Demkov-Osherov model reformulated in terms of conventional scattering theory

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One of the few exactly solvable time-dependent quantum-mechanics problems was first analyzed by Demkov and Osherov 30 years ago (Zh. Éksp. Teor. Fiz. **53**, 1589 (1967) [Sov. Phys. JETP **26**, 916 (1968)]). This model problem describes the interaction of a set of approximate stationary states with an additional state whose energy, in zeroth approximation, is a linear function of time. The Demkov-Osherov model is reexamined here using conventional Fourier transform methods. Emphasis on forward propagation in time eliminates the need for a Laplace transform of the wave function, as well as the resultant choice of contours for the evaluation of transition amplitudes. The evolution operator for the model Hamiltonian is expressed in terms of a single, frequency-dependent Sturmian. Such Sturmian functions are of considerable current interest in the analysis of nonadiabatic phenomena. [S1050-2947(98)07707-5]

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I. INTRODUCTION

Many physical processes in atomic collision physics can be analyzed treating the heavy nuclei classically and solving a nonstationary Schrödinger equation for the electrons. However, the difficulties inherent in obtaining analytical solutions to such problems has led to widespread use of approximation methods based on a few idealized models that are known to have exact solutions. Principal among these are the Landau-Zener model [1] and the Demkov-Osherov model [2,3].

If the Hamiltonian depends only weakly on time, inelastic processes occur at times when two (or more) instantaneous energy eigenvalues are nearly degenerate. The Landau-Zener model describes transitions among a pair of adiabatic states whose instantaneous energies vary linearly with time, except near their point of intersection where they avoid one another and do not cross. The model yields accurate transition probabilities if the energy splitting at the quasi-intersection is small compared to the energy splittings to other levels (that is, provided the two interacting states are energetically isolated.) When a physical system has many such isolated intersections, the Landau-Zener formula can sometimes be applied to each intersection separately, with inelastic processes described by multiplying the probabilities for passing either adiabatically or diabatically through each quasi-intersection.

Remarkably, the Landau-Zener formula is sometimes useful even when avoided crossings are not isolated [4]. Demkov and Osherov introduced a model for transitions between a number of approximate stationary states and another state of a different kind whose energy, in zeroth approximation, is a linear function of time. The scattering matrix for this multilevel problem resolves precisely into products of separate Landau-Zener factors, independent of the strength of the interaction between any pair of quasi-intersecting levels. The Demkov-Osherov solution has successfully modeled a number of ion-atom and atom-atom collision processes.

The original solution of this model problem employs Laplace transforms with integration contours chosen according to the initial conditions [2]. In that approach, the system is chosen to be in an initial eigenstate. Because applications often require arbitrary initial states, especially when the continuum is involved, a solution that avoids separate contours for each initial eigenstate is desirable. Standard scattering theory employing the time evolution operator is one way to achieve this objective.

In this paper, the Demkov-Osherov model is reformulated in terms of conventional scattering theory. Emphasis on forward propagation in time replaces the Laplace transform in the original formulation by a simpler Fourier transform. The need for a transition-specific choice of contours is thereby eliminated. An exact integral expression for the forward-evolution operator results from this analysis; its evaluation using the method of stationary phase in the limit of infinite elapsed time yields explicit expressions for the magnitudes and phases of the resultant scattering amplitudes. The integral expression for the forward evolution operator and the phases of the scattering amplitudes have not been given previously.

In addition to its utility as a model, the analysis of Demkov and Osherov may have far-reaching implications for the study of nonstationary quantum-mechanics problems in general. Recent advances in ion-atom collision theory make use of the Fourier transform methods described herein [5]. Difficult questions of boundary conditions in the frequency domain are simply answered in the context of the model. Furthermore, the model naturally replaces adiabatic states in the time domain by a Sturmian in the frequency domain. In fact, the forward-evolution operator is most simply expressed in terms of a single frequency-dependent Sturmian. Such Sturmian states are now widely used in time-dependent quantum-mechanics problems [5,6], and the analysis presented below provides the simplest intuitive illustration of their utility.

II. THE MODEL HAMILTONIAN

The Hamiltonian studied by Demkov and Osherov describes the interaction of a set of approximate stationary states, $|i\rangle$, with an additional state, $|0\rangle$, whose energy, in zeroth approximation, is a linear function of time. The interaction among these states is assumed to be constant. The Hermitian Hamiltonian is accordingly parametrized by the matrix elements

$$\langle 0|H(t)|0\rangle=\beta t, \quad \langle 0|H(t)|i\rangle=h_i,$$
$$\langle i|H(t)|0\rangle=h_i^*, \quad \langle i|H(t)|j\rangle=\epsilon_i\delta_{i,j}. \tag{1}$$

Assuming that the states are complete and orthonormal,

$$|0\rangle\langle 0|+\sum_i |i\rangle\langle i|=1, \quad \langle 0|0\rangle=1, \quad \langle 0|i\rangle=0,$$
$$\langle i|j\rangle=\delta_{i,j}, \tag{2}$$

this Hamiltonian is expressed in terms of a projection operator V as

$$H(t)=H_0+\beta tV, \quad H_0=H(0), \quad V\equiv|0\rangle\langle 0|, \tag{3}$$

where $\beta>0$ is assumed for simplicity. Atomic units are used throughout this work.

Schrödinger's equation for the Demkov-Osherov model is then

$$\left(i\frac{\partial}{\partial t}-H_0\right)|\Psi(t)\rangle=\beta tV|\Psi(t)\rangle. \tag{4}$$

We transform Eq. (4) to the frequency domain by focusing on the forward propagation in time of an initial solution $|\Psi(t_0)\rangle$. To this end, we left multiply Eq. (4) by the step function

$$\theta(t-t_0)=\begin{cases}0, & t<t_0\\ 1, & t\geqslant t_0\end{cases} \tag{5}$$

and make use of the commutator

$$\left[\theta(t-t_0),\frac{\partial}{\partial t}\right]=-\delta(t-t_0) \tag{6}$$

to find

$$\left(i\frac{\partial}{\partial t}-H_0\right)|\Psi(t)\rangle\theta(t-t_0)-i|\Psi(t)\rangle\delta(t-t_0)$$
$$=\beta tV|\Psi(t)\rangle\theta(t-t_0). \tag{7}$$

Upon defining the Fourier transform function $\Psi(\omega)$

$$|\Psi(t)\rangle\theta(t-t_0)=\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t}|\Psi(\omega)\rangle, \tag{8}$$

Eq. (7) becomes

$$\int_{-\infty}^{\infty}d\omega\, e^{-i\omega t}(\omega-H_0)|\Psi(\omega)\rangle-i|\Psi(t)\rangle\delta(t-t_0)$$
$$=\beta tV|\Psi(t)\rangle\theta(t-t_0). \tag{9}$$

The inverse Fourier transform of this equation is

$$2\pi(\omega-H_0)|\Psi(\omega)\rangle-ie^{i\omega t_0}|\Psi(t_0)\rangle$$
$$=\beta V\int_{-\infty}^{\infty}dt\, e^{i\omega t}t|\Psi(t)\rangle\theta(t-t_0). \tag{10}$$

We rewrite the right-hand side of this expression as

$$\beta V\int_{-\infty}^{\infty}dt\, e^{i\omega t}t|\Psi(t)\rangle\theta(t-t_0)=-2\pi i\beta V\frac{\partial}{\partial\omega}|\Psi(\omega)\rangle \tag{11}$$

and find, after rearranging terms, the differential form

$$i\beta V\frac{\partial}{\partial\omega}|\Psi(\omega)\rangle+(\omega-H_0)|\Psi(\omega)\rangle=\frac{i}{2\pi}e^{i\omega t_0}|\Psi(t_0)\rangle. \tag{12}$$

Equation (12) is the appropriate Fourier transform of Eq. (4) and is the principal result of this section. The initial condition, $|\Psi(t_0)\rangle$, appears explicitly as an inhomogeneity in the frequency domain. The inhomogeneous term was not included in Demkov and Osherov's original solution, since they focused on the transform of the full wave function $|\Psi(t)\rangle$ without regard to forward (or backward) propagation in time.

A solution of the homogeneous equation

$$i\beta V\frac{\partial}{\partial\omega}|\Psi_h(\omega)\rangle+(\omega-H_0)|\Psi_h(\omega)\rangle=0 \tag{13}$$

may always be added to any particular solution of Eq. (12). However, the integral in Eq. (8) must be zero for $t<t_0$, and this requires that $|\Psi(\omega)\rangle$ have the form

$$|\Psi(\omega)\rangle=e^{i\omega t_0}|\tilde{\Psi}(\omega)\rangle, \tag{14}$$

where $|\tilde{\Psi}(\omega)\rangle$ is an analytic function in the upper half of the complex ω plane. [Specifically, $|\tilde{\Psi}(\omega)\rangle$ must have no poles or branch points in the upper half plane and must vanish in the upper half plane as $|\omega|\to\infty$.] We will show below that this requirement of analyticity determines a boundary condition in the frequency domain that, in turn, determines the contribution of the homogeneous term to $|\Psi(\omega)\rangle$.

Our solution of Eq. (12) is presented in Sec. IV, below. The solution is most readily expressed in terms of a Sturmian, as defined in the next section.

III. THE STURMIAN

Following standard practice, we define a Sturmian, $|S(\omega)\rangle$, as the solution of

$$(\omega-H_0)|S(\omega)\rangle=\tau(\omega)\beta V|S(\omega)\rangle, \tag{15}$$

where $\tau(\omega)$ is the Sturmian eigenvalue.

Note that if τ is fixed at the value $\tau=t$ and ω is treated as the eigenvalue, $\omega=E(t)$, then Eq. (15) is identical to the adiabatic approximation to Eq. (4). Accordingly, $\tau(\omega)$ is simply the inverse of the usual ''adiabatic'' eigenspectrum, $E_\mu(t)$. Similarly, the Sturmian, $|S(\omega)\rangle$, evaluated at $\omega=E_\mu(t)$ is equal (to within normalization) to the μth adiabatic state at time t.

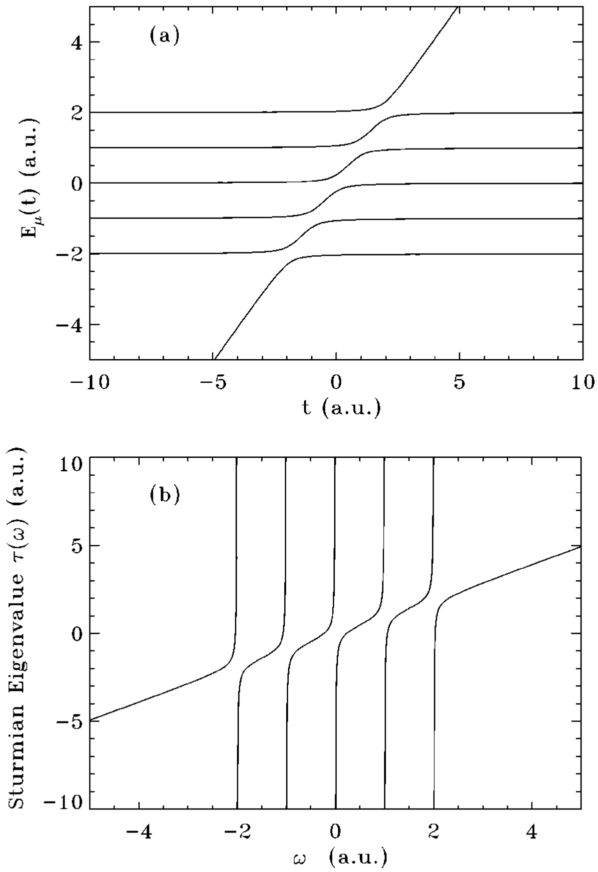

FIG. 1. (a) Adiabatic energies for a model Hamiltonian with $\beta=1$ and $h_i=1/4$, and (b) the corresponding Sturmian eigenvalue.

The Sturmian for the Demkov-Osherov model is readily constructed by projecting Eq. (15) onto $\langle 0|$ and $\langle i|$, and then using Eqs. (1) and (2):

$$\omega\langle 0|S(\omega)\rangle - \sum_i h_i\langle i|S(\omega)\rangle = \beta\tau(\omega)\langle 0|S(\omega)\rangle, \quad (16)$$

$$-h_i^*\langle 0|S(\omega)\rangle + (\omega-\epsilon_i)\langle i|S(\omega)\rangle = 0. \quad (17)$$

Solving Eq. (17) for $\langle i|S(\omega)\rangle$ and substituting the result into Eq. (16) yields the secular equation

$$\left[\omega - \sum_i \frac{|h_i|^2}{\omega-\epsilon_i} - \beta\tau(\omega)\right]\langle 0|S(\omega)\rangle = 0. \quad (18)$$

A nontrivial solution of Eq. (15) exists only when the eigenvalue satisfies

$$\tau(\omega) = \frac{1}{\beta}\left[\omega - \sum_i \frac{|h_i|^2}{\omega-\epsilon_i}\right]. \quad (19)$$

For the Demkov-Osherov model, the one Sturmian eigenvalue τ is a single-valued function of ω with simple poles on the real ω axis. This circumstance is illustrated in Fig. 1. Figure 1(a) shows the adiabatic eigenspectrum for a model consisting of five equally spaced ϵ_i levels, with $h_i=1/4$ and $\beta=1$. The corresponding $\tau(\omega)$, as given by Eq. (19), is shown in Fig. 1(b).

The Sturmian is now obtained, to within normalization, from Eq. (17) and the completeness relation Eq. (2):

$$|S(\omega)\rangle = \left[|0\rangle + \sum_i \frac{h_i^*}{\omega-\epsilon_i}|i\rangle\right]\langle 0|S(\omega)\rangle. \quad (20)$$

The normalization factor may be selected to eliminate the poles at $\omega=\epsilon_i$ [e.g., so that $\langle S(\omega)|S(\omega)\rangle=1$]. However, the normalization constant will play no role in our solution, so that it is simpler to choose

$$\langle 0|S(\omega)\rangle = 1. \quad (21)$$

The Sturmian and its eigenvalue have poles on the real ω axis, and careful treatment of these poles will be essential to the evaluation of the Fourier transform Eq. (8) and to the imposition of the analyticity requirement Eq. (14). For the sake of clarity, we introduce here two alternative Sturmians obtained by shifting all diagonal elements of $H(t)$ infinitesimally below

$$|S^-(\omega)\rangle = \left[|0\rangle + \sum_i \frac{h_i^*}{\omega-\epsilon_i+i\eta}|i\rangle\right] \quad (22)$$

and above the real axis

$$|S^+(\omega)\rangle = \left[|0\rangle + \sum_i \frac{h_i^*}{\omega-\epsilon_i-i\eta}|i\rangle\right] \quad (23)$$

with the understanding that the limit $\eta\to 0^+$ will eventually be taken. The corresponding Sturmian eigenvalues are

$$\tau_\pm(\omega) = \frac{1}{\beta}\left[\omega \mp i\eta - \sum_i \frac{|h_i|^2}{\omega-\epsilon_i\mp i\eta}\right]. \quad (24)$$

IV. SOLUTION IN THE FREQUENCY DOMAIN

We now return to Eq. (12) and project it onto $\langle 0|$ and $\langle i|$ to obtain

$$i\beta\frac{d}{d\omega}\langle 0|\Psi(\omega)\rangle + \langle 0|\omega-H_0|\Psi(\omega)\rangle = \frac{i}{2\pi}e^{i\omega t_0}\langle 0|\Psi(t_0)\rangle, \quad (25)$$

$$\langle i|\omega-H_0|\Psi(\omega)\rangle = \frac{i}{2\pi}e^{i\omega t_0}\langle i|\Psi(t_0)\rangle. \quad (26)$$

Shifting the diagonal elements of H_0 infinitesimally into the lower half plane, using the completeness relation Eq. (2) and the matrix elements Eq. (1), then gives

$$i\beta\frac{d}{d\omega}\langle 0|\Psi(\omega)\rangle+(\omega+i\eta)\langle 0|\Psi(\omega)\rangle-\sum_i h_i\langle i|\Psi(\omega)\rangle=\frac{i}{2\pi}e^{i\omega t_0}\langle 0|\Psi(t_0)\rangle, \tag{27}$$

$$-h_i^*\langle 0|\Psi(\omega)\rangle+(\omega-\epsilon_i+i\eta)\langle i|\Psi(\omega)\rangle=\frac{i}{2\pi}e^{i\omega t_0}\langle i|\Psi(t_0)\rangle. \tag{28}$$

The second of these may be solved directly for $\langle i|\Psi(\omega)\rangle$:

$$\langle i|\Psi(\omega)\rangle=\frac{1}{\omega-\epsilon_i+i\eta}\left[h_i^*\langle 0|\Psi(\omega)\rangle+\frac{i}{2\pi}e^{i\omega t_0}\langle i|\Psi(t_0)\rangle\right]. \tag{29}$$

Substituting this result into Eq. (27) and rearranging terms, we find

$$\left[i\beta\frac{d}{d\omega}+\omega+i\eta-\sum_i\frac{|h_i|^2}{\omega-\epsilon_i+i\eta}\right]\langle 0|\Psi(\omega)\rangle =\frac{ie^{i\omega t_0}}{2\pi}\left[\langle 0|\Psi(t_0)\rangle+\sum_i\frac{h_i\langle i|\Psi(t_0)\rangle}{\omega-\epsilon_i+i\eta}\right]. \tag{30}$$

This result is simply expressed in terms of the Sturmian and its eigenvalue using Eqs. (23) and (24)

$$\left[i\frac{d}{d\omega}+\tau_-(\omega)\right]\langle 0|\Psi(\omega)\rangle=\frac{i}{2\pi\beta}e^{i\omega t_0}\langle S^+(\omega)|\Psi(t_0)\rangle. \tag{31}$$

Equation (31) is readily integrated to give

$$\langle 0|\Psi(\omega)\rangle=\frac{e^{i\phi(\omega)}}{2\pi\beta}\left[C+\int_{-\infty}^{\omega}d\nu\; e^{-i\phi(\nu)+i\nu t_0}\langle S^+(\nu)|\Psi(t_0)\rangle\right], \tag{32}$$

where the constant C remains to be determined, and

$$\phi(\omega)\equiv\int^{\omega}d\omega'\,\tau_-(\omega') =\frac{1}{\beta}\left[\frac{\omega^2}{2}+i\eta\omega-\sum_i|h_i|^2\ln(\omega-\epsilon_i+i\eta)\right]. \tag{33}$$

Equations (29) and (32) provide a solution of Schrödinger's equation (12) in the frequency domain:

$$|\Psi(\omega)\rangle=|0\rangle\langle 0|\Psi(\omega)\rangle+\sum_i|i\rangle\langle i|\Psi(\omega)\rangle. \tag{34}$$

Upon substituting our results and rearranging terms, we find

$$|\Psi(\omega)\rangle=C\frac{e^{i\phi(\omega)}}{2\pi\beta}|S^-(\omega)\rangle+\frac{i}{2\pi}\sum_i|i\rangle\frac{e^{i\omega t_0}}{\omega-\epsilon_i+i\eta}\times\langle i|\Psi(t_0)\rangle+|S^-(\omega)\rangle\frac{e^{i\phi(\omega)}}{2\pi\beta}\times\int_{-\infty}^{\omega}d\nu\; e^{-i\phi(\nu)+i\nu t_0}\langle S^+(\nu)|\Psi(t_0)\rangle. \tag{35}$$

The first term on the right-hand side of this equation is a solution of the homogeneous Eq. (13). The remaining two terms are proportional to the driving term in Eq. (12), and so result from incorporating the step function in Eq. (8).

The difference between the present formulation and the original solution of Demkov and Osherov may now be clarified. By considering the transform of the full wave function, Demkov and Osherov's solution consists entirely of the homogeneous term in Eq. (35). Owing to the ω^2 contribution to the phase, Eq. (33), this homogeneous term diverges as $|\omega|\to\infty$ in the second and fourth quadrants of the complex ω plane. Accordingly, Demkov and Osherov terminated the contour in the first and third quadrants. Our focus on forward propagation instead yields the analyticity requirement, Eq. (14), so that the homogeneous term in $|\Psi(\omega)\rangle$ must be set to zero; i.e.,

$$C=0, \tag{36}$$

which is equivalent to the boundary condition

$$\lim_{\omega\to-\infty}|\Psi(\omega)\rangle=0. \tag{37}$$

The second term on the right-hand side of Eq. (35) clearly satisfies Eq. (14), since the poles have been shifted into the lower half of the complex ω plane. That the third term in Eq. (35) also satisfies Eq. (14), and so contributes to the Fourier transform only if $t>t_0$, is not obvious and so requires further comment here. Recall from Eq. (22) that $|S^-(\omega)\rangle$ is an analytic function of ω in the upper half plane; we therefore need to consider only the analytic properties of the factor

$$F(\omega)=e^{i\phi(\omega)-i\omega t_0}\int_{-\infty}^{\omega}d\nu\; e^{-i\phi(\nu)+i\nu t_0}\langle S^+(\nu)|\Psi(t_0)\rangle. \tag{38}$$

Upon differentiating this factor, recalling Eq. (24), and rearranging terms, one finds

$$\left[1-\frac{1}{\omega-\beta t_0+i\eta}\sum_i\frac{|h_i|^2}{\omega-\epsilon_i+i\eta}+\frac{i\beta}{\omega-\beta t_0+i\eta}\frac{d}{d\omega}\right]F(\omega)=i\beta\frac{\langle S^+(\omega)|\Psi(t_0)\rangle}{\omega-\beta t_0+i\eta}. \tag{39}$$

This is a first-order differential equation with coefficients that are analytic in the upper half plane. It follows that $F(\omega)$ is also analytic in the upper half plane, except possibly for the point at $|\omega|=\infty$. Equation (39) may furthermore be inverted to determine an asymptotic expansion of $F(\omega)$ near $|\omega|=\infty$:

$$\frac{F(\omega)}{i\beta}=\left[1-\frac{1}{\omega-\beta t_0+i\eta}\sum_i\frac{|h_i|^2}{\omega-\epsilon_i+i\eta}+\frac{i\beta}{\omega-\beta t_0+i\eta}\frac{d}{d\omega}\right]^{-1}\frac{\langle S^+(\omega)|\Psi(t_0)\rangle}{\omega-\beta t_0+i\eta}$$

$$=\left[1+\frac{1}{\omega-\beta t_0+i\eta}\sum_i\frac{|h_i|^2}{\omega-\epsilon_i+i\eta}-\frac{i\beta}{\omega-\beta t_0+i\eta}\frac{d}{d\omega}+\cdots\right]\frac{\langle S^+(\omega)|\Psi(t_0)\rangle}{\omega-\beta t_0+i\eta} \tag{40}$$

$$=\frac{\langle 0|\Psi(t_0)\rangle}{\omega}+O(\omega^{-2}). \tag{41}$$

$F(\omega)$ accordingly decreases as $1/\omega$ in the limit $|\omega|\to\infty$. This completes our proof that the final term in Eq. (35) satisfies the analyticity requirement of Eq. (14).

V. THE EVOLUTION OPERATOR

The two remaining terms in Eq. (35) derive from operations upon an arbitrary initial state $|\Psi(t_0)\rangle$. Combining Eqs. (35) and (36) with the Fourier transform in Eq. (8) yields an evolution operator for forward propagation, $U_F(t,t_0)$, defined by

$$|\Psi(t)\rangle\theta(t-t_0)=U_F(t,t_0)|\Psi(t_0)\rangle \tag{42}$$

with the explicit form

$$U_F(t,t_0)=U_F^0(t,t_0)+\frac{1}{2\pi\beta}\int_{-\infty}^{\infty}d\omega|S^-(\omega)\rangle e^{i\phi(\omega)-i\omega t}\times\left[\int_{-\infty}^{\omega}d\nu\, e^{-i\phi(\nu)+i\nu t_0}\langle S^+(\nu)|\right], \tag{43}$$

where

$$U_F^0(t,t_0)=\frac{i}{2\pi}\sum_i|i\rangle\int_{-\infty}^{\infty}d\omega\frac{e^{-i\omega(t-t_0)}}{\omega-\epsilon_i+i\eta}\langle i|. \tag{44}$$

The integral in Eq. (44) is readily evaluated, giving

$$U_F^0(t,t_0)=\theta(t-t_0)\sum_i|i\rangle e^{-i\epsilon_i(t-t_0)}\langle i|, \tag{45}$$

which represents free evolution of the states $|i\rangle$ in the absence of interaction with the state $|0\rangle$.

The nontrivial part of the time evolution is contained in the second term of Eq. (43). This exact form of the forward evolution operator for the Demkov-Osherov model has not been given previously and is the principal result of this paper.

VI. EVALUATION OF THE TRANSITION AMPLITUDES

The form of the evolution operator given above yields directly the time-dependent amplitudes

$$\langle 0|U_F(t,t_0)|0\rangle=\frac{1}{2\pi\beta}\int_{-\infty}^{\infty}d\omega\, e^{i\phi(\omega)-i\omega t}\times\int_{-\infty}^{\omega}d\nu\, e^{-i\phi(\nu)+i\nu t_0}, \tag{46}$$

$$\langle i|U_F(t,t_0)|0\rangle=\frac{h_i^*}{2\pi\beta}\int_{-\infty}^{\infty}d\omega\frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}\times\int_{-\infty}^{\omega}d\nu\, e^{-i\phi(\nu)+i\nu t_0}, \tag{47}$$

$$\langle 0|U_F(t,t_0)|i\rangle=\frac{h_i}{2\pi\beta}\int_{-\infty}^{\infty}d\omega\, e^{i\phi(\omega)-i\omega t}\times\int_{-\infty}^{\omega}d\nu\frac{e^{-i\phi(\nu)+i\nu t_0}}{\nu-\epsilon_i+i\eta}, \tag{48}$$

$$\langle i|U_F(t,t_0)|j\rangle=\theta(t-t_0)\delta_{i,j}e^{-i\epsilon_i(t-t_0)}+\frac{h_i^*h_j}{2\pi\beta}\times\int_{-\infty}^{\infty}d\omega\frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}\int_{-\infty}^{\omega}d\nu\frac{e^{-i\phi(\nu)+i\nu t_0}}{\nu-\epsilon_j+i\eta}. \tag{49}$$

The S-matrix elements are proportional to the above amplitudes in the limits $t\to\infty$ and $t_0\to-\infty$. However, the evolution operator Eq. (43) and the resultant transition amplitudes are given here in the Schrödinger picture [7], while the S matrix is generally written in the interaction picture. To preserve this convention, we extract the asymptotic phases from the transition amplitudes and define the S matrix for this model by

$$S_{ij}=\lim_{\substack{t\to\infty\\ t_0\to-\infty}}\exp\left[i\int^{t}E_i(t')dt'\right]\langle i|U(t,t_0)|j\rangle \times\exp\left[-i\int^{t_0}E_j(t')dt'\right], \tag{50}$$

where $E_i(t)$ is the *adiabatic* energy corresponding to the state i in the limit $t\to\infty$ (or $t_0\to-\infty$). The required phase factors are

$$\lim_{t_0\to-\infty}\int^{t_0}E_0(t')dt'=\frac{\beta}{2}t_0^2-\sum_i \frac{|h_i|^2}{\beta}\ln(-1/t_0), \tag{51}$$

$$\lim_{t_0\to-\infty}\int^{t_0}E_i(t')dt'=\epsilon_i t_0+\frac{|h_i|^2}{\beta}\ln(-1/t_0), \tag{52}$$

$$\lim_{t\to\infty}\int^{t}E_0(t')dt'=\frac{\beta}{2}t^2+\sum_i \frac{|h_i|^2}{\beta}\ln(t), \tag{53}$$

$$\lim_{t\to\infty}\int^{t}E_i(t')dt'=\epsilon_i t-\frac{|h_i|^2}{\beta}\ln(t). \tag{54}$$

We now turn to the evaluation of the U matrix in the limits $t_0\to-\infty$ and $t\to\infty$. Consider first the integral entering Eqs. (46) and (47)

$$I_0(\omega)\equiv\lim_{t_0\to-\infty}\int_{-\infty}^{\omega}d\nu\, e^{-i\phi(\nu)+i\nu t_0}. \tag{55}$$

The integrand of this expression oscillates rapidly for large values of $|t_0|$, so that the only nonvanishing contributions as $t_0\to-\infty$ result from values of ν for which the phase is stationary; i.e., for which

$$\frac{d\phi(\nu)}{d\nu}=\tau_-(\nu)=t_0. \tag{56}$$

The stationary phase points can be extracted directly from Eq. (24):

$$\nu_0=\beta t_0+\frac{1}{\beta t_0}\sum_i |h_i|^2+O(t_0^{-2}), \tag{57}$$

$$\nu_i=\epsilon_i-\frac{|h_i|^2}{\beta t_0}+O(t_0^{-2}). \tag{58}$$

Following Eckart [8], the integral $I_0(\omega)$ is then

$$I_0(\omega)=\sqrt{-2\pi i}\lim_{t_0\to-\infty}\left[\frac{\theta(\omega-\nu_0)e^{-i\phi(\nu_0)+i\nu_0 t_0}}{\sqrt{(d\tau_-/d\nu)_{\nu=\nu_0}}}+\sum_i \frac{\theta(\omega-\nu_i)e^{-i\phi(\nu_i)+i\nu_i t_0}}{\sqrt{(d\tau_-/d\nu)_{\nu=\nu_i}}}\right]. \tag{59}$$

Differentiation of Eq. (24) yields

$$\left.\frac{d\tau_-}{d\nu}\right|_{\nu=\nu_0}=\frac{1}{\beta}+O(t_0^{-1}), \tag{60}$$

$$\left.\frac{d\tau_-}{d\nu}\right|_{\nu=\nu_i}=\frac{\beta t_0^2}{|h_i|^2}+\frac{1}{\beta}\left[1+\sum_{j\neq i}\frac{|h_j|^2}{(\epsilon_i-\epsilon_j)^2}\right]+O(t_0^{-1}). \tag{61}$$

Accordingly, only the stationary phase point $\nu=\nu_0$ contributes to $I_0(\omega)$ as $t_0\to-\infty$, with the result

$$I_0(\omega)=\theta(\omega-\beta t_0)\sqrt{-2\pi i\beta}e^{i\beta t_0^2/2}\prod_i a_i(\epsilon_i-\beta t_0)^{i|h_i|^2/\beta}, \tag{62}$$

where a_i is the Landau-Zener amplitude for a $|0\rangle\to|0\rangle$ transition near the crossing with level i:

$$a_i=\sqrt{p_i}=e^{-\pi|h_i|^2/\beta}. \tag{63}$$

For the amplitudes in Eqs. (46) and (47), we then have

$$\lim_{t_0\to-\infty}\langle 0|U_F(t,t_0)|0\rangle=\frac{e^{i\beta t_0^2/2}}{\sqrt{2\pi i\beta}}\prod_j a_j(\epsilon_j-\beta t_0)^{i|h_j|^2/\beta}\times\int_{\beta t_0}^{\infty}d\omega e^{i\phi(\omega)-i\omega t}, \tag{64}$$

$$\lim_{t_0\to-\infty}\langle i|U_F(t,t_0)|0\rangle=\frac{h_i^* e^{i\beta t_0^2/2}}{\sqrt{2\pi i\beta}}\prod_j a_j(\epsilon_j-\beta t_0)^{i|h_j|^2/\beta}\times\int_{\beta t_0}^{\infty}d\omega\frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}. \tag{65}$$

We next turn to the integral contributing to Eqs. (48) and (49):

$$I_i(\omega)\equiv\lim_{t_0\to-\infty}\int_{-\infty}^{\omega}d\nu\frac{e^{-i\phi(\nu)+i\nu t_0}}{\nu-\epsilon_i+i\eta}. \tag{66}$$

Near the stationary phase point ν_0, given by Eq. (57), the integrand in this expression vanishes as $1/t_0$. The stationary phase points ν_j with $j\neq i$ also do not contribute in the limit, due to amplitude factors akin to Eq. (61). Accordingly, the only contribution to $I_i(\omega)$ comes from the vicinity of the pole at $\nu=\epsilon_i$. Defining $x=(\epsilon_i-\nu)t_0$, the integral can be written

$$I_i(\omega)\equiv\theta(\omega-\epsilon_i)\overline{I_i}, \tag{67}$$

$$\overline{I_i}=\lim_{t_0\to-\infty}e^{i\epsilon_i t_0}\int_{-\infty}^{-(\omega-\epsilon_i)t_0}dx\frac{e^{-i\phi(\epsilon_i-x/t_0)}e^{-ix}}{x-i\eta t_0}. \tag{68}$$

Note that as $t_0\to-\infty$, the only dependence of this integral on ω is contained in the step function. Expanding the phase $\phi(\epsilon_i-x/t_0)$ in Eq. (33) to lowest order in $1/t_0$ gives the limiting form

$$\overline{I_i}=e^{i\epsilon_i t_0}e^{-i\epsilon_i^2/2\beta}(-1/t_0)^{i|h_i|^2/\beta}\prod_{j\neq i}(\epsilon_i-\epsilon_j+i\eta)^{i|h_j|^2/\beta}\times\int_{-\infty}^{\infty}dx\, e^{-ix}(x-i\eta t_0)^{i|h_i|^2/\beta-1}. \tag{69}$$

The remaining integral along the real x axis is evaluated by extending the contour into the lower half of the complex x plane and distorting it along the negative imaginary axis to encircle the pole. The integral along the negative imaginary axis is proportional to Hankel's contour integral for the Gamma function [9]:

$$\int_{-\infty}^{\infty} dx\, e^{-ix}(x-i\eta t_0)^{i|h_i|^2/\beta-1}$$

$$=(i)^{i|h_i|^2/\beta}\int_c dz(-z)^{i|h_i|^2/\beta}\exp[-z]$$

$$=\frac{2\pi}{i}\frac{\sqrt{a_i}}{\Gamma(1-i|h_i|^2/\beta)}, \tag{70}$$

and yields

$$\overline{I_i}=\frac{2\pi}{i}e^{i\epsilon_i t_0}e^{-i\epsilon_i^2/2\beta}(-1/t_0)^{i|h_i|^2/\beta}$$

$$\times\frac{\sqrt{a_i}}{\Gamma(1-i|h_i|^2/\beta)}\prod_{j\neq i}(\epsilon_i-\epsilon_j+i\eta)^{i|h_j|^2/\beta}. \tag{71}$$

As $\eta\to 0^+$, each term in the product may be separated into its amplitude and phase:

$$(\epsilon_i-\epsilon_j+i\eta)^{i|h_j|^2/\beta}=e^{i|h_j|^2(\ln|\epsilon_i-\epsilon_j|)/\beta}$$

$$\times\begin{cases}1, & \epsilon_i>\epsilon_j\\ e^{-\pi|h_j|^2/\beta}, & \epsilon_i<\epsilon_j\,.\end{cases} \tag{72}$$

For the amplitudes in Eqs. (48) and (49) we then have

$$\lim_{t_0\to-\infty}\langle 0|U(t,t_0)|i\rangle=\frac{\overline{I_i}h_i}{2\pi\beta}\int_{\epsilon_i}^{\infty}d\omega\, e^{i\phi(\omega)-i\omega t}, \tag{73}$$

$$\lim_{t_0\to-\infty}\langle i|U(t,t_0)|j\rangle=\delta_{i,j}e^{-i\epsilon_i(t-t_0)}$$

$$+\frac{\overline{I_j}h_i^*h_j}{2\pi\beta}\int_{\epsilon_j}^{\infty}d\omega\frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}. \tag{74}$$

Equations (64), (65), (73), and (74) give expressions for the transition amplitudes in terms of one-dimensional integrals. The remaining integrals are readily evaluated in the limit $t\to\infty$ using the techniques described above. Evaluation of the integral entering Eqs. (64) and (73)

$$J_0(\omega_0)\equiv\lim_{t\to\infty}\int_{\omega_0}^{\infty}d\omega\, e^{i\phi(\omega)-i\omega t} \tag{75}$$

closely follows the argument used above for $I_0(\omega)$, and yields

$$J_0(\omega_0)=\sqrt{2\pi i\beta}e^{-i\beta t^2/2}\prod_i(\beta t-\epsilon_i)^{-i|h_i|^2/\beta}. \tag{76}$$

This result, combined with Eq. (64), gives the transition amplitude

$$\lim_{\substack{t\to\infty\\ t_0\to-\infty}}\langle 0|U(t,t_0)|0\rangle=e^{i\beta(t_0^2-t^2)/2}\prod_i e^{i|h_i|^2\ln(-t_0/t)/\beta}a_i\,. \tag{77}$$

The corresponding extreme-diabatic S-matrix element is then [recall Eq. (50)]

$$S_{00}=\prod_i a_i \tag{78}$$

with corresponding probability [recall Eq. (63)]

$$|S_{00}|^2=\prod_i p_i \tag{79}$$

as found earlier by Demkov and Osherov.

Combining Eqs. (50), (71), (73), and (76) we then have, for the $i\to 0$ transition

$$S_{0i}=\sqrt{\frac{2\pi}{i\beta}}\frac{h_i e^{i\gamma}\sqrt{a_i}}{\Gamma(1-i|h_i|^2/\beta)}\prod_k^{\epsilon_k>\epsilon_i}a_k\,, \tag{80}$$

where

$$\gamma\equiv-\epsilon_i^2/2\beta-\frac{(\ln\beta)}{\beta}\sum_j|h_j|^2+\sum_{k\neq i}\frac{|h_k|^2}{\beta}\ln|\epsilon_i-\epsilon_k|. \tag{81}$$

The transition probability is then [10]

$$|S_{0i}|^2=(1-p_i)\prod_k^{\epsilon_k>\epsilon_i}p_k\,, \tag{82}$$

which is the desired result.

The remaining integral entering Eqs. (65) and (74),

$$J_i(\omega_0)=\int_{\omega_0}^{\infty}d\omega\frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}, \tag{83}$$

is evaluated following the above argument for $I_i(\omega)$, giving

$$J_i(\omega_0)=\theta(\epsilon_i-\omega_0)\overline{J_i},$$

$$\overline{J_i}=\frac{2\pi}{i}e^{-i\epsilon_i t}e^{i\epsilon_i^2/2\beta}(1/t)^{-i|h_i|^2/\beta}$$

$$\times\frac{1}{\sqrt{a_i}\Gamma(1+i|h_i|^2/\beta)}\prod_{j\neq i}(\epsilon_i-\epsilon_j+i\eta)^{-i|h_j|^2/\beta}. \tag{84}$$

Combining this result with Eqs. (50) and (65) yields

$$S_{i0}=-i\sqrt{\frac{2\pi}{i\beta}}\frac{h_i^*e^{i\delta}}{\sqrt{a_i}\Gamma(1+i|h_i|^2/\beta)}\prod_k^{\epsilon_k\leqslant\epsilon_i}a_k\,, \tag{85}$$

where

$$\delta \equiv +\epsilon_i^2/2\beta - \frac{(\ln\beta)}{\beta}\sum_j |h_j|^2 - \sum_{k\neq i}\frac{|h_k|^2}{\beta}\ln|\epsilon_i-\epsilon_k|. \tag{86}$$

The probability for a transition from state $|0\rangle$ to state $|i\rangle$ is

$$|S_{i0}|^2 = (1-p_i)\prod_k^{\epsilon_k<\epsilon_i} p_k \tag{87}$$

as expected for a multicrossing model.

For inelastic transitions between the stationary states, $j \to i$ with $i\neq j$, Eqs. (50), (65), (83), and (84) yield

$$S_{ij} = -\frac{2\pi}{\beta}h_i^* h_j \theta(\epsilon_i-\epsilon_j) \times \frac{e^{i\Delta}\sqrt{a_j}}{\sqrt{a_i}\Gamma(1+i|h_i|^2/\beta)\Gamma(1-i|h_j|^2/\beta)}\prod_k^{\epsilon_i\geq\epsilon_k>\epsilon_j} a_k, \tag{88}$$

where

$$\Delta = +\frac{1}{2\beta}(\epsilon_i^2-\epsilon_j^2) + \sum_{k\neq j}\frac{|h_k|^2}{\beta}\ln|\epsilon_j-\epsilon_k| - \sum_{\ell\neq i}\frac{|h_\ell|^2}{\beta}\ln|\epsilon_i-\epsilon_\ell|. \tag{89}$$

The transition probability is then

$$|S_{ij}|^2 = \theta(\epsilon_i-\epsilon_j)(1-p_j)\left[\prod_k^{i>k>j} p_k\right](1-p_i). \tag{90}$$

Evaluation of the amplitude for elastic scattering in state $|i\rangle$ requires particular care, due to the coincidence of the poles in Eq. (49),

$$U_{ii}^\infty \equiv \lim_{\substack{t\to\infty\\ t_0\to-\infty}}\langle i|U(t,t_0)|i\rangle = e^{-i\epsilon_i(t-t_0)} + \frac{|h_i|^2}{2\pi\beta} \times \int_{-\infty}^{\infty} d\omega \frac{e^{i\phi(\omega)-i\omega t}}{\omega-\epsilon_i+i\eta}\int_{-\infty}^{\omega} d\nu \frac{e^{-i\phi(\nu)+i\nu t_0}}{\nu-\epsilon_i+i\eta}. \tag{91}$$

Setting $\omega=\epsilon_i+x/t$ and $\nu=\epsilon_i-y/t_0$ and evaluating the integrands for large t and $-t_0$ gives

$$U_{ii}^\infty = e^{-i\epsilon_i(t-t_0)}\left[1+\frac{|h_i|^2}{2\pi\beta}(-t/t_0)^{i|h_i|^2/\beta} \times \int_{-\infty}^{\infty} dx\, e^{-ix}(x)^{-i|h_i|^2/\beta-1} \times \int_{-\infty}^{-xt_0/t} dy\, e^{-iy}(y)^{i|h_i|^2/\beta-1}\right]. \tag{92}$$

Now setting $y=xz$ gives

$$U_{ii}^\infty = e^{-i\epsilon_i(t-t_0)}\left[1+\frac{|h_i|^2}{2\pi\beta}(-t/t_0)^{i|h_i|^2/\beta} \times \int_{-\infty}^{\infty} dx\frac{e^{-ix}}{x}\int_{-\infty}^{-t_0/t} dz\, e^{-ixz}(z)^{i|h_i|^2/\beta-1}\right]. \tag{93}$$

The integral over x is evaluated by simple contour integration

$$\int_{-\infty}^{\infty} dx\frac{e^{-ix(1+z)}}{x} = -2\pi i\,\theta(1+z), \tag{94}$$

leaving

$$U_{ii}^\infty = e^{-i\epsilon_i(t-t_0)}\left[1-i\frac{|h_i|^2}{\beta}(-t/t_0)^{i|h_i|^2/\beta} \times \int_{-1}^{-t_0/t} dz\,(z)^{i|h_i|^2/\beta-1}\right]. \tag{95}$$

The remaining integral over z is elementary, and the final result for the elastic scattering amplitude is

$$S_{ii} = a_i \tag{96}$$

with corresponding probability

$$|S_{ii}|^2 = p_i \tag{97}$$

as expected.

VII. DISCUSSION AND CONCLUSIONS

While the transition probabilities resulting from our analysis are all contained in Demkov and Osherov's original work, our exact expression for the evolution operator and the time-dependent transition amplitudes have not been given previously. The double integral representation for the evolution operator is evaluated in the limits of large times to obtain the exact S matrix for this model. More importantly, the analytical result indicates that the exact evolution operator is represented by a single frequency dependent Sturmian. Single Sturmian approximations have been used recently to describe ionization processes in ion-atom and electron-atom collisions. Our reexamination of the Demkov-Osherov model shows how a single Sturmian represents an entire chain of avoided crossings of adiabatic levels.

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[1] L. D. Landau, Phys. Z. Sowjetunion **1**, 88 (1932); C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[2] Y. N. Demkov and V. I. Osherov, Zh. Éksp. Teor. Fiz. **53**, 1589 (1967) [Sov. Phys. JETP **26**, 916 (1968)].
[3] See, also, Yu. N. Demkov and V. N. Ostrovskii, *Zero-Range Potentials and Their Applications in Atomic Physics* (Plenum, New York, 1988).
[4] See, for example, D. A. Harmin, Phys. Rev. A **56**, 232 (1997).
[5] J. H. Macek and S. Y. Ovchinnikov, Phys. Rev. A **50**, 468 (1994).
[6] R. Shakeshaft, J. Phys. B **18**, L611 (1985); Phys. Rev. A **34**, 244 (1986); **34**, 5119 (1986).
[7] See, for example, Eugen Merzbacher, *Quantum Mechanics*, 2nd ed. (Wiley, New York, 1970), p. 473, Eq. (18.86); Charles J. Joachain, *Quantum Collision Theory* (North-Holland, Amsterdam, 1975), Chap. 13.
[8] Carl Eckart, Rev. Mod. Phys. **20**, 399 (1948).
[9] *Handbook of Mathematical Physics*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), Eq. (6.1.4).
[10] See *Handbook of Mathematical Physics* (Ref. [9]), Eq. (6.1.31).