Multi-channel scattering problems with arbitrary coupling: Analytical approach for exact solution using Green’s functions

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We have proposed an analytical approach for exact solution of multi-channel scattering problems, in presence of arbitrary coupling. Our solution is quite general and is valid for any set of potentials, if the Green’s functions of the uncoupled potentials are known in the range of coordinate where coupling is non-zero. In this paper, it is shown that using our model, it is possible to express N-channel problem by N independent ‘single’ channel problems and hence one can have a realistic solution of multi-channel scattering problem with arbitrary coupling. In this paper we have shown that transition probability from first diabatic potential to any other potential can be easily calculated using a very simple analytical formula - which only require values of eigenfunction of first uncoupled potential and values of Green’s function of other uncoupled potential, in the range of coordinate where coupling is non-zero.

Keywords: Quantum mechanics; scattering; multi-channel; analytical model; Green’s function
I. INTRODUCTION

Nonadiabatic transition due to potential curve crossing is one of the most known mechanisms to induce electronic transitions\textsuperscript{1–14}. This is truly an interdisciplinary topic and appears in various fields of physics, chemistry and biology\textsuperscript{2,3,5,7,15}. The theory of non-adiabatic transitions dates back to 1932, when the pioneering works were done by Landau\textsuperscript{16}, Zener\textsuperscript{17} and Stueckelberg\textsuperscript{18} and by Rosen and Zener\textsuperscript{19}. Since then there are huge number of research papers in this area\textsuperscript{1–14}. For example, Osherov and Voronin analyzed the problem where two diabatic potentials are constant with exponential coupling\textsuperscript{20}. C. Zhu analyzed the problem where two diabatic potentials are exponential with exponential coupling\textsuperscript{21}. In our earlier publications we have reported analytical solution in those cases where two or more arbitrary potentials are coupled by Dirac Delta interactions\textsuperscript{15,22–27}. The Dirac Delta function coupling model has the great advantage that it can be solved exactly\textsuperscript{15,22–28}. Recently we have extended our research to deal with the cases where two potentials are coupled by any arbitrary interaction\textsuperscript{28}. The main problem in this area is the fact that the calculation of the N-channel Green’s function is impossible for a general system. In our most recent paper it is shown that if we use Dirac Delta coupling model, it is possible to express N-channel problem by N independent ‘single’ channel problem and hence one can have a realistic solution of multi-channel scattering problem\textsuperscript{29}. Using the same model it is also shown that the transition probability from first diabatic potential to any other potential can be easily calculated by using single equation with two boundary conditions\textsuperscript{29}. In the most recent paper, using the same model, we have shown that the transition probability from first diabatic potential to any other potential can be easily calculated using a very simple analytical formula - which only require value of eigenfunction of first uncoupled potential and value of Green’s function of other uncoupled potential, at the crossing\textsuperscript{29}. In this paper we again consider the same problem of two or more arbitrary diabatic potentials with arbitrary coupling, but we will discuss about a far simpler method, where the transition probability from first diabatic potential to any other potential can be easily calculated using a very simple analytical formula - which only require values of eigenfunction of first uncoupled potential and values of Green’s function of other uncoupled potential, in the range of coordinate where coupling is non-zero.
II. MULTI-CHANNEL SCATTERING PROBLEMS

A. Two Channel Scattering Problems

The time-independent Schrödinger equation for any two state system is given by

$$\begin{pmatrix} H_{11}(x) & V_{12}(x) \\ V_{21}(x) & H_{22}(x) \end{pmatrix} \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \end{pmatrix} = E \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \end{pmatrix}. \quad (1)$$

The above two equations can be expressed as follows

$$\psi_2(x) = V_{12}(x)^{-1} [E - H_{11}(x)] \psi_1(x) \quad \text{and}$$

$$\psi_2(x) = [E - H_{22}(x)]^{-1} V_{21}(x) \psi_1(x). \quad (2)$$

After eliminating $\psi_2(x)$ from the above two equations we get

$$[E - H_{11}(x)] \psi_1(x) - V_{12}(x) [E - H_{22}(x)]^{-1} V_{21}(x) \psi_1(x) = 0. \quad (3)$$

The above equations simplify considerably if $V_{12}(x)$ and $V_{21}(x)$ are expressed as a sum Dirac delta functions of appropriate strengths, which can be expressed using operator notation as $V = \sum_{i=1}^{N} K_{12}^i |x_i\rangle \langle x_i|$. The weight factor $K_{12}^i$ varies depending on the scheme of discretization used. The above equation now become

$$\left( [E - H_{11}(x)] - \sum_{i=1}^{N} \sum_{j=1}^{N} K_{12}^i K_{12}^j |x_i\rangle \langle x_i| [E - H_{22}]^{-1} |x_j\rangle \langle x_j| \right) \psi_1(x) = 0. \quad (4)$$

This may be written as

$$\left[ H_{11}(x) + \sum_{i=1}^{N} K_{12}^i 2 \delta(x - x_i) G_2^0(x_i, x_i; E) \right] \psi_1(x) = E \psi_1(x), \quad (5)$$

where

$$G_2^0(x_i, x_i; E) = \langle x_i| [E - H_{22}]^{-1} |x_i\rangle. \quad (6)$$

So the effect of second potential is entering into the above equation in terms of Dirac Delta functions and $K_{12}^i 2 G_2^0(x_i, x_i; E)$ in general is a complex valued function. If we express $H_{11}(x)$ in terms of kinetic energy and potential energy $[V_1(x)]$ terms, the above equation becomes

$$- \frac{\hbar^2}{2m} \frac{d^2 \psi_1(x)}{dx^2} + V_1(x) \psi_1(x) + \sum_{i=1}^{N} K_{12}^i 2 \delta(x - x_i) G_2^0(x_i, x_i; E) \psi_1(x) = E \psi_1(x). \quad (7)$$
If we take the complex conjugate of the above equation we get
\[-\frac{\hbar^2}{2m} \frac{d^2 \psi_1^*(x)}{dx^2} + V_1(x) \psi_1^*(x) + \sum_{i=1}^{N} K_{12}^i \delta(x-x_i) G_2^0(x_i, x_i; E) \psi_1^*(x) = E \psi_1^*(x). \quad (8)\]

Multiplying \(\psi_1^*(x)\) from the left to Eq. (7) and multiplying \(\psi_1(x)\) from the left to Eq. (8) we get
\[-\frac{\hbar^2}{2m} \psi_1^*(x) \frac{d^2 \psi_1(x)}{dx^2} - V_1(x) \psi_1^*(x) \psi_1(x) + \sum_{i=1}^{N} K_{12}^i \psi_1^*(x) \delta(x-x_i) G_2^0(x_i, x_i; E) \psi_1(x) = E \psi_1^*(x) \psi_1(x), \quad (9)\]

and
\[-\frac{\hbar^2}{2m} \psi_1(x) \frac{d^2 \psi_1^*(x)}{dx^2} + V_1(x) \psi_1(x) \psi_1^*(x) + \sum_{i=1}^{N} K_{12}^i \psi_1(x) \delta(x-x_i) G_2^0(x_i, x_i; E) \psi_1^*(x) = E \psi_1(x) \psi_1^*(x). \quad (10)\]

Now subtracting Eq. (10) from Eq. (9) we get
\[-\frac{\hbar^2}{2m} \left[ \psi_1^*(x) \frac{d^2 \psi_1(x)}{dx^2} - \psi_1(x) \frac{d^2 \psi_1^*(x)}{dx^2} \right] + \sum_{i=1}^{N} K_{12}^i \left( G_2^0(x_i, x_i; E) - G_2^0(x_i, x_i; E)^* \right) \psi_1(x) \psi_1^*(x) \delta(x-x_i) = 0. \quad (11)\]

After simplification of Eq. (11), we get
\[-\frac{\hbar^2}{2m} \left[ \psi_1^*(x) \frac{d \psi_1(x)}{dx} - \psi_1(x) \frac{d \psi_1^*(x)}{dx} \right] + \sum_{i=1}^{N} K_{12}^i \left( G_2^0(x_i, x_i; E) - G_2^0(x_i, x_i; E)^* \right) \psi_1(x) \psi_1^*(x) \delta(x-x_i) = 0. \quad (12)\]

Integrating the above equation from \(x_i - \epsilon\) to \(x_i + \epsilon\).
\[\frac{\hbar^2}{2m} \left[ \psi_1^*(x) \frac{d \psi_1(x)}{dx} - \psi_1(x) \frac{d \psi_1^*(x)}{dx} \right]_{x_i-\epsilon}^{x_i+\epsilon} = K_{12}^i \left( G_2^0(x_i, x_i; E) - G_2^0(x_i, x_i; E)^* \right) \psi_1(x_i) \psi_1^*(x_i). \quad (13)\]

After simplification we get
\[\frac{\hbar}{2mi} \left[ \psi_1^*(x) \frac{d \psi_1(x)}{dx} - \psi_1(x) \frac{d \psi_1^*(x)}{dx} \right]_{x_i-\epsilon}^{x_i+\epsilon} = \frac{2K_{12}^i}{\hbar} \Im \left[ G_2^0(x_i, x_i; E) \right] \psi_1(x_i) \psi_1^*(x_i). \quad (14)\]

So the transition probability from one diabatic potential to another at \(x_i\) is given by
\[T_{12}^{i\epsilon}(E) = \frac{2K_{12}^i}{\hbar} \Im \left[ G_2^0(x_i, x_i; E) \right] \psi_1(x_i) \psi_1^*(x_i). \quad (15)\]

This is a very simple formula, for using \(T_{12}^{i\epsilon}(E)\) one only needs to know the value of \(G_2^0(x_i, x_i; E)\) and \(\psi_1(x)\) at \(x = x_i\). But for calculating the total transition probability from one diabatic potential to another, we have to add contributions from several points for which
coupling potential is effectively non-zero. So the total transition probability will be given by

\[ T_{12}(E) = \sum_{i=1}^{N} T_{i2}^i(E). \]  

(16)

**B. Three Channel Scattering Problems**

The time-independent Schrödinger equation for three state system is given by

\[
\begin{pmatrix}
    H_{11}(x) & V_{12}(x) & V_{13}(x) \\
    V_{21}(x) & H_{22}(x) & 0 \\
    V_{31}(x) & 0 & H_{33}(x)
\end{pmatrix}
\begin{pmatrix}
    \psi_1(x) \\
    \psi_2(x) \\
    \psi_3(x)
\end{pmatrix}
= E
\begin{pmatrix}
    \psi_1(x) \\
    \psi_2(x) \\
    \psi_3(x)
\end{pmatrix}. 
\]  

(17)

This above matrix equation can be written in the following form

\[ [H_{11}(x) - E] \psi_1(x) + V_{12}(x)\psi_2(x) + V_{13}(x)\psi_3(x) = 0, \]

\[ [H_{22}(x) - E] \psi_2(x) + V_{21}(x)\psi_1(x) = 0 \quad \text{and} \quad [H_{33}(x) - E] \psi_3(x) + V_{31}(x)\psi_1(x) = 0. \]  

(18)

The above equation after rearranging is given below

\[ [E - H_{11}(x)] \psi_1(x) - V_{12}(x)\psi_2(x) - V_{13}(x)\psi_3(x) = 0, \]

\[ \psi_2(x) = [E - H_{22}(x)]^{-1} V_{21}(x)\psi_1(x) \quad \text{and} \quad \psi_3(x) = [E - H_{33}(x)]^{-1} V_{31}(x)\psi_1(x). \]  

(19)

(20)

(21)

After eliminating both \( \psi_2(x) \) and \( \psi_3(x) \) from Eq. (19) we get

\[
\left( H_{11}(x) + V_{12}(x) [E - H_{22}(x)]^{-1} V_{21}(x) + V_{13}(x) [E - H_{33}(x)]^{-1} V_{31}(x) \right) \psi_1(x) = E\psi_1(x). 
\]  

(22)

The above equations are true for any general \( V_{12}, V_{21}, V_{13} \) and \( V_{31} \). The above equation simplify considerably if \( V_{12}, V_{13}, V_{31} \) and \( V_{21} \) are Dirac Delta functions, which we write in operator notation as \( V_{12} = V_{21} = \sum_{i=1}^{N} K_{12}^i |x_i\rangle \langle x_i| \) and \( V_{13} = V_{31} = \sum_{j=1}^{N} K_{13}^j |x_j\rangle \langle x_j| \). The above equation now becomes

\[
\left( H_{11}(x) + \sum_{i=1}^{N} K_{12}^i \delta(x - x_i) G_2^0(x_i, x_i; E) + \sum_{j=1}^{N} K_{13}^j \delta(x - x_j) G_3^0(x_j, x_j; E) \right) \psi_1(x) = E\psi_1(x). 
\]  

(23)
So the effect of second and third potential is entering into the above equation in terms of Dirac Delta functions. Now one can use a method similar to that used in last section, to calculate the transition probability \([T_{12}(E)]\) from first potential to the second potential. The analytical expression for \(T_{12}(E)\) becomes

\[
T_{12}(E) = \sum_{i=1}^{N} T_{12}^{x_i}(E),
\]

where

\[
T_{12}^{x_i}(E) = \frac{2K^{0}}{\hbar}Im \left[ G_2^0(x_i, x_i; E) \right] \psi_1(x_i) \psi_1^*(x_i). \tag{25}
\]

Similarly transition probability \([T_{13}(E)]\) from first potential to the third potential is given by

\[
T_{13}(E) = \sum_{j=1}^{N} T_{13}^{x_j}(E),
\]

where

\[
T_{13}^{x_j}(E) = \frac{2K^{0}}{\hbar}Im \left[ G_3^0(x_j, x_j; E) \right] \psi_1(x_j) \psi_1^*(x_j). \tag{27}
\]

C. \(N\) Channel Scattering Problems

The time-independent Schrödinger equation for a \(N\) state system, given by

\[
\begin{pmatrix}
H_{11}(x) & V_{12}(x) & V_{13}(x) & \ldots & V_{1N}(x) \\
V_{21}(x) & H_{22}(x) & 0 & 0 & 0 \\
V_{31}(x) & 0 & H_{33}(x) & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
V_{N1}(x) & 0 & 0 & \ldots & H_{NN}(x)
\end{pmatrix}
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x) \\
\vdots \\
\psi_N(x)
\end{pmatrix} = E
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x) \\
\vdots \\
\psi_N(x)
\end{pmatrix}. \tag{28}
\]

The above matrix equation can be written in the following form

\[
[H_{11}(x) - E] \psi_1(x) + \sum_{n=2}^{n=N} V_{1n}(x) \psi_n(x) = 0 \quad \text{and}
\]

\[
[H_{nn}(x) - E] \psi_n(x) + V_{n1}(x) \psi_1(x) = 0.
\]

The above equations after rearrangement are given below

\[
[E - H_{11}(x)] \psi_1(x) - \sum_{n=2}^{n=N} V_{1n}(x) \psi_n(x) = 0 \quad \text{and}
\]

\[
\psi_n(x) = [E - H_{nn}(x)]^{-1} V_{n1}(x) \psi_1(x) \quad \text{for } n > 1. \tag{31}
\]
After eliminating $\psi_n(x)$ from Eq.(30) we get

$$\left( H_{11}(x) + \sum_{n=2}^{N} V_{1n}(x) [E - H_{nn}(x)]^{-1} V_{n1}(x) \right) \psi_1(x) = E\psi_1(x) .$$

(32)

The above equations are true for any general $V_{1n}$ and $V_{n1}$. The above equation simplify considerably if $V_{1n}$ and $V_{n1}$ are Dirac Delta functions, which we write in operator notation as $V_{1n} = V_{n1} = \sum_{i=1}^{N} K_{1n}^{i} |x_{n}^{i}\rangle \langle x_{n}^{i}|$. The above equation now becomes

$$\left( H_{11}(x) + \sum_{n=2}^{N} \sum_{i=1}^{N} K_{1n}^{i} \delta(x - x_{n}^{i}) G_{n}^{0}(x_{n}^{i}, x_{n}^{i}; E) \right) \psi_1(x) = E\psi_1(x) .$$

(33)

So the effect of all other potentials are entering into the above equation in terms of Dirac Delta functions. Now one can use a method similar to that used in last section, to calculate the transition probability $[T_{1n}(E)]$ from first potential to the n-th potential. The analytical expression for $T_{1n}(E)$ becomes

$$T_{1n}(E) = \sum_{i=1}^{N} T_{1n}^{x_i}(E) ,$$

(34)

where

$$T_{1n}^{x_i}(E) = \frac{2K_{1n}^{0} \delta}{\hbar} \text{Im} \left[ G_{n}^{0}(x_{i}, x_{i}; E) \right] \psi_1(x_{i}) \psi_{1}^{*}(x_{i}) .$$

(35)

III. CONCLUSIONS:

We have proposed a very simple general method for finding an exact analytical solution for the multi-channel quantum scattering problem in presence of arbitrary coupling. Our solution is quite general and is valid for any potential. We have shown that transition probability from first diabatic potential to any other potential can be easily calculated using a very simple analytical formula - which only require values of eigenfunction of first uncoupled potential and values of Green’s function of other uncoupled potential, in the range of coordinate where coupling is non-zero.

ACKNOWLEDGMENTS

A.C. would like to thank Prof. M. S. Child for his kind interest, suggestions and encouragements.
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