Arrangement-channel approach to reactive systems: A new coupling scheme

Michael Baer and Yaakov Shima
Soreq Nuclear Research Center, Yavne 70600, Israel
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In this work we present a new scheme for coupling the different arrangement channels in a three-dimensional $n$-channel (where $n > 2$) reactive system. Whereas the old scheme was found to yield a nonunitary $S$ matrix when employed to a three-channel system, the new scheme yields a unitary $S$ matrix and relevant results for the $H + H_2$ ($J=0$) reactive system.

I. INTRODUCTION

More than a decade ago, Baer and Kouri\cite{1} presented their arrangement-channel approach for reactive scattering, which is basically a coupled system of Lippmann-Schwinger equations—each equation for one arrangement channel. The coupling, as will also be briefly shown in this work, was done explicitly by introducing a matrix $W$ with elements which may (or may not) depend on the coordinates. This set of equations was later modified by Kouri and Levin\cite{2} and generalized by Tobocman.\cite{3} So far, this set of equations was only applied to two-channel systems such as the $e$-H problem\cite{4} or various collinear reactive systems.\cite{5} In all the cases treated so far, the $W$ matrix was assumed to be of the form\cite{4,d}

$$W = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix},$$

and the results obtained with this coupling scheme were similar to those obtained by other methods.

Difficulties were encountered once this simple structure was employed in a three-channel problem. From the numerical treatment of the $H + H_2$ reactive system by the present authors,\cite{5} it was soon recognized that the final $S$ matrix is not unitary. In the present work we report on a different coupling scheme, which yields a unitary $S$ matrix and relevant results for the reactive $H + H_2$ system (for $J=0$), as calculated on the Porter-Karplus potential.\cite{6}

II. THEORY

A. The coupled Lippmann-Schwinger integral equation for reactive systems

The reactance operator $R$ with the elements $R_{\lambda',\lambda}$ is defined as\cite{5}

$$R_{\lambda',\lambda} | X_{\lambda} \rangle = V_{\lambda'} | \psi_{\lambda} \rangle,$$

where $\lambda$ and $\lambda'$ are two different arrangement channels; thus, $\lambda$ may stand for the $(A,BC)$ arrangement channel and $\lambda'$ for the $(B,AC)$ or $(C,AB)$ arrangement channels, $| X_{\lambda} \rangle$ denotes a real unperturbed solution of the Schrödinger equation, and $| \psi_{\lambda} \rangle$ is a solution of the full Schrödinger equation with $\lambda$ being the initial channel and $V_{\lambda'}$ the perturbation potential. If $H$ is the full Hamiltonian and $H_{\lambda'}$ is the $\lambda'$ arrangement unperturbed Hamiltonian, then

$$H = H_{\lambda'} + V_{\lambda'}, \quad \lambda' = \lambda, \nu, k$$

where $V_{\lambda'}$ fulfills the requirement that

$$\lim_{\rho_{\lambda'} \to \infty} V_{\lambda'}(\rho_{\lambda'}, \ldots) = 0, \quad \rho_{\lambda'} \to \infty.$$

Here $\rho_{\lambda'}$ is the distance between the free atom and the center of mass of the diatomic, as measured in the $\lambda'$ arrangement.

Let us now consider the integral representation of the Schrödinger equations for $| \psi_{\lambda} \rangle$,

$$| \psi_{\lambda} \rangle = | X_{\lambda} \rangle + G V_{\lambda'} | X_{\lambda'} \rangle,$$

where $G$ is the full Green function defined as

$$G = (E - H + i\epsilon)^{-1}.$$

Multiplying both sides of Eq. (4) by $V_{\lambda'}$ and employing the definition of $R_{\lambda',\lambda}$, we get the integral representation for $R_{\lambda',\lambda}$:

$$R_{\lambda',\lambda} = V_{\lambda'} G V_{\lambda'}.$$

Next we do the following.

(a) Apply for any $\lambda''$ the identity

$$E - H + i\epsilon \equiv E - H_{\lambda''} + i\epsilon - V_{\lambda''},$$

which leads to an integral equation for $G$,

$$G = G_{\lambda''} + G_{\lambda''} V_{\lambda''} G.$$

(b) Introduce the matrix $W$ with the elements $W_{\lambda',\lambda''}$, which may or may not depend on the coordinates. The choice of these elements is so far not restricted, except for the condition

$$\sum_{\lambda''} W_{\lambda',\lambda''} = 1,$$

which should hold for any value $\lambda'$. The summation index $\lambda''$ runs over all arrangements. Multiplying Eq. (8) by $W_{\lambda',\lambda''}$, summing over $\lambda''$, and making use of Eq. (9) leads to a generalized equation for $G$, i.e.,

$$G = \sum_{\lambda''} W_{\lambda',\lambda''} G_{\lambda''} + \sum_{\lambda''} W_{\lambda',\lambda''} G_{\lambda''} V_{\lambda''} G.$$

Substituting Eq. (10) in Eq. (6) we get (see Appendix A).
the result

\[ R_{\lambda\lambda} = V_{\lambda} W_{\lambda\lambda} + V_{\lambda} \sum_{\lambda'} W_{\lambda\lambda'} G_{\lambda'} R_{\lambda'\lambda} . \]  

(11)

In all previous studies the \( W \) matrix elements were assumed to be constant and the channel permuting choice was applied, namely,

\[ W_{\lambda \lambda'} = \delta_{\lambda \lambda'} - 1 . \]  

(12)

Thus, in the three-channel case we may have for \( W \) the following elements:

\[
W = \begin{bmatrix}
0 & 1 & 0 \\
0 & 0 & 1 \\
1 & 0 & 0
\end{bmatrix} .
\]  

(13)

In a recent numerical treatment of the \( H + H_2 \) system, this choice was found to lead to a nonsymmetric \( R \) matrix.\(^5\) In the present work we suggest a choice for which the \( R \) matrix was found to be symmetric (other schemes, more symmetrical than the one presented in Eq. (12), have been discussed in the literature\(^7\)).

**B. The construction of the \( W \) matrix**

As is well noticed, the matrix elements are responsible for the coupling among the different arrangement channels. This coupling can be done in many ways, but a necessary condition imposed on these elements is that the resulting \( R \) matrix be symmetric or, what is the same thing, that the \( S \) matrix be unitary.

In order to be able to refer in a more convenient way to the \( W \) matrix elements, Eq. (11) is written explicitly for the three-channel case:

\[ R_{\lambda\lambda} = V_{\lambda} W_{\lambda\lambda} + V_{\lambda} W_{\lambda\lambda'} G_{\lambda'} R_{\lambda\lambda'} + V_{\lambda} W_{\lambda\lambda''} G_{\lambda''} R_{\lambda\lambda''} , \]  

(14a)

\[ R_{\nu\nu} = V_{\nu} W_{\nu\nu} + V_{\nu} W_{\nu\nu'} G_{\nu'} R_{\nu\nu'} + V_{\nu} W_{\nu\nu''} G_{\nu''} R_{\nu\nu''} , \]  

(14b)

\[ R_{\kappa\kappa} = V_{\kappa} W_{\kappa\kappa} + V_{\kappa} W_{\kappa\kappa'} G_{\kappa'} R_{\kappa\kappa'} + V_{\kappa} W_{\kappa\kappa''} G_{\kappa''} R_{\kappa\kappa''} . \]  

(14c)

In this notation \( W_{\lambda\lambda} \) is responsible for the coupling of the \( \lambda \) channel to itself, \( W_{\lambda\nu} \) is responsible for the coupling of the \( \lambda \) channel to the \( \nu \) channel, and \( W_{\lambda\kappa} \) is responsible for the coupling of the \( \lambda \) channel to the \( \kappa \) channel. We now make the assumption that the three matrix elements \( W_{\lambda\lambda} \), \( W_{\lambda\nu} \), and \( W_{\lambda\kappa} \) depend only on the \( \gamma \) angle defined as (see Fig. 1)

\[ \gamma_{\lambda} = \cos^{-1}\left( \tilde{\mathbf{R}}_{\lambda} \cdot \mathbf{\hat{r}}_{\lambda} \right) . \]  

(15)

Since the \( \lambda \) channel is mainly coupled to the \( \nu \) channel for \( 0 \leq \gamma_{\lambda} \leq \pi/2 \) and to the \( \kappa \) channel for \( \pi/2 < \gamma_{\lambda} < \pi \), a reasonable choice for the \( W_{\lambda\lambda}, W_{\lambda\nu}, \gamma_{\lambda}, \nu, \kappa \) elements is as follows:

\[ W_{\lambda\nu}(\gamma_{\lambda}) = \begin{cases} 
1, & 0 \leq \gamma_{\lambda} \leq (\pi/2 - \gamma_{\lambda})_0 \\
0, & \text{otherwise},
\end{cases} \]  

(16a)

\[ W_{\lambda\kappa}(\gamma_{\lambda}) = \begin{cases} 
1, & (\pi/2 + \gamma_{\lambda})_0 \leq \gamma_{\lambda} \leq \pi \\
0, & \text{otherwise} ,
\end{cases} \]  

(16b)

\[ W_{\lambda\lambda}(\gamma_{\lambda}) = \begin{cases} 
1, & (\pi/2 - \gamma_{\lambda})_0 \leq \gamma_{\lambda} \leq (\pi/2 + \gamma_{\lambda})_0 \\
0, & \text{otherwise} .
\end{cases} \]  

(16c)

Here \( \gamma_{0} \) is an angle which may or may not be equal to zero. This choice is in accordance with the basic requirement for the \( W \) matrix elements, namely,

\[ \sum_{\lambda'} W_{\lambda\lambda'}(\gamma_{\lambda}) = 1 . \]  

(9')

A similar structure is assumed for the other two rows of the \( W \) matrix, namely, \( W_{\nu\lambda'} \) and \( W_{\kappa\lambda'} \) except that the \( W_{\nu\lambda'} \)'s are assumed to be a function of \( \gamma_{\nu} \) and \( W_{\kappa\lambda'} \) are assumed to be a function of \( \gamma_{\kappa} \) (see Fig. 1)

**III. CONCLUSIONS**

In this work we proposed a new coupling scheme for the reactive Lippmann-Schwinger integral equations. Instead of coupling each arrangement channel to one (single) other channel in a permutative way as has been discussed frequently in the literature\(^2,3,7,8\), we suggested explicitly coupling each channel to all other channels. The coupling is controlled by the three \( \gamma \) angles defined in Eq. (15).

We carried out preliminary calculations for the three-dimensional three-channel reactive \( H + H_2 \) system and obtained unitary \( S \) matrices, a feature never obtained with the previous coupling scheme.\(^9\) The results for \( J = 0 \) were close to those obtained by Schatz and Kuppermann.\(^10\)

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**APPENDIX A: DERIVATION OF THE COUPLED \( R \)-OPERATOR EQUATION**

In Sec. II we showed that the Green function \( G \) can be written as

\[ G = \sum_{\lambda'} W_{\lambda\lambda'} G_{\lambda'} + \sum_{\lambda'} W_{\lambda\lambda'} G_{\lambda'} V_{\lambda'} G , \]  

(A1)
We also gave a general expression for the $R$ operator:

$$R_{\lambda \lambda} = V_{\lambda'} + V_{\lambda'} G V_{\lambda} .$$  \hfill (A2)

Substituting Eq. (A1) in Eq. (A2) leads to

$$R_{\lambda \lambda} = V_{\lambda'} + V_{\lambda'} \left[ \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} + \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} V_{\lambda''} G \right] V_{\lambda}$$

$$= V_{\lambda'} \left[ 1 + \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} (V_{\lambda''} - V_{\lambda''}) \right] + V_{\lambda'} \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} (V_{\lambda''} + V_{\lambda''} G V_{\lambda}) .$$  \hfill (A3)

Since the expression in the parentheses in the last term is $R_{\lambda' \lambda}$ we get

$$R_{\lambda \lambda} = V_{\lambda'} \left[ 1 + \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} (V_{\lambda''} - V_{\lambda''}) \right] + V_{\lambda'} \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} R_{\lambda'' \lambda} .$$  \hfill (A4)

Next we consider the expression in the large parentheses.\(^1\) It can be shown that

$$1 + \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} (V_{\lambda''} - V_{\lambda''}) = 1 + \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} (G_{\lambda''}^{-1} - G_{\lambda''}^{-1})$$

$$= \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} G_{\lambda''}^{-1} ,$$  \hfill (A5)

where use was made of the fact that

$$\sum_{\lambda''} W_{\lambda \lambda''} = 1 .$$  \hfill (A6)

In the final summation in Eq. (A5) the term $\lambda'' = \lambda$ yields $W_{\lambda \lambda}$, whereas those terms with $\lambda'' \neq \lambda$ become negligibly small once operating on asymptotic state $|X_{\lambda''}\rangle$. Consequently we have for $R_{\lambda \lambda}$ the following expression:

$$R_{\lambda \lambda} = V_{\lambda'} W_{\lambda \lambda} + V_{\lambda'} \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} R_{\lambda'' \lambda} .$$  \hfill (A7)

We have not determined $\bar{\lambda}$, which is still free. In what we did in the text, $\bar{\lambda}$ was assumed to be equal to $\lambda'$, and therefore Eq. (A7) becomes

$$R_{\lambda \lambda} = V_{\lambda'} W_{\lambda \lambda} + V_{\lambda'} \sum_{\lambda''} W_{\lambda \lambda''} G_{\lambda''} R_{\lambda'' \lambda} .$$  \hfill (A8)

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\(^5\) Y. Shima and M. Baer (unpublished).


