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Exact solution of time-dependent Schrodinger equation for two state problem in Laplace domain

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A R T I C L E I N F O

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A B S T R A C T

The present work focuses on the exact solution of the time dependent Schrodinger equation involving two potentials coupled by a Dirac Delta potential. The problem involving the partial differential equations in two variables can be reduced to a single integral equation in Laplace domain and by knowing the wave function at the origin we can derive the wave function everywhere. Solutions for the bound state and partly unbound state along with propagator are derived for the first potential.

1. Introduction

Nonadiabatic transitions due to crossing of potential energy curves is one of the most effective phenomena involved in different type of electronic transitions. It is an interdisciplinary concept which occurs in various fields of physics, chemistry and biology [1–3]. Common examples to the processes which involves such kind of transitions are variety of atomic and molecular processes, chemical reactions and spectroscopic processes. In our earlier published research [4] we have solved the problem of crossing of two diabatic curves and there is a coupling between the two curves which is responsible for transitions from one curve to another and gave an exact model of curve crossing problem. This article explains a general multi crossing problem which is very important in view of applications to various practical problems involving chemical dynamics beyond the diatomic systems. Recently we have published our research to deal with the cases where two potentials are coupled by any arbitrary interaction [5–11]. Out of all existing numerical as well as analytical methods the use of Dirac Delta potentials to model different physical problems has its own established importance. The physical significance of the choice of Dirac Delta function is that, using Dirac Delta function as a coupling between two states it is possible to get an exact analytical solution for any problem which is not possible for any other function [4–8]. The other advantage of Dirac Delta functions is that any arbitrary coupling which can be any kind of function can be expressed as a collection of Dirac Delta function and then it can be used to calculate the transition probability [9–11]. All these methods as well as different applications of Dirac Delta function proved it to be useful as a analytical solvable model in variety of applications involving novel concepts of physics and chemistry. In the present work we developed an alternative approach of study of nonadiabatic transitions involving time dependent Schroedinger equations for two state scattering problem coupled by Dirac Delta potential where the coupling is time independent but can be extended to the time dependent coupling as well which is in the pipeline.

2. Methodology

We start with the case where two constant potential as represented by time dependent Schrodinger equations are coupled to each other by a time independent coupling. The 1D Schrodinger equation in this case can be written as

$$i\frac{\partial}{\partial t}\begin{bmatrix}\phi_1(x,t)\\ \phi_2(x,t)\end{bmatrix}=\begin{bmatrix}H_{11} & V_{12}\\ V_{21} & H_{22}\end{bmatrix}\begin{bmatrix}\phi_1(x,t)\\ \phi_2(x,t)\end{bmatrix}. \quad (1)$$

The above equation is equivalent to the following equation

$$i\frac{\partial\phi_1(x,t)}{\partial t}=H_{11}\,\phi_1(x,t)+V_{12}\,\phi_2(x,t) \quad (2)$$

$$i\frac{\partial\phi_2(x,t)}{\partial t}=H_{22}\,\phi_2(x,t)+V_{21}\,\phi_1(x,t), \quad (3)$$

if V_{12} and V_{21} is the coupling between the potentials represented by $V_{12}=V_{21}=2k_0\delta(x)$, then the above equations reduces to

$$i\frac{\partial\phi_1(x,t)}{\partial t}=H_{11}\,\phi_1(x,t)+2k_0\delta(x)\,\phi_2(x,t) \quad (4)$$

$$i\frac{\partial\phi_2(x,t)}{\partial t}=H_{22}\,\phi_2(x,t)+2k_0\delta(x)\,\phi_1(x,t), \quad (5)$$

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taking the Laplace transform of Eq. (4), it can be written as

$$H_{11}\,\bar{\phi}_1(x,s)+2k_0\delta(x)\bar{\phi}_2(x,s)=is\,\bar{\phi}_1(x,s)-i\,\phi_1(x,0). \tag{6}$$

In a similar way Eq. (5) can also be written as

$$H_{22}\,\bar{\phi}_2(x,s)+2k_0\delta(x)\bar{\phi}_1(x,s)=is\,\bar{\phi}_2(x,s)-i\,\phi_2(x,0). \tag{7}$$

We put wave packet at time $t=0$ on the first potential, hence for second state in our problem $\phi_2(x,0)=0$, hence above equation reduced to

$$H_{22}\,\bar{\phi}_2(x,s)+2k_0\delta(x)\bar{\phi}_1(x,s)=is\,\bar{\phi}_2(x,s). \tag{8}$$

Eq. (8) can be rewritten as

$$(is-H_{22})\,\bar{\phi}_2(x,s)=2k_0\delta(x)\bar{\phi}_1(x,s), \tag{9}$$

or

$$\bar{\phi}_2(x,s)=(is-H_{22})^{-1}2k_0\delta(x)\bar{\phi}_1(x,s), \tag{10}$$

using the value of $\bar{\phi}_2(x,s)$ from above equation, Eq. (6) can be rewritten as

$$H_{11}\,\bar{\phi}_1(x,s)+2k_0^2\delta(x)G_2^0(0,0,s)\bar{\phi}_1(x,s)=is\,\bar{\phi}_1(x,s)-i\,\phi_1(x,0), \tag{11}$$

where $G_2^0(0,0,s)=\langle x_c|(is-H_{22})^{-1}|x_c\rangle$ is the Green's function for the second state. Eq. (11) is a single equation in Laplace domain which has the effect of second state in it, in terms of Green's function. We will now solve Eq. (11) by using a method similar to one discussed in ref. [12], hence the above equation at the point of coupling can be further reduced to the following two equation given by

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} &= is\,\bar{\phi}_1(x,s)-i\,\phi_1(x,0)\\ \frac{\partial\bar{\phi}_1(x,s)}{\partial x}\Big|_{x=0^+}-\frac{\partial\bar{\phi}_1(x,s)}{\partial x}\Big|_{x=0^-} &= 2k_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s). \end{aligned} \tag{12}$$

In order to solve Eq. (12), we should consider the homogeneous solution in order to satisfy the discontinuity condition at the point of coupling. Its solution is given by

$$\bar{\phi}_1(x,s)=\eta(s)\exp(i\sqrt{is}|x|)+\frac{1}{2\sqrt{is}}\int dx'\exp(i\sqrt{is}|x-x'|)\phi_1(x',0) \tag{13}$$

where $\eta(s)$ is an arbitrary function of s. Eq. (13) is the homogeneous solution of Eq. (12) with a constant $\eta(s)$which is to be determined using boundary conditions. Using the wave function given by Eq. (13) in Eq. (12), at the point of coupling we get

$$2i\sqrt{is}\,\eta(s)=2k_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s) \tag{14}$$

or

$$\eta(s)=\frac{k_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s)}{i\sqrt{is}} \tag{15}$$

with $k_0=-b_0$ *where* b_0 *is a positive real number*

$$\eta(s)=\frac{b_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s)}{i\sqrt{is}}. \tag{16}$$

In the above equation $k_0=-b_0$ is the strength of the coupling between two states which we will consider as a positive real number for any numerical calculation. Hence, the wave function can be written as

$$\bar{\phi}_1(x,s)=\frac{b_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s)}{i\sqrt{is}}\exp(i\sqrt{is}|x|)+\frac{1}{2\sqrt{is}}\int dx'\exp(i\sqrt{is}|x-x'|)\phi_1(x',0) \tag{17}$$

at point of coupling i.e. $x=0$, the above equation reduces to

$$\bar{\phi}_1(0,s)=\frac{b_0^2G_2^0(0,0,s)\bar{\phi}_1(0,s)}{i\sqrt{is}}+\frac{1}{2\sqrt{is}}\int dx'\exp(i\sqrt{is}|x'|)\phi_1(x',0) \tag{18}$$

Eq. (18) is a integral equation in Laplace domain which will determine the wave function at the point of coupling, so if the wave function can be determined at the origin then it can be determined everywhere. It is always preferable to have the solution of above equation in time domain but since we formulate this problem and its solution for any arbitrary potential and for different potentials we have different analytical expressions for Green's function so it is worth to express the solution in Laplace domain instead of time domain.

2.1. Derivation of the propagator for constant b_0

The solution in operator form can also be represented as

$$\bar{\phi}_1(x,s)=\int_{-\infty}^{\infty}dx'G(x,x',s)\phi_1(x',0) \tag{19}$$

where G is an propagator. To find the propagator we will make use of Eqs. (12) and (18) to find

$$\begin{aligned}\eta(s) &= \frac{{b_0}^2G_2^0(0,0,s)\bar{\phi}_1(0,s)}{i\sqrt{is}}\\ &= \frac{-b_0^2G_2^0(0,0,s)}{2\sqrt{s}}\frac{1}{\sqrt{s}+\sqrt{i}b_0^2G_2^0(0,0,s)}\\ &\times\int_{-\infty}^{\infty}dx'\ \exp(i\sqrt{is}|x'|\phi_1(x',0)\end{aligned} \tag{20}$$

from Eqs. (13) and (21) we get

$$G(x,x',s)=\frac{-b_0^2G_2^0(0,0,s)\exp(i\sqrt{is}(|x|+|x'|)}{2\sqrt{s}(\sqrt{s}+\sqrt{i}b_0^2G_2^0(0,0,s)}+\frac{\exp(i\sqrt{is}|x-x'|)}{2\sqrt{is}} \tag{21}$$

further we will see that this propagator is equivalent to one derived by us in our previous research using Feynman approach [4] and is presented in next section

2.2. Consistency between derived operator and Green's function using Feynman approach

We start with Eq. (11) given as

$$H_{11}\,\bar{\phi}_1(x,s)+2k_0^2\delta(x)G_2^0(0,0,s)\bar{\phi}_1(x,s)=is\,\bar{\phi}_1(x,s)-i\,\phi_1(x,0), \tag{22}$$

further this equation can be written as

$$[-is+H_{11}-k_1\delta(x)]\bar{\phi}_1(x,s)=-i\phi_1(x,0), \tag{23}$$