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Exact analytical solution for coupled time-independent Schrödinger equations with certain model potentials

Chaoyuan Zhu
Division of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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Abstract. An exact analytical solution is obtained for coupled time-independent Schrödinger equations with model potentials: $V_{11}(x) = V_1 + \beta V_0\,\mathrm{e}^{-\alpha x}$, $V_{22}(x) = V_2 + \frac{1}{\beta} V_0\,\mathrm{e}^{-\alpha x}$ and $V_{12}(x) = V_{21}(x) = V_0\,\mathrm{e}^{-\alpha x}$. This is made possible by solving a single fourth-order ordinary differential equation derived from the original coupled equations. Exact closed-form solutions for the non-adiabatic transition matrices (or scattering matrices) are found for scattering boundary conditions with three, two and one open channels, respectively. How to apply the present results to deal with general potentials is also briefly analysed.

1. Introduction

Coupled time-independent Schrödinger equations

$$\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} + [E - V_{11}(x)]\psi_1(x) = V_{12}(x)\psi_2(x) \tag{1.1a}$$

and

$$\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_2}{\mathrm{d}x^2} + [E - V_{22}(x)]\psi_2(x) = V_{21}(x)\psi_1(x) \tag{1.1b}$$

for $-\infty < x < \infty$, construct a starting point of analytical treatment for non-adiabatic collisions in atomic and molecular physics. Since exact analytical solutions in closed form for the coupled equations are not generally possible, exactly solvable model problems play a very important role for developing various approximation methods. The present work is an illustration toward this aim with the following two diabatic potentials and coupling:

$$V_{11}(x) = V_1 + \beta V_0\,\mathrm{e}^{-\alpha x} \qquad V_{22}(x) = V_2 + \frac{1}{\beta} V_0\,\mathrm{e}^{-\alpha x} \tag{1.2}$$

and

$$V_{12}(x) = V_{21}(x) = V_0\,\mathrm{e}^{-\alpha x} \tag{1.3}$$

where α, β and V_0 are assumed to be positive with $V_2 > V_1$. A central task in the present paper is to find exact analytical solutions of non-adiabatic transition matrices (or scattering matrices) for three cases:

(i) Three open channels for $E > V_2$,

(ii) Two open channels for $V_2 > E > V_3$,

(iii) One open channel for $V_3 > E > V_1$,

where three energy thresholds V_1, V_2 and V_3 (see equation (2.8)) are shown in figure 1. Two diabatic potentials are crossing, parallel, and non-crossing and non-parallel respectively for $\beta > 1$, $\beta = 1$ and $\beta < 1$. These three situations correspond to quite different types of non-adiabatic transitions in the diabatic representation. In contrast, their counterparts of the two adiabatic potentials show very smooth dependence on β because of exponentially divergent coupling in equation (1.3). Figure 1 shows the two adiabatic potentials for $\beta = 1$ with two tendencies that V_3 approaches V_2 for $\beta \to \infty$ and V_3 approaches V_1 for $\beta \to 0$.

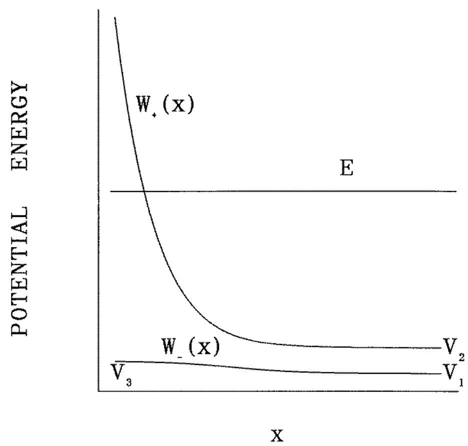

Figure 1. Two adiabatic potentials $W_+(x)$ and $W_-(x)$ with $\beta = 1$ in (1.2).

Two categories might be classified for finding an exact analytical solution of the ordinary differential equation. The first is that an exact analytical solution can be obtained for the whole region of the variable (say x here) through various transformations. For example, Osherov and Voronin [1] illustrated a fascinating example in which the compact solution has been obtained for equations (1.1) in the case where two diabatic potentials ($V_{11}(x)$ and $V_{22}(x)$) are constants with the same type of coupling term as in (1.3). The present work is actually stimulated from their work. A significant importance of the present model potentials is that three cases of crossing, parallel, non-crossing and non-parallel are considered as a whole, it provides an opportunity for establishing the unified semiclassical approach to the non-adiabatic collisions of atomic and molecular physics. The model potentials introduced by Osherov and Voronin [1] correspond to the parallel case only. Moreover, the lower adiabatic potential $W_-(x)$ (see figure 1) is now convergent as x approaches negative infinity, while it is divergent negatively in [1]. This means that the arbitrariness of the phase encountered in [1] can be removed in the present model for the semiclassical applications. The second is that an exact analytical solution is not possible for the whole region of the variable, but is possible for the asymptotic region through various transformations. Then, physical quantities such as eigenvalues, scattering matrices and so on can still be solved in an exact analytical form, providing that the connection problem of the asymptotic solution is known. The Stokes phenomenon [2] of asymptotic solution of the ordinary differential equation provides a powerful tool to deal with these kinds of problems [3–5]. Generalizing the real variable to the complex variable and tracing the asymptotic solution around the complex plane, the connection matrix which connects the asymptotic solution in the complex plane can be expressed in terms of Stokes constants. In a remarkable recent work Zhu and Nakamura [5] found an exact analytical solution of the Stokes constants for the second-order ordinary differential equation with the coefficient function as the fourth-order polynomial. In this way, exact analytical solutions of scattering matrices were obtained for the two-state linear curve crossing problems [6] ($V_{11}(x)$ and $V_{22}(x)$ in equations (1.2) are linearly dependent on the variable x with constant coupling $V_{12}(x)$ in equation (1.3)). The two ways mentioned above are complementary to deal with the differential equation analytically.

An exact analytical solution for a differential equation is very important not only in a mathematical aspect, but also in setting up an excellent foundation for a semiclassical approximation [7]. For instance, the WKB elastic phase shift for the scattering problem on a single potential is analytically formulated by the exact connection based on the Airy function with a one-turning-point problem. The well known Bohr–Sommerfeld quantization formula for a potential well and the tunnelling formula for a potential barrier can be produced by the exact connection based on the Weber function with a two-turning-point problem. Moreover, semiclassical solutions of the scattering matrices for the two-state curve crossing problems have been found from the exact connection based on the four-transition-point problem [8, 9]. An underlying idea in semiclassical theory is that exact analytical solutions first based on certain model potentials can be generalized to a wide class of real potentials which share the same essential features as the model potentials. Even for a numerical computational program, it is very obvious that an exact analytical solution can provide the most reliable and accurate check.

Section 2 reduces coupled equations (1.1) to a single fourth-order ordinary differential equation and its solution is related to a certain special function called the G-function [10]. Four independent solutions are given. Section 3 presents exact analytical solutions for non-adiabatic transition matrices for the three cases mentioned above. The conclusion is given in section 4.

2. Exact solution in terms of the G-function

Following the notation used by Osherov and Voronin [1], we introduce a new variable

$$\rho = \frac{\sqrt{8mV_0}}{\hbar\alpha}\,\mathrm{e}^{-\frac{1}{2}\alpha x} \tag{2.1}$$

with dimensionless wave numbers

$$q_i = \frac{\sqrt{2m}}{\hbar\alpha}\sqrt{E - V_i} \qquad i = 1, 2\,. \tag{2.2}$$

Then, the coupled equations (1.1) turn out to be of the form

$$\left(\rho^2\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \rho\frac{\mathrm{d}}{\mathrm{d}\rho} + 4q_1^2 - \beta\rho^2\right)\psi_1(\rho) = \rho^2\psi_2(\rho) \tag{2.3a}$$

and

$$\left(\rho^2\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \rho\frac{\mathrm{d}}{\mathrm{d}\rho} + 4q_2^2 - \frac{1}{\beta}\rho^2\right)\psi_2(\rho) = \rho^2\psi_1(\rho). \tag{2.3b}$$

Making the further substitution $z = (\beta + 1/\beta)\rho^2/4$ and eliminating ψ_2 in (2.3*a*), we obtain a single fourth-order differential equation for ψ_1,

$$\left[\prod_{i=1}^{4}\left(z\frac{\mathrm{d}}{\mathrm{d}z} - b_i\right) - z\prod_{i=1}^{2}\left(z\frac{\mathrm{d}}{\mathrm{d}z} - a_i + 1\right)\right]\psi_1(z) = 0 \tag{2.4}$$

with a relation for ψ_2,

$$\left[\left(z\frac{\mathrm{d}}{\mathrm{d}z} - b_1\right)\left(z\frac{\mathrm{d}}{\mathrm{d}z} - b_2\right) - \frac{\beta}{\beta + 1/\beta}z\right]\psi_1(z) = \frac{z}{\beta + 1/\beta}\psi_2(z) \tag{2.5}$$

where

$$\begin{aligned} &b_1 = \mathrm{i}q_1 \qquad b_2 = -\mathrm{i}q_1 \qquad b_3 = 1 + \mathrm{i}q_2 \qquad b_4 = 1 - \mathrm{i}q_2 \\ &a_1 = 1 + \mathrm{i}\gamma \qquad \text{and} \qquad a_2 = 1 - \mathrm{i}\gamma \end{aligned} \tag{2.6}$$

with

$$\gamma = \sqrt{\frac{\beta q_2^2 + q_1^2/\beta}{\beta + 1/\beta}} \equiv \frac{\sqrt{2m}}{\hbar\alpha}\sqrt{E - V_3} \tag{2.7}$$

and

$$V_3 = \frac{\beta V_2 + V_1/\beta}{\beta + 1/\beta}\,. \tag{2.8}$$

The general solution of (2.4) can be related to a linear combination of four independent Meijer functions (denoted as the G-function) [11],

$$\psi_1(z) = c_1 G_{24}^{40}\left(z\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) + c_2 G_{24}^{40}\left(z\mathrm{e}^{\mathrm{i}2\pi}\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) + c_3 G_{24}^{41}\left(z\mathrm{e}^{\mathrm{i}\pi}\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) + c_4 G_{24}^{41}\left(z\mathrm{e}^{\mathrm{i}\pi}\middle|^{a_2a_1}_{b_1b_2b_3b_4}\right) \tag{2.9}$$

where $c_i (i = 1–4)$ are arbitrary constants, $b_i (i = 1 \sim 4)$ and $a_j (j = 1, 2)$ are defined in (2.6). This solution has an irregular singularity only at $z = \infty$. In order to find a non-adiabatic transition matrix we must investigate the asymptotic connection of the G-function between the ranges of $z \to 0$ (corresponding to $x \to \infty$) and $z \to \infty$ (corresponding to $x \to -\infty$). Explicit asymptotic expressions for the G-function in (2.9) can be found as follows [12]:

$$G_{24}^{40}\left(z\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) = \frac{\sqrt{\pi}}{z^{1/4}}\mathrm{e}^{-2\sqrt{z}} \tag{2.10a}$$

$$G_{24}^{40}\left(z\,\mathrm{e}^{\mathrm{i}2\pi}\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) = \frac{\sqrt{\pi}}{\mathrm{i}z^{1/4}}\,\mathrm{e}^{2\sqrt{z}} \tag{2.10b}$$

$$G_{24}^{41}\left(z\,\mathrm{e}^{\mathrm{i}\pi}\middle|^{a_1a_2}_{b_1b_2b_3b_4}\right) = (z\,\mathrm{e}^{\mathrm{i}\pi})^{a_1-1}A(a_1, a_2) \tag{2.10c}$$

and

$$G_{24}^{41}\left(z\,\mathrm{e}^{\mathrm{i}\pi}\middle|^{a_2a_1}_{b_1b_2b_3b_4}\right) = (z\,\mathrm{e}^{\mathrm{i}\pi})^{a_2-1}A(a_2, a_1) \tag{2.10d}$$

for $z \to \infty$, where

$$A(a_1, a_2) = \frac{\Gamma(1+b_1-a_1)\Gamma(1+b_2-a_1)\Gamma(1+b_3-a_1)\Gamma(1+b_4-a_1)}{\Gamma(1+a_2-a_1)}. \tag{2.11}$$

For $z \to 0$, we have

$$G_{24}^{40}\left(z\middle|_{b_1b_2b_3b_4}^{a_1a_2}\right) = B(b_1,b_2)z^{b_1}(1+\nu z) + B(b_2,b_1)z^{b_2}(1+\nu^* z) + D(b_3,b_4)z^{b_3} + D(b_4,b_3)z^{b_4} \tag{2.12a}$$

$$G_{24}^{40}\left(z\,\mathrm{e}^{\mathrm{i}2\pi}\middle|_{b_1b_2b_3b_4}^{a_1a_2}\right) = B(b_1,b_2)\,\mathrm{e}^{\mathrm{i}2\pi b_1}z^{b_1}(1+\nu z) + B(b_2,b_1)\,\mathrm{e}^{\mathrm{i}2\pi b_2}z^{b_2}(1+\nu^* z) + D(b_3,b_4)\,\mathrm{e}^{\mathrm{i}2\pi b_3}z^{b_3} + D(b_4,b_3)\mathrm{e}^{i2\pi b_4}z^{b_4} \tag{2.12b}$$

$$G_{24}^{41}\left(z\,\mathrm{e}^{\mathrm{i}\pi}\middle|_{b_1b_2b_3b_4}^{a_1a_2}\right) = \frac{\pi B(b_1,b_2)}{\sin\pi(a_1-b_1)}\,\mathrm{e}^{\mathrm{i}\pi b_1}z^{b_1}(1+\nu z) + \frac{\pi B(b_2,b_1)}{\sin\pi(a_1-b_2)}\,\mathrm{e}^{\mathrm{i}\pi b_2}z^{b_2}(1+\nu^* z) + \frac{\pi D(b_3,b_4)}{\sin\pi(a_1-b_3)}\,\mathrm{e}^{\mathrm{i}\pi b_3}z^{b_3} + \frac{\pi D(b_4,b_3)}{\sin\pi(a_1-b_4)}\,\mathrm{e}^{\mathrm{i}\pi b_4}z^{b_4} \tag{2.12c}$$

and

$$G_{24}^{41}\left(z\,\mathrm{e}^{\mathrm{i}\pi}\middle|_{b_1b_2b_3b_4}^{a_2a_1}\right) = \frac{\pi B(b_1,b_2)}{\sin\pi(a_2-b_1)}\,\mathrm{e}^{\mathrm{i}\pi b_1}z^{b_1}(1+\nu z) + \frac{\pi B(b_2,b_1)}{\sin\pi(a_2-b_2)}\,\mathrm{e}^{\mathrm{i}\pi b_2}z^{b_2}(1+\nu^* z) + \frac{\pi D(b_3,b_4)}{\sin\pi(a_2-b_3)}\,\mathrm{e}^{\mathrm{i}\pi b_3}z^{b_3} + \frac{\pi D(b_4,b_3)}{\sin\pi(a_2-b_4)}\,\mathrm{e}^{\mathrm{i}\pi b_4}z^{b_4} \tag{2.12d}$$

where $\nu = \beta/[(\beta+1/\beta)(1+\mathrm{i}2q_1)]$ with

$$B(b_1,b_2) = \frac{\Gamma(b_2-b_1)\Gamma(b_3-b_1)\Gamma(b_4-b_1)}{\Gamma(a_1-b_1)\Gamma(a_2-b_1)} \tag{2.13}$$

and

$$D(b_3,b_4) = \frac{\Gamma(b_1-b_3)\Gamma(b_2-b_3)\Gamma(b_4-b_3)}{\Gamma(a_1-b_3)\Gamma(a_2-b_3)} \tag{2.14}$$

where $\Gamma(\,)$ means the gamma function. It should be noted that the first two terms in (2.12) are expanded up to the first order while the last two terms are only required to the zeroth order. Now, by setting up $c_2 = 0$ in (2.9) we can eliminate the unphysical solution (2.10b) which is exponentially divergent at $z \to \infty$. Inserting equations (2.10) and (2.12) into (2.9) and (2.5) with carefully algebraic calculation, we finally obtain the asymptotic solutions for $\psi_1(x)$ and $\psi_2(x)$,

$$\psi_1(x) = c_3\mu^{\mathrm{i}\gamma}A(a_1,a_2)\,\mathrm{e}^{-\pi\gamma}\exp(-\mathrm{i}\alpha\gamma x) + c_4\mu^{-\mathrm{i}\gamma}A(a_2,a_1)\,\mathrm{e}^{\pi\gamma}\exp(\mathrm{i}\alpha\gamma x) \quad \text{for} \quad x \to -\infty \tag{2.15a}$$

and

$$\psi_2(x) = -\beta\psi_1(x) \qquad \text{for} \quad x \to -\infty \tag{2.15b}$$

with

$$\psi_1(x) = B(b_1, b_2)\mu^{\mathrm{i}q_1}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_1}}{\sin\pi(a_1-b_1)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_1}}{\sin\pi(a_2-b_1)}\right]\exp(-\mathrm{i}\alpha q_1 x)$$
$$+ B(b_2, b_1)\mu^{-\mathrm{i}q_1}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_2}}{\sin\pi(a_1-b_2)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_2}}{\sin\pi(a_2-b_2)}\right]\exp(\mathrm{i}\alpha q_1 x)$$
$$\text{for}\quad x\to\infty \tag{2.16a}$$

and

$$\psi_2(x) = D(b_3, b_4)\mu^{\mathrm{i}q_2}(\beta + 1/\beta)(b_3-b_1)(b_3-b_2)$$
$$\times\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_1-b_3)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_2-b_3)}\right]\exp(-\mathrm{i}\alpha q_2 x)$$
$$+ D(b_4, b_3)\mu^{-\mathrm{i}q_2}(\beta + 1/\beta)(b_4-b_1)(b_4-b_2)$$
$$\times\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_4}}{\sin\pi(a_1-b_4)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_4}}{\sin\pi(a_2-b_4)}\right]\exp(\mathrm{i}\alpha q_2 x)\qquad\text{for}\quad x\to\infty \tag{2.16b}$$

where

$$\mu = \frac{2mV_0}{\hbar^2\alpha^2}(\beta + 1/\beta)\,. \tag{2.17}$$

Equations (2.15) and (2.16), which are interrelated by c_1, c_3 and c_4, basically define the connection of the asymptotic solution, and include all the information for finding the non-adiabatic transition matrix in the next section.

3. Exact solutions of non-adiabatic transition matrices

In the previous section we have found exact asymptotic solutions for the wavefunctions $\psi_1(x)$ and $\psi_2(x)$ which are given in the diabatic representation. As is well known, the non-adiabatic transition matrix (or scattering matrix) is defined in terms of the wavefunctions in an adiabatic representation in which the correct physical boundary conditions can be imposed. The transformation matrix between two representations can be found in the literature (for example, [13]),

$$\begin{pmatrix}\Psi_1(x)\\ \Psi_2(x)\end{pmatrix} = \begin{pmatrix}\cos\theta(x) & \sin\theta(x)\\ -\sin\theta(x) & \cos\theta(x)\end{pmatrix}\begin{pmatrix}\psi_1(x)\\ \psi_2(x)\end{pmatrix} \tag{3.1}$$

where

$$\theta(x) = \frac{1}{2}\arctan\frac{2V_{12}(x)}{V_{11}(x) - V_{22}(x)}\,. \tag{3.2}$$

When $x\to\infty$ the diabatic coupling $V_{12}\to 0$, i.e. $\theta\to 0$. Thus, two representations are identical,

$$\Psi_1(x) = \psi_1(x)\qquad\text{for}\quad x\to\infty \tag{3.3}$$

and

$$\Psi_2(x) = \psi_2(x) \qquad \text{for} \quad x \to \infty \tag{3.4}$$

where $\psi_1(x)$ and $\psi_2(x)$ are given in (2.16). On the other hand, for $x \to -\infty$ we have $\theta = \frac{1}{2}\arctan\frac{2}{\beta - 1/\beta}$. From equation (3.1) we can obtain the wavefunctions in an adiabatic representation,

$$\Psi_1(x) = \frac{1}{\sqrt{1+\beta^2}}[\psi_1(x) - \beta\psi_2(x)] = \sqrt{1+\beta^2}\psi_1(x) \qquad \text{for} \quad x \to -\infty \tag{3.5}$$

and

$$\Psi_2(x) = \frac{1}{\sqrt{1+\beta^2}}[\beta\psi_1(x) + \psi_2(x)] = 0 \qquad \text{for} \quad x \to -\infty \tag{3.6}$$

where $\psi_1(x)$ and $\psi_2(x)$ are given by (2.15). As is demonstrated in figure 1, there is one closed channel which corresponds to (3.6) and one possible open channel ($E > V_3$) which corresponds to (3.5) in the asymptotic region of $x \to -\infty$.

An alternative way to find asymptotic solutions of wavefunctions is directly based on the two adiabatic potentials,

$$\begin{aligned} W_\pm(x) =& (V_{11}(x) + V_{22}(x))/2 \pm \sqrt{(V_{11}(x) - V_{22}(x))^2/4 + V_{12}^2(x)} \\ =& (V_1 + V_2)/2 + (\beta + 1/\beta)V_0\,\mathrm{e}^{-\alpha x}/2 \\ &\pm \sqrt{(V_1 - V_2 + (\beta - 1/\beta)V_0\,\mathrm{e}^{-\alpha x})^2/4 + V_0^2\,\mathrm{e}^{-2\alpha x}} \end{aligned} \tag{3.7}$$

with wavenumbers

$$Q_\pm(x) = \frac{\sqrt{2m}}{\hbar}\sqrt{E - W_\pm(x)} \tag{3.8}$$

which lead to the following asymptotic expressions:

$$\lim_{x\to\infty} Q_+(x) = \alpha q_2 \qquad \lim_{x\to\infty} Q_-(x) = \alpha q_1 \qquad \text{and} \qquad \lim_{x\to-\infty} Q_-(x) = \alpha\gamma \tag{3.9}$$

with which we can directly write down asymptotic expressions for the wavefunctions in the adiabatic representation,

$$\Psi_1(x) = \frac{1}{\sqrt{\alpha q_1}}(A_1\,\mathrm{e}^{\mathrm{i}\alpha q_1 x} + B_1\,\mathrm{e}^{-\mathrm{i}\alpha q_1 x}) \qquad \text{for} \quad x \to \infty \tag{3.10a}$$

$$\Psi_2(x) = \frac{1}{\sqrt{\alpha q_2}}(A_2\,\mathrm{e}^{\mathrm{i}\alpha q_2 x} + B_2\,\mathrm{e}^{-\mathrm{i}\alpha q_2 x}) \qquad \text{for} \quad x \to \infty \tag{3.10b}$$

and

$$\Psi_1(x) = \frac{1}{\sqrt{\alpha\gamma}}(A_3\,\mathrm{e}^{-\mathrm{i}\alpha\gamma x} + B_3\,\mathrm{e}^{\mathrm{i}\alpha\gamma x}) \qquad \text{for} \quad x \to -\infty \tag{3.10c}$$

where $A_i(i = 1, 2, 3)$ represents outgoing wave amplitude and $B_i(i = 1, 2, 3)$ represents incoming wave amplitude if the corresponding channel is open. The non-adiabatic transition matrix is simply defined by the connection between the A_i and B_i. Their relations with the three arbitrary constants c_1, c_2 and c_3 in the previous section can be found by comparing (3.10) with (3.3)–(3.5) together with (2.15) and (2.16), for A_i we simply write

$$\frac{1}{\sqrt{\alpha q_1}} A_1 = B(-q_1)\mu^{-\mathrm{i}q_1}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_2}}{\sin\pi(a_1-b_2)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_2}}{\sin\pi(a_2-b_2)}\right] \tag{3.11a}$$

$$\frac{1}{\sqrt{\alpha q_2}} A_2 = (\beta+1/\beta)R(-q_2)\mu^{-\mathrm{i}q_2}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_4}}{\sin\pi(a_1-b_4)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_4}}{\sin\pi(a_2-b_4)}\right] \tag{3.11b}$$

and

$$\frac{1}{\sqrt{\alpha\gamma}} A_3 = \sqrt{\beta^2+1}c_3\,\mathrm{e}^{-\pi\gamma}A(\gamma)\mu^{\mathrm{i}\gamma}\,. \tag{3.11c}$$

For B_i we have

$$\frac{1}{\sqrt{\alpha q_1}} B_1 = B(q_1)\mu^{\mathrm{i}q_1}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_1}}{\sin\pi(a_1-b_1)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_1}}{\sin\pi(a_2-b_1)}\right] \tag{3.12a}$$

$$\frac{1}{\sqrt{\alpha q_2}} B_2 = (\beta+1/\beta)R(q_2)\mu^{\mathrm{i}q_2}\left[c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_1-b_3)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_2-b_3)}\right] \tag{3.12b}$$

and

$$\frac{1}{\sqrt{\alpha\gamma}} B_3 = \sqrt{\beta^2+1}\,c_4\,\mathrm{e}^{\pi\gamma}A(-\gamma)\mu^{-\mathrm{i}\gamma} \tag{3.12c}$$

where A and B (see equations (2.11) and (2.13)) can be rewritten as

$$A(\gamma) = \frac{\Gamma[\mathrm{i}(q_1-\gamma)]\Gamma[-\mathrm{i}(q_1+\gamma)]\Gamma[1+\mathrm{i}(q_2-\gamma)]\Gamma[1-\mathrm{i}(q_2+\gamma)]}{\Gamma[1-\mathrm{i}2\gamma]} \tag{3.13}$$

and

$$B(q_1) = \frac{\Gamma[-2\,\mathrm{i}q_1]\Gamma[1-\mathrm{i}(q_1-q_2)]\Gamma[1-\mathrm{i}(q_1+q_2)]}{\Gamma[1+\mathrm{i}(\gamma-q_1)]\Gamma[1-\mathrm{i}(\gamma+q_1)]} \tag{3.14}$$

with R given by

$$R(q_2) = \frac{\Gamma[-2\,\mathrm{i}q_2]\Gamma[\mathrm{i}(q_1-q_2)]\Gamma[-\mathrm{i}(q_1+q_2)]}{\Gamma[\mathrm{i}(\gamma-q_2)]\Gamma[-\mathrm{i}(\gamma+q_2)]}\,. \tag{3.15}$$

3.1. Three-channel case ($E > V_2$)

Since $E > V_2$, the three channels denoted as in (3.10) are open. The non-adiabatic transition matrix is defined by the connection between the outgoing amplitudes $A_i (i = 1\text{–}3)$ and incoming amplitudes $B_i (i = 1\text{–}3)$ as follows:

$$\begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} = \begin{pmatrix} N_{11} & N_{12} & N_{13} \\ N_{21} & N_{22} & N_{23} \\ N_{31} & N_{32} & N_{33} \end{pmatrix} \begin{pmatrix} B_1 \\ B_2 \\ B_3 \end{pmatrix}. \tag{3.16}$$

By eliminating c_1, c_3 and c_4 from (3.11) and (3.12), we can find

$$\begin{aligned}
N_{11} &= \mu^{-2\,\mathrm{i}q_1} \frac{B(-q_1)}{B(q_1)} \frac{\sinh\pi(q_1-\gamma)\sinh\pi(q_1+q_2)}{\sinh\pi(q_1+\gamma)\sinh\pi(q_1-q_2)} \\
N_{12} &= \frac{\mu^{-\mathrm{i}q_1-\mathrm{i}q_2}}{\beta+1/\beta}\sqrt{\frac{q_1}{q_2}}\,\frac{B(-q_1)}{R(q_2)}\,\frac{\sinh\pi(\gamma-q_2)\sinh(2q_1\pi)}{\sinh\pi(q_1+\gamma)\sinh\pi(q_1-q_2)} \\
N_{13} &= \frac{\mathrm{i}\pi\,\mu^{-\mathrm{i}q_1+\mathrm{i}\gamma}}{\sqrt{1+\beta^2}}\sqrt{\frac{q_1}{\gamma}}\,\frac{B(-q_1)}{A(-\gamma)}\,\frac{\sinh(2\gamma\pi)\sinh(2q_1\pi)\sinh\pi(q_1+q_2)}{\sinh^2\pi(q_1+\gamma)\sinh\pi(\gamma+q_2)\sinh\pi(q_1-\gamma)} \\
N_{21} &= N_{12} \\
N_{22} &= \mu^{-2\,\mathrm{i}q_2} \frac{R(-q_2)}{R(q_2)} \frac{\sinh\pi(\gamma-q_2)\sinh\pi(q_1+q_2)}{\sinh\pi(\gamma+q_2)\sinh\pi(q_1-q_2)} \\
N_{23} &= \mathrm{i}\pi\sqrt{1+1/\beta^2}\,\mu^{-\mathrm{i}q_2+\mathrm{i}\gamma}\sqrt{\frac{q_2}{\gamma}}\,\frac{R(-q_2)}{A(-\gamma)}\,\frac{\sinh(2\gamma\pi)\sinh(2q_2\pi)\sinh\pi(q_1+q_2)}{\sinh^2\pi(q_2+\gamma)\sinh\pi(\gamma+q_1)\sinh\pi(q_2-\gamma)} \\
N_{31} &= N_{13} \\
N_{32} &= N_{23} \\
N_{33} &= \mu^{2\mathrm{i}\gamma}\frac{A(\gamma)}{A(-\gamma)}\frac{\sinh\pi(q_1-\gamma)\sinh\pi(\gamma-q_2)}{\sinh\pi(q_1+\gamma)\sinh\pi(\gamma+q_2)}
\end{aligned} \tag{3.17}$$

where $B(q_1)$, $R(q_2)$ and $A(\gamma)$ are defined by (3.13)–(3.15). It is not difficult to prove that the symmetrical matrix N_{ij} in (3.17) satisfies the unitarity condition as a requirement of the scattering matrix.

3.2. Two-channel case ($V_2 > E > V_3$)

In this case, since $q_2^2 < 0$ we can rewrite

$$q_2 = \mathrm{i}|q_2|\,. \tag{3.18}$$

Now, Ψ_2 in (3.10*b*) becomes a closed channel which requires a physical boundary condition as

$$B_2 = 0\,. \tag{3.19}$$

From equation (3.12*b*) this leads to

$$c_1 + c_3\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_1-b_3)} + c_4\frac{\pi\,\mathrm{e}^{\mathrm{i}\pi b_3}}{\sin\pi(a_2-b_3)} = 0 \tag{3.20}$$

which indicates that there are only two arbitrary constants out of three c_1, c_3 and c_4. The non-adiabatic transition matrix is defined by two open channels,

$$\begin{pmatrix} A_1 \\ A_3 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} B_1 \\ B_3 \end{pmatrix} . \tag{3.21}$$

By using (3.11) and (3.12) with the constraint of (3.20), we can find

$$\begin{aligned} M_{11} &= \mu^{-2\,\mathrm{i}q_1} \frac{B(-q_1)}{B(q_1)} \frac{\sinh \pi(q_1-\gamma) \sinh \pi(q_1+q_2)}{\sinh \pi(q_1+\gamma) \sinh \pi(q_1-q_2)} \\ M_{12} = M_{21} &= \frac{\mu^{\mathrm{i}\gamma - iq_1}}{\pi} \sqrt{\beta^2+1} \frac{A(\gamma)}{B(q_1)} \sqrt{\frac{\gamma}{q_1}} \frac{\sinh \pi(q_1-\gamma) \sinh \pi(\gamma-q_2)}{\sinh \pi(q_1-q_2)} \\ M_{22} &= \mu^{2\,\mathrm{i}\gamma} \frac{A(\gamma)}{A(-\gamma)} \frac{\sinh \pi(q_1-\gamma) \sinh \pi(\gamma-q_2)}{\sinh \pi(q_1+\gamma) \sinh \pi(\gamma+q_2)} . \end{aligned} \tag{3.22}$$

Recall that $q_2 = \mathrm{i}|q_2|$. Again one can prove that M_{ij} in equation (3.22) is a unitarity matrix.

3.3. One-channel case ($V_3 > E > V_1$)

In this case we have one more closed channel which is Ψ_1 in (3.10c) because of $\gamma^2 < 0$. This requires a physical boundary condition as

$$B_3 = 0 . \tag{3.23}$$

From equation (3.12c) this leads to one more constraint

$$c_4 = 0 . \tag{3.24}$$

With the two constraints of (3.20) and (3.24), we define the non-adiabatic transition matrix by only one open channel,

$$A_1 = SB_1 \equiv \mathrm{e}^{\mathrm{i}2\eta} B_1 \tag{3.25}$$

with

$$\eta = -q_1 \ln \mu - \arg B(q_1) - \arctan[\tan(|\gamma|\pi)/\tanh(q_1\pi)] + \arctan[\tan(|q_2|\pi)/\tanh(q_1\pi)] \tag{3.26}$$

which can be regarded as the non-adiabatic scattering phase shift.

4. Conclusions

By employing a special function which is called the G-function, we have found exact analytical solutions for coupled Schrödinger equations with the model potentials proposed in (1.2) and (1.3). Exact closed-form solutions for the non-adiabatic transition matrices provide an excellent foundation to investigate non-adiabatic transitions with general potentials analytically. In order to demonstrate a wide class of applications to realistic systems, we would like to take an example in the following. Since the lower adiabatic potential $W_-(x)$ approaches the energy threshold V_3 quickly in the negative direction of the coordinate x, we put a repulsive potential to replace $W_-(x)$ up to a certain negative point x_0. Thus, in the region $x < x_0$ wave propagation along the lower adiabatic potential can be assumed to decouple with the upper adiabatic potential; and a simple semiclassical connection based on one turning point can be applied to this region. In the region $x > x_0$ the non-adiabatic transition can be described by the present results of the non-adiabatic transition matrix. By using this kind of semiclassical analysis, the non-adiabatic transition probability can be easily obtained as follows:

$$P_{12} = \frac{\sinh(2q_1\pi)\sinh(2q_2\pi)\cos^2\eta}{\sinh^2\pi(q_1-q_2)} \times \left[\frac{\sinh^2(2\gamma\pi)\sinh^2\pi(q_1+q_2)}{4\sinh\pi(q_1-\gamma)\sinh\pi(q_1+\gamma)\sinh\pi(\gamma-q_2)\sinh\pi(\gamma+q_2)} - \cos^2\eta\right]^{-1} \tag{4.1}$$

where

$$\eta = \sigma + \arg A(\gamma) \tag{4.2}$$

in which $A(\gamma)$ is given in (3.13) and σ can be interpreted as a difference of phase integrals along two adiabatic potentials. Note that (3.17) are used for deriving (4.1). This presents a very rigorous semiclassical result directly based on the coupled time-independent Schrödinger equations. In contrast, a lot of sophisticated mathematical methods have been developed in the literature which provide semiclassical approaches based on the coupled time-dependent Schrödinger equations [14–16]. The relationship of time-independent and time-dependent schemes has been clearly reviewed in a recent paper [17]. However, the present result in (4.1) is very general and can provide a basis for further semiclassical approaches to non-adiabatic scattering problems.

It is an essential feature of the present method that exact solutions of non-adiabatic transition matrices first derived from model potentials can be applied to a wide class of general potentials. This idea is not restricted in the coupled Schrödinger equations, i.e. the two-state case; and it must be applicable even for the multi-state problem, in principle. To establish semiclassical theory based on the present results will be a very interesting subject and will be investigated in a future publication.

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