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MODIFICATION OF THE "AMPLITUDE DENSITY FUNCTION" METHOD

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A modification of the numerical method of Secrest and Johnson for solving integral equations appearing in collision problems with a local interaction potential is presented. It arose from a combination of the well known "amplitude density function" formalism and the "homogeneous integral solution" method of Sams and Kouri. It is shown that this modification leads to considerable savings in the computations.

1. Introduction

In 1966 Secrest and Johnson proposed [1] the "amplitude density function" formalism, describing the nonrearrangement scattering problems, the main idea of which consists in replacing the scattering problem with many separate problems with weaker interaction potential. Within this formalism the authors have developed a numerical method which was next applied to the investigation of the collision between a structureless particle and a harmonic oscillator [2]. They also considered the collision of a structureless particle with a rigid rotator [3]. The applications of this method to more complicated collision models are not known in the literature. This is understandable because of the large amount of time involved in computing the matrix inversions needed. However, it seems to be possible to improve this method. The present work is an attempt in this direction. We believe that our results make the "amplitude density function" method more suitable for solving collision problems, and, in our opinion, it should be more exploited because of its large numerical stability.

In Section 2 we summarize the main points of the "amplitude density function" formalism. In order to solve the integral equations which occur there we apply the procedure of Sams and Kouri (Section 3). As a result, we arrive at the numerical method described in detail in Sections 4 and 5.

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2. Formalism of the "amplitude density function"

The amplitude density functions are defined by the following formula:

$$F_i^{\pm I}(x) = \int g^{1/2}\Phi_i^*(y)V(x, y)\Psi^{\pm I}(x, y)dy,$$

where $\Psi^{\pm I}(x, y)$ is the solution of the collision problem

$$[H_1(x)+H_2(x, y)+V(x, y)-E]\Psi(x, y) = 0 \tag{1}$$

satisfying the outgoing wave condition. By $H_1(x)$ we denote this part of the complete Hamiltonian which depends only on the distance x of the colliding objects. For the remaining variables we use y. I is the index labelling the solutions of Eq. (1) without the interaction potential $V(x, y)$. The signs "+" or "−" mark their forms as $\Phi_I(y)n_I(x)$ or $\Phi_I(y)m_I(x)$, respectively. $\Phi_i(y)$ are the eigenfunctions of the Hamiltonian $H_2(x, y)$ to the eigenvalues E_{2i}, $n_i(x)$, $m_i(x)$ are independent solutions of the equation

$$[H_1(x)+E_{2i}-E]R(x) = 0, \tag{2}$$

and g is the determinant of the metric tensor. The amplitude density functions can be obtained as the solutions of the integral equations which may be written in the matrix notation[1]

$$\overline{F}^{\pm}(x) = \begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} \overline{V}(x) - \int \overline{F}^{\pm}(x')\bar{c}\overline{m}(x_<)\overline{n}(x_>)\overline{V}(x)dx', \tag{3}$$

where

$$[\overline{F}^{\pm}(x)]_{ij} = F_j^{\pm i}(x), \quad [\overline{m}(x)]_{ij} = \delta_{ij}m_i(x),$$
$$[\overline{n}(x)]_{ij} = \delta_{ij}n_i(x), \quad [\bar{c}]_{ij} = \delta_{ij}c_i, \quad [\overline{V}(x)]_{ij} = V_{ij}(x),$$
$$V_{ij}(x) = \int g^{1/2}\Phi_j^*(y)V(x, y)\Phi_i(y)dy,$$

c_i are the coefficients in the appropriate Green's function of the operator H_1+H_2-E [1] and $x_<(x_>)$ is smaller (bigger) from x and x'.

The infinite dimension of the matrices occurring in Eq. (3) is reduced for practical applications to a particular integer N, whereas the infinite integration range with respect to x is replaced by a finite range S. The knowledge of the amplitude density functions enables one to determine the reflection, $R_j^{\pm i} = [\overline{R}^{\pm}]_{ij}$, and the transition, $T_j^{\pm i} = [\overline{T}^{\pm}]_{ij}$, coefficients from the formulae

$$\overline{R}^{\pm} = \int \overline{F}^{\pm}(x)\bar{c}\begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} dx, \tag{4}$$

$$\overline{T}^{\pm} = \int \overline{F}^{\pm}(x)\bar{c}\begin{bmatrix} \overline{m}(x) \\ \overline{n}(x) \end{bmatrix} dx. \tag{5}$$

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[1] Eq. (3) as well as the majority of other equations in this paper are in effect two equations condensed into one. For "+" one takes the upper function in the square bracket and for "−" the lower one.

These coefficients determine completely the asymptotic forms of the functions $\Psi^{\pm i}(x, y)$

$$\lim_{x\to\infty} \Psi^{\pm i}(x, y) = \Phi_i(y)\begin{bmatrix} n_i(x) \\ m_i(x) \end{bmatrix} - \sum_j \begin{bmatrix} T_j^{+i} \\ R_j^{-i} \end{bmatrix} \Phi_j(y) n_j(x),$$

$$\lim_{x\to-\infty} \Psi^{\pm i}(x, y) = \Phi_i(y)\begin{bmatrix} n_i(x) \\ m_i(x) \end{bmatrix} - \sum_j \begin{bmatrix} R_j^{+i} \\ T_j^{-i} \end{bmatrix} \Phi_j(y) m_j(x).$$

Therefore, they contain full information about the investigated collision process.

The most important consequences of introducing the amplitude density functions for description of the collision phenomena are connected with the validity of the following relations

$$\overline{F}^{\pm C} = \overline{F}^{\pm A} + \overline{F}^{\pm B} + \overline{a}^{\pm}\overline{F}^{-A} + \overline{b}^{\pm}\overline{F}^{+B}, \tag{6}$$

$$\overline{R}^{\pm C} = \overline{R}^{\pm A} + \overline{R}^{\pm B} + \overline{a}^{\pm}\begin{bmatrix} \overline{T}^{-A} \\ \overline{R}^{-A} \end{bmatrix} + \overline{b}^{\pm}\begin{bmatrix} \overline{R}^{+B} \\ \overline{T}^{+B} \end{bmatrix}, \tag{7}$$

$$\overline{T}^{\pm C} = \overline{T}^{\pm A} + \overline{T}^{\pm B} + \overline{a}^{\pm}\begin{bmatrix} \overline{R}^{-A} \\ \overline{T}^{-A} \end{bmatrix} + b^{\pm}\begin{bmatrix} \overline{T}^{+B} \\ \overline{R}^{+B} \end{bmatrix}. \tag{8}$$

The amplitude density functions $\overline{F}^{\pm C}$, $\overline{F}^{\pm A}$, $\overline{F}^{\pm B}$ are defined as the solutions of Eq. (3) in which $\overline{V}(x)$ has been replaced by $\overline{V}^C(x)$, $\overline{V}^A(x)$ and $\overline{V}^B(x)$, respectively, where

$$[\overline{V}^{\alpha}(x)]_{ij} = \begin{cases} V_{ij}(x) & \text{for } x \in \alpha, \\ 0 & \text{for } x \notin \alpha, \end{cases}$$

where $\alpha = A, B, C$ are the intervals of the variable x satisfying $A+B = C$. The coefficients $\overline{a}^{\pm}$ and $\overline{b}^{\pm}$ are the solutions of the systems of linear equations

$$\overline{a}^{\pm} = -\overline{b}^{\pm}\overline{R}^{+B} - \begin{bmatrix} \overline{R}^{+B} \\ \overline{T}^{-B} \end{bmatrix}, \tag{9}$$

$$\overline{b}^{\pm} = -\overline{a}^{\pm}\overline{R}^{-A} - \begin{bmatrix} \overline{T}^{+A} \\ \overline{R}^{-A} \end{bmatrix}. \tag{10}$$

The matrices $\overline{R}^{\pm\alpha}$ and $\overline{T}^{\pm\alpha}$ are defined analogously to $\overline{R}^{\pm}$ and $\overline{T}^{\pm}$. Due to (6)—(8) one can obtain the functions $\overline{F}^{\pm}(x)$ by solving the $2(M+1)$ integral equations for $\overline{F}^{\pm\alpha_i}(x)$, where $\{\alpha_i\}$ $(i = 0, 1, \ldots, M)$ forms a partition of the interval S into $M+1$ subintervals.

It is worth noticing that the presented formalism does not contain any restrictions on the partition of S (i.e., on the length and number of the α_i). This fact will be exploited in the next section concerning the determination of the functions $\overline{F}^{\pm\alpha}(x)$.

3. *Application of the "homogeneous integral solution" method to the amplitude density functions*

The integral equations for the amplitude density functions $\overline{F}^{\pm\alpha}(x)$

$$\overline{F}^{\pm\alpha}(x) = \begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} \overline{V}^{\alpha}(x) - \int_{x_1}^{x_u} \overline{F}^{\pm\alpha}(x')\overline{c}\overline{m}(x_<)\overline{n}(x_>)\overline{V}^{\alpha}(x)dx', \tag{11}$$

where x_l, x_u are the lower and upper bounds of the α interval, can be written in two equivalent forms

$$\overline{F}^{\pm\alpha}(x) = \begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} \overline{V}^{\alpha}(x) - \int_{x_l}^{x} \overline{F}^{\pm\alpha}(x')\bar{c}[\overline{m}(x')\overline{n}(x) - \overline{m}(x)\overline{n}(x')]$$

$$\times \overline{V}^{\alpha}(x)dx' - \int_{x_l}^{x_u} \overline{F}^{\pm\alpha}(x')\bar{c}\overline{m}(x)\overline{n}(x')\overline{V}^{\alpha}(x)dx', \tag{12}$$

and

$$\overline{F}^{\pm\alpha}(x) = \begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} \overline{V}^{\alpha}(x) - \int_{x}^{x_u} \overline{F}^{\pm\alpha}(x')\bar{c}[\overline{m}(x)\overline{n}(x') - \overline{m}(x')\overline{n}(x)]$$

$$\times \overline{V}^{\alpha}(x)dx' - \int_{x_l}^{x_u} \overline{F}^{\pm\alpha}(x')\bar{c}\overline{m}(x')\overline{n}(x)\overline{V}^{\alpha}(x)dx'. \tag{13}$$

Following Sams and Kouri [4] we seek the solutions of this equation as a sum

$$\overline{F}^{\pm\alpha}(x) = \overline{F}_0^{\pm\alpha}(x) + \overline{F}_1^{\pm\alpha}(x). \tag{14}$$

Choosing the integral equations

$$\overline{F}_0^{+\alpha}(x) = \overline{n}(x)\overline{V}^{\alpha}(x) - \int_{x}^{x_u} \overline{F}_0^{+\alpha}(x')\bar{c}[\overline{m}(x)\overline{n}(x') - \overline{m}(x')\overline{n}(x)]\overline{V}^{\alpha}(x)dx', \tag{15}$$

$$\overline{F}_0^{-\alpha}(x) = \overline{m}(x)\overline{V}^{\alpha}(x) - \int_{x_l}^{x} \overline{F}_0^{-\alpha}(x')\bar{c}[\overline{m}(x')\overline{n}(x) - \overline{m}(x)\overline{n}(x')]\overline{V}^{\alpha}(x)dx' \tag{16}$$

for defining the "homogeneous integral solutions" $\overline{F}_0^{\pm\alpha}(x)$ we get (by inserting (14)—(16) into (12), (13)) the following integral equations for $\overline{F}_1^{\pm\alpha}(x)$

$$\overline{F}_1^{+\alpha}(x) = -\int_{x}^{x_u} \overline{F}_1^{+\alpha}(x')\bar{c}[\overline{m}(x)\overline{n}(x') - \overline{m}(x')\overline{n}(x)]\overline{V}^{\alpha}(x)dx'$$

$$- \int_{x_l}^{x_u} [\overline{F}_0^{+\alpha}(x') + \overline{F}_1^{+\alpha}(x')]\bar{c}\overline{m}(x')\overline{n}(x)\overline{V}^{\alpha}(x)dx', \tag{17}$$

$$\overline{F}_1^{-\alpha}(x) = -\int_{x_l}^{x} \overline{F}_1^{-\alpha}(x')\bar{c}[\overline{m}(x')\overline{n}(x) - \overline{m}(x)\overline{n}(x')]\overline{V}^{\alpha}(x)dx'$$

$$- \int_{x_l}^{x_u} [\overline{F}_0^{-\alpha}(x') + \overline{F}_1^{-\alpha}(x')]\bar{c}\overline{m}(x)\overline{n}(x')\overline{V}^{\alpha}(x)dx'. \tag{18}$$

The functions thus defined $\overline{F}_0^{\pm\alpha}(x)$ and $\overline{F}_1^{\pm\alpha}(x)$ are connected by the relation

$$\overline{F}_1^{\pm\alpha}(x) = \overline{C}^{\pm\alpha}\overline{F}_0^{\pm\alpha}(x) \tag{19}$$

in which $\overline{C}^{\pm\alpha}$ are constant matrices satisfying the equation

$$\overline{C}^{\pm\alpha} = -(\overline{1} + \overline{C}^{\pm\alpha})\overline{T}_0^{\pm\alpha}$$

hence

$$\bar{C}^{\pm\alpha} = -\bar{T}_0^{\pm\alpha}(\bar{1}+\bar{T}_0^{\pm\alpha})^{-1},$$

where

$$\bar{T}_0^{+\alpha} = \bar{T}_0^{+\alpha}(x_l), \quad \bar{T}_0^{-\alpha} = \bar{T}_0^{-\alpha}(x_u),$$

$$\bar{T}_0^{+\alpha}(x) = \int_x^{x_u} \bar{F}_0^{+\alpha}(x')\bar{c}\bar{m}(x')dx',$$

$$\bar{T}_0^{-\alpha}(x) = \int_{x_l}^{x} \bar{F}_0^{-\alpha}(x')\bar{c}\bar{n}(x')dx'. \tag{20}$$

Inserting (19) into (14) we get the following relation for the amplitude density functions $\bar{F}^{\pm\alpha}(x)$

$$\bar{F}^{\pm\alpha}(x) = (\bar{Q}^{\pm\alpha})^{-1}\bar{F}_0^{\pm\alpha}(x), \tag{21}$$

where

$$(\bar{Q}^{\pm\alpha})^{-1} = \bar{1}+\bar{C}^{\pm\alpha},$$

hence

$$\bar{Q}^{\pm\alpha} = \bar{1}+\bar{T}_0^{\pm\alpha},$$

and analogously for the matrices $\bar{R}^{\pm\alpha}$ and $\bar{T}^{\pm\alpha}$

$$\bar{T}^{\pm\alpha} = (\bar{Q}^{\pm\alpha})^{-1}\bar{T}_0^{\pm\alpha}, \tag{22}$$

$$\bar{R}^{\pm\alpha} = (\bar{Q}^{\pm\alpha})^{-1}\bar{R}_0^{\pm\alpha}, \tag{23}$$

where

$$\bar{R}_0^{+\alpha} = \bar{R}_0^{+\alpha}(x_l), \quad \bar{R}_0^{-\alpha} = \bar{R}_0^{-\alpha}(x_u),$$

$$\bar{R}_0^{+\alpha}(x) = \int_x^{x_u} \bar{F}_0^{+\alpha}(x')\bar{c}\bar{n}(x')dx',$$

$$\bar{R}_0^{-\alpha}(x) = \int_{x_l}^{x} \bar{F}_0^{-\alpha}(x')\bar{c}\bar{m}(x')dx'. \tag{24}$$

These relations are of fundamental importance for the modification of the numerical Secrest-Johnson method presented in this paper. They indicate the possibility of replacing Eqs. (11) by (15), (16). Applying a procedure analogous to that described by Eastes and Secrest [5] one can solve Eqs. (15) and (16) with a relatively small expenditure of effort.

5. *Numerical method*

It is convenient to write the equations for the functions $\bar{F}_0^{\pm\alpha}(x)$ in the form

$$\bar{F}_0^{\pm\alpha}(x) = \bar{Q}^{\pm\alpha}(x)\begin{bmatrix}\bar{n}(x)\\ \bar{m}(x)\end{bmatrix}\bar{V}^{\alpha}(x) - \bar{R}_0^{\pm\alpha}(x)\begin{bmatrix}\bar{m}(x)\\ \bar{n}(x)\end{bmatrix}\bar{V}^{\alpha}(x). \tag{25}$$

After preparing these equations for the numerical treatment and denoting by $\mathcal{S} = \{x_i\}_{i=0}^{M}$ the $M+1$ point set of a quadrature formula employed to the integrals in Eq. (3), by ω_i

the weight of point x_i in the quadrature used and by $\alpha = \{x_{l+1}\}_{i=0}^{L}$ the $L+1$ element subsequence of $\mathcal{S}$ ($x_{l+L} = x_u$) we get:

1. for $L > 0$

$$\overline{F}_0^{+\alpha}(x_{u-k}) = \overline{Q}^{+\alpha}(x_{u-k+1})\overline{n}(x_{u-k})\overline{V}(x_{u-k}) - \overline{R}_0^{+\alpha}(x_{u-k+1})\overline{m}(x_{u-k})\overline{V}(x_{u-k}), \tag{26}$$

$$\overline{F}_0^{-\alpha}(x_{l+k}) = \overline{Q}^{-\alpha}(x_{l+k-1})\overline{m}(x_{l+k})\overline{V}(x_{l+k}) - \overline{R}_0^{-\alpha}(x_{l+k-1})\overline{n}(x_{l+k})\overline{V}(x_{l+k}), \tag{27}$$

$$\text{for } k = 1, 2, \ldots L$$

and

$$\overline{F}_0^{+\alpha}(x_u) = \overline{n}(x_u)\overline{V}(x_u), \tag{28}$$

$$\overline{F}_0^{-\alpha}(x_l) = \overline{m}(x_l)\overline{V}(x_l), \tag{29}$$

where

$$\overline{Q}^{+\alpha}(x_{u-r}) = \overline{1} + \overline{T}_0^{+\alpha}(x_{u-r}), \tag{30}$$

$$\overline{Q}^{-\alpha}(x_{l+r}) = \overline{1} + \overline{T}_0^{-\alpha}(x_{l+r}), \tag{31}$$

$$\overline{R}_0^{+\alpha}(x_{u-r}) = \sum_{i=0}^{r} \omega_{u-i}\overline{F}_0^{+\alpha}(x_{u-i})\overline{c}\overline{n}(x_{u-i}), \tag{32}$$

$$\overline{R}_0^{-\alpha}(x_{l+r}) = \sum_{i=0}^{r} \omega_{l+i}\overline{F}_0^{-\alpha}(x_{l+i})\overline{c}\overline{m}(x_{l+i}), \tag{33}$$

$$\overline{T}_0^{+\alpha}(x_{u-r}) = \sum_{i=0}^{r} \omega_{u-i}\overline{F}_0^{+\alpha}(x_{u-i})\overline{c}\overline{m}(x_{u-i}), \tag{34}$$

$$\overline{T}_0^{-\alpha}(x_{l+r}) = \sum_{i=0}^{r} \omega_{l+r}\overline{F}_0^{-\alpha}(x_{l+r})\overline{c}\overline{n}(x_{l+r}), \quad \text{for } r = 1, 2, \ldots L \tag{35}$$

and

$$\overline{Q}^{+\alpha}(x_u) = \overline{Q}^{-\alpha}(x_l) = \overline{1}, \tag{36}$$

$$\overline{R}_0^{+\alpha}(x_u) = \overline{R}_0^{-\alpha}(x_l) = \overline{0}, \tag{37}$$

$$\overline{T}_0^{+\alpha}(x_u) = \overline{T}_0^{-\alpha}(x_l) = \overline{0}. \tag{38}$$

2. for $L = 0$ (i.e., for $x_l = x_u = x$)

$$\overline{F}_0^{\pm\alpha}(x) = \begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix} \overline{V}(x). \tag{39}$$

$$\overline{Q}^{\pm\alpha}(x) = \overline{1} + \omega\overline{F}_0^{\pm\alpha}(x)\overline{c}\begin{bmatrix} \overline{m}(x) \\ \overline{n}(x) \end{bmatrix}, \tag{40}$$

$$\overline{R}_0^{\pm\alpha}(x) = \omega\overline{F}_0^{\pm\alpha}(x)\overline{c}\begin{bmatrix} \overline{n}(x) \\ \overline{m}(x) \end{bmatrix}. \tag{41}$$

In the formulae concerning case 1 use has been made of the fact that the integrands in (15) and (16) vanish for $x = x'$. As a consequence of this we may find the functions $\overline{F}_0^{\pm\alpha}(x)$ and the coefficients $\overline{R}_0^{\pm\alpha}$ and $\overline{T}_0^{\pm\alpha}$ (see (20)—(24)) without matrix inversion. The special case of one-point sets α was considered by Secrest and Johnson. Therefore the

formulae given in point 2 can be transformed into the equations of their method. In particular one can show that two Eqs. (21) can be reduced in this case to one equation of the form

$$\bar{A}(x) = [\bar{1} + \omega \bar{V}(x) \bar{c} \bar{m}(x) \bar{n}(x)]^{-1} \bar{V}(x), \tag{42}$$

where

$$\bar{A}^{+}(x) = \bar{A}^{-}(x) \equiv \bar{A}(x), \quad \bar{A}^{\pm}(x) = \begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} \bar{F}^{\pm\alpha}(x).$$

To prove this we multiply Eqs. (21) on the left:

$$\begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} \bar{F}^{\pm\alpha}(x) = \begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} (\bar{Q}^{\pm\alpha})^{-1} \begin{bmatrix} \bar{n}(x) \\ \bar{m}(x) \end{bmatrix} \begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} \bar{F}_0^{\pm\alpha}(x),$$

and we calculate

$$\begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} \bar{F}_0^{\pm\alpha}(x) = \bar{V}(x),$$

$$\begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} (\bar{Q}^{\pm\alpha})^{-1} \begin{bmatrix} \bar{n}(x) \\ \bar{m}(x) \end{bmatrix} = \left\{ \begin{bmatrix} [\bar{n}(x)]^{-1} \\ [\bar{m}(x)]^{-1} \end{bmatrix} \left(\bar{1} + \begin{bmatrix} \bar{n}(x) \\ \bar{m}(x) \end{bmatrix} \bar{V}(x) \bar{c} \begin{bmatrix} \bar{m}(x) \\ \bar{n}(x) \end{bmatrix} \right) \times \begin{bmatrix} \bar{n}(x) \\ \bar{m}(x) \end{bmatrix} \right\}^{-1} = \left\{ \bar{1} + \omega \bar{V}(x) \bar{c} \begin{bmatrix} \bar{m}(x) \\ \bar{n}(x) \end{bmatrix} \begin{bmatrix} \bar{n}(x) \\ \bar{m}(x) \end{bmatrix} \right\}^{-1}$$

$$= \left\{ \bar{1} + \omega \bar{V}(x) \bar{c} \begin{bmatrix} \bar{m}(x) \\ \bar{m}(x) \end{bmatrix} \begin{bmatrix} \bar{n}(x) \\ \bar{n}(x) \end{bmatrix} \right\}^{-1}.$$

It follows from the above arguments that we can solve a given scattering problem within the "amplitude density function" formalism in many different ways. They are determined by a partition of the set $\mathcal{S}$ and in practice they differ from each other in the number of the $N \times N$ matrices which must be inverted. This is exhibited by scheme I which contains the list of the needed operation for calculating the coefficients $\bar{R}^{\pm}$ and $\bar{T}^{\pm}$ if we have split the $M+1$ element set $\mathcal{S}$ into K subsets α_i among which there are J one-point sets.

Scheme I

	Formulae	Number of matrix inversions
1. The evaluation of $6(K-J)$ matrices $\bar{Q}^{\pm\alpha_i}$, $\bar{R}_0^{\pm\alpha_i}$ and $\bar{T}_0^{\pm\alpha_i}$ for α_i formed by more than one element	(26)—(38)	—
2. The evaluation of $4K$ matrices $\bar{T}^{\pm\alpha_i}$ and $\bar{R}^{\pm\alpha_i}$		
a) $4J$ matrices for one-point α_i	(42), (4), (5)	J
b) $4(K-J)$ matrices for the α_i which contain more than one point	(22), (23)	$2(K-J)$
3. The evaluation of 4 matrices $\bar{R}^{\pm}$ and $\bar{T}^{\pm}$	(9), (10), (7), (8)	$2(K-1)$

For $K = M+1$ ($J = K$) we can exclude steps 1 and 2b but the whole number of matrix inversions has then its greatest value $3M+1$. The other cases involve less calculations. The amount of calculations necessary is proportional to the size of K. For these reasons the most suitable choice for K is $K = 1$ ($J = 0$) when scheme I reduces to steps 1 and 2b and becomes equivalent (in the case when the trapezoid rule is used) to the Eastes--Secrest method [5] formulated for the amplitude density functions. The use of too large intervals α_i, however, can lead to some computational difficulties, the details of which are described in the next section.

5. *Calculations and discussion*

In order to show the most important practical implications of the presented considerations we investigated in some more details the model of a collinear collision of a homonuclear diatomic molecule with a structureless particle. For this case the respective constituents of Eqs. (1)—(3) take the form (see Appendix)

$$H_1(x) = -\frac{1}{m}\frac{\partial^2}{\partial x^2}, \tag{43}$$

$$H_2(y) = -\frac{\partial^2}{\partial y^2} + y^2, \tag{44}$$

$$V(x, y) = Ae^{-2\beta|x|}(e^{\beta y} + e^{-2\beta y_{eq}}e^{-\beta y}), \tag{45}$$

$$[\overline{m}]_{ij} = \delta_{ij}e^{-ik_i x}, \tag{46}$$

$$[\overline{n}]_{ij} = \delta_{ij}e^{ik_i x}, \tag{47}$$

where

$$k_i = [m(E-E_{2i})]^{1/2}, \tag{48}$$

$$E_{2i} = 2i+1, \tag{49}$$

$$c_i = -\frac{m}{2ik_i}, \quad g = 1$$

and $\Phi_i(y)$ are the harmonic oscillator eigenfunctions. As a solution of this collision model we have calculated the transition probabilities of the molecule from the state i to j with a simultaneous reflection (P^{R}) or transmission (P^{T}) of the incoming particle through the potential barrier defined by

$$P^{\mathrm{R}}_{i-j} = \frac{k_j}{k_i}|R^{-i}_j|^2, \tag{50}$$

$$P^{\mathrm{T}}_{i-j} = \frac{k_j}{k_i}|T^{-i}_j + \delta_{ij}|^2. \tag{51}$$

These probabilities fulfil the relations

$$\sum_{j=0}^{N_0} (P^{\mathrm{R}}_{i-j} + P^{\mathrm{T}}_{i-j}) = 1 \quad \text{for } i = 0, 1, \ldots, N_0 \tag{52}$$

where N_0+1 is the number of open channels (i.e., the number of the molecule states for which $E_{2i} < E$), and

$$P^{\mathrm{R}}_{i-j} = P^{\mathrm{R}}_{j-i}, \tag{53}$$

$$P^{\mathrm{T}}_{i-j} = P^{\mathrm{T}}_{j-i}. \tag{54}$$

Eq. (53) expresses the detailed balance relation and (54) results from the symmetry of the interaction potential (45). These relations may serve as a basis for the verification of the calculated probabilities. The probabilities evaluated for $m = 1, y_{\mathrm{eq}} = 1$ and different sets of parameters E, A and β are collected in Table I. The Table contains also the information about how the total interval S was partitioned into K subintervals α_i. It is seen that the results of the tests no. 2, 6 and 8 do not satisfy (53) and (54) which means that they are incorrect. The computations failed also in test no. 5 due to a computer overflow. The origin of the difficulties can be understood if we compare the results of different tests:

a) From the results of tests no. 2 and 3 it is evident that as expected the difficulties are connected with the closed channels

b) No. 1, 2, 9 and 10 illustrate the fact that a decrease in the range of the potential improves the accuracy of the results

c) Finally if one compares the tests 2 and 4 or 6, 8 and 7 one can see that the stability of the method depends strongly on how the interval S is partitioned. It is also worth noting that with a proper partitioning of S, i.e., when (53) and (54) are satisfied, (52) holds too.

Thus we see from the tests that the maximum lengths of the intervals α_i which lead to correct probabilities depend on the range of the interaction potential and on the number of closed channels included in the calculations. For closed channels the solutions of Eq. (2), $n_i(x)$ and $m_i(x)$, become real exponential functions. During the realization of step 1 in schema I these functions may have very large values which may lead either to a computer overflow or to almost singular matrices $\overline{Q}^{\pm\alpha}$. Obviously in such a case it is impossible to calculate the correct matrices $\overline{R}^{\pm\alpha}$ and $\overline{T}^{\pm\alpha}$. The probability of such difficulties increases with the lengths of the intervals α_i. Thus in the frame of the present method the above mentioned numerical instabilities can be always avoided by means of an appropriate partitioning of the interval S into small fragments α_i. Moreover, the partitioning of S enables one to use an additional protection against numerical difficulties. This may be achieved by modification of the numerical procedure which cancels to some degree the large arguments of the exponential functions. This modification is an extension, for sets α_i with more than one element, of the modification given by Secrest and Johnson [3]. It consists in

TABLE I

Numerical tests for calculation of probabilities P^{R}_{i-j} and P^{T}_{i-j}; $m = 1$, $y_{eq} = 1$

Test No	Energy E	Potential constants		Number of channels		Interval S	Partition of $\mathscr{S}$		Probabilities		Sum of probabilities[b]	
		A	β	open	closed		$\{L_i\}_{i=1}^{K}$ [a]	K	P^{R}_{0-1}/P^{R}_{1-0}	P^{T}_{0-1}/P^{T}_{1-0}	$\sum^0$	$\sum^1$
1	4.9	5	0.3	2	1	(−60, 60)	601	1	0.563 (−2) 0.563 (−2)	0.747 (−5) 0.747 (−5)	0.100 (1)	0.100 (1)
2	4.9	5	0.1	2	1	(−80, 80)	102, 597, 102	3	0.118 (3) 0.561 (−8)	0.454 (2) 0.646 (−7)	0.164 (3)	0.997
3	4.9	5	0.1	2	—	(−80, 80)	102, 597, 102	3	0.167 (−7) 0.167 (−7)	0.179 (−17) 0.179 (−17)	1.00	1.00
4	4.9	5	0.1	2	1	(−80, 80)	356, 89, 356	3	0.156 (−7) 0.156 (−7)	0.173 (−17) 0.173 (−17)	1.00	1.00
5	3.9	4	0.1	2	1	(−60, 60)	601	1	—	—	—	—
6	3.9	4	0.1	2	1	(−60, 60)	242, 117, 242	3	0.931 (−2) 0.497 (−4)	0.214 (−13) 0.773 (−14)	0.977	0.984
7	3.9	4	0.1	2	1	(−60, 60)	152, 107, 83, 107, 152	5	0.114 (−9) 0.114 (−9)	0.147 (−19) 0.147 (−19)	1.00	1.00
8	3.9	4	0.1	2	1	(−60, 60)	266, 69, 266	3	0.810 (2) 0.290 (−1)	0.697 (−10) 0.540 (−12)	0.814 (2)	0.211 (1)
9	4.9	7	0.15	2	1	(−70, 70)	52, 597, 52	3	0.104 (−4) 0.104 (−4)	0.496 (−16) 0.496 (−16)	1.00	1.00
10	6.0	7	0.13	2	1	(−70, 70)	52, 597, 52	3	0.132 (−4) 0.132 (−4)	0.147 (−14) 0.147 (−14)	1.00	1.00

[a] L_i — the number of points in α_i, [b] $\sum^i \equiv \sum_{j=0}^{1} (P^{R}_{i-j} + P^{T}_{i-j})$.

replacing the matrices $\overline{n}(x)$ and $\overline{m}(x)$ by $\tilde{\overline{n}}^{\alpha}(x)$ and $\tilde{\overline{m}}^{\alpha}(x)$ given by

$$\tilde{\overline{m}}^{\alpha}(x) = \overline{Z}^{\alpha}\overline{m}, \quad \tilde{\overline{n}}^{\alpha}(x) = (\overline{Z}^{\alpha})^{-1}\overline{n},$$

where

$$[\overline{Z}^{\alpha}]_{ij} = \delta_{ij}\mathrm{e}(k_i x_p),$$

$$\mathrm{e}(k_i x_p) = \begin{cases} 1 & \text{for } k_i \text{ real,} \\ \exp(-k_i x_p) & \text{for } k_i \text{ imaginary,} \end{cases}$$

(x_p is a point from α). The remaining quantities and some of the equations must then be changed in the following way

$$\tilde{\overline{F}}^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{F}^{\pm\alpha}$$

$$\tilde{\overline{F}}_0^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{F}_0^{\pm\alpha}$$

$$\tilde{\overline{R}}^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{R}^{\pm\alpha} \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix}$$

$$\tilde{\overline{R}}_0^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{R}_0^{\pm\alpha} \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix}$$

$$\tilde{\overline{T}}^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{T}^{\pm\alpha} \begin{bmatrix} \overline{Z}^{\alpha} \\ (\overline{Z}^{\alpha})^{-1} \end{bmatrix}$$

$$\tilde{\overline{T}}_0^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{T}_0^{\pm\alpha} \begin{bmatrix} \overline{Z}^{\alpha} \\ (\overline{Z}^{\alpha})^{-1} \end{bmatrix}$$

$$\tilde{\overline{a}}^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{a}^{\pm} \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ (\overline{Z}^{\alpha})^{-1} \end{bmatrix}$$

$$\tilde{\overline{b}}^{\pm\alpha} = \begin{bmatrix} (\overline{Z}^{\alpha})^{-1} \\ \overline{Z}^{\alpha} \end{bmatrix} \overline{b}^{\pm} \begin{bmatrix} \overline{Z}^{\alpha} \\ \overline{Z}^{\alpha} \end{bmatrix}$$

$$\tilde{\overline{a}}^{\pm\alpha} = -\tilde{\overline{b}}^{\pm\alpha}\tilde{\overline{R}}^{+\alpha} - \begin{bmatrix} \tilde{\overline{R}}^{+\alpha} \\ \tilde{\overline{T}}^{-\alpha} \end{bmatrix}$$

$$\tilde{\overline{b}}^{\pm\alpha_i} = -\tilde{\overline{a}}^{\pm\alpha_i}\overline{W}^{\alpha_i}\tilde{\overline{R}}^{-\alpha_{i-1}}\overline{W}^{\alpha_i} - \begin{bmatrix} (\overline{W}^{\alpha_i})^{-1}\tilde{\overline{T}}^{+\alpha_{i-1}}\overline{W}^{\alpha_i} \\ \overline{W}^{\alpha_i}\tilde{\overline{R}}^{-\alpha_{i-1}}\overline{W}^{\alpha_i} \end{bmatrix}$$

$$\overline{W}^{\alpha_i} = \overline{Z}^{\alpha_i}(\overline{Z}^{\alpha_{i-1}})^{-1}.$$

It is easy to see that the effectiveness of the above modification diminishes with enlarging of the intervals α_i. In particular there is no reason to apply it in the case of the partition with $K = 1$. However, with a proper choice of α_i it may be quite useful.

The difficulties considered here can be also overcome by the use of a procedure analogous to that applied in [5]. Following Eastes and Secrest we may modify the matrices $\bar{R}_0^{\pm\alpha}(x)$, $\bar{Q}^{\pm\alpha}(x)$ and $\bar{T}_0^{\pm\alpha}(x)$

$$\tilde{\bar{Q}}^{\pm\alpha}(x) = \bar{S}^{\pm}\bar{Q}^{\pm\alpha}(x), \tag{55}$$

$$\tilde{\bar{R}}_0^{\pm\alpha}(x) = \bar{S}^{\pm}\bar{R}_0^{\pm\alpha}(x), \tag{56}$$

$$\tilde{\bar{T}}_0^{\pm\alpha}(x) = \bar{S}^{\pm}\bar{T}_0^{\pm\alpha}(x), \tag{57}$$

during their numerical determination by means of constant matrices $\bar{S}^{\pm}$ which can be chosen as

$$\bar{S}^{\pm} = [\bar{Q}^{\pm\alpha}(x_f)]^{-1},$$

where x_f is a point from the interval α. These modifications, performed in an appropriate number, prevent the occurrence of singular $\bar{Q}^{\pm\alpha}$ and they leave the matrices $\bar{T}^{\pm\alpha}$ and $\bar{R}^{\pm\alpha}$ unchanged

$$\bar{R}^{\pm\alpha} = (\bar{Q}^{\pm\alpha})^{-1}\bar{R}_0^{\pm\alpha} = (\tilde{\bar{Q}}^{\pm\alpha})^{-1}\tilde{\bar{R}}_0^{\pm\alpha},$$

$$\bar{T}^{\pm\alpha} = (\bar{Q}^{\pm\alpha})^{-1}\bar{T}_0^{\pm\alpha} = (\tilde{\bar{Q}}^{\pm\alpha})^{-1}\tilde{\bar{T}}_0^{\pm\alpha}.$$

In order to get the modifying matrices $\bar{S}^{\pm}$ we have to do the matrix inversions. Thereby the whole number of matrix inversions becomes larger than the number given in the preceding section (see Table II). It should be noted however that the latter modification does not reduce the large arguments of the exponential functions and these are the most important source of the numerical difficulties. Therefore one may expect that in the cases where a large number of closed channels is included this modification will be less effective than the reduction of the length of the intervals α_i.

TABLE II

Number of needed matrix inversions in calculation of the probabilities P_{i-j}^{R} and P_{i-j}^{T} for the case $E = 3.9$, $m = 1$, $A = 4$, $\beta = 0.1$, $y_{eq} = 1$, $S = (-60, 60)$, $M = 599$

Secrest-Johnson method $K = 600$	Present modification of Secrest-Johnson method $K = 5$ $J = 0$	Eastes-Secrest method $K = 1$
1199[a]	14[a]	1[a]+4[b]

[a] these numbers are less than indicated in scheme I because in our calculation we need the matrices $\bar{R}^{-}$ and $\bar{T}^{-}$ only, [b] the number of modification (55)—(57).

6. *Summary*

The presented numerical method of solving collision problems is formulated in the frame of the "amplitude density function" formalism introduced by Secrest and Johnson. According to this formalism a collision problem with an interaction potential $V(x, y)$

given for an interval S of the x variable (the distance between the colliding objects) can be separated into many independently solvable problems with the potentials $V^{\alpha_i}(x, y)$ ($i = 1, 2, \ldots, M$) vanishing outside of the intervals α_i, which form a partition of S into M fragments. Although no restrictions are imposed on the partition of the interval S, Secrest and Johnson chose for numerical applications only the special case of intervals α_i containing one point. Thereby they avoided the necessity of solving any integral equation. Though in this case the solving of the partial problems with the potentials V^{α_i} requires inversions of matrices labeled by collision channels only, the number of these inversions is often very large. In the present modification of the Secrest-Johnson method other possible partitions of the interval S are exploited and, for solving the integral equations occurring then, the "homogeneous integral solution" method of Sams and Kouri is applied. The dimension of the matrices which should be inverted remains unchanged but the number of inversions can be considerably diminished. The numerical tests performed for the simple model of a collinear diatomic-atom collision support this statement. Here we should notice that in all reported tests the number of matrix inversions needed in the modified Secrest-Johnson method was larger than the number of inversions required by the method of Eastes and Secrest, in which the procedure of Sams and Kouri is used for solving the whole problem with potential $V(x, y)$. However, as we have pointed out in Section 5 the present method is numerically more stable and therefore it seems quite likely that it will be superior to the Eastes-Secrest method in cases where a large number of closed channels is needed. A more extensive numerical investigation of this problem is certainly desirable and it will be undertaken in the near future as a continuation of the present work.

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APPENDIX

The time independent Schrodinger equation for a collinear collision between a homonuclear diatomic molecule BC and a structureless particle A (see Fig. 1) has in the center-

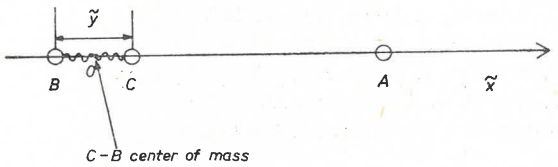

Fig. 1. Spatial arrangement of colliding objects

-of-mass coordinates the form

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \tilde{y}^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial \tilde{x}^2}+\tilde{V}_{B-C}(\tilde{y})+\tilde{V}_{BC-A}(\tilde{x},\tilde{y})\right]\Psi=\tilde{E}\Psi, \tag{A1}$$

where M is the reduced mass of the molecule BC, μ is the reduced mass of the molecule--particle system and $\tilde{E}$ is the total energy.

We assume the following models of the interaction potentials

$$\tilde{V}_{B-C} = \tfrac{1}{2} k(\tilde{y}-\tilde{y}_{eq})^2$$

($\tilde{y}_{eq}$ is the distance between the atoms B and C in equilibrium)

$$\tilde{V}_{BC-A} = \tilde{V}_{B-A}+\tilde{V}_{C-A},$$

where

$$\tilde{V}_{B-A} = \begin{cases} \tilde{A}e^{-\tilde{\beta}(\tilde{x}-\frac{1}{2}\tilde{y})} & \text{for } \tilde{x} \geqslant 0 \\ \tilde{A}e^{-\tilde{\beta}(-\tilde{x}+\frac{1}{2}\tilde{y})} & \text{for } \tilde{x} < 0, \end{cases}$$

$$\tilde{V}_{C-A} = \begin{cases} \tilde{A}e^{-\tilde{\beta}(\tilde{x}+\frac{1}{2}\tilde{y})} & \text{for } \tilde{x} \geqslant 0 \\ \tilde{A}e^{-\tilde{\beta}(-\tilde{x}-\frac{1}{2}\tilde{y})} & \text{for } \tilde{x} < 0. \end{cases}$$

Due to the transformation given by

$$\tilde{x} = \delta x, \quad \tilde{y} = \delta y+\tilde{y}_{eq}, \quad \tilde{y}_{eq} = \delta y_{eq},$$

$$\tilde{\beta} = 2\beta/\delta, \quad \tilde{A} = \varepsilon A e^{-\frac{1}{2}\tilde{\beta}\tilde{y}_{eq}}, \quad \tilde{E} = \varepsilon E, \quad \tilde{V}_{BC-A} = \varepsilon V_{BC-A},$$

where

$$\delta = \left(\frac{\hbar}{M^{1/2}k^{1/2}}\right)^{1/2}, \quad \varepsilon = \frac{\hbar k^{1/2}}{2M^{1/2}},$$

we may rewrite Eq. (A1) in the form

$$\left[-\frac{1}{m}\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + y^2 + Ae^{-2\beta|x|}(e^{\beta y}+e^{-2\beta y_{eq}}e^{-\beta y})\right]\Psi = E\Psi,$$

where $m = \mu/M$.

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