Application of the log-derivative method to variational calculations for inelastic and reactive scattering

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The log-derivative algorithm of Johnson is further generalized to evaluate transition amplitudes of orders up to third between states of free or bound character. These quantities appear in particular as constituents of a variety of low-order variational expressions for the reactance matrix which are based on the Lippmann–Schwinger type equations of scattering theory. The new algorithm is exploited to investigate relative accuracy of a number of these expressions on simple inelastic scattering test problems. Some findings of previous investigations, e.g., that of superior convergence of the expressions involving expansions of the amplitude density over the expressions based on expansions of the wave function, are revised. Superiority of the symmetric expressions over the asymmetric ones is demonstrated. The features of the new algorithm, such as relatively high efficiency and low storage requirements, make it well suited to variational calculations for reactive scattering. An exemplary implementation is presented to solving the Baer–Kouri–Levin–Tobocman (BKLT) equations for the collinear $H + H_2 \leftrightarrows H_2 + H$ reaction. Two new elements which improve the previous numerical treatment of these equations are exposed: the use of the Schwinger variational expression for the reactance matrix instead of the expression of the method of moments for the amplitude density and the use of distortion potentials producing inelastic transitions.

I. INTRODUCTION

A renewed interest in variational methods for determination of scattering matrices is observed recently in connection with the search for effective techniques of solving rigorously atom–diatom reactive collision problems formulated in the frame of the arrangement channel quantum mechanics.[1–4] A variety of such methods has been investigated computationally on simple potential scattering problems[5–7] with the motivation of providing some guidelines for their utilization in more advanced calculations. Actually, applications of basis set (variational) methods to reactive scattering calculations started much earlier, with the first successful numerical implementations of the Baer–Kouri–Levin–Tobocman (BKLT) equations to collinear reactions,[8–11] which were made with the method named in Ref. 5, the method of moments for the amplitude density. Though later efforts to promote the use of the BKLT equations concentrated rather on improving the structure of these equations itself, i.e., on making the arrangement channel permuting coupling scheme more flexible and symmetric,[12,13] the methodological investigations have been continued on analogous equations in the Fock coupling scheme (resulting from the Miller's formulation[14]). Systematic studies of various discrete and continuous basis set approaches[15,16] on one-dimensional (1D), i.e., collinear, reactive collision problems had led to an implementation of the Schwinger variational principle[17] and to a conclusion of feasibility of corresponding 3D calculations with the aid of this method.[16] Unfortunately, dealing with multichannel Green's functions in the proposed implementation appeared to be too cumbersome and the procedure was not further pursued. The first basis set calculations for 3D reactive scattering[18–20] were performed again with the method of moments. This method, similar to the above mentioned implementation of the Schwinger method, combines a distorted-wave description of scattering within particular arrangements with a basis set treatment of rearrangement process and also involves Green's functions for respective distorted-wave Hamiltonians. With the simple choices of the distortion potentials made in Refs. 8–11 and 18–20, only one-channel Green's functions had to be generated. However, incorporation of multichannel, i.e., producing inelastic transitions, distortion potentials was suggested[19] as one of desirable improvements to be made in further development of the method.[21] Thus, the problem of efficient evaluation of matrix elements involving multichannel Green's functions returned. It became even more important when utilization of higher-order variational functionals was started. Much effort has been devoted to efficient treatment of multichannel Green's functions in the work by Kouri, Schwenke, Truhlar, and collaborators[22–24] on utilization of the Newton variational principle.[25]

Difficulties with the Green's functions, encountered in the earlier implementation of the Schwinger principle,[16] have given rise to the most recent tendency to completely eliminate these functions from the variational calculations for reactive scattering. This tendency has naturally led to an increase of interest in the Kohn principle.[26] Novel ways of using this principle have been found and demonstrated to be appropriate for treating large scale problems.[27–32]

The successful applications of the new Kohn-type procedures to reactive scattering calculations, reported recently,[28–31] should not, however, discourage us from seeking more efficient ways of implementing to these calculations the variational methods based on the Lippmann–Schwinger (L–S) equations. Inspiration for continuing efforts in this direction comes from the studies of McKoy and co-workers

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on the relationship between the Kohn and the Schwinger variational principles,[33–35] which have shown that the latter principle is capable of giving higher-order accuracy results. Moreover, the expressions for the scattering matrices resulting from the Schwinger principle, though considerably more complicated than the Kohn-type expressions, are definitely simpler than those resulting from the Newton principle. Thus, it is our opinion that despite the enormous progress which has been already made in establishing the generalized Newton method[22–24] utilization of the Schwinger principle in atom–diatom reactive scattering calculations is at least worth reconsidering; more so as the arguments raised against the Schwinger method in some of the computational studies mentioned above (Ref. 5) seem not to be fully justified (cf. Ref. 6 and Secs. IV and VI B of this paper).

The main purpose of the present paper is to call attention to some simplifications which are possible in evaluation of the various matrix elements involved in the Schwinger or Schwinger-like expressions for the reactance matrix when an invariant imbedding approach[36,37] is followed. The particular aproach proposed is the L-matrix propagation method which has been introduced and exploited in a series of previous papers devoted to improving[38] and extending the Johnson's log-derivative method[39] to reactive[40–42] and half-collision problems.[43–45]

II. CONTENTS OF THE PAPER

In Sec. III, a brief analysis is presented of the variational expressions for the reactance matrix based on L–S-type integral equations, including the generalized L–S equations with nonsymmetric matrix potentials.[1–4] A number of relations existing between these expressions is written explicitly, symmetry properties of the expressions are exposed, and an attempt is made to assess theoretically relative performance of the methods exploiting these expressions. Of practical importance seems to be what is implied concerning the relation of the method of moments to the Schwinger method. Namely, it is recognized that both (!) methods use variationally stable expressions and both expressions are of the same order (this means roughly, of comparable complexity). Of the two, however, only the Schwinger expression gives results of correct symmetry irrespective of the size of basis set employed. On this ground, one may expect that the Schwinger method should offer a definite improvement over the method of moments, especially in solving multichannel problems. However, the conclusions reached from the computational studies of Ref. 5 do not seem to support such an expectation. Thus, a need for further tests of the methods, clarifying the relations between them, arises. Performing such tests on simple model problems was the second goal of the present work. A discussion on the results is given in Sec. VI B. The prediction of superiority of symmetric variational expressions over asymmetric expressions (of the same order) is fully confirmed and the conclusion of Ref. 5 on superiority of the methods based on expanding the amplitude density over the methods involving expansions of the wave function is found not to be generally valid.

Sections IV and V are devoted to the main theme of the paper—a presentation of a new generalized log-derivative algorithm and a description of how it can be implemented to variational calculations. In Sec. IV, transition amplitudes—the constituents of the variational expressions—are introduced, categorized, and converted to respective integrals over one, i.e., over an appropriate scattering coordinate. In Sec. V A, **J** integrals—the counterparts of the transition amplitudes within the L-matrix formalism—are defined and their relations to the "true" amplitudes of orders up to third and for transitions of three types—free–free, bound–bound, and bound–free—are determined. In Sec. V B, a sketchy derivation of invariant imbedding relations for accumulation of the **J** integrals over subsequent sectors of the integration range is presented and a hybrid approximate-solution approximate-potential algorithm for these integrals is constructed.

The following are the attractive features of the algorithm:

(i) All the **J** integrals, also those related to the second- and third-order transition amplitude, i.e., involving Green's functions, are evaluated in one-way propagation along the integration coordinate, simultaneously with the related log-derivative matrix. A few working quantities, related to current propagation step only, have to be kept in storage. This is in contrast to the standard, i.e., noninvariant imbedding approaches which require determination of the Green's functions,[15,19] or of the "half-integrated Green's functions"[23,24] for the entire range prior to evaluation of the integrals.

(ii) The algorithm is stable with respect to inclusion of closed channels into propagation; so, it applies equally well to one- and to multichannel problems.

(iii) The growth of errors with increasing energy in calculations is linear or close to linear for all quantities generated. For comparison, cubic growth of errors with energy is characteristic for the standard Numerov[46] and for the purely approximate-solution log-derivative algorithms.[45]

A numerical illustration to the point (iii) is provided in Sec. VI A. All features of the algorithm are exploited in the numerical investigations of the variational methods, reported in Sec. VI B. Part of the algorithm, including formulas for evaluation of the first-order bound–free and second-order bound–bound transition amplitudes, has been already presented and tested on half-collision problems in Refs. 43–45. In Sec. VI C, this algorithm is implemented to solving the BKLT equations for the collinear $H + H_2 \rightleftarrows H_2 + H$ reaction. There are two new elements in the implementation: (i) the use of the Schwinger variational expression for the reactance matrix and (ii) the use of inelastic distortion potentials. Both are demonstrated to lead to an improvement of the previous numerical treatment of the BKLT equations.

III. VARIATIONAL EXPRESSIONS FOR THE REACTANCE MATRIX BASED ON THE LIPPMANN–SCHWINGER EQUATIONS

Let us consider a three-atom collision system described by Hamiltonian $\mathscr{H}$ and, to begin with, take into account the range of total energy E, where only one two-cluster, i.e., atom–diatom arrangement channel is accessible. The system with the two clusters infinitely separated is described by the asymptotic form of $\mathscr{H}$, H_0. The following basic partition of

$\mathscr{H}$ is assumed at any collision stage:

$$\mathscr{H} = H_0 + \mathscr{V}. \tag{1}$$

It is convenient to divide the corresponding potential $\mathscr{V}$ into two parts, distortion and coupling potentials (each vanishing asympototically),

$$\mathscr{V} = V_0 + V \tag{2}$$

and introduce yet another partition

$$\mathscr{H} = H + V \quad \text{with } H = H_0 + V_0. \tag{3}$$

Let $|\Psi\rangle$ denote an N_0-dimensional row vector of standing-wave type scattering states of $\mathscr{H}$, i.e., the solution of the following L–S equation:

$$(I - GV)|\Psi\rangle = |\psi\rangle, \tag{4}$$

where G is the respective Green's operator related to the distorted Hamiltonian H;

$$G = \mathscr{P}[1/(E-H)] \tag{5}$$

and $|\psi\rangle$ is the vector of the distorted-wave states

$$|\psi\rangle = (I + GV_0)|\psi_0\rangle \tag{6}$$

corresponding to the N_0 free-wave states of H_0 grouped in the vector $|\psi_0\rangle$. N_0 is the number of rovibrational channels open at given E. The reactance matrix $\mathscr{R}$ describing the asymptotic form of $|\Psi\rangle$,

$$\mathscr{R} = \langle\psi_0|\mathscr{V}\Psi\rangle, \tag{7}$$

can be written in the two-potential form

$$\mathscr{R} = {}^0\mathscr{R} + {}^1\mathscr{R}$$

with ${}^0\mathscr{R} = \langle\psi_0|V_0\psi\rangle$ and ${}^1\mathscr{R} = \langle V^\dagger\psi|\Psi\rangle = \langle\psi|\zeta\rangle$. (8)

In the second formula for the matrix ${}^1\mathscr{R}$, the vector of amplitude density states is introduced

$$|\zeta\rangle = V|\Psi\rangle. \tag{9}$$

The symbol of Hermitian conjugation is written above to make the relations formally applicable also to reactive collisions treated within the arrangement channel quantum mechanics [i.e., in terms of (not necessarily Hermitian) matrix operators acting on vector wave functions built by a decomposition of ordinary wave functions into pieces associated with different arrangement channels[1–4]]. Allowing for more than one atom–diatom clustering in the collision process, one has to include into consideration a number of appropriate free-wave and distorted-wave Hamiltonians, distortion and coupling potentials. To distinguish between them, the superscript "c"($=\alpha,\beta,\gamma$) will be added to respective symbols H_0, H, V_0, and V. Equation (4), considered as the generalized L–S equation of the arrangement channel approach, is a matrix equation with respect to the arrangement channel index, i.e.,

$$G = \{G^{cc'}\}, \quad V = \{V^{cc'}\}, \quad |\Psi\rangle = \{|\Psi^{c\bar{c}}\rangle\},$$
$$|\psi\rangle = \{|\psi^{c\bar{c}}\rangle\}, \quad \text{and } |\psi_0\rangle = \{|\psi_0^{c\bar{c}}\rangle\}.$$

where $G^{cc'} = G^c\delta_{c,c'}$ with $G^c = \mathscr{P}[1/(E-H^c)]$,

$$|\psi^{c\bar{c}}\rangle = \delta_{c,\bar{c}}|\psi^{\bar{c}}\rangle, \quad |\psi_0^{c\bar{c}}\rangle = \delta_{c,\bar{c}}|\psi_0^{\bar{c}}\rangle,$$

and $\bar{c}$ is the index of the initial arrangement. The elements $V^{cc'}$ are constructed, essentially from the channel coupling potentials V^c, accordingly to the assumed scheme of the decomposition of the ordinary total wave function. Most of the schemes[1–4,12,13] lead to non-Hermitian matrix operators V, i.e.,

$$(V^\dagger)^{cc'} = (V^{c'c})^\dagger = V^{c'c} \neq V^{cc'}. \tag{10}$$

Because of these non-Hermitian operators, it is necessary to introduce, in addition to Eq. (4), the equation in which the potential V is replaced with $V^\dagger$. The solution of this equation and all quantities related to it will be denoted by adding the left subscript " + " to letters denoting the quantities introduced for Eq. (4). Obviously, the respective reactance matrices $\mathscr{R}$ and ${}_+\mathscr{R}$ are simply transpositions of one another

$$\mathscr{R} = ({}_+\mathscr{R})^T. \tag{11}$$

This relation expresses automatically symmetry of the matrix $\mathscr{R}$ for (nonreactive) problems described by the ordinary L–S equations (when the subscript " + " can be omitted). The proof of symmetry of the matrices $\mathscr{R}$ or ${}_+\mathscr{R}$ (more precisely, ${}^1\mathscr{R}$ or ${}^1_+\mathscr{R}$) in the generalized case requires considering additionally some rules of construction of the matrix potentials and consists essentially in showing that the generalized L–S equation is equivalent to the ordinary Schrödinger equation.[1–4]

The quantity to be determined variationally is the matrix ${}^1\mathscr{R}$. In the following discussion on this matter, the standpoint of R. R. Lucchese *et al.*[33] is adopted which allows for a unified presentation of a variety of iteration–variation expressions used for determination of matrix elements

$$M(R,S,K) := \langle R|F\rangle \tag{12}$$

involving solutions of the L–S-type integral equations

$$(I-K)|F\rangle = |S\rangle, \quad K = GV. \tag{13}$$

The general iteration–variation approximation to such matrix elements, given in Ref. 33, reads

$$M^n_{i,j}(R,S,K = GV;\bar{B},B) = \sum_{l=0}^{n-1}\langle R|K^lS\rangle + \langle R|(G,V)_{j-1}B\rangle \times [D^n_{i,j}(K;\bar{B},B)]^{-1}\langle\bar{B}|[G,V]_iS\rangle, \tag{14}$$

where

$$D^n_{i,j}(K;\bar{B},B) := \langle\bar{B}|[G,V]_i(I-K)(G,V)_{j-2n-1}B\rangle \tag{14a}$$

$$= \langle\bar{B}|[(G,V^\dagger)_{i-2n-1}]^\dagger \times V(GV)^n(I-GV)(G,V)_{j-2n-1}B\rangle. \tag{14b}$$

The first term results from applying the n-term Born series approximation to $|F\rangle$ and the second term is a variational approximation to the residual integral

$$M(R,S,K) - \sum_{l=0}^{n-1}\langle R|K^lS\rangle = M[(K^n)^\dagger R,S,K] = \langle R|K^nF\rangle = \langle\bar{F}_n|S\rangle, \tag{15}$$

where $\langle\bar{F}_n|$ is defined as satisfying the equation

$$\langle\bar{F}_n|(I-K) = \langle R|K^n. \tag{16}$$

More precisely, the second term gives the stationary value of

the following bilinear functional:

$$\mathscr{M}^n[\overline{F}^t_n,F^t]:=\langle R\,|K^nF^t\rangle+\langle\overline{F}^t_n|S\rangle-\langle\overline{F}^t_n|(I-K)F^t\rangle$$

$$\{\mathscr{M}^n[\overline{F}_n,F]=M[(K^n)^\dagger R,S,K],\quad \text{for } n=0,1,...\} \tag{17}$$

within the class of trial states represented by the following expansions:

$$|F^t\rangle=(G,V)_{j-2n-1}|B\rangle a;\quad |\overline{F}^t_n\rangle=(V^\dagger,G)_i|\overline{B}\rangle\bar{a}, \tag{18}$$

where $|B\rangle$ and $|\overline{B}\rangle$ denote row vectors of given (usually bound-type) states; a and $\bar{a}$ are the corresponding vectors of expansion coefficients; the symbol $(,)_i$ denotes the following operations:

$$(A,B)_i=\begin{cases}(AB)^k, & \text{if } i=2k\\ (AB)^kA, & \text{if } i=2k+1;\end{cases} \tag{19}$$

and

$$[A,B]_i=[(B^\dagger,A^\dagger)_i]^\dagger. \tag{19a}$$

Expression (14) applied in particular to the two (matrices of) matrix elements for ${}^1\mathscr{R}$ [cf. Eq. (8)] gives the following two expressions for the reactance matrix $\mathscr{R}$:

$$\widetilde{\mathscr{R}}^n_{i,j}(\overline{B},B)={}^0\mathscr{R}+M^n_{i,j}(V^\dagger\psi,\psi,GV;\overline{B},B); \tag{20}$$

$$\widehat{\mathscr{R}}^n_{i,j}(\overline{B},B)={}^0\mathscr{R}+M^n_{i,j}(\psi,V\psi,VG;\overline{B},B). \tag{21}$$

$|B\rangle$ and $|\overline{B}\rangle$ have in the generalized case the matrix structure

$$|B\rangle=\{|B^{cc'}\rangle\},\quad |B^{cc'}\rangle=\underset{1\times M^c}{|B^c\rangle}\,\delta_{c,c'}. \tag{22}$$

There exists, of course, a relation between the two (sets of) approximations to the reactance matrix $\widetilde{\mathscr{R}}^n_{i,j}$ and $\widehat{\mathscr{R}}^n_{i,j}$ which are based on the L–S equation for the wave function ($F=\Psi$) and for the amplitude density ($F=\zeta$), respectively. This relation can be established by exploiting the following property of the operation (19):

$$(A,B)_i=(A,B)_{2k+1}(B,A)_{i-2k-1}=(A,B)_{2k}(A,B)_{i-2k},\quad \text{for } 2k+1,2k\leqslant i \tag{23}$$

and reads

$$\widetilde{\mathscr{R}}^n_{i,j}(\overline{B},B)=[{}_+\widehat{\mathscr{R}}^n_{j-1,i+1}(B,\overline{B})]^T. \tag{24}$$

One can also show that the matrices $\widetilde{\mathscr{R}}^n_{i,j}$ satisfy the following symmetry relation if $j=i$:

$$\widetilde{\mathscr{R}}^n_{i,i}(\overline{B},B)=[{}_+\widetilde{\mathscr{R}}^n_{i,i}(B,\overline{B})]^T. \tag{25}$$

and that the following "index raising" relations hold:

$$\widetilde{\mathscr{R}}^n_{2k,j}(V^\dagger\overline{B},B)=\widetilde{\mathscr{R}}^n_{2k+1,j}(\overline{B},B); \tag{26}$$

$$\widetilde{\mathscr{R}}^n_{i,2l}(\overline{B},VB)=\widetilde{\mathscr{R}}^n_{i,2l+1}(\overline{B},B); \tag{27}$$

$$\widehat{\mathscr{R}}^n_{2k,2k+1}(\overline{B},VB)=\widetilde{\mathscr{R}}^n_{2k+1,2k+1}(\overline{B},B). \tag{28}$$

An intermediate result in the proof of Eq. (24) is formula (14b) for the matrix $D^n_{i,j}$.

Noting that Eq. (16) with $K=GV$ and $\langle R\,|=\langle V^\dagger\psi|$ gives basically the amplitude density state $\langle\overline{F}_0|=\langle{}_+\zeta\,|$, one can readily find out that in the derivation of the expression $\widetilde{\mathscr{R}}^n_{i,j}(\overline{B},B)$ the following states:

$$|f(j,n)\rangle:=[(G,V)_{j-2n-1}]^{-1}|F\rangle=[(V,G)_j]^{-1}(VG)^nV|\Psi\rangle, \tag{29}$$

and

$$\langle\bar{f}(i,n)|:=\langle\overline{F}_n|([G,V]_i)^{-1}=\langle{}_+\zeta\,|(GV)^n([G,V]_i)^{-1} \tag{29a}$$

have been actually expanded in the bases $|B\rangle$ and $\langle\overline{B}|$, respectively. The states expanded in the derivation of $\widehat{\mathscr{R}}^n_{i,j}$ are obtained after exchanging in the above formulas the operators $V\rightleftarrows G$ and replacing the states $|\Psi\rangle\to|\zeta\rangle$, $\langle{}_+\zeta\,|\to\langle{}_+\Psi|$.

The significance of the relations presented above lies in that they can serve (i) to make some predictions concerning practical usefulness of the methods convertible to the expressions of $\widetilde{\mathscr{R}}^n_{i,j}$ or $\widehat{\mathscr{R}}^n_{i,j}$ type, or (ii) to confirm or verify some findings concerning relative performance of the expressions already tested. To the latter belong the expressions $\widetilde{\mathscr{R}}^n_{2n+1,2n+1}(B,B)$ of the lowest orders $n=0,1$ which correspond to the Schwinger[33] and to the Newton[33,34] variational methods, respectively, and the expression $\widetilde{\mathscr{R}}^n_{2n,2n}(B,B)$ with $n=1$ which was proposed (in T-operator versions) in Refs. 34 and 47 and recommended recently (under the term reactance operator variational principle) in Ref. 5. One should note also that the expression of the S-matrix version of the Kohn variational principle, as proposed in Refs. 27 and 28 (not in Refs. 29 and 30), has the structure of the expression $\widetilde{\mathscr{R}}^1_{1,1}$, proposed for the first time in Ref. 34. A more extensive list of assignments of the $\widetilde{\mathscr{R}}^n_{i,j}$—or $\widehat{\mathscr{R}}^n_{i,j}$—expressions to the methods investigated recently[5–7] is given in Table I. It is perhaps worth noting that all the methods of moments, for the wave function (ΨM), for the amplitude density (ζM), for the scattered wave function ($\bar{C}M$), and for the scattered amplitude density ($\bar{\zeta}M$), presented in Ref. 5 as nonvariational, appear in Table I as equivalent to the expressions $\widetilde{\mathscr{R}}^0_{0,1}$, $\widehat{\mathscr{R}}^0_{0,1}$, $\widetilde{\mathscr{R}}^1_{2,1}$, and $\widehat{\mathscr{R}}^1_{2,1}$, respectively. So, these methods are in fact both variationally correct (first-order errors of both trial states, i.e., of trial amplitude density and of trial wave function in the cases of $\widetilde{\mathscr{R}}^0_{0,1}$ and $\widehat{\mathscr{R}}^0_{0,1}$, do not produce first-order contributions to the error of the reactance matrix) and stationary. In this context, the existence of the simple connection between the ΨM method and the Schwinger method, noted in Ref. 5, becomes much less surprising; it is an example of validity of the general relation (26). The equivalence of the methods ΨM and ζM in application to problems with $V=V^\dagger$, experienced also in Ref. 5, follows from Eq. (24).

Postponing further discussion on relations between the methods listed in Table I to Sec. VI B, we would like to close the present section with some remarks on three lines of proceeding which seem acceptable and useful when a comparison of convergence properties of the various $\widetilde{\mathscr{R}}^n_{i,j}(\overline{B},B)$ and $\widehat{\mathscr{R}}^n_{i,j}(\overline{B},B)$ expressions with respect to the length of the bases B and $\overline{B}$ is attempted. First, one may compare expressions of different orders involving, however, expansions of the same states $|f\rangle$ and $\langle\bar{f}|$ in given bases $|B\rangle$ and $\langle\overline{B}|$. This is the most obvious test, but the result is obvious too. The expressions of higher orders should reveal faster convergence with the bases length (except perhaps for cases of completely inappropriate choices of these bases). Still open remains the related practical question to indicate the most effective expression, i.e., to compromise between accuracy and computational effort, both increasing with the order index n.

TABLE I. A list of basis set methods which use the expressions of $\tilde{\mathscr{R}}^n_{i,j}(B,B)$ or $\hat{\mathscr{R}}^n_{i,j}(B,B)$ type.

Method	Notation of Ref. 5	Variational expression	States expanded[a] $\langle\bar{f}\| = a^T\langle B\|, \|f\rangle = \|B\rangle a$	
Of moments for wave function	ΨM	$\tilde{\mathscr{R}}^0_{0,1}(B,B)$	$\langle\zeta\|$	$\|\Psi\rangle$
Of moments for amplitude density	ζM	$\hat{\mathscr{R}}^0_{0,1}(B,B)$	$\langle\Psi\|$	$\|\zeta\rangle$
Refined Born approximation for amplitude density	ζIV	$\hat{\mathscr{R}}^0_{0,1}(\bar{B},B)$ $\langle\bar{B}\| = \langle V(I-VG)B\|$	$\langle\Psi\|$	$\|\zeta\rangle$
Refined Born approximation for wave function	ΨIV	$\tilde{\mathscr{R}}^0_{1,1}(\bar{B},B)$ $\langle\bar{B}\| = \langle(I-GV)B\|$	$\langle\Psi\|$	$\|\Psi\rangle$
Schwinger	ΨS	$\tilde{\mathscr{R}}^0_{1,1}(B,B)$	$\langle\Psi\|$	$\|\Psi\rangle$
Newton for amplitude density	ζS	$\tilde{\mathscr{R}}^1_{2,2}(B,B)$	$\langle\zeta\|$	$\|\zeta\rangle$
Newton for wave function	$\cdots$	$\tilde{\mathscr{R}}^1_{3,3}(B,B)$	$\langle\Psi\|$	$\|\Psi\rangle$
Takatsuka–McKoy	$\tilde{C}S$	$\tilde{\mathscr{R}}^2_{3,3}(B,B)$	$\langle GV\Psi\|$	$\|GV\Psi\rangle$
Takatsuka–McKoy for amplitude density	$\tilde{\zeta}S$	$\tilde{\mathscr{R}}^3_{4,4}(B,B)$	$\langle VG\zeta\|$	$\|VG\zeta\rangle$
Of moments for scattered wave function	$\tilde{C}M$	$\tilde{\mathscr{R}}^1_{2,1}(B,B)$	$\langle\zeta\|$	$\|GV\Psi\rangle$
Of moments for scattered amplitude density	$\tilde{\zeta}M$	$\hat{\mathscr{R}}^1_{2,1}(B,B)$	$\langle\Psi\|$	$\|VG\zeta\rangle$

[a] cf. Eqs. (29) and (29a). It is assumed here that $V = V^\dagger$.

The second possibility is to compare expressions of the same order involving expansions of the same states, but in different bases $|B\rangle$ and/or $\langle\bar{B}|$. Such a comparison, however, gives merely information on adequacy of the bases employed to describe given states $|f\rangle$ and $\langle\bar{f}|$. Finally, one may try to compare expressions of given order based on expansions of different states $|f\rangle$ and/or $\langle\bar{f}|$. However, one should be aware that conclusions drawn from such a comparison are likely to be highly basis dependent. Therefore it seems reasonable at least to optimize nonlinear basis parameters (if present) before comparing convergence of the expressions $\tilde{\mathscr{R}}^n_{i,j}$ (or $\hat{\mathscr{R}}^n_{i,j}$) which differ only in the indices i and/or j. Without any tests, however, one may predict that the expressions $\tilde{\mathscr{R}}^n_{i,j}(\bar{B},B)$ with $i=j$ and $\bar{B}=B$ should be superior to others since they give results of proper symmetry [i.e., satisfying the relation (11)] irrespective of the basis length [cf. Eq. (25)].

IV. TRANSITION AMPLITUDES

Directing further consideration towards evaluation of (some of) the variational expressions of the previous section and towards practical demonstration of the relations existing between them, let us introduce the following nth order transition amplitudes between states $|S\rangle$ and $|\bar{S}\rangle$ having free or bound character (i.e., $|S\rangle, |\bar{S}\rangle = |\psi\rangle, |B\rangle$):

$$T^n_{\bar{S},S} := \langle\bar{S}|V(GV)^{n-1}S\rangle, \quad \hat{T}^n_{\bar{S},S} := \langle\bar{S}|(VG)^{n-1}S\rangle, \quad \text{for } n = 1,2,\ldots, \tag{30}$$

and $\bar{T}^n_{\bar{S},S} := \langle\bar{S}|(GV)^{n-2}GS\rangle$, for $n = 2,3,\ldots$.

In terms of these amplitudes, all the $\tilde{\mathscr{R}}^n_{i,j}$—and $\hat{\mathscr{R}}^n_{i,j}$—expressions can be rewritten. Of particular interest are the cases (cf. Table I)

$$\tilde{\mathscr{R}}^n_{2n+1,2n+1}(\bar{B},B) = {}^0\mathscr{R} + \sum_{l=1}^{n} T^l_{\psi,\psi} + T^{n+1}_{\psi,B}\left[T^{n+1}_{\bar{B},B} - T^{n+2}_{\bar{B},B}\right]^{-1} \times ({}_+T^{n\pm1}_{\psi,\bar{B}})^T, \quad \text{for } n = 0,1, \tag{31}$$

$$\tilde{\mathscr{R}}^n_{2n,2n}(\bar{B},B) = {}^0\mathscr{R} + \sum_{l=1}^{n} T^l_{\psi,\psi} + \hat{T}^{n+1}_{\psi,B}\left[\bar{T}^{n+1}_{\bar{B},B} - \bar{T}^{n+2}_{\bar{B},B}\right]^{-1} \times ({}_+\hat{T}^{n\pm1}_{\psi,\bar{B}})^T, \quad \text{for } n = 1, \tag{32}$$

$$\hat{\mathscr{R}}^n_{2n,2n+1}(\bar{B},B) = {}^0\mathscr{R} + \sum_{l=1}^{n} T^l_{\psi,\psi} + \hat{T}^{n+1}_{\psi,B}\left[\hat{T}^{n+1}_{\bar{B},B} - \hat{T}^{n+2}_{\bar{B},B}\right]^{-1} \times ({}_+T^{n\pm1}_{\psi,\bar{B}})^T, \quad \text{for } n = 0,1, \tag{33}$$

$$\tilde{\mathscr{R}}^{2n}_{2n+1,2n+1}(\bar{B},B) = {}^0\mathscr{R} + \sum_{l=1}^{2n} T^l_{\psi,\psi} + T^{n+1}_{\psi,B}\left[T^1_{\bar{B},B} - T^2_{\bar{B},B}\right]^{-1} \times ({}_+T^{n\pm1}_{\psi,\bar{B}})^T, \quad \text{for } n = 1, \tag{34}$$

$$\widetilde{\mathscr{R}}^{2n+1}_{2n+2,2n+2}(\bar{B},B) = {}^{0}\mathscr{R} + \sum_{l=1}^{2n+1} T^{l}_{\psi,\psi} + \hat{T}^{n+2}_{\psi,B}[\bar{T}^{2}_{B,B} - \bar{T}^{3}_{B,B}]^{-1} \times ({}_{+}\hat{T}^{n+2}_{\psi,\bar{B}})^{T}, \quad \text{for } n = 1. \tag{35}$$

Consistent with the previous notation, the symbols with the left subscript " + " appearing above denote respective amplitudes for transitions caused by the potential $V^{\dagger}$.

The following are the basic steps necessary for evaluation of the transition amplitudes: (i) introduction of coordinate representation of states and operators involved in the transitions; (ii) partial integration of the amplitudes over internal coordinates via expanding respective integrands in appropriate basis functions in these coordinates; and (iii) integration over remaining, i.e., scattering coordinates.

To describe given atom–diatom arrangement channel c, two vectors $\mathbf{x}_c$ and ξ_c are introduced which join the atoms in the molecule and the center of mass of the molecule with the unbounded atom, respectively, and are scaled by appropriate mass-dependent factors to give the kinetic energy operator for both the bounded and unbounded motions with common and channel independent reduced mass μ. The sets of $\mathbf{x}_c$ —and ξ_c—vectors corresponding to different channels are connected by orthogonal transformations—the kinematic rotations.[48] In these coordinates, the Hamiltonian H^{c}_{0} reads

$$H^{c}_{0}(\mathbf{x}_c,\xi_c) = -\hbar^2/(2\mu)(\Delta_{\mathbf{x}_c} + \Delta_{\xi_c}) + V^{c}_{\text{vib}}. \tag{36}$$

In order to separate out the motion in the channel scattering coordinate x_c, $x_c := |\mathbf{x}_c|$, spherical components of $\mathbf{x}_c$ are exploited giving the Laplacian $\Delta_{\mathbf{x}_c}$ in the form

$$\Delta_{\mathbf{x}_c} = x_c^{-d}\frac{\partial}{\partial x_c}x_c^{d}\frac{\partial}{\partial x_c} + x_c^{-2}\Delta_0(\Omega_d), \tag{37}$$

where the index d is connected with the spatial dimensionality of the problem D, $d = D - 1$, and $\Delta_0(\Omega_d)$ is the Laplacian on the unit sphere depending on d angular coordinates denoted by Ω_d. Thus, H^{c}_{0} can be partitioned in the required way

$$H^{c}_{0}(x_c,y_c) = -\hbar^2/(2\mu)x_c^{-d}\frac{\partial}{\partial x_c}x_c^{d}\frac{\partial}{\partial x_c} + H^{c}_{\text{rovib}}(x_c,y_c), \tag{38}$$

where $y_c := (\hat{\mathbf{x}}_c,\xi)$ denotes the internal coordinates describing the bounded ro- (if $d \neq 0$) vibrational motion.

As mentioned above, evaluation of the scalar product $\langle|\rangle$ is carried out in two successive integrations. To denote them, the following symbols will be used:

$$[X|Y]_c := J^{c}\int dy_c\, X^{T}Y; \tag{39}$$

$$(X|Y)_c := \int dx_c\, X^{T}Y, \tag{39a}$$

where $J^{c} = x_c^{d}$ and $J^{c}\,dx_c\,dy_c$ equals, of course, the volume element $dv = d\mathbf{x}_c\,d\xi_c$.

Let $\varphi^{c}(x_c,y_c)$ denote an N^{c}-dimensional row vector of functions which are assumed to form an orthonormal set with respect to the scalar product $[|]_c$, i.e.,

$$[\varphi^{c}|\varphi^{c}]_c = \mathbf{I}^{c}, \quad \varphi^{c}(x_c,y_c) := [J^{c}(x_c)]^{-1/2}\tilde{\varphi}^{c}(y_c). \tag{40}$$

A suitable choice of $\tilde{\varphi}^{c}(y_c)$ is the set on N^{c} eigenfunctions of the Hamiltonian H^{c}_{rovib}:

$$H^{c}_{\text{rovib}}\tilde{\varphi}^{c} = \tilde{\varphi}^{c}[\epsilon^{c} + \hbar^2/(2\mu x_c^2)\mathbf{l}^{c}], \tag{41}$$

ϵ^{c} is the corresponding diagonal matrix of rovibrational energies of the diatom and $\mathbf{l}^{c}$ is the diagonal matrix of eigenvalues of the respective angular momentum operator for atom–diatom relative rotation. $\mathbf{I}^{c}$ denotes hereafter the $N^{c}\times N^{c}$ unit matrix.

In the basis φ^{c}, the Green's function $G^{c}(x_c,y_c;\bar{x}_c,\bar{y}_c)$ and the vectors of functions $\psi^{c}_{1\times N^{c}_{0}}(x_c,y_c)$, $\psi^{c}_{0_{1\times N^{c}_{0}}}(x_c,y_c)$, $B^{c}_{1\times M^{c}}(x_c,y_c)$, and $\bar{B}^{c}_{1\times M^{c}}(x_c,y_c)$ are represented by the matrices $\mathbf{G}^{c}_{N^{c}\times N^{c}}(x_c;\bar{x}_c)$, $\boldsymbol{\psi}^{c}_{N^{c}\times N^{c}_{0}}(x_c)$, $\mathbf{m}^{c}_{N^{c}\times N^{c}_{0}}(x_c)$, $\bar{\mathbf{B}}^{c}_{N^{c}\times M^{c}}(x_c)$, and $\bar{\mathbf{B}}^{c}_{N^{c}\times M^{c}}(x_c)$, respectively, i.e.,

$$\mathbf{G}^{c}(x_c;\bar{x}_c) = \left[\varphi^{c}(x_c,y_c)\Big|\int d\bar{y}_c\, G^{c}(x_c,y_c;\bar{x}_c,\bar{y}_c)\varphi^{c}(\bar{x}_c,\bar{y}_c)\right]_c,$$

$$\boldsymbol{\psi}^{c} := [\varphi^{c}|\psi^{c}]_c, \quad \mathbf{m}^{c} := [\varphi^{c}|\psi^{c}_{0}]_c, \quad \mathbf{B}^{c} := [\varphi^{c}|B^{c}]_c, \quad \bar{\mathbf{B}}^{c} := [\varphi^{c}|\bar{B}^{c}]_c. \tag{42}$$

The matrices representing the operators V and $V^{\dagger}$ are

$$\mathbf{V}^{c} := [\varphi^{c}|V^{cc}\varphi^{c}]_c, \quad \mathbf{V}^{cc'} := [\varphi^{c}|V^{cc'}B^{c'}]_c, \quad {}_{+}\mathbf{V}^{cc'} := [\varphi^{c}|(V^{\dagger})^{cc'}B^{c'}]_c. \tag{43}$$

The matrix $\boldsymbol{\psi}^{c}(x_c)$ satisfies the equation

$$\mathbf{D}^{c}(x_c)\boldsymbol{\psi}^{c}(x_c) = 0\ \mathbf{I}^{c}, \tag{44}$$

where

$$\mathbf{D}^{c}(x_c) := 2\mu/\hbar^2[\varphi^{c}|(E - H^{c})\varphi^{c}]_c = \mathbf{D}^{c}_{0}(x_c) - \mathbf{V}^{c}_{0}(x_c), \tag{44a}$$

$$\mathbf{D}^{c}_{0}(x_c) := \mathbf{I}^{c}d^2/dx_c^2 - \mathbf{l}^{c}/x_c^2 + (\mathbf{k}^{c})^2, \tag{44b}$$

$$(\mathbf{k}^{c})^2 := 2\mu/\hbar^2(E\mathbf{I}^{c} - \epsilon^{c}), \tag{44c}$$

and the following boundary conditions:

$$\boldsymbol{\psi}^{c}(x_c = 0) = 0\ \mathbf{I}^{c}, \quad \boldsymbol{\psi}^{c}(x_c) \underset{x_c\to\infty}{\sim} \mathbf{m}^{c}(x_c) + \mathbf{n}^{c}(x_c)\,{}^{0}\mathscr{R}^{c}, \tag{45}$$

where $\mathbf{m}^{c}$ and $\mathbf{n}^{c}$ denote, respectively, regular and irregular solutions of Eq. (44) with the operator $\mathbf{D}^{c}_{0}$ standing in place of $\mathbf{D}^{c}$. The solutions are normalized to give Wronskian $W[\mathbf{m}^{c},\mathbf{n}^{c}]$ equal to $-\mathbf{I}^{c}$. The respective boundary value problem for the matrix Green's function reads

$$\mathbf{D}^{c}(x_c)\mathbf{G}^{c}(x_c;\bar{x}_c) = 2\mu/\hbar^2\mathbf{I}^{c}\delta(x_c - \bar{x}_c), \tag{46}$$

$$\mathbf{G}^{c}(x_c = 0;\bar{x}_c) = 0\ \mathbf{I}^{c}, \quad \mathbf{G}^{c}(x_c;\bar{x}_c) \underset{x_c\to\infty}{\sim} \mathbf{n}^{c}(x_c)\mathbf{g}^{c}(\bar{x}_c). \tag{47}$$

After integration over the internal coordinates, the formulas for the amplitudes of inelastic (i.e., purely nonreactive $V^{cc'} = \delta_{c,c'}V^{cc}$) transitions read like the following formula for $(T^{n}_{\bar{S},S})^{cc}$:

$$(T^{n}_{\bar{S},S})^{cc} = [\bar{\mathbf{S}}^{c}|\mathbf{V}^{c}(\mathbf{G}^{c}\mathbf{V}^{c})^{n-1}\mathbf{S}^{c}]_c, \tag{48}$$

where $\mathbf{S}^{c}$ and $\bar{\mathbf{S}}^{c}$ stand for one of the matrices $\boldsymbol{\psi}^{c}$, $\mathbf{B}^{c}$, or $\bar{\mathbf{B}}^{c}$. The following formulas are obtained for the lowest-order amplitudes of reactive transitions (listed are the formulas used in the tests described in Sec. VI C):

$$(T^1_{B,B})^{cc'} = (\mathbf{B}^c|\mathbf{V}^{cc'})_c = ({}_+\mathbf{V}^{c'c}|\mathbf{B}^{c'})_{c'};$$
$$(T^1_{\psi,B})^{cc'} = (\psi^c|\mathbf{V}^{cc'})_c;$$
$$(T^2_{B,B})^{cc'} = \sum_{c''} ({}_+\mathbf{V}^{c''c}|\mathbf{G}^{c''}\mathbf{V}^{c''c'})_{c''}; \tag{49}$$
$$(\hat{T}^1_{BB})^{cc'} = (\mathbf{B}^c|\mathbf{B}^c)_c\delta_{c,c'};$$
$$(\hat{T}^1_{\psi,B})^{cc'} = (\psi^c|\mathbf{B}^c)_c\delta_{c,c'};\quad (\hat{T}^2_{B,B})^{cc'} = ({}_+\mathbf{V}^{c'c}|\mathbf{G}^{c'}\mathbf{B}^{c'})_{c'}.$$

At the last stage, the evaluation of the transition amplitudes requires solving the boundary value problems (44) and (45) and Eqs. (46) and (47) and evaluating the integrals (48) and (49) over the channel scattering coordinates. These two tasks can be performed in succession, which seems to be the common practice now, or simultaneously as recommended in the present paper. The way proposed—a generalized version of Johnson's log-derivative method[39]—is a particular realization of the well-known invariant imbedding approach to solving linear two-point boundary value problems.[36,37] The advantages, listed in Sec. II, will become apparent after more detailed presentation of the method in the next section.

V. DETERMINATION OF THE TRANSITION AMPLITUDES BY THE GENERALIZED LOG-DERIVATIVE (L-MATRIX PROPAGATION) METHOD

A. The transition amplitudes in the L-matrix formulation

Let $[x^0,x^\infty]$ denote the range of the x_c coordinate relevant for the scattering process under consideration and let $[x',x'']$ be a subinterval of $[x^0,x^\infty]$, i.e., $[x',x'']\subseteq[x^0,x^\infty]$. For the sake of clarity, the channel index will be omitted in this section.

The following are the three basic boundary value problems considered in the L-matrix formalism:[40,43]

$$[\mathbf{I}d^2/dx^2 + \mathbf{C}(x)]\psi^\alpha_{x',x''}(x) = \delta_{\alpha,0}\phi(x),$$
$$\text{for } \alpha = +,-,0; \tag{50}$$
$$\psi^\pm_{x',x''}(x') = \begin{cases}\mathbf{I}\\ \mathbf{0}\end{cases},\quad \psi^\pm_{x',x''}(x'') = \begin{cases}\mathbf{0}\\ \mathbf{I}\end{cases}; \tag{50a}$$
$$\psi^0_{x',x''}(x') = \psi^0_{x',x''}(x'') = \mathbf{0}, \tag{50b}$$

where $\mathbf{C}_{N\times N}$ and $\phi_{N\times M}$ are matrices of given functions and $\mathbf{C}$ is assumed to be symmetric. In terms of the solutions $\underset{N\times N}{\psi^{\pm}_{x',x''}}$, the L-matrix propagator is defined

$$\mathbf{L}_{x',x''} := \begin{pmatrix}\mathbf{L}^{(1)}_{x',x''} & \mathbf{L}^{(2)}_{x',x''}\\ \mathbf{L}^{(3)}_{x',x''} & \mathbf{L}^{(4)}_{x',x''}\end{pmatrix} := \begin{pmatrix}\dot{\psi}^+_{x',x''}(x') & \dot{\psi}^-_{x',x''}(x')\\ \dot{\psi}^+_{x',x''}(x'') & \dot{\psi}^-_{x',x''}(x'')\end{pmatrix}. \tag{51}$$
$$(\mathbf{L}^{(2)}_{x',x''})^T = -\mathbf{L}^{(3)}_{x',x''},\quad (\mathbf{L}^{(i)}_{x',x''})^T = \mathbf{L}^{(i)}_{x',x''},\quad \text{for } i = 1,4, \tag{52}$$

and through the solution $\psi^0_{x',x''}$, the matrix Green's function $\mathbf{G}^0_{x',x''}(x;\bar{x})$ which vanishes at both boundaries, i.e., for $x = x'$ and for $x = x''$, is introduced;

$$\psi^0_{x',x''}(x) = \int_{x'}^{x''} d\bar{x}\,\mathbf{G}^0_{x',x''}(x;\bar{x})\phi(\bar{x}). \tag{53}$$

An overdot denotes hereafter a derivative with respect to x.

The following (matrices of) integrals involving the solutions of the above problems are of interest here:

$$\mathbf{J}^\alpha_{x',x''} := (\psi^\alpha_{x',x''}|\phi),\quad \text{for } \alpha = +,-, \tag{54}$$
$$\mathbf{J}^0_{x',x''} := (\bar{\psi}^0_{x',x''}|\phi), \tag{55}$$
$$\mathbf{J}^{0,0}_{x',x''} := (\bar{\psi}^0_{x',x''}|\chi\psi^0_{x',x''}), \tag{56}$$
$$\mathbf{J}^{a,b}_{x',x''} := (\psi^a_{x',x''}|\chi\psi^b_{x',x''}),$$
$$\text{for } a = \alpha,0(\alpha),\quad b = \beta,0,0(\beta),\text{ and } \alpha,\beta = +,-, \tag{57}$$

where $\underset{N\times\bar{M}}{\bar{\psi}^0_{x',x''}}$ and $\underset{N\times N}{\psi^{0(\beta)}_{x',x''}}$ denote solutions of Eqs. (50)–(50b) with $\alpha = 0$ corresponding to the inhomogeneities $\bar{\phi}(x)$ and $\phi(x) = \chi(x)\psi^\beta_{x',x''}(x)$, respectively; $\bar{\phi}_{N\times\bar{M}}$ and $\chi_{N\times N}$ are given matrices of functions. $(|)$ denotes the scalar product defined in Eq. (39a), but with the range of integration confined to the interval $[x',x'']$.

Now, assigning to $\mathbf{C}$ in Eq. (50) the respective part of the operator $\mathbf{D}$ from the problems of the previous section [Eqs. (44)–(47)] and imposing conditions (45) and (47) at the respective boundaries of the interval $[x^0,x^\infty]$, one can determine the connection between the solutions of those problems, the matrices $\psi(x)$ and $\mathbf{G}(x;\bar{x})$, and the solutions of the above problems with $\alpha = -,0$ and $[x',x''] = [x^0,x^\infty]$ (cf. Ref. 45);

$$\psi(x) = \psi^-_{x^0,x^\infty}(x)\psi(x^\infty)$$
$$= \psi^-_{x^0,x^\infty}(x)[\mathbf{m}(x^\infty) + \mathbf{n}(x^\infty)^0\mathscr{R}], \tag{58}$$

where

$${}^0\mathscr{R} = [\dot{\mathbf{n}}(x^\infty) - \mathbf{L}^{(4)}_{x^0,x^\infty}\mathbf{n}(x^\infty)]^{-1}$$
$$\times[\mathbf{L}^{(4)}_{x^0,x^\infty}\mathbf{m}(x^\infty) - \dot{\mathbf{m}}(x^\infty)], \tag{59}$$
$$\mathbf{G}(x;\bar{x}) = 2\mu/\hbar^2\{\mathbf{G}^0_{x^0,x^\infty}(x;\bar{x}) + \psi^-_{x^0,x^\infty}(x)(\mathbf{L}^n - \mathbf{L}^{(4)}_{x^0,x^\infty})^{-1}$$
$$\times[\psi^-_{x^0,x^\infty}(\bar{x})]^T\},\quad \text{for } x,\bar{x}\in[x^0,x^\infty], \tag{60}$$

where

$$\mathbf{L}^n := \dot{\mathbf{n}}(x^\infty)[\mathbf{n}(x^\infty)]^{-1}. \tag{60a}$$

On the basis of this connection, some of the transition amplitudes $(T^n_{\bar{S},S})^{cc'}$ can be expressed in terms of the $\mathbf{J}$ integrals [Eqs. (54)–(57)]. To these belong the amplitudes of orders up to third for nonreactive transitions of bound–bound ($\bar{S} = \bar{B},S = B$), free–bound ($\bar{S} = \psi,S = B$), and free–free ($\bar{S} = \psi,S = \psi$) types

$$(T^n_{\bar{B},B})^{cc} = \left(\frac{2\mu}{\hbar^2}\right)^{n-1}\begin{cases}\mathbf{J}^0 + \bar{\mathbf{d}}^T\mathbf{J}^-, & \text{for } n = 2,\\ \mathbf{J}^{0,0} + (\bar{\mathbf{J}}^{-,0})^T\mathbf{d} + \bar{\mathbf{d}}^T\mathbf{J}^{-,0} + \bar{\mathbf{d}}^T\mathbf{J}^{-,-}\mathbf{d}, & \text{for } n = 3,\end{cases} \tag{61a}$$
$$\tag{61b}$$
$$(T^n_{\psi,\psi})^{cc} = \left(\frac{2\mu}{\hbar^2}\right)^{n-1}[\psi(x^\infty)]^T(\cdots)^{(n)}\psi(x^\infty) \tag{62}$$

with

$$(\cdots)^{(n)} := \begin{cases}\mathbf{J}^{-,-}, & \text{for } n = 1, \quad (62a)\\ \mathbf{J}^{-,0(-)} + (\mathbf{d}^-)^T(\cdots)^{(1)}, & \text{for } n = 2, \quad (62b)\\ \mathbf{J}^{0(-),0(-)} + \mathbf{J}^{-,0(-)}\mathbf{d}^- + (\mathbf{d}^-)^T(\cdots)^{(2)}, & \text{for } n = 3, \quad (62c)\end{cases}$$

$$(T^{n}_{\psi,B})^{cc} = \left(\frac{2\mu}{\hbar^2}\right)^{n-1} [\psi(x^{\infty})]^{T} (\cdots)^{(n)} \tag{63}$$

with

$$(\cdots)^{(n)} := \begin{cases} \mathbf{J}^{-}, & \text{for } n=1, \quad (63a) \\ \mathbf{J}^{-,0} + (\mathbf{d}^{-})^{T}(\cdots)^{(1)}, & \text{for } n=2, \quad (63b) \\ \mathbf{J}^{0(-),0} + \mathbf{J}^{-,0(-)}\mathbf{d} + (\mathbf{d}^{-})^{T}(\cdots)^{(2)}, & \\ \quad \text{for } n=3, & (63c) \end{cases}$$

where

$$\mathbf{d} := (\mathbf{L}^{n} - \mathbf{L}^{(4)})^{-1}\mathbf{J}^{-}, \quad \bar{\mathbf{d}} := (\mathbf{L}^{n} - \mathbf{L}^{(4)})^{-1}\bar{\mathbf{J}}^{-},$$
$$\mathbf{d}^{-} := (\mathbf{L}^{n} - \mathbf{L}^{(4)})^{-1}\mathbf{J}^{-,-}, \tag{64}$$

and all the $\mathbf{J}$ integrals and the matrix $\mathbf{L}^{(4)}$ refer to the interval $[x',x''] = [x^0,x^{\infty}]$ and $\boldsymbol{\phi} = \mathbf{V}^{c}\mathbf{B}^{c}$, $\bar{\boldsymbol{\phi}} = \mathbf{V}^{c}\bar{\mathbf{B}}^{c}$, $\boldsymbol{\chi} = \mathbf{V}^{c}$. $\bar{\mathbf{J}}^{-}$ and $\bar{\mathbf{J}}^{-,0}$ denote the quantities obtained after replacing $\boldsymbol{\phi}$ with $\bar{\boldsymbol{\phi}}$ in the respective formulas (54) and (57). The above formulas apply also to the analogous amplitudes of $\hat{T}$ and $\bar{T}$ type [cf. Eqs. (30)], if only appropriately modified substitutions for the matrices $\boldsymbol{\phi}$ and $\bar{\boldsymbol{\phi}}$ are made, and can be easily adapted to the reactive amplitudes which are needed for evaluation of the zeroth order expressions $\tilde{\mathscr{R}}^{0}_{1,1}$ or $\hat{\mathscr{R}}^{0}_{0,1}$. [These are the amplitudes listed in Eqs. (49).]

Concerning the other reactive transition amplitudes which would appear in the higher-order expressions $\tilde{\mathscr{R}}^{n}_{i,j}$ [cf. Eqs. (31)–(35)], an essential complication arises from the fact that these amplitudes involve within one matrix element Green's functions or distorted-wave functions corresponding to different arrangement channels, e.g.,

$$(T^{(3)}_{B,B})^{cc'} = \sum_{\bar{c},\bar{c}} \langle B^{c}|V^{c\bar{c}}G^{\bar{c}}V^{\bar{c}\bar{c}}G^{\bar{c}}V^{\bar{c}c'}B^{c'}\rangle,$$

$$(T^{(2)}_{\psi,B})^{cc'} = \sum_{\bar{c}} \langle \psi^{c}|V^{c\bar{c}}G^{\bar{c}}V^{\bar{c}c'}B^{c'}\rangle,$$

$$(T^{(1)}_{\psi,\psi})^{cc'} = \langle \psi^{c}|V^{cc'}\psi^{c'}\rangle.$$

Such matrix elements cannot be expressed entirely in terms of the above $\mathbf{J}$ integrals because of the assumed local character of the operator $\boldsymbol{\chi}$.

B. The algorithm for the J integrals

The log-derivative related algorithms for evaluation of the integrals $\mathbf{J}^{-,-}$, $\mathbf{J}^{0}$, and $\mathbf{J}^{-}$ involved in the first-order free–free and free–bound and in the second-order bound–bound transition amplitudes, have been derived in the previous papers.[43,45] Here, these algorithms will be generalized to the additional five integrals $\mathbf{J}^{0,0}$, $\mathbf{J}^{-,0}$, $\mathbf{J}^{-,0(-)}$, $\mathbf{J}^{0(-),0}$, and $\mathbf{J}^{0(-),0(-)}$, which are involved in the amplitudes up to third order [cf. formulas (61a)–(62)]. The generalization is essentially a matter of deriving appropriate recurrence relations for accumulation of the required integrals over subsequent sectors (or half-sectors) of the integration range and applying these relations to so-called half-sector L matrices and half-sector J integrals—the specific quantities arising from discretizing the boundary value problems (50)–(50b) as described in Refs. 40, 43, and 45.

The derivation of the recurrence relations is straightforward if one exploits the following linear superposition relations for the solutions of problems (50)–(50b) on intervals $[x',x'']$, $[x',y]$, and $[y,x'']$, where $x' \leqslant y \leqslant x''$;

$$\psi^{\alpha}_{x',x''}(x) = \begin{cases} \psi^{-}_{x',y}(x)\,{}_{-}\mathbf{a}^{\alpha}_{x',y} + \psi^{+}_{x',y}(x)\,{}_{+}\mathbf{a}^{\alpha}_{x',y} + \delta_{\alpha,0}\psi^{0}_{x',y}(x), & \text{for } x\in[x',y] \\ \psi^{-}_{y,x''}(x)\,{}_{-}\mathbf{a}^{\alpha}_{y,x''} + \psi^{+}_{y,x''}(x)\,{}_{+}\mathbf{a}^{\alpha}_{y,x''} + \delta_{\alpha,0}\psi^{0}_{y,x''}(x), & \text{for } x\in[y,x''], \quad \alpha = +,-,0, \end{cases} \tag{65a}$$

$$\psi^{0(\beta)}_{x',x''}(x) = \begin{cases} \psi^{-}_{x',y}(x)\,{}_{-}\mathbf{a}^{0(\beta)}_{x',y} + \psi^{0(-)}_{x',y}(x)\,{}_{-}\mathbf{a}^{\beta}_{x',y} + \psi^{0(+)}_{x',y}(x)\,{}_{+}\mathbf{a}^{\beta}_{x',y}, & \text{for } x\in[x',y] \\ \psi^{+}_{y,x''}(x)\,{}_{+}\mathbf{a}^{0(\beta)}_{y,x''} + \psi^{0(-)}_{y,x''}(x)\,{}_{-}\mathbf{a}^{\beta}_{y,x''} + \psi^{0(+)}_{y,x''}(x)\,{}_{+}\mathbf{a}^{\beta}_{y,x''}, & \text{for } x\in[y,x''], \quad \beta = +,-. \end{cases} \tag{65b}$$

The coefficients assuring continuity of the solutions $\psi^{\alpha}_{x',x''}(x)$, $\alpha = +,-,0,0(\beta)$, and of their derivatives at the point y are

$$-\mathbf{a}^{\alpha}_{x',y} = {}_{+}\mathbf{a}^{\alpha}_{y,x''} = -\mathbf{l}_{x',y,x''}\cdot \begin{cases} \mathbf{L}^{(3)}_{x',y}, & \text{for } \alpha = +, \\ (-\mathbf{L}^{(2)}_{y,x''}), & \text{for } \alpha = -, \\ (\mathbf{J}^{-}_{x',y} + \mathbf{J}^{+}_{y,x''}), & \text{for } \alpha = 0, \end{cases}$$
$${}_{+}\mathbf{a}^{+}_{x',y} = -\mathbf{a}^{-}_{y,x''} = \mathbf{I}, \quad {}_{+}\mathbf{a}^{-}_{x',y} = -\mathbf{a}^{+}_{y,x''} = \mathbf{0},$$
$${}_{+}\mathbf{a}^{0}_{x',y} = -\mathbf{a}^{0}_{y,x''} = \mathbf{0},$$
$$-\mathbf{a}^{0(\beta)}_{x',y} = {}_{+}\mathbf{a}^{0(\beta)}_{y,x''} = -\mathbf{l}_{x',y,x''}\left[(\mathbf{J}^{-,-}_{x',y} + \mathbf{J}^{+,+}_{y,x''})\,{}_{-}\mathbf{a}^{\beta}_{x',y} + \mathbf{J}^{+,-}_{y,x''}\,{}_{-}\mathbf{a}^{\beta}_{y,x''} + \mathbf{J}^{-,+}_{x',y}\,{}_{+}\mathbf{a}^{\beta}_{x',y}\right], \quad \text{for } \beta = +,-, \tag{66}$$

where

$$\mathbf{l}_{x',y,x''} := (\mathbf{L}^{(4)}_{x',y} - \mathbf{L}^{(1)}_{y,x''})^{-1}. \tag{66a}$$

Two examples of the recurrence relations obtained by inserting the relations (65a)–(66a) into the formulas (54)–(57) are listed below:

$$\mathbf{J}^{-,-}_{x',x''} = \mathbf{J}^{-,-}_{y,x''} + \mathbf{J}^{-,+}_{y,x''}\mathbf{l}_{x',y,x''}\mathbf{L}^{(2)}_{y,x''} - \mathbf{L}^{(3)}_{y,x''}\mathbf{l}_{x',y,x''}\mathbf{J}^{+,-}_{y,x''} - \mathbf{L}^{(3)}_{y,x''}\mathbf{l}_{x',y,x''}(\mathbf{J}^{-,-}_{x',y} + \mathbf{J}^{+,+}_{y,x''})\mathbf{l}_{x',y,x''}\mathbf{L}^{(2)}_{y,x''}, \tag{67}$$

$$\mathbf{J}^{-,0}_{x',x''} = \mathbf{J}^{-,0}_{y,x''} - \mathbf{J}^{-,+}_{y,x''}\mathbf{l}_{x',y,x''}(\mathbf{J}^{-}_{x',y} + \mathbf{J}^{+}_{y,x''}) - \mathbf{L}^{(3)}_{y,x''}\mathbf{l}_{x',y,x''} \times (\mathbf{J}^{-,0}_{x',y} + \mathbf{J}^{+,0}_{y,x''}) + \mathbf{L}^{(3)}_{y,x''}\mathbf{l}_{x',y,x''} \times (\mathbf{J}^{-,-}_{x',y} + \mathbf{J}^{+,+}_{y,x''})\mathbf{l}_{x',y,x''}(\mathbf{J}^{-}_{x',y} + \mathbf{J}^{+}_{y,x''}). \tag{68}$$

The first relation was given previously in Ref. 43 in terms of the matrices $\mathbf{T}^{\beta}_{N\times N}$ and $\mathbf{Q}^{\beta}_{N\times N}$;

$$\mathbf{T}^{\beta}_{x',x''} := \dot{\psi}^{0(\beta)}_{x',x''}(x''), \quad \mathbf{Q}^{\beta}_{x',x''} := \dot{\psi}^{0(\beta)}_{x',x''}(x'), \quad \text{for } \beta = +,-, \tag{69}$$

which can be shown (cf. Ref. 45) to be connected with the $\mathbf{J}$

integrals as follows:

$$\mathbf{Q}^{\beta} = -\mathbf{J}^{+,\beta}, \quad \mathbf{T}^{\beta} = \mathbf{J}^{-,\beta}, \quad \beta = +,- . \tag{69a}$$

At the second stage of derivation of the algorithms, the boundary problems (50)–(50b), converted to integral equation form, are discretized on subsequent sectors of the integration range $[x^0,x^\infty]$, i.e., on the intervals $[x_{2p-2}, x_{2p} = x_{2p-2} + 2h]$ for $p = 1,...,L$, where $x_0 = x^0$ and $x_{2L} = x^\infty$, by means of the modified Simpson quadrature formula,[49] and counterparts of the **L** matrix and of the **J** integrals are introduced on intervals consisting of two points x_l and $x_{l+1} = x_l + h$ for $l = 2p-2$, $2p-1$, and $p = 1,...,L$, i.e., of the boundary points of the half-sectors. The precise definition and the formulas for the blocks of the half-sector **L** matrix

$$\mathbf{L}_{l,l+1} = \begin{pmatrix} \mathbf{L}^{(1)}_{l,l+1} & \mathbf{L}^{(2)}_{l,l+1} \\ \mathbf{L}^{(3)}_{l,l+1} & \mathbf{L}^{(4)}_{l,l+1} \end{pmatrix},$$

are given in Refs. 40 and 45. The half-sector **J** integrals are defined by analogy to the formulas (54)–(57), e.g.,

$$\mathbf{J}^{a,b}_{l,l+1}: = \{\psi^{a}_{l,l+1}|\chi\psi^{b}_{l,l+1}\}, \quad \text{for } a = \alpha,0(\alpha), \quad b = \beta,0,0(\beta), \quad \alpha,\beta = +,-, \tag{70}$$

where

$$\{\mathbf{X}_{l,l+1}|\mathbf{Y}\}: = \sum_{k=l}^{l+1} \omega_k [\mathbf{X}_{l,l+1}(x_k)]^T \mathbf{Y}(x_k), \tag{70a}$$

$$\omega_k = 2h/3 \ (h/3), \quad \text{for odd (even) } k. \tag{70b}$$

The half-sector functions $\psi^{a}_{l,l+1}(x_k)$ assume the values[45]

$$\psi^{\pm}_{l,l+1}(x_l) = \begin{cases} \mathbf{q}^p_l \\ \mathbf{0} \end{cases}, \quad \psi^{\pm}_{l,l+1}(x_{l+1}) = \begin{cases} \mathbf{0} \\ \mathbf{q}^p_{l+1} \end{cases}, \tag{71}$$

$$\psi^{0}_{l,l+1}(x_k) = \eta_k \mathbf{q}^p_k \phi(x_k), \tag{72}$$

$$\psi^{0(\pm)}_{l,l+1}(x_k) = \eta_k \mathbf{q}^p_k \chi(x_k) \psi^{\pm}_{l,l+1}(x_k), \quad \text{for } k = l,l+1 \text{ and } l = 2p-2,2p-1, \tag{73}$$

where

$$\mathbf{q}^p_k: = [\mathbf{I} + \eta_k \mathbf{C}^p(x_k)]^{-1}, \tag{74}$$

$$\mathbf{C}^p(x_k) = \mathbf{C}(x_k) - \mathbf{C}^p_{\text{ref}}, \tag{75}$$

$$\mathbf{C}^p_{\text{ref}}: = \text{diag}[\mathbf{C}(x_{2p-1})]: = (\mathbf{k}^p)^2, \tag{76}$$

$$\eta_k = h^2/6 \ (0), \quad \text{for odd (even) k.} \tag{77}$$

Since the resultant expressions for the half-sector **J** integrals are to be inserted at the final stage into the recurrence relations (67) and (68) and into even more complicated relations for $\mathbf{J}^{-,0(-)}$, $\mathbf{J}^{0(-),0}$, $\mathbf{J}^{0,0}$, and $\mathbf{J}^{0(-),0(-)}$, it is important to note that many of these integrals, namely the integrals $\mathbf{J}^{\alpha,\beta}_{l,l+1}$, $\mathbf{J}^{\alpha,0(\beta)}_{l,l+1}$, and $\mathbf{J}^{0(\alpha),0(\beta)}_{l,l+1}$ with $\alpha,\beta = +,-$, but $\alpha \neq \beta$ vanish. Further simplification in the form of the algorithm is achieved by making use of the relations

$$\mathbf{J}^{-}_{l-1,l} = \mathbf{J}^{+}_{l,l+1}, \quad \mathbf{J}^{-,-}_{l-1,l} = \mathbf{J}^{+,+}_{l,l+1}, \quad \mathbf{J}^{0}_{l-1,l} = \mathbf{J}^{0}_{l,l+1}$$

(and of analogous relations for the other types of the **J** integrals) and by introducing the following working quantities:

$$\mathbf{t}_l: = h(\mathbf{J}^{-}_{0,l} + \mathbf{J}^{+}_{l,l+1}), \quad \mathbf{t}^{(2)}_l: = h(\mathbf{J}^{-,0}_{0,l} + \mathbf{J}^{+,0}_{l,l+1}),$$

$$\mathbf{t}^{(3)}_l: = h(\mathbf{J}^{0(-),0}_{0,l} + \mathbf{J}^{0(+),0}_{l,l+1}), \quad \mathbf{u}_l: = h(\mathbf{J}^{-,-}_{0,l} + \mathbf{J}^{+,+}_{l,l+1}),$$

$$\mathbf{u}^{(2)}_l: = h(\mathbf{J}^{-,0(-)}_{0,l} + \mathbf{J}^{+,0(+)}_{l,l+1}), \quad \mathbf{u}^{(3)}_l: = h(\mathbf{J}^{0(-),0(-)}_{0,l} + \mathbf{J}^{0(+),0(+)}_{l,l+1}), \quad \mathbf{j}^{(2)}_l: = h(\mathbf{J}^{0}_{0,l} + \mathbf{J}^{0}_{l,l+1}),$$

$$\mathbf{j}^{(3)}_l: = h(\mathbf{J}^{0,0}_{0,l} + \mathbf{J}^{0,0}_{l,l+1}).$$

$\mathbf{J}^{\alpha}_{0,l}$ and $\mathbf{J}^{a,b}_{0,l}$ with $\alpha = -,0$ and $a,b = -,0,0(-)$ denote the quantities assembled according to appropriate recurrence relations from the half-sector integrals. For even values of l, these quantities give approximations to the respective **J** integrals in the interval $[x_0,x_l]$. Obviously, $\mathbf{J}^{\alpha}_{0,0} = \mathbf{0}$ and $\mathbf{J}^{a,b}_{0,0} = \mathbf{0}$ for all values of the indices α, a, and b. Through the notation chosen for the working quantities, the **J** integrals are classified according to the type and order of the transition amplitudes to which they are primarily related [cf. Eqs. (61a)–(64)]. The letters **t**, **u**, and **j** are used to denote bound–free, free–free, and bound–bound transitions, respectively. The order index $n = 1$ is omitted.

The formulas of the algorithm concerning the amplitudes of the lowest orders considered within the three types are

$$\mathbf{t}_0 = h^2/3\phi_0, \quad \mathbf{j}^{(2)}_0 = \mathbf{0}, \quad \mathbf{u}_0 = h^2/3\chi_0,$$

$$\mathbf{t}_l = \mathbf{s}^p \mathbf{z}^{-1}_{l-1} \mathbf{t}_{l-1} + \begin{cases} h^2/6\mathbf{g}^p_l \phi_l, & \text{for } l = 2p-1 \\ 2h^2/3\phi_l, & \text{for } l = 2p, \end{cases}$$

$$\mathbf{j}^{(2)}_l = \mathbf{j}^{(2)}_{l-1} - \bar{\mathbf{t}}^T_{l-1} \mathbf{z}^{-1}_{l-1} \mathbf{t}_{l-1} + \begin{cases} h^4/36\bar{\phi}^T_l \mathbf{g}^p_l \phi_l, & \text{for } l = 2p-1 \\ \mathbf{0}, & \text{for } l = 2p, \end{cases}$$

$$\mathbf{u}_l = \mathbf{s}^p \mathbf{z}^{-1}_{l-1} \mathbf{u}_{l-1} \mathbf{z}^{-1}_{l-1} \mathbf{s}^p + \begin{cases} h^2/48\mathbf{g}^p_l \chi_l \mathbf{g}^p_l, & \text{for } l = 2p-1 \\ 2h^2/3\chi_l, & \text{for } l = 2p, \end{cases} \quad p = 1,...,L,$$

$$\mathbf{J}^{-}_{0,2L} = (\mathbf{t}_{2L} - h^2/3\phi_{2L})/h,$$

$$\mathbf{J}^{-,-}_{0,2L} = (\mathbf{u}_{2L} - h^2/3\chi_{2L})/h, \quad \mathbf{J}^{0}_{0,2L} = \mathbf{j}^{(2)}_{2L}/h.$$

The formulas for the higher-order amplitudes read

$$\mathbf{t}^{(2)}_0 = \mathbf{t}^{(3)}_0 = \mathbf{0}, \quad \mathbf{u}^{(2)}_0 = \mathbf{u}^{(3)}_0 = \mathbf{0}, \quad \mathbf{j}^{(3)}_0 = \mathbf{0},$$

$$\mathbf{t}^{(2)}_l = \mathbf{s}^p[(\mathbf{t}^{(2)}_l)] + \begin{cases} h^4/288(\cdots)\phi_l, & \text{for } l = 2p-1, \\ \mathbf{0}, & \text{for } l = 2p, \end{cases}$$

where $[(\mathbf{t}^{(2)}_l)]: = \mathbf{z}^{-1}_{l-1}\mathbf{t}^{(2)}_{l-1} - (\cdots)\mathbf{t}_{l-1}$,

$$\mathbf{t}^{(3)}_l = \mathbf{s}^p\{\mathbf{z}^{-1}_{l-1}\mathbf{t}^{(3)}_{l-1} - (:::)\mathbf{t}_{l-1} - \mathbf{z}^{-1}_{l-1}\mathbf{u}_{l-1}[(\mathbf{t}^{(2)}_l)]\} + \begin{cases} h^6/13\,824(\cdots)\chi_l \mathbf{g}^p_l \phi_l, & \text{for } l = 2p-1, \\ \mathbf{0}, & \text{for } l = 2p, \end{cases}$$

$$\mathbf{u}^{(2)}_l = \mathbf{s}^p[(\mathbf{u}^{(2)}_l)]\mathbf{s}^p + \begin{cases} h^4/2304(\cdots)\chi_l \mathbf{g}^p_l, & \text{for } l = 2p-1, \\ \mathbf{0}, & \text{for } l = 2p, \end{cases}$$

where $[(\mathbf{u}^{(2)}_l)]: = (:::) - \mathbf{z}^{-1}_{l-1}\mathbf{u}_{l-1}(\cdots)$,

$$\mathbf{u}^{(3)}_l = \mathbf{s}^p[(\vdots\vdots\vdots) - \mathbf{z}^{-1}_{l-1}\mathbf{u}_{l-1}(:::) - [(\mathbf{u}^{(2)}_l)]\mathbf{u}_{l-1}\mathbf{z}^{-1}_{l-1}]\mathbf{s}^p + \begin{cases} h^6/110\,592\mathbf{g}^p_l \chi_l(\cdots)\chi_l \mathbf{g}^p_l, & \text{for } l = 2p-1, \\ \mathbf{0}, & \text{for } l = 2p, \end{cases}$$

$$\mathbf{j}^{(3)}_l = \mathbf{j}^{(3)}_{l-1} + \bar{\mathbf{t}}^T_{l-1}(\cdots)\mathbf{t}_{l-1} - \bar{\mathbf{t}}^T_{l-1}\mathbf{z}^{-1}_{l-1}\mathbf{t}^{(2)}_{l-1} - (\bar{\mathbf{t}}^{(2)}_{l-1})^T \times \mathbf{z}^{-1}_{l-1}\mathbf{t}_{l-1} + \begin{cases} h^6/1728\bar{\phi}^T_l(\cdots)\phi_l, & \text{for } l = 2p-1, \\ \mathbf{0}, & \text{for } l = 2p, \quad p = 1,...,L \end{cases}$$

$$1/h(\mathbf{t}_{2L}^{(2)},\mathbf{t}_{2L}^{(3)},\mathbf{u}_{2L}^{(2)},\mathbf{u}_{2L}^{(3)},\mathbf{j}_{2L}^{(3)}) = (\mathbf{J}_{0,2L}^{-,0},\mathbf{J}_{0,2L}^{0(-),0},\mathbf{J}_{0,2L}^{-,0(-)},\mathbf{J}_{0,2L}^{0(-),0(-)},\mathbf{J}_{0,2L}^{0,0}),$$

where

$$(\cdots):=\mathbf{z}_{l-1}^{-1}\mathbf{u}_{l-1}\mathbf{z}_{l-1}^{-1},\quad (:::):=\mathbf{z}_{l-1}^{-1}\mathbf{u}_{l-1}^{(2)}\mathbf{z}_{l-1}^{-1},$$

$$(\vdots\,\vdots\,\vdots):=\mathbf{z}_{l-1}^{-1}\mathbf{u}_{l-1}^{(3)}\mathbf{z}_{l-1}^{-1},$$

$$(-\cdot-):=\mathbf{g}_l^p\boldsymbol{\chi}_l\mathbf{g}_l^p,\quad \mathbf{g}_l^p:=8\mathbf{q}_l^p,\quad \boldsymbol{\phi}_l:=\boldsymbol{\phi}(x_l),\quad \boldsymbol{\chi}_l:=\boldsymbol{\chi}(x_l),$$

$\bar{\mathbf{t}}_l$ and $\bar{\mathbf{t}}_l^{(2)}$ are counterparts of $\mathbf{t}_l$ and $\mathbf{t}_l^{(2)}$, respectively, for the inhomogeneity $\bar{\boldsymbol{\phi}}_l$ (the formulas for them are omitted).

The evaluation of the integrals proceeds simultaneously with propagation of the log-derivative matrix $\mathbf{L}^{(4)}$ to which the matrix $\mathbf{z}$ occurring above is related;

$$\mathbf{z}_l:=h\,\mathbf{L}_{0,l}^{(4)}+\mathbf{l}^p-h\omega_l\mathbf{q}_l^p\mathbf{C}_l^p,\quad \text{for } l=2p-1,$$

and

$$\mathbf{z}_l=\tilde{\mathbf{z}}_l+\mathbf{a}^p,\quad \text{for } l=2p,$$

where

$$\tilde{\mathbf{z}}_l:=h(\mathbf{L}_{0,l}^{(4)}-\omega_l\mathbf{C}_l),$$

$$\mathbf{a}^p:=\mathbf{l}^p+h^2/3\mathbf{C}_{\text{ref}}^p,$$

$$\mathbf{C}_l:=\mathbf{C}(x_l),\quad \mathbf{C}_l^p:=\mathbf{C}^p(x_l),$$

$$\mathbf{l}^p:=h\,|\mathbf{k}^p|\begin{cases}\cot(h\,|\mathbf{k}^p|), & \text{if } (\mathbf{k}^p)^2>0\\ \coth(h\,|\mathbf{k}^p|), & \text{if } (\mathbf{k}^p)^2<0.\end{cases}$$

The formulas for propagation of $\mathbf{z}$ read[38,45]

$$\left.\begin{aligned}&\tilde{\mathbf{z}}_0=\gamma\mathbf{I},\quad \gamma\gg 1,\\ &\mathbf{z}_{l-1}=\tilde{\mathbf{z}}_{l-1}+\mathbf{a}^p\\ &\mathbf{z}_l=2\mathbf{l}^p-8\mathbf{I}+\mathbf{g}_l^p-\mathbf{s}^p\mathbf{z}_{l-1}^{-1}\mathbf{s}^p\end{aligned}\right\},\quad \text{for } l=2p-1,$$

$$\tilde{\mathbf{z}}_l=\mathbf{a}^p-2h^2/3\mathbf{C}_l-\mathbf{s}^p\mathbf{z}_{l-1}^{-1}\mathbf{s}^p,\quad \text{for } l=2p,\quad p=1,\ldots,L.$$

The matrices $\mathbf{s}^p$ for $p=1,\ldots,L$, related to the nondiagonal blocks of the half-sector $\mathbf{L}$ propagators, i.e., to $\mathbf{L}_{l,l+1}^{(2)}=-(\mathbf{L}_{l,l+1}^{(3)})^T$ for $l=2p-2,2p-1$, are given by the formulas

$$\mathbf{s}^p=h\,|\mathbf{k}^p|\begin{cases}[\sin(h\,|\mathbf{k}^p|)]^{-1}, & \text{if } (\mathbf{k}^p)^2>0\\ [\sinh(h\,|\mathbf{k}^p|)]^{-1}, & \text{if } (\mathbf{k}^p)^2<0.\end{cases}$$

The part of the above algorithm including the formulas for $\mathbf{z}$, $\mathbf{t}$, and $\mathbf{j}^{(2)}$ was presented in Ref. 45 as the "half-hybrid" version of the generalized log-derivative algorithm for second-order (bound–bound) transition amplitudes and the formulas for $\mathbf{u}$ ($\mathbf{J}^{-,-}$) give a hybrid version of the algorithm derived for $\mathbf{T}^-$ ($=\mathbf{J}^{-,-}$) in Ref. 43. (The factor of $4h^2/3$ appearing there in place of the present factor $h^2/48$ is incorrect). The term "hybrid" refers here to the use of the sector-reference potentials $\mathbf{C}_{\text{ref}}^p$. Two terms, "hybrid" and half-hybrid, were introduced in Ref. 45 to distinguish between algorithms which do and do not use additional reference inhomogeneities. Superiority of the hybrid and especially of the half-hybrid versions of the log-derivative method over the purely approximate-solutions versions has been shown in that paper. This gave a motivation for presenting here the new generalization of the method in the hybrid version. An approximate-solution version can be, however, readily obtained by setting $\mathbf{C}_{\text{ref}}^p=\mathbf{0}$, $\mathbf{l}^p=\mathbf{I}$, and $\mathbf{s}^p=\mathbf{I}$ for $p=1,\ldots,L$.

It often happens (cf. the problem of Sec. VI C) that the range of the functions $\boldsymbol{\phi}(x)$ and $\boldsymbol{\chi}(x)$ occurring in the $\mathbf{J}$ integrals is much shorter than the range of variation of the matrix $\mathbf{C}$ in the coupled equations (50) for which the log-derivative matrix must be found. Thus, the interval $[x^0,x^\infty]$ can be divided into two intervals $[x^0,x^e]$ and $[x^e,x^\infty]$ in such a way that $\boldsymbol{\phi}(x)\approx\mathbf{0}$ and $\boldsymbol{\chi}(x)\approx\mathbf{0}$ for $x\in[x^e,x^\infty]$ and, in consequence, all the half-sector $\mathbf{J}$ integrals in the second interval vanish. Instead of continuing propagation of the $\mathbf{J}$ integrals throughout the second interval, it is recommended in such cases to start propagation of all the four blocks of the matrix $\mathbf{L}_{x^e,x^\infty}$ and, at the end, to "add" this matrix, using appropriate recurrence relations[45] to the quantities determined in the first interval. For completeness, the formulas for evaluation of the matrices $\mathbf{L}_{x^e,x^\infty}^{(1)}$ and $\mathbf{L}_{x^e,x^\infty}^{(3)}=-(\mathbf{L}_{x^e,x^\infty}^{(2)})^T$ are listed below (their approximate-solution counterparts were given in Refs. 40 and 41):

$$\mathbf{L}_{0,1}^{(1)}=-\mathbf{l}^1/h+h/3\mathbf{C}_0^1,\quad \mathbf{L}_{0,1}^{(3)}=-\mathbf{s}^1/h,$$

$$\mathbf{L}_{0,l}^{(3)}=\mathbf{s}^p\mathbf{z}_{l-1}^{-1}\mathbf{L}_{0,l-1}^{(3)},$$

$$\mathbf{L}_{0,l}^{(1)}=\mathbf{L}_{0,l-1}^{(1)}+h(\mathbf{L}_{0,l-1}^{(3)})^T\mathbf{L}_{0,l}^{(3)},$$

$$\text{for } l=2,2p-1,2p,\text{ and } p=2,\ldots\bar{L},$$

where $\bar{L}$ denotes the number of sectors of length $2h$ in the range $[x^e,x^\infty]$.

Of the features of the above algorithm, announced in Sec. II, the most attractive in comparison with the currently available techniques[19–24] may be that of low storage requirements. Indeed, the procedure completely avoids evaluation of the functions $\psi_{x^0,x^\infty}^-(x)\left[\psi_{x^0,x^\infty}^+(x)\right]$ and $\psi_{x^0,x^\infty}^0(x)$, whereas counterparts of these functions in the standard approaches (cf., the finite difference boundary value method[23,24])—the regular (irregular) distorted-wave solutions and the "half-integrated Green's functions", respectively—have to be calculated and stored for x points covering the entire scattering range $[x^0,x^\infty]$. Advantages of this and of the other features of the proposed algorithm can be fully taken in variational treatments of inelastic scattering problems employing any of the expressions for the reactance matrix listed in Eqs. (31)–(35). Concerning exploition of the new algorithm in variational calculations for reactive scattering, it should be noted that quite large savings are possible when the Schwinger or a Schwinger-like (i.e., zeroth order) expression is chosen for evaluation. The higher-order expressions involve reactive transition amplitudes which, as was mentioned in the previous subsection, cannot be handled by the present algorithm without extending it to integrals $\mathbf{J}_{x',x''}^{a,b}$ [cf. Eqs. (56) and (57)] with nonlocal operators $\boldsymbol{\chi}$. Such an extension, however, would lead inevitably to a considerable enlargement of the present storage requirements.

VI. NUMERICAL TESTS

The goal of this section is threefold and is specified in the titles of the three subsections. In order to establish a common reference for the test problems considered in these subsections, let us put together the various partitions of the total Hamiltonian introduced in the text

$$\mathscr{H}=H_0^c+\mathscr{V}^c=H^c+V^c=T_{x_c}+H_{(\text{ro-})\text{vib}}^c+V_0^c+V^c,\tag{78}$$

and the respective operators appearing in the Schrödinger equation represented in the basis of the eigenfuctions of $H^c_{(\text{ro-})\text{vib}}$:

$$\mathscr{D} := 2\mu/\hbar^2[\varphi^c|(E-\mathscr{H})\varphi^c]_c$$
$$= \mathbf{D}^c_0 + \mathscr{V}^c = \mathbf{D}^c + \mathbf{V}^c = \mathbf{D}^c_0 + \mathbf{V}^c_0 + \mathbf{V}^c. \quad (79)$$

T_{x_c} denotes the kinetic energy operator for the motion along the channel scattering coordinate. The channel index "c" will be necessary only in the Sec. VI C.

A. A demonstration of accuracy of the new generalization of the log-derivative algorithm

The test problem is the simplified version of the Secrest–Johnson model of vibrational excitation in atom–diatom nonreactive collisions[49] in which the particular operators of Eq. (78) take the form

$$T_x = (-1/m)\partial^2/\partial x^2, \quad H_{\text{vib}} = -\partial^2/\partial y^2 + y^2,$$
$$V_0 = \exp(-\alpha x), \quad V = \alpha y \exp(-\alpha x). \quad (80)$$

α and m are the parameters of the model. The transition probabilities in this model can be determined analytically[49] within the distorted-wave Born approximation which gives a good opportunity to check numerical accuracy of the respective approximation to the reactance matrix

$$\mathscr{R}^{DWB1} = {}^0\mathscr{R} + T^1_{\psi,\psi}, \quad (81)$$

and, indirectly, the accuracy of the integral $\mathbf{J}^{-,-}$ [cf. Eqs. (62) and (62a)]. In Ref. 43, the performance of the approximate-solution version of the log-derivative algorithm for this integral was tested on the same problem. Superior accuracy of the present hybrid version and, in particular, a considerable reduction in growth of errors with energy are demonstrated in Table II. Since the integral $\mathbf{J}^{-,-}$ is involved in evaluation of all the new integrals considered in Sec. V, it is obvious that also in cases of these integrals the hybrid algorithm should give more accurate results than the approximate-solution version.

B. An illustration of relative performance of the variational methods on simple nonreactive scattering problems

The test problems are the N (= 1,2)-channel problems with the operators (79) in the form

$$(\mathbf{D}_0)_{i,j} = \delta_{i,j}(d^2/dx^2 + E - \epsilon_i),$$
$$\text{for } i,j = 1,\ldots,N \text{ and } N = 1,2 \quad (82)$$

$$(\mathscr{V})_{i,i} = \begin{cases} v_i\{1-\exp[-\beta_i(x-\tilde{x}_i)]\}^2 - v_i, \\ \quad \text{for } i = 1,2 \text{ if } N = 2, & (82a) \\ \gamma_i \exp(-\nu_i x), \quad \text{for } i = 1 \text{ if } N = 1, & (82b) \end{cases}$$

$$(\mathscr{V})_{1,2} = \gamma_{1,2}\exp(-\nu_{1,2}x) \quad (82c)$$

$$(\mathbf{V}_0)_{i,j} = \begin{cases} \delta_{i,j}(\mathscr{V})_{i,j} \quad \text{for } i,j = 1,2 \text{ if } N = 2, & (82d) \\ \text{or } 0 & (82e) \\ 0, \quad \text{for } i = j = 1 \text{ if } N = 1. & (82f) \end{cases}$$

The values of the parameters chosen in the $N = 2$-channel problem are $(\epsilon_i, v_i, \beta_i, \tilde{x}_i) = (0,2.0,1.8,0.8)$, $(0.5,1.0,1.5,1.0)$ for $i = 1,2$, respectively, and $\gamma_{1,2} = 0.5$, $\nu_{1,2} = 2.0$; $E = 1$ and the integration range $[x^0, x^\infty]$ is $[0,12]$. For the $N = 1$ problem, $E = (0.55)^2$, $\epsilon_1 = 0$, $\gamma_1 = -2$, $\nu_1 = 1$, and $[x^0, x^\infty] = [0,20]$. The bases $\underset{N\times M}{\mathbf{B}}(x)$ and $\underset{N\times M}{\overline{\mathbf{B}}}(x)$, $\mathbf{B} = \overline{\mathbf{B}}$, used in the tests are of the form

$$\mathbf{B}(x) = \mathbf{I} \otimes \mathbf{b}(x), \quad (83)$$

TABLE II. Accuracy test of the nonhybrid[a] (nH) and hybrid (H) log-derivative algorithms for the $\mathbf{J}^{-,-}$ integral on the distorted-wave version of the Secrest–Johnson problem [cf. Eqs. (76), (78), and (79)].

Parameters		Energy	Step size	Error of $P_{0\to1}$[c] $\lvert P^{\text{calc}}_{0\to1}/P^{\text{exact}}_{0\to1} - 1\rvert/h^4$		
m	α	E	h[b]	nH	H	$P^{\text{exact}}_{0\to1}$[d]
2/3	0.3	8.0	0.2	0.58(−1)[e]	0.20(−1)	0.354 12
		10.8365		0.11(+1)	0.32(−1)	1.233 97
		12.8365		0.16(+1)	0.41(−1)	2.174 13
1/13	0.1287	6.0	0.4	0.29(−2)	0.30(−3)	0.030 72
		6.0	0.2	0.29(−2)	0.30(−3)	
		8.0		0.60(−2)	0.49(−3)	0.110 81
		12.8365		0.20(−1)	0.94(−3)	0.474 61
		16.8365		0.24(−1)	0.13(−2)	0.889 13
		18.8365		0.46(−1)	0.15(−2)	1.119 88
		18.8365	0.1	0.40(−1)	0.15(−2)	
5/4	0.2973	12.7882		0.49(+1)	0.64(−1)	1.041 89

[a] The purely approximate-solution version of Ref. 43.
[b] The integration range was [−30, 170] in the cases with $\alpha = 0.1287$ and [−20. 80] in the remaining cases.
[c] The probability of the $v = 0 \to v = 1$ excitation.
[d] Obtained by the Jackson-Mott formula (Refs. 49 and 50).
[e] The numbers in parentheses denote powers of 10.

$$(\mathbf{b})_i = x^i \exp(-\alpha x), \quad \text{for } i = 1,2,...,m, \quad N \times m = M. \tag{83a}$$

Mean-square relative errors of the reactance matrices obtained from the variational expressions $\tilde{\mathscr{R}}^n_{i,j}(B,B)$ with $n \leqslant 3$,

$$\text{error } (\mathscr{R}) := \left\{ \sum_{k,l=1}^{N} (\mathscr{R}^{\text{cal}}_{k,l}/\mathscr{R}^{\text{exact}}_{k,l} - 1)^2 \right\}^{1/2} / N^2, \tag{84}$$

where $\mathscr{R}^{\text{cal}}_{k,l} := (\tilde{\mathscr{R}}^n_{i,j})_{k,l} = (\hat{\mathscr{R}}^n_{j-1,i+1})_{l,k}$ are plotted vs the number of the basis functions used in these expressions in Figs. 1–3. $\mathscr{R}^{\text{exact}} = 2.200\,38$ for the $N = 1$-channel problem and

$$\mathscr{R}^{\text{exact}} = \begin{pmatrix} 2.246\,47 & -0.221\,17 \\ -0.221\,17 & 1.689\,19 \end{pmatrix}$$

for the $N = 2$-channel problem.

Figure 1 gives a comparison of convergence rates yielded on the one-channel problem by the expressions $\hat{\mathscr{R}}^0_{0,1}$, $\tilde{\mathscr{R}}^0_{1,1}$, and $\tilde{\mathscr{R}}^1_{3,3}$ corresponding to the method of moments, the Schwinger, and the Newton methods, respectively, for two values of the nonlinear parameter in the basis functions $\alpha = 1.5$ and $\alpha = 0.5$. The relations shown between the methods are perfectly clear if analyzed along the lines given in Sec. III. The expression $\tilde{\mathscr{R}}^1_{3,3}$ as the proper first-order counterpart of the expression $\tilde{\mathscr{R}}^0_{1,1}$—in the sense of involving expansions of the same quantities (cf. Table I)—yields better convergence in both cases. The relation between the method of moments and the Schwinger method changes, however, essentially with the value of α as it concerns the expressions based on expansions of different quantities. Since the maxima of the subsequent functions in the basis $\mathbf{b}$ are shifted by a distance equal to $1/\alpha$, it is obvious that for approximating the wave function in the Schwinger method a smaller α should be used than for assuring simultaneously a good representation of the wave function and of the localized amplitude density, as required in the method of moments. The

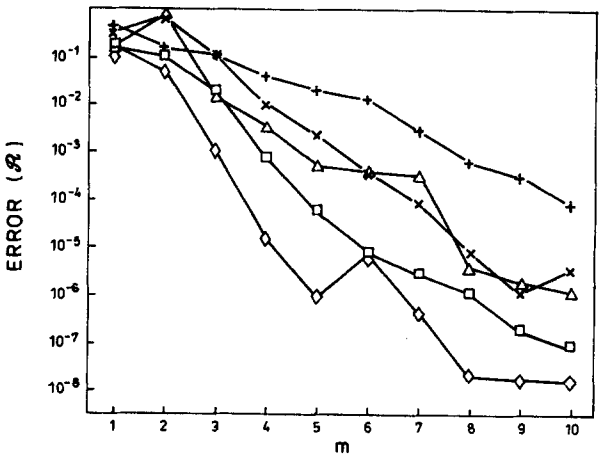

FIG. 2. The best convergence rates yielded on the $N = 2$-channel problem, Eqs. (82), (82a), (82c), and (82e) by the asymmetric expressions $\hat{\mathscr{R}}^0_{0,1}$ (+) and $\tilde{\mathscr{R}}^1_{2,3}$ (×), and by the symmetric expressions $\tilde{\mathscr{R}}^0_{1,1}$ (△), $\tilde{\mathscr{R}}^1_{3,3}$ (◇), and $\tilde{\mathscr{R}}^1_{2,2}$ (□). The values of the parameter α are 3.4, 3.4, 1.0, 1.0, and 3.0, respectively.

convergence in the Schwinger method is the best and superior to the convergence of the method of moments when $\alpha = 0.5$. It worsens systematically with increasing the value of α, i.e., when the basis becomes more and more localized near the origin. The fastest convergence in the method of moments is achieved with $\alpha = 1.5$. This convergence is better than the convergence in the Schwinger method obtained with the same α, but definitely worse than the convergence obtained with α optimal for this method (compare the respective full lines in Fig. 1). The last fact testifies undoubtedly to the superiority of the symmetric expression of the Schwinger method $\tilde{\mathscr{R}}^0_{1,1}$ over the asymmetric expression of the method of moments $\hat{\mathscr{R}}^0_{0,1}$. This conclusion contradicts

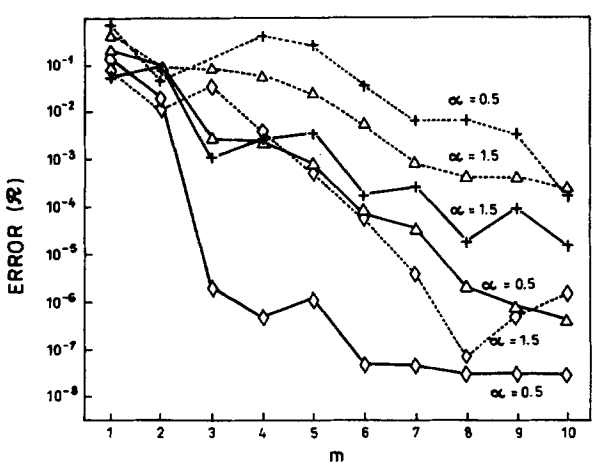

FIG. 1. Mean-square relative errors of the reactance matrix [Eq. (84)] yielded on the $N = 1$-channel problem, Eqs. (82), (82b), and (82f), by the expressions $\hat{\mathscr{R}}^0_{0,1}$ (+), $\tilde{\mathscr{R}}^0_{1,1}$ (△), and $\tilde{\mathscr{R}}^1_{3,3}$ (◇) vs the basis length [cf. Eq. (83) and (83a)] for two values of the parameter α. The value $\alpha = 1.5$ gives the best convergence of the expression $\hat{\mathscr{R}}^0_{0,1}$ and the value $\alpha = 0.5$ is optimal for the expressions $\tilde{\mathscr{R}}^0_{1,1}$ and $\tilde{\mathscr{R}}^1_{3,3}$.

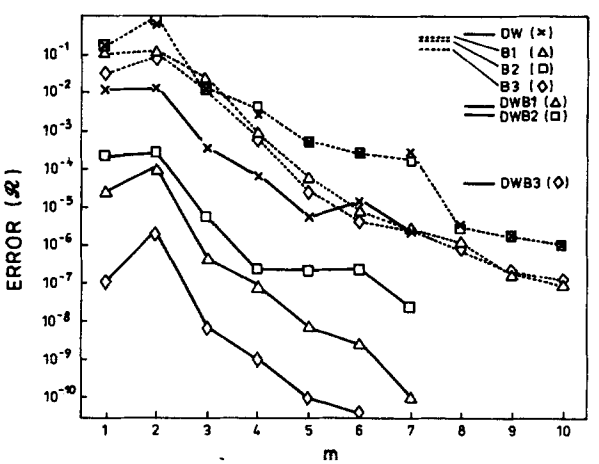

FIG. 3. Convergence rates yielded by the expressions $\hat{\mathscr{R}}^0_{1,1}$ (×), $\tilde{\mathscr{R}}^2_{3,3}$ (□), $\tilde{\mathscr{R}}^1_{2,2}$ (△), and $\tilde{\mathscr{R}}^3_{4,4}$ (◇) on the $N = 2$-channel problem with the distortion potential [Eq. (82d)]—the full lines—and without the distortion potential—the dotted lines. The values of α used (close to) optimal for the four expressions are 1.0, 1.0, 3.0, and 3.0, respectively. The convergence of the related distorted-wave Born and Born series is shown in the right side of the figure.

the conclusion of Ref. 5 drawn from tests on the same model. As an explanation, one should state that the values of α used preferably in those investigations $\alpha = 2.5$, 1.5 favor expansion of the amplitude density.

In Fig. 2 are shown the best convergence rates yielded on the two-channel problem with $\mathbf{V}_0 = \mathbf{0}$ by the asymmetric expression $\hat{\mathscr{R}}^0_{0,1}$ and $\hat{\mathscr{R}}^1_{1,3}$, and by the symmetric expressions $\tilde{\mathscr{R}}^0_{1,1}$, $\tilde{\mathscr{R}}^1_{3,3}$, and $\tilde{\mathscr{R}}^1_{2,2}$. The expression $\hat{\mathscr{R}}^1_{1,3}$ is the first-order counterpart of the expression $\hat{\mathscr{R}}^0_{0,1}$ [cf. Eq. (33)] in the same sense as used above in the case of the expressions $\tilde{\mathscr{R}}^1_{3,3}$ and $\tilde{\mathscr{R}}^0_{1,1}$. Thus, it is not surprising that the optimal values of the parameter α are the same for both expressions within these two pairs. Again, the first-order expressions $\hat{\mathscr{R}}^1_{1,3}$ and $\tilde{\mathscr{R}}^1_{3,3}$ converge faster than their lower-order counterparts $\hat{\mathscr{R}}^0_{0,1}$ and $\tilde{\mathscr{R}}^0_{1,1}$, respectively, and, among the expression of the same order, the symmetric expressions are superior to the asymmetric ones. A new contribution to the discussion follows from comparing the two symmetric expressions of the same order $\tilde{\mathscr{R}}^1_{3,3}$ and $\tilde{\mathscr{R}}^1_{2,2}$, which correspond to the two versions of the Newton method involving expansions of the wave function and of the amplitude density, respectively. Superiority of the wave function version is clearly seen in Fig. 2. In order to give an explanation to it, one should resort to the relations (26)–(28), which applied to the present case give

$$\tilde{\mathscr{R}}^1_{3,3}(\mathbf{B},\mathbf{B}) = \tilde{\mathscr{R}}^1_{2,2}(\mathbf{VB},\mathbf{VB}) \quad (\mathbf{V} = \mathbf{V} - \mathbf{V}_0).$$

This means, of course, that both versions of the method would perform identically if the basis used in the expression $\tilde{\mathscr{R}}^1_{3,3}$ were multiplied by the potential matrix before inserting it into the expression $\tilde{\mathscr{R}}^1_{2,2}$. Interpreted less literally, the above relation says that given basis $\mathbf{B}$, serving to represent the product of the matrices $\mathbf{V}$ and ψ in the amplitude density version, has to account for a larger amount of information than in the wave function version, where it serves to approximate only the matrix ψ and the relation of this matrix to the amplitude density matrix, ξ ($= \mathbf{V}\psi$), is treated exactly. Only in cases exceptionally simple, such as the one-channel problem considered above, the basis of the form (83) is capable of fulfilling equally well both roles. This is because in this problem the replacement $\mathbf{B} \rightarrow \mathbf{VB}$ is only a matter of shifting appropriately the parameter α. (This is also why the results shown in Fig. 1 as obtained by the wave function version with $\alpha = 0.5$ and 1.5 coincide with the results presented in Ref. 5 as obtained by the amplitude density version with $\alpha = 1.5$ and 2.5, respectively). Obviously, in multichannel cases or even in one-channel cases, but with potentials, e.g., of Morse type, the higher requirements of the amplitude density version are harder to meet with bases of simple forms. This must result, of course, in lower convergence rates of this version in comparison to the wave function version.

Superior convergence properties of the wave function version of the Newton method on one-channel test problems were noticed and discussed for the first time in Ref. 6.

Figure 3 is enclosed to compare convergence properties of the Takatsuka–McKoy expression $\tilde{\mathscr{R}}^2_{3,3}$ [cf. Eq. (34)] and of its amplitude density analog $\tilde{\mathscr{R}}^3_{4,4}$ [cf. Eq. (35)] with properties of the Schwinger $\tilde{\mathscr{R}}^0_{1,1}$ and of the Newton $\tilde{\mathscr{R}}^1_{2,2}$ expressions, respectively. Though such a comparison does not match the scheme of testing the methods proposed in Sec. III, the motivation for it comes from the particular connection which exists between the quantities expanded in these two sets of expressions (cf. Table I). Whereas expansions of the total wave function and of the total amplitude density function are involved in the expressions $\tilde{\mathscr{R}}^0_{1,1}$ and $\tilde{\mathscr{R}}^1_{2,2}$, respectively, only the scattered parts of these functions $\tilde{\Psi} := \Psi - \psi = G\mathcal{V}\Psi$ and $\tilde{\xi} := \xi - \mathcal{V}\psi = \mathcal{V}G\xi$ are represented in a basis, i.e., treated approximately, in the expressions $\tilde{\mathscr{R}}^2_{3,3}$ and $\tilde{\mathscr{R}}^3_{4,4}$, respectively. This gives a good reason to expect that the latter expressions are better suited than the former to problems in which the scattered functions are only small corrections to respective unscattered functions or, in other words, for which the Born series converges well. The above two-channel problem with the distortion potential $\mathbf{V}_0$ chosen in the form (82d) can be considered a problem of such type where the role of unscattered functions is played by respective distorted-wave solutions. The results of the tests performed on this problem with the four expressions are represented in Fig. 3 by the points joined with the full lines. It is demonstrated that almost no change in convergence rate with the basis length, but a considerable improvement in overall accuracy of the calculated reactance matrices can be achieved if the expression $\tilde{\mathscr{R}}^2_{3,3}$ is used instead of $\tilde{\mathscr{R}}^0_{1,1}$ or the expression $\tilde{\mathscr{R}}^3_{4,4}$ instead of $\tilde{\mathscr{R}}^1_{2,2}$. The superior accuracy of the expressions $\tilde{\mathscr{R}}^2_{3,3}$ and $\tilde{\mathscr{R}}^3_{4,4}$ originates indeed in the accuracy and high convergence rate of the related distorted-wave Born (DWB) series which is also demonstrated in Fig. 3. The difference in errors between the reactance matrices obtained in the DWB2 and in the DW approximations is close to the distance between the lines representing the errors of the matrices obtained from the expressions $\tilde{\mathscr{R}}^2_{3,3}$ and $\tilde{\mathscr{R}}^0_{1,1}$; a similar relation can be noticed between the errors of the DWB3 and the DWB1 approximations and the errors yielded by the expressions $\tilde{\mathscr{R}}^3_{4,4}$ and $\tilde{\mathscr{R}}^1_{2,2}$. Obviously, the subtraction of the unscattered wave or amplitude density functions which is, in a rough description, the way the expressions $\tilde{\mathscr{R}}^2_{3,3}$ and $\tilde{\mathscr{R}}^3_{4,4}$ have been derived from the expressions $\tilde{\mathscr{R}}^0_{1,1}$ and $\tilde{\mathscr{R}}^1_{2,2}$, respectively, should not be expected to lead to any significant improvement in cases characterized by slow convergence of the Born or distorted-wave Born series. This is confirmed by the results of the tests performed on the two-channel problem in the formulation not using the distortion potential, i.e., with $\mathbf{V}_0 = 0$ (the dotted lines in Fig. 3), for which the Born series converges poorly. Slow convergence of the Born series for the one-channel problem used in the tests of Ref. 5 is the reason why the advantages of the Takatsuka–McKoy expressions could not be noticed in those investigations.

C. Solving variationally the BKLT equations. An illustration of usefulness of the log-derivative algorithms in reactive scattering calculations.

The test problem is the collinear $\mathrm{H} + \mathrm{H}_2 \rightleftarrows \mathrm{H}_2 + \mathrm{H}$ reaction described by the Hamiltonian

$$\mathscr{H}(x_c,y_c) = -\hbar^2/(2\mu)(\partial^2/\partial x_c^2 + \partial^2/\partial y_c^2) + \bar{\mathcal{V}}(x_c,y_c), \tag{85}$$

where $\bar{\mathcal{V}}$ denotes the electronic energy potential surface for

the three H atoms (the Porter–Karplus potential[51] was used in the tests). The detailed definition of the (x_c,y_c) coordinates for the two arrangements in this reaction $c=\alpha,\beta$ as well as the formula for the angle of the kinematic rotation

$$\begin{pmatrix} x_\beta \\ y_\beta \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos\chi & \sin\chi \\ -\sin\chi & \cos\chi \end{pmatrix} \begin{pmatrix} x_\alpha \\ y_\alpha \end{pmatrix} \tag{86}$$

can be found, e.g., in Ref. 8.

As Eqs. (78) imply, the potential $\bar{\mathscr{V}}$ is partitioned in each arrangement channel into vibrational, distortion, and exchange potentials

$$\bar{\mathscr{V}} = V^c_{\rm vib} + \mathscr{V}^c = V^c_{\rm vib} + V^c_0 + V^c, \quad \text{for } c=\alpha,\beta, \tag{87}$$

where

$$V^c_{\rm vib}(y_c) = \bar{\mathscr{V}}(x^\infty_c,y_c), \quad \text{for } y_c\in[y^0_c\simeq 0, y^{\max}_c].$$

$[y^0_c,y^{\max}_c]$ denotes the range of the y_c coordinate which is important for dynamics of the process at given energy (well below the three-body dissociation limit). The following two choices of the distortion potentials were considered:

$$\text{(i)}\quad V^c_0(x_c) = \bar{\mathscr{V}}(x_c,y^{\rm eq}_c) - V^c_{\rm vib}(y^{\rm eq}_c), \tag{88}$$

where $y^{\rm eq}_c$ denotes the position of the minimum of $V^c_{\rm vib}$ (cf. Ref. 8);

$$\text{(ii)}\quad V^c_0(x_c,y_c) = \begin{cases} \bar{\mathscr{V}}(x_c,y_c) - V^c_{\rm vib}(y_c), & \text{for } y_c\in[y'(x_c),y''(x_c)] \\ V^c_0[x_c,y'(x_c)], & \text{for } y_c\in[y^0_c,y'(x_c)] \\ V^c_0[x,y''_c(x_c)], & \text{for } y_c\in[y''(x_c),\min(y^{\max}_c,x_c\tan\chi)], \end{cases} \tag{89}$$

where $[y'_c(x_c),y''_c(x_c)]$ is an interval around the line $y_c(x_c)=y^{\rm eq}_c$ chosen as follows:

$$y'_c(x_c) = 0.75y^{\rm eq}_c,$$

$$y''_c(x_c) = \begin{cases} y^{\rm eq}_c + 0.25y^{\rm eq}_c(x_c - x^{\rm eq}_c)/(x^e_c - x^{\rm eq}_c), \\ \quad \text{for } x_c\in[x^0_c,x^e_c] \\ 1.25y^{\rm eq}_c, \quad \text{for } x_c\in[x^e_c,x^\infty_c]. \end{cases} \tag{89a}$$

$[x^0_c,x^e_c]$ is the range of the x_c coordinate where exchange interaction occurs (i.e., $V^c\neq 0$). The coordinates $x^{\rm eq}_\alpha$ and $x^{\rm eq}_\beta$ correspond to the point of intersection of the lines $y_\alpha(x_\alpha) = y^{\rm eq}_\alpha$ and $y_\beta(x_\beta)=y^{\rm eq}_\beta$. The values used in the tests are $x^0_c = 0.7$ Å, $x^e_c = 2.5$ Å, and $x^\infty_c = 9.5$ Å for $c=\alpha,\beta$.

The BKLT equations are examples of the generalized L–S equations (cf. Sec. III) which correspond to the use of the channel permuting coupling scheme in construction of the matrix potentials. For the present problem, this scheme gives

$$V = \begin{pmatrix} 0 & V^\alpha \\ V^\beta & 0 \end{pmatrix}, \quad V^\dagger = \begin{pmatrix} 0 & V^\beta \\ V^\alpha & 0 \end{pmatrix}. \tag{90}$$

The equations with the potentials V and $V^\dagger$ were solved for the reactance matrices using the expressions of the method of moments $\hat{\mathscr{R}}^0_{0,1}$ and ${}_+\hat{\mathscr{R}}^0_{0,1}$, respectively, and also the expression $\tilde{\mathscr{R}}^0_{1,1}$ or ${}_+\tilde{\mathscr{R}}^0_{1,1}$ of the Schwinger method. Since both expressions of the two methods should converge in principle to the same result, the reactance matrices obtained with the given basis were subject to a symmetrization such as the following:

$${}_1\hat{\mathscr{R}}^0_{0,1} := [\hat{\mathscr{R}}^0_{0,1}(B,B) + {}_+\hat{\mathscr{R}}^0_{0,1}(B,B)]/2. \tag{91}$$

It should be stressed, however, that this operation gives strictly symmetric reactance matrices only in the case of the Schwinger method which is a consequence of relation (25). Because of the same relation, separate evaluation of the expression ${}_+\tilde{\mathscr{R}}^0_{1,1}$ becomes unnecessary. This reduces, of course, the number of the transition amplitudes which have to be evaluated. Namely, two second-order amplitudes

$$(\hat{T}^2_{B,B})^{\alpha\beta} = ({}_+\mathbf{V}^{\beta\alpha}|\mathbf{G}^\beta\mathbf{B}^\beta)_\beta$$

and $({}_+\hat{T}^2_{B,B})^{\alpha\beta} = (\mathbf{V}^{\beta\alpha}|\mathbf{G}^\beta\mathbf{B}^\beta)_\beta$

and three first-order amplitudes

$$(\hat{T}^1_{\psi,B})^{\beta\beta} = ({}_+\hat{T}^1_{\psi,B})^{\beta\beta}, \ ({}_+T^1_{\psi,B})^{\beta\alpha},$$

and $(T^1_{\psi,B})^{\beta\alpha}$,

have to be evaluated to determine the matrix ${}_1\tilde{\mathscr{R}}^0_{0,1}$, and only one second-order transition amplitude

$$(T^2_{B,B})^{\alpha\alpha} = ({}_+\mathbf{V}^{\beta\alpha}|\mathbf{G}^\beta\mathbf{V}^{\beta\alpha})_\beta,$$

in addition to the three first-order amplitudes $(T^1_{\psi,B})$, $({}_+T^1_{\psi,B})^{\beta\alpha}$, and $(T^1_{B,B})^{\beta\alpha}$ is necessary for calculating the matrix ${}_1\tilde{\mathscr{R}}^0_{1,1}$. (Obviously, twice as many amplitudes would be necessary for asymmetric reactive systems.) The translational bases $\mathbf{B}^c(x_c)$ for $c=\alpha,\beta$ were chosen in the form

$$\mathbf{B}^c(x_c) = \mathbf{I}^c \otimes \mathbf{b}^c(x_c),$$

$$(\mathbf{b}^c)_i = [2/(x^e_c - x^0_c)]^{1/2}\sin[i\pi(x_c - x^0_c)/(x^e_c - x^0_c)],$$

$$\text{for } i = 1,\ldots,m. \tag{92}$$

In evaluation of the transition amplitudes, $L=75$ and $\bar{L}=140$ sectors were used in the exchange $[x^0_\beta,x^e_\beta]$ and in the inelastic $[x^e_\beta,x^\infty_\beta]$, regions of the x_β coordinate, respectively.

All the reactance matrices generated both the symmetrized and the unsymmetrized were converted to the corresponding probability matrices and the accuracy of the latter was estimated relative to the results yielded by the standard approaches, i.e., based on the ordinary Schrödinger equation like the R matrix propagation method,[41,52] using the following error formula:

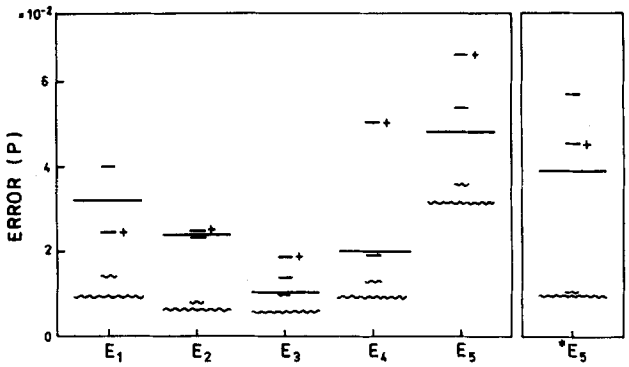

FIG. 4. Variational solutions of the BKLT equations for the collinear $H + H_2 \rightleftarrows H_2 + H$ reaction. Errors of the probability matrices [Eq. (93)] obtained by the method of moments with the matrix potentials $V(-)$ and $V^{\dagger}(-+)$ [Eq. (90)] and by the Schwinger method ($\sim$). The longer straight and waved lines show errors of the symmetrized results obtained from the matrices ${}_1\hat{\mathscr{R}}^0_{0,1}$ and ${}_1\hat{\mathscr{R}}^0_{1,1}$, respectively. E_i for $i = 1,\ldots, 5$ denote the following values of the total energy (measured from the bottom of the potential valley corresponding to infinite separation of H and H_2): 0.897 60, 1.0, 1.1, 1.2, and 1.3966 eV. $N^{\beta}_0(=N^{\alpha}_0) = 2$ for E_i with $i = 1,\ldots, 4$ and $N^{\beta}_0(=N^{\alpha}_0) = 3$ for E_5. The asterisk means that the multichannel distortion potential [Eq. (89)] was used in the calculation. In all cases $N^{\beta}(=N^{\alpha}) = 8$ vibrational and $m = 10$ translational basis functions [cf. Eq. (92)] were employed.

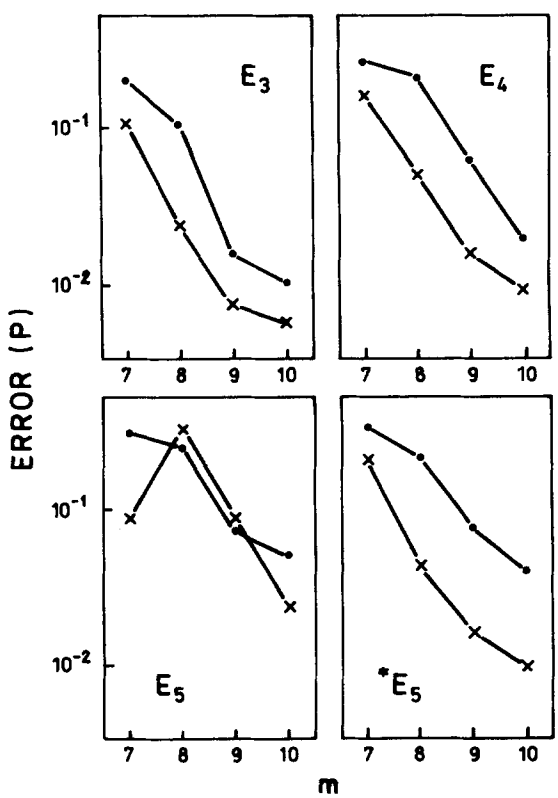

FIG. 5. Covergence with the translational basis size of the symmetrized results obtained by the method of moments (●) and by the Schwinger method (×) in some of the cases shown in Fig. 4.

$$\text{error}\,(P) := \left\{ \sum_{C=\alpha,\beta} \sum_{i,j=1}^{N^{\alpha}_0} \left[P^{ac}_{i,j}/(P^{ac}_{i,j})_{\text{ref}} - 1 \right]^2 \right\}^{1/2} \Big/ \left[2(N^{\alpha}_0)^2\right], \quad N^{\alpha}_0 = N^{\beta}_0. \tag{93}$$

The errors of the symmetrized and of the unsymmetrized results obtained at five energies, mostly in the two open channel range, by the method of moments and by the Schwinger method with $m = 10$ translational and $N^{\beta}(=N^{\alpha}) = 8$ vibrational basis functions are compared in Fig. 4. A comparison of the two methods with respect to the convergence with the translational basis length is given in Fig. 5. Both figures demonstrate clearly the superiority of the Schwinger method. The errors of the probability matrices are reduced on an average by a factor of 2. This gain in accuracy may be considered not large, but it should be said that the tests performed, being to our knowledge the first attempt to implement the Schwinger variational principle to solving the BKLT equations, had only preliminary character. For example, no search for bases optimal for the two methods was made and, as demonstrated in the previous subsection, this might affect strongly the picture of relative accuracy of these methods. The second aspect of the tests concerned the use of multichannel distortion potentials in the numerical treatment of the BKLT equations. No attempts were made to give any prescription on how to find the best distortion potential, but the tests with the rather arbitrary choice (ii) indicate the effectiveness of using such potentials. Larger advantages in accuracy and in convergence rate than those demonstrated in Figs. 4 and 5 (compare the panels denoted by E_5 and $*E_5$) can certainly be expected in cases of reactive systems which behave less adiabatically than the $H_2 + H$ system outside the exchange region of the configuration space. The point to be stressed again is that with the log-derivative algorithm, the multichannel distortion potential (ii) could be treated equally as easily as the one-channel potential (i).

ACKNOWLEDGMENT

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