Exact analytical solution of the quantum Rosen-Zener-Demkov model

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(Received 7 January 1993)

An exact analytical solution in terms of the Meijer functions is obtained from the quantum Rosen-Zener-Demkov model for nonadiabatic transitions. The N matrix for the nonadiabatic transitions, the S matrices, and the probabilities for elastic and inelastic atomic collision channels are found.

PACS number(s): 03.65.Nk, 34.10.+x, 34.50.−s

I. INTRODUCTION

The Demkov model [1], as well as the model by Rosen and Zener [2] to which it closely related, is well known in the theory of atomic and molecular collisions. It applies to a wide class of problems ranging from charge transfer in atomic collisions to vibrational transitions in molecular scattering. Unlike the avoided-crossing model by Landau, Zener, and Stueckelberg [3], in the Demkov model the zero-order terms are independent of the nuclear separation while the interaction between them is described by an exponential coupling.

Previous studies of the Demkov model have utilized semiclassical and quasiclassical methods [1,2,4–6]. Here we present an exact quantum-mechanical solution to the model with exponential coupling. This makes the model an ideal reference problem for many applications in collision theory and enables one to quantitatively identify the ranges of validity of various approximate solutions.

II. FORMULATION OF THE PROBLEM

The radial quantum equations describing the nonadiabatic transitions in atomic collisions are of the form

$$\begin{aligned}&\left[-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+V_{11}(R)-E\right]\psi_1(R)+V_{12}(R)\psi_2(R)=0\ ,\\&\left[-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}+V_{22}(R)-E\right]\psi_2(R)+V_{21}(R)\psi_1(R)=0\ ,\end{aligned}\tag{2.1}$$

where $V_{11}(R), V_{22}(R)$ are the so-called diabatic terms, $V_{12}(R)$ is a coupling between diabatic states, R is the internuclear separation, m is the reduced mass, and E is the collision energy. Equations (2.1) are written in the diabatic representation and were obtained after separating out the angle variables and truncating the basis [3].

As indicated above, there are two different mechanisms for the nonadiabatic transitions at atomic and molecular collisions. According to the first mechanism elaborated in works by Landau, Zener, Stueckelberg *et al.* the nonadiabatic transition is localized in the region of the intersection of the diabatic terms $V_{11}(R)$ and $V_{22}(R)$, which are approximated by linear functions of R, the coupling V_{12} being considered constant. This mechanism adequately describes the situation provided the nonadiabatic transition is accompanied by a large energy transfer, i.e., asymptotically the energetic states of the reagents and products are well separated. However, there exists a large majority of collisional atomic and molecular processes accompanied by small changes of the electronic or vibrational energy. Typical examples of this sort of process are the nonresonant charge exchange $A^+ + B \rightarrow A + B^+$, the nonresonant excitation transfer $A^* + B \rightarrow A + B^*$, the exchange chemical reactions $A + BC(v) \rightarrow AB(v') + C$, etc. These processes result in nonadiabatic transitions occurring as a rule at large separations, which permits the use of asymptotic forms for the potentials V_{11}, V_{22} and the coupling V_{12}.

In accordance with the semiclassical Demkov model [1] we shall approximate the coupling V_{12} by an exchange interaction with an exponential asymptote

$$V_{12}(R)=V_{21}(R)=V\exp(-\alpha R)\ .\tag{2.2}$$

Additionally, we shall assume that $V_{ii}(R)$ vary much more slowly than $V_{12}(R)$. For the above $V_{ii}(R)$ and $V_{12}(R)$, the physical boundary conditions for Eqs. (2.1) are conveniently specified in the basis that is determined by the functions

$$\begin{pmatrix}\Psi_1(R)\\ \Psi_2(R)\end{pmatrix}=\begin{pmatrix}\cos\beta(R) & \sin\beta(R)\\ -\sin\beta(R) & \cos\beta(R)\end{pmatrix}\begin{pmatrix}\psi_1(R)\\ \psi_2(R)\end{pmatrix}\ .\tag{2.3}$$

Here

$$\beta(R)=\tfrac{1}{2}\arctan\frac{2V_{12}(R)}{V_{11}-V_{22}}\ ,\tag{2.4}$$

and the adiabatic terms of the system are

$$U_{1,2}(R)=\tfrac{1}{2}\{V_{11}+V_{22}\pm[(V_{11}-V_{22})^2+4V_{12}^2]^{1/2}\}\ .\tag{2.5}$$

Write down these conditions in the form

$$\begin{aligned}&\Psi_{1,2}(R)=0\ ,\quad R\rightarrow 0\ ,\\&\Psi_{1,2}(R)=k_{1,2}^{-1/2}\{A_{1,2}e^{i(k_{1,2}R-l\pi/2)}\\&\qquad\qquad -B_{1,2}e^{-i(k_{1,2}R-l\pi/2)}\}\ ,\quad R\rightarrow\infty\ ,\end{aligned}\tag{2.6}$$

where $k_i=\{2m[E-V_{ii}(\infty)]\}^{1/2}/\hbar$, $E>V_{ii}(\infty)$, and l is the orbital angular momentum. The asymptotic expres-

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sions (2.6) define the S matrix through the relation

$$\mathbf{A}=S\mathbf{B}\ , \tag{2.7}$$

where $\mathbf{A}=(A_1,A_2)$ and $\mathbf{B}=(B_1,B_2)$. To find out the S matrix consider Eqs. (2.1) near a point R_c defined by the equation

$$\tfrac{1}{2}|V_{11}(R_c)-V_{22}(R_c)|=V\exp(-\alpha R_c)\ . \tag{2.8}$$

In the vicinity of R_c the diagonal elements $V_{ii}(R)$ are assumed to be constants V_{ii}^0 since they vary more slowly as compared to $V_{12}(R)$. Within the above assumptions the system of quantum equations (2.1) takes the form

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_{11}^0-E\right]\psi_1(x)+V_0\exp(-\alpha x)\psi_2(x)=0\ ,$$
$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_{22}^0-E\right]\psi_2(x)+V_0\exp(-\alpha x)\psi_1(x)=0\ , \tag{2.9}$$

where $x=(R-R_c)$ and $V_0=V\exp(-\alpha R_c)$. For sake of definiteness take $V_{22}\geq V_{11}$. The semiclassical counterpart of Eqs. (2.9) was first considered by Demkov [1]. The relation to the Rosen-Zener model is clarified by the trajectory equation

$$\exp(-\alpha x)\simeq\frac{2E}{\cosh(\alpha v t)}\ ,\quad v=\left[\frac{2E}{m}\right]^{1/2}\ , \tag{2.10}$$

provided the turning point is sufficiently remote, where t is time. The system (2.9) is to be solved with boundary conditions for the adiabatic functions (see Fig. 1)

$$\Psi_1(x)=q_1^{-1/2}\left[a_3\exp\left[i\int^x q_1(x)dx\right]-b_3\exp\left[-i\int^x q_1(x)dx\right]\right]\ ,$$
$$\Psi_2(x)=0\ ,\quad x\to-\infty\ , \tag{2.11}$$
$$\Psi_{1,2}(x)=\tilde{q}_{1,2}^{-1/2}(a_{1,2}e^{i\tilde{q}_{1,2}x}-b_{1,2}e^{-i\tilde{q}_{1,2}x})\ ,\quad x\to\infty\ ,$$

where

$$q_i(x)=\{2m[E-U_i^0(x)]\}^{1/2}/\hbar\ ,\quad \tilde{q}_i=q_i(\infty)\ ,$$
$$U_i^0(x)=\tfrac{1}{2}\{V_{11}^0+V_{22}^0\mp[(V_{11}^0-V_{22}^0)^2+4V_0^2e^{-2\alpha x}]^{1/2}\}\ . \tag{2.12}$$

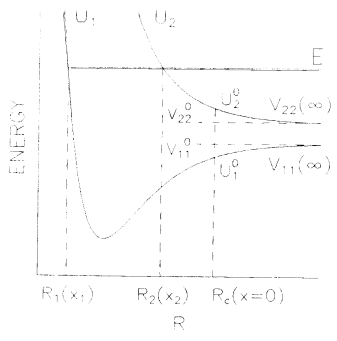

FIG. 1. Schematic diagram of diabatic V_{11}^0, V_{22}^0 and adiabatic U_1^0, U_2^0, U_1, U_2 electronic terms.

Further, for simplicity, the asymptotes $U_i(R\to\infty)$ and $U_i^0(x\to\infty)$ are assumed to be coinciding, resulting in $\tilde{q}_i=k_i=\{2m[E-V_{ii}(\infty)]\}^{1/2}/\hbar$.

If the energy $E>V_{11}(\infty),V_{22}(\infty)$ (see Fig. 1), then three channels are open in the collision process: two channels at $x\to\infty$ $[\Psi_1(\infty),\Psi_2(\infty)]$ and one channel $[\Psi_1(-\infty)]$ at $x\to-\infty$. The corresponding N matrix for the nonadiabatic transitions is of 3×3 dimension. At $V_{11}(\infty)<E<V_{22}(\infty)$ the N matrix is reduced to a 2×2 matrix.

If the exact terms, i.e., $U_1(R)$ and $U_2(R)$ from Eq. (2.5), are considered at small R's, the boundary conditions should be specified at $R=0$. In this case, at $E>V_{11}(\infty),V_{22}(\infty)$ the total S matrix combined from the nonadiabatic N matrix and the diagonal matrix of the adiabatic evolution at $R\ll R_c$ is of 2×2 dimension. At $V_{11}(\infty)<E<V_{22}(\infty)$ the one-channel potential scattering occurs.

Finally, Eqs. (2.9) can be regarded as a sample of an exactly solvable two-channel s-wave scattering problem. In this case the zero boundary condition for $\Psi_{1,2}$ should be specified at $x=0$, and the S matrix at $E>V_{11}(\infty),V_{22}(\infty)$ is of 2×2 dimension. All these S matrices in the above order will be given below.

III. THE SOLUTION OF QUANTUM EQUATIONS

Introduce a new variable ρ and dimensionless wave numbers

$$\rho=(-8mV_0e^{-\alpha x})^{1/2}/\hbar\alpha\ ,\quad q_{1,2}=\tilde{q}_{1,2}/\alpha\ . \tag{3.1}$$

Then quantum equations (2.9) take the form

$$\left[\rho^2\frac{d^2}{d\rho^2}+\rho\frac{d}{d\rho}+4q_1^2\right]\psi_1+\rho^2\psi_2=0\ ,$$
$$\left[\rho^2\frac{d^2}{d\rho^2}+\rho\frac{d}{d\rho}+4q_2^2\right]\psi_2+\rho^2\psi_1=0\ . \tag{3.2}$$

Make one more variable substitution, $\rho=4z^{1/4}$, and eliminate the function ψ_2 from Eqs. (3.2). For the function ψ_1 we obtain the equation

$$-\prod_{n=1}^{4}\left[z\frac{d}{dz}-b_n\right]\psi_1+z\psi_1=0\ , \tag{3.3}$$

where $b_{1,2}=\pm iq_1/2$ and $b_{3,4}=1/2\pm iq_2/2$. The general solution of (3.3) represented as a linear combination of four Meijer functions [7]

$$\psi_1(\rho)=c_{\rm I}G_{04}^{40}(e^{-2\pi i}(\rho/4)^4|b_q)+c_{\rm II}G_{04}^{40}((\rho/4)^4|b_q)$$
$$+c_{\rm III}G_{04}^{40}(e^{2\pi i}(\rho/4)^4|b_q)$$
$$+c_{\rm IV}G_{04}^{40}(e^{4\pi i}(\rho/4)^4|b_q)\ , \tag{3.4}$$

where $G_{04}^{40}(e^{2\pi ir}(\rho/4)^4|b_q)$ $(r=-1,0,1,2$ and $b_q=b_1, b_2,b_3,b_4)$ are four fundamental solutions of Meijer equation (3.3) in the region of irregular singular point $\rho=\infty$. The function $\psi_2(\rho)$ has the form similar to Eq. (3.4) where the substitution $q_1\leftrightarrow q_2$ should be performed

$$\psi_2(\rho)=c_{\rm I}G_{04}^{40}(e^{-2\pi i}(\rho/4)^4|b_q')-c_{\rm II}G_{04}^{40}((\rho/4)^4|b_q')$$
$$+c_{\rm III}G_{04}^{40}(e^{2\pi i}(\rho/4)^4|b_q')$$
$$-c_{\rm IV}G_{04}^{40}(e^{4\pi i}(\rho/4)^4|b_q')\ , \qquad (3.5)$$

with $b_q'=iq_2/2,-iq_2/2,\frac{1}{2}+iq_1/2,\frac{1}{2}-iq_1/2$. Thus the general solution of Eq. (3.2) and hence of system (2.9) can be written in the form

$$\psi=\begin{bmatrix}\psi_1\\ \psi_2\end{bmatrix}=\sum_{L=\rm I}^{\rm IV}c_L\psi^L\ , \qquad (3.6)$$

where in accordance with (3.4) and (3.5) the vector function ψ^L is composed of the fundamental solutions $G_{04}^{40}(e^{2\pi ir}(\rho/4)^4|b_q)$ and $G_{04}^{40}(e^{2\pi ir}(\rho/4)^4|b_q')$.

The next step is to find out the asymptotes of the functions ψ^L ($L=$I–IV) at $\rho\to 0$ ($x\to\infty$) and $\rho\to\infty$ ($x\to-\infty$). To this end invoke the well-known asymptotes of the Meijer G-functions [7]. For ψ^L we obtain

$$\psi^L=\begin{bmatrix}\dfrac{a_1^L}{\sqrt{2q_1}}\rho^{-2iq_1} & -\dfrac{b_1^L}{\sqrt{2q_1}}\rho^{2iq_1}\\ \dfrac{a_2^L}{\sqrt{2q_2}}\rho^{-2iq_2} & -\dfrac{b_2^L}{\sqrt{2q_2}}\rho^{2iq_2}\end{bmatrix}\ ,\quad \rho\to 0\ , \qquad (3.7)$$

$$\psi^L=\frac{1}{\sqrt{\rho}}\left\{(a_3^Le^{i\rho}-b_3^Le^{-i\rho})\begin{bmatrix}1\\1\end{bmatrix}\right.$$
$$\left.+(a_4^Le^{\rho}+b_4^Le^{-\rho})\begin{bmatrix}1\\-1\end{bmatrix}\right\}\ ,\quad \rho\to\infty\ . \qquad (3.8)$$

The exponentially small terms $b_4^Le^{-\rho}$ are obtained from $G_{04}^{40}((\rho/4)^4|b_q)$ and $G_{04}^{40}((\rho/4)^4|b_q')$. The necessary constants are

$$a_1^L=\Gamma(iq_1)\Gamma[\tfrac{1}{2}+i(q_1+q_2)/2]$$
$$\times\Gamma[\tfrac{1}{2}+i(q_1-q_2)/2]2^{4iq_1}e^{ir\pi q_1}\sqrt{2q_1}\ ,$$
$$a_2^L=\pm q_1^L(q_1\leftrightarrow q_2)\ ,$$
$$a_3^{\rm I}=-(2\pi)^{3/2}e^{i\pi/4}\ ,\quad a_4^{\rm IV}=(2\pi)^{3/2}e^{-i\pi/2}\ , \qquad (3.9)$$
$$b_1^L=-a_1^L(q_1\to -q_1)\ ,\quad b_2^L=-a_2^L(q_2\to -q_2)\ ,$$
$$b_3^{\rm III}=-(2\pi)^{3/2}e^{-i\pi/4}\ ,\quad b_4^{\rm IV}=(2\pi)^{3/2}\ ,$$

where the sign (+) is for $L=$I,III and the sign (−) is for $L=$II,IV. The others constants equal zero.

The consequent determination of the S matrix requires constructing of a linear combination similar to (3.6) for the adiabatic functions (2.3)

$$\Psi=\begin{bmatrix}\Psi_1\\ \Psi_2\end{bmatrix}=\sum_{L=\rm I}^{\rm IV}c_L\Psi^L\ . \qquad (3.10)$$

The angle β goes to $\pi/4$ at $\rho\to\infty$ and to zero at $\rho\to 0$. Note that the solution $\Psi^{\rm IV}$ in (3.6) and (3.10) growing exponentially at $\rho\to\infty$ ($x\to-\infty$) does not satisfy the physical boundary condition for $\Psi(11)$, and therefore $c^{\rm IV}=0$ in linear combination (3.10).

IV. DETERMINATION OF THE N AND S MATRICES

A. Three-channel nonadiabatic N matrix: $E>V_{11}(\infty),V_{22}(\infty)$

Let us define the channels 1,2,3 and the elements of the nonadiabatic N matrix for the inelastic processes as follows (see Fig. 1). Let

$$\frac{1}{\sqrt{2q_1}}(\rho^{2iq_1}-N_{11}\rho^{-2iq_1}) \qquad (4.1)$$

stand for the ingoing and outgoing waves, respectively, in channel 1; then the outgoing waves in channels 2 and 3 are

$$-N_{12}\frac{\rho^{-2iq_2}}{\sqrt{2q_2}}\ ,\quad -N_{13}\frac{e^{i\rho}}{\sqrt{\rho}}\ , \qquad (4.2a)$$

respectively. Similarly, for the ingoing wave in channels 2 and 3 we define

$$\frac{1}{\sqrt{2q_2}}(\rho^{2iq_2}-N_{22}\rho^{-2iq_2})\ ,$$
$$-N_{21}\frac{\rho^{-2iq_1}}{\sqrt{2q_1}}\ ,\quad -N_{23}\frac{e^{i\rho}}{\sqrt{\rho}}\ ; \qquad (4.2b)$$
$$\frac{1}{\sqrt{\rho}}(e^{-i\rho}-N_{33}e^{i\rho})\ ,$$
$$-N_{32}\frac{\rho^{-2iq_2}}{\sqrt{2q_2}}\ ,\quad -N_{31}\frac{\rho^{-2iq_1}}{\sqrt{2q_1}}\ , \qquad (4.2c)$$

respectively. Three-channel nonadiabatic N matrix connects the coefficients of the ingoing and outgoing waves centered at $x=0$, i.e.,

$$\mathbf{a}=N\mathbf{b}\ ,\quad \mathbf{a}=(a_1,a_2,a_3)\ ,\quad \mathbf{B}=(b_1,b_2,b_3) \qquad (4.3)$$

in accordance with (2.11). Vector equation (4.3) reduces to three simple algebraic problems

$$a_i^L=\sum_k N_{ik}b_k^L\quad (i,k=1,2,3;\ L=\rm I,II,III)\ . \qquad (4.4)$$

A simple way to calculate the N matrix is to choose the c_L coefficients providing successive ingoing waves in each of the three channels and outgoing ones in the rest channels according to (4.2a)–(4.2c). Simple calculation leads to the following expressions for the elements of the N matrix:

$$N_{11}=-2^{8iq_1}e^{-\pi q_1}\frac{\Gamma^2[\frac{1}{2}+i(q_1-q_2)/2]\Gamma(iq_1)}{\Gamma^2[\frac{1}{2}-i(q_1+q_2)/2]\Gamma(-iq_1)}\ ,$$

$$N_{22}=N_{11}(q_1\leftrightarrow q_2),\quad N_{33}=ie^{-\pi(q_1+q_2)},$$

$$N_{12}=N_{21}=2^{4i(q_1+q_2)}e^{-\pi(q_1+q_2)/2}\frac{\Gamma[\frac{1}{2}+i(q_1-q_2)/2]\Gamma[\frac{1}{2}+i(q_2-q_1)/2]\Gamma[\frac{1}{2}+i(q_1+q_2)/2]}{\Gamma(\frac{1}{2}-i(q_1+q_2)/2)\Gamma(-iq_1)\Gamma(-iq_2)(q_1q_2)^{1/2}}\ , \tag{4.5}$$

$$N_{13}=N_{31}=-\sqrt{2\pi/q_1}2^{4iq_1}e^{i\pi/4}e^{-\pi(q_1+q_2)/2}\frac{\Gamma[\frac{1}{2}+i(q_1-q_2)/2]}{\Gamma[\frac{1}{2}-i(q_1+q_2)/2]\Gamma(-iq_1)}\ ,$$

$$N_{23}=N_{32}=N_{13}(q_1\leftrightarrow q_2)\ ,$$

where $\Gamma(x)$ is the gamma function. The N matrix given the above expression is symmetrical and unitary.

B. Two-channel nonadiabatic N^0 matrix: $V_{11}(\infty)<E<V_{22}(\infty)$

In the energy region under consideration, channel 2 is closed while channels 1 and 3 are open, i.e., the N matrix (4.5) is reduced to a N^0 matrix of the 2×2 dimension. In this case linear combination (3.10) has to fulfill the condition $\Psi_2(\rho)\to 0$ at $\rho\to 0$ and $\rho\to\infty$. The N^0 matrix is defined by the relation

$$\mathbf{a}=N^0\mathbf{b}\ ,\quad \mathbf{a}=(a_1,a_3)\ ,\quad \mathbf{b}=(b_1,b_3) \tag{4.6}$$

and is an analytical continuation of the corresponding submatrix of N by the parameter q_2 ($q_2\to iq_2$). As a result we obtain

$$N^0_{11}=-2^{8iq_1}e^{-\pi q_1}\frac{\Gamma^2(\frac{1}{2}+q_2/2+iq_1/2)\Gamma(iq_1)}{\Gamma^2(\frac{1}{2}+q_2/2-iq_1/2)\Gamma(-iq_1)}\ ,$$

$$N^0_{33}=ie^{-i\pi q_2}e^{-\pi q_1}\ ,$$

$$N^0_{13}=N^0_{31}=-\sqrt{2\pi/q_1}2^{4iq_1}e^{i\pi/4}e^{-\pi q_2/2}e^{-\pi q_1}\times\frac{\Gamma(\frac{1}{2}+q_2/2+iq_1/2)}{\Gamma(\frac{1}{2}+q_2/2-iq_1/2)\Gamma(-iq_1)}\ . \tag{4.7}$$

Like the N matrix, the N^0 matrix is symmetrical and unitary.

C. The total two-channel S matrix: $E>V_{11}(\infty)$, $V_{22}(\infty)$

As noted above, the total S matrix appears when the exact terms $U_1(R)$ and $U_2(R)$ are taken into account in the region of small R. It describes both nonadiabatic transitions characterized by the N matrix and the adiabatic evolution of the states Ψ_1 and Ψ_2 at small R. In order to calculate the S matrix, we shall invoke the matching method. In the spirit of that method we shall suppose that the quasiclassical and adiabatic approximation apply outside the domain of nonadiabatic transitions. Then there exist the turning points $R_1(x_1)$ and $R_2(x_2)$ on the U_1 and U_2 terms (see Fig. 1), and $\psi_{1,2}$ are represented as a sum of quasiclassical waves

$$\psi_{1q}=N_1k_1^{-1/2}(x)\sin\left[\int_{x_1}^{x}k_1(x)dx+\pi/4\right]\sin\beta - N_2k_2^{-1/2}(x)\sin\left[\int_{x_2}^{x}k_2(x)dx+\pi/4\right]\cos\beta\ ,$$

$$\psi_{2q}=N_1k_1^{-1/2}(x)\sin\left[\int_{x_1}^{x}k_1(x)dx+\pi/4\right]\cos\beta + N_2k_2^{-1/2}(x)\sin\left[\int_{x_2}^{x}k_2(x)dx+\pi/4\right]\sin\beta \tag{4.8}$$

in the range between $x_1(R_1)$, $x_2(R_2)$, and $x=0(R=R_c)$. After using the quasiclassical representations for the Meijer G functions, the exact functions $\psi_1(x)$ and $\psi_2(x)$ (3.4) and (3.5) to the left from R_c can be presented in the analogous form. To be specific, we shall assume that only the U_1 term is modified at small R. Matching $\psi_{1q}(x)$ and $\psi_1(x)$ and using of the asymptotic expansions of the Meijer G functions (3.7) and (3.9) at $\rho\to 0$ gives after routine algebra the following S matrix for the boundary conditions (2.6)

$$S=\begin{vmatrix} N'_{11}+\dfrac{N'_{13}N'_{31}}{e^{-2i\eta}-N_{33}} & N'_{12}+\dfrac{N'_{13}N'_{32}}{e^{-2i\eta}-N_{33}} \\ N'_{21}+\dfrac{N'_{23}N'_{31}}{e^{-2i\eta}-N_{33}} & N'_{22}+\dfrac{N'_{23}N'_{32}}{e^{-2i\eta}-N_{33}} \end{vmatrix}\ , \tag{4.9}$$

where

$$N'_{ij}=N_{ij}\exp[-(\xi_i+\xi_j)]\ ,\quad N'_{i3}=N_{i3}\exp(-i\xi_i)\quad (i,j=1,2)\ , \tag{4.10}$$

$$\xi_i=q_i\ln\left[-\frac{8mV_0}{\hbar^2\alpha^2}\right]\ . \tag{4.11}$$

The phase η is the so-called matching phase and the phase ξ_i emerges in going from the variable ρ to the variable x by (3.1).

The above S matrix expressions enable one to calculate the probabilities of the nonadiabatic transitions. For example, the nonadiabatic transition probability from the state Ψ_1 to the state Ψ_2, i.e., the nonresonant charge-exchange probability has the form

$$P_{12}=|S_{12}|^2 = \frac{\sinh(\pi q_1)\sinh(\pi q_2)\cos^2\eta}{\cosh^2\frac{\pi(q_1-q_2)}{2}\left[\cosh^2\frac{\pi(q_1+q_2)}{2}-\cos^2\eta\right]} . \tag{4.12}$$

This expression agrees with that of the work [6] where, however, the phase η was not defined. In the case of the resonant charge exchange, i.e., $q_1=q_2=q$, the probability reduces to

$$P_{12}=\frac{\sinh^2(\pi q)\cos^2\eta}{\cosh^2(\pi q)-\cos^2\eta} . \tag{4.13}$$

At high collision energy when

$$q_1-q_2\simeq\frac{2(U_2-U_1)}{\hbar\alpha V}=\frac{2\Delta U(\infty)}{\hbar a V} \tag{4.14}$$

takes place, Eq. (4.13) coincides with the semiclassical Rosen-Zener-Demkov (RZD) probability for the nonresonant charge exchange process $A+B^+\rightarrow A^++B$

$$P_{\mathrm{RZD}}=\frac{\sin^2\sigma}{\cosh^2\delta} , \tag{4.15}$$

where

$$\delta=\Delta U(\infty)/\hbar\alpha V , \quad \sigma=\eta-\pi/2 . \tag{4.16}$$

In this limit Eq. (4.13) coincides with the semiclassical nonresonant charge-exchange probability

$$P_{12}^0=\sin^2\sigma . \tag{4.17}$$

Concluding this section, we note that if the terms $U_1(R)$ and $U_2(R)$ are modified at large R, too, then the S matrix (4.9) is replaced by the S' matrix

$$S'=\begin{bmatrix}\exp(i\eta_1) & 0\\ 0 & \exp(i\eta_2)\end{bmatrix}S\begin{bmatrix}\exp(i\eta_1) & 0\\ 0 & \exp(i\eta_2)\end{bmatrix} , \tag{4.18}$$

where η_1 and η_2 are the adiabatic phases for the U_1 and U_2 terms in the range of $R>R_c$.

D. One-channel S^0 matrix: $V_{11}(\infty)<E<V_{22}(\infty)$

Within this energy range, elastic scattering in the adiabatic term U_1 occurs, the scattering being distorted by the nonadiabatic coupling with the adiabatic term U_2. The elastic S matrix is equal to the matrix element S_{11} subjected to the analytical continuation as a function of parameter q_2 ($q_2\rightarrow iq_2$)

$$S^0=e^{2i\gamma}=S_{11}(q_2\rightarrow iq_2) = \left[N'_{11}+\frac{N'_{13}N'_{31}}{e^{-2i\eta}-N_{33}}\right]_{(q_2\rightarrow iq_2)} . \tag{4.19}$$

With the use of Eq. (4.5), this expression can be recast in the form

$$e^{2i\gamma}=e^{2i(\xi_2+\phi_{22})}\left[\frac{(1+e^{-\pi q_1})+i(1-e^{-\pi q_1})\tan\sigma}{(1+e^{-\pi q_1})-i(1-e^{-\pi q_1})\tan\sigma}\right] . \tag{4.20}$$

The elastic phase γ is

$$\gamma=\xi_2+\phi_{22}+\arctan\left[\frac{(1-e^{-\pi q_1})\tan\sigma}{1+e^{-\pi q_1}}\right] , \tag{4.21}$$

$$\phi_{22}=4q_1\ln 2+\arg\Gamma(iq_1)+2\arg\Gamma(\tfrac{1}{2}-q_2/2+iq_1/2) .$$

The elastic S^0 matrix displays well-known features of the low-energy scattering of the particles.

E. Two-channel $\tilde{S}$ matrix for the s-wave scattering

Of certain interest is the $\tilde{S}$ matrix for the quantum problem (2.9) regarded as a model for the two-channel s-wave scattering under zero boundary conditions at $x=0$. For the wave functions $\phi_1=\psi_1+\psi_2$ and $\phi_2=\psi_1-\psi_2$ the system (2.9) has the form

$$\left[-\frac{1}{2m}\frac{d^2}{dx^2}-E+\mu+V_0e^{-\alpha x}\right]\phi_1=\nu\phi_2 , \quad \left[-\frac{1}{2m}\frac{d^2}{dx^2}-E+\mu-V_0e^{-\alpha x}\right]\phi_2=\nu\phi_1 , \tag{4.22}$$

where $\mu=(V_{11}^0+V_{22}^0)/2$ and $\nu=(V_{11}^0-V_{22}^0)/2$. The $\tilde{S}$ matrix for the system (4.22) is a generalization of the one-channel S matrix for an exponential potential [8]. The boundary conditions for either (2.9) or (4.22) lead to the equations

$$\boldsymbol{\psi}(\rho_0)=\mathbf{0} \text{ or } \boldsymbol{\phi}(\rho_0)=\mathbf{0} , \quad \rho_0=(-8mV_0)^{1/2}/\hbar\alpha , \tag{4.23}$$

which are, according to (3.6), equivalent to the system

$$\sum_{L=\mathrm{I}}^{\mathrm{IV}} c_L\psi_{1,2}^L(\rho_0)=0 . \tag{4.24}$$

This system enables one to replace any pair of the c_L coefficients in Eq. (3.6) with linear combinations of two others and, as a result, to introduce a new basis of fundamental solutions

$$\boldsymbol{\psi}^M=\sum_{L=1}^{\mathrm{IV}} Q_{ML}\boldsymbol{\psi}^L \quad (M=1,2) , \tag{4.25}$$

where the rectangular matrix Q_{ML} consists of 2×2 determinants of the form

$$\begin{vmatrix}\psi_i^L(\rho_0) & \psi_k^L(\rho_0)\\ \psi_i^{L'}(\rho_0) & \psi_k^{L'}(\rho_0)\end{vmatrix} .$$

The basis (4.25) specifies the coefficients A_L^M and B_L^M and defines the $\tilde{S}$ matrix similar to the S matrix (4.9)

$$A_i^M=\sum_k\tilde{S}_{ik}B_k^M \quad (i,k=1,2;\ M=1,2) . \tag{4.26}$$

The actual calculation of the elements $\tilde{S}_{ik}$ is appropriate to perform by choosing the two yet indefinite c_L

coefficients in a way providing an ingoing wave in channel either 1 or 2, i.e.,

$$\psi\sim\begin{pmatrix}\frac{1}{\sqrt{\alpha q_1}}(e^{-i\alpha q_1 x}-\tilde{S}_{11}e^{i\alpha q_1 x})\\ -\frac{1}{\sqrt{\alpha q_2}}\tilde{S}_{12}e^{i\alpha q_2 x}\end{pmatrix},$$
$$\psi\sim\begin{pmatrix}-\frac{1}{\sqrt{\alpha q_1}}\tilde{S}_{21}e^{i\alpha q_1 x}\\ \frac{1}{\sqrt{\alpha q_2}}(e^{-i\alpha q_2 x}-\tilde{S}_{22}e^{i\alpha q_2 x})\end{pmatrix}. \tag{4.27}$$

The final result can be formulated as follows. Define vectors $\mathbf{V}_1,\mathbf{V}_2,\mathbf{v}_1,\mathbf{v}_2$ and a matrix $\hat{M}$

$$\mathbf{V}_{1,2}=\begin{pmatrix}A_{1,2}\\ B_{1,2}\\ C_{1,2}\\ D_{1,2}\end{pmatrix},\quad \mathbf{v}_1=\begin{pmatrix}r\\ 0\\ m\\ n\end{pmatrix},\quad \mathbf{v}_2=\begin{pmatrix}0\\ r\\ p\\ q\end{pmatrix},$$
$$\hat{M}=\begin{pmatrix}\alpha^{\mathrm{I}} & \alpha^{\mathrm{II}} & \alpha^{\mathrm{III}} & \alpha^{\mathrm{IV}}\\ \beta^{\mathrm{I}} & \beta^{\mathrm{II}} & \beta^{\mathrm{III}} & \beta^{\mathrm{IV}}\\ \gamma^{\mathrm{I}} & \gamma^{\mathrm{II}} & \gamma^{\mathrm{III}} & \gamma^{\mathrm{IV}}\\ \delta^{\mathrm{I}} & \delta^{\mathrm{II}} & \delta^{\mathrm{III}} & \delta^{\mathrm{IV}}\end{pmatrix}. \tag{4.28}$$

They obey equations $\mathbf{V}_{1,2}=\hat{M}\mathbf{v}_{1,2}$. The coefficients $\alpha^L,\beta^L,\gamma^L,\delta^L$ $(L=\mathrm{I},\ldots,\mathrm{IV})$ are determined from asymptotic expansions of the Meijer G functions at $x\to\infty$, as in Eqs. (3.9), and they are

$$\alpha^L=-\sqrt{\alpha/2}\,A^{2iq_1}b_1^L,\quad \beta^L=\sqrt{\alpha/2}\,A^{-2iq_1}a_1^L,$$
$$\gamma^L=-\sqrt{\alpha/2}\,A^{2iq_2}b_2^L,\quad \delta^L=\sqrt{\alpha/2}\,A^{-2iq_2}a_2^L, \tag{4.29}$$
$$A=(-8mV_0)^{1/2}/\hbar\alpha .$$

The quantities r,m,n,p,q are the determinants composed of the boundary values of $\psi_{1,2}^L(x=0)$

$$r=\begin{vmatrix}\psi_1^{\mathrm{IV}}(\rho_0) & \psi_2^{\mathrm{IV}}(\rho_0)\\ \psi_1^{\mathrm{III}}(\rho_0) & \psi_2^{\mathrm{III}}(\rho_0)\end{vmatrix},$$
$$m=-r(\mathrm{III}\to\mathrm{I}),\quad p=m(\mathrm{I}\to\mathrm{II}), \tag{4.30}$$
$$n=-r(\mathrm{IV}\to\mathrm{I}),\quad q=n(\mathrm{I}\to\mathrm{II}).$$

The sufficient development of the Meijer G functions permits calculations r,m,n,p,q with any degree of accuracy. Then the elements of the $\tilde{S}$ matrix have the form

$$\tilde{S}_{11}=\begin{vmatrix}B_1 & C_1\\ B_2 & C_2\end{vmatrix}D^{-1},\quad \tilde{S}_{12}=\begin{vmatrix}D_1 & C_1\\ D_2 & C_2\end{vmatrix}D^{-1},$$
$$\tilde{S}_{21}=\begin{vmatrix}A_1 & B_1\\ A_2 & B_2\end{vmatrix}D^{-1},\quad \tilde{S}_{22}=\begin{vmatrix}A_1 & D_1\\ A_2 & D_2\end{vmatrix}D^{-1}, \tag{4.31}$$

$$D=\begin{vmatrix}C_1 & A_1\\ C_2 & A_2\end{vmatrix}.$$

Thus all of the N and S matrices mentioned in Sec. II, for the nonadiabatic transitions described by the quantum Rosen-Zener-Demkov model have been found out.

V. CONCLUSION

The Rosen-Zener-Demkov model in its original semiclassical form as well as in other modifications [4,5,9] is frequently used for interpreting experimental data on nonresonant charge exchange in ion-atom collisions. Investigated in most detail have been the charge-exchange processes in collisions of alkali-metal ions with atoms such as [10]

$$\begin{aligned}&\mathrm{K}^+(^1S)+\mathrm{Rb}(^2S)\to\mathrm{K}(^2S)+\mathrm{Rb}+(^1S)+0.163\ \mathrm{eV},\\ &\mathrm{Li}^+(^1S)+\mathrm{Na}(^2S)\to\mathrm{Li}(^2S)+\mathrm{Na}^+(^1S)+0.253\ \mathrm{eV},\end{aligned} \tag{5.1}$$

etc. Recently, this semiclassical model also has been used for interpreting complicated numerical calculations of the probabilities and cross sections of chemical reactions involving light-atom transfer [11]

$$\begin{aligned}&\mathrm{Cl}+\mathrm{HBr}(v=0)\to\mathrm{Br}+\mathrm{HCl}(v=2),\\ &\mathrm{Br}+\mathrm{HCl}(v=0)\to\mathrm{Cl}+\mathrm{HBr}(v=2),\end{aligned} \tag{5.2}$$

with special attention being paid to resonances in the energy range near threshold. The discrepancies seen between the experimental data and the exact numerical calculations, on the one hand, may to a degree be due to breakdown of semiclassical version of the model at low collision energies. The expressions given in this paper for the N and S matrices, and the resulting probabilities, provide, in contrast, an adequate representation of these processes, especially in the threshold energy range.

In addition, the exact results given in Eqs. (4.5) and (4.7) can be exploited as local elements in numerical calculations for other real problems in collision theory. In this case, depending on the applicability of the exponential approximation, significant improvements in the time requested for the calculations may be expected. In the best case, the problem may reduce to numerical matching of the adiabatic wave functions inside the collision region with the exact quantum amplitudes from the coupled equations (2.9) or (4.22). As a result, the calculation for a real system will simplify in practice to a calculation of the adiabatic motion whose results in quasiclassical range of parameters can be controlled by means of Eqs. (4.9) and (4.19).

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