Multichannel Scattering Problem with Non-trivial
Asymptotic Non-adiabatic Coupling

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Abstract. The multichannel scattering problem in an adiabatic representation is considered. The non-adiabatic coupling matrix is assumed to have a non-trivial constant asymptotic behavior at large internuclear separations. The asymptotic solutions at large internuclear distances are constructed. It is shown that these solutions up to the first order of perturbation theory are identical to the asymptotic solutions of the re-projection approach, which was proposed earlier as a remedy for the electron translation problem in the context of the Born-Oppenheimer treatment.

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1. Introduction

1.1. Background

The adiabatic approach is one of the most widely used methods for a theoretical study of a low-energy quantum collision problem in atomic and molecular physics [1]. In the context of the two-atom collision problem, this consists of using the eigenfunctions of an electronic sub-Hamiltonian as the basis for expanding the total wave function, which then leads to the resulting multichannel equations.

One of the main approximations within this approach includes the Born-Oppenheimer approximation [2], which corresponds to neglecting all non-adiabatic couplings. The adiabatic representation is complete if all the couplings are kept in the formalism and, therefore, yields in principle the exact solution to the Schrödinger equation. The main, and computationally challenging, difficulty of solving the scattering problem in the adiabatic representation is related to the strong non-adiabatic couplings between the channels. Critically, these may happen in the region of an (avoided) crossing of electronic energy levels which, as a rule, appear at finite inter-atomic distances. One of the methods to overcome that difficulty is by a reformulation of the problem into the diabatic representation or into the more flexible split diabatic representation (see, for example, [3, 4] and references therein). Another source of non-trivial non-adiabatic couplings is associated with the so-called molecular-state problem (sometimes also called the electronic translation problem), which appears in the formalism as the non-zero limit of the non-adiabatic coupling matrix elements when the internuclear distance tends to infinity [5, 6, 7, 8, 9, 10]. It is well understood [9, 10, 11, 12] that the physical reason for these non-vanishing asymptotic couplings is due to the fact that the adiabatic approach is based on the molecular representation and, hence, on the molecular coordinates, typically, the Jacobi molecular coordinates, in which electrons are measured from the centre of nuclear mass. The problem is that the molecular coordinates which are used to describe fixed-nuclei molecular states of the collision complex at small and intermediate distances are not suited for the description of the free atoms in the asymptotic region. The difference arises from the fact that the inter-atomic vectors connecting the centres of mass of colliding atoms do not coincide with the internuclear vectors which connect the centres of mass of the respective nuclei. This results in non-zero asymptotic couplings in coupled channel equations calculated in the molecular representation. Thus, non-zero asymptotic couplings in coupled channel equations are fundamental features of the standard Born-Oppenheimer approach. This property, if present, makes the simple Born-Oppenheimer asymptotic form of the scattering wave function in the adiabatic representation no longer valid.

One of the successful methods for constructing a suitable asymptotic form of the wave function in the adiabatic representation is provided by the re-projection procedure [9, 10, 11, 12]. This procedure utilises the physically motivated asymptotic form of the total wave function which here is represented in the channel specific Jacobi coordinates by the atomic eigenstates of non-interacting atoms. The asymptotic form of the wave
function in the adiabatic representation is then calculated by re-projecting this total asymptotic wave function onto the adiabatic (molecular) basis. Although this procedure is well established, with respect to the adiabatic representation itself it requires the use of an outer information on the asymptotic form of the total wave function. On the other hand, a complete adiabatic representation must automatically generate the correct asymptotic form of the wave function in the adiabatic representation. The asymptotic wave function should be calculated from the asymptotic solutions of the adiabatic coupled channel equations in the region of large internuclear distances. However, as to the best of our knowledge, such a method of constructing the asymptotic wave function, which plays the role of boundary conditions in the adiabatic representation formalism, is not properly addressed in the literature. This motivated us to undertake the present study.

The paper is organised as follows. The definition of the problem is given in the following subsection. The two channel model is considered in section two since it demonstrates the exact analytic solution of the asymptotic two-channel equations in all required details. In section three we consider the general situation when the asymptotic non-adiabatic coupling matrix couples an arbitrary number of channels $N$. Section four concludes the paper. The proof of a technical statement about the roots of the specific polynomial with matrix coefficients appeared in the formalism is given in the appendix.

1.2. Multichannel adiabatic equations and Born-Oppenheimer asymptotic states

The issue under consideration is the scattering problem for the set of equations

$$\left[-\frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{r^2} + V_j(r) - E\right]F_j(r) = \sum_{n \geq 1} \left[2P_{jn}(r)\frac{d}{dr} + W_{jn}(r)\right]F_n(r),$$

(1)

defined for integer $\ell \geq 0$ and real non-negative $r$, $0 \leq r < \infty$. The coefficients $V_j(r)$, $P_{jn}(r)$ and $W_{jn}(r)$ will be defined below. In order to correctly formulate the problem, the set (1) has to be supplied by appropriate boundary conditions. While the boundary condition at $r = 0$ is natural: $F_j(0) = 0$, the asymptotic ($r \to \infty$) form of $F_j(r)$ is far from trivial and depends on the decay rate of the coefficients $V_j(r)$, $P_{jn}(r)$ and $W_{jn}(r)$ when $r \to \infty$.

The set of equations (1) conventionally represents the Schrödinger equation for a system of two atoms by using the so-called adiabatic expansion (1) for the total wave function $\Psi$ of the system. The molecular basis set $\phi_k$ generates the expansion of the total wave function

$$\Psi(r, \xi) = Y_{\ell m_\ell}(\hat{r}) \sum_{n \geq 1} \frac{F_n(r)}{r} \phi_n(\xi, r),$$

(2)

where $Y_{\ell m_\ell}$ are the standard spherical functions, for which $\ell$ and $m_\ell$ denote the total angular momentum quantum numbers, $r$ is the internuclear relative position vector,
the unit vector \( \hat{r} \) is given by \( r/r \), where \( r = |r| \), while \( \xi \) represents the electronic degrees of freedom. The above expansion assumes the following form of the two-atomic Hamiltonian

\[
H = -\frac{\hbar^2}{2M} \nabla_r^2 + h(r, \xi),
\]

(3)

with \( M \) denoting the nuclei reduced mass. The sub-Hamiltonian \( h(r, \xi) \) contains all interaction potentials and governs the dynamics of electrons in the field of the “frozen” nuclei. The molecular basis set \( \phi_n(\xi, r) \) is then formed by eigenfunctions of the Hamiltonian \( h(r, \xi) \)

\[
h(r, \xi)\phi_n(\xi, r) = \lambda_n(r)\phi_n(\xi, r).
\]

(4)

The eigenfunctions obey the orthonormality and completeness conditions

\[
\langle \phi_j | \phi_n \rangle = \delta_{jn}, \quad \sum_{n \geq 1} |\phi_n(\xi, r)\rangle \langle \phi_n(\xi', r)\rangle = \delta(\xi - \xi'),
\]

(5)

where \( \delta_{jn} \) is the Kroneker symbol and \( \delta(\xi - \xi') \) is the delta-function. The relative internuclear position vector \( r \) serves here as a parameter. Throughout the paper it is assumed that the eigenfunctions \( \phi_k(\xi, r) \) and the eigenvalues \( \lambda_k(r) \) depend on the magnitude \( r = |r| \) of the vector \( r \). This property is quite common in most applications \[8\], and corresponds, for example, to the case when only molecular \( \Sigma \) states contribute to the problem. These assumption can also be adapted to a more general case, which involves some additional small complications to the coupling matrices \[10\]. Finally, it is assumed that the elements of the molecular basis \( \phi_j \) are chosen to be real, which is always possible since the sub-Hamiltonian \( h(r, \xi) \) is Hermitian.

The matrices in equations (1) can now be expressed in terms of the molecular basis by the following equations:

\[
V_j(r) = \frac{2M}{\hbar^2} \lambda_j(r),
\]

(6)

\[
P_{jn}(r) = \frac{2M}{\hbar^2} \langle \phi_j | \frac{\partial}{\partial r} | \phi_n \rangle, \quad W_{jn}(r) = \frac{2M}{\hbar^2} \langle \phi_j | \frac{\partial^2}{\partial r^2} | \phi_n \rangle.
\]

(7)

Here, the brackets in matrix elements mean an integration over the electronic degrees of freedom \( \xi \). The completeness of the basis leads to the familiar relationship for matrices \( P_{jn}(r) \) and \( W_{jn}(r) \)

\[
W_{jn}(r) = \sum_{m \geq 1} P_{jm}(r) P_{mn}(r) + \frac{dP_{jn}(r)}{dr}.
\]

(8)

Since the eigenfunctions \( \phi_j \) are real, the matrix \( P_{jn}(r) \) is antisymmetric, i.e. \( P_{jn}(r) = -P_{nj}(r) \), and, hence, it is off-diagonal \( P_{jj}(r) = 0 \). The constant parameter \( E \) in (1) represents a reduced total energy in the colliding system.

The asymptotic behavior of the potentials \( V_j(r) \) and the matrices \( P_{jn}(r) \) is essential for the asymptotic analysis of the solution to the equation (1). The asymptote of \( V_j(r) \) determines the asymptotic thresholds \( \epsilon_j \)

\[
\epsilon_j = \lim_{r \to \infty} V_j(r).
\]

(9)
In this paper we assume that the potentials $V_j(r)$ are short-range, that means
\[
\lim_{r \to \infty} r^{1+\delta}[V_j(r) - \epsilon_j] = 0 \quad (10)
\]
for $\delta > 0$. The matrix $P_{jn}(r)$ determines the asymptotic couplings $a_{jn}$ through the formula
\[
a_{jn} = \lim_{r \to \infty} P_{jn}(r). \quad (11)
\]
As for potentials, it is required
\[
\lim_{r \to \infty} r^{1+\delta}[P_{jn}(r) - a_{jn}] = 0 \quad (12)
\]
for $\delta > 0$. These “short-range” conditions lead to the following asymptotic properties of the matrices in the equations (1)
\[
V_j(r) \sim \epsilon_j + O(r^{-(1+\delta)}), \quad (13)
\]
\[
P_{jn}(r) \sim a_{jn} + O(r^{-(1+\delta)}), \quad (14)
\]
\[
W_{jn}(r) \sim \sum_{m \geq 1} a_{jm}a_{mn} + O(r^{-(1+\delta)}). \quad (15)
\]
From these properties, the equations (11) can be recast into the form
\[
\left[-\frac{d^2}{dr^2} + \epsilon_j - E\right] F_j(r) = \sum_{n \geq 1} \left[2 a_{jn} \frac{d}{dr} + \sum_{m \geq 1} a_{jm}a_{mn}\right] F_n(r) + Q_j(r, F). \quad (16)
\]
In the last equation, all the terms of the order $O(r^{-(1+\delta)})$ and less have been denoted by $Q_j(r, F)$. It follows from formal scattering theory [13] that terms of the order $O(r^{-(1+\delta)})$ do not affect the asymptotic behaviour of the solution as $r \to \infty$. Therefore, in the current problem, studying the asymptote of the solution to (16), setting $Q_j(r, F) = 0$ gives the correct asymptotic form of the solution to the equation (1).

Depending on the values of the asymptotic couplings $a_{jn}$, two cases should be distinguished: (i) $a_{jn} = 0$ for all $j, n$; and (ii) there exists a number $N$ such that $a_{jn} \neq 0$ for $j, n \leq N$ and $a_{jn} = 0$, if $j > N$ or $n > N$. The former case (i) is somewhat “conventional” and corresponds to the Born-Oppenheimer type of asymptotic states [14]. As such, due to (10) and (12), the set of equations given in (16) becomes decoupled in the limit $r \to \infty$, and takes the form
\[
\left[-\frac{d^2}{dr^2} + \epsilon_j - E\right] F_j(r) = 0. \quad (17)
\]
The two linearly independent solutions of (17) are
\[
F_j^\pm(r, k_j) = \exp\{\pm ik_jr\}, \quad (18)
\]
where the channel momenta $k_j$ are given by
\[
k_j = \sqrt{E - \epsilon_j} \geq 0. \quad (19)
\]
These solutions provide us with the basis for the asymptotic form of the solution to the equation (11) as $r \to \infty$

$$F_j(r) \sim k_j^{-1/2}[b_j^+ F_j^+(r, k_j) + b_j^- F_j^-(r, k_j)]. \quad (20)$$

The scattering matrix can now be defined as the transformation between incoming and outgoing amplitudes

$$(-1)^{\ell+1} b_j^+ = \sum_n S_{jn} b_n^- . \quad (21)$$

The latter case (ii) is significantly more complicated, and is studied in the subsequent sections.

2. Two channel model

As the first step in solving the problem of constructing the asymptotic form of the solution to the equation (11) a model with two channels is considered. In matrix form, this model is written as

$$\left\{ -I \left[ \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} \right] - 2 P(r) \frac{d}{dr} - W(r) + V(r) - IE \right\} F(r) = 0, \quad (22)$$

where $F = (F_1(r), F_2(r))^T$, the matrices $I$, $P$, and $V$ are defined as

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad P(r) = \begin{bmatrix} 0 & p(r) \\ -p(r) & 0 \end{bmatrix}, \quad V = \begin{bmatrix} V_1(r) & 0 \\ 0 & V_2(r) \end{bmatrix} \quad (23)$$

and $W(r) = P^2(r) + \frac{d}{dr} P(r)$. Since the asymptotic coupling has to be non-trivial at $r \to \infty$, we have:

$$\lim_{r \to \infty} p(r) = a \neq 0. \quad (24)$$

In contrast to (17), the set of equations (22) remain coupled when $r \to \infty$, and asymptotically takes the form

$$\left( -I \frac{d^2}{dr^2} - 2 A \frac{d}{dr} - A^2 - K^2 \right) \Phi(r) = 0. \quad (25)$$

Here $\Phi = \{\Phi_1(r), \Phi_2(r)\}^T$ and $A$ and $K^2$ are $2 \times 2$ constant matrices defined as

$$A = \begin{bmatrix} 0 & a \\ -a & 0 \end{bmatrix}, \quad K^2 = \begin{bmatrix} k_1^2 & 0 \\ 0 & k_2^2 \end{bmatrix}. \quad (26)$$

The next step is to construct a set of linearly independent solutions to equation (25). These solutions we represent by the following expression for components

$$\Phi_j(r) = c_j \exp \{iqr\} , \quad j = 1, 2, \quad (27)$$

where $q$ and $c_j$ should be determined such that the vector-function $\Phi(r)$ obeys equation (25). With $\phi_j$ expressed in this form, the set of differential equations (25) is reduced to the following set of linear algebraic equations

$$(q^2 - k_1^2 + a^2)c_1 + i2aqc_2 = 0,$$

$$(q^2 - k_2^2 + a^2)c_2 - i2aqc_1 = 0. \quad (28)$$
The parameter $q$ should now be defined in such a way that this set of homogeneous equations has a non-trivial solution. This can be achieved if the determinant of the system (28) is zero, leading to the following bi-quadratic equation

$$q^4 - (k_1^2 + k_2^2 + 2a^2)q^2 + (k_1^2 - a^2)(k_2^2 - a^2) = 0.$$  \hfill (29)

The four solutions to (29) are given by

$$q_1^\pm = \pm \frac{1}{\sqrt{2}} \sqrt{k_1^2 + k_2^2 + 2a^2 + \sqrt{(k_1^2 + k_2^2 + 2a^2)^2 - 4(k_1^2 - a^2)(k_2^2 - a^2)}},$$  \hfill (30)

$$q_2^\pm = \pm \frac{1}{\sqrt{2}} \sqrt{k_1^2 + k_2^2 + 2a^2 - \sqrt{(k_1^2 + k_2^2 + 2a^2)^2 - 4(k_1^2 - a^2)(k_2^2 - a^2)}}. \hfill (31)$$

The case of small $a$ is of interest, since in the atomic collision problem $a$ is proportional to the square root of the ratio of the electron to the nuclear mass. In this case, the asymptotes of $q_n$, when $a \to 0$, can easily be evaluated from (30), (31) and have the form

$$q_n^\pm = \pm k_n \pm \frac{1 \pm 2k_1^2k_2^2}{2k_n} a^2 + O(a^4), \quad n = 1, 2. \hfill (32)$$

These formulae show that in the limit $a \to 0$ the quantities $q_n$ approach the momenta $k_n$. It is important to emphasize that $q_n^\pm - (\pm k_n) = O(a^2)$.

The set of equations (28) for two-component vectors $C^{a\pm}$ can now be solved by inserting values of $q_n^\pm$ into (28). The resulting solution is represented by the following expressions:

$$C_1^{a\pm} = \begin{bmatrix} c_1^{a\pm} \\ c_2^{a\pm} \end{bmatrix} = N(a, q_1^{a\pm}, k_1) \begin{bmatrix} 1 \\ -(q_1^{a\pm})^2 - k_1^2 + a^2 \end{bmatrix} \frac{1}{i2aq_1^2}, \hfill (33)$$

$$C_2^{a\pm} = \begin{bmatrix} c_1^{a\pm} \\ c_2^{a\pm} \end{bmatrix} = N(a, q_2^{a\pm}, k_2) \begin{bmatrix} (q_2^{a\pm})^2 - k_2^2 + a^2 \end{bmatrix} \frac{1}{i2aq_2^2}. \hfill (34)$$

where the normalisation factor $N$ is calculated from

$$N(a, q, k) = \left\{ 1 + \frac{(q^2 - k^2 + a^2)^2}{4a^2q^2} \right\}^{-1/2} \hfill (35)$$

using the relevant values of $q$ and $k$. As earlier for $q_n^\pm$ quantities, consider the situation when $a \to 0$. In this case, the following behaviour of the components of the vectors $C^{a\pm}, \quad n = 1, 2$ is obtained

$$c_j^{a\pm} = \delta_{jn} \pm ia \frac{2k_n}{k_1^2 - k_2^2} [1 - \delta_{jn}] + O(a^2), \quad j = 1, 2. \hfill (36)$$

The four solutions derived for equation (25)

$$\Phi^{a\pm}(r, q_n^\pm) = C_n^{a\pm} \exp \{i q_n^\pm r\}, \quad n = 1, 2 \hfill (37)$$

are the set of asymptotic states which were necessary to construct the asymptote to the solution of the two-channel equation (22)

$$F(r) \sim \sum_{n=1}^{2} q_n^{-1/2} [b_n^+ \Phi^{a+}(r, q_n^+) + b_n^- \Phi^{a-}(r, q_n^-)], \quad r \to \infty. \hfill (38)$$
Analogously to the definition (21) given in the preceding section, the $2 \times 2$ scattering matrix is introduced as the transformation matrix for incoming $b_j^-$ and outgoing $b_j^+$ amplitudes

$$(-1)^{l+1} b_j^+ = \sum_{n=1}^{2} S_{jn}(a) b_n^-.$$  (39)

The asymptotic representation (38) can be simplified if the asymptotes (32) and (36) for $q_n^\pm$ and $C_n^\pm$ as $a \to 0$ are used in (37). Neglecting terms of the order $O(a^2)$ leads to the following form of the components of the asymptotic solution (38)

$$F_j(r) \sim \sum_{n=1}^{2} \frac{k_n}{2} \left[ b_n^+ t_{jn}^+ F_n^+ (r, k_n) + b_n^- t_{jn}^- F_n^- (r, k_n) \right].$$  (40)

Here, the $t_{jn}^\pm$ coefficients are defined as

$$t_{jn}^\pm = \delta_{jn} \pm i a \frac{2k_n}{k_1^2 - k_2^2} [1 - \delta_{jn}], \quad j, n = 1, 2.$$  (41)

It is easily verified that formulae (40) and (41) are identical to the representation of the asymptotic solution that is obtained by the re-projection method (see, for instance, formulae (18) and (21) from the paper [14]).

It is worth noting that in the limit $a \to 0$ the coefficients $t_{jn}^\pm$ take the Kroneker-delta $\delta_{jn}$ form and, consequently, the representation (40) turns into (20). For the scattering matrix this limit yields $S_{jn}(a) \to S_{jn}$ with $S_{jn}$ defined by (21).

### 3. General case of multichannel equations

In this section we consider the general situation, i.e. the case (ii) described in subsection 1.2, when $N$ states remain asymptotically coupled as $r \to \infty$. Here, the set of equations (11), (16) is asymptotically split into two pieces: the nontrivial $N \times N$ system for components $F_j$, $j = 1, \ldots, N$; and the trivial decoupled set of the form (17) for components $F_j$, $j > N$. The latter leads to the asymptotic form of the components $F_j$, $j > N$, given in Eq. (20). The asymptotic form of the former components for $j = 1, \ldots, N$ should be constructed by solving the relevant set of equations with non-trivial asymptotic coupling. As it was argued in subsection 1.2, this set is obtained from (11) or (16) by neglecting all terms of the order $O(r^{-1-\delta})$ and less. The resulting asymptotic $N \times N$ set of equations for the vector-function $\Phi(r) = \{\Phi_1(r), \ldots, \Phi_N(r)\}^T$ is, in the matrix form, given by:

$$\left( -I \frac{d^2}{dr^2} - 2A \frac{d}{dr} - A^2 - K^2 \right) \Phi(r) = 0.$$  (42)

The $N \times N$ matrices $I$, $K^2$ and $A$ are given by their matrix elements

$$[I]_{jn} = \delta_{jn}, \quad [K^2]_{jn} = \delta_{jn} k_n^2, \quad [A]_{jn} = a_{jn}.$$  (43)

In the same way as discussed in section 2 by using the substitution

$$\Phi(r) = C \exp \{iqr\}$$  (44)
with the unknown constant $q$ and vector $\mathbf{C} = \{C_1, \ldots, C_N\}$, the set of differential equations given in (42) can be reduced to a set of linear algebraic equations:

$$\left(q^2 \mathbf{I} - 2q i \mathbf{A} - \mathbf{A}^2 - \mathbf{K}^2\right) \mathbf{C} = 0. \quad (45)$$

The non-trivial solution to (45) exists if and only if the determinant, which is a polynomial of degree $2N$, of that system is zero

$$D(q) \equiv \det \left(q^2 \mathbf{I} - 2q i \mathbf{A} - \mathbf{A}^2 - \mathbf{K}^2\right) = 0. \quad (46)$$

It is shown in the Appendix that the equation (46) can be satisfied only for real values of $q$. Since the matrix $\mathbf{A}$ is antisymmetric with respect to the matrix transposition $\mathbf{A}^T = -\mathbf{A}$, the following property

$$\left(q^2 \mathbf{I} - 2q i \mathbf{A} - \mathbf{A}^2 - \mathbf{K}^2\right)^T = \left(q^2 \mathbf{I} + 2q i \mathbf{A} - \mathbf{A}^2 - \mathbf{K}^2\right) \quad (47)$$

shows that the left hand side of (46) is even function of real $q$, i.e. $D(-q) = D(q)$. Therefore, the $2N$ roots of equation (46) form the symmetric real set $\pm q_1, \ldots, \pm q_N$, such that $D(\pm q_n) = 0$, $n = 1, \ldots, N$. For definiteness, the signs of $q_n$ are fixed in such a way that $q_n \geq 0$, $n = 1, \ldots, N$. The $2N$ vectors $\mathbf{C}^{n\pm}$, $n = 1, \ldots, N$ can now be calculated as the solutions to equation (46) by inserting $\pm q_n$ quantities. These quantities determine $2N$ solutions to the equation (42) of the form

$$\Phi^{n\pm}(r, q_n) = \mathbf{C}^{n\pm} \exp\{\pm i q_n r\}. \quad (48)$$

All ingredients which are necessary for constructing the asymptotic ($r \to \infty$) boundary conditions for the equation (1) are now available. The components $\Phi_j^{n\pm}$ of states (48) for $j = 1, \ldots, N$ together with components $F_j^{\pm}$ from (18) for $j > N$ form the basis for those asymptotic boundary conditions for the components $F_j(r)$ of the solution to the equations (1)

$$F_j(r) \sim \sum_{n=1}^{N} q_n^{-1/2} \left[ b_n^- \Phi_j^- (r, q_n) + b_n^+ \Phi_j^+ (r, q_n) \right] , \quad j = 1, \ldots, N, \quad (49)$$

$$F_j(r) \sim k_j^{-1/2} \left[ b_j^- F^- (r, k_j) + b_j^+ F^+ (r, k_j) \right] , \quad j > N. \quad (50)$$

These boundary conditions are our main result that completes the definition of the scattering problem for the set of equations (11) in the general situation.

The respective $S$-matrix is then defined as the transformation matrix between the incoming and outgoing amplitudes in scattering channels

$$(-1)^{\ell+1} b^{+\ell}_{j} = \sum_{n \geq 1} S_{jn}(\mathbf{A}) b_{n}^{-\ell}. \quad (51)$$

As in the preceding section, we consider the special case when the coupling matrix $\mathbf{A}$ is small. Here, it is useful to introduce the scalar coupling constant $a$ in such a way that $\mathbf{A} = a \hat{\mathbf{A}}$ in order to explicitly characterize the order of the coupling matrix. For small coupling constant $a \to 0$, the solution to the equation (45) can be obtained perturbatively. $\mathbf{C}$ and $q$ are represented as

$$q = q_0 + a q_1 + O(a^2), \quad \mathbf{C} = \mathbf{C}^{(0)} + a \mathbf{C}^{(1)} + O(a^2) \quad (52)$$
To solve the second equation (54), we take
\[ Cq \text{ is required to guaranty the existence of a non-trivial solution to (54).} \]
The corresponding eigenvectors \( C \) correspond to \( K^2 \), respectively. The eigenvalues set of \( K^2 \) is \( k_1^2, \ldots, k_N^2 \) and the corresponding eigenvectors \( C^{(0)n}, n = 1, \ldots, N \), are given by components as \( C^{(0)n}_j = \delta_{jn} \). To solve the second equation (54), we take \( C^{(0)} = C^{(0)n} \) and \( q_0^2 = k_n^2 \) which leads to \( q_0 = \pm k_n \). Since \( \text{Ker}(k_n^2 - K^2) \) is not trivial, the resolution condition
\[ \mp 2k_n \langle (q_1 - iA)C^{(0)n}, C^{(0)n} \rangle = 0 \] is required to guaranty the existence of a non-trivial solution to (54). Here, \( \langle \cdot, \cdot \rangle \) means the standard inner product in \( C^N \). Evaluating the inner product gives \( q_1 = i\hat{a}_{nn} \), hence \( q_1 = 0 \), since \( \hat{a}_{jn} \) is off-diagonal. The equation (54) takes now the form
\[ (k_n^2 - K^2)C^{(1)n\pm} = \pm 2ik_n \hat{A}C^{(0)n}. \] For the components, it is given by
\[ (k_n^2 - k_j^2)C^{(1)n\pm}_j = \pm 2ik_n \hat{a}_{jn} \] for \( j \neq n \), while
\[ C^{(1)n\pm}_n = 0 \] according to the standard convention of the perturbation theory \[15\]. From equations (57), (58), it is seen that
\[ C^{(1)n\pm}_j = \pm \frac{2ik_n}{k_n^2 - k_j^2} \hat{a}_{jn}(1 - \delta_{jn}). \] Finally, from (52), the following expressions are obtained for \( q \) and for components of \( C \)
\[ q = \pm k_n + O(a^2), \quad n = 1, \ldots, N, \] \[ C^{n\pm}_j = \delta_{jn} \pm \frac{2ik_n}{k_n^2 - k_j^2} a_{jn}(1 - \delta_{jn}) + O(a^2), \quad j, n = 1, \ldots, N. \] Here it has been taken into account that \( a\hat{a}_{jn} = a_{jn} \). With these representations the explicit form for the leading terms of the components of the asymptotic states \( \Phi^{n\pm} \) are obtained
\[ \Phi^{n\pm}_j(r, q_n) = t^{\pm} jn \exp\{i\pm ik_hr\} + O(a^2) \] with \( t^{\pm} jn \) defined as
\[ t^{\pm} jn = \delta_{jn} \pm \frac{2ik_n}{k_n^2 - k_j^2} a_{jn}(1 - \delta_{jn}). \] The respective asymptotic \( (r \to \infty) \) boundary conditions (49) for components \( F_j(r) \) with \( j = 1, \ldots, N \) now become
\[ F_j(r) \sim \sum_{n=1}^{N} k_n^{-1/2} \left[ b_n^- t^{\pm}_jn \exp\{-ik_hr\} + b_n^+ t^{\pm}_jn \exp\{ik_hr\} \right] + O(a^2). \]
It is noted that the latter formula is identical to the formula (18) that is obtained in [14] within the re-projection procedure. The $t$-matrix components (63) are also identical to the respective $t$-matrix components from [14] if the definitions (13), (9) and (19) are taken into account.

The derived formulae (60) and (61) give the leading with respect to the coupling constant $a$ terms for $q$ and $C$. Subsequent terms of the decompositions can be obtained (if it is necessary) by implementing the standard prescription of the perturbation theory [15]. It is also worth mentioning that the case of degenerate asymptotic scattering channels can be treated with the relevant variant of the perturbation theory, and, therefore, may require applying additional corrections in the construction of asymptotic boundary conditions, as shown, for example, in [16].

4. Conclusion

We have presented a general formalism of constructing the asymptotic boundary conditions for solutions to the adiabatic multi-channel scattering problem in the case when the non-adiabatic coupling matrix remains non-trivial at large internuclear distances. These asymptotic conditions generalise the Born-Oppenheimer form of the asymptotic boundary conditions, which commonly used in the case of asymptotic decoupling of equations. The non-zero asymptotic non-adiabatic coupling matrix elements are fundamental features of the Born-Oppenheimer approach, so the construction of the asymptotic solutions to the coupled channel equations with such couplings is not only of general, but also of practical importance for calculations of inelastic cross sections. The calculations of inelastic cross sections with non-zero asymptotic non-adiabatic couplings have been successfully accomplished by means of the re-projection method for a number of collisional processes, e.g., in collisions of Li + Na [12], He + H [16], Mg + H [17], Li$^+$ + He and Li + He$^+$ [18]. The asymptotic solutions (63), (64) derived via the general formalism of the present paper are identical to the asymptotic solutions used in the re-projection method [9, 10, 12, 14] within the first order of perturbation theory. Therefore, numerical calculations of inelastic cross sections would lead to identical results. Thus, there is no need to repeat any numerical calculations in the present paper.

The formulation of the scattering problem for multichannel coupled equations with the conditions derived in the present paper covers two most important cases of short-range and constant long-range asymptotic behavior of the non-adiabatic coupling matrix. The case of as slow as $O(r^{-1})$ vanishing of the non-adiabatic coupling matrix and/or adiabatic potentials is of interest, particularly, for the hyper-spherical adiabatic approach [4]. The solution of the asymptotic boundary condition problem in that case requires some specific new technique and will be explained elsewhere.

The derived asymptotic form of the solution to the adiabatic coupled equations opens a way for using the recently developed potential splitting approach for solving the multichannel scattering problem in both the diabatic and adiabatic forms of the
multichannel equations [19, 20].

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Appendix

In order to show that the equation (46) can possess the nontrivial solution only for real values of the parameter \( q \) the equivalent fact that \( \text{Ker}(q^2 \mathbf{I} - 2q i \mathbf{A} - \mathbf{A}^2 - K^2) \) can be non-trivial only for real values of \( q \) is proven. Begin from the identity

\[
q^2 \mathbf{I} - 2q i \mathbf{A} - \mathbf{A}^2 - K^2 = (q \mathbf{I} - i \mathbf{A})^2 - K^2
\]

(65)

and the fact that \( i \mathbf{A} \) is Hermitian. Let \( q = \alpha + i \beta \) be complex and \( \mathbf{C} \in \text{Ker}((q \mathbf{I} - i \mathbf{A})^2 - K^2) \), then

\[
\langle [(q \mathbf{I} - i \mathbf{A})^2 - K^2] \mathbf{C}, \mathbf{C} \rangle = 0,
\]

(66)

where \( \langle ., . \rangle \) is the standard inner product in \( \mathbb{C}^N \). Since the left hand side of this equation is represented as

\[
\langle (\alpha - i \mathbf{A})^2 \mathbf{C}, \mathbf{C} \rangle - \langle (\beta^2 + K^2) \mathbf{C}, \mathbf{C} \rangle + 2i\beta\langle (\alpha - i \mathbf{A}) \mathbf{C}, \mathbf{C} \rangle
\]

(67)

equation (66) is equivalent to the following two equations

\[
\langle (\alpha - i \mathbf{A})^2 \mathbf{C}, \mathbf{C} \rangle - \langle (\beta^2 + K^2) \mathbf{C}, \mathbf{C} \rangle = 0,
\]

(68)

\[
\beta\langle (\alpha - i \mathbf{A}) \mathbf{C}, \mathbf{C} \rangle = 0.
\]

(69)

If \( \beta \neq 0 \) and \( \mathbf{C} \neq 0 \), from (69) it follows that

\[
(\alpha - i \mathbf{A}) \mathbf{C} = 0.
\]

The latter reduces the left hand side of (68) to \( -\langle (\beta^2 + K^2) \mathbf{C}, \mathbf{C} \rangle \). The matrix \( \beta^2 + K^2 \) is obviously positive defined for \( \beta \neq 0 \), hence \( -\langle (\beta^2 + K^2) \mathbf{C}, \mathbf{C} \rangle < 0 \), which contradicts equation (68). As a result, it is proven that for complex \( q \) with \( \text{Im} \, q = \beta \neq 0 \), equation (66) can be satisfied only for \( \mathbf{C} = 0 \) and, consequently, \( \text{Ker}((q \mathbf{I} - i \mathbf{A})^2 - K^2) \) is trivial.

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