Inverted box spectrum for the Nikitin model

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We demonstrate that the quantum-mechanical equations of the Nikitin exponential model can be exactly solved at the energies coinciding with the inverted spectrum of an infinite box. Assuming specific potential parameters, the N matrix has been derived for the second level in closed form. The general solution in the Bessel representation has been found for the third and fourth levels. The results show a logarithmic anomaly in the amplitude behavior at the threshold of three-channel–two-channel transformation.

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I. INTRODUCTION

For a long time nonadiabatic dynamics has been one of the most popular topics in quantum mechanics [1–3]. Most of the modern research in the field of atomic and molecular physics deals with numerical simulations of the real systems [4–12]; however, analytical studies of the physical models are rather rare. The analytical results are useful to control numerical codes and to describe complicated phenomena where otherwise elaborate exact quantum-mechanical solutions are required. Important examples of recent analytical work can be found in the explicit determination of the Stokes constant connection for the linear potential model [3], the exact study of some special models with exponential potentials [13–16], and the solution of the coupled equations for conic and glancing intersection problems [17–20].

In general, problems that can be analytically solved require rigorous limitations for the model parameters. In particular, the results obtained in Ref. [16] are applicable only to some special energy values and for a flat diabatic potential in the excited state. In the same paper, we suggested that the class of exactly solvable exponential models can be considerably extended. The current paper is an extension of our exponential model study in Ref. [16], which will be cited below as paper I. In the present paper, we demonstrate how the model limitations can be significantly reduced.

The current paper is organized as follows: Section II formulates the physical problem of the general Nikitin exponential model in the Bessel representation. In Sec. III, we reduce the problem to the Heun equation, find its solution by the Erdelyi method, and determine the spectrum for the solvable cases. The details of the N-matrix calculation are presented for the second level of this spectrum. Section IV gives the solution in the coordinate representation, Sec. V describes the asymptotic behavior of the basis set, and Sec. VI gives the N-matrix closed expression. The conclusions and perspectives for further studies can be found in Sec. VII. The Appendixes contain the formal solutions for the third and fourth levels and also the evaluation of the main integrals.

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II. FORMULATION OF THE PROBLEM: BESSEL REPRESENTATION

We take the Schrödinger equation for the general Nikitin model in the form

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+\begin{pmatrix} U_1-V_1e^{-\alpha x}, & Ve^{-\alpha x} \\ Ve^{-\alpha x}, & U_2-V_2e^{-\alpha x}\end{pmatrix}\right]\boldsymbol{\psi}=E\boldsymbol{\psi}. \tag{1}$$

In the Nikitin model, the potential energy matrix is characterized by the same exponent α appearing in the various matrix elements. One example of a quantum-mechanically exact analytical solution for a two-state exponential model, in which the exponent of diabatic coupling is one-half of that of the diabatic potential curve, can be found in Ref. [15].

As in paper I, the Bessel representation

$$\psi_{1,2}=\oint_L pF_{1,2}(p)Z_{i\nu}(p\rho)dp \tag{2}$$

reduces system (1) to the equation

$$\left(\frac{d^2}{dp^2}+\frac{1+4\mu^2}{4}\frac{p^4-4\varepsilon p^2+\lambda}{p^2(p^2-a_1)(p^2-a_2)}\right)f=0, \tag{3}$$

where the variable

$$\rho^2=\frac{8mV}{(\hbar\alpha)^2}e^{-\alpha x}, \tag{4}$$

parameters

$$\nu^2=\frac{8m}{(\hbar\alpha)^2}(E-U_1),\quad \mu^2=\frac{8m}{(\hbar\alpha)^2}(E-U_2),\quad \beta_i=\frac{V_i}{V}, \tag{5}$$

$$a_{1,2}=\frac{\beta_1+\beta_2}{2}\mp\sqrt{\left(\frac{\beta_1-\beta_2}{2}\right)^2+1}, \tag{6}$$

$$\varepsilon=\frac{\frac{1}{4}(\beta_1+\beta_2)+(\beta_1\mu^2+\beta_2\nu^2)}{1+4\mu^2},\quad \lambda=\frac{(\beta_1\beta_2-1)(1+4\nu^2)}{1+4\mu^2}, \tag{7}$$

and amplitudes

$$F_1(p)=\frac{f(p)}{p^{1/2}(p^2-a_1)(p^2-a_2)},\quad F_2=(\beta_1-p^2)F_1(p) \quad (8)$$

coincide completely with the corresponding ones in paper I.

The integrals (2) must converge, and the contour increments must satisfy the conditions

$$F_i(p)\frac{dZ_{i\nu}(p\rho)}{dp}p^n\bigg|_L=0,\qquad \frac{d}{dp}[F_i(p)p^n]Z_{i\nu}(p\rho)\bigg|_L=0,$$

$$n=1-3,$$

$$F_i(p)p^nZ_{i\nu}(p\rho)|_L=0,\quad n=0,2. \quad (9)$$

III. REDUCTION TO THE HEUN EQUATION: SPECTRUM OF SOLVABLE CASES

The substitution of the variable and the function

$$\zeta=\frac{p^2}{a_2},\quad \phi=p^{-1/2+i\nu}f \quad (10)$$

transforms Eq. (3) to the Heun form [21]

$$\frac{d^2\phi}{d\zeta^2}+\frac{1-i\nu}{\zeta}\frac{d\phi}{d\zeta}+\frac{\mu^2-\nu^2}{4}\frac{\zeta-\beta_1/a_2}{\zeta(\zeta-1)(\zeta-a_1/a_2)}\phi=0. \quad (11)$$

The further variable substitution

$$z=\frac{\zeta-1}{a_1/a_2-1}=\frac{p^2-a_2}{a_1-a_2} \quad (12)$$

transforms Eq. (11) to the Heun equation

$$\frac{d^2\phi}{dz^2}+\frac{1-i\nu}{z-a_2/(a_2-a_1)}\frac{d\phi}{dz}+\frac{\mu^2-\nu^2}{4}\frac{z-(a_2-\beta_1)/(a_2-a_1)}{z(z-1)[z-a_2/(a_2-a_1)]}\phi=0. \quad (13)$$

The general Heun equation (see Refs. [21–24]) is given as

$$\frac{d^2}{dx^2}H(x)+\left(\frac{\gamma}{x}+\frac{\delta}{x-1}+\frac{\varepsilon}{x-a}\right)\frac{\partial}{\partial x}H(x)+\frac{\alpha\beta x-q}{x(x-1)(x-a)}H(x)=0, \quad (14)$$

where the parameters are connected by Fuchs's relation

$$\gamma+\delta+\varepsilon=\alpha+\beta+1. \quad (15)$$

The Heun equation describes the exponential model with parametrization

x	a	q	α	β	γ	δ	ε
ζ	$\frac{a_1}{a_2}$	$\frac{(\mu^2-\nu^2)}{4}\frac{\beta_1}{a_2}$	$\frac{i}{2}(\mu-\nu)$	$-\frac{i}{2}(\mu+\nu)$	$1-i\nu$	0	0

(16)

for Eq. (11) and with

x	a	q	α	β	γ	δ	ε
z	$\frac{a_2}{a_2-a_1}$	$\frac{1}{4}\frac{(\mu^2-\nu^2)(a_2-\beta_1)}{a_2-a_1}$	$\frac{i}{2}(\mu-\nu)$	$-\frac{i}{2}(\mu+\nu)$	0	0	$1-i\nu$

(17)

for Eq. (13).

Using the operator Λ (see Ref. [25]),

$$\Lambda=x(x-1)(x-a)\frac{d^2}{dx^2}+[\gamma(x-1)(x-a)+\delta x(x-a)+\varepsilon x(x-1)]\frac{d}{dx}+\alpha\beta x-q, \quad (18)$$

we try to find the solutions to the equation

$$\Lambda H=0 \quad (19)$$

as the expansion series

$$H=\sum_m d_mW_m, \quad (20)$$

where W_m are the solutions of the associated hypergeometric equation

$$x(x-1)\left[\frac{d^2W_m}{dx^2}+\left(\frac{\gamma}{x}+\frac{\delta}{x-1}\right)\frac{dW_m}{dx}\right]+(\alpha+m)(\beta-\varepsilon-m)W_m=0. \quad (21)$$

We will use the notations r_m, s_m, and t_m in place of a, b, and c for the Gauss equation parameters, and following Erdelyi [25] take them in the form

$$r_m = \alpha + m, \quad s_m = \beta - \varepsilon - m, \quad t_m = \gamma, \tag{22}$$

where m is an integer number. Erdelyi has found the uniform representation of Kummer's solutions [26] $W_{i,m}$, $i=1,\ldots,6$, such that the functional equation

$$\Lambda W_{i,m} = A_m W_{i,m-1} + B_m W_{i,m} + C_m W_{i,m+1} \tag{23}$$

is satisfied at the following universal (independent of the number i) values of the parameters A_m, B_m, and C_m:

$$A_m = \frac{m(m+\alpha-\beta)(m+\alpha-\gamma)(m+\alpha-1)}{(2m+\alpha-\beta+\varepsilon)(2m+\alpha-\beta+\varepsilon-1)}, \tag{24}$$

$$B_m = a(\alpha+m)(\beta-\varepsilon-m) - q + \frac{m(m+\alpha-\beta)(m+\alpha-\gamma)(m-\beta+\varepsilon)}{(2m+\alpha-\beta+\varepsilon)(2m+\alpha-\beta+\varepsilon-1)} + \frac{(m-\beta+\varepsilon+\alpha)(m+\varepsilon)(m-\beta+\varepsilon+\gamma)(m+\alpha)}{(2m+\alpha-\beta+\varepsilon)(2m+\alpha-\beta+\varepsilon+1)}, \tag{25}$$

$$C_m = \frac{(m-\beta+\varepsilon+\alpha)(m+\varepsilon)(m-\beta+\varepsilon+\gamma)(m-\beta+\varepsilon+1)}{(2m+\alpha-\beta+\varepsilon)(2m+\alpha-\beta+\varepsilon+1)}. \tag{26}$$

Now, following the strategy of paper I, we take for the basis set in Eq. (20) the solutions $W_{5,m}$:

$$W_{5,m} = \frac{\Gamma(r_m)\Gamma(1-t_m+r_m)}{\Gamma(1+r_m-s_m)} x^{-r_m} \times {}_2F_1\left(r_m,\ 1-t_m+r_m,\ 1+r_m-s_m,\ \frac{1}{x}\right). \tag{27}$$

Substituting parameters from Eq. (22) we get

$$W_{5,m} = \frac{\Gamma(\alpha+m)\Gamma(1-\gamma+\alpha+m)}{\Gamma(1+\alpha-\beta+\varepsilon+2m)} x^{-\alpha-m} {}_2F_1\left(\alpha+m,\ 1-\gamma+\alpha+m,\ 1+\alpha-\beta+\varepsilon+2m,\ \frac{1}{x}\right). \tag{28}$$

The equation

$$\sum_m d_m \Lambda W_{i,m} = 0 \tag{29}$$

results in the recurrence relation [21,22,25]

$$C_{m-1}d_{m-1} + B_m d_m + A_{m+1}d_{m+1} = 0. \tag{30}$$

The conditions to find the solution as a finite sum of k hypergeometric functions are given by

$$C_{k-1} = 0, \quad \det(M) = 0, \tag{31}$$

where M is a three-diagonal $k\times k$ matrix,

$$M = \begin{pmatrix} B_0 & A_1 & & & & & \\ C_0 & B_1 & A_2 & & & & \\ & C_1 & B_2 & & & & \\ & & C_2 & \cdots & & & \\ & & & \cdots & A_{k-3} & & \\ & & & & B_{k-3} & A_{k-2} & \\ & & & & C_{k-3} & B_{k-2} & A_{k-1} \\ & & & & & C_{k-2} & B_{k-1} \end{pmatrix}. \tag{32}$$

The solution to Eq. (30) is as follows:

$$d_0 = 1, \quad d_1 = -B_0/A_1, \quad \ldots, \quad d_{m+1} = -(C_{m-1}d_{m-1} + B_m d_m)/A_{m+1}, \quad \ldots. \tag{33}$$

The complete list of the Heun equation solutions includes 192 solutions (see Ref. [24]). Analysis of this list shows that, as in paper I, the only parametrization which leads to the physical solutions is that of Eq. (17). The parameters given by Eq. (17) will be used below.

The first condition of Eq. (31) gives

$$\nu = -ik. \tag{34}$$

This is an inverted box spectrum.

IV. SOLUTION TO THE EXPONENTIAL MODEL FOR TWO ${}_2F_1$ FUNCTIONS

In paper I, we studied the first level ($k=1$) with the limitation $\beta_1=0$ induced by this choice because of Eq. (31).

For $k=2$, the second condition of Eq. (31) results in the following relation between energy and the potential parameter β_1:

$$\beta_1 = \frac{2}{\mu}. \tag{35}$$

The expression for the coefficient d_1,

$$d_1 = \frac{\beta_1 - \beta_2 + 2i}{a_2 - a_1}, \tag{36}$$

follows from Eq. (33). The parameters r_0, s_0, and t_0 for the associated hypergeometric equation with $m=0$,

$$r_0 = -1 + \frac{i\mu}{2}, \quad s_0 = -\frac{i\mu}{2}, \quad t_0 = 0, \tag{37}$$

the parameters r_1, s_1, and t_1 for the equation with $m=1$,

$$r_1 = \frac{i\mu}{2}, \quad s_1 = -1 - \frac{i\mu}{2}, \quad t_1 = 0, \tag{38}$$

and the solution W_5

$$W_{5,m=0} = z^{1-i\mu/2}\ {}_2F_1\left(-1+\frac{i\mu}{2},\ \frac{i\mu}{2},\ i\mu,\ \frac{1}{z}\right), \tag{39}$$

$$W_{5,m=1} = \frac{(i\mu-2)}{4(1+i\mu)} z^{-i\mu/2} \, {}_2F_1\left(\frac{i\mu}{2},\ 1+\frac{i\mu}{2},\ 2+i\mu,\ \frac{1}{z}\right) \tag{40}$$

follow from the basic definitions given above. In expressions (39) and (40) the coefficient

$$\frac{\Gamma\left(-1+\frac{i\mu}{2}\right)\Gamma\left(\frac{i\mu}{2}\right)}{\Gamma(i\mu)} \tag{41}$$

is omitted. As a result we get the solution to Eq. (11) in the form

$$\phi(\zeta) = H(\zeta) = W_{5,m=0} + d_1 W_{5,m=1}. \tag{42}$$

The solutions to the exponential model for the cases of three and four hypergeometric functions are given in Appendix A.

Calculating the diabatic wave functions $\psi_{1,2}(x)$ in coordinate representation, we take, in analogy to paper I,

$$L_{1,2} = (\sqrt{a_{2,1}}+i\infty, \sqrt{a_{2,1}}+, \sqrt{a_{2,1}}+i\infty), \quad Z_{i\nu} = H_2^{(1)},$$
$$L_{3,4} = (\sqrt{a_{2,1}}-i\infty, \sqrt{a_{2,1}}+, \sqrt{a_{2,1}}-i\infty), \quad Z_{i\nu} = H_2^{(2)}. \tag{43}$$

As in paper I we modify the integrals of Eq. (2) using analytical continuation of the functions $W_{5,m}(z)$ in the neighborhood of $z=0$ for the contours L_1 and L_3 and analytical continuation in the neighborhood of $z=1$ for the contours L_2 and L_4 (see Ref. [26]). Considering the case when both of two adiabatic channels are open at $\rho\to\infty$, i.e., the condition

$$a_2 > a_1 > 0 \tag{44}$$

is satisfied, we get the following four independent solutions of the problem:

$$\boldsymbol{\psi}^{(n)}(\rho) = \boldsymbol{\psi}^{(n)}(r_0,s_0,\rho) + c_E \boldsymbol{\psi}^{(n)}(r_1,s_1,\rho), \quad n=1,\ldots,4, \tag{45}$$

with

$$c_E = d_1 \frac{2-i\mu}{4(1+i\mu)} = \frac{\beta_1-\beta_2+2i}{a_2-a_1}\frac{2-i\mu}{4(1+i\mu)}, \tag{46}$$

where we use the following definitions:

$$\psi_1^{(1,3)}(r,s,\rho) = c(r,s)\left(-\frac{H_2^{(1,2)}(\sqrt{a_2}\rho)}{\sqrt{a_2}} + \frac{2rs}{a_2-a_1}a_2^{1/2}\int_{\sqrt{a_2}}^{\infty} p^{-1} \times {}_2F_1(1-r,1-s,2,z)H_2^{(1,2)}(p\rho)dp\right), \tag{47}$$

$$\psi_2^{(1,3)}(r,s,\rho) = c(r,s)\left(\sqrt{a_2}H_2^{(1,2)}(\sqrt{a_2}\rho) - \frac{2rs}{a_2-a_1}a_2^{1/2}\int_{\sqrt{a_2}}^{\infty} p \times {}_2F_1(1-r,1-s,2,z)H_2^{(1,2)}(p\rho)dp\right) + \beta_1\psi_1^{(1,3)}, \tag{48}$$

$$\psi_1^{(2,4)}(r,s,\rho) = e^{i\pi r}c(r,s)\left(-\frac{H_2^{(1,2)}(\sqrt{a_1}\rho)}{\sqrt{a_1}} + \frac{2rs}{a_1-a_2}a_1^{1/2}\int_{\sqrt{a_1}}^{\pm i\infty} p^{-1} \, {}_2F_1(1-r,1-s,2,1-z)H_2^{(1,2)}(p\rho)dp\right), \tag{49}$$

$$\psi_2^{(2,4)}(r,s,\rho) = e^{i\pi r}c(r,s)\left[\sqrt{a_1}H_2^{(1,2)}(\sqrt{a_1}\rho) - \frac{2rs}{a_1-a_2}a_1^{1/2}\int_{\sqrt{a_1}}^{\pm i\infty} p \, {}_2F_1(1-r,1-s,2,1-z)H_2^{(1,2)}(p\rho)dp\right] + \beta_1\psi_1^{(2,4)}, \tag{50}$$

$$c(r,s) = \frac{\Gamma(1+r-s)}{\Gamma(1-s)\Gamma(1+r)}. \tag{51}$$

The general solution will be used below in the form

$$\boldsymbol{\psi}(\rho) = C_1\boldsymbol{\psi}^{(1)}(\rho) + C_2\boldsymbol{\psi}^{(2)}(\rho) + C_3\boldsymbol{\psi}^{(3)}(\rho) + C_4\boldsymbol{\psi}^{(4)}(\rho). \tag{52}$$

V. ASYMPTOTIC BEHAVIOR OF SOLUTIONS

A. Asymptotic behavior at $\rho\to 0$

We found the asymptotic form of the basis set $\boldsymbol{\psi}^{(n)}(\rho)$ at $\rho\to 0$ using the methodology of paper I. For this we isolate the singularity $\mp 4i/\pi x^2$ of the Hankel functions $H_2^{(1,2)}(x)$,

$$H_2^{(1,2)}(x) = \mp\frac{4i}{\pi x^2} + \tilde{H}_2^{(1,2)}(x). \tag{53}$$

The behavior of the function $\tilde{H}_2^{(1,2)}(x)$ at $x\to 0$ is given by (see Ref. [27])

$$\tilde{H}_2^{(1,2)}(x) = \mp\frac{i}{\pi} + \frac{1}{16}\frac{2\pi \pm i[4\ln(x/2)+4\gamma-3]}{\pi}x^2 + O(x^4), \quad x\to 0. \tag{54}$$

The singular term $4i/\pi x^2$ of the Hankel function expansion generates the singularity of amplitudes (47)–(50) at $\rho\to 0$ and the constant term i/π results in nonphysical behavior of the first channel amplitudes. The contributions of these two terms to the basis set (45) at $\rho\to 0$ are expressed in terms of the following functions:

$$I(r,s) = \tilde{c}(r,s)\sqrt{a_2}\left(\frac{a_1-a_2}{a_2} + 2rs\int_{\sqrt{a_2}}^{\infty} {}_2F_1(1-r,1-s,2,z)\frac{dp}{p}\right), \tag{55}$$

$$\tilde{I}(r,s) = \tilde{c}(r,s)\sqrt{a_2}\left(\frac{a_2-a_1}{a_2^2} - 2rs\int_{\sqrt{a_2}}^{\infty} {}_2F_1(1-r,1 - s,2,z)\frac{dp}{p^3}\right), \tag{56}$$

$$J(r,s) = -\tilde{c}(r,s)\sqrt{a_1}e^{i\pi r}\left(\frac{a_2-a_1}{a_1} + 2rs\int_{\sqrt{a_1}}^{i\infty} {}_2F_1(1-r,1 - s,2,1-z)\frac{dp}{p}\right), \tag{57}$$

$$\tilde{J}(r,s) = -\tilde{c}(r,s)\sqrt{a_1}e^{i\pi r}\left(\frac{a_1-a_2}{a_1^2} - 2rs\int_{\sqrt{a_1}}^{i\infty} {}_2F_1(1-r,1 - s,2,1-z)\frac{dp}{p^3}\right), \tag{58}$$

$$K(r,s) = \tilde{c}(r,s)\sqrt{a_1}e^{i\pi r}\left(\frac{a_2-a_1}{a_1} + 2rs\int_{\sqrt{a_1}}^{-i\infty} {}_2F_1(1-r,1-s,2,1 - z)\frac{dp}{p}\right), \tag{59}$$

$$\tilde{K}(r,s) = \tilde{c}(r,s)\sqrt{a_1}e^{i\pi r}\left(\frac{a_1-a_2}{a_1^2} - 2rs\int_{\sqrt{a_1}}^{-i\infty} {}_2F_1(1-r,1-s,2,1 - z)\frac{dp}{p^3}\right), \tag{60}$$

where

$$\tilde{c}(r,s) = c(r,s)\frac{4i}{\pi(a_2-a_1)}. \tag{61}$$

With the definitions

$$I = I(r_0,s_0) + c_E I(r_1,s_1), \tag{62}$$

$$\tilde{I} = \tilde{I}(r_0,s_0) + c_E \tilde{I}(r_1,s_1), \tag{63}$$

$$J = J(r_0,s_0) + c_E J(r_1,s_1), \tag{64}$$

$$\tilde{J} = \tilde{J}(r_0,s_0) + c_E \tilde{J}(r_1,s_1), \tag{65}$$

$$K = K(r_0,s_0) + c_E K(r_1,s_1), \tag{66}$$

$$\tilde{K} = \tilde{K}(r_0,s_0) + c_E \tilde{K}(r_1,s_1), \tag{67}$$

we get the singular contributions to the basis set in the form

$$\begin{pmatrix}\psi_{s,1}^{(1)}\\ \psi_{s,2}^{(1)}\end{pmatrix} = \begin{pmatrix}\frac{1}{\rho^2}\tilde{I}\\ \frac{1}{\rho^2}I + \beta_1\psi_{s,1}^{(1)}\end{pmatrix}, \tag{68}$$

$$\begin{pmatrix}\psi_{s,1}^{(3)}\\ \psi_{s,2}^{(3)}\end{pmatrix} = \begin{pmatrix}-\frac{1}{\rho^2}\tilde{I}\\ -\frac{1}{\rho^2}I + \beta_1\psi_{s,1}^{(3)}\end{pmatrix}, \tag{69}$$

$$\begin{pmatrix}\psi_{s,1}^{(2)}\\ \psi_{s,2}^{(2)}\end{pmatrix} = \begin{pmatrix}\frac{1}{\rho^2}\tilde{J}\\ \frac{1}{\rho^2}J + \beta_1\psi_{s,1}^{(2)}\end{pmatrix}, \tag{70}$$

$$\begin{pmatrix}\psi_{s,1}^{(4)}\\ \psi_{s,2}^{(4)}\end{pmatrix} = \begin{pmatrix}\frac{1}{\rho^2}\tilde{K}\\ \frac{1}{\rho^2}K + \beta_1\psi_{s,1}^{(4)}\end{pmatrix} \tag{71}$$

and the constant contributions to the first state functions in the form

$$\psi_{\tilde{s},1}^{(1)} = -\frac{1}{4}I, \quad \psi_{\tilde{s},1}^{(3)} = \frac{1}{4}I, \quad \psi_{\tilde{s},1}^{(2)} = -\frac{1}{4}J, \quad \psi_{\tilde{s},1}^{(4)} = -\frac{1}{4}K. \tag{72}$$

The regular behavior at $\rho \to 0$ of the second channel amplitudes is determined by the $\tilde{H}_2^{(1,2)}(x)$ contributions to Eqs. (47)–(50). In evaluating the regular terms we will use the following definitions:

$$I_r^{(1,2)}(r,s) = c(r,s)\frac{\sqrt{a_2}}{a_2-a_1}\left((a_2-a_1)\tilde{H}_2^{(1,2)}(\sqrt{a_2}\rho) - 2rs\int_{\sqrt{a_2}}^{\infty} {}_2F_1(1-r,1-s,2,z)\tilde{H}_2^{(1,2)}(p\rho)p\, dp\right), \tag{73}$$

$$J_r(r,s) = e^{i\pi r}c(r,s)\frac{\sqrt{a_1}}{a_1-a_2}\left((a_1-a_2)\tilde{H}_2^{(1)}(\sqrt{a_1}\rho) - 2rs\int_{\sqrt{a_1}}^{i\infty} {}_2F_1(1-r,1-s,2,1-z)\tilde{H}_2^{(1)}(p\rho)p\, dp\right), \tag{74}$$

$$K_r(r,s) = e^{i\pi r}c(r,s)\frac{\sqrt{a_1}}{a_1-a_2}\left((a_1-a_2)\tilde{H}_2^{(2)}(\sqrt{a_1}\rho) - 2rs\int_{\sqrt{a_1}}^{-i\infty} {}_2F_1(1-r,1-s,2,1-z)\tilde{H}_2^{(2)}(p\rho)p\, dp\right), \tag{75}$$

and

$$I_r^{(1,2)} = I_r^{(1,2)}(r_0,s_0) + c_E I_r^{(1,2)}(r_1,s_1), \tag{76}$$

$$J_r = J_r(r_0,s_0) + c_E J_r(r_1,s_1), \tag{77}$$

$$K_r = K_r(r_0,s_0) + c_E K_r(r_1,s_1). \tag{78}$$

Combining the singular and regular parts, we get

$$\psi_1^{(1)} = \frac{1}{\rho^2}\tilde{I} - \frac{1}{4}I + O(\rho^2 \ln \rho), \quad \psi_2^{(1)} = \frac{1}{\rho^2}I + \beta_1\psi_1^{(1)} + I_r^{(1)}, \tag{79}$$

$$\psi_1^{(3)} = -\frac{1}{\rho^2}\tilde{I} + \frac{1}{4}I + O(\rho^2 \ln \rho), \quad \psi_2^{(3)} = -\frac{1}{\rho^2}I + \beta_1\psi_1^{(3)} + I_r^{(2)}, \tag{80}$$

$$\psi_1^{(2)} = \frac{1}{\rho^2}\tilde{J} - \frac{1}{4}J + O(\rho^2 \ln \rho), \quad \psi_2^{(2)} = \frac{1}{\rho^2}J + \beta_1\psi_1^{(2)} + J_r, \tag{81}$$

$$\psi_1^{(4)} = \frac{1}{\rho^2}\tilde{K} - \frac{1}{4}K + O(\rho^2 \ln \rho), \quad \psi_2^{(4)} = \frac{1}{\rho^2}K + \beta_1\psi_1^{(4)} + K_r. \tag{82}$$

The integral calculation (see Appendix B) gives

$$I = C_{sc}\Bigg[4(-2-\mu i + a_1\mu)(a_2-a_1)\sqrt{a_1}\,{}_2F_1\left(\frac{i\mu}{2},\ -\frac{i\mu}{2},\ 2,\ -\frac{a_1}{a_2-a_1}\right) + i\mu(-\mu i + \mu a_2 - 2)a_1^{3/2}\,{}_2F_1\left(1+\frac{i\mu}{2},\ 1-\frac{i\mu}{2},\ 3,\ -\frac{a_1}{a_2-a_1}\right)\Bigg],$$

$$\tilde{I} = -\frac{I}{\beta_1}, \tag{83}$$

$$J = C_{sc}\Bigg[4(-\mu i + \mu a_2 - 2)(a_2-a_1)\sqrt{a_2}e^{-\pi\mu/2}\,{}_2F_1\left(\frac{i\mu}{2},\ -\frac{i\mu}{2},\ 2,\ \frac{a_2}{a_2-a_1}\right)_+ - i\mu(-2-\mu i + a_1\mu)\,e^{-\pi\mu/2}a_2^{3/2}\,{}_2F_1\left(1+\frac{i\mu}{2},\ 1-\frac{i\mu}{2},\ 3,\ \frac{a_2}{a_2-a_1}\right)_+\Bigg],$$

$$\tilde{J} = -\frac{J}{\beta_1}, \tag{84}$$

$$K = C_{sc}\Bigg[-4(-\mu i + \mu a_2 - 2)(a_2-a_1)\sqrt{a_2}e^{-\pi\mu/2}\,{}_2F_1\left(\frac{i\mu}{2},\ -\frac{i\mu}{2},\ 2,\ \frac{a_2}{a_2-a_1}\right)_- + i\mu(-2-\mu i + a_1\mu)\,e^{-\pi\mu/2}a_2^{3/2}\,{}_2F_1\left(1+\frac{i\mu}{2},\ 1-\frac{i\mu}{2},\ 3,\ \frac{a_2}{a_2-a_1}\right)_-\Bigg],$$

$$\tilde{K} = -\frac{K}{\beta_1}, \tag{85}$$

with

$$C_{sc} = -\frac{i(\mu+2i)\Gamma(\mu i)}{\mu\sqrt{a_1 a_2}(a_2-a_1)^2\sinh(\pi\mu/2)\Gamma^2(i\mu/2)}. \tag{86}$$

The argument of the hypergeometric functions in the expressions for J and K, $a_2/(a_2-a_1)$, is greater than unity. The indices $\pm$ in Eqs. (84) and (85) designate the upper and lower sides of the complex plane cut drawn from unity to $+\infty$.

Finally, the behavior of the basis set diabatic amplitudes (45) at $\rho\to 0$ is given by the following expressions:

$$\psi_1^{(1)} = -\left(\frac{1}{\beta_1\rho^2} + \frac{1}{4}\right)I + O(\rho^2 \ln \rho), \quad \psi_2^{(1)} = I_r^{(1)} - \frac{\beta_1}{4}I, \tag{87}$$

$$\psi_1^{(3)} = \left(\frac{1}{\beta_1\rho^2} + \frac{1}{4}\right)I + O(\rho^2 \ln \rho), \quad \psi_2^{(3)} = I_r^{(2)} + \frac{\beta_1}{4}I, \tag{88}$$

$$\psi_1^{(2)} = -\left(\frac{1}{\beta_1\rho^2} + \frac{1}{4}\right)J + O(\rho^2 \ln \rho), \quad \psi_2^{(2)} = J_r - \frac{\beta_1}{4}J, \tag{89}$$

$$\psi_1^{(4)} = -\left(\frac{1}{\beta_1\rho^2} + \frac{1}{4}\right)K + O(\rho^2 \ln \rho), \quad \psi_2^{(4)} = K_r - \frac{\beta_1}{4}K, \tag{90}$$

where the asymptotic behavior of the basis set's regular parts $I_r^{(1)}$, J_r, $I_r^{(2)}$, and K_r is given by (see Appendix C)

$$I_r^{(1)} = r_1^-\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{i\mu} + r_1^+\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{-i\mu}, \tag{91}$$

$$J_r = r_2^-\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{i\mu} + r_2^+\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{-i\mu}, \tag{92}$$

$$I_r^{(2)} = r_3^-\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{i\mu} + r_3^+\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{-i\mu}, \tag{93}$$

$$K_r = r_4^-\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{i\mu} + r_4^+\frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{-i\mu} \tag{94}$$

with

$$r_1^- = \frac{4\sqrt{a_2}e^{\pi\mu/2}2^{i\mu}(a_2-a_1)^{i\mu/2}}{\sqrt{\mu}\sinh(\pi\mu)(\mu-2i)\Gamma^2(i\mu/2)}, \tag{95}$$

$$r_1^+ = -\frac{d_1\sqrt{\mu a_2}e^{-\pi\mu/2}2^{i\mu}\Gamma^2(i\mu/2+1/2)(a_2-a_1)^{-i\mu/2}}{(\mu-2i)\pi^2}, \tag{96}$$

$$r_2^- = -\frac{\sqrt{a_1}e^{(-\pi\mu)}}{\sqrt{a_2}}r_1^-, \tag{97}$$

$$r_3^- = -e^{(-\pi\mu)}r_1^-, \tag{98}$$

$$r_4^- = \frac{\sqrt{a_1}e^{(-\pi\mu)}}{\sqrt{a_2}}r_1^-, \tag{99}$$

$$r_2^+ = \frac{\sqrt{a_1}}{\sqrt{a_2}}r_1^+, \tag{100}$$

$$r_3^+ = -e^{(\pi\mu)}r_1^+, \tag{101}$$

$$r_4^+ = -\frac{\sqrt{a_1}}{\sqrt{a_2}}r_1^+. \tag{102}$$

It follows from Eqs. (87)–(90) that the basic condition for the solution to have physical meaning has the form

$$(C_1 - C_3)I + C_2 J + C_4 K = 0. \tag{103}$$

B. Asymptotic behavior at $\rho \to \infty$

The asymptotic form of the basis set at $\rho \to \infty$ is obtained from the first term in large parentheses of Eqs. (47)–(50) as

$$\psi_1^{(1)} = D_2 \frac{e^{i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{104}$$

$$\psi_2^{(1)} = D_2(\beta_1 - a_2)\frac{e^{i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{105}$$

$$\psi_1^{(2)} = -D_1 \frac{e^{i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \tag{106}$$

$$\psi_2^{(2)} = -D_1(\beta_1 - a_1)\frac{e^{i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \tag{107}$$

$$\psi_1^{(3)} = -D_2 \frac{e^{-i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{108}$$

$$\psi_2^{(3)} = -D_2(\beta_1 - a_2)\frac{e^{-i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{109}$$

$$\psi_1^{(4)} = D_1 \frac{e^{-i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \tag{110}$$

$$\psi_2^{(4)} = D_1(\beta_1 - a_1)\frac{e^{-i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \tag{111}$$

where

$$D_1 = \frac{2(2i - \mu - 4ic_E + 4c_E\mu)\Gamma(\mu i)\exp(-\pi\mu/2)}{\Gamma^2(i\mu/2)\mu(\mu - 2i)}\sqrt{\frac{2}{\pi a_1}},$$

$$D_2 = \frac{2(2i - \mu + 4ic_E - 4c_E\mu)\Gamma(\mu i)}{\Gamma^2(i\mu/2)\mu(\mu - 2i)}\sqrt{\frac{2}{\pi a_2}}. \tag{112}$$

VI. N-MATRIX EVALUATION

To calculate the N matrix we change the diabatic basis set to the adiabatic one by the rotation

$$\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix} = \boldsymbol{R}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}. \tag{113}$$

The matrix $\boldsymbol{R}$ diagonalizes the potential of the Eq. (1) and is given by the expression

$$\boldsymbol{R} = \begin{pmatrix}\cos g, & -\sin g\\ \sin g, & \cos g\end{pmatrix}, \tag{114}$$

where

$$\tan 2g = \frac{2Ve^{-\alpha x}}{U_2 - U_1 - (V_2 - V_1)e^{-\alpha x}}. \tag{115}$$

The asymptotic amplitudes of the normalized incoming and outgoing adiabatic waves are related by the N matrix.

At $\rho \to 0$ the angle $g=0$ and adiabatic amplitudes coincide with the diabatic ones. At $\rho \to \infty$ we have

$$\cos g = \sqrt{\frac{-\beta_1 + a_2}{a_2 - a_1}}, \tag{116}$$

$$\sin g = -\sqrt{\frac{-a_1 + \beta_1}{a_2 - a_1}}, \tag{117}$$

and as a consequence

$$\varphi_1^{(1)} = 0, \quad \varphi_2^{(1)} = l_2^+ \frac{e^{i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{118}$$

$$\varphi_1^{(2)} = l_1^+ \frac{e^{i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \quad \varphi_2^{(2)} = 0, \tag{119}$$

$$\varphi_1^{(3)} = 0, \quad \varphi_2^{(3)} = l_2^- \frac{e^{-i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \tag{120}$$

$$\varphi_1^{(4)} = l_1^- \frac{e^{-i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}}, \quad \varphi_2^{(4)} = 0, \tag{121}$$

where

$$l_2^+ = \frac{D_2}{\sin g}, \quad l_1^+ = D_1(a_2 - a_1)\sin g, \quad l_2^- = -l_2^+, \quad l_1^- = -l_1^+. \tag{122}$$

It can be shown that

$$\frac{l_2^+}{l_1^+} = i\sqrt{\frac{a_2}{a_1}}e^{\pi\mu/2}. \tag{123}$$

The general physical solution in the adiabatic representation has the following asymptotic behavior at $\rho \to 0$:

$$\varphi_1 = 0, \quad \varphi_2 = a_1^+ \frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{-i\mu} + a_1^- \frac{1}{\sqrt{\mu}}\left(\frac{\rho}{4}\right)^{+i\mu}, \quad \rho \to 0, \tag{124}$$

and at $\rho \to \infty$

$$\varphi_1 = a_3^+ \frac{e^{+i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}} + a_3^- \frac{e^{-i(\sqrt{a_1}\rho+\pi/4)}}{\sqrt{\sqrt{a_1}\rho}},$$

$$\varphi_2 = a_2^+ \frac{e^{+i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}} + a_2^- \frac{e^{-i(\sqrt{a_2}\rho+\pi/4)}}{\sqrt{\sqrt{a_2}\rho}}, \quad \rho \to \infty. \tag{125}$$

Taking the N-matrix definition

$$\begin{pmatrix} a_1^+ \\ a_2^+ \\ a_3^+ \end{pmatrix} = N \begin{pmatrix} a_1^- \\ a_2^- \\ a_3^- \end{pmatrix}, \tag{126}$$

and using the relations

$$a_1^- = C_1 r_1^- + C_2 r_2^- + C_3 r_3^- + C_4 r_4^-,$$

$$a_1^+ = C_1 r_1^+ + C_2 r_2^+ + C_3 r_3^+ + C_4 r_4^+,$$

$$a_2^- = C_3 l_2^-,$$

$$a_3^- = C_4 l_1^-,$$

$$a_2^+ = C_1 l_2^+,$$

$$a_3^+ = C_2 l_1^+, \tag{127}$$

which follow from Eqs. (52), (87)–(94), and (118)–(121) and condition (103), we finally obtain

$$N_{11} = -\frac{r_1^+(I\sqrt{a_1} - J\sqrt{a_2})}{r_1^-(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{128}$$

$$N_{12} = \frac{r_1^+ J\sqrt{a_2}(-e^{-\pi\mu} + e^{\pi\mu})}{l_2^+(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{129}$$

$$N_{21} = \frac{l_2^+ J\sqrt{a_2}}{r_1^-(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{130}$$

$$N_{22} = -\frac{e^{-\pi\mu}(J\sqrt{a_2} + I\sqrt{a_1})}{I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2}}, \tag{131}$$

$$N_{13} = \frac{r_1^+\sqrt{a_1}(e^{-\pi\mu}+1)(J+K)}{l_1^+(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{132}$$

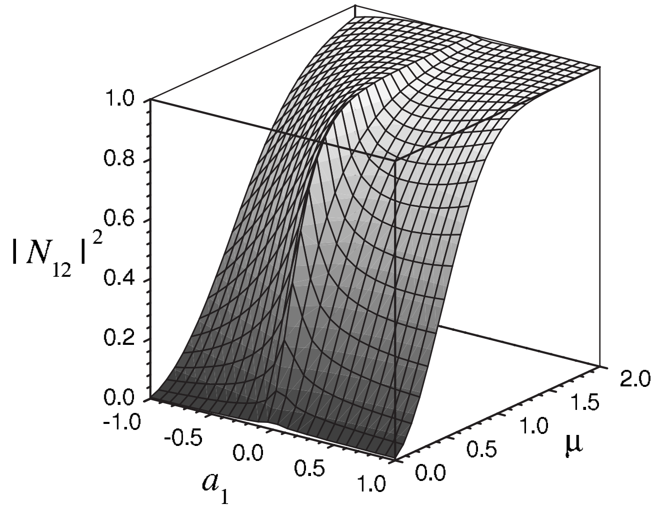

FIG. 1. Probability of transition between channels 1 and 2.

$$N_{31} = -\frac{l_1^+ I\sqrt{a_2}}{r_1^-(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{133}$$

$$N_{32} = \frac{l_1^+ I(e^{-\pi\mu} - 1)\sqrt{a_2}}{l_2^+(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{134}$$

$$N_{23} = \frac{l_2^+\sqrt{a_1}e^{-\pi\mu}(J+K)}{l_1^+(I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2})}, \tag{135}$$

$$N_{33} = -\frac{I\sqrt{a_1}e^{-\pi\mu} - K\sqrt{a_2}}{I\sqrt{a_1}e^{-\pi\mu} + J\sqrt{a_2}}. \tag{136}$$

The N matrix is unitary and symmetric. The symmetry proof is given in Appendix D.

In the physical case, when channel 3 is closed, the value of a_1 is negative. It can be shown that in this case the correct 2×2 N matrix is also given by matrix elements (128)–(131) when the negative variable a_1 is replaced by $|a_1|\exp(+i\pi)$.

The shapes of the N_{12}, N_{13}, and N_{23} surfaces above the plane (μ, a_1) are depicted in Figs. 1–3. All of the N-matrix elements have a singularity along the line $a_1=0$. The behavior of N_{23} is given by the following limit:

$$\lim_{a_1\to 0} N_{23} = \frac{2\pi}{\ln\dfrac{2a_1\mu}{\mu^2+4}}e^{-\pi\mu/2}. \tag{137}$$

VII. CONCLUSION

The energy spectrum and solutions to the exponential Nikitin model as contour Bessel integrals of hypergeometric function finite series are the main results of this work. The levels obtained coincide with the inverted spectrum of the infinite potential box, the size of which is determined by the model characteristic length. The solution for the first level has been considered in Ref. [16]. Here we have found the

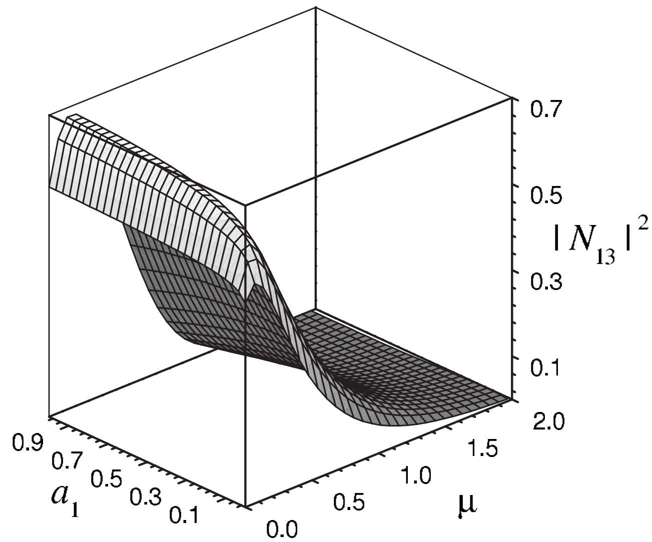

FIG. 2. Probability of transition between channels 1 and 3.

closed expression of the N matrix for the second level and the Bessel representation of the solutions for the third and fourth levels.

The general exponential Nikitin model contains four dimensionless parameters. In the present paper, we demonstrate a method aimed at the exact solution to basic equations when these parameters are subject to two conditions that depend on the level number and vary along the spectrum. The results obtained can be used for a large number of physical situations by applying the proper N-matrix parametrization. In particular, the N-matrix analytical representation as a function of two physical variables—the momentum μ in the lower channel at $x\to\infty$ and the adiabatic potential amplitude a_1 in the upper channel at $x\to-\infty$—can be conveniently applied to similar problems. In these coordinates, the N surface has a singularity along the line dividing attractive and repulsive upper state potentials. Upon a normal approach to this line, the system undergoes a three-channel–two-channel transformation and the N-matrix amplitudes show logarithmic behavior. These results are of interest if the transitions in complicated systems are studied by dimension truncation.

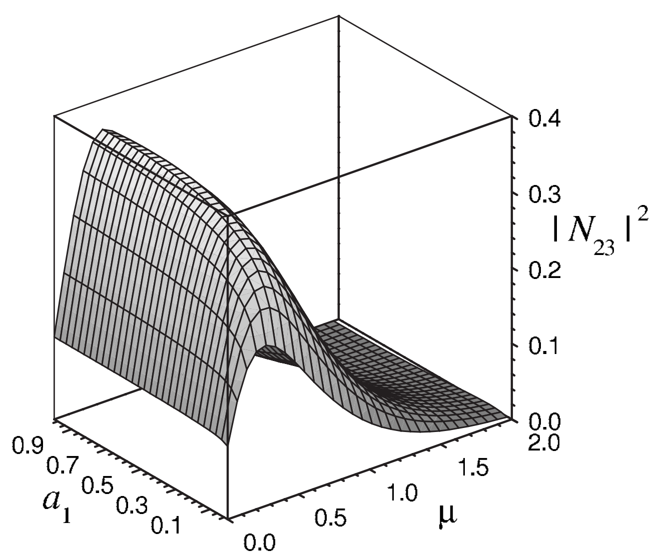

FIG. 3. Probability of transition between channels 2 and 3.

The results obtained can be applied to study the accuracy of the adiabatic approximation. For the model considered, this fundamental problem can be formulated in the low-energy range. It includes finding the Erdelyi basis set asymptotes, the asymptotic solution of the recurrence relations, and the study of convergence in the Heun function series.

We believe that the current approach will be helpful for other model studies.

APPENDIX A

1. Parameters of the Bessel representation for the third level: Three $_2F_1$ functions

In the case $k=3$ we get the equations

$$\nu=-3i, \tag{A1}$$

$$\beta_2=-\frac{1}{64}\beta_1(\mu^2+1)(\beta_1^2\mu^2+\beta_1^2-16), \tag{A2}$$

and the parameters r_0, s_0, and t_0 for the hypergeometric equation with $m=0$,

$$r_0=-\frac{3}{2}+\frac{i\mu}{2},\quad s_0=\frac{1}{2}-\frac{i\mu}{2},\quad t_0=0, \tag{A3}$$

the parameters r_1, s_1, and t_1 for the hypergeometric equation with $m=1$,

$$r_1=-\frac{1}{2}+\frac{i\mu}{2},\quad s_1=-\frac{1}{2}-\frac{i\mu}{2},\quad t_1=0, \tag{A4}$$

the parameters r_2, s_2, and t_2 for the hypergeometric equation with $m=2$,

$$r_2=\frac{1}{2}+\frac{i\mu}{2},\quad s_2=-\frac{3}{2}-\frac{i\mu}{2},\quad t_2=0, \tag{A5}$$

and solutions W_5,

$$W_{5,m=0}=x^{3/2-i\mu/2}\,{}_2F_1\left(-\frac{1}{2}+\frac{i\mu}{2},\ -\frac{3}{2}+\frac{i\mu}{2},\ -1+i\mu,\ \frac{1}{z}\right), \tag{A6}$$

$$W_{5,m=1}=\frac{i(3-i\mu)}{4\mu}x^{1/2-i\mu/2}\times{}_2F_1\left(\frac{1}{2}+\frac{i\mu}{2},\ -\frac{1}{2}+\frac{i\mu}{2},\ 1+i\mu,\ \frac{1}{z}\right), \tag{A7}$$

$$W_{5,m=2}=\frac{i(3-i\mu)(i\mu-1)}{16\mu(2+i\mu)}x^{-1/2-i\mu/2}\times{}_2F_1\left(\frac{3}{2}+\frac{i\mu}{2},\ \frac{1}{2}+\frac{i\mu}{2},\ 3+i\mu,\ \frac{1}{z}\right), \tag{A8}$$

$$H(\zeta) = W_{5,m=0} + d_1 W_{5,m=1} + d_2 W_{5,m=2}. \tag{A9}$$

The coefficients d_1 and d_2 are obtained in the form

$$d_1 = \frac{-i(Q\mu + 2i - 3iQ + 2iA)\mu}{(-i+\mu)(A-1)}, \tag{A10}$$

$$d_2 = \frac{1}{2}[-\mu(3i+\mu)(\mu-3i)^2Q^2 - 2i\mu(\mu-3i) \times(\mu+5i)(1+A)Q + 2(A-1)^2(i+\mu)^2 + 32iA\mu]/[(-i+\mu)(i+\mu)(A-1)^2] \tag{A11}$$

with

$$A = a_1/a_2, \quad Q = \beta_1/a_2. \tag{A12}$$

2. Parameters of the Bessel representation for the fourth level: Four $_2F_1$ functions

In this case we set $k=4$ and get the following equations:

$$\nu = -4i, \tag{A13}$$

$$\beta_2 = \frac{1}{48}\beta_1(4+\mu^2)(4 \mp \beta_1\mu) \pm \frac{1}{4}\mu, \tag{A14}$$

parameters

$$r_0 = -2 + \frac{i\mu}{2}, \quad s_0 = 1 - \frac{i\mu}{2}, \quad t_0 = 0, \tag{A15}$$

$$r_1 = -1 + \frac{i\mu}{2}, \quad s_1 = -\frac{i\mu}{2}, \quad t_1 = 0, \tag{A16}$$

$$r_2 = \frac{i\mu}{2}, \quad s_2 = -1 - \frac{i\mu}{2}, \quad t_2 = 0, \tag{A17}$$

$$r_3 = 1 + \frac{i\mu}{2}, \quad s_3 = -2 - \frac{i\mu}{2}, \quad t_3 = 0, \tag{A18}$$

and solutions

$$W_{5,m=0} = x^{2-i\mu/2}\, {}_2F_1\left(-1 + \frac{i\mu}{2},\ -2 + \frac{i\mu}{2},\ -2 + i\mu,\ \frac{1}{z}\right), \tag{A19}$$

$$W_{5,m=1} = \frac{4-i\mu}{4(1-i\mu)}x^{1-i\mu/2}\, {}_2F_1\left(\frac{i\mu}{2},\ -1 + \frac{i\mu}{2},\ i\mu,\ \frac{1}{z}\right), \tag{A20}$$

$$W_{5,m=2} = \frac{(4-i\mu)(i\mu-2)}{16(1+\mu^2)}x^{-i\mu/2} \times {}_2F_1\left(1 + \frac{i\mu}{2},\ \frac{i\mu}{2},\ 2 + i\mu,\ \frac{1}{z}\right), \tag{A21}$$

$$W_{5,m=3} = \frac{i\mu(4-i\mu)(i\mu-2)}{64(3+i\mu)(1+\mu^2)}x^{-1-i\mu/2} \times {}_2F_1\left(2 + \frac{i\mu}{2},\ 1 + \frac{i\mu}{2},\ 4 + i\mu,\ \frac{1}{z}\right), \tag{A22}$$

$$H(\zeta) = W_{5,m=0} + d_1 W_{5,m=1} + d_2 W_{5,m=2} + d_3 W_{5,m=3}. \tag{A23}$$

Here the coefficients d_1, d_2, and d_3 are obtained in the form

$$d_1 = \frac{(-i\mu Q - 4Q + 3 + 3A)(\mu + i)}{(A-1)(\mu - i)}, \tag{A24}$$

$$d_2 = \frac{1}{2}[(i+\mu)(16+\mu^2)(4i-\mu)Q^2 - 4i(1+A)(\mu+5i)(i+\mu) \times(\mu-4i)Q + 12i(5\mu+4i)A + 6(2i+\mu)^2(1+A^2)]/[(4 + \mu^2)(A-1)^2], \tag{A25}$$

$$d_3 = \frac{1}{6}[i(1+\mu^2)(16+\mu^2)^2(4i-\mu)Q^3 + (1+A)(1+\mu^2)(16 + \mu^2)(3\mu+28i)(\mu-4i)Q^2 + 2i(3\mu^3 + 24i\mu^2 - 78\mu + 96i - 8\mu^3A + 50i\mu^2A - 260\mu A + 320iA + 3\mu^3A^2 + 24iA^2\mu^2 - 78\mu A^2 + 96iA^2)(\mu-4i)(i+\mu)Q + 12(i+\mu) \times(1+A)(2\mu^2 + 11i\mu + 16)(\mu-4i)A - 6\mu(i+\mu)(2i + \mu)^2(1+A)(1+A^2)]/[\mu(4+\mu^2)(i-\mu)(A-1)^3]. \tag{A26}$$

APPENDIX B

Here we use the integrals

$$\int_0^\infty {}_2F_1(1-r,1-s,2,-x)dx = \frac{1}{rs}, \tag{B1}$$

$$\int_0^\infty {}_2F_1(1-r,1-s,2,-x)\frac{x\,dx}{x+c} = \frac{\Gamma(-r)\Gamma(-s)}{\Gamma(1-r-s)} \times {}_2F_1(-r,-s,1-r-s,1-c), \tag{B2}$$

$$\int_0^\infty {}_2F_1(1-r,1-s,2,-x)\frac{x\,dx}{(x+c)^2} = \frac{\Gamma(1-r)\Gamma(1-s)}{\Gamma(2-r-s)} \times {}_2F_1(1-r,1-s,2-r-s,1-c), \tag{B3}$$

and the relations

$$r + s = r_0 + s_0 = r_1 + s_1 = -1. \tag{B4}$$

For calculating I and $\tilde{I}$, we use the transformations

$$x = -z = \frac{p^2 - a_2}{a_2 - a_1},$$

$$\frac{dp}{p} = \frac{1}{2}\frac{dx}{x+c} = \frac{1}{2c}\left(1 - \frac{x}{x+c}\right)dx,$$

$$\frac{dp}{p^3} = \frac{1}{2(a_2-a_1)}\frac{dx}{(x+c)^2} = \frac{1}{c(a_2-a_1)}\left(\frac{dp}{p} - \frac{x\,dx}{2(x+c)^2}\right), \tag{B5}$$

with

$$c = \frac{a_2}{a_2-a_1} > 0, \tag{B6}$$

and for calculating J, $\tilde{J}$, K, and $\tilde{K}$, we use

$$x = -1 + z = \frac{p^2-a_1}{a_1-a_2},$$

$$\frac{dp}{p} = \frac{1}{2}\frac{dx}{x+c} = \frac{1}{2c}\left(1 - \frac{x}{x+c}\right)dx,$$

$$\frac{dp}{p^3} = \frac{1}{2(a_1-a_2)}\frac{dx}{(x+c)^2} = \frac{1}{c(a_1-a_2)}\left(\frac{dp}{p} - \frac{x\,dx}{2(x+c)^2}\right), \tag{B7}$$

with

$$c = \frac{a_1}{a_1-a_2} < 0. \tag{B8}$$

For the contour

$$p \in (\sqrt{a_1}, +i\infty) \tag{B9}$$

the singularity

$$x = -c \tag{B10}$$

is located above the integration contour in the complex plane of the variable x. We deform the contour to the line

$$x \in (0,\infty) \tag{B11}$$

and displace the singularity above this line. Thus, in this case we take

$$c = \frac{a_1}{a_1-a_2} - i\varepsilon, \quad \varepsilon > 0, \quad \varepsilon \to 0. \tag{B12}$$

For the contour

$$p \in (\sqrt{a_1}, -i\infty) \tag{B13}$$

the singularity

$$x = -c \tag{B14}$$

is located below the integration contour in the complex plane of the variable x. We deform the contour to the line

$$x \in (0,\infty) \tag{B15}$$

and displace the singularity below this line. Thus, in this case we take

$$c = \frac{a_1}{a_1-a_2} + i\varepsilon, \quad \varepsilon > 0, \quad \varepsilon \to 0. \tag{B16}$$

As a result we get the expressions in Eqs. (83)–(85).

APPENDIX C

To find the necessary integrals for the first and third solutions, we use the variable

$$x = z = \frac{p^2-a_2}{a_1-a_2}, \tag{C1}$$

and the accurate relations

$$\begin{aligned}\frac{d}{dp}{}_2F_1(-r,-s,1,x) &= \frac{2p}{a_1-a_2}\frac{d}{dx}{}_2F_1(-r,-s,1,x)\\ &= \frac{2p}{a_1-a_2} rs\,{}_2F_1(1-r,1-s,2,x).\end{aligned} \tag{C2}$$

Modifying the integral in Eq. (73),

$$\begin{aligned}&\int_{\sqrt{a_2}}^{\infty} {}_2F_1(1-r,1-s,2,x)\tilde{H}_2^{(1,2)}(p\rho)p\,dp\\ &= \frac{a_1-a_2}{2rs}\int_{\sqrt{a_2}}^{\infty}\left(\frac{d}{dp}{}_2F_1(-r,-s,1,x)\right)\tilde{H}_2^{(1,2)}(p\rho)dp\\ &= \frac{a_2-a_1}{2rs}\left(\tilde{H}_2^{(1,2)}(\sqrt{a_2}\rho) + \int_{\sqrt{a_2}}^{\infty}{}_2F_1(-r,-s,1,x)\right.\\ &\quad\left.\times\frac{d\tilde{H}_2^{(1,2)}(p\rho)}{d(p\rho)}d(p\rho)\right),\end{aligned} \tag{C3}$$

we obtain

$$\begin{aligned}I_r^{(1,2)}(r,s) = -c(r,s)\sqrt{a_2}\int_{\sqrt{a_2}}^{\infty}{}_2F_1(-a,-b,1,x)\\ \times\frac{d\tilde{H}_2^{(1,2)}(p\rho)}{d(p\rho)}d(p\rho), \quad \arg(x) = \pi.\end{aligned} \tag{C4}$$

For the second and fourth solutions, an analogous procedure with the variable

$$x = 1 - z = \frac{p^2-a_1}{a_2-a_1} \tag{C5}$$

results in the expressions

$$\begin{aligned}J_r(r,s) = -e^{i\pi r}c(r,s)\sqrt{a_1}\int_{\sqrt{a_1}}^{\infty}{}_2F_1(-r,-s,1,x)\\ \times\frac{d\tilde{H}_2^{(1)}(p\rho)}{d(p\rho)}d(p\rho), \quad \arg(x) = 0,\end{aligned} \tag{C6}$$

$$\begin{aligned}K_r(r,s) = -e^{i\pi r}c(r,s)\sqrt{a_1}\int_{\sqrt{a_1}}^{\infty}{}_2F_1(-r,-s,1,x)\\ \times\frac{d\tilde{H}_2^{(2)}(p\rho)}{d(p\rho)}d(p\rho), \quad \arg(x) = 2\pi.\end{aligned} \tag{C7}$$

To calculate the integrals in the expressions (C4), (C6), and (C7) we replace the hypergeometric function by its asymptotic value at $|x|\to\infty$:

$$ {}_2F_1(-r,-s,1,x)=\frac{\Gamma(r-s)}{\Gamma(-s)\Gamma(1+r)}w_5+\frac{\Gamma(s-r)}{\Gamma(-r)\Gamma(1+s)}w_6, $$

$$ w_5=(x^{-1}e^{i\pi})^{-r}{}_2F_1(-r,-r,1+s-r,x^{-1})\approx(x^{-1}e^{i\pi})^{-r}, $$

$$ w_6=(x^{-1}e^{i\pi})^{-s}{}_2F_1(-s,-s,1+r-s,x^{-1})\approx(x^{-1}e^{i\pi})^{-s}. \tag{C8} $$

The result is as follows:

$$ I_r^{(1,2)}(r,s)=-c(r,s)\sqrt{a_2}\int_0^\infty\left[\frac{\Gamma(r-s)}{\Gamma(-s)\Gamma(1+r)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-r}+\frac{\Gamma(s-r)}{\Gamma(-r)\Gamma(1+s)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-s}\right]\frac{d\widetilde{H}_2^{(1,2)}(y)}{dy}dy, \tag{C9} $$

$$ J_r(r,s)=-e^{i\pi r}c(r,s)\sqrt{a_1}\int_0^\infty\left[\frac{\Gamma(r-s)}{\Gamma(-s)\Gamma(1+r)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-r}e^{-i\pi r}+\frac{\Gamma(s-r)}{\Gamma(-r)\Gamma(1+s)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-s}e^{-i\pi s}\right]\frac{d\widetilde{H}_2^{(1)}(y)}{dy}dy, \tag{C10} $$

$$ K_r(r,s)=-e^{i\pi r}c(r,s)\sqrt{a_1}\int_0^\infty\left[\frac{\Gamma(r-s)}{\Gamma(-s)\Gamma(1+r)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-r}e^{+i\pi r}+\frac{\Gamma(s-r)}{\Gamma(-r)\Gamma(1+s)}\left(\frac{(a_2-a_1)\rho^2}{y^2}\right)^{-s}e^{+i\pi s}\right]\frac{d\widetilde{H}_2^{(2)}(y)}{dy}dy. \tag{C11} $$

At $\rho\to0$, only those terms of the integrals (C9)–(C11) are significant that contain the pure imaginary r or s. Using for these integrals the accurate expressions

$$ \int_0^\infty y^{i\mu}\frac{d\widetilde{H}_2^{(1)}(y)}{dy}dy=\frac{\mu^2 2^{i\mu}e^{-\pi\mu/2}\Gamma^2(i\mu/2)}{2\pi(\mu+2i)}, \tag{C12} $$

$$ \int_0^\infty y^{i\mu}\frac{d\widetilde{H}_2^{(2)}(y)}{dy}dy=-\frac{\mu^2 2^{i\mu}e^{\pi\mu/2}\Gamma^2(i\mu/2)}{2\pi(\mu+2i)}, \tag{C13} $$

we finally get

$$ I_r^{(1)}(r_0,s_0)=\frac{4\sqrt{a_2}e^{\pi\mu/2}2^{-i\mu}(a_2-a_1)^{i\mu/2}}{\mu\sinh(\pi\mu)(\mu-2i)\Gamma^2(i\mu/2)}\rho^{i\mu}, \tag{C14} $$

$$ J_r(r_0,s_0)=-\frac{\sqrt{a_1}e^{-\pi\mu}}{\sqrt{a_2}}I_r^{(1)}(r_0,s_0), \tag{C15} $$

$$ I_r^{(2)}(r_0,s_0)=-e^{-\pi\mu}I_r^{(1)}(r_0,s_0), \tag{C16} $$

$$ K_r(r_0,s_0)=\frac{\sqrt{a_1}e^{-\pi\mu}}{\sqrt{a_2}}I_r^{(1)}(r_0,s_0), \tag{C17} $$

$$ I_r^{(1)}(r_1,s_1)=\frac{16\sqrt{a_2}e^{-\pi\mu/2}2^{3i\mu}\Gamma^2(i\mu/2+3/2)}{i(1+i\mu)(4+\mu^2)\pi^2(a_2-a_1)^{i\mu/2}}\rho^{-i\mu}, \tag{C18} $$

$$ J_r(r_1,s_1)=\frac{\sqrt{a_1}}{\sqrt{a_2}}I_r^{(1)}(r_1,s_1), \tag{C19} $$

$$ I_r^{(2)}(r_1,s_1)=-e^{\pi\mu}I_r^{(1)}(r_1,s_1), \tag{C20} $$

$$ K_r(r_1,s_1)=-\frac{\sqrt{a_1}}{\sqrt{a_2}}I_r^{(1)}(r_1,s_1). \tag{C21} $$

APPENDIX D

The symmetry of the N matrix is represented by the relations:

$$ N_{12}=N_{21}\Rightarrow(e^{\pi\mu}-e^{-\pi\mu})r_1^-r_1^+-(l_2^+)^2=0, \tag{D1} $$

$$ N_{13}=N_{31}\Rightarrow\sqrt{a_1}(e^{-\pi\mu}+1)(J+K)r_1^-r_1^++(l_1^+)^2I\sqrt{a_2}=0, \tag{D2} $$

$$ N_{23}=N_{32}\Rightarrow I(e^{-\pi\mu}-1)\sqrt{a_2}(l_1^+)^2-(J+K)e^{-\pi\mu}(l_2^+)^2\sqrt{a_1}=0. \tag{D3} $$

These three equations are mutually dependent. Equation (D2) is a combination of Eqs. (D1) and (D3). The proof of Eq. (D1) is straightforward. To check Eq. (D3) we have to calculate the sum $J+K$. This sum contains the difference between hypergeometric functions on the upper and lower sides of the complex plane cut. To calculate the difference we use the analytical continuation of the hypergeometric functions in the vicinity of unity (see [26]).

At

$$ z>1,\quad \varepsilon\to0, \tag{D4} $$

we get

$$ {}_2F_1\left(\frac{i\mu}{2},\ -\frac{i\mu}{2},\ 2,\ z+i\varepsilon\right) - {}_2F_1\left(\frac{i\mu}{2},\ -\frac{i\mu}{2},\ 2,\ z-i\varepsilon\right) = \frac{i\pi(1-z)^2\ {}_2F_1(2+i\mu/2,\ 2-i\mu/2,\ 3,\ 1-z)}{\Gamma(-i\mu/2)\Gamma(i\mu/2)} \tag{D5} $$

and

$$ {}_2F_1\left(1+\frac{i\mu}{2},\ 1-\frac{i\mu}{2},\ 3,\ z+i\varepsilon\right) - {}_2F_1\left(1+\frac{i\mu}{2},\ 1-\frac{i\mu}{2},\ 3,\ z-i\varepsilon\right) = \frac{-4i\pi(1-z)\ {}_2F_1(2+i\mu/2,\ 2-i\mu/2,\ 2,\ 1-z)}{\Gamma(1-i\mu/2)\Gamma(1+i\mu/2)}. \tag{D6} $$

Further simplification is possible:

$$ {}_2F_1(2+i\mu/2,\ 2-i\mu/2,\ 2,\ z) = \frac{{}_2F_1(i\mu/2,\ -i\mu/2,\ 2,\ z)}{(1-z)^2}, \tag{D7} $$

$$ {}_2F_1(2+i\mu/2,\ 2-i\mu/2,\ 3,\ z) = \frac{{}_2F_1(1+i\mu/2,\ 1-i\mu/2,\ 3,\ z)}{1-z}. \tag{D8} $$

Finally we get

$$ J+K = I\sqrt{\frac{a_1}{a_2}}(1-e^{-\pi\mu}). \tag{D9} $$

Using this expression and Eq. (123), the proof of Eq. (D3) is straightforward.

[1] M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).
[2] E. E. Nikitin and S. Y. Umanskii, *Theory of Slow Atomic Collision* (Springer, Berlin, 1984).
[3] H. Nakamura, *Nonadiabatic Transition: Concepts, Basic Theories and Applications* (World Scientific, Singapore, 2002).
[4] *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996).
[5] *Theory of Chemical Reactions Dynamics*, edited by A. Lagana and G. Lendvay (Kluwer Academic, Dordrecht, 2004).
[6] B. K. Kendrick, Phys. Rev. Lett. **79**, 2431 (1997).
[7] B. K. Kendrick and R. T. Pack, J. Chem. Phys. **106**, 3519 (1997).
[8] S. Mahapatra and H. J. Koppel, Phys. Rev. Lett. **81**, 3116 (1998).
[9] S. Mahapatra, H. J. Koppel, and L. S. Cederbaum, J. Phys. Chem. A **105**, 2321 (2001).
[10] A. J. C. Varandas and L. P. Viegas, Chem. Phys. Lett. **367**, 625 (2003).
[11] J. C. Juanes-Marcos and S. C. Althorpe, Chem. Phys. Lett. **381**, 743 (2003).
[12] J. C. Juanes-Marcos and S. C. Althorpe, J. Chem. Phys. **122**, 204324 (2005).
[13] C. Zhu, J. Phys. A **29**, 1293 (1996).
[14] V. I. Osherov and H. Nakamura, J. Chem. Phys. **105**, 2770 (1996).
[15] V. I. Osherov and H. Nakamura, Phys. Rev. A **59**, 2486 (1999).
[16] V. I. Osherov and V. G. Ushakov, Phys. Rev. A **73**, 022713 (2006).
[17] A. I. Voronin and V. I. Osherov, Sov. Phys. JETP **39**, 62 (1974).
[18] A. I. Voronin, S. P. Karkach, V. I. Osherov, and V. G. Ushakov, Sov. Phys. JETP **44**, 465 (1976).
[19] V. I. Osherov, V. G. Ushakov, and A. I. Voronin, J. Phys. B **13**, 1507 (1980).
[20] V. I. Osherov and V. G. Ushakov, Phys. Rev. A **75**, 032716 (2007).
[21] *Heun's Differential Equations*, edited by A. Ronveaux (Oxford University Press, New York, 1995).
[22] *Higher Transcendental Functions*, edited by A. Erdelyi (Robert E. Krieger, Malabar, FL, 1981), Vol. III.
[23] S. Slavyanov and W. Lay, *Special Functions: A Unified Theory Based on Singularities* (Oxford University Press, New York, 2000).
[24] R. S. Maier, Math. Comput. **76**, 811 (2007).
[25] A. Erdelyi, Q. J. Math. **os-15**, 62 (1944).
[26] Y. Luke, *The Special Functions and Their Approximations* (Academic, New York, 1969), Vol. 1.
[27] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, New York, 1944).