Three state scattering problem: Exact analytical solution approach

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Abstract

Using Dirac Delta function couplings we have proposed a simple analytical approach to find exact analytical solution to scattering problems where the interacting states can be two, three or even $n$ in number. The analytical method presented here requires the knowledge of six boundary conditions and with the use of these the transition probability form one diabatic potential to another diabatic potential is calculated by a simple analytical formula.

Keywords: Quantum mechanics; scattering; multi-channel; analytical model; boundary conditions

1. Introduction

In various kind of atomic and molecular dynamic processes there are different type of transitions which occurs effectively in between molecular states and indeed it is not wrong to say that potential energy curve crossings are involved in such kind of processes. Non adiabatic transitions(transitions between two adiabatic states or diabatic states) generally occur between bound states$^1$. Various dynamic processes which occurs in fields of biology, chemistry and physics, non adiabatic transitions plays a very important role

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in change of state/phase\textsuperscript{2, 3, 4, 5, 6}. Apart from above, various spectroscopic, collision processes and various reactions are governed by non adiabatic transitions at crossing or avoided crossing of the potential energy surfaces\textsuperscript{7}. Other processes like radiationless transitions in condense matter physics, fluorescence quenching, self-trapping of excitons, laser assisted collision reactions are some of the examples\textsuperscript{8, 9} where non adiabatic transitions due to curve crossing or avoided crossing plays important role. Other important fields of study where non adiabatic transition plays an important role include the Zener transition in flux driven metallic rings\textsuperscript{10}, superconducting Josephson junctions\textsuperscript{11}, nuclear collisions and reactions in nuclear physics\textsuperscript{12}, electron-proton transfer processes in biological molecules\textsuperscript{13}. Non adiabatic transition also plays a very important role in neutrino conversion in the sun and provide an evidence for its existence in the mutability of the universe\textsuperscript{14}. It was also commented by Sason S. sheik\textsuperscript{15} that curve crossing /avoided crossing could be interpret as a general mechanism of rearrangement of electrons by molecules leading to the formation and breaking of bonds. Non adiabatic transition are also studied as a mechanism of dissociation of molecules on metal surfaces as reported by R. Kosloff\textsuperscript{16} in his studies. The first report on non adiabatic transition comes into existence in 1932, when the prime works were published by Landau\textsuperscript{17}, Zener\textsuperscript{18} and Stueckelberg\textsuperscript{19} and by Rosen and Zener\textsuperscript{20}. From 1932 onwards we have numerous research papers in this area using analytical as well as computational approach\textsuperscript{21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33}. We have also explored the area of non adiabatic transition using analytical methods (Our Dirac Delta coupling model) and reported analytical solution in those cases where two or more arbitrary potentials are coupled by Dirac Delta interactions\textsuperscript{34, 35, 36, 37, 38, 39, 40, 41, 42, 43}. This Dirac Delta function coupling model has a plus point that we can get exact analytical solution using such model. Recently we have extended our research to deal with the cases where two potentials are coupled by any arbitrary interaction\textsuperscript{44}. The present work is an extension of two state scattering problem to three state scattering problem where we have to find the six boundary conditions and with the help of these six boundary conditions we can calculate the transition probability from one diabatic potential to another diabatic potential by the use of a simple analytical formula. we have examine our approach succesfully by considering the three simple examples of constant, linear and exponentiel potentials and calulated the transition probability from one diabatic state to another diabatic state. In a similar fashion we can extend
the three state to four, five and so on to multi state scattering problem and can find the transition probability between any two states with the help of simple formula.

2. Three Channel scattering Problems

We consider a particle moving on any of the three diabatic curves and we calculate the probability of the particle on the same diabatic curve after a time $t$. The probability amplitude for the particle can be written as

$$\Psi(x) = \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \\ \psi_3(x,t) \end{pmatrix}. $$

(1)

where $\psi_1(x,t)$, $\psi_2(x,t)$ and $\psi_3(x,t)$ are the probability amplitude for the three states. The matrix equation for this system is given by

$$H = \begin{pmatrix} H_{11}(x) & V_{12}(x) & V_{13}(x) \\ V_{21}(x) & H_{22}(x) & 0 \\ V_{31}(x) & 0 & H_{33}(x) \end{pmatrix}, $$

(2)

where $H_{11}(x)$, $H_{22}(x)$, $H_{33}(x)$, $V_{12}(x)$, $V_{21}(x)$, $V_{31}(x)$ and $V_{13}(x)$ are defined by

$$H_{11}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_1(x), $$

(3)

$$H_{22}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_2(x), $$

$$H_{33}(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_3(x), $$

$$V_{12}(x) = V_{21}(x) = K_0 \delta(x - x_c) \quad \text{and} \quad V_{13}(x) = V_{31}(x) = K_0 \delta(x - x_c). $$

In the above equation $V_1(x)$, $V_2(x)$ and $V_3(x)$ are determined by the shape of that diabatic curve. The time-independent Schrödinger equation for this problem will look like as given below

$$\begin{pmatrix} H_{11}(x) & K_0 \delta(x - x_c) & K_0 \delta(x - x_c) \\ K_0 \delta(x - x_c) & H_{22}(x) & 0 \\ K_0 \delta(x - x_c) & 0 & H_{33}(x) \end{pmatrix} \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \\ \psi_3(x) \end{pmatrix} = E \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \\ \psi_3(x) \end{pmatrix}. $$

(4)
Converting this matrix equation into following three equations will give us

\[
H_{11}(x)\psi_1(x) + K_0\delta(x - x_c)\psi_2(x) + K_0\delta(x - x_c)\psi_3(x) = E\psi_1(x),
\]
\[
K_0\delta(x - x_c)\psi_1(x) + H_{22}(x)\psi_2(x) = E\psi_2(x) \quad \text{and}
\]
\[
K_0\delta(x - x_c)\psi_1(x) + H_{33}(x)\psi_3(x) = E\psi_3(x).
\]

Now, we obtain three boundary conditions by integrating the above three equations form \( x_c - \eta \) to \( x_c + \eta \) (where \( \eta \to 0 \)) and get the following

\[
-\frac{\hbar^2}{2m} \left[ \frac{d\psi_1(x)}{dx} \right]_{x_c - \eta}^{x_c + \eta} + K_0\psi_2(x_c) + K_0\psi_3(x_c) = 0,
\]
\[
-\frac{\hbar^2}{2m} \left[ \frac{d\psi_2(x)}{dx} \right]_{x_c - \eta}^{x_c + \eta} + K_0\psi_1(x_c) = 0 \quad \text{and}
\]
\[
-\frac{\hbar^2}{2m} \left[ \frac{d\psi_3(x)}{dx} \right]_{x_c - \eta}^{x_c + \eta} + K_0\psi_1(x_c) = 0.
\]

In addition to above three boundary conditions, we have three more boundary conditions stated as

\[
\psi_1(x_c - \eta) = \psi_1(x_c + \eta)
\]
\[
\psi_2(x_c - \eta) = \psi_2(x_c + \eta) \quad \text{and}
\]
\[
\psi_3(x_c - \eta) = \psi_3(x_c + \eta).
\]

Now, in total we have six boundary conditions. Using these six boundary conditions we have obtained the transition probability from one diabatic potential to the other in the case of coupling between (a) three constant potentials, (b) three linear potentials and (c) three exponential potentials.

**Exact analytical solution for constant potential case:**

The time-independent Schrödinger equation for the first potential in the region 1, i.e. \( x < x_c \), is given by

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} + V_1(x)\psi_1(x) = E\psi_1(x).
\]

The solution of the above equation is given by

\[
\psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x},
\]
where \( k_1 = \sqrt{\frac{2m}{\hbar^2}(E - V_1)} \). The time-independent Schrödinger equation for the first potential in region 2, i.e. \((x > x_c)\), is given by

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_1(x)}{\partial x^2} + V_1(x)\psi_1(x) = E\psi_1(x).
\]

(10)

The solution of above equation in region 2, given by

\[
\psi_1(x) = Ce^{ik_1x}.
\]

(11)

Similarly, for second potential the time-independent Schrödinger equation in region 1, i.e. \((x < x_c)\), is given by

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(x)}{\partial x^2} + V_2(x)\psi_2(x) = E\psi_2(x).
\]

(12)

The physically acceptable solution of the above equation is given by

\[
\psi_2(x) = D_1e^{-ik_2x},
\]

(13)

where \( k_2 = \sqrt{\frac{2m}{\hbar^2}(E - V_2)} \). In region 2, i.e. \((x > x_c)\), the time-independent Schrödinger equation for the second potential is given by

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_2(x)}{\partial x^2} + V_2(x)\psi_2(x) = E\psi_2(x).
\]

(14)

The physically acceptable solution of the above equation is given by

\[
\psi_2(x) = F_1e^{ik_2x}.
\]

(15)

The time-independent Schrödinger equation for the third potential in region 1, i.e. \((x < x_c)\), is given by

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_3(x)}{\partial x^2} + V_3(x)\psi_3(x) = E\psi_3(x).
\]

(16)

The physically acceptable solution of the above equation is given by

\[
\psi_3(x) = D_2e^{-ik_3x},
\]

(17)

where \( k_3 = \sqrt{\frac{2m}{\hbar^2}(E - V_3)} \). In region 2, i.e. \((x > x_c)\), the time-independent Schrödinger equation for the third potential is given by

\[
- \frac{\hbar^2}{2m} \frac{\partial^2 \psi_3(x)}{\partial x^2} + V_3(x)\psi_3(x) = E\psi_3(x).
\]

(18)
The physically acceptable solution of the above equation is given by
\[ \psi_3(x) = F_2 e^{ik_3x}. \]  
(19)

Now we put \( x_c = 0 \) and using six boundary conditions mentioned above we have derived analytical expression for transition probabilities from first potential to the second and third potential. The transition probability from the first potential to the second potential \( T_{1\to2} \) is given by
\[ T_{1\to2} = \frac{2k_2}{k_1} \left| \frac{k_1}{k_2} \frac{1}{k_{10m} + k_{20m} + k_{30m}} \right|^2 \]  
(20)

The transition probability from the first potential to the third potential \( T_{1\to3} \) is given by
\[ T_{1\to3} = \frac{2k_3}{k_1} \left| \frac{k_1}{k_3} \frac{1}{k_{10m} + k_{20m} + k_{30m}} \right|^2 \]  
(21)

The total transition probability from the first potential to both the second potential and the third potential is given by
\[ T = T_{1\to2} + T_{1\to3} \]  
(22)

In our numerical calculation we use atomic unit. \( V_1(x) = 0.0, V_2(x) = 2.0 \) and \( V_3(x) = 3.0 \). So \( \hbar = 1 \) unit. The value of \( K_0 \) we took is 1.0 unit. In our calculation \( m \) is taken to be unity. The Schematic diagram for three potential case is shown in Figure 1, while the result of our calculation are shown in Figure 2 and Figure 3. \( T_{1\to2} \) and \( T_{1\to3} \) represents the plot of transition probability from 1st diabatic potential to 2nd and 3rd diabatic potential respectively.

**Exact analytical solution for Linear potential case:**

The time-independent Schrödinger equation for the case where a linear potential is coupled to another two linear potentials through a Dirac delta potential (Schematic diagram is shown in Figure 4).

\[
\begin{pmatrix}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_1 x & K_0 \delta(x - x_c) & K_0 \delta(x - x_c) \\
K_0 \delta(x - x_c) & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_2 x & 0 \\
K_0 \delta(x - x_c) & 0 & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_3 x
\end{pmatrix}
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x)
\end{pmatrix}
= E
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x)
\end{pmatrix}.
\]  
(23)
The Eq. (23) can be split into three equations

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_1 x \right) \psi_1(x) + K_0 \delta(x) \psi_2(x) + K_0 \delta(x) \psi_3(x) = E \psi_1(x) , \tag{24}
\]

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_2 x \right) \psi_2(x) + K_0 \delta(x) \psi_1(x) = E \psi_2(x) \quad \text{and}
\]

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_3 x \right) \psi_3(x) + K_0 \delta(x) \psi_1(x) = E \psi_3(x) .
\]

The time-independent Schrödinger equation for the first diabatic potential is given below

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_1 x \right) \psi_1(x) = E \psi_1(x) . \tag{25}
\]

In region 1 ( \( x < x_c \) ) the physically acceptable solution is

\[
\psi_1(x) = (A + B) A_i \left[ 2^{\frac{1}{3}}(E + x) \right] + i(A - B) B_i \left[ 2^{\frac{1}{3}}(E - x) \right] . \tag{26}
\]

Here, \( A_i[z] \text{ and } B_i[z] \) denotes the Airy functions. In the above expression \( A \) denotes the probability amplitude for the motion along the positive direction and \( B \) denotes the probability amplitude for the motion along the negative direction. So the acceptable solution in region 2 ( \( x > x_c \) ), is

\[
\psi_1(x) = CA \left[ 2^{\frac{1}{3}}(E - x) \right] . \tag{27}
\]

In this region the net flux is zero.

The time-independent Schrödinger equation for the second diabatic potential is given below

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_2 x \right) \psi_2(x) = E \psi_2(x) . \tag{28}
\]

In region 1 ( \( x < x_c \) ) the physically acceptable solution is

\[
\psi_2(x) = D_1 A_i \left[ 2^{\frac{1}{3}}(E - x) \right] . \tag{29}
\]

In this region the net flux is zero. In region 2 ( \( x > x_c \) ) the physically acceptable solution is given below

\[
\psi_2(x) = F_1 \left( A_i \left[ 2^{\frac{1}{3}}(E - x) \right] - iB_i \left[ 2^{\frac{1}{3}}(E - x) \right] \right) . \tag{30}
\]
The time-independent Schrödinger equation for the third diabatic potential is given below

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + p_3 x \right) \psi_3(x) = E \psi_3(x).
\]  

(31)

In region 1 \((x < x_c)\) the physically acceptable solution is

\[
\psi_3(x) = D_2 A_i \left[ (-0.5 - 0.866025 i) (-2E - x) \right].
\]  

(32)

In this region the net flux is zero. In region 2 \((x > x_c)\) the physically acceptable solution is

\[
\psi_3(x) = F (A_i \left[ (-0.5 - 0.866025 i) (-2E - x) \right] - iB_i \left[ (-0.5 - 0.866025 i) (-2E - x) \right])
\]  

(33)

Using the six boundary conditions mentioned above (here we put \(x_c = 0\)), we calculate the transition probability from one diabatic potential to all the other diabatic potentials. The result of our calculation is shown in Figure 5 and Figure 6. In our numerical calculation we use atomic unit. So \(\hbar = 1\) unit. The value of \(K_0\) we took is 1.0 unit. In our calculation \(m\) is taken to be unity. \(T_{1\rightarrow2}\) and \(T_{1\rightarrow3}\) represents the plot of transition probability from 1st diabatic potential to 2nd and 3rd diabatic potential respectively.

The schematic diagram which represents the one exponential potential coupled to other two exponential potentials in the diabatic representation is shown in Figure 7. Here, we start with the time-independent Schrödinger equation for a three state system

\[
\begin{pmatrix}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_1 x} & K_0 \delta(x - x_c) & K_0 \delta(x - x_c) \\
K_0 \delta(x - x_c) & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_2 x} & 0 \\
K_0 \delta(x - x_c) & 0 & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{b x}
\end{pmatrix}
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x)
\end{pmatrix}
= E
\begin{pmatrix}
\psi_1(x) \\
\psi_2(x) \\
\psi_3(x)
\end{pmatrix}
\]  

(34)

Eq.(34) can be split into

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_1 x} \right) \psi_1(x) + K_0 \delta(x - x_c) \psi_2(x) + K_0 \delta(x - x_c) \psi_3(x) = E \psi_1(x)
\]  

(35)

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_2 x} \right) \psi_2(x) + K_0 \delta(x - x_c) \psi_1(x) = E \psi_2(x)
\]

and

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{b x} \right) \psi_3(x) + K_0 \delta(x - x_c) \psi_1(x) = E \psi_3(x).
\]
For the first diabatic potential, the time-independent Schrödinger equation is given by
\[
\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_{1}x}\right)\psi_1(x) = E\psi_1(x). \quad (36)
\]
In the region 1, \(x < x_c\), the physically acceptable solution is given by
\[
\psi_1(x) = A e^{-\sqrt{2E} \pi i (2 \sqrt{2 e^x}) \Gamma(1+2 i \sqrt{2E})} + B e^{\sqrt{2E} \pi i (2 \sqrt{2 e^x}) \Gamma(1-2 i \sqrt{2E})}. \quad (37)
\]
In the region 2, where \(x > x_c\) the physically acceptable solution is given by
\[
\psi_1(x) = C K_{-2 i \sqrt{2E}}(2 \sqrt{2 e^x}). \quad (38)
\]
For the second diabatic potential, the time-independent Schrödinger equation is given by
\[
\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_0 e^{a_{2}x}\right)\psi_2(x) = E\psi_2(x) \quad (39)
\]
In the region 1, \(x < x_c\) the physically acceptable solution is given by
\[
\psi_2(x) = F_1 (-1)^{-i \sqrt{2E}} I_{-2 i \sqrt{2E}}(2 \sqrt{2 e^x}) \Gamma(1 - 2 i \sqrt{2E}) \quad (40)
\]
In the region 2, where \(x > x_c\) the physically acceptable solution is given by
\[
\psi_2(x) = D_1 K_{-2 i \sqrt{2E}}(2 \sqrt{2 e^x}). \quad (41)
\]
For the third diabatic potential, the time-independent Schrödinger equation is given by
\[
\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + e^{bx}\right)\psi_3(x) = E\psi_3(x) \quad (42)
\]
In the region 1, \(x < x_c\) the physically acceptable solution is given by
\[
\psi_3(x) = F_2 (-1)^{(-2.82845)i \sqrt{2E}} I_{-5.65685i \sqrt{2E}}(5.65685 \sqrt{2.71828 - 0.5x}) \Gamma\left[1 - (5.65685i \sqrt{2E})\right] \quad (43)
\]
In the region 2, where \(x > x_c\) the physically acceptable solution is given by
\[
\psi_3(x) = D_2 K_{-2 i \sqrt{2E}}(2 \sqrt{2 e^{-x/2}}). \quad (44)
\]
Using six boundary conditions as mentioned above and putting \(x_c = 0\), we have calculated the transition probability from one exponential potential to all other exponential potentials. The result of our calculation is shown in Figure 8 and Figure 9. In our numerical calculation we use atomic unit. So \(\hbar = 1\). The values of \(K_0\) we took is 0.1. In our calculation the value of \(m\) is taken to be unity. \(T_{1\rightarrow 2}\) and \(T_{1\rightarrow 3}\) represents the plot of transition probability form 1st diabatic potential to 2nd and 3rd diabatic potential respectively.

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3. Conclusions:

In the present work we have proposed a general method for finding the exact analytical solution for the three state quantum scattering problem and given a simple analytical formula. This analytical formula requires the use of six boundary conditions and with the help of these six boundary conditions the transition probability from one diabatic potential to another diabatic potential can be calculated. We have also solved few simple examples of i.e. three constant potentials, three linear potential and three exponential potentials coupled by Dirac Delta coupling and calculated the transition probability from one diabatic potential to another diabatic potential. Same approach can be applicable to calculate the transition probability from \( i^{th} \) diabatic potential to \( j^{th} \) diabatic potential where \( i = 1, 2, 3...n \) and \( j = 2, 3, 4...n + 1 \). This method can be further generalised to solve the general multi channel scattering problem.

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