled equations even in the presence of the continuum. To reflect these similarities and differences, we call Eqs. (30a) the GBF equations. These equations are one of the main results of this work.

Equation (29) is the *adiabatic* SS expansion. One can similarly expand the solution to Eq. (19) in terms of the DSSs [3]. The coefficients $d_n(t)$ in such a *diabatic* SS expansion are related to $a_n(t)$ by

$$d_n(t) = \sum_m T_{mn}(\tau) a_m(t). \tag{32}$$

Substituting Eq. (24) into Eq. (31) one obtains another useful representation for $\hat{\lambda}_{t,nm}$:

$$\hat{\lambda}_{t,nm} = \sum_l T_{ln}^{-1}(\tau)\hat{\lambda}_t T_{ml}(\tau). \tag{33}$$

### C. Nonadiabatic couplings

In order to turn Eqs. (30a) into a practically useful tool one needs to develop techniques to work with the matrix operator $\hat{\lambda}_{t,nm}$. We shall not discuss here how this operator could be implemented numerically; for the numerical solution of the problem, it is easier to return to the diabatic representation and use the algorithms described in [3]. On the other hand, Eqs. (30a) are more convenient for constructing the asymptotic solution for $\epsilon \to 0$. The key technical element that furnishes further progress in this direction is Leibniz's formula for the operator $\hat{\lambda}_t$; see Appendix A. Using Eq. (A6), we obtain from Eq. (31)

$$\hat{\lambda}_{t,nm} = \sum_{p=0}^{\infty} \frac{(-2i\epsilon)^p \Gamma(3/2)}{p!\,\Gamma(3/2-p)} \frac{\mathcal{P}_{nm}^{(p)}(\tau)}{2ik_n(\tau)} \hat{\lambda}_t^{1-2p}, \tag{34}$$

where

$$\mathcal{P}_{nm}^{(p)}(\tau) = \int_0^a (\phi_n(r;\tau)\tilde{\phi}_n(r;\tau)) \begin{pmatrix} -\mathcal{F} & 1 \\ 1 & 0 \end{pmatrix} \frac{\partial^p}{\partial \tau^p} \begin{pmatrix} \phi_m(r;\tau) \\ \tilde{\phi}_m(r;\tau) \end{pmatrix} dr. \tag{35}$$

Equation (34) is an expansion of $\hat{\lambda}_{t,nm}$ in powers of the adiabatic parameter $\epsilon$, with matrices (35) having the meaning of nonadiabatic couplings. The physical grounds for such an expansion root in the difference of scales in the dependence on time of the ASSs and solutions to Eqs. (30a) and (30b). For comparison, we recall that there are nonadiabatic couplings only of the first order in $\epsilon$ in the original BF equations. Using Eq. (22), one finds

$$\mathcal{P}_{nm}^{(0)}(\tau) = 2ik_n(\tau)\delta_{nm}, \tag{36}$$

and thus the zeroth-order term in Eq. (34) does not couple the ASSs. The first-order coupling matrix $\mathcal{P}_{nm}^{(1)}(\tau)$ is explicitly given by

$$\mathcal{P}_{nn}^{(1)}(\tau) = i\dot{k}_n(\tau), \tag{37a}$$

$$\mathcal{P}_{nm}^{(1)}(\tau) = -\mathcal{P}_{mn}^{(1)}(\tau) = i[k_n(\tau)+k_m(\tau)]\int_0^a \phi_n(r;\tau)\dot{\phi}_m(r;\tau)dr - \phi_n(a;\tau)\dot{\phi}_m(a;\tau) + \dot{k}_m(\tau)\frac{\phi_n(a;\tau)\phi_m(a;\tau)}{k_n(\tau)+k_m(\tau)}, \quad n \neq m. \tag{37b}$$

Here and in the following, overdots denote differentiation with respect to "slow" time $\tau$. If both $n$ and $m$ correspond to bound states, the last equation can be rewritten as

$$\mathcal{P}_{nm}^{(1)}(\tau) = i[k_n(\tau)+k_m(\tau)]\int_0^{\infty} \phi_n(r;\tau)\dot{\phi}_m(r;\tau)dr, \quad n \neq m. \tag{38}$$

In the integral term here one can recognize the matrix of nonadiabatic couplings between bound states in the BF equations. Using perturbation theory for SSs [8], one can obtain another representation for the off-diagonal part of $\mathcal{P}_{nm}^{(1)}(\tau)$:

$$\mathcal{P}_{nm}^{(1)}(\tau) = -2i\frac{\int_0^a \phi_n(r;\tau)\dot{U}(r,\tau)\phi_m(r;\tau)dr}{k_n(\tau)-k_m(\tau)}, \quad n \neq m. \tag{39}$$

Using Eq. (23), one obtains from Eq. (35) a recurrence relation

$$\mathcal{P}_{nm}^{(p+1)}(\tau) = \frac{d\mathcal{P}_{nm}^{(p)}(\tau)}{d\tau} - \sum_l \frac{\mathcal{P}_{ln}^{(1)}(\tau)\mathcal{P}_{lm}^{(p)}(\tau)}{2ik_l(\tau)}. \tag{40}$$

Thus all coupling matrices with $p>1$ can be expressed in terms of $\mathcal{P}_{nm}^{(1)}(\tau)$. These equations establish a framework suitable for developing a regular procedure to successively take higher-order nonadiabatic effects into account.

### D. Transition points

Using Eq. (36), let us rewrite Eq. (34) as

$$\hat{\lambda}_{t,nm} = \delta_{nm}\hat{\lambda}_t - \epsilon\frac{\mathcal{P}_{nm}^{(1)}(\tau)}{2k_n(\tau)}\hat{\lambda}_t^{-1} + O(\epsilon^2). \tag{41}$$

The first term on the right-hand side corresponds to pure adiabatic evolution and does not cause nonadiabatic transitions. The coupling terms become negligible in the adiabatic limit $\epsilon \to 0$ everywhere in complex $\tau$ plane except for the localized regions near singular points of the function $\mathcal{P}_{nm}^{(1)}(\tau)/k_n(\tau)$. Nonadiabatic transitions occur via strong interaction between ASSs near such points, so they are called the transition points. We note that the localization of regions of strong nonadiabatic couplings important for the evaluation of probabilities of nonadiabatic transitions is typical for adiabatic and semiclassical approximations [14,15]. Using Eq. (39), one can distinguish three types of transition points in the present case: (i) turning points, where $k_n(\tau)=0$, (ii) crossing points, where $k_n(\tau)=k_m(\tau)$, and (iii) singularities of the potential $V(r,\tau)$ as a function of $\tau$, if any, where $\dot{U}(r,\tau)=\infty$. At turning points, one of the ASSs is promoted to the continuum or, on the contrary, is captured from the continuum and becomes a bound state. The term is probably not commonly accepted in the nonstationary context, but this is how in classical and quantum mechanics one calls points where the momentum turns zero. In this paper, we consider only transitions via turning points, since this mechanism is specific for transitions from a bound state to the continuum. Crossing points are in fact branch points of the multivalued function $k(\tau)$. They are known to play the key role in treating nonadiabatic transitions between discrete states [14]. The

analysis of transitions to the continuum via crossing points on the basis of the present approach is postponed to a future study.

## IV. UNDERBARRIER TRANSITIONS

If the external field never becomes strong enough to statically break the system, the ASS representing the initial state at $t \to -\infty$ remains bound during all the evolution. This condition is formalized as [see Fig. 2(a)]

$$\mathrm{Re}\, k_0(\tau) = 0, \quad \mathrm{Im}\, k_0(\tau) > 0, \quad -\infty < \tau < \infty. \tag{42}$$

In this case, for a transition to the continuum the system must absorb a finite energy. Such a process has an exponentially small probability in the adiabatic regime, which resembles the tunneling through a potential barrier in the stationary case, so we call it the underbarrier transition.

We consider the situation when $\mathrm{Im}\, k_0(\tau)$ has only one minimum on the real axis at $\tau_{\min}$; see Fig. 2(a). Let function $k_0(\tau)$ have a pair of complex-conjugate simple zeros $\tau_0$ and $\tau_0^*$ with $\mathrm{Im}\, \tau_0 > 0$; it is assumed that $\mathrm{Im}\, \tau_0 = O(\epsilon^0)$. For small $\delta\tau = \tau - \tau_0$ we have

$$k_0(\tau) = \alpha\delta\tau + O(\delta\tau^2), \quad \alpha = \dot{k}_0(\tau_0), \tag{43a}$$

$$\phi_0(r;\tau) = \delta\tau^{1/2}\chi(r) + O(\delta\tau^{3/2}), \quad \chi^2(a) = -2i\alpha, \tag{43b}$$

where $\alpha = O(\epsilon^0)$ and the function $\chi(r)$ does not depend on $\tau$. Equations (43b) follow from Eq. (43a) and the normalization condition (22) for $n=m=0$. Introduce the notation

$$s(\tau_1, \tau_2) = \int_{\tau_1}^{\tau_2} E_0(\tau) d\tau. \tag{44}$$

Stokes $l$ and anti-Stokes $\tilde{l}$ lines emanating from $\tau_0$ are defined by

$$\mathrm{Re}\, s(\tau_0, \tau) = 0, \quad \tau \in l, \tag{45a}$$

$$\mathrm{Im}\, s(\tau_0, \tau) = 0, \quad \tau \in \tilde{l}. \tag{45b}$$

Let $l_2$ be the Stokes line connecting points $\tau_0$ and $\tau_0^*$; see Fig. 2(b). It crosses the real axis under a right angle; the point where this happens is denoted by $\tau_x$. Let $\varphi$ be the angle between $l_2$ and the downward direction at $\tau_0$. Making a branch cut from $\tau_0$ upward, we have

$$\arg \delta\tau = -\pi/2 + \varphi, \quad \delta\tau \to 0, \quad \tau \in l_2. \tag{46}$$

All phases are fixed by the convention

$$\arg \alpha = \pi - 3\varphi/2. \tag{47}$$

Using Eq. (43a) we obtain

$$s(\tau_0, \tau) = \frac{1}{6}\alpha^2\delta\tau^3 + O(\delta\tau^4). \tag{48}$$

Thus

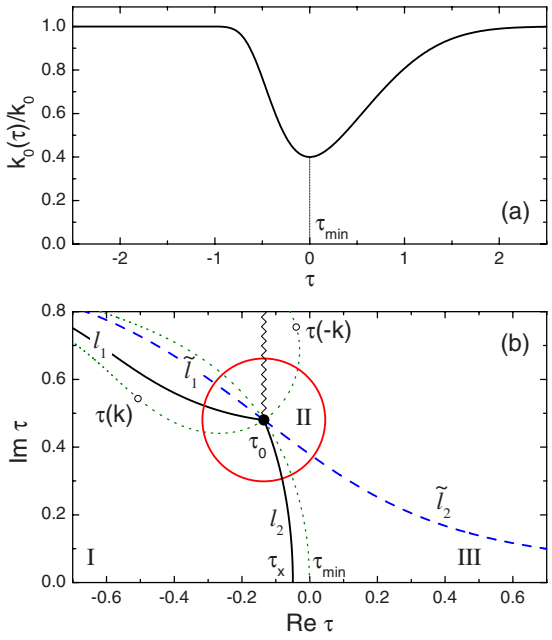


FIG. 2. (Color online) (a) The behavior of the adiabatic momentum eigenvalue $k_0(\tau)$ in the underbarrier case; see Eqs. (42). (b) The analytic structure of the function $k_0(\tau)$ in complex $\tau$ plane near a first-order turning point $\tau_0$. The zigzag line shows the branch cut. Solid (dashed) lines are Stokes (anti-Stokes) lines defined by Eqs. (45a), (45b), (49), and (50). Dotted lines are defined by $\arg k_0(\tau) = 0$, $\pi/2$, $\pi$, and $-\pi/2$. The first of them passes through the point $\tau(k)$; the others follow in counterclockwise order around $\tau_0$.

$$\arg s(\tau_0, \tau) = \pi/2, \quad \tau \in l_2. \tag{49}$$

We introduce one more Stokes line $l_1$ and two anti-Stokes lines $\tilde{l}_1$ and $\tilde{l}_2$ defined by

$$\arg s(\tau_0, \tau) = \begin{cases} -3\pi/2, & \tau \in l_1, \\ -2\pi, & \tau \in \tilde{l}_1, \\ \pi, & \tau \in \tilde{l}_2. \end{cases} \tag{50}$$

Let us define three zones in the upper half plane [see Fig. 2(b)]: zone I (III) is bounded by the real axis and lines $l_1$ and $l_2$ ($l_2$ and $\tilde{l}_2$), excluding a segment belonging to zone II; zone II is a vicinity of $\tau_0$ of radius $|\delta\tau| = O(\epsilon^{1/3})$. For calculating the spectrum of ejected particles it is necessary to construct the asymptotic solution to the GBF equations (30a) and (30b) in all these zones. We consider them separately. The technique of the derivation differs from the more familiar case of adiabatic approximation for the discrete spectrum [14,19], because Eqs. (30a) are nonlocal in time, so we believe that it is appropriate to give some details here. We shall consistently use $\tau$ instead of $t$ as a time variable in order to keep track of the adiabatic parameter $\epsilon$ in all formulas.

### A. Asymptotic solution in zone I

The ASSs are regular functions of $\tau$ in zone I; hence,

$$\mathcal{P}_{nm}^{(p)}(\tau) = O(\epsilon^0), \quad p = 0,1,\ldots . \tag{51}$$

In this case, Eq. (34) is indeed an expansion in powers of $\epsilon$, so in adiabatic approximation the higher-order terms can be neglected. Substitution of Eq. (41) into Eq. (30a) gives

$$[\hat{\lambda}_t - ik_n(\tau)]a_n(t) = \epsilon \sum_m \frac{\mathcal{P}_{nm}^{(1)}(\tau)}{2k_n(\tau)} \hat{\lambda}_t^{-1} a_m(t) + O(\epsilon^2). \tag{52}$$

The solutions to these equations satisfying initial conditions (30b) are sought in the form

$$a_n(t) = \bar{a}_n(\tau)\exp[-i\epsilon^{-1}s(\tau_x,\tau)], \tag{53}$$

where $\bar{a}_n(\tau)$ are slowly varying amplitudes. Substituting this ansatz into Eq. (52) and using Eqs. (B6), we find (up to an inessential constant phase factor)

$$a_0(t) = \exp[-i\epsilon^{-1}s(\tau_x,\tau)][1 + O(\epsilon)], \tag{54a}$$

$$a_{n\neq 0}(t) = \frac{\epsilon \mathcal{P}_{nm}^{(1)}(\tau)\exp[-i\epsilon^{-1}s(\tau_x,\tau)]}{2k_n(\tau)k_0(\tau)[k_n(\tau) - k_0(\tau)]}[1 + O(\epsilon)]. \tag{54b}$$

Thus in zone I

$$a_{n\neq 0}(t) = O(\epsilon) \times a_0(t); \tag{55}$$

i.e., coefficients $a_{n\neq 0}(t)$ are of the order of the error term in $a_0(t)$. As follows from the derivation in Appendix B, the validity of Eqs. (54a) and (54b) requires

$$\epsilon^{-1}|E_0| \gg 1, \tag{56}$$

which is satisfied in the adiabatic limit $\epsilon \to 0$.

### B. Asymptotic solution in zone II

The radius of zone II, $|\delta\tau| = O(\epsilon^{1/3})$, tends to zero as $\epsilon \to 0$; therefore, the ASS eigenvalues and eigenfunctions in this zone can be substituted by their expansions near the turning point $\tau_0$. The behavior of the ASS with $n=0$ is given by Eqs. (43a) and (43b). Note that the normalization factor in $\phi_0(r;\tau)$ vanishes at $\tau = \tau_0$ as $\delta\tau^{1/2}$. All the other ASSs are regular functions of $\tau$, and their expansions near $\tau_0$ start with terms $\sim \delta\tau^0$.

Because of the vanishing of $k_0(\tau)$ and $\phi_0(r;\tau)$ at $\tau = \tau_0$, Eq. (34) is no longer a good representation for $\hat{\lambda}_{t,nm}$. Indeed, consider, e.g., the operator $\hat{\lambda}_{t,00}$. Let us introduce a new variable in zone II:

$$z = e^{i\pi}\epsilon^{-1/3}\alpha^{2/3}\delta\tau, \quad z = O(\epsilon^0). \tag{57}$$

This change of variables can be implemented in the operator $\hat{\lambda}_t$ using Eq. (A3):

$$\hat{\lambda}_t = e^{i\pi/2}(\epsilon\alpha)^{1/3}\hat{\lambda}_z. \tag{58}$$

Thus $\hat{\lambda}_t$ scales as $\epsilon^{1/3}$ in zone II. Using Eqs. (43a) and (43b), we obtain from Eq. (35)

$$\mathcal{P}_{00}^{(p)}(\tau) = \frac{2i\alpha\Gamma(3/2)\delta\tau^{1-p}}{\Gamma(3/2-p)} + O(\delta\tau^{2-p}), \quad p = 0,1,\ldots . \tag{59}$$

Substituting these equations into Eq. (34), one finds that all terms in the sum for $\hat{\lambda}_{t,00}$ are in fact of the same order $\epsilon^{1/3}$, so the approximation (41) cannot be used. Another expansion for $\hat{\lambda}_{t,nm}$ suitable in zone II can be obtained by substituting the aforementioned expansions for ASSs near $\tau_0$ into Eq. (31) and using Eq. (22).

As a preliminary step, let us clarify the relative order of magnitudes of the different terms in Eqs. (30a) as $\epsilon \to 0$. Using Eqs. (22), (31), (43a), and (43b), we obtain that the leading-order terms in the expansions for $\hat{\lambda}_{t,nm}$ in zone II scale as

$$\hat{\lambda}_{t,00} \sim \epsilon^{1/3}, \quad \hat{\lambda}_{t,0n} \sim \epsilon^{1/2}, \quad n \neq 0, \tag{60a}$$

$$\hat{\lambda}_{t,n0} \sim \epsilon^{5/6}, \quad \hat{\lambda}_{t,nm} \sim \epsilon^{1/3}, \quad n,m \neq 0. \tag{60b}$$

Assuming that (this is confirmed by the result below)

$$a_{n\neq 0}(t) = O(\epsilon^{5/6}) \times a_0(t), \tag{61}$$

Eqs. (30a) in zone II can be presented in the form

$$[\hat{\lambda}_{t,00} - i\alpha\delta\tau]a_0(t) = O(\epsilon^{2/3}) \times a_0(t), \tag{62a}$$

$$\hat{\lambda}_{t,n0}a_0(t) - ik_n(\tau_0)a_n(t) = O(\epsilon^{7/6}) \times a_0(t), \quad n \neq 0. \tag{62b}$$

Thus in the leading-order approximation the equation for $a_0(t)$ is decoupled from the other equations. We now need to specify the expansions (60a) and (60b) for the operators $\hat{\lambda}_{t,00}$ and $\hat{\lambda}_{t,n0}$:

$$\hat{\lambda}_{t,00} = e^{i\pi/2}(\epsilon\alpha)^{1/3}z^{-1/2}\hat{\lambda}_z z^{1/2} + O(\epsilon^{2/3}), \tag{63a}$$

$$\hat{\lambda}_{t,n0} = C_n\epsilon^{5/6}\hat{\lambda}_z^{-1}z^{1/2} + O(\epsilon^{7/6}), \quad n \neq 0, \tag{63b}$$

where the coefficient $C_n$ does not depend on $\epsilon$ [it can be expressed in terms of $k_n(\tau_0)$, $\phi_n(r;\tau_0)$, and $\chi(r)$, but its explicit form is not needed for the following]. The substitution of Eqs. (57) and (63a) into Eq. (62a) reduces this equation to Eq. (C1) discussed in Appendix C. The solution reads

$$a_0(t) = \mathcal{N}z^{-1/2}A(z)[1 + O(\epsilon^{1/3})], \tag{64}$$

where $\mathcal{N}$ is a constant. Zone II overlaps with zone I in the region $|z| \gg 1$. Matching the solutions (54a) and (64) in this region using Eqs. (48) and (C4c), we find $\mathcal{N} = \exp(-\epsilon^{-1}\Delta)$, where

$$\Delta = is(\tau_x,\tau_0) = i\int_{\tau_x}^{\tau_0} E_0(\tau)d\tau. \tag{65}$$

This parameter is real and positive; see Eq. (49). Substituting Eqs. (63b) and (64) into Eq. (62b), one can express $a_{n\neq 0}(t)$ in terms of $a_0(t)$. Summarizing, in zone II we obtain

$$a_0(t) = \exp(-\epsilon^{-1}\Delta) z^{-1/2} A(z)[1 + O(\epsilon^{1/3})], \tag{66a}$$

$$a_{n\neq 0}(t) = \frac{C_n \epsilon^{5/6}}{ik_n(\tau_0)} \exp(-\epsilon^{-1}\Delta) \hat{\lambda}_z^{-1} A(z)[1 + O(\epsilon^{1/3})], \tag{66b}$$

which confirm the assumption (61). Note that in this case the error term in $a_0(t)$ exceeds the value of $a_{n\neq 0}(t)$. As can be seen from the derivation, the validity of Eqs. (66a) and (66b) requires

$$\epsilon^{-1}\Delta \gg 1, \tag{67}$$

which ensures that the turning point $\tau_0$ can be treated as isolated—i.e., separately from its complex-conjugate counterpart $\tau_0^*$.

As follows from Eqs. (46), (47), and (57), the argument of $z$ is equal to $\pi/2$ and $7\pi/6$ on the Stokes lines $l_1$ and $l_2$, respectively; see Fig. 2(b). The large $|z|$ asymptotics of the function (66a) between these lines contains only one term $\sim\exp(iz^3)$ [see Eq. (C4c)], which turns into function (54a) in zone I. This term exponentially grows as $\tau$ moves away from the turning point $\tau_0$ along lines $l_1$ and $l_2$, so one could expect a Stokes phenomenon to occur on these lines. Indeed, an additional term $\sim 1/z^3$ appears in the large $|z|$ asymptotics of function (66a) above line $l_1$ [see Eq. (C4b)], and consequently a corresponding additional term should appear in Eq. (54a) when $\tau$ leaves zone I by crossing line $l_1$. This term is subdominant with respect to the exponential term in the sector between lines $l_1$ and $\tilde{l}_1$, and hence Eqs. (54a) and (54b) remain valid in this sector too.

### C. Asymptotic solution in zone III

The argumentation of Sec. IV A applies to zone III as well. However, before analytically continuing Eqs. (54a) and (54b) to zone III we have to consider the Stokes phenomenon on line $l_2$. It can be shown that an additional term appears in the asymptotics of $a_0(t)$ when $\tau$ crosses this line moving from zone I to zone III which is given by

$$\Delta a_0(t) = \frac{i\epsilon \exp(-\epsilon^{-1}\Delta)}{2\alpha k_0^2(\tau)(\tau - \tau_0)^{3/2}} \times \left[ \chi(a)\phi_0(a;\tau) - ik_0(\tau) \int_0^a \chi(r)\phi_0(r;\tau)dr \right]. \tag{68}$$

One can easily verify that on the boundary between zones II and III this function turns into the term $\sim 1/z^3$ in the large $|z|$ asymptotics of function (66a) [see Eq. (C4d)]. The function $\Delta a_0(t)$ must be added to Eq. (54a) in zone III, but this does not change the asymptotics of $a_0(t)$ since $\Delta a_0(t)$ is smaller than the error term in Eq. (54a). We note in passing that Eq. (68) gives an example of exponentially small terms mentioned at the end of Appendix B. Thus Eqs. (54a) and (54b) remain valid in zone III too. This in particular means that the probability to stay in the initial state, $P_0 \equiv |a_0(t\to\infty)|^2$, in the leading-order approximation is equal to unity. It can be shown that Eq. (68) gives the leading-order term in the asymptotics of $a_0(t)$ in the remaining part of the region shown in Fig. 2(b)—namely, above the anti-Stokes lines $\tilde{l}_1$ and $\tilde{l}_2$ and outside zone II. The character of the asymptotics here is changed: a rapidly varying exponential function (54a) is replaced by a slowly varying function (68). This completes the construction of the asymptotic solution to the GBF equations (30a) and (30b) in the underbarrier case.

### D. Spectrum of ejected particles

The spectrum of ejected particles is given by Eq. (11), where according to Eq. (29) one has to substitute

$$\psi(a,t) = \sum_n a_n(t)\phi_n(a;\tau). \tag{69}$$

The leading-order contribution comes from the term with $n=0$. Thus we need to calculate the integral

$$I(k) = \int_{-\infty}^{\infty} a_0(t)\phi_0(a;\tau)\exp(i\epsilon^{-1}E\tau)d\tau, \tag{70}$$

where $a_0(t)$ is given by Eq. (54a) in zones I and III and by Eq. (66a) in zone II. The integrand in Eq. (70) is a rapidly oscillating function of $\tau$ on the real axis. To evaluate this integral, we deform the integration path by shifting it into the upper half plane. The procedure and argumentation depend on the value of the momentum $k$. We divide the whole interval $0 \le k < \infty$ into two overlapping parts and consider them separately.

*Small momenta:* $0 \le k \le O(\epsilon^{1/3})$. In this case, the integral is accumulated in zone II. We deform the integration path to make it passing through the turning point $\tau_0$. Substituting Eqs. (43b) and (66a) into Eq. (70) and using Eq. (C5), we obtain

$$P(k) = \frac{4\pi \exp(-2\epsilon^{-1}\Delta)}{\epsilon|\alpha|} k^2 \exp\left[ -k^2 \frac{\mathrm{Im}\ \tau_0}{\epsilon} + k^3 \frac{2\sin(3\varphi/2)}{3\epsilon|\alpha|} \right]. \tag{71}$$

This spectrum has a maximum at $k = O(\epsilon^{1/2})$, which lies within the interval under consideration. Substituting Eq. (71) into Eq. (12), we find

$$P_c = \frac{\sqrt{\pi\epsilon}\exp(-2\epsilon^{-1}\Delta)}{2|\alpha|(\mathrm{Im}\ \tau_0)^{3/2}}. \tag{72}$$

The relative error of these results is $O(\epsilon^{1/3})$.

*Large momenta:* $O(\epsilon^{1/3}) \le k < \infty$. In this case, the integral can be evaluated using the steepest-descent method. Substituting Eq. (54a) into Eq. (70), it can be seen that the saddle points are defined by

$$E_0(\tau) = E. \tag{73}$$

Let us introduce a function $\tau(k)$ which is inverse to $k_0(\tau)$:

$$k = k_0(\tau) \to \tau = \tau(k). \tag{74}$$

As follows from Eq. (43a), $\tau(k)$ is a single-valued function in some vicinity of $k=0$. Equations (74) establish a map be

+tween complex $k$ and $\tau$ planes. The image of $k=0$ under this map is $\tau=\tau_0$. The images of the real and imaginary axes in the $k$ plane behave as shown by dotted lines in Fig. 2(b). For any real and positive $k$ from the interval under consideration, Eq. (73) has two solutions $\tau(k)$ and $\tau(-k)$; see Fig. 2(b). The first of them lies in zone I, while the second lies in the region where Eq. (54a) does not hold. Thus there is only one saddle point $\tau=\tau(k)$ in the integrand in (70). Calculating its contribution, we obtain

$$P(k)=\frac{2\pi k|\phi_0(a;\tau(k))|^2}{\epsilon|\dot{k}_0(\tau(k))|}\exp\left[\frac{2}{\epsilon}\mathrm{Im}\int_{\tau_x}^{\tau(k)}[E_0(\tau)-E]d\tau\right]. \tag{75}$$

The relative error of this result is $O(\epsilon)$. We note that the lower limit of integration, $\tau_x$, in the exponent can be replaced by any real value, e.g., Re $\tau(k)$.

The images of the intervals of "small" and "large" momenta under the map (74) fall in zones II and I, respectively. The function $a_0(t)$ has different asymptotics in these zones; that is why the two intervals of $k$ require separate treatments. However, it can be easily verified using Eqs. (43a) and (43b) that Eq. (75) reduces to Eq. (71) for $0\le k\le O(\epsilon^{1/3})$. This fact is by far not evident *a priori*; one could expect that the spectra (71) and (75) coincide at $k=O(\epsilon^{1/3})$, since zones I and II overlap at $\delta\tau=O(\epsilon^{1/3})$, but their coincidence at $k=O(\varepsilon^{1/2})$, where the maximum of $P(k)$ is located, must have a more subtle explanation. Anyway, we come to the conclusion that Eq. (75) gives the leading-order adiabatic approximation for the spectrum of ejected particles in the underbarrier case uniformly for all values of $k$.

Now, when this result is obtained and we know that it could be simply derived by substituting Eq. (54a) into Eq. (70) and calculating the integral using the steepest-descent method [in doing so, one still has to find a good reason to discard the second solution $\tau(-k)$ of Eq. (73)], one may ask, what is all the analysis of this section needed for? The answer is, to avoid mutually compensating errors of such a simple "derivation."

## V. OVERBARRIER TRANSITIONS

The initial state can be temporarily promoted to the continuum if the maximum amplitude of the external field exceeds some critical value. We consider the situation when the function $k_0(\tau)$ has two real zeros $\tau_1<\tau_2$ satisfying $\tau_2-\tau_1=O(\epsilon^0)$ and [see Fig. 3(a)]

$$\mathrm{Re}\ k_0(\tau)=0,\quad -\infty<\tau<\infty, \tag{76a}$$

$$\mathrm{Im}\ k_0(\tau)>0,\quad \tau<\tau_1\quad\text{or}\quad \tau_2<\tau, \tag{76b}$$

$$\mathrm{Im}\ k_0(\tau)<0,\quad \tau_1<\tau<\tau_2. \tag{76c}$$

In this case, the ASS representing the initial state becomes antibound and hence unstable during the interval $\tau_1<\tau<\tau_2$. A transition to the continuum can occur via its decay without absorbing an additional energy, which will be termed the overbarrier transition.

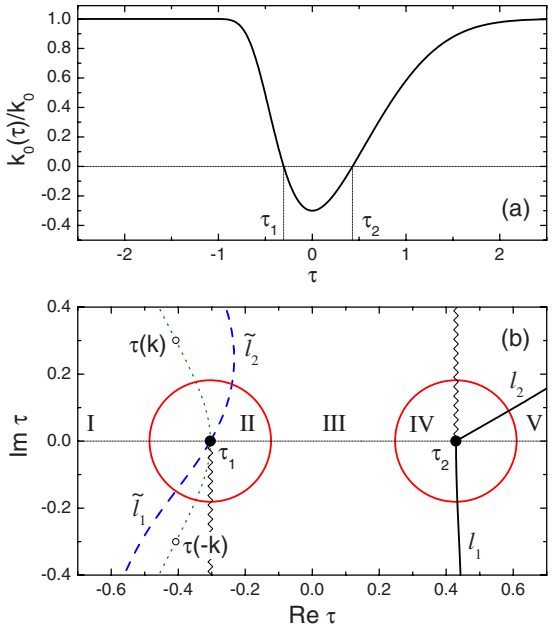


FIG. 3. (Color online) (a) The behavior of the adiabatic momentum eigenvalue $k_0(\tau)$ in the overbarrier case; see Eqs. (76a)–(76c). (b) The analytic structure of the function $k_0(\tau)$ in complex $\tau$ plane near two real first-order turning points $\tau_1$ and $\tau_2$. Zigzag lines show branch cuts. Solid (dashed) lines are Stokes (anti-Stokes) lines defined by Eqs. (79) and (80). Dotted lines passing through points $\tau(k)$ and $\tau(-k)$ are defined by arg $k_0(\tau)=0$ and $\pi$, respectively.

Let us introduce some notation and definitions similar to the underbarrier case. For small $\delta\tau_i=\tau-\tau_i$, $i=1,2$, similarly to Eqs. (43a) and (43b) we have

$$k_0(\tau)=\alpha_i\delta\tau_i+O(\delta\tau_i^2),\quad \alpha_i=\dot{k}_0(\tau_i), \tag{77a}$$

$$\phi_0(r;\tau)=\delta\tau_i^{1/2}\chi_i(r)+O(\delta\tau_i^{3/2}),\quad \chi_i^2(a)=-2i\alpha_i, \tag{77b}$$

where $\alpha_i=O(\epsilon^0)$ and the functions $\chi_i(r)$ do not depend on $\tau$. The turning points $\tau_1$ and $\tau_2$ lie on the real axis, so one should specify a way to circumvent them via the complex plane. We postulate on physical grounds the following general rule: the image of the branch cut from a real turning point under the map $k=k_0(\tau)$ should lie in the left half of the complex $k$ plane. Then the branch cuts from $\tau_1$ and $\tau_2$ should go as shown in Fig. 3(b). All phases are fixed by the conventions

$$\arg\alpha_1=-\pi/2,\quad \arg\delta\tau_1=0\quad\text{for positive}\quad\delta\tau_1, \tag{78a}$$

$$\arg\alpha_2=-3\pi/2,\quad \arg\delta\tau_2=2\pi\quad\text{for positive}\quad\delta\tau_2. \tag{78b}$$

We introduce two anti-Stokes lines emanating from $\tau_1$ and defined by

$$\arg s(\tau_1,\tau)=\begin{cases}3\pi, & \tau\in\tilde{l}_1,\\ 0, & \tau\in\tilde{l}_2,\end{cases} \tag{79}$$

and two Stokes lines emanating from $\tau_2$ and defined by

$$\arg s(\tau_2,\tau)=\begin{cases}3\pi/2, & \tau\in l_1,\\ 7\pi/2, & \tau\in l_2.\end{cases} \tag{80}$$

Recall the definition (44). Finally, we define five zones in the complex $\tau$ plane [see Fig. 3(b)]: zone I (V) lies to the left (right) of lines $\tilde{l}_1$ and $\tilde{l}_2$ ($l_1$ and $l_2$), zone III lies in between zones I and V, and zone II (IV) is a vicinity of $\tau_1$ ($\tau_2$) of radius $|\delta\tau_i|=O(\epsilon^{1/3})$.

### A. Asymptotic solution of the generalized Born-Fock equations

The technique of constructing the asymptotic solution to the GBF equations is similar to the underbarrier case, so we omit details of the derivation and present only final results. The equation for $a_0(t)$ is again decoupled from the other equations in the leading-order approximation, so we shall not consider $a_{n\neq 0}(t)$ and the error term in $a_0(t)$. Similarly to Eq. (54a), in zone I we have

$$a_0(t)=\exp[-i\epsilon^{-1}s(\tau_1,\tau)]. \tag{81}$$

In zone II we obtain

$$a_0(t)=z_1^{-1/2}A(z_1),\quad z_1=e^{i\pi/3}\epsilon^{-1/3}\alpha_1^{2/3}\delta\tau_1, \tag{82}$$

which is similar to Eq. (66a), except for the exponential factor. The solution in zone III can be obtained similarly to Eq. (68):

$$a_0(t)=\frac{-i\epsilon}{2\alpha_1 k_0^2(\tau)(\tau-\tau_1)^{3/2}}\times\left[\chi_1(a)\phi_0(a;\tau)-ik_0(\tau)\int_0^a\chi_1(r)\phi_0(r;\tau)dr\right]. \tag{83}$$

In zone IV, the equation for $a_0(t)$ reduces to Eq. (C6) discussed in Appendix C. The solution reads

$$a_0(t)=\frac{\epsilon^{1/2}\chi_1(a)\chi_2(a)}{2\alpha_1\alpha_2(\tau_2-\tau_1)^{3/2}}z_2^{-1/2}B(z_2),\quad z_2=e^{-i\pi/3}\epsilon^{-1/3}\alpha_2^{2/3}\delta\tau_2. \tag{84}$$

Finally, the solution in zone V is given by

$$a_0(t)=\frac{e^{-3i\pi/4}(2\pi\epsilon)^{1/2}\chi_1(a)\chi_2(a)}{2\alpha_1\alpha_2(\tau_2-\tau_1)^{3/2}}\exp[-i\epsilon^{-1}s(\tau_2,\tau)]. \tag{85}$$

Thus the probability to stay in the initial state is

$$P_0=\frac{2\pi\epsilon}{|\alpha_1\alpha_2|(\tau_2-\tau_1)^3}. \tag{86}$$

Using Eqs. (77a), (77b), (C4), and (C8) it can be verified that all these solutions coincide with each other in regions where the corresponding zones overlap. The validity of Eqs. (81) and (85) requires (56). The second condition (67) in the overbarrier case can be presented in the form

$$P_0\ll 1. \tag{87}$$

This ensures that the two turning points $\tau_1$ and $\tau_2$ can be treated as isolated.

### B. Spectrum of ejected particles

The momentum distribution of ejected particles can be obtained from Eqs. (11) and (69). One needs to evaluate the integral (70), where the function $a_0(t)$ is defined by the above equations. Zones IV and V do not contribute in the leading order, since $a_0(t)$ contains there an additional small factor $\epsilon^{1/2}$, which reveals the time asymmetry of the process. This means that the interference of wave packets created around moments $\tau_1$ and $\tau_2$ is not observable in the adiabatic regime because of low contrast. We again consider "small" and "large" momenta separately.

*Small momenta:* $0\le k\le O(\epsilon^{1/3})$. In this case, the integral (70) is accumulated in zone II. Using Eq. (82), we obtain

$$P(k)=\frac{4\pi}{\epsilon|\alpha_1|}k^2\exp\left[-\frac{2k^3}{3\epsilon|\alpha_1|}\right]. \tag{88}$$

This spectrum has a maximum at $k=O(\epsilon^{1/3})$, which lies within the interval under consideration. Substituting Eq. (88) into Eq. (12), we find in the leading order $P_c=1$. The relative error of these results is $O(\epsilon^{1/3})$.

*Large momenta:* $O(\epsilon^{1/3})\le k<\infty$. In this case, the integral (70) is accumulated in zone I, where $a_0(t)$ is given by Eq. (81). It can be evaluated using the steepest-descent method. Similarly to the underbarrier case, there is only one saddle point $\tau=\tau(k)$ in the integrand for real and positive $k$, where function $\tau(k)$ is defined by Eqs. (74). The second solution $\tau=\tau(-k)$ to Eq. (73) lies in zone II, where Eq. (81) does not hold; see Fig. 3(b). Calculating its contribution, we obtain

$$P(k)=\frac{2\pi k|\phi_0(a;\tau(k))|^2}{\epsilon|\dot{k}_0(\tau(k))|}\exp\left[\frac{2}{\epsilon}\mathrm{Im}\int_{\tau_1}^{\tau(k)}[E_0(\tau)-E]d\tau\right]. \tag{89}$$

The relative error of this result is $O(\epsilon^1)$. Using Eqs. (77a) and (77b), one can verify that Eq. (89) coincides with Eq. (88) for $0\le k\le O(\epsilon^{1/3})$. Thus we again conclude that Eq. (89) gives the leading-order adiabatic approximation for the spectrum of ejected particles in the overbarrier case uniformly for all values of $k$. Taking into account that the lower limit of integration $\tau_1$ in Eq. (89) can be replaced by any real value, we arrive at a much stronger conclusion: Eqs. (75) and (89) coincide; i.e., in the leading-order approximation the spectra of ejected particles in the underbarrier and overbarrier cases are given by the same asymptotic formula. This formula is another main result of the work.

## VI. COMPARISON WITH PREVIOUS APPROACHES AND DISCUSSION

The adiabatic approximation for the present problem in the underbarrier case was first considered by Chaplik [26].

His approach was based on the expansion of the solution in terms of the bound and scattering eigenstates of the momentary Hamiltonian $H(\tau)$, which leads to the BF equations. In this representation, to obtain the spectrum of ejected particles one has to take into account not only nonadiabatic couplings between the initial discrete state and the continuum, but also between states of the continuum. We recall that in the present approach the initial ASS is decoupled from the other states in the leading-order approximation, which is an important technical advantage. The result of [26] in the present notation reads

$$P(k) = \frac{|g|^2 2^{1/2}\pi \exp(-2\epsilon^{-1}\Delta)}{\epsilon|\alpha|} k^2 \exp\left[-k^2 \frac{\mathrm{Im}\ \tau_0}{\epsilon}\right], \tag{90}$$

where $|g|^2$ is a universal numerical factor which does not depend on the potential $V(r,\tau)$. It was shown [26] that $|g|^2$ is a limiting value of a function of two variables for which a prohibitively involved integro-differential equation was obtained, but the solution was not found. The analysis of [26] was then extended to nonzero angular momenta and potentials with a Coulomb tail [27]. Later, following an earlier paper by Demkov [28], Devdariani [29] considered the underbarrier case in the ZRP model. He succeeded in obtaining a closed-form asymptotic formula for the spectrum. Comparing it with Eq. (90) and taking into account the universal character of the factor $|g|^2$, he found

$$|g|^2 = 2^{3/2}. \tag{91}$$

It can be seen that Eqs. (90) and (91) coincide with Eq. (71) in the interval $0 \le k \le O(\epsilon^{1/2})$. This is the interval where function $P(k)$ reaches its maximum and the integral in Eq. (12) is accumulated; therefore, Eqs. (90) and (91) agree also with Eq. (72). We now can summarize a relation between the results of [26,29] and the present results. Equations (90) and (91) give the leading-order adiabatic approximation for the spectrum of ejected particles in the interval $0 \le k \le O(\epsilon^{1/2})$. The fact that the analysis of [26] applies only to this restricted interval was recognized there. Equation (71) gives the same spectrum in a wider interval $0 \le k \le O(\epsilon^{1/3})$. Finally, Eq. (75) applies to the whole interval $0 \le k < \infty$, thus giving a complete solution to the problem.

The above discussion strictly follows the asymptotic approach, which implies that $\epsilon \to 0$. However, in applications the adiabatic parameter $\epsilon$ always has a finite value. Then the accuracy of Eq. (71), and hence of Eqs. (90) and (91), may be limited by the accuracy of replacing $k_0(\tau)$ and $\phi_0(r;\tau)$ by the first terms in expansions (43a) and (43b). On the other hand, Eq. (75) does not rely upon this approximation; its validity requires only conditions (56) and (67). As we shall see, in addition to being more general analytically Eq. (75) is always more accurate numerically. This situation resembles a relation between the famous Landau-Zener formula [13,16], which gives the probability of a nonadiabatic transition between discrete states under the approximation of linear potentials and constant coupling in a diabatic representation, and a more general formula obtained by Dykhne [14].

The present problem in the overbarrier case was first considered in the ZRP model by Demkov [28]. His results in our notation coincide with Eqs. (86) and (88), where one has to substitute $\alpha_1 = \alpha_2$, in accordance with the implication of [28]. Later, Demkov and co-worker extended the approach of [28] to more general situations (see [30], and references therein), which culminated in a complete analysis of the ZRP model uniformly from the underbarrier to overbarrier case [29]. These developments where motivated by applications to the process of electron detachment in collisions of negative ions with neutral atoms [35,36]. A number of studies have shown that the ZRP model qualitatively explains the main physical mechanisms governing this process and fairly well reproduces the experimental results; see the review in [37]. Interestingly, for some reasons the ZRP model leads to the probability to stay in the initial state (86) and the spectrum of ejected particles (88) in the interval $0 \le k \le O(\epsilon^{1/3})$ *coinciding* with the present results obtained for a general potential. Thus the range of applicability of the ZRP model turns out to be effectively wider than one could expect, which probably explains its success. Regarding a relation between Eqs. (88) and (89), the arguments of the preceding paragraph fully apply to the overbarrier case too.

The approaches to the theory of nonadiabatic transitions to the continuum based on the BF or GBF equations start with expanding the solution to the TDSE in terms of some complete basis. This step in itself is exact; an approximation is introduced in solving the resulting coupled time-dependent equations. An alternative approach was proposed and developed by Solov'ev [31]. In this approach, the solution is sought in the form of an expansion (see the second unnumbered equation in [31]) which cannot be justified *a priori*. This expansion is rather a smart guess inspired by the Demkov-Osherov model [33], which is acknowledged by the author [31]. Assuming this form of the solution, Solov'ev derived a formula for the spectrum which seems to apply to the most general situation. In application to the present problem, this formula reduces to Eqs. (75) and (89). The formulation of [31] raises many questions which, I admit, are caused not by its internal inconsistency, but by the too lapidary style of the presentation. That is probably why this fundamental work is not as widely known as it deserves. The fact that the present quite different derivation agrees with the results of [31] adds confidence to both approaches. Whether other mechanisms of nonadiabatic transitions identified in the present work are accounted for by the approach of [31] remains an open question.

## VII. ILLUSTRATIVE EXAMPLES

### A. Model

To illustrate our results, we consider the dissociation of a model diatomic molecule by an electric field pulse. We are interested in situations when the characteristic time of the pulse is comparable to or exceeds the period of internuclear vibrations, which is when our adiabatic approximation is expected to work. In this case, one can safely ignore the electronic degrees of freedom by adiabatically separating them out. We adopt a frequently used model [38–41] in which the

molecule is represented by a rotationless Morse oscillator with the potential

$$V(r) = D[e^{-2\eta(R-R_0)} - 2e^{-\eta(R-R_0)}], \tag{92}$$

and its interaction with the electric field $F(\tau)$ is described by

$$U(r,\tau) = \mu(r)F(\tau), \tag{93}$$

where $\mu(r)$ is the molecular dipole moment. Here $R=r/\sqrt{m}$ is the internuclear distance, $m$ is the reduced mass, and $r$ is the mass-scaled coordinate which is introduced to bring the problem to the form implied by Eqs. (1) and (2). For the dissociation into two neutral atoms the dipole moment $\mu(r)$ rapidly decays as $r$ grows, so the total potential $V(r,\tau)$ can be safely cut off at a sufficiently large distance to satisfy the key assumption (4) of our formulation. We use parameters of the Morse potential corresponding to the ground electronic state of HF [40]: $D=0.2101$, $\eta=1.22$, and $R_0=1.75$. The reduced mass for HF is $m=1732$. The function $\mu(r)$ for this molecule is modeled by [40]

$$\mu(r) = qRe^{-\xi R^4}, \tag{94}$$

with $q=0.4541$ and $\xi=0.0064$; all parameters are in atomic units. The potential (92) supports 22 bound states. In the presence of excited states there exist indirect paths leading to the continuum via excitation which competes with the direct mechanism discussed above. In order to simplify the comparison of the present asymptotic theory with the numerical results, we decrease the reduced mass used in the calculations to $m=3$, leaving all the other parameters unchanged. Then there remains only one bound state in the unperturbed system with $E_0 \approx -0.043\,816$, which is taken to be the initial state. Also for the sake of simplicity we consider structureless Gaussian pulses with

$$F(\tau) = F_0 e^{-\tau^2}, \quad \tau = t/T. \tag{95}$$

Comparing this with Eq. (3), the asymptotic parameter is specified as $\epsilon = 1/T$. We emphasize that the above simplifications are essential neither for our numerical scheme nor for the asymptotic analysis; their only purpose is to focus the presentation on its main subject.

We are going to compare accurate numerical calculations for this model with the adiabatic approximation and discuss the dependence of the results on the duration $T$ and amplitude $F_0$ of the pulse. Condition (56) now reads $T|E_0| \gg 1$, which means $T \gg 23$. The critical value of the amplitude for which the initial ASS eigenvalue $k_0(\tau)$ satisfies $k_0(0)=0$, and hence has a second-order zero at the maximum of the pulse and which thus sets up the boundary between underbarrier and overbarrier cases, is $F_c \approx 0.091$. These numbers define scales in the variation of $T$ and $F_0$ of interest here. The numerical results were obtained by solving the problem in the diabatic representation [3]. The calculations were done with the cutoff radius $a=15$ and only 15 radial basis functions, which results in 30 Siegert pseudostates; see [3,6]. The time step used to solve the coupled equations is 0.1. These parameters ensure that the results reported below are converged to much better than on the scale of the figures, so for brevity we shall refer to them as "exact." The distribution of the DSS momentum eigenvalues $k_n$ for this model is shown in Fig. 1.

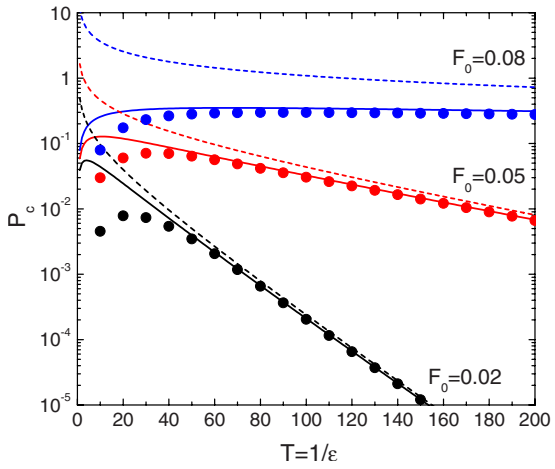


FIG. 4. (Color online) The total probability of transitions to the continuum in the underbarrier case. Solid circles: exact numerical results. Solid lines: present adiabatic approximation; see Eqs. (12) and (75). Dashed lines: adiabatic approximation developed by Chaplik [26] with the coefficient found by Devdariani [29]; see Eq. (72).

### B. Underbarrier case

In the underbarrier case, we consider three values of the field amplitude $F_0=0.02$, 0.05, and 0.08, all below the critical value $F_c$. We note that even the smallest of them is well beyond the perturbative regime. The ASS eigenvalues $k_n(\tau)$ for $F_0=0.05$ at the maximum of the pulse are shown by squares in Fig. 1.

The probability of dissociation $P_c$ as a function of $T$ is shown in Fig. 4. One can see that the present adiabatic approximation rapidly converges to the exact numerical results as $T$ grows beyond the maximum of the curve $P_c(T)$. This agrees with condition (56), since on the physical grounds maximum dissociation is expected to occur when $T|E_0| \approx 1$—i.e., for $T \approx 23$—which is confirmed by the calculations. One can also notice that the convergence is slowing down as $F_0$ approaches the critical value $F_c$. This is explained by the second condition (67) required for the validity of the present adiabatic approximation. Indeed, for the aforementioned values of $F_0$ we have $\Delta \approx 2.7\times10^{-2}$, $6.7\times10^{-3}$, and $3.0\times10^{-4}$, respectively, so condition (67) is satisfied for larger $T$ as $F_0$ becomes closer to $F_c$. Finally, one can observe that in all cases the present adiabatic approximation converges to the exact results much faster than the approximation based on formulas of Chaplik, Eq. (90), and Devdariani, Eq. (91) [see Eq. (72)], and the gain in accuracy becomes more essential as $F_0$ approaches $F_c$.

The convergence of the spectra of ejected particles as $T$ grows for the same three values of $F_0$ is illustrated in Fig. 5. Even for $T=20$, which is only the onset of the adiabatic regime, the present adiabatic approximation is in qualitative agreement with the exact numerical results. For $T=80$, which corresponds to $T|E_0| \approx 3.5$, the agreement becomes quantita-

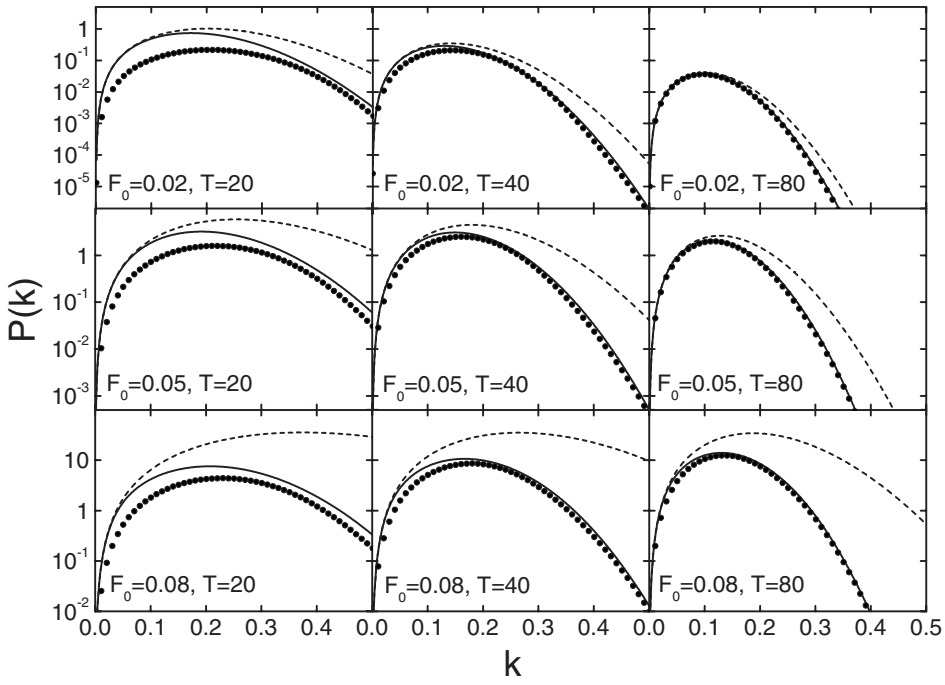


FIG. 5. Momentum distributions of ejected particles in the underbarrier case. Solid circles: exact numerical results. Solid lines: present adiabatic approximation, Eq. (75). Dashed lines: adiabatic approximation developed by Chaplik [26] with the coefficient found by Devdariani [29]; see Eqs. (90) and (91).

tive even for the least favorable case $F_0=0.08$. Note that the results obtained from Eq. (75) converge to the exact results uniformly in $k$. The spectra obtained from Eqs. (90) and (91) also converge as $T$ grows, but much slower and only in a limited interval $0\leq k\leq O(\epsilon^{1/2})$. [In fact, because of the evenness of the pulse (95), the angle $\varphi$ defined by Eq. (46) is equal to zero, so in the present case Eqs. (90) and (91) converge in a wider interval $0\leq k\leq O(\epsilon^{1/3})$ where Eq. (71) applies.] The numerical advantage of Eq. (75) over Eqs. (90) and (91) is evident from Figs. 4 and 5.

### C. Overbarrier case

Let us consider three values of the field amplitude $F_0=0.10$, 0.13, and 0.20 above the critical value $F_c$, which corresponds to the overbarrier case. The ASS eigenvalues $k_n(\tau)$ for $F_0=0.20$ at the maximum of the pulse are shown by diamonds in Fig. 1. Note that for such a strong field there exists a pair of incoming-outgoing eigenvalues that lie closer to the real axis, which indicates the appearance of a field-induced resonance state.

The probability to stay in the initial state $P_0$ as a function of $T$ is shown in Fig. 6. Similar results for the total probability of dissociation $P_c$ are shown in Fig. 7. Even though in the present case $P_0+P_c=1$, since there are no excited states, and the exact results do satisfy this relation to a very good accuracy, the asymptotic formulas (86) and (89) preserve the unitarity only in the leading order in $\epsilon$, so the results for $P_0$ and $P_c$ should be compared separately. Again, one can see that the present adiabatic approximation converges to the exact numerical results as $T$ grows beyond the onset of the adiabatic regime $T\approx 23$. For $F_0=0.10$, which is close to the critical value $F_c$, the convergence is slower since condition (87) is satisfied for larger $T$. One can notice slight modulations in the exact results for $F_0=0.13$, which become much more pronounced for $F_0=0.20$. This is probably explained by an interference between the direct mechanism and the dissociation via excitation to the intermediate field-induced resonance state mentioned above.

The convergence of the spectra of ejected particles for the same three values of $T$ as in Fig. 5 is illustrated in Fig. 8. The conclusion is similar to the underbarrier case: a good quan-

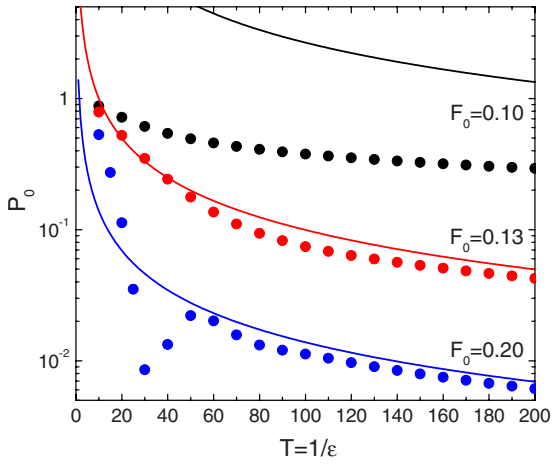


FIG. 6. (Color online) The probability to stay in the initial state in the overbarrier case. Solid circles: exact numerical results. Solid lines: present adiabatic approximation [see Eq. (86)], which coincides with the result obtained by Demkov for the ZRP model [28].

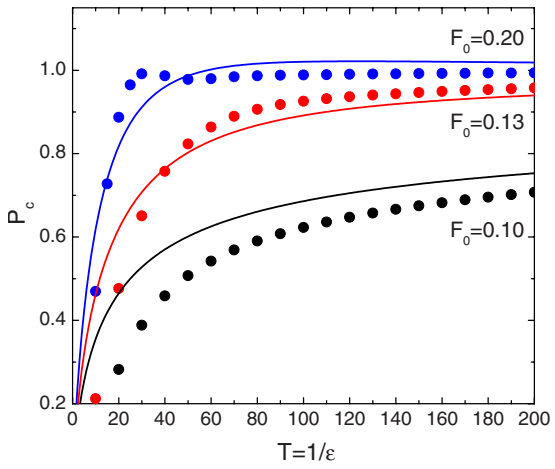


FIG. 7. (Color online) The total probability of transitions to the continuum in the overbarrier case. Solid circles: exact numerical results. Solid lines: present adiabatic approximation; see Eqs. (12) and (89).

titative agreement between the asymptotic and exact results uniformly in $k$ is already achieved for $T=80$, even in the least favorable case $F_0=0.10$. An effect of the field-induced resonance state on the spectrum can be clearly seen for $F_0=0.20$ and $T=20$, but it fades away and disappears as $T$ grows. The approximation (88), which coincides with the result for the ZRP model [28], converges much slower and only in a limited interval $0 \leq k \leq O(\epsilon^{1/3})$.

## VIII. CONCLUSIONS

The Siegert-state expansion approach initiated in [3] opens new perspectives for theoretical studies of transitions to the continuum in nonstationary quantum systems. In [3,11,12], the computational advantages of the approach in a diabatic representation were emphasized. In the present paper, we introduced the adiabatic representation which opens the way to an analytical treatment of the problem in the adiabatic approximation. One of the main results of this work is the derivation of the generalized Born-Fock equations (30a) describing the time evolution of the coefficients in the expansion of the solution to the TDSE (1) in terms of the adiabatic Siegert states. In contrast to the original Born-Fock equations, these equations enable one to treat discrete and continuous spectra on an equal footing. Some general techniques to work with the driving pseudo-differential operator in these equations are discussed. By constructing the asymptotic solutions to these equations for $\epsilon \to 0$, where $\epsilon$ is the adiabatic parameter characterizing the ratio of slow to fast time scales in the system, we developed the adiabatic approximation for transitions that occur via turning points, where the initial-state adiabatic momentum eigenvalue turns zero. The asymptotic formulas (75) and (89) for the spectra of ejected particles in underbarrier (when the initial state remains bound during all the evolution) and overbarrier (when the initial state is temporarily promoted to the continuum) cases are obtained. It turns out that in the leading-order approximation both cases are described by the same formula which is another main result of this work. This formula generalizes the well-known results of Stueckelberg

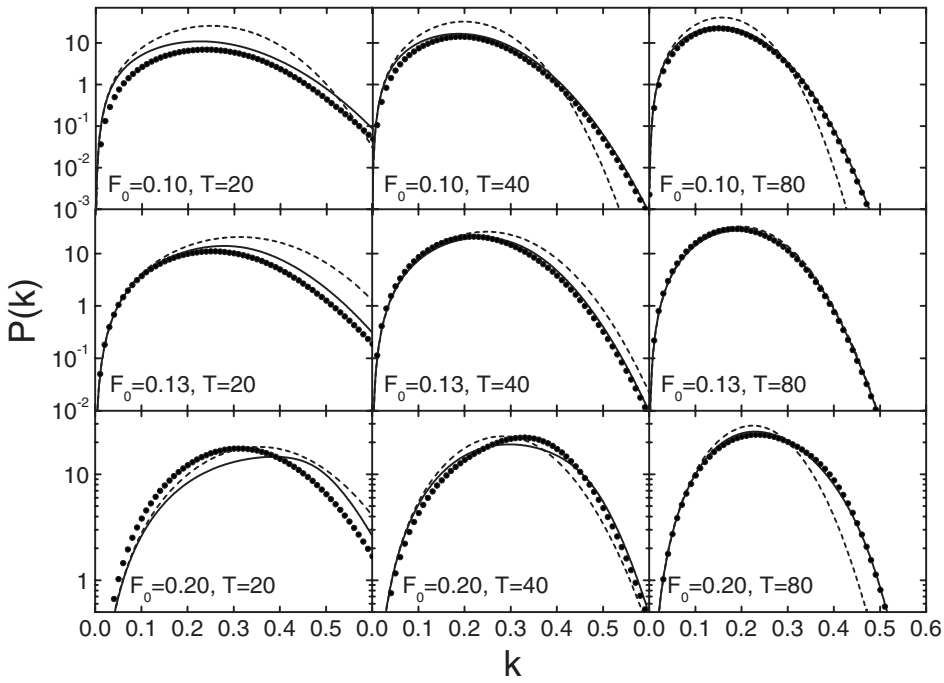


FIG. 8. Momentum distributions of ejected particles in the overbarrier case. Solid circles: exact numerical results. Solid lines: present adiabatic approximation; see Eq. (89). Dashed lines: Eq. (88), which coincides with the spectrum obtained by Demkov for the ZRP model [28].

[15] and Dykhne [14] for transitions between discrete states to transitions to the continuum. It is uniform in the momentum $k$ of ejected particles and thus gives a complete asymptotic solution to the problem. In the interval $0 \le k \le O(\epsilon^{1/2})$ in the underbarrier case, it reduces to the formula derived by Chaplik [26] with the coefficient found by Devdariani [29]; in the interval $0 \le k \le O(\epsilon^{1/3})$ in the overbarrier case, it coincides with the formula obtained by Demkov for the zero-range potential model [28]. This formula coincides with what follows for the present problem from a general formula obtained by Solov'ev [31], which confirms this important result by a quite different and independent method. The results are illustrated by calculations for a model describing the dissociation of a diatomic molecule by an electric field pulse. Good agreement between exact numerical calculations and the asymptotic formula in the adiabatic regime is demonstrated.

The next goal in the development of the Siegert-state expansion approach is to extend it to the three-dimensional case. A recent generalization of the theory of Siegert pseudostates to nonzero angular momenta [10] makes the extension possible. This will be a subject of the fourth paper of the series.

## ACKNOWLEDGMENTS

I thank E. A. Solov'ev for useful discussions on the results of [31] and the theory of nonadiabatic transitions in general. A financial support from the Russian Science Support Foundation is gratefully acknowledged.

## APPENDIX A: LEIBNIZ'S FORMULA FOR THE OPERATOR $\hat{\lambda}_t$

Similarly to Eq. (16), one can define powers of the operator $\hat{\lambda}_t$:

$$\hat{\lambda}_t^n f(t) = \int_{-\infty}^{\infty} (ik)^n f(E) e^{-iEt} \frac{dE}{2\pi}. \tag{A1}$$

In particular, in the time domain one explicitly obtains [3]

$$\hat{\lambda}_t^{-1} f(t) = \frac{e^{-3i\pi/4}}{\sqrt{2\pi}} \int_{-\infty}^{t} \frac{f(t')}{(t-t')^{1/2}} dt' \tag{A2}$$

and

$$\hat{\lambda}_t f(t) = \frac{2e^{3i\pi/4}}{\sqrt{2\pi}} \frac{d}{dt} \int_{-\infty}^{t} \frac{f(t')}{(t-t')^{1/2}} dt'. \tag{A3}$$

Consider the action of $\hat{\lambda}_t$ on a product of two functions. From the definition (16) we have

$$\hat{\lambda}_t[f(t)g(t)] = \int_{-\infty}^{\infty} ikf(E-E')g(E') e^{-iEt} \frac{dEdE'}{(2\pi)^2}. \tag{A4}$$

Substituting here

$$k = k'\left(1 + \frac{E-E'}{E'}\right)^{1/2} = k' \sum_{p=0}^{\infty} \frac{\Gamma(3/2)}{p!\,\Gamma(3/2-p)} \left(\frac{E-E'}{E'}\right)^p, \tag{A5}$$

where $k'$ and $E'$, as well as $k$ and $E$, are related by Eqs. (17), we obtain Leibniz's formula for the operator $\hat{\lambda}_t$:

$$\hat{\lambda}_t[f(t)g(t)] = \sum_{p=0}^{\infty} \frac{(-2i)^p \Gamma(3/2)}{p!\,\Gamma(3/2-p)} \frac{d^p f(t)}{dt^p} \hat{\lambda}_t^{1-2p} g(t). \tag{A6}$$

Taking into account a relation between $\hat{\lambda}_t$ and the Riemann-Liouville fractional derivative of order 1/2 [42],

$$\hat{\lambda}_t = \sqrt{2} e^{3i\pi/4}\, {}_{-\infty}D_t^{1/2}, \tag{A7}$$

one can see that Eq. (A6) agrees with Leibniz's formula for ${}_{-\infty}D_t^{1/2}$ [43].

## APPENDIX B: ACTION OF THE OPERATORS $\hat{\lambda}_t^{-1}$ AND $\hat{\lambda}_t$ ON THE ADIABATIC ANSATZ

From Eqs. (A2) and (A3) for Im $E \ge 0$ we obtain [recall Eqs. (17)]

$$\hat{\lambda}_t^{-1} e^{-iEt} = \frac{e^{-iEt}}{ik}, \tag{B1a}$$

$$\hat{\lambda}_t e^{-iEt} = ike^{-iEt}. \tag{B1b}$$

Consider the action of these operators on the adiabatic ansatz

$$F(t) = f(\tau) \exp\left[-i\epsilon^{-1} \int_{\tau_x}^{\tau} E(\tau') d\tau'\right], \tag{B2}$$

where $f(\tau)$ is a smooth slowly varying amplitude function, $E(\tau) = k(\tau)^2/2$ is an adiabatic energy eigenvalue, and $\tau_x$ is an arbitrary fixed "slow" time moment [recall Eq. (3)]. The problem reduces to evaluation of the integral

$$\int_{-\infty}^{\tau} f(\tau') \exp\left[-i\epsilon^{-1} \int_{\tau_x}^{\tau'} E(\tau'') d\tau''\right] \frac{d\tau'}{(\tau-\tau')^{1/2}} = 2\int_0^{\infty} f(\tau - z^2) \exp\left[-i\epsilon^{-1} \int_{\tau_x}^{\tau-z^2} E(\tau'') d\tau''\right] dz, \tag{B3}$$

where $z = (\tau - \tau')^{1/2}$. The asymptotics of the last integral for $\epsilon \to 0$ can be obtained using the steepest-descent method. The saddle points are determined by

$$zE(\tau - z^2) = 0. \tag{B4}$$

This equation is satisfied at $z=0$ and at the turning points, where $E(\tau - z^2) = 0$. Let us assume that

$$\text{Im}\, E(\tau') \ge 0, \quad E(\tau') \ne 0, \quad -\infty < \tau' \le \tau. \tag{B5}$$

The first of these conditions is needed for convergence of the integral (B3); the second means that there are no turning points for real $\tau'$ in the specified interval. Calculating the

contribution from $z=0$ to the integral and substituting the result into Eqs. (A2) and (A3), we obtain (for brevity, we omit the "slow" time argument $\tau$ on the right-hand side)

$$\hat{\lambda}_t^{-1}F(t) = \frac{F(t)}{ik}\left[1 - \frac{i\epsilon}{k^2}\left(\frac{\dot{f}}{f} - \frac{3\dot{k}}{2k}\right) - \frac{\epsilon^2}{2k^4}\left(\frac{3\ddot{f}}{f} - \frac{5\ddot{k}}{k} - \frac{5\dot{k}^2}{k^2}\right) + O(\epsilon^3)\right], \tag{B6a}$$

$$\hat{\lambda}_t F(t) = ikF(t)\left[1 + \frac{i\epsilon}{k^2}\left(\frac{\dot{f}}{f} - \frac{\dot{k}}{2k}\right) + \frac{\epsilon^2}{2k^4}\left(\frac{\ddot{f}}{f} - \frac{18\dot{k}\dot{f}}{kf} - \frac{\ddot{k}}{k} + \frac{29\dot{k}^2}{k^2}\right) + O(\epsilon^3)\right]. \tag{B6b}$$

Comparing these formulas with Eqs. (B1), we see that in the leading order in $\epsilon$ the operators $\hat{\lambda}_t^{-1}$ and $\hat{\lambda}_t$ act on the adiabatic ansatz (B2) as on a simple exponential function. Complex zeros of $E(\tau)$ as well as complex singular points of $f(\tau)$, if any, lead to the appearance of exponentially small terms in the asymptotics of (B3) which do not change formulas (B6).

## APPENDIX C: COMPARISON EQUATIONS FOR A FIRST-ORDER TURNING POINT

Consider the equation

$$(\hat{\lambda}_z - z)A(z) = 0. \tag{C1}$$

Up to some inessential change of notation, this equation coincides with the key equation in Demkov's treatment of the ZRP model [28]. It can be solved by Laplace's contour integral method. Its solutions can be expressed in terms of the Airy function, but for finding their asymptotics it is more convenient to work directly with contour integrals. The solution satisfying $A(z\to+\infty)\to 0$ is given by

$$A(z) = \frac{e^{i\pi/4}}{\sqrt{2\pi}}\int_{\mathcal{C}} \exp\left(-\frac{q^3}{3} - \frac{iq^2z}{2}\right) q\, dq, \tag{C2}$$

where the contour $\mathcal{C}$ is defined by

$$\mathcal{C} = (e^{2i\pi/3}\times\infty, 0] + [0, \infty). \tag{C3}$$

As can be seen from Eq. (C2), $A(z)$ is an entire function of $z$. Its asymptotics for large $|z|$ can be found using the steepest-descent method. There are two saddle points $q=0$ and $q=-iz$. Depending on the argument of $z$, the steepest-descent contour obtained by a deformation of contour (C3) passes through either both or only one of them. The asymptotics in the whole complex plane for $|z|\to\infty$ is given by

$$A(z) = z^{-5/2}, \quad 0 \le \arg z < \pi/6, \tag{C4a}$$

$$A(z) = z^{-5/2} + z^{1/2}e^{iz^3/6}, \quad \pi/6 < \arg z < \pi/2, \tag{C4b}$$

$$A(z) = z^{1/2}e^{iz^3/6}, \quad \pi/2 < \arg z < 7\pi/6, \tag{C4c}$$

$$A(z) = -z^{-5/2} + z^{1/2}e^{iz^3/6}, \quad 7\pi/6 < \arg z < 3\pi/2, \tag{C4d}$$

$$A(z) = -z^{-5/2}, \quad 3\pi/2 < \arg z \le 2\pi, \tag{C4e}$$

where the terms $z^{-5/2}$ and $z^{1/2}e^{iz^3/6}$ represent contributions from the two saddle points. One can notice that a Stokes phenomenon occurs on the boundaries of the sectors; the contribution experiencing a jump there must be multiplied by 1/2. The function $A(z)$ defines the asymptotic solution to the GBF equations (30a) near turning points where an initially bound state is promoted to the continuum. The Fourier transform of $A(z)$ for arg $E=0$ is [recall Eqs. (17)]

$$A(E) = \int_{-\infty}^{\infty} A(z)e^{iEz}dz = e^{i\pi/4}\sqrt{2\pi}\exp(-k^3/3). \tag{C5}$$

This function can be analytically continued to any complex $E$.

We also need to consider a related inhomogeneous equation

$$(\hat{\lambda}_z - z)B(z) = 1. \tag{C6}$$

The solution reads

$$B(z) = -i\int_0^{\infty} \exp\left(-\frac{q^3}{3} - \frac{iq^2z}{2}\right) q\, dq. \tag{C7}$$

Its asymptotics for $|z|\to\infty$ is given by

$$B(z) = -z^{-1}, \quad 0 \le \arg z < \pi/6, \tag{C8a}$$

$$B(z) = -z^{-1} - (2\pi z)^{1/2}e^{iz^3/6 + i\pi/4}, \quad \pi/6 < \arg z < 5\pi/6, \tag{C8b}$$

$$B(z) = -z^{-1}, \quad 5\pi/6 < \arg z \le 2\pi. \tag{C8c}$$

The function $B(z)$ defines the asymptotic solution to Eqs. (30a) near turning points where a state is captured from the continuum and becomes a bound state.


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