On the reactive infinite order sudden approximation
S matrix

M. Baer

Applied Mathematics, Soreq Nuclear Research Center, Yavne, Israel 76000

D. J. Kouri

Department of Chemistry and Department of Physics, University of Houston Central Campus, Houston, Texas 77004

J. Jellinek

Department of Chemistry and the James Franck Institute, University of Chicago, Chicago, Illinois 60637

(Received 27 June 1982; accepted 29 July 1983)

We reconsider the S matrix in the l-labeled version of the reactive infinite order sudden (RIOS) approximation. The roles of the ∂S, γS, and Bw are clarified and a general expression obtained for the S matrix which results from averaging over all possible Bw.

I. INTRODUCTION

The reactive order sudden approximation applied to reactive scattering has been formulated and applied by a number of groups reflecting different points of view. Of these, one which has been extensively been applied to a variety of systems (e.g., H + H2, F + H2, F + D2, D + H2) is the l-labeled reactive infinite order sudden (RIOS) formalism. In that approach, the RIOS equations were derived by making the IOS approximation to the close coupling reactive scattering formalism due to Kuppermann, Schatz, and Baer and Kuppermann and Schatz. This involved the simplification of their complicated matching techniques. Part of the RIOS matching involved the choice of a matching surface, determined by a parameter Bw, which fixed the relation between the internal angle γl in arrangement λ to the internal angle γl in arrangement ν. In the RIOS method, the results in general could vary with Bw (although numerical evidence indicates that the dependence of Bw is rather weak). In the original paper by Khere, Kouri, and Baer the final expressions for the RIOS S matrix, for reaction from arrangement λ to ν involved an integral over the final configuration internal angle γw which is determined by γw through Bw. However, intuitively, it appeared more natural to integrate over γw and the calculations reported in subsequent papers all used expressions in which the λ-ν reactive S-matrix elements were evaluated via integration over the initial arrangement internal angle γl. The purpose of this paper is to provide the justification for the expressions actually used in the RIOS calculations which have been carried out. This paper is organized as follows. In Sec. II we indicate the expression given in the KKB paper and consider the specific case where Bw is taken equal to one (which is the value used by Schatz and Kuppermann in the close coupling calculations for H + H2 and by Khare, Kouri, and Baer in their RIOS study of H + H2). In Sec. III we consider a more general and superior analysis involving effectively averaging over Bw and thereby obtain a general expression for the RIOS S-matrices. Finally, we show how this may be reduced to the expression actually used in the calculations for the F + H2, F + D2, and D + H2 systems. In Sec. IV we give our conclusions.

II. THE RIOS EXPRESSION FOR THE S-MATRIX FOR Bw EQUAL TO ONE

The detailed derivation of the l-labeled RIOS approximation from exact close coupling formalism was given in KKB. In that paper, they began with the exact close coupling formalism of Kuppermann, Schatz, and Baer and Schatz and Kuppermann and obtained the RIOS approximation by substituting the l-labeled IOS approximation to the wave function in the various arrangements. They then carried out the matching and asymptotic analysis just as in a close coupling treatment thereby obtaining the resulting RIOS formulas for the scattering matrix. It is in the very last step of the KKB analysis that one may introduce a more general treatment in order to provide a framework for obtaining the expression used in actual calculations. Since only the last step in the KKB derivation is essential to our consideration we refer the reader to KKB for the preceding steps in arriving at this formula. The result of introducing the IOS approximation into the close coupling expressions for the wave function in the various arrangements and requiring that they match on a general matching surface is

\[ \sum_{\nu} Y_{\mu l}^* \left( \gamma_l, \gamma_w, B_w \right) \mathbf{S}_{\nu l}^{y^*} \left( \gamma_w, B_w \right) \left( \gamma_l, \gamma_w, B_w \right) = \sum_{1}^{m} \left( \frac{2l+1}{2j^*+1} \right) \langle \phi_{j^*}^* \left| N_{\nu} \right| \phi_{j^*} \left| J_{\nu} \right| \left[ \Delta_m \left( \gamma_w, B_w \right) \right] \times Y_{\nu l}^* \left( \gamma_w, 0 \right) \mathbf{S}_{\nu l}^y \left( \gamma_w, B_w \right) \rangle. \]

This is Eq. (105) in KKB except written for the S matrix instead of the R matrix. In this expression we
have taken the initial arrangement to be $\lambda$ and $\nu$ is the final arrangement, the internal angle $\gamma_\nu$ is determined by the initial arrangement internal angle $\gamma_\lambda$ and the matching surface, characterized by the parameter $B_{\nu,\lambda}$.

$S_{\nu,\lambda}^{\mu,\alpha}$ is the physical $S$ matrix for the transition $\lambda j_i \lambda j_i - \nu j_\nu j_\nu$, $S_{\nu,\lambda}^{\mu,\alpha}(\gamma_\nu, B_{\nu,\lambda})$ is the fixed-internal angle IOS $S$ matrix for the transition $\lambda j_i - \nu j_\nu$, with orbital quantum number $l_i$; $\nu_\lambda$ is the $\lambda$ arrangement internal angle and $\gamma_\nu(\gamma_\nu, B_{\nu,\lambda})$ is the $\nu$ arrangement internal angle. To which the $\lambda$ arrangement IOS solution is matched. The angle $\Delta_\lambda(\nu_\lambda, B_{\nu,\lambda})$ is the rotation relating the $\lambda$ and $\nu$ arrangement $z$ axes. In this expression, KKB took the independent variable to be $\nu_\lambda$, multiplied both sides by $2\pi Y_{\nu_\lambda,0}(\gamma_\nu, 0) \sin \gamma_\nu$ and integrated over $\gamma_\nu$ for fixed $B_{\nu,\lambda}$, treating $\nu_\lambda$ as a function of $\nu_\lambda$ and $B_{\nu,\lambda}$. The result is

$$S_{\nu,\lambda}^{\mu,\alpha}(B_{\nu,\lambda}) = \sum_{l_i} \left( \frac{2l_i + 1}{2\lambda + 1} \right) \langle 0j_i \Omega_i | J_l \Omega_i | 0j_i \Omega_i \rangle \times \int_0^{2\pi} d\gamma_\nu \sin \gamma_\nu d\nu_\lambda d\nu_\lambda \left[ \Delta_\lambda(\nu_\lambda, B_{\nu,\lambda}) \right] Y_{\nu_\lambda,0}(\gamma_\nu, 0) \times Y_{\nu_\lambda,0}(\gamma_\nu, 0) \left| S_{\nu,\lambda}^{\mu,\alpha}(\gamma_\nu, B_{\nu,\lambda}) \right|,$$

which is Eq. (109) of KKB (except written for the $S$ matrix rather than the $R$ matrix). From a computational viewpoint, it is simpler to have expressions in which one integrates over the initial arrangement angle $\gamma_\lambda$. The case where $B_{\nu,\lambda}$ equals one is simple and since it has been used in calculations on $H + H_2$ and $D + H_2$, we consider it in detail. We shall multiply both sides of Eq. (1) by $2\pi Y_{\nu_\lambda,0}(\gamma_\nu, B_{\nu,\lambda}, 0) \sin \gamma_\nu d\gamma_\nu$ and integrate over $d(\cos \gamma_\nu)$ from $-1$ to $+1$. Now when $B_{\nu,\lambda}$ equals one, it may be shown that

$$\cos \gamma_\nu(\gamma_\nu, B_{\nu,\lambda} = 1) = \cos (\pi - \gamma_\nu) \cos \gamma_\nu,$$

and

$$\gamma_\nu = -\cos \gamma_\nu,$$

Then we obtain for the left-hand side the expression

$$\sum_{l_i} S_{\nu,\lambda}^{\mu,\alpha}(B_{\nu,\lambda}) \times \int_0^{2\pi} d(\cos \gamma_\nu) Y_{\nu_\lambda,0}(\gamma_\nu, 0) \times Y_{\nu_\lambda,0}(-\cos \gamma_\nu, 0)$$

and

$$2\pi \int_0^{2\pi} d(\cos \gamma_\nu) Y_{\nu_\lambda,0}(\gamma_\nu, 0) Y_{\nu_\lambda,0}(-\cos \gamma_\nu, 0) = \delta_{\nu_\lambda,\nu_\lambda}.$$
\[ \int_{-1}^{1} d(\cos \gamma) W(\gamma) = 1, \]  

so that

\[ S_{\gamma \gamma, \lambda \lambda} = 2 \pi \sum_{i=0}^{\infty} \left( \frac{2i+1}{2i+1} \right) \left( \left| \langle 0 \left| \Omega_{1} \right| J_{0} \rangle \right| \right)^{2} \left| \langle 0 \left| \Omega_{2} \right| J_{0} \rangle \right|^{2} \]

\[ \times \int_{-1}^{1} \int_{-1}^{1} d(\cos \gamma_{1}) d(\cos \gamma_{2}) W(\gamma_{1}) Y_{i_{1}, \rho_{1}}^{*}(\gamma_{1}, 0) d_{\rho_{1}, \rho_{2}}(\Delta_{\lambda, \gamma_{1}, \gamma_{2}}) S_{\rho_{2}}(\gamma_{1}, \gamma_{2}) Y_{i_{2}, \rho_{2}}(\gamma_{2}, 0). \]  

Equation (16) is the general expression for a physical S matrix element as obtained from the RIOSA assuming the \( \lambda \) channel is the initial channel. The characteristic feature of this expression is that \( \gamma_{1} \) and \( \gamma_{2} \) are completely independent, so that fixing one does not impose any restriction on the other.

The introduction of some kind of dependence between the two angles can be done only in an \( \textit{ad hoc} \) fashion by multiplying the integrand by \( 2Q(\gamma_{1}, \gamma_{2}) \) where \( Q(\gamma_{1}, \gamma_{2}) \) is a conditional probability function fulfilling the condition

\[ \int_{-1}^{1} Q(\gamma_{1} | \gamma_{2}) d(\cos \gamma_{2}) = 1. \]  

Consequently, Eq. (16) becomes

\[ S_{\gamma \gamma, \lambda \lambda} = 4 \pi \sum_{i=0}^{\infty} \left( \frac{2i+1}{2i+1} \right) \left( \left| \langle 0 \left| \Omega_{1} \right| J_{0} \rangle \right| \right)^{2} \left| \langle 0 \left| \Omega_{2} \right| J_{0} \rangle \right|^{2} \]

\[ \times \int_{-1}^{1} \int_{-1}^{1} d(\cos \gamma_{1}) d(\cos \gamma_{2}) W(\gamma_{1}) Q(\gamma_{1} | \gamma_{2}) Y_{i_{1}, \rho_{1}}^{*}(\gamma_{1}, 0) d_{\rho_{1}, \rho_{2}}(\Delta_{\lambda, \gamma_{1}, \gamma_{2}}) S_{\rho_{2}}(\gamma_{1}, \gamma_{2}) Y_{i_{2}, \rho_{2}}(\gamma_{2}, 0). \]  

The reason for multiplying by \( 2Q(\gamma_{1}, \gamma_{2}) \) (and not simply by \( Q(\gamma_{1}, \gamma_{2}) \)) is to avoid “overnormalization.” Thus, if we take a constant conditional probability \( Q(\gamma_{1}, \gamma_{2}) = \frac{1}{2} \) for which Eq. (18) must become identical to Eq. (16), we in fact obtain Eq. (16) only if the integrand is multiplied by \( 2Q(\gamma_{1}, \gamma_{2}) \). Equation (18) is in the appropriate form to obtain a single \( B_{\lambda \nu} \) equation. For a given \( \gamma_{1} \), choosing a single fixed value for \( B_{\lambda \nu} \) yields a single value \( \gamma_{2} \) according to

\[ \gamma_{2} = \gamma_{2}(B_{\lambda \nu}, \gamma_{1}). \]

This can be introduced into Eq. (18) by taking \( Q(\gamma_{1}, \gamma_{2}) \) to be a Dirac \( \delta \) function:

\[ Q(\gamma_{1}, \gamma_{2}) = \delta(\cos \gamma_{2} - \cos \gamma_{2}(B_{\lambda \nu}, \gamma_{1})). \]  

Substituting Eq. (20) into Eq. (18) yields

\[ S_{\gamma \gamma, \lambda \lambda} = 4 \pi \sum_{i=0}^{\infty} \left( \frac{2i+1}{2i+1} \right) \left( \left| \langle 0 \left| \Omega_{1} \right| J_{0} \rangle \right| \right)^{2} \left| \langle 0 \left| \Omega_{2} \right| J_{0} \rangle \right|^{2} \]

\[ \times \int_{-1}^{1} d(\cos \gamma_{1}) W(\gamma_{1}) Y_{i_{1}, \rho_{1}}^{*}(\gamma_{1}, B_{\lambda \nu}, \gamma_{1}) 0) d_{\rho_{1}, \rho_{2}}(\Delta_{\lambda, \gamma_{1}, \gamma_{2}}) S_{\rho_{2}}(B_{\lambda \nu}, \gamma_{1}) Y_{i_{2}, \rho_{2}}(\gamma_{2}, 0). \]  

Equation (21) is the expression for the physical \( S \) matrix element obtained by fixing \( B_{\lambda \nu} \) and choosing the \( \lambda \) channel to be the initial channel. Comparing Eq. (21) to Eq. (7), it is noticed that the two are identical (when \( B_{\lambda \nu} = 1 \)) if \( W(\gamma_{1}) \) is taken to be a constant equal to \( (1/2) \).

IV. CONCLUSION

In this paper a general IOSA expression for reactive \( S \)-matrix elements is derived. It is established that the expression which follows from the present extension of the KKB theory\(^1\) consists of a double integral over the initial angle \( \gamma_{1} \) and the final angle \( \gamma_{2} \) where the primitive \( S \)-matrix elements, i.e., \( S_{\gamma_{1}, \gamma_{2}, \lambda \lambda} \) are weighted by the corresponding initial and final spherical harmonics. In addition, the integral includes \( d_{\rho_{1}, \rho_{2}}(\Delta_{\lambda, \gamma_{1}, \gamma_{2}}) \) which is due to the transformation from reagent to product coordinates and a \( \gamma_{1}, \gamma_{2} \) dependent weighting function \( Q(\gamma_{1}, \gamma_{2}) \), defined as \( W(\gamma_{1}) Q(\gamma_{1}, \gamma_{2}) \), which is introduced in order to carry out a general average over the two angles. The integral is now symmetric with respect to \( \gamma_{1} \) and \( \gamma_{2} \). The major advantage of this expression over the KKB expression is that in this one the dependence on the undetermined \( B_{\lambda \nu} \) parameter is eliminated. A single \( B_{\lambda \nu} \) dependent expression is also obtained by assuming that for each \( \gamma_{1} \), there corresponds a single value of \( \gamma_{2} \). The present single \( B \) expression and the KKB expression, differ in general from each other and only for \( B_{\lambda \nu} = 1 \) may they coincide.

1V. Khare, D. J. Kouri, and M. Baer, J. Chem. Phys. 71, 1169 (1979). Hereafter we refer to this paper as KKB.


12. N. Abu-Salbi, D. J. Kouri, Y. Shima, and M. Baer (to be published).


