The coupled equations problem of the quantum theory of atom–diatom reactive scattering

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Various formulations of the coupled equations in the quantum theory of atom–diatom reactive scattering—based on the ordinary Schrödinger equation and on the generalized equations of the arrangement channel quantum mechanics—are summarized with emphasis on symmetry properties of these formulations. New simplified and/or symmetrized versions are presented of the coupled ordinary differential equations derived previously (using the mixed Jacobi/hyperspherical coordinates) from the two distinct generalized Schrödinger equations which incorporate the arrangement channel permuting and the Fock arrangement coupling scheme, respectively. Inhomogeneous coupled equations arising from the close-coupling description of some related half-collision processes are also included in the considerations. Numerical approaches to solution of the coupled equations problems are recapitulated. The log–derivative method is presented in various versions. The material included in the presentation supplements previous reviews on numerical methods for molecular scattering calculations in that: (i) more information is given on implementations of the invariant imbedding technique; and (ii) determination of scattering wave functions and evaluation of some first- and second-order transition amplitudes involving these functions are considered in addition to determination of the scattering matrices.

1. Introduction

In the description of molecular reactive scattering, the problem of accounting for the change of chemical identity between reagents and products is essential. Two formal approaches to this problem have become important in the quantum theory of atom–diatom reactive scattering. In the traditional *ordinary Schrödinger equation approach*, the difference between reagents and products is accounted for essentially by appropriate design of coordinate system, i.e., on the 'kinematical level' of description. In the approach offered by the arrangement channel quantum mechanics (for a recent review, see Kouri and Baer (1986)), called here the *generalized Schrödinger equation approach*, the problem of existence of different asymptotia in reactive collisions is resolved on the 'dynamical level', by intervening into the structure of the equation of motion.

Most of the coordinate systems which have been especially designed or adapted to description of atom–diatom reactive scattering fall into the category of natural reaction coordinates (Marcus 1966, Light 1971) or into the category of hyperspherical coordinates (Smith 1960a, b, Johnson 1980). The essential difference between these categories concerns construction of the so-called scattering coordinate. In general terms, this is a coordinate which measures the progress the collision system has made from (or to) the condensation stage to (or from) the fragmentation stage. There are, of course, three different atom–diatom fragmentations—arrangement channels—possible in a triatomic system and the three-atom dissociation channel which is usually excluded from consideration.

In the natural reaction coordinate systems, the scattering coordinate is defined separately for every atom–diatom arrangement channel, usually as an arc length along some reference curve in the space of relative configurations of the three atomic nuclei which is placed possibly close to the path of minimum electronic energy within a respective arrangement channel region ('tube') of this space. Obviously, when the Schrödinger equation for the nuclear motion on a given potential surface is solved in the natural reaction coordinates, the necessity arises for matching the solutions from the different arrangement channel tubes at some surfaces in the condensation (strong interaction) region of the configuration space. The natural reaction coordination systems have been particularly popular and useful in solving collinear models of reactive collisions (see the reviews: Walker and Light (1980), Kuppermann (1981), Baer (1982), Basilevsky and Ryaboy (1982)). In a rigorous description of reactive collisions, usefulness of the natural reaction coordinates approach has been found to be rather severely limited by considerable complexity and possible inaccuracies of the matching procedure.

In the hyperspherical coordinate systems, the scattering coordinate—the hyperradius—is defined to describe simultaneously all the fragmentation channels possible in a collision system. There is no need for troublesome matching of solutions arising in the strong interaction region. The hyperspherical coordinates become inadequate, however, in describing the system at the fragmentation stage, with atom and diatom fragments infinitely separated. This causes some complications in asymptotic analysis of solutions of the Schrödinger equation.

In the generalized Schrödinger equation approach, a decomposition of the total wavefunction into pieces—each describing only one atom–diatom arrangement channel—is made which corresponds, in a sense, to the division of the configuration space into the separate arrangement channel regions in the natural reaction coordinate-ordinary Schrödinger approach. The matching of the total wave function generated in the different arrangement channel regions is replaced with a coupling of the different arrangement channel components of the total wavefunction which is introduced explicitly into the generalized Schrödinger equation, usually in the form of potential-like terms. The choice of coordinate representation is not as essential for overall adequacy of description of reactive collision as in the case of the ordinary Schrödinger equation but it still matters a lot when the generalized equation is to be practically solved. Of some importance is the fact that each component of the total wavefunction may be represented in its own coordinate system, most suitable for describing a given atom–diatom arrangement. All the channel coordinate systems may have a common scattering coordinate or three different channel scattering coordinates may be employed.

Concerning practical approaches aimed at solving eventually the ordinary or the generalized Schrödinger equation, two categories of methods may be distinguished: *close-coupling methods* and *variational methods*. Actually, methods of both categories have been (or could have been) derived on a basis of some variational principle connected with the quantum-mechanical equations of motion. The difference lies in the assumed form of trial solutions of these equations, the 'best' of which is sought for by any individual method.

In the close-coupling methods, trial wavefunctions or their arrangement channel components are in the form of expansions in some basis functions which span the parts of the entire configuration space available to the collision system on surfaces with fixed values of the scattering coordinate or the parts of the particular arrangement channel

regions on surfaces with fixed values of respective channel scattering coordinates. The basis functions may be modified, stepwise or continuously, with changing the parameters of the surfaces and the expansion coefficients have to be, of course, functions of the scattering coordinate(s). For the coefficient functions which correspond to the actual (approximate) solution of the ordinary or of the generalized Schrödinger equation, sets of coupled equations—differential or integro-differential in cases with multiple scattering coordinates—are obtained. The number of equations in a set is made finite by retaining only the most closely coupled ones—the close-coupling approximation. Obviously, the strength of coupling depends on the shape of the potential surface, on properties of the basis functions and on the coordinate system employed. For usefulness of the close-coupling methods, it is important that a kind of (quasi-)separability exists in the collision system between motion along the scattering coordinate and motions along the remaining coordinates in the coordinate system chosen which allows truncation of the coupled equations to a small set.

In the variational methods, trial solutions are expanded in basis functions which describe all degrees of freedom of the collision system. From the condition of stationarity of the functional employed, sets of algebraic equations are obtained for the expansion coefficients. Since the choice of coordinates and of basis functions is not limited by any quasi-separability requirement these direct variational (algebraic) methods are potentially more flexible than the close-coupling methods in describing collision systems at the condensation stage and therefore are particularly suitable for reactive systems. Some remarkable research has been carried out in recent years on utilization of the algebraic approach in atom–diatom reactive scattering calculations. Methods have been developed using various versions of the Kohn principle, for the scattering S matrix (Zhang and Miller 1987, 1989), for the log–derivative matrix (Manolopoulos *et al.* 1989), and for the Wigner R matrix (Linderberg *et al.* 1989). These methods can be exploited to carry out calculations within the generalized as well as within the ordinary Schrödinger equation approaches. A parallel (actually an earlier) trend in the search for efficient algebraic methods for molecular reactive scattering calculations has been concerned with the generalized Lippmann–Schwinger equations rather than with the Schrödinger equations and has resulted in developing methods which use the Schwinger or Schwinger-like expressions for the reactance matrix (Schwenke *et al.* 1988, Zhang *et al.* 1988) and the methods based on the Newton variational principle (Schwenke *et al.* 1988, 1989) and on the scattering wave variational principle (Sun *et al.* 1990a, b).

The close-coupling methods, being undoubtedly the most powerful and convenient methods of investigating non-reactive molecular scattering processes (see Lester (1976)), have played the leading role in advancing the description of reactive atom–diatom collisions from the stage of collinear models to the present level of rigorous quantum-mechanical treatment in full dimensionality (see the reviews: Wyatt (1979), Walker and Light (1980), Schatz (1986)). These methods continue to be useful tools in the branch of reactive scattering investigations (see Pack and Parker (1987, 1989), Parker *et al.* 1987, Bačic *et al.* 1990, Darakjian *et al.* 1991) despite the rapid development and impressive achievements of the algebraic approach. Using a close-coupling method seems to be the most natural choice within the ordinary Schrödinger equation approach. Numerous formulations of the coupled equations for atom–diatom reactive scattering have appeared in the literature. Representative of the class of formulations using natural reaction coordinates and involving matching procedures are those by Elkowitz and Wyatt (1975) (see also Wyatt (1979)), by Schatz and

Kuppermann (1976) (see also Kuppermann (1981)), and by Walker *et al.* (1976) (see also Light and Walker (1976a), Walker and Light (1980)). Formulations using hyperspherical coordinates were proposed by Kuppermann and co-workers (Kuppermann *et al.* 1980, Kuppermann and Hipes 1986, Cuccaro *et al.* 1989), by Hauke *et al.* (1980) and Römelt (1980) for collinear reactions, and by Pack and Parker (1987, 1989).

Within the generalized Schrödinger approach, the close-coupling methods have had much less popularity. Several interesting attempts, however, have been made to derive coupled equations within this approach in an ordinary differential equation form (Diestler 1971, Stechel *et al.* 1979, Top and Shapiro 1983, Schwenke *et al.* 1987). Successful calculations based on one of such formulations (which also employs hyperspherical coordinates) have been reported by Schatz (1988).

There has been a considerable interest and a number of papers (Kulander and Light 1980, 1986, Band *et al.* 1981, Heather and Light 1982, 1983, Kouri and Truhlar 1989, Schatz 1989, Zhang and Miller 1990, Soares Neto and Linderberg 1991) devoted to extending the quantum-mechanical time-independent description of dynamics of triatomic systems on a single dissociative electronic energy potential surface to half-collision processes in these systems which are initiated by weak interactions between bound and dissociative states. Direct dissociation of triatomic molecules by weak matter–radiation interaction is an example of such processes. In the usual perturbation theory description, this is a first-order process with respect to the weak primary (matter–radiation) interaction.

There are also a variety of interesting physical processes amenable to a treatment on second-order perturbation theory level (see Singer *et al.* (1987, 1989), Lee and Freed (1989), Zhang and Miller (1990)) in which the system moves on a dissociative surface only at an intermediate stage and undergoes two (weak) transitions from and to bound states at initial and at final stages, respectively. Application of the close-coupling approximation to description of these first and second-order processes gives rise to some boundary value problems for inhomogeneous coupled equations (Band *et al.* 1981).

In the first part of this paper, the coupled (ordinary differential) equations problems for atom–diatom reactive scattering and for related half-collision and collision mediated processes are presented in forms general enough to account for all essential features and complexities (as compared with analogous problems for non-reactive scattering) which are associated with coordinate and basis set choices typical for the ordinary and for the generalized Schrödinger equation approaches. Thus, such points as curvilinearity and non-orthogonality of coordinates and non-orthonormality of bases are of concern. The procedure of scaling of basis functions (see Webster and Light (1989) and references therein) devised for lessening the impact of curvilinearity of coordinates on the structure of the coupled equations is briefly reviewed. Known and exploited so far in the context of the ordinary Schrödinger equation, the procedure is adapted here and demonstrated to also be useful in cases of the generalized equations. Emphasis in the presentation is, however, on symmetry properties of the coupled equations, especially of those arising from the generalized approach, as it is the aspect of great importance for its own as well as for the design of efficient numerical methods for solving these equations. In particular, self-adjointness of the coupled equations derived from the generalized Schrödinger equation in the Fock arrangement coupling scheme (Schwenke *et al.* 1987) is examined and a new intrinsically symmetric formulation of these equations is presented. The considerations on the coupled equations (included in Section 3) are preceded by a short introduction (Section 2)

providing some necessary details on the two—the ordinary and the generalized Schrödinger equations based—formalisms in application to description of atom–diatom reactive scattering.

The second part of this paper is devoted to numerical solution of the coupled equations. Some general remarks on this matter—a recapitulation of ideas involved in construction of adequate algorithms—are given in Section 4. Considerations of Sections 5.1. and 5.2. are concentrated essentially on one—the log–derivative—method which has found since its publication (Johnson 1973) innumerable applications to molecular scattering calculations (see Manolopoulos and Wyatt (1989), Bačic *et al.* (1990), Darakjian *et al.* (1991)) and which has been subjected in recent years to several modifications and generalizations (Mrugała and Secrest 1983a, b, Mrugała 1983, 1985, 1989, 1990, Manolopoulos 1986, 1988, Alexander *et al.* 1989a, b, Darakjian and Hayes 1990). Newly modified versions, among them—for direct evaluation of energy derivatives of the scattering matrices, and a new extension—to determination of scattering wavefunctions and of so-called 'half-integrated Green's functions' (see Schwenke *et al.* (1988), Sun *et al.* (1990))—are included in the present review with the hope of making the method even more useful (widely applicable). In Section 5.3., two other methods, widely used in close-coupling calculations, are reviewed briefly and compared with the log–derivative method.

2. The quantum-mechanical time-independent description of atom–diatom reactive scattering: an outline

The problem of interest here consists basically in solving the time-independent Schrödinger equation for relative motion of three atomic nuclei on a given electronic-energy potential surface V in the range of total energy E where different two-cluster fragmentation, i.e. atom–diatom arrangement channels are accessible but the three-atom dissociation channel is deeply closed (and therefore can be discarded)

$$(E - H)\Psi = 0. \tag{1}$$

The problem necessitates considering different asymptotia of the total Hamiltonian H, $H_{a'}^0$ which describe the two clusters of the three different arrangement channels, denoted hereafter with $a = \alpha, \beta, \gamma$, at infinite separation. As a kind of extrapolation of these asymptotic Hamiltonians to any finite atom–diatom separations, the channels Hamiltonians H_a are usually introduced

$$H_a = T + V_a, \qquad \text{for } a = \alpha, \beta, \gamma, \tag{2}$$

where T denotes the kinetic energy operator (after removal of the centre-of-mass term) and V_a is a part of the potential V which involves the potential of the respective diatom V_a^{vib}, and a distortion potential V_a^{dist}, i.e., $V_a = V_a^{\text{vib}} + V_a^{\text{dist}}$. By construction, the channel Hamiltonians mainly govern the non-reactive, i.e., elastic and purely inelastic, transitions in the collision system; for the transitions with atomic rearrangements, the potentials V^a, $V^a = V - V_a$ for $a = \alpha, \beta, \gamma$, become primarily responsible. The implied partitions of the total Hamiltonian are

$$H = H_a + V^a, \qquad \text{for } a = \alpha, \beta, \gamma, \tag{3}$$

where

$$H_a = H_a^0 + V_a^{\text{dist}}.$$

There are standard coordinate systems in the six-dimensional space of relative configurations of a three-body system in terms of which the particular channel Hamiltonians H_a for $a = \alpha, \beta, \gamma$ can be conveniently represented. These are the sets of scaled Jacobi coordinates (see, e.g., Smith (1960b)). To describe configurations of atoms in given atom–diatom arrangement channel a, two vectors are introduced in a laboratory fixed coordinate frame, $\mathbf{r}_a$ and $\mathbf{R}_a$, which join the atoms in the molecule and the centre of mass of the molecule with the unbounded atom, respectively, and are scaled by appropriate mass-dependent factors to give the kinetic energy operator T with one and channel independent reduced mass μ

$$T(\mathbf{R}_a, \mathbf{r}_a) = -\frac{\hbar^2}{2\mu}(\Delta_{\mathbf{R}_a} + \Delta_{\mathbf{r}_a}) = -\frac{\hbar^2}{2\mu}\Delta(\mathbf{R}_a, \mathbf{r}_a), \qquad \text{for } a = \alpha, \beta, \gamma. \tag{4}$$

The three sets of the vectors $(\mathbf{R}_a, \mathbf{r}_a)$ corresponding to the different channels 'a' are connected by orthogonal transformations—the kinematic rotations (Smith 1960b). Expressing the Laplacians $\Delta_{\mathbf{R}_a}$ and $\Delta_{\mathbf{r}_a}$ in the respective spherical coordinates of the vectors $\mathbf{R}_a$ and $\mathbf{r}_a$, $(R_a, \Theta_{\mathbf{R}_a}, \varphi_{\mathbf{R}_a})$ and $(r_a, \Theta_{\mathbf{r}_a}, \varphi_{\mathbf{r}_a})$, one can write the asymptotic Hamiltonian of the channel a

$$H_a^0 = \lim_{R_a \to \infty} H_a = \lim_{R_a \to \infty} H,$$

in the form

$$H_a^0(R_a, \bar{y}_a) = -\frac{\hbar^2}{2\mu}\frac{1}{R_a^2}\frac{\partial}{\partial R_a} R_a^2 \frac{\partial}{\partial R_a} + H_a^{\text{ro--vib}}(R_a, \bar{y}_a), \tag{5}$$

$$\bar{y}_a = (r_a, \hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a), \qquad \hat{\mathbf{r}}_a = (\Theta_{\mathbf{r}_a}, \varphi_{\mathbf{r}_a}), \qquad \hat{\mathbf{R}}_a = (\Theta_{\mathbf{R}_a}, \varphi_{\mathbf{R}_a}),$$

where the operator describing the unbounded motion in this channel, i.e., the motion along the R_a coordinate—the channel scattering coordinate, is clearly separated from the operator describing the bounded ro–vibrational motion

$$H_a^{\text{ro--vib}}(R_a, \bar{y}_a) = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r_a^2}\frac{\partial}{\partial r_a} r_a^2 \frac{\partial}{\partial r_a} - \frac{\hat{\mathbf{l}}^2(\hat{\mathbf{R}}_a)}{R_a^2} - \frac{\hat{\mathbf{j}}^2(\hat{\mathbf{r}}_a)}{r_a^2}\right) + V_a^{\text{vib}}(r_a). \tag{6}$$

$\hbar\hat{\mathbf{j}}$ and $\hbar\hat{\mathbf{l}}$ denote here the respective angular momentum operators associated with diatomic and with atom–diatom relative rotations. The form (5) of H_a^0 is basic for specifying the so called scattering boundary conditions for solutions of the Schrödinger equation (1), i.e. the form which the function Ψ should assume in the asymptotic regions of the configuration space corresponding in the three atom–diatom arrangement channels, defined as the regions where R_a goes to infinity while r_a remains finite for $a = \alpha, \beta, \gamma$.

Let $\Psi^{a'n'}$ be the solution which describes the collision process at energy E in the case when the initial arrangement of the system is a' and the initial inelastic channel within this arrangement is n'. n' is the collection of quantum numbers characterizing a bound state of $H_{a'}^{\text{ro--vib}}$. Let $\bar{\varepsilon}_{a'n'}$ denote the corresponding ro–vibrational energy of the a'th diatom. Now, let us introduce a vector

$$\underset{1 \times N_{\text{op}}^{a'}}{\Psi^{a'}},$$

consisting of the solutions $\Psi^{a'n'}$ which correspond to all open at the energy E channels $n'(\bar{\varepsilon}_{a'n'} < E)$. Denoting

$$\bar{\Psi}^{aa'} = \lim_{R_a \to \infty} \Psi^{a'}, \tag{7}$$

one can write

$$\bar{\Psi}^{aa'}(R_a, \bar{y}_a) = (\bar{c}_a)^{-1/2} \bar{\varphi}^a(\bar{y}_a)(\mathbf{m}^a(R_a)\delta_{a,a'} - \mathbf{n}^a(R_a)\mathbf{Y}^{aa'}). \tag{7a}$$

$\bar{c}_a(=R_a^2 r_a^2)$ is the factor coming from the Jacobian in the $(R_a, \bar{y}_a)$ coordinates, $J_a = \bar{c}_a \sin \Theta_{\mathbf{R}_a} \sin \Theta_{r_a}$. $\bar{\varphi}^a_{1 \times N^a}$ is a set of N^a eigenfunctions of the Hamiltonian $\tilde{H}_a^{\text{ro}-\text{vib}} = (\bar{c}_a)^{+1/2} H_a^{\text{ro}-\text{vib}}(\bar{c}_a)^{-1/2}$. More specifically, the functions in the set $\bar{\varphi}^a$ assume the form

$$(\bar{\varphi}^a)_n = \bar{\chi}_{\text{av}_n j_n}(r_a)\mathscr{Y}^{JM}_{l_n j_n}(\hat{r}_a, \hat{R}_a), \qquad n = (v, j, l), \tag{8}$$

with $\mathscr{Y}^{JM}_{lj}$ denoting the standard eigenfunctions of the angular part of $\tilde{H}_a^{\text{ro}-\text{vib}}$ in the total angular momentum representation (J, M, l, and j are the quantum numbers associated with the operators $\hat{\mathbf{J}}^2 = (\hbar\hat{\mathbf{j}} + \hbar\hat{\mathbf{l}})^2$, $\hat{J}_z$, $\hat{\mathbf{l}}^2$, and $\hat{\mathbf{j}}^2$, respectively) and with $\bar{\chi}_{\text{av}j}$ satisfying the vibrational equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r_a^2} + \frac{\hbar^2 j(j+1)}{2\mu r_a^2} + V_a^{\text{vib}}(r_a) - \bar{\varepsilon}_{\text{av}j} \right] \bar{\chi}_{\text{av}j}(r_a) = 0. \tag{8a}$$

$\mathbf{m}^a$ and $\mathbf{n}^a$ occurring in equation (7a) denote, respectively, regular and irregular solutions of the radial equation

$$\left(\mathbf{I}^a \frac{\mathrm{d}^2}{\mathrm{d}R_a^2} + \mathbf{k}_a^2 - \frac{1}{R_a^2} \mathbf{l}_a^2 \right) \mathbf{f}(R_a) = 0, \tag{9}$$

where

$$\mathbf{k}_a^2 = \frac{2\mu}{\hbar^2}(E\mathbf{I}^a - \bar{\varepsilon}_a), \tag{9a}$$

$\bar{\varepsilon}_a$ and $\mathbf{l}_a^2$ are diagonal matrices of the ro–vibrational energies $\bar{\varepsilon}_{an}$ and of the eigenvalues $l_n(l_n + 1)$ of the orbital angular momentum operator $\hat{\mathbf{l}}^2$, respectively. $\mathbf{I}^a$ is the $N^a \times N^a$ unit matrix.

$\mathbf{Y}^{aa'}$ in equation (7a) stands for a block of one of the standard matrices of the scattering theory $\mathbf{S}$, $\mathbf{T}$, or $\mathbf{K}$. Each of these matrices is connected with a definite form of the solutions $\mathbf{m}^a$ and $\mathbf{n}^a$ (see, e.g., Lester (1971)). In the case of the reactance matrix, i.e., when $\mathbf{Y}^{aa'} = \mathbf{K}^{aa'}$, the matrices $\mathbf{m}^a$ and $\mathbf{n}^a$ are constructed from the spherical Riccati–Bessel and Riccati–Neuman functions, respectively. The convenient normalization in this case (which will be assumed in the next Section) is

$$\mathbf{m}^a \left(\frac{\mathrm{d}}{\mathrm{d}R_a} \mathbf{n}^a \right) - \left(\frac{\mathrm{d}}{\mathrm{d}R_a} \mathbf{m}^a \right) \mathbf{n}^a = \mathbf{I}^a.$$

The matrix $\mathbf{Y}$ gives (directly or after a simple transformation) the probability amplitudes for all transition possible in the collision system at given energy E. So, by determining this matrix the scattering problem is essentially solved.

As mentioned in the Introduction, there are two formalisms which gives a choice within which solutions of the atom–diatom reactive scattering problem may be sought.

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In the first, the ordinary Schrödinger equation, equation (1), is directly dealt with; in the second, a generalized form of this equation becomes a central object (Evans *et al.* 1983)

$$(\mathbb{E} - \mathbb{H})\bar{\bar{\Psi}} = \mathbb{O}. \tag{10}$$

The Hamiltonian $\mathbb{H}$ in the generalized equation is a 3×3 matrix of operators $H^{aa'}$

$$(\mathbb{H})^{aa'} = H^{aa'}, \qquad \text{with } a, a' = \alpha, \beta, \gamma, \tag{10a}$$

which satisfy the condition

$$\sum_a H^{aa'} = H, \qquad \text{for } a' = \alpha, \beta, \gamma. \tag{10b}$$

$\mathbb{E} = E\mathbb{1}$, where $\mathbb{1}$ denotes the 3×3 matrix identity operator.

Any solution $\bar{\bar{\Psi}}$ of the generalized Schrödinger equation is a 3×1 vector of components Ψ^a with $a = \alpha, \beta, \gamma$ which summed up give a solution of the ordinary equation

$$\sum_a \Psi^a = \Psi, \qquad \text{or } \sum_a \Psi^a \equiv 0.$$

The generalized Hamiltonian is usually given in the form

$$\mathbb{H} = \mathbb{H}_0 + \mathbb{V}, \tag{11}$$

where

$$(\mathbb{H}_0)^{aa'} = \delta_{a,a'} H_a, \tag{11a}$$

and $\mathbb{V}$ is a matrix potential

$$(\mathbb{V})^{aa'} = V^{aa'}, \qquad \text{with } a, a' = \alpha, \beta, \gamma. \tag{11b}$$

The operators $V^{aa'}$ are constructed from the potentials V^a (see equation (3)) in a way guaranteeing the condition (10b) and meeting the requirement (which has been the motivation for developing the arrangement channel quantum mechanics)—that the related Lippmann–Schwinger equations have well-behaved kernels (i.e. amenable to approximations with finite rank kernels). A variety of possible constructions of $V^{aa'}$ is included in the following formula

$$V^{aa'} = W_{aa'} V^{a'}, \qquad \sum_a W_{aa'} = 1, \qquad \text{for any } a', \tag{12}$$

where $W_{aa'}$ are elements of a 3×3 matrix $\mathbb{W}$—the arrangement Channel Coupling Array (CCA)—introduced by Baer and Kouri (1973) (see also the reviews: Kouri (1985), Kouri and Baer (1986)). Most of the arrays $\mathbb{W}$ considered so far (Baer 1989) lead to non-symmetric matrices $\mathbb{V}$, i.e. $(\mathbb{V}^T)^{aa'} = V^{a'a} \neq V^{aa'}$. In particular, highly non-symmetric matrices $\mathbb{V}$ result from the use of the channel permuting arrays which are characteristic for (the original form of) the Baer–Kouri–Levin–Tobocman (BKLT) equations (see, for example, the review by Barrett *et al.* (1983)). An array leading to a symmetric generalized potential was proposed recently by Neuhauser and Baer (1988).

An important case of a generalized Hamiltonian is the Hamiltonian in which the matrix $\mathbb{V}$ couples the different arrangement channels according to the Fock (F) scheme (Schwenke *et al.* 1987, Zhand *et al.* 1988). In this case

$$V^{aa'} = \delta_{a,a'} V^a + (1 - \delta_{a,a'})(H - E). \tag{13}$$

Actually, the Fock scheme had been used in nuclear physics (for references, see for example, Adhikari (1983)) and in electron scattering theory (see, e.g., Burke and Seaton (1971)) and introduced into the field of molecular reactive scattering (Micha 1965, Miller 1969) long before the arrangement channel mechanics arose (Kouri *et al.* 1977, Evans *et al.* 1981, 1983). The Hamiltonian in the Fock scheme does not always satisfy the mathematical requirements of this theory but has the advantage of being always Hermitian (Tobocman 1975, Adhikari 1983).

In connection with description of the half-collision processes in triatomic systems and of the second-order collision mediated processes mentioned in the Introduction, evaluation of the following (standing wave) transition amplitudes, $\mathbf{K}^b$ and $K^{\bar{b}b}$, respectively, will be considered in further parts of this paper

$$\mathbf{K}^b = \langle \Psi | X \zeta^b \rangle, \tag{14}$$

$$K^{\bar{b}b} = \left\langle \zeta^{\bar{b}} | \bar{X} \left(\text{p.v.} \frac{1}{E-H} \right) X \zeta^b \right\rangle, \tag{15}$$

Ψ denotes here the set of the scattering states (see quation (7))

$$\Psi_{1 \times N_{\text{op}}} = \left(\Psi^\alpha_{1 \times N^\alpha_{\text{op}}}, \quad \Psi^\beta_{1 \times N^\beta_{\text{op}}}, \quad \Psi^\gamma_{1 \times N^\gamma_{\text{op}}} \right),$$

ζ^b and $\zeta^{\bar{b}}$ are triatomic bound states. X and $\bar{X}$ denote the interactions between the bound and the scattering states and 'p.v.' is the abbreviation of 'principal value'.

3. Symmetric formulation of the coupled equations problem

3.1. *The ordinary Schrödinger equation approach*

Let us start with a sketchy derivation of the coupled equations and, following original papers on this matter (Burke *et al.* 1962, 1966), let us present the derivation as being based on the Kohn variational principle (Kohn 1948). The formulation of this principle for the matrix $\mathbf{K}$ will be convenient here.

Let Ψ denote a row vector of exact solutions (in any coordinate representation) of the Schrödinger equation (1) which satisfy the boundary conditions with the matrix $\mathbf{K}$, described (in the Jacobi coordinates representation) in the previous section. The Kohn principle states that the following functional $[K]$

$$[K] = \mathbf{K}_{t_1} + \frac{2\mu}{\hbar^2} \langle \Psi_{t_2} | (E-H) \Psi_{t_1} \rangle, \tag{16}$$

is stationary around its exact value, $\mathbf{K}$, with respect to variations of the exact solutions, $\delta\Psi_i, \delta\Psi_i = \Psi_{t_i} - \Psi$ for $i = 1, 2$, of which the variation $\delta\Psi_2$ is completely arbitrary and the variation $\delta\Psi_1$ is restricted only by the requirement that the trial solution Ψ_{t_i} should satisfy the correct boundary conditions with the trial reactance matrix $\mathbf{K}_{t_i}$. Since the first variation of the functional $[K]$, $\delta[K]$, can be shown to assume the form

$$\delta[K] = \frac{2\mu}{\hbar^2} (\langle \delta\Psi_2 | (E-H) \Psi_{t_i} \rangle + \langle (E-H) \Psi_{t_2} | \delta\Psi_1 \rangle), \tag{17}$$

the condition of stationarity of $[K]$, $\delta[K] = 0$, becomes equivalent to the requirement of vanishing of the two (matrices of) integrals

$$\langle \delta\Psi_i | (E-H) \Psi_{t_i} \rangle = 0, \qquad \text{for } i = 1, 2. \tag{18}$$

For the present purpose, it suffices to consider only a single condition of the above form

$$I = \frac{2\mu}{\hbar^2} \langle \delta\Psi | (E-H)\Psi_t \rangle = 0, \tag{19}$$

where the omission of the subscript 'i' means that both the variation $\delta\Psi$ and the trial solution Ψ_t will be treated as completely arbitrary.

Let (x, y) be a system of suitable curvilinear, in general, coordinates in the configuration space of the atom–diatom system (i.e. in the space spanned by the Cartesian coordinates of the mass-scaled Jacobi vectors $\mathbf{R}_a$ and $\mathbf{r}_a$). x denotes a scattering coordinate in terms of which the coupled equations are to derive and y stands for a set of 'internal' coordinates. (y is, of course, a single coordinate when a collinear model of collision is assumed). Let us divide the set y into two subsets, $y = (q, \rho)$, in a way to be specified below. For a Laplacian in the (x, y) coordinates, the following general expression should be employed

$$\Delta = \frac{1}{J} P^{\mathrm{T}} J G P, \tag{20}$$

where $P^{\mathrm{T}}(P)$ denotes a row (column) vector of derivative operators

$$P^{\mathrm{T}} = (P_x, P_y^{\mathrm{T}}) = (P_x, P_q^{\mathrm{T}}, P_\rho^{\mathrm{T}}) = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial q_1}, \dots, \frac{\partial}{\partial \rho_1}, \dots \right),$$

G is the respective contravariant matrix tensor, and J is the Jacobian, $J = (\det G)^{-1/2}$.

The class of coordinate systems which are of interest in the context of close-coupling treatments of reactive scattering can be specified as follows:

  (i)   the Jacobian assumes the following factorized form

$$J = j(x, q)\sigma(\rho); \tag{21}$$

  (ii) the element G^{xx} is independent of any internal coordinate from the subset ρ, i.e.
$$G^{xx} = G^{xx}(x, q);$$

  (iii) among the internal coordinates from the subset q, there may be some which are non-orthogonal to the x coordinate, i.e. the block G^{xq} of the metric G is allowed not to vanish;

  (iv) apart from G^{xq} (and G^{qx}), all off-diagonal blocks of G, i.e. $G^{x\rho}$ and $G^{q\rho}$ (and their transposes) vanish.

The trial functions to be inserted into the integral I assume in the (x, y) coordinates the following 'separable' form

$$\text{A031G}_t(x, y) = \underset{1 \times N}{\check{\phi}(y; x)} \psi(x), \qquad \delta\Psi(x, y) = \check{\phi}(y; x)\delta\psi, \tag{22}$$

which involves (in the vector $\check{\phi}$) a set of given (usually real) basis functions in the space of internal coordinates. This makes possible a conversion of I to an integral over the scattering coordinate only

$$I = (\delta\psi | \mathscr{D}\psi), \tag{23}$$

with

$$\mathscr{D}\psi = \left(\check{\phi} \left| \frac{2\mu}{\hbar^2} (E-H)\Psi_t \right. \right]. \tag{23a}$$

The symbols $(\,|\,)$ and $(\,|\,]$ introduced here have the meaning

$$(Y|Z) = \int dx \, Y^T Z, \qquad (Y|Z] = \int J \, dy \, Y^T Z. \qquad (24)$$

In view of arbitrariness of $\delta\psi$, the desired coupled equations for the unknown (vector of) functions ψ follow from the condition (19)

$$\mathscr{D}\psi = 0. \qquad (25)$$

The ordinary differential operator $\mathscr{D}$ takes, in general, the form

$$\mathscr{D} = \sum_{k=0}^{n(=2)} \mathbf{a}_k(x) \frac{d^k}{dx^k}, \qquad (25\,a)$$

where $\mathbf{a}_k$ are real $N \times N$ matrices. The following features of $\mathscr{D}$ are desirable when designing efficient and accurate numerical methods for solving equation (25) is attempted:

  (i) that $\mathscr{D}$ should involve a possibly small number of coupling terms. Obviously, not only the size N of the matrices $\mathbf{a}_k$ is meant here but their structure too. Equations with $\mathbf{a}_2(x) \equiv \mathbf{I}$ and, possibly, with $\mathbf{a}(x) \equiv \mathbf{0}$ are of special interest.

  (ii) that $\mathscr{D}$ should be a formally self-adjoint differential operator (see Dunford and Schwartz (1963)), i.e.

$$\mathscr{D} = \mathscr{D}^\dagger, \qquad (26)$$

where

$$\mathscr{D}^\dagger \psi = \sum_{k=0}^{n(=2)} (-1)^k \frac{d^k}{dx^k} \mathbf{a}_k^T \psi. \qquad (26\,a)$$

The well-known Lagrange identity (see, for example, Hartman (1964))

$$\phi^T \mathscr{D}\psi - (\mathscr{D}^\dagger \phi)^T \psi = \frac{d}{dx}(W_{n(=2)}[\phi, \psi]), \qquad (27)$$

$$W_n[\phi, \psi] = \sum_{k=0}^{n} \sum_{j=0}^{k-1} (-1)^j (\phi^T \mathbf{a}_k)^{(j)} \psi^{(k-j-1)}, \qquad (27\,a)$$

(superscripts in parentheses denote hereafter derivatives with respect to x), which holds for any functions ψ and ϕ in domains of $\mathscr{D}$ and $\mathscr{D}^\dagger$, respectively, and yields in the case of the self-adjoint operator $\mathscr{D}$ the following relation for ψ and ϕ satisfying equation (25)

$$W_{n(=2)}[\phi, \psi] \equiv \text{const.} \qquad (28)$$

Satisfying this relation of conservation of the (generalized) Wronskian by solutions of the coupled equations (25) is essential for the approximate solutions Ψ_t of the original Schrödinger equation to satisfy strictly the microscopic reversibility and the flux conservation relations.

   Translated into properties of the matrices $\mathbf{a}_k$, self-adjointness of the operator $\mathscr{D}$ means

$$\mathbf{a}_2 = \mathbf{a}_2^T, \qquad \mathbf{a}_1 = \mathbf{a}_2^{(1)} + \tfrac{1}{2}(\mathbf{a}_1 - \mathbf{a}_1^T), \qquad \mathbf{a}_0 = \mathbf{a}_0^T - (\mathbf{a}_1^T)^{(1)} + \mathbf{a}_2^{(2)}. \qquad (29)$$

Obviously, assuring the properties (i) and (ii) simultaneously is the goal which should be kept in mind when the choice of coordinate system and of the basis functions is decided. A great deal can be achieved in this respect by scaling the total wavefunctions

(or equivalently, the basis functions) with a proper coordinate system dependent factor—the idea which has been exploited with particular success by Light and co-workers in their formulation of the coupled equations in natural reaction coordinates (Light and Walker 1976a, Stechel *et al.* 1988, Webster and Light 1989). Following the work of these authors, let us define the scaling factor c as

$$c = G^{xx}j, \tag{30}$$

scale with it the basis $\check{\phi}$

$$\check{\phi}(y, x) = [c(x, q)]^{-1/2} \varphi(y; x), \tag{30a}$$

and convert the scaled Laplacian, $c^{-1/2}\Delta c^{-1/2}$, to the form

$$c^{-1/2}\Delta c^{-1/2} = \frac{1}{J} P^{\mathrm{T}}\sigma\check{G}P - \frac{1}{J}\{c^{-1/2}P^{\mathrm{T}}\sigma\check{G}Pc^{+1/2}\}, \tag{30b}$$

where

$$\check{G} = \frac{1}{G^{xx}}G, \tag{30c}$$

and the curly parentheses are to indicate that the operators act only within them.

Exploiting further the assumptions made above on the (x, y) coordinate system and introducing yet another scalar product

$$[Y|Z] = \int \sigma \, dy \, Y^{\mathrm{T}}Z, \tag{31}$$

one can write $\mathscr{D}\psi$ of equation (23 a) in the form

$$\mathscr{D}\psi = \left[\varphi \left| \frac{2\mu}{\hbar^2} \frac{1}{G^{xx}}(E - \check{H})\varphi\psi \right. \right], \tag{32}$$

where

$$\check{H} = c^{1/2}Hc^{-1/2} = -\frac{\hbar^2}{2\mu}G^{xx}\left(\frac{1}{\sigma}P^{\mathrm{T}}\sigma\check{G}P - V^{\mathrm{ext}}\right) + V, \tag{32a}$$

with

$$V^{\mathrm{ext}} = \{c^{-1/2}P^{\mathrm{T}}\check{G}Pc^{1/2}\}. \tag{32b}$$

The following expressions can be easily obtained for the coefficient matrices $\mathbf{a}_k$ of the operator $\mathscr{D}$ (see equation (25 a))

$$\mathbf{a}_2(x) = \mathbf{S}(x), \qquad \mathbf{a}_1(x) = 2[\bar{\mathbf{A}}(x) + \mathbf{C}(x)], \qquad \mathbf{a}_0(x) = \bar{\mathbf{P}}(x) + \bar{\mathbf{B}}(x) + \check{\mathbf{W}}(x), \tag{33}$$

where

$$\mathbf{S} = [\varphi|\varphi], \qquad \bar{\mathbf{A}} = [\varphi|P_x\varphi], \qquad \bar{\mathbf{B}} = [\varphi|P_xP_x\varphi], \tag{33a}$$

$$\mathbf{C} = \tfrac{1}{2}[\varphi|(P_q^{\mathrm{T}}\check{G}^{qx} + \check{G}^{xq}P_q)\varphi], \tag{33b}$$

$$\bar{\mathbf{P}} = [\varphi|(P_x\bar{G}^{xq}P_q + P_q^{\mathrm{T}}\bar{G}^{qx}P_x)\varphi], \tag{33c}$$

$$\check{\mathbf{W}} = \left[\varphi \left| \frac{2\mu}{\hbar^2}\frac{1}{G^{xx}}(E - V)\varphi \right. \right] - [\varphi|V^{\mathrm{ext}}\varphi]$$

$$+ \left[\varphi \left| \left(P_q^{\mathrm{T}}\check{G}^{qq}P_q + \frac{1}{\sigma}P_\rho^{\mathrm{T}}\sigma\check{G}^{\rho\rho}P_\rho\right)\varphi \right. \right]. \tag{33d}$$

S is evidently a symmetric matrix. The matrix $\bar{\mathbf{W}}$ is also symmetric and the matrix $\mathbf{C}$ can be converted to the skew-symmetric form

$$\mathbf{C} = \tfrac{1}{2}([\varphi|\check{G}^{xq}P_q\varphi] - [\check{G}^{xq}P_q\varphi|\varphi]), \tag{33e}$$

provided the basis φ is such that the functions $\check{G}^{xq}\varphi$, $\check{G}^{qq}P_q\varphi$, and $\sigma\check{G}^{\rho\rho}P_\rho\varphi$ vanish at the boundary of the integration range over the internal coordinates (q, ρ). Concerning the other matrices, the following properties can be easily shown

$$\begin{rcases} \bar{\mathbf{A}} = \mathbf{A} + \tfrac{1}{2}\mathbf{S}^{(1)}, & \text{where } \mathbf{A} = \tfrac{1}{2}(\bar{\mathbf{A}} - \bar{\mathbf{A}}^{\mathrm{T}}), \\[2mm] \bar{\mathbf{B}} = \mathbf{A}^{(1)} + \tfrac{1}{2}\mathbf{S}^{(2)} - \mathbf{B}, & \text{where } \mathbf{B} = [P_x\varphi|P_x\varphi], \\[2mm] \bar{\mathbf{P}} = \mathbf{C}^{(1)} + \mathbf{P}, & \text{where } \mathbf{P} = \tfrac{1}{2}(\bar{\mathbf{P}} + \bar{\mathbf{P}}^{\mathrm{T}}). \end{rcases} \tag{34}$$

and

Thus,

$$\begin{rcases} \mathbf{a}_1 = 2(\mathbf{A} + \mathbf{C} + \tfrac{1}{2}\mathbf{S}^{(1)}), \\[2mm] \mathbf{a}_0 = \mathbf{W} + \mathbf{P} + \tfrac{1}{2}\mathbf{a}_1^{(1)}, & \text{where } \mathbf{W} = \bar{\mathbf{W}} - \mathbf{B}, \end{rcases} \tag{35}$$

and it is a simple matter to check that the self-adjointness relations (29) are satisfied. Due to the scaling (30)–(30 c), all the complications have been eliminated which the use of curvilinear coordinates might cause in the structure of the coupled equations except for that related to the non-orthogonality of these coordinates (the occurrence of the matrices $\mathbf{C}$ and $\mathbf{P}$). The extra potential-type coupling arising from the scaling, V^{ext} (see equation (32 b)), cannot be considered a complication, of course. The main achievement lies in that the matrix $\mathbf{a}_2$ becomes the unit matrix if only the basis φ is orthonormal with respect to the scalar product [|] (see equation (33 a)). The first derivative coupling, the matrix $\mathbf{a}_1$, may have three origins:

(i) non-orthogonality of the scattering coordinate to the internal coordinates,
(ii) non-orthonormality of the basis in the internal coordinates, and
(iii) 'non-diabaticity' of the basis, i.e. its (parametrical) dependence on the scattering coordinate.

Whereas non-orthogonal bases and coordinates can be easily avoided in formulation of the coupled equations for atom–diatom reactive scattering, within the ordinary Schrödinger approach the use of bases modified suitably along the scattering coordinate is essential for keeping the number of these equations on a reasonable level (Walker and Light 1980). Indeed, all the well-known formulations of this category (Elkowitz and Wyatt 1975, Schatz and Kupperman 1976, Walker *et al.* 1976, Pack and Parker 1987, Cuccaro *et al.* 1989) do employ orthogonal coordinates and orthogonal but non-diabatic bases.

Formulation of the coupled equations problem is completed by specifying appropriate boundary conditions for the solutions $\psi(x)$. Let $\Psi^{a'}(x, y)$ be the set of the trial functions Ψ_t which are to describe the collision process at given energy E for all possible (open) initial inelastic channels in the system being initially in the arrangement channel a'

$$\underset{1 \times N_{\mathrm{op}}^{a'}}{\Psi^{a'}(x, y)} = \underset{1 \times N}{\check{\phi}(y; x)} \, \underset{N \times N_{\mathrm{op}}^{a'}}{\psi^{a'}(x)}.$$

Assume that the scattering coordinate x is defined in such a way that $x \to \infty$ in the asymptotic regions of the configuration space associated with the three arrangement channels α, β, and γ. An adequately chosen basis $\varphi(y; x)$ should have the property that it splits when $x \to \infty$ into three groups $\varphi^a(y; x)$, for $a = \alpha, \beta, \gamma$, each describing the internal motion in one atom–diatom channel only. Then, grouping accordingly the rows in the matrix $\psi^{a'}$, $[\psi^{a'}]^T = [(\psi^{\alpha a'})^T, (\psi^{\beta a'})^T, (\psi^{\gamma a'})^T]$, one can decompose the total wavefunctions $\Psi^{a'}$ into parts $\Psi^{aa'}$ with $a = \alpha, \beta, \gamma$, each of which describes at $x \to \infty$ only the respective channel a

$$\Psi^{a'}(x, y) = \sum_a \Psi^{aa'}(x, y),$$

where

$$\Psi^{aa'}(x, y) = \underset{1 \times N^a}{\varphi^a(y; x)} \underset{N^a \times N^a_{op}}{\psi^{aa'}(x)}, \qquad \left(\sum_a N_a = N \right).$$

Obviously, each component $\Psi^{aa'}(x, y)$ for $a = \alpha, \beta, \gamma$, should match the correct form $\bar{\Psi}^{aa'}(R_a, \bar{y}_a)$, given in equation (7 a). The matching is done at a sufficiently large value of x, x_∞, by imposing the following continuity conditions

$$(\check{\phi}^a | \Psi^{aa'}] = (\check{\phi}^a | \bar{\Psi}^{aa'}]|_{x = x_\infty}, \tag{36 a}$$

$$(\check{\phi}^a | (GP)_x \Psi^{aa'}] = (\check{\phi}^a | (GP)_x \bar{\Psi}^{aa'}]|_{x = x_\infty}, \tag{36 b}$$

where

$$(GP)_x = G^{xx} P_x + G^{xq} P_q.$$

The resulting conditions for the functions $\psi^{aa'}(x)$, $a = \alpha, \beta, \gamma$, read

$$g^a(x_\infty) \psi^{aa'}(x_\infty) = m^a(x_\infty) \delta_{a, a'} - n^a(x_\infty) K^{aa'}, \tag{37 a}$$

$$S^{aa}(x_\infty) \frac{d}{dx} \psi^{aa'}(x_\infty) + [\bar{A}^{aa}(x_\infty) + C^{aa}(x_\infty) + d^a(x_\infty)] \psi^{aa'}(x_\infty)$$

$$= \dot{m}^a(x_\infty) \delta_{a, a'} - \dot{n}^a(x_\infty) K^{aa'}. \tag{37 b}$$

where

$$g^a = (\check{\phi}^a | \check{\phi}^a] = \left[\varphi^a \middle| \frac{1}{G^{xx}} \varphi^a \right], \qquad (\check{\phi}^a = c^{-1/2} \varphi^a), \tag{37 c}$$

$$d^a = (\varphi^a | \{ c^{-1/2} (GP)_x c^{-1/2} \} \varphi^a] - \tfrac{1}{2} [\varphi^a | \{ P_q^T \check{G}^{xq} \} \varphi^a], \tag{37 d}$$

$$m^a(x) = (\check{\phi}^a(y; x) | \{ \bar{c}_a [R_a(x, y), r_a(x, y)] \}^{-1/2} \varphi^a [y_a(x, y)] m^a [R_a(x, y)]], \tag{37 e}$$

$$\dot{m}^a = (\check{\phi}^a | (GP)_x (\bar{c}_a)^{-1/2} \bar{\varphi}^a m^a]. \tag{37 f}$$

The matrices n^a and $\dot{n}^a$ are defined by formulae analogous to equations (37 e) and (37 f), respectively, obtained by replacing m^a with n^a. S^{aa}, $\bar{A}^{aa}$, and C^{aa} denote the blocks of the respective matrices defined in equations (32 a, b) which correspond to the subset φ^a of the entire basis φ. Obviously, $S^{aa} = I^a$ and $\bar{A}^{aa} = A^{aa}$ for orthonormal bases φ^a and $C^{aa} = 0$ (since $G^{xq} = 0$) for orthogonal coordinates (x, y). The conditions (37 a, b) allow one to determine the (approximate) reactance matrix K after integration of the coupled equations in the interval $[x_0, x_\infty]$, where x_0 is a value of the x coordinate corresponding to all three atoms being close together. The condition which should be imposed on the

functions $\psi^{aa'}(x)$ at the x_0 boundary results from the requirement of finiteness of the total wave function and is

$$\psi^{aa'}(x_0) \cong 0. \tag{38}$$

Example

The coupled equations in the Delves hyperspherical coordinates

$$x = r_a^2 + R_a^2, \qquad y_a = (\eta_a, \hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a),$$

where

$$\eta_a = \mathrm{tg}^{-1}\frac{r_a}{R_a}, \qquad \hat{\mathbf{r}}_a = (\Theta_{\mathbf{r}_a}, \varphi_{\mathbf{r}_a}), \qquad \hat{\mathbf{R}}_a = (\Theta_{\mathbf{R}_a}, \varphi_{\mathbf{R}_a}).$$

Actually, these are three sets of coordinates, (x, y_a) for $a = \alpha, \beta, \gamma$, each of which is really convenient to use only in a part of the entire configuration space, namely in the part of the respective arrangement channel region which extends outside the exchange (strong interaction) region but not too far into the asymptotic region. A detailed analysis of the usefulness of the Delves coordinates in solving the Schrödinger equation for atom–diatom reactive scattering (in three dimensions) was presented by Pack and Parker (1987). In the method proposed by these authors, the Delves coordinate sets are employed as intermediates between a set of (adiabatically adjusting principal axis) hyperspherical coordinates appropriate to describe the exchange region and the sets of the Jacobi coordinates appropriate in the asymptotic regions. Some points of their approach will be followed here.

Let us take one set (x, y_a) and confine ourselves to the part of the ath arrangement channel region of the configuration space which corresponds to intermediate and large (but not too large) values of the hyperradius x. (x, y_a) is a set of orthogonal coordinates and the corresponding diagonal elements of the tensor G are

$$G^{xx} = 1, \qquad G_a^{\eta\eta} = G^{\eta_a\eta_a} = x^{-2}, \qquad G_a^{\theta_R\theta_R} = (x\cos\eta_a)^{-2}, \qquad G_a^{\theta_r\theta_r} = (x\sin\eta_a)^{-2},$$

$$G_a^{\varphi_R\varphi_R} = (x\cos\eta_a\sin\Theta_{\mathbf{R}_a})^{-2}, \qquad G_a^{\varphi_r\varphi_r} = (x\sin\eta_a\sin\Theta_{\mathbf{r}_a})^{-2}.$$

Partitioning the internal coordinates y_a into sets $q_a = (\eta_a)$ and $\rho_a = (\hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a)$, one can write the Jacobian as $J_a = c_a\sigma_a$, where $c_a = \frac{1}{4}x^5\sin^2 2\eta_a$ and $\sigma_a = \sin\Theta_{\mathbf{R}_a}\sin\Theta_{\mathbf{r}_a}$. With this choice of the scaling factor c_a (see equations (21) and (30)), the operator $\breve{H}$ of equation (32 a) assumes the form

$$\breve{H}(x, y_a) = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{1}{x^2}\frac{\partial}{\partial\eta_a^2} - \frac{\hat{\mathbf{j}}^2(\hat{\mathbf{r}}_a)}{x^2\sin^2\eta_a} - \frac{\hat{\mathbf{l}}^2(\hat{\mathbf{R}}_a)}{x^2\cos^2\eta_a} + \frac{1}{4x^2}\right) + V.$$

Note that $V^{\mathrm{ext}} = -1/4x^2$ and that after rejecting the terms with $\hat{\mathbf{j}}^2$ and $\hat{\mathbf{l}}^2$ one obtains the respective scaled Hamiltonian for collinear reactions in the (x, η_a) coordinates (although $J_a = c_a = x$ in this case). Assuming that $\cos^2\eta_a \cong 1$ in the region of interest one can form the basis φ and its part

$$\underset{1\times N^a}{\varphi^a(y_a; x)},$$

of the following functions $(\varphi^a)_n$ (cf. the functions $(\bar{\varphi}^a)_n$ defined in equations (8, 8 a))

$$(\varphi^a)_n = \chi_{av_nj_n}(\eta_a; x)\mathscr{Y}_{l_nj_n}^{JM}(\hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a),$$

where $\chi_{\mathrm{av}j}$ are solutions of the equation

$$\left\{ -\frac{\hbar^2}{2\mu x^2} \left[\frac{\partial^2}{\partial \eta_a^2} - \frac{j(j+1)}{\sin^2 \eta_a} \right] + V_a^{\mathrm{vib}}(x \sin \eta_a) - \varepsilon_{\mathrm{av}j}(x) \right\} \chi_{\mathrm{av}j}(\eta_a; x) = 0.$$

The basis φ^a is orthonormal with respect to the scalar product $[\,|\,]_a$ (see equations (31) and (50)). For the corresponding coefficient matrices of the coupled equations, one gets (see equations (33, 34))

$$\mathbf{S}^{aa} = \mathbf{I}^a, \qquad \bar{\mathbf{A}}^{aa} = \mathbf{A}^{aa}, \qquad \mathbf{C}^{aa} = \mathbf{P}^{aa} = 0,$$

and

$$\bar{\mathbf{W}}^{aa}(x) = \left(\frac{2\mu}{\hbar^2} E + \frac{1}{4x^2} \right) \mathbf{I}^a - \frac{2\mu}{\hbar^2} \boldsymbol{\varepsilon}_a(x) - \left[\varphi^a \left| \left[\frac{2\mu}{\hbar^2} (V - V_a^{\mathrm{vib}}) + \frac{\mathbf{l}_a^2}{x^2 \sin^2 \eta_a} \right] \varphi^a \right. \right].$$

The matching of the solutions generated in the Delves coordinates to the asymptotic solutions in the Jacobi coordinates according to equations $(37\,a, f)$ involves the matrices

$$\mathbf{g}^a(x) = \mathbf{I}^a, \qquad \mathbf{d}^a(x) = -\frac{5}{2x} \mathbf{I}^a,$$

$$\boldsymbol{m}^a(x) = x^{1/2} [\varphi^a(y_a; x) | \bar{\varphi}^a[\bar{y}_a(x, y_a)] \mathbf{m}^a(x \cos \eta_a)],$$

$$\dot{\boldsymbol{m}}^a(x) = x^{1/2} \left[\varphi^a(y_a; x) \left| \frac{\partial}{\partial x} \bar{\varphi}^a[\bar{y}_a(x, y_a)] \mathbf{m}^a(x \cos \eta_a) \right. \right] - \frac{2}{x} \boldsymbol{m}^a(x).$$

Use has been made here of the fact that

$$\bar{c}_a[R_a(x, y_a), r_a(x, y_a)] = \tfrac{1}{4} x^4 \sin^2 2\eta_a,$$

and

$$\left(\frac{c_a}{\bar{c}_a} \right)^{1/2} = x^{1/2}.$$

Concerning description of the half-collision and the collision mediated processes, the following close-coupling approximant is obtained for the vector of transition amplitudes from the triatomic bound state, ζ^b, to the scattering states in the arrangement channel a, Ψ^a

$$\mathbf{K}^{ab} = (\psi^a | \phi^b),$$

where   (39)

$$\phi^b_{N \times 1} = (\check{\phi} | X \zeta^b].$$

An analogous formula for the amplitude $K^{\bar{b}b}$, $K^{\bar{b}b} = (\psi^{\bar{b}} | \phi^b)$, involves a vector of functions $\psi^{\bar{b}}(x)$ coming from the respective close-coupling expansion of the state $\Psi^{\bar{b}}$

$$\Psi^{\bar{b}}(x, y) = \check{\phi}(y; x)_{1 \times N} \psi^{\bar{b}}(x)_{N \times 1}.$$

The following inhomogeneous equation is obtained for $\psi^{\bar{b}}$

$$\mathscr{D} \psi^{\bar{b}} = \frac{2\mu}{\hbar^2} \phi^{\bar{b}},$$

where (40)

$$\phi^{\bar{b}} = (\varphi | \bar{X} \zeta^{\bar{b}}],$$

$\psi^{\bar{b}}(x_0) = 0$ and appropriate conditions for $\psi^{\bar{b}}(x_\infty)$ and for $(d/dx)\psi^{\bar{b}}(x_\infty)$ are obtained in a way analogous to that described above in the homogeneous equations case. Obviously, no free-wave related term appears in these conditions

$$\psi^{\bar{b}}(x_\infty) = -\mathbf{n}(x_\infty)\mathbf{K}^{\bar{b}}, \qquad (41\,a)$$

$$\frac{d}{dx}\psi^{\bar{b}}(x_\infty) + [\mathbf{A}(x_\infty) + \mathbf{C}(x_\infty) + \mathbf{d}(x_\infty)]\psi^{\bar{b}} = -\dot{\mathbf{n}}^c(x_\infty)\mathbf{K}^{\bar{b}}. \qquad (41\,b)$$

$\mathbf{n}$, $\dot{\mathbf{n}}$, and $\mathbf{d}$ denote here block diagonal matrices formed from the respective blocks $\mathbf{n}^a$, $\dot{\mathbf{n}}^a$, and $\mathbf{d}^a$ for $a = \alpha, \beta, \gamma$, defined in equations $(37\,c\text{-}f)$; $\mathbf{g}^a(x_\infty)$ and $\mathbf{S}^{aa}(x_\infty)$ are assumed to be the unit matrices; and

$$\left(\mathbf{K}^{\bar{b}}_{1 \times N}\right)^{\mathrm{T}} = \left[\left(\mathbf{K}^{\alpha\bar{b}}_{1 \times N^\alpha}\right)^{\mathrm{T}}, \left(\mathbf{K}^{\beta\bar{b}}_{1 \times N^\beta}\right)^{\mathrm{T}}, \left(\mathbf{K}^{\gamma\bar{b}}_{1 \times N^\gamma}\right)^{\mathrm{T}}\right].$$

3.2. *The generalized Schrödinger equation approach*

Proceeding to the derivation of coupled equations from the generalized Schrödinger equation, called here 'the generalized coupled equations', let us modify appropriately the above formulation of the Kohn variational principle. This means replacing the ordinary Hamiltonian in the functional $[K]$ with a generalized one, $\mathbb{H}$, and taking Ψ_{t_1} and Ψ_{t_2} as trial solutions of the Schrödinger equation with the Hamiltonian $\mathbb{H}$ and of the adjoint equation with $\mathbb{H}^{\mathrm{T}}$, $\mathbb{H}^{\mathrm{T}} = \mathbb{H}_0 + \mathbb{V}^{\mathrm{T}}$ respectively. Both Ψ_{t_i} for $i = 1, 2$ should have in the modified functional the following matrix form

$$\bar{\bar{\Psi}}_t \atop {3 \times N_{\mathrm{op}}} = \begin{bmatrix} \Psi_t^\alpha \\ \Psi_t^\beta \\ \Psi_t^\gamma \end{bmatrix} = \begin{bmatrix} \Psi_t^{\alpha\alpha} & \Psi_t^{\alpha\beta} & \Psi_t^{\alpha\gamma} \\ \Psi_t^{\beta\alpha} & \Psi_t^{\beta\beta} & \Psi_t^{\beta\gamma} \\ \Psi_t^{\gamma\alpha} & \Psi_t^{\gamma\beta} & \Psi_t^{\gamma\gamma} \end{bmatrix}, \qquad N_{\mathrm{op}} = \sum_{a'} N_{\mathrm{op}}^{a'}.$$

As before, $\bar{\bar{\Psi}}_{t_1}$ is required to satisfy the correct boundary conditions with the trial $\mathbf{K}$ matrix, $\mathbf{K}_{t_1}$, i.e., the functions $\Psi_{t_1}^{aa'}$, when expressed in the Jacobi coordinates $(R_a, \bar{y}_a)$, should assume at $R_a \to \infty$ the form $\bar{\Psi}^{aa'}(R_a, \bar{y}_a)$ (see equation $(7\,a)$) with $\mathbf{K}_{t_1}^{aa'}$ standing in place of $\mathbf{Y}^{aa'}$. The first variation of the modified functional is also given by equation (17) but with $\mathbb{H}$ and $\mathbb{H}^{\mathrm{T}}$ standing in place of H's in the first and in the second term, respectively. The condition of stationarity of $[K]$ brings into consideration the following integral I (see equation (19))

$$I = \frac{2\mu}{\hbar^2} \sum_{a,a'} \langle \delta\Psi^a | (\mathbb{E} - \mathbb{H})^{aa'} \Psi_t^{a'} \rangle, \qquad (42)$$

where

$$(\mathbb{E} - \mathbb{H})^{aa'} = \begin{cases} E - H, & \text{for the } F \text{ scheme,} \\ (E - H_a)\delta_{a,a'} - V^{a'} W_{aa'}, & \text{for the } CCA \text{ schemes.} \end{cases}$$

For the two (classes of) coupling schemes, the integral I can be converted to the forms

$$_{(F)}I = \frac{1}{2} \sum_{a,a'} (I_a^{aa'} + I_{a'}^{aa'}) - \sum_{a,a'} {}_{(F)}\hat{I}^{aa'}, \qquad (43)$$

$$_{(CCA)}I = \sum_a I_a^{aa} - \sum_{a,a'} {}_{(CCA)}\hat{I}^{aa'}, \qquad (44)$$

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where

$$I_{\bar{a}}^{aa'} = \frac{2\mu}{\hbar^2} \langle \delta \Psi^a | (E - H_{\bar{a}}) \Psi_t^{a'} \rangle, \qquad \text{for } \bar{a} = a, a', \tag{45}$$

$$_{(s)}\hat{I}^{aa'} = \frac{2\mu}{\hbar^2} \langle \delta \Psi^a |_{(s)} V^{aa'} \Psi_t^{a'} \rangle, \tag{46}$$

with

$$_{(s)}V^{aa'} = \begin{cases} \frac{1}{2}(V^a + V^{a'}), & \text{for } s = F, \\ V^{a'} W_{aa'}, & \text{for } s = CCA. \end{cases} \tag{46a}$$

In the form of $_{(F)}I$, use has been made of arbitrariness in choice of the partitioned form (3) of the total Hamiltonian H.

Concerning coordinate representation of the generalized Schrödinger equation, the essentially new aspect is that different coordinate sets may be employed simultaneously in this equation (i.e. also in the condensation region of the configuration space) to represent different arrangement channel components of $\overline{\overline{\Psi}}$ (and $\mathbb{H}$).

Most suitable are, of course, the three sets of the (mass-scaled) Jacobi coordinates. However, a common scattering coordinate has to be introduced for all channels if coupled equations in the form of ordinary differential equations are reguired. Let (x, y_a) for $a = \alpha, \beta, \gamma$ be three sets of such coordinates, each set belonging to the class specified above. To distinguish between the metric tensors, the Jacobians, and between the other quantities characterizing these coordinate sets, the subscript 'a' will be added to the respective symbols introduced for the (x, y) system (similarly as it was done in the example of the previous subsection).

Obviously, the choice of coordinate representation determines, to some extent, possible choices of basis function for expansion of the total wavefunction. Let

$$\underset{1 \times N^a}{\check{\phi}^a(y_a; x)},$$

for $a = \alpha, \beta, \gamma$ denote bases which are suitable for expansion of the particular arrangement channel components of the total wavefunction. Now, two things remain to be done:

(i) the functions $\Psi_t^{a'}(x, y_{a'})$ and $\delta \Psi^a(x, y_a)$ occurring in the integrals $I_{\bar{a}}^{aa'}$ with $\bar{a} = a, a'$ and $_{(s)}\hat{I}^{aa'}$ with $s = F$ or CCA and $a, a' = \alpha, \beta, \gamma$ are to expand in the respective bases $\check{\phi}^{a'}$ and $\check{\phi}^a$

$$\Psi_t^{a'}(x, y_{a'}) = \check{\phi}^{a'}(y_{a'}; x)\psi^{a'}(x), \qquad \delta \Psi^a(x, y_a) = \check{\phi}^a(y_a; x)\psi^a(x),$$

and

(ii) integration over all but the x coordinate is to be performed in these integrals in order to convert them to the forms

$$I_{\bar{a}}^{aa'} = (\delta \psi^a | \mathscr{D}_{\bar{a}}^{aa'} \psi^{a'}), \qquad \text{for } \bar{a} = a, a', \tag{47}$$

$$_{(s)}\hat{I}^{aa'} = (\delta \psi^a |_{(s)} \mathscr{V}^{aa'} \psi^{a'}), \qquad \text{for } s = F \text{ or } CCA, \tag{48}$$

where

$$\mathscr{D}_{\bar{a}}^{aa'} \psi^{a'} = \left(\check{\phi}^a \left| \frac{2\mu}{\hbar^2} (E - H_{\bar{a}}) \Psi_t^{a'} \right]_{\bar{a}}, \tag{47a}$$

$$_{(s)}\mathscr{V}^{aa'} = \left(\check{\phi}^a \left| \frac{2\mu}{\hbar^2} {}_{(s)}V^{aa'} \check{\phi}^{a'} \right]_{\tilde{a}}, \qquad \tilde{a} = a \text{ or } a'. \tag{48 a}$$

The symbols $(\,|\,)$ and $(\,|\,]_a$ have here the same meaning as defined in equation (24). The subscript added to the latter indicates which of the three sets of (internal) coordinates is chosen for performing integration in the particular integrals, e.g.

$$(\mathbf{Y}^a | \mathbf{Z}^{a'}]_a = \int J_a \, dy_a [\mathbf{Y}^a(x, y_a)]^\mathrm{T} \mathbf{Z}^{a'}[x, y_{a'}(x, y_a)].$$

Arbitrariness in this respect should be exploited, of course, to facilitate the operation. The choice made in equation (47 a) is the most convenient one as it means that the integration is carried out in the coordinates in which the channel Hamiltonian $H_{\tilde{a}}$ assumes the simplest form. In equation (48 a), the two choices, $\tilde{a} = a$ and $\tilde{a} = a'$, seem to be equally convenient.

With the goal of simplifying the operators $\mathscr{D}_{\tilde{a}}^{a,a'}$, let us adapt to the present situation the scaling procedure described above. This means scaling both bases, $\check{\phi}^a$ and $\check{\phi}^{a'}$, which are inserted into the integrals $I_{\tilde{a}}^{aa'}$ for $\bar{a} = a, a'$, with the same factor $(c_{\bar{a}})^{-1/2}$

$$\check{\phi}^a = (c_{\bar{a}})^{-1/2} \varphi_{\bar{a}}^a, \qquad \text{where } c_{\bar{a}} = j_{\bar{a}} G_{\bar{a}}^{xx}. \tag{49}$$

Two kinds of scaled bases appear in that way: $\varphi_a^{\bar{a}}$ with $a \neq \bar{a}$ and $\varphi_a^a = \varphi^a$, and

$$\varphi_{\bar{a}}^a = \left(\frac{c_{\bar{a}}}{c_a} \right)^{1/2} \varphi^a. \tag{49 a}$$

Concerning the bases φ^a for $a = \alpha, \beta, \gamma$, let us make the following assumptions:

(i) each basis φ^a is diabatic, i.e. $\varphi^a = \varphi^a(y_a)$. Using diabatic bases becomes practical in the context of the generalized Schrödinger equation. This is because each basis φ^a serves to describe internal (i.e. bounded) motion within one arrangement channel only. The need for bases modified along the scattering coordinate in the ordinary Schrödinger equation approach is compensated by the explicit coupling of the various arrangement channel components of the total wavefunction, incorporated into the structure of the generalized equation.

(ii) each basis φ^a is orthonormal

$$[\varphi^a | \varphi^a]_a = \mathbf{I}^a, \tag{50}$$

where

$$[\mathbf{Y} | \mathbf{Z}]_a = \int \sigma_a(\rho_a) \, dq_a \, d\rho_a \, \mathbf{Y}^\mathrm{T} \mathbf{Z}.$$

This does not guarantee, of course, orthogonality of the bases φ^a and $\varphi^{a'}$ describing different arrangement channels a and a'. They should, however, become orthogonal asymptotically, i.e.

$$[\varphi^a(y_a) | \varphi^{a'}(y_{a'}(x, y_a))]_a \xrightarrow[x \to \infty]{} 0, \qquad \text{for } a \neq a'.$$

As a result of the scaling, one gets the operators $\mathscr{D}_{\bar{a}}^{aa'}$ for $\bar{a} = a, a'$ and $a, a' = \alpha, \beta, \gamma$ in the form

$$\mathscr{D}_{\bar{a}}^{aa'} = \mathscr{S}_{\bar{a}}^{aa'} \frac{d^2}{dx^2} + 2(\mathscr{A}_{\bar{a}}^{aa'} + \mathscr{C}_{\bar{a}}^{aa'}) \frac{d}{dx} + \mathscr{W}_{\bar{a}}^{aa'} + \mathscr{B}_{\bar{a}}^{aa'} + \mathscr{P}_{\bar{a}}^{aa'}, \tag{51}$$

where the $N^a \times N^{a'}$ coefficient matrices are given by the formula

$$\mathscr{X}_{\tilde{a}}^{aa'} = [\varphi_{\tilde{a}}^a | (*) \varphi_{\tilde{a}}^{a'}]_{\tilde{a}},\tag{51 a}$$

with the following operators standing in place of $(*)$

$$I, \qquad P_x, \qquad P_x P_x, \qquad \tfrac{1}{2}(P_{q\tilde{a}}^{\mathrm{T}} \check{G}_{\tilde{a}}^{qx} + \check{G}_{\tilde{a}}^{xq} P_{q\tilde{a}}), \qquad (P_x \check{G}_{\tilde{a}}^{xq} P_q + P_{q\tilde{a}}^{\mathrm{T}} \check{G}_{\tilde{a}}^{qx} P_x), \tag{51 b}$$

$$\left[\frac{2\mu}{\hbar^2} \frac{1}{G_{\tilde{a}}^{xx}} (E - V_{\tilde{a}}) + \left(P_{q\tilde{a}}^{\mathrm{T}} \check{G}_{\tilde{a}}^{qq} P_q + \frac{1}{\sigma_{\tilde{a}}} P_{\rho\tilde{a}}^{\mathrm{T}} \sigma_{\tilde{a}} \check{G}_{\tilde{a}}^{\rho\rho} P_{\rho\tilde{a}} \right) - \{ c_{\tilde{a}}^{-1/2} P_{\tilde{a}}^{\mathrm{T}} \check{G}_{\tilde{a}} P_{\tilde{a}} c_{\tilde{a}}^{+1/2} \} \right], \tag{51 c}$$

for $\mathscr{X} = \mathscr{S}, \mathscr{A}, \mathscr{B}, \mathscr{C}, \mathscr{P}$, and $\mathscr{W}$, respectively.

Finally, from the condition $_{(s)}I = 0$ ($s = F$ or CCA) the coupled equations for the functions $\psi(x)$, $\psi^{\mathrm{T}} = [(\psi^\alpha)^{\mathrm{T}}, (\psi^\beta)^{\mathrm{T}}, (\psi^\gamma)^{\mathrm{T}}]$, are obtained. They can be written in the general form (25) by composing the operator

$$\underset{N \times N}{\mathscr{D}},$$

of the blocks

$$\underset{N^a \times N^{a'}}{\mathscr{D}^{aa'}}, \qquad \mathscr{D} = \{\mathscr{D}^{aa'}\}_{a, a'},$$

where

$$\mathscr{D}^{aa'} = \begin{cases} \tfrac{1}{2}(\mathscr{D}_a^{aa'} + \mathscr{D}_{a'}^{aa'}) - {}_{(F)}\mathscr{V}^{aa'}, & \text{for } F \text{ scheme}, \\ \mathscr{D}_a^{aa} - {}_{(CCA)}\mathscr{V}^{aa'}, & \text{for } CCA \text{ scheme}. \end{cases} \tag{52}$$

For the purpose of further discussion, let us write the operator $\mathscr{D}$ in the form

$$\mathscr{D} = \mathscr{S}(x) \frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2[\mathscr{A}(x) + \mathscr{C}(x)] \frac{\mathrm{d}}{\mathrm{d}x} + \mathscr{W}(x) + \mathscr{B}(x) + \mathscr{P}(x) - \mathscr{V}(x). \tag{53}$$

All the matrices introduced here have the block structure

$$\mathscr{X} = \{\mathscr{X}^{aa'}\}_{a, a'}. \tag{54}$$

where

$$\mathscr{X}^{aa'} = \tfrac{1}{2}(\mathscr{X}_a^{aa'} + \mathscr{X}_{a'}^{aa'}), \qquad \text{for } \mathscr{X} = \mathscr{S}, \mathscr{A}, \mathscr{B}, \mathscr{C}, \mathscr{P}, \mathscr{W},$$

and the respective matrices $\mathscr{X}_{\tilde{a}}^{aa'}$ with $\tilde{a} = a, a'$ are defined in equation (51 a–c). The difference between the F and the CCA coupling schemes is not indicated in equation (53). The important fact to remember is that only diagonal blocks of all the matrices $\mathscr{X}$ (excluding $\mathscr{V}$) enter the coupled equations in the cases of the CCA schemes.

Analysing more closely the operator $\mathscr{D}$ of equation (53), one can state that:

(i) The diagonal blocks of the matrices $\mathscr{A}(x)$ and $\mathscr{B}(x)$ vanish (everywhere), i.e. $\mathscr{A}^{aa} \equiv 0$ and $\mathscr{B}^{aa} \equiv 0$. In fact, this concerns all the matrices $\mathscr{A}_{a'}^{aa'}$ and $\mathscr{B}_{a'}^{aa'}$, i.e. $\mathscr{A}_{a'}^{aa'} \equiv 0$ and $\mathscr{B}_{a'}^{aa'} \equiv 0$, and is a consequence of the assumed diabaticity of the bases φ^a for $a = \alpha, \beta, \gamma$. The off-diagonal blocks of the matrices $\mathscr{A}$ and $\mathscr{B}$ are, however, non-vanishing (except asymptotically)

$$\mathscr{A}^{aa'} = \tfrac{1}{2}\mathscr{A}_a^{aa'}, \qquad \mathscr{B}^{aa'} = \tfrac{1}{2}\mathscr{B}_a^{aa'}. \tag{55}$$

This is because the functions $\varphi_{a'}^{a'}$ with $a \neq a'$ acquire dependence on the x coordinate through the scaling factor and through the transformation $y_{a'} = y_{a'}(x, y_a)$ which is implied in equation (51 a).

(ii) The matri2x $\mathscr{S}$ is symmetric and has simple diagonal blocks

$$\mathscr{S}^{aa}(x) \equiv \mathbf{I}^a, \qquad \text{for } a = \alpha, \beta, \gamma. \tag{56}$$

(iii) The matrices $\mathscr{C}$ and $\mathscr{W}$ are skew-symmetric and symmetric, respectively. Strictly speaking, these properties are guaranteed under some additional assumptions concerning the bases φ^a, analogous to those mentioned above in the case of the matrices $\mathbf{C}$ and $\bar{\mathbf{W}}$ (see equations (33 d, e)).

(iv) The following relations hold

$$\bar{\mathscr{A}} = \mathscr{A} + \tfrac{1}{2}\mathscr{S}^{(1)}, \qquad \text{where} \quad \mathscr{A} = \tfrac{1}{2}(\bar{\mathscr{A}} - \bar{\mathscr{A}}^{\mathrm{T}}),$$

$$\bar{\mathscr{B}} = \mathscr{A}^{(1)} + \mathscr{S}^{(2)}, \qquad \text{where} \quad \mathscr{A}^{(1)} = \tfrac{1}{2}(\bar{\mathscr{B}} - \bar{\mathscr{B}}^{\mathrm{T}}), \tag{57}$$

$$\bar{\mathscr{P}} = \mathscr{P} + \mathscr{C}^{(1)}, \qquad \text{where} \quad \mathscr{P} = \tfrac{1}{2}(\bar{\mathscr{P}} + \bar{\mathscr{P}}^{\mathrm{T}}).$$

These relations differ from those concerning the coupled equations in the ordinary Schrödinger equation approach, equation (34), only in that there is no counterpart of the (symmetric) matrix $\mathbf{B}$ here.

(v) The matrix $\mathscr{V}$ representing the matrix operator $_{(s)}\mathbb{V}$ is the transposition of the matrix $\mathscr{V}^{\mathrm{T}}$ representing the potential $_{(s)}\mathbb{V}^{\mathrm{T}}[(_{(s)}\mathbb{V}^{\mathrm{T}})^{aa'} = _{(s)}V^{a'a}]$. So, the matrix $\mathscr{V}$ is symmetric if it represents the (generalized) potential in the Fock coupling scheme (when $s = F$). In the case of the CCA schemes, symmetry of this matrix depends on properties of the particular arrangement channel array $\mathbb{W}$ employed. Obviously, $(\mathscr{V}^{aa})^{\mathrm{T}} = \mathscr{V}^{aa}$ in any scheme.

(vi) In the CCA schemes, the operator $\mathscr{D}$ simplifies to the form

$$_{(CCA)}\mathscr{D} = \mathbf{I}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2\underline{\mathscr{C}}\frac{\mathrm{d}}{\mathrm{d}x} + \underline{\mathscr{L}}^{(1)} + \underline{\mathscr{W}} + \underline{\mathscr{P}} - {}_{(CCA)}\mathscr{V}, \tag{53 a}$$

where the underlined letters denote the block-diagonal parts of the respective matrices. The replacement of $_{(CCA)}\mathscr{V}$ with $_{(CCA)}\mathscr{V}^{\mathrm{T}}$ in this form leads to the adjoint operator $_{(CCA)}\mathscr{D}^{\dagger}$ (see equation (26 a)).

In summary, one can state that the coupled equations derived here from the generalized Schrödinger equation are self-adjoint if the (generalized) potential in this equation is symmetric. Consequently, the form of these coupled equations is rather simple, especially in the case of the CCA-type schemes (see equation (53 a)).

It should be pointed out that assuring self-adjointness of the coupled equations in the Fock scheme has been possible only due to the use in the derivation of the particular symmetrized form of the integral $_{(F)}I$, equation (43). If the unsymmetrized form of this integral were exploited

$$_{(F)}I = \sum_{a,a'} I_a^{a'a} - \sum_{a,a'} \bar{\bar{I}}^{a'a}, \tag{58}$$

where

$$\bar{\bar{I}}^{a'a} = \left\langle \delta\Psi^{a'} \left| \frac{2\mu}{\hbar^2} V^a \Psi^a \right. \right\rangle, \tag{58 a}$$

the coupled equations would involve an operator—let us denote it with $\bar{\bar{\mathscr{D}}} = \{\bar{\bar{\mathscr{D}}}^{a'a}\}_{a',a}$—composed of the following blocks $\bar{\bar{\mathscr{D}}}^{a'a}$

$$\bar{\bar{\mathscr{D}}}^{a'a} = \mathscr{D}_a^{a'a} - \bar{\bar{\mathscr{V}}}^{a'a}, \tag{59}$$

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where

$$\bar{\bar{\mathcal{V}}}^{a'a} = \left(\check{\phi}^{a'} \left| \frac{2\mu}{\hbar^2} V^a \check{\phi}^a \right. \right]_{\tilde{a}}, \qquad \tilde{a} = a' \text{ or } a. \tag{59 a}$$

Writing these blocks explicitly

$$\bar{\bar{\mathcal{D}}}^{a'a} = \mathcal{S}_a^{a'a} \frac{d^2}{dx^2} + 2\mathcal{C}_a^{a'a} \frac{d}{dx} + \bar{\mathcal{P}}_a^{a'a} + \bar{\mathcal{W}}_a^{a'a} - \bar{\bar{\mathcal{V}}}^{a'a}, \tag{60}$$

one realizes easily that the coefficient matrices in the operator $\bar{\bar{\mathcal{D}}}$ fail to satisfy the self-adjointness relations (29).

It seems rather unlikely that the lack of self-adjointness of the operator $\bar{\bar{\mathcal{D}}}$ could be cured simply by a modification of the scalar product $(\,|\,)$ (see equation (24)). If one defines a product $(\,|\,)_s$

$$(\mathbf{Y}|\mathbf{Z})_s = (s\mathbf{Y}|\mathbf{Z}) = \int_{x'}^{x''} s \, dx \, \mathbf{Y}^T \mathbf{Z},$$

with s being a symmetric positive definite matrix, and denotes with $\mathcal{D}^{\#}$ the operator adjoint to $\mathcal{D}$ with respect to this product (see equations (25 a), (27), (27 a))

$$(\phi|\mathcal{D}\psi)_s = (\mathcal{D}^{\#}\phi|\psi)_s + W_{n(=2)}[s\phi, \psi]|_{x'}^{x''},$$

i.e. $\mathcal{D}^{\#} = s^{-1}\mathcal{D}^{\dagger}s$, one finds easily that in order to guarantee that $\mathcal{D}$ be self-adjoint in the generalized sense, i.e. that $\mathcal{D}^{\#} = \mathcal{D}$, the coefficient matrices have to satisfy the following relations

$$\mathbf{a}_2 = s^{-1}\mathbf{a}_2^T s, \qquad \mathbf{a}_1 = -s^{-1}[\mathbf{a}_1^T s - 2(\mathbf{a}_2^T s)^{(1)}],$$

$$\mathbf{a}_0 = s^{-1}[\mathbf{a}_0^T s - (\mathbf{a}_1^T s)^{(1)} + (\mathbf{a}_2^T s)^{(2)}].$$

So, choosing $s = \{\mathcal{S}_a^{a'a}\}_{a,a'}$ and replacing the operator $\bar{\bar{\mathcal{D}}}$ with $s^{-1}\bar{\bar{\mathcal{D}}}$ one would get $\mathbf{a}_2 = \mathbf{I}$ in this modified operator but even if there were no first derivative coupling, i.e. $\mathbf{a}_1 = \mathbf{0}$, and the matrix $\mathbf{a}_0$ were self-adjoint, i.e. $\mathbf{a}_0 = \mathbf{a}_0^{\#} = s^{-1}\mathbf{a}_0^T s$, the above relations would not be satisfied because of the absence of the derivatives $s^{(1)}$ and $s^{(2)}$.

Despite of not being self-adjoint, the operator $\bar{\bar{\mathcal{D}}}$ may be useful in practice because of the relatively simple structure of the first derivative coupling term. This coupling does not occur at all in $\bar{\bar{\mathcal{D}}}$ if all the channel internal coordinates are orthogonal to the scattering coordinate. Delves' hyperspherical coordinates are an example of such coordinates. The coupled equations with the operator $\bar{\bar{\mathcal{D}}}$ expressed in these coordinates are solved in the method used by Schatz (1988).

In fact, all the Fock scheme related formulations of the coupled ordinary differential equations proposed so far (Diestler 1971, Stechel *et al.* 1979, Schwenke *et al.* 1987, Schatz 1988) do involve the operator $\bar{\bar{\mathcal{D}}}$ (or a version of it) and therefore should be categorized as non-symmetric ones.

A symmetrized and simplified version of the formulation by Schwenke, Truhlar, and Kouri (1987) will be presented below using the operator $\mathcal{D}$ derived above, equation (53).

Example
The generalized coupled equations in the mixed hyperspherical/Jacobi coordinates

$$x = R_a^2 + r_a^2, \qquad y_a = \bar{y}_a = (r_a, \hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a), \qquad \text{for } a = \alpha, \beta, \gamma.$$

Here $q_a = (r_a)$ and $\rho_a = (\hat{\mathbf{r}}_a, \hat{\mathbf{R}}_a)$. These are non-orthogonal coordinates with $G_a^{xq} = r_a/x$, $G_a^{xx} = 1$, and $G_a^{qq} = 1$. The Jacobians J_a, the metrics σ_a, and the scaling factors c_a (see equation (21) and (30)) are

$$J_a = c_a \sigma_a, \qquad c_a = x(x^2 - r_a^2)^{1/2} r_a^2, \qquad \sigma_a = \sin \Theta_{\mathbf{R}_a} \sin \Theta_{r_a} \qquad \text{for } a = \alpha, \beta, \gamma.$$

The part of the operator $(2\mu/\hbar^2)(E - H_{\bar{a}})$ occurring in the definition of the matrix $\mathscr{W}_{\bar{a}}^{aa'}$ (see equations (51 a) and (51 c)) now read

$$\frac{2\mu}{\hbar^2}[E - \check{H}_{\bar{a}}^{\text{ro}-\text{vib}}(x, \bar{y}_{\bar{a}}) - V_{\bar{a}}^{\text{dist}}] - V_{\bar{a}}^{\text{ext}},$$

where

$$\check{H}_{\bar{a}}^{\text{ro}-\text{vib}}(x, \bar{y}_{\bar{a}}) = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r_{\bar{a}}^2} - \frac{\hat{\mathbf{l}}^2(\hat{\mathbf{r}}_{\bar{a}})}{r_{\bar{a}}^2} - \frac{\hat{\mathbf{l}}^2(\hat{\mathbf{R}}_{\bar{a}})}{x^2 - r_{\bar{a}}^2}\right) + V_{\bar{a}}^{\text{vib}}(r_{\bar{a}}),$$

$$V_{\bar{a}}^{\text{ext}} = \{c_{\bar{a}}^{-1/2} P_{\bar{a}}^{\text{T}} G_{\bar{a}} P_{\bar{a}} c_{\bar{a}}^{1/2}\} = \frac{1}{4}\left(\frac{1}{x^2} + \frac{1}{x^2 - r_{\bar{a}}^2}\right).$$

The bases $\varphi^a(y_a)$ for $a = \alpha, \beta, \gamma$ are chosen as consisting of the eigenfunctions of (the bound states of) the respective channel Hamiltonians $\check{H}_a^{\text{ro}-\text{vib}}$ (see equation (8)), i.e.

$$\varphi^a(y_a) = \bar{\varphi}^a(\bar{y}_a), \qquad \varphi_{\bar{a}}^a = \left(\frac{x^2 - r_{\bar{a}}^2}{x^2 - r_a^2}\right)^{1/4} \frac{r_{\bar{a}}}{r_a} \bar{\varphi}^a.$$

Thus, the following expression is obtained for the matrix $\mathscr{W}_{\bar{a}}^{aa'}(\bar{a} = a, a')$

$$\mathscr{W}_{\bar{a}}^{aa'} = \mathbf{e}_{\bar{a}}^{aa'} - \mathbf{v}_{\bar{a}}^{aa'} - \frac{1}{4x^2}\mathscr{S}_{\bar{a}}^{aa'},$$

where

$$\mathbf{e}_a^{aa'} = \mathbf{k}_a^2 \mathscr{S}^{aa'}, \qquad \mathbf{e}_{a'}^{aa'} = \mathscr{S}_{a'}^{aa'} \mathbf{k}_{a'}^2,$$

$$\mathbf{v}_{\bar{a}}^{aa'} = \left[\varphi_{\bar{a}}^a \middle| \left(\frac{2\mu}{\hbar^2} V_{\bar{a}}^{\text{dist}} + \frac{\mathbf{l}_{\bar{a}}^2 + \frac{1}{4}}{x^2 - r_{\bar{a}}^2}\right) \varphi_{\bar{a}}^{a'}\right]_{\bar{a}}.$$

The diagonal matrices $\mathbf{k}_{\bar{a}}^2$ and $\mathbf{l}_{\bar{a}}^2$ are defined in Section 2. The respective expressions for the matrices $\mathscr{C}_{\bar{a}}^{aa'}$, $\mathscr{P}_{\bar{a}}^{aa'}$, and $\mathscr{A}_a^{aa'}$ are

$$\mathscr{C}_{\bar{a}}^{aa'} = \frac{1}{2}\left[\left[\varphi_{\bar{a}}^a \middle| \frac{r_{\bar{a}}}{x} \frac{\partial}{\partial r_{\bar{a}}} \varphi_{\bar{a}}^{a'}\right]_{\bar{a}} - \left[\frac{\partial}{\partial r_{\bar{a}}} \varphi_{\bar{a}}^{a'} \middle| \frac{r_{\bar{a}}}{x} \varphi_{\bar{a}}^a\right]_{\bar{a}}\right], \qquad \text{for } \bar{a} = a, a',$$

$$\mathscr{P}_{a'}^{\bar{a}a'} = -\frac{1}{x^2}\left[\varphi_{a'}^a \middle| r_{a'} \frac{\partial}{\partial r_{a'}} \varphi^{a'}\right]_{a'},$$

$$\mathscr{P}_a^{\bar{a}a'} = \left[\varphi^a \middle| \left(\frac{1}{x}\frac{\partial}{\partial x} + \frac{2r_a}{x}\frac{\partial^2}{\partial x \partial r_a} - \frac{r_a}{x^2}\frac{\partial}{\partial r_a}\right) \varphi_a^{a'}\right]_a,$$

$$\mathscr{A}_a^{aa'} = \left[\varphi^a \middle| \frac{\partial}{\partial x} \varphi_a^{a'}\right]_a.$$

These are the most complex expressions which have to be evaluated to formulate the self-adjoint coupled equations in the Fock scheme

$$\left[\mathscr{S}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + 2\left(\mathscr{A} + \mathscr{C} + \tfrac{1}{2}\mathscr{S}^{(1)}\right)\frac{\mathrm{d}}{\mathrm{d}x} + \mathscr{A}^{(1)} + \mathscr{C}^{(1)} + \tfrac{1}{2}\mathscr{S}^{(2)} + \mathscr{W}\right]\psi = 0, \qquad (61)$$

where

$$\mathscr{W} = \mathscr{\overline{W}} + \mathscr{P} - {}_{(F)}\mathscr{V}.$$

The precise way of constructing the blocks of all the matrices occurring here follows from equations (54), (51 a, c), (55), and (57), e.g. $\mathscr{A}^{aa'} = \frac{1}{4}[\mathscr{\overline{A}}_a^{aa'} - (\mathscr{\overline{A}}_{a'}^{a'a})^T]$. As will be seen in the next Section, the matrices $\mathscr{A}^{(1)}$, $\mathscr{C}^{(1)}$, and $\mathscr{P}^{(2)}$ are not actually needed in the process of solving the equations. Besides the self-adjointness property, the point which makes different the coupled equations (61) from those given by Schwenke et al. (1987) is the simple form of the matrix $\mathscr{P}$, equation (56). Replacing ${}_{(F)}\mathscr{V}$ with ${}_{(CCA)}\mathscr{V}$ and retaining only diagonal blocks of all other matrices in equation (61) one gets the respective equations in the CCA coupling schemes (see equation (53 a). Their simplicity is apparent too: $\mathscr{A} = \mathscr{A}^{(1)} = \mathscr{P}^{(1)} = \mathscr{P}^{(2)} = 0$ and $\mathscr{P} = I$. Because of the latter property the present form of the CCA coupled equations seems to be more convenient than that given by Schwenke et al. (1987).

The only other formulation of the coupled equations in a CCA scheme proposed so far is that by Top and Shapiro (1982). Because of the coordinates used, however, their formulation applies only to two-arrangement-channel cases.

For the sake of completeness one should mention that the boundary conditions (36 a, b) apply also to the solutions of the generalized coupled equations. The only adjustment necessary is to make it explicit that there are three sets of internal coordinates, y_a for $a = \alpha, \beta, \gamma$, instead of one, y, and that each basis $\check{\phi}^a$ (and φ^a) is defined in its own coordinates y_a; e.g., equation (36 b) should in the generalized case read

$$(\check{\phi}^a|(G_a P_a)_x \Psi^{aa'}]_a = (\check{\phi}^a|(G_a P_a)_x \overline{\Psi}^{aa'}]_a|_{x = x_\infty}.$$

In the above example of symmetric formulation of the (generalized) coupled equations in the mixed hyperspherical/Jacobi coordinates, the conditions (37 a) and (37 b) take the following form

$$\psi^{aa'}(x_\infty) = m^a(x_\infty)\delta_{a,a'} - n^a(x_\infty)K^{aa'}, \tag{62 a}$$

$$\frac{d}{dx}\psi^{aa'}(x_\infty) + \left[\mathscr{C}^{aa}(x_\infty) - \frac{5}{2x_\infty}I^a\right]\psi^{aa'}(x_\infty) = \dot{m}^a(x_\infty) - \dot{n}^a(x_\infty)K^{aa'}, \tag{62 b}$$

where

$$m^a(x) = \left[\overline{\varphi}^a\left|\left(\frac{c_a}{c_{\bar{a}}}\right)^{1/2}\overline{\varphi}^a m^a\right]_a,\right.$$

$$\dot{m}^a(x) = -\frac{2}{x}m^a(x) + \left[\overline{\varphi}^a\left|\left(\frac{c_a}{c_{\bar{a}}}\right)^{1/2}\left(\frac{\partial}{\partial x} + \frac{r_a}{x}\frac{\partial}{\partial r_a}\right)\overline{\varphi}^a m^a\right]_a,\right.$$

$$\bar{c}_a[R_a(x, r_a), r_a] = (x^2 - r_a^2)r_a^2,$$

n^a and $\dot{n}^a$ are obtained after replacing m^a with n^a in the formulas for m^a and $\dot{m}^a$, respectively.

To close this Section, let us stress again that the ordinary and the generalized Schrödinger equations for atom–diatom reactive scattering can be converted, via the close-coupling approximation, to sets of ordinary differential equations which are self-adjoint even if curvilinear non-orthogonal coordinates and non-orthogonal basis functions are employed. The most complicated coupled equations arise from the generalized Schrödinger equation in the Fock scheme which is a result of the inherent non-orthogonality of bases involved in the derivation. In particular, the first derivative coupling term seems unavoidable in these equations (though this opinion is not

necessarily shared by others; see, Lill *et al.* 1983) if they are required to yield strictly symmetric reactance matrices irrespective of the overall accuracy ot the employed close-coupling expansions.

4. Numerical methods for solving the coupled equations

Let us start with presenting a view of the numerous methods developed over the years for handling the coupled equations of the quantum theory of molecular scattering (see the articles by Gordon, Lester, Light, and Secrest in *Methods in Computational Physics*, 1971, **10**, and the reviews: Secrest 1979, Wyatt 1979, Thomas *et al.* 1981, Allison 1988) in a wider context of methods applicable to linear two-point boundary value problems for systems of ordinary differential equations. Systems of N second-order equations and separated boundary conditions—N at each boundary point—are assumed in what follows.

A short reminder will be helpful of the general classification of the methods (see, for example, Scott (1973)) according to the technique adopted for imposing the boundary conditions. There are so-called: (*a*) boundary value and (*b*) initial value techniques, and among the latter techniques (see, for example, Meyer (1973)): (bi) linear superposition (version of shooting for linear problems), (bii) invariant imbedding, and (bii)′ Riccati transformations techniques.

In methods employing the boundary value techniques, hereafter referred to as *global methods*, a system of algebraic equations is constructed which gives a finite difference approximation to the differential equations over the entire region of integration and simultaneously accounts for the boundary conditions.

The initial value techniques consist generally of replacing a given boundary value problem with a number of initial value problems which are next solved in a propagative (step-by-step) manner. Hence, the term *propagative methods* is commonly used. If the linear superposition principle is chosen to be directly exploited (as in the shooting technique) then the initial value problems are essentially for generating a basis in the $2N$-dimensional space of all solutions of the original differential equations or only in the N-dimensional subspace within which the solution satisfying the required boundary conditions must lie.

The initial value problems of the invariant imbedding technique arise as a result of treating a given two-point boundary value problem as a member of a family of analogous problems with the distance between the two boundaries being a parameter of the family—the parameter of imbedding (see Casti and Kalaba (1973) and references therein). Relations between the members of the family corresponding to larger and larger values of the imbedding parameter, called recurrence relations or addition formulas (Allen and Wing 1970, 1974, Denman 1971, Nelson and Ray 1979) when the parameter changes stepwise, assume a form of some differential equations in the limiting case of continuous growth of this parameter. Solutions of the boundary value problem on the interval of zero-length, entirely determined by the boundary conditions, serve as initial conditions to these equations.

One of the $(N \times N$ matrix) differential equations with respect to the imbedding parameter is of Riccati type which indicates that a connection of the invariant imbedding technique exists with the Riccati transformation method of solving linear boundary value problems (Bellman and Angel 1972, Meyer 1973, Scott 1973). In some textbooks (e.g., Meyer (1973), Scott (1973)), the Riccati transformation method has been even presented as a particular (non-classical) realization of the idea of invariant imbedding, namely, as an implicit imbedding of a given boundary value problem into a

family of initial value problems for the same differential equations where the role of imbedding parameters is assigned to the set of initial conditions unspecified in the original problem. Actually, both the (classical) invariant imbedding and the Riccati transformation techniques offer the same prescriptions only for completing solution of the problem at the boundaries of the entire integration range.

The initial value problems arising in any method of category (bii) or (bii)' may be divided into two groups. The basic group consists of four problems which can be solved independently of the others and yield certain *propagators of solutions of the* original *coupled equations* over the interval of integration. Under the term 'propagator over an interval', a $2N \times 2N$ matrix is meant which connects values of any solution of the system of N coupled equations and of its derivative at the endpoints of the interval. The initial value problems for determining the propagator are, of course, those which may appear in the same form in an invariant imbedding and in a Riccati transformation method. The other initial value problems are mostly for determining the solution of the original boundary value problem at internal points of the integration range.

In the linear superposition methods, the role of a propagator is naturally fulfilled by a matrix of fundamental solutions of any set of $2N$ first-order differential equations which is equivalent to the original system of second-order equations. Such a propagator is called standard hereafter.

Any difference between the linear superposition and the invariant imbedding techniques may be attributed to some properties of the related propagators. The most important practical difference between the two techniques concerns their capabilities of handling boundary value problems which are described as mathematically unstable or stiff (Davey 1983). These are problems with solutions being composed of functions (of some elementary solutions of the differential equations) which grow or decay exponentially at widely differing rates. Standard propagators generated numerically (as solutions of respective linear initial value problems) tend to become singular matrices in such cases. This may happen, of course, only because of finite accuracy of numerical operations. A counteraction is necessary and it is usually taken in the form of some transformations (orthonormalization, triangularization) performed on the propagator from time to time in the course of its generation. Procedures ortho- normalizing columns of standard propagators continuously and automatically have also been suggested (Davey 1983, Mayer 1986).

No problem with exponential solutions is encountered (though other instabilities may arise) in solving numerically the initial value problems for invariant imbedding type propagators.

Concerning interconnections between the various techniques, it has been demon- strated also (e.g., Bellman and Angel (1972)) that in application to (linear) boundary value problems for three-point (matrix) difference equations the Riccati transformation method becomes equivalent to a version of the Gaussian elimination method for systems of linear algebraic equations with (block) tridiagonal matrices. Algebraic equations of such a structure frequently arise from applying the boundary value techniques to boundary value problems for systems of differential equations. This links the global methods with the propagative Riccati transformation and invariant imbedding methods of solving these problems.

Among the methods specialized to scattering problems, representative of the global methods is the finite difference boundary value method developed by Truhlar and Kuppermann (1971) and by Zhang *et al.* (1988). It should be mentioned here that the sense of the term 'global method' is actually broader than that conveyed above.

Boundary value techniques may be applied directly to the Schrödinger equation as a partial differential equation, i.e. not necessarily in conjunction with the close-coupling approximation. Such attempts were made in some early reactive scattering calculations (e.g. Diestler and McKoy (1968), see also Light (1971)). Moreover, the global methods based on finite difference approximations to ordinary or partial differential operators bear a strong resemblance to some variational methods employing spacially confined (i.e. finite element type) basis functions (see Linderberg *et al.* (1989)).

However, the overwhelming majority of the methods tried and finally established for use in close-coupling calculations for molecular scattering are of propagative type. The chief argument in favour of propagative methods has been the fact that our interest in a given scattering process is actually focused on the fragmentation stage and the relevant information may be obtained if the wavefunction for the process is only known in respective asymptotic regions of the configuration space. Thus, any costs would be superfluous (storage requirements and/or amount of computational work) associated with determining solutions of the coupled equations explicitly within the entire scattering range. While it seems not always possible to avoid such costs in the global methods they can be eliminated quite naturally when a propagative technique is employed. One simply confines oneself to determining respective propagator (or even a part of it) over the scattering range.

No doubt, the development of propagative methods for scattering was stimulated by the formulation of the close-coupling theory of ro–vibrational energy transfer in non-reactive molecular (mostly, atom–diatom) collisions (for a review, see Lester (1976)). Two features of the coupled equations problems arising in this theory have been particularly important: (i) the simple form of the equations—ordinary differential equations of second-order with (i)′ no first derivative term and with (i)″ potential type coupling elements which vary rapidly in a not large and in part classically inaccessible condensation region and change rather slowly outside this region of scattering coordinate; (ii) the need (caused by anisotropy of interaction between colliding partners) for inclusion of a large number of equations into a system, among them also equations corresponding to closed collision channels.

Because of participation of the closed channels and the existence of the non-classical regions the problems belong to the mathematically unstable ones. The invariant imbedding technique seems the ideal remedy for instability of the scattering problems. Indeed, resorting to this technique resulted in developing methods which are now among the most popular in the field, such as the log–derivative method of Johnson (1973). Even more widely used (since designed at once for more general problems) is the R-matrix propagation method of Light and Walker (1976b); see also: Zvijac and Light (1976), Stechel *et al.* (1978, 1979), Schneider and Walker (1979), Wyatt (1979), Kulander and Light (1980), Garrett and Truhlar (1981), Lill *et al.* (1983). Classical examples of numerical procedures based on the idea of invariant imbedding are: the amplitude density functions method which was used in the first accurate multichannel calculations for (a model of) molecular collisions reported in 1966 by Secrest and Johnson (see also Secrest (1971)) and the state path sum method of Manz (1974)—later modified and renamed to the S-matrix propagation method (Hauke *et al.* 1980). Each of the methods quoted generates a definite propagator of solutions of the coupled equations. A propagator is, of course, the matrix R in the method of Light and co-workers. The propagator associated with the log–derivative method, strictly, with its later generalizations, is called the L matrix (or propagator). Hence, the alternate name—the L-matrix propagation method—appears in Section 5.

Though usefulness of the invariant imbedding technique in treating the coupled equations problems for molecular scattering was realized quite early there was also an intensive search in the 1970s for more standard procedures suitable to these problems, i.e. for methods generating standard type propagators and using stabilizing transformations of some kind. These are the methods reviewed by Secrest (1979) and recently by Allison (1988) under the heading 'solution following' methods.

Besides the instability a large size of the problem has been an element of difficulty in devising adequate numerical methods for naturally increased efficiency requirements. The algorithms constructed consist of operations which serve essentially the following two purposes: (*a*) determination of propagators (of standard or invariant imbedding type) over subsequent sectors of integration interval, and (*b*) assembling of the sector propagators according to respective (the ordinary linear superposition or invariant imbedding recurrence) relations to get the corresponding global propagator over the entire interval of interest. For efficiency, it is desirable, of course, that the sector propagators can be evaluated as accurately as possible with few operations and simultaneously that the total number of sectors cannot be large. The obvious thing to do for accomplishing that is to take advantage of the characteristiq behaviour of the potential coupling, i.e. of the feature (i)″ of the problems. In that way, the two approaches have arisen to the determination of sector propagators (see again the 1979 review by Secrest): the 'approximate-potential' approach which allows relatively large sectors in the regions of slowly varying potentials and the 'approximate-solution' approach which is particularly appropriate in the nonclassical regions. In the former approach, the sector propagators are determined from analytical solutions of differential equations obtained by approximate decoupling of the original equations within particular sectors and by insertion of simple reference potentials. In the latter approach, the propagators are determined from algebraic equations which come from a discretization, i.e. an approximate treatment mostly of the derivative operator in the original equations. The R-matrix propagation method and the (original) log–derivative method are representative examples of the two different approaches.

Having recapitulated Secrest's well-known classification of the propagative methods for molecular scattering calculations (as being based on the two criterions: the type of the propagator generated in a given method and the approach taken to its evaluation), let us recall finally the work in 1981 of Thomas *et al.* comparing the performance of these methods on some representative non-reactive collision test problems. This comparison revealed superiority of the log–derivative algorithm of Johnson to any other purely approximate-solution procedure available at that time. In the non-classical regions, this algorithm performed also better than all the approximate-potential methods tested. High efficiency of the log–derivative method, in the original version applicable only to the simplest coupled equations problems describing usually non-rearrangement collisions, has been an inspiration for extending applicability of this method to more involved problems arising in the theory of reactive scattering and half-collision processes. Reviewing the research done on this matter and presenting some new contributions are the goals of the next Section.

In the first place, a suitable analytical frame for construction of generalized log–derivative algorithms had to be provided. This is the L-matrix formalism which is reviewed in Section 5.1.

A complete set of initial value problems is presented, in the discrete (recurrence relation) form, which in addition to the basic L-propagator (and the log–derivative matrix as a part of it) also allow determination of the actual solution of a given coupled

equations problem at any point within the range of integration. Such information is not necessary, as mentioned above, if the solution represents the total wavefunction for the collision system, i.e. if the problem being solved comes from applying the close-coupling approximation to the appropriate, ordinary or generalized Schrödinger equation. However, some auxiliary boundary value problems for coupled ordinary differential equations which account for only a part of all transitions possible in a given reactive collision system arise (see, for example, Schwenke *et al.* 1988, 1989) when variational methods are applied to respective generalized Lippmann–Schwinger equations. Solutions of these problems enter various matrix elements (listed, for example, in Mrugała (1990)) which constitute the Schwinger or the Schwinger-like variational expressions for the scattering matrices. Knowledge of these functions along the entire integration range is usually necessary to start evaluation of those matrix elements which involve nonlocal operators.

Matrix elements which are single integrals with integrands including solutions of boundary value problems for homogeneous or inhomogeneous coupled equations can be evaluated in the course of the generation of propagators for these equations, avoiding the step of explicit determination of the solutions. Appropriate recurrence relations for accumulation of such integrals over subsequent sectors of the integration interval simultaneously with addition of the sector L-propagators are also presented in Section 5.1, in connection with evaluation of the first- and second-order transition amplitudes for half-collision and collision mediated processes and in connection with evaluation of the energy derivative of the scattering S matrix. The latter quantity appears in the definition of the collision lifetime matrix (Smith 1960a) which has proved useful in the analysis of resonances in multichannel collisions (Kuppermann and Kaye 1981, Bisseling *et al.* 1987, Kaye and Kuppermann 1988, Darakjian *et al.* 1991) and half-collisions (Mrugała·1988, 1989, Parlant *et al.* 1990). A relatively new trend in the lifetime matrix calculations is the direct evaluation, i.e. omitting numerical differentiation, of the energy derivatives of the scattering matrix (Walker and Hayes 1988, 1989, Darakjian and Hayes 1990). In Section 5.1, this idea is viewed in the context of the more general task of evaluation of first-order transition amplitudes of free–free type.

A part of Section 5.1 is devoted to a description of how the coupled equations, in particular those derived from the generalized Schrödinger equation in the Fock scheme (i.e. with the use of non-orthogonal bases), should be prepared for numerical treatment, i.e. transformed with preservation of self-adjointness property to representations which are most convenient for discretization.

In Section 5.2, the generalized log–derivative algorithms are presented for evaluation of the propagator L, for determination of solutions of some basic boundary value problems for homogeneous and inhomogeneous coupled ordinary differential equations, and for evaluation of some integrals involving these solutions. The algorithms are written in the version appropriate for equations in the diabatic representation and a (new) convenient way of their adaptation to equations in so-called quasi-diabatic representations is described. All algorithms presented have a hybrid approximate-solution approximate-potential character and are easily convertible to purely approximate-solution versions. Computational experience gathered so far with the various generalized algorithms is summarized.

In Section 5.3, a comparison of the generalized log–derivative algorithms is made (*a*) with algorithms of the R-matrix propagation method and (*b*) with the renormalized Numerov algorithms (being here a collection of invariant imbedding algorithms derived on the basis of the well-known Numerov scheme and on the basis of the

schemes adapted to the Schrödinger equation as proposed by Raptis and Allison (1978) and by Ixaru and Rizea (1980)).

5. The L-matrix propagation (generalized log–derivative) method

5.1. The L-matrix formalism

In order to describe the invariant imbedding -matrix propagation method in application to the coupled equations derived in Section 3 one should start by introducing appropriate standard propagators of solutions of these equations and with collecting some basic facts concerning the standard propagators. For this purpose, it will be convenient to have the equations rewritten in a first-order differential equation form.

Let

$$DX = 0, \tag{63}$$

with

$$X = \begin{pmatrix} \psi \\ \lambda \end{pmatrix}, \quad \text{and } D = J\frac{d}{dx} + M, \tag{63a}$$

be such a form, where D is a self-adjoint operator, i.e. the $2N \times 2N$ coefficient matrices J and M satisfy the relations $J = -J^T$ and $M = M^T + J^{(1)}$. The most general form of J considered here will be

$$J = \begin{pmatrix} \mathbf{j}_0 & \mathbf{j} \\ -\mathbf{j} & \mathbf{0} \end{pmatrix}, \tag{63c}$$

with $\mathbf{j}_0$ and $\mathbf{j}$ being $N \times N$ skew-symmetric and symmetric positive definite matrices, respectively

$$\mathbf{j}_0 = -\mathbf{j}_0^T, \quad \mathbf{j} = \mathbf{j}^T. \tag{63d}$$

Equivalence of equation (63) with equation (25) is established, for example, by setting

$$\lambda \equiv \psi^{(1)}, \quad J = \begin{pmatrix} \frac{1}{2}(\mathbf{a}_1 - \mathbf{a}_1^T) & \mathbf{a}_2 \\ -\mathbf{a}_2 & 0 \end{pmatrix}, \quad \text{and } M = \begin{pmatrix} \mathbf{a}_0 & \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_1^T) \\ 0 & \mathbf{a}_2 \end{pmatrix}. \tag{63e}$$

The following operator D corresponds then to the coupled equations in the Fock scheme (equation (61))

$$_{(F)}D = \begin{pmatrix} \mathscr{F} & \mathscr{S} \\ -\mathscr{S} & 0 \end{pmatrix}\frac{d}{dx} + \begin{pmatrix} \mathscr{W} + \frac{1}{2}(\mathscr{F}^{(1)} + \mathscr{S}^{(2)}) & \mathscr{S}^{(1)} \\ 0 & \mathscr{S} \end{pmatrix}, \tag{64}$$

where

$$\mathscr{F} = 2(\mathscr{A} + \mathscr{C}).$$

The matrix of fundamental solutions of equation (63) $\Omega(x, x')$

$$\underset{2N \times 2N}{\Omega} = \begin{pmatrix} \mathbf{\Omega}_1 & \mathbf{\Omega}_2 \\ \mathbf{\Omega}_3 & \mathbf{\Omega}_4 \end{pmatrix},$$

which is normalized to the unit matrix at a point x'

$$D\Omega(x, x') = 0, \quad \Omega(x', x') = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}, \tag{65}$$

is called a standard propagator of solutions of the coupled equations (equations (63) or (25)). Any solution $X(x)$ of an inhomogeneous equation involving the operator D

$$DX = Y, \tag{66}$$

is propagated between endpoints of an interval $[a, b]$ according to the relation

$$X(b) = \Omega(b, a)X(a) + \omega(b, a), \tag{67}$$

where

$$\omega(b, a) = \int_a^b \Omega(b, x)J^{-1}(x)Y(x)\,\mathrm{d}x. \tag{67\,a}$$

The inhomogeneity term Y is a $2N \times 1$ matrix of given functions. Obviously, the propagator Ω itself satisfies the above relation giving the following group property

$$\Omega(x'', x') = \Omega(x'', y)\Omega(y, x'). \tag{68}$$

(Here $[a, b] = [y, x']$ and x' is an arbitrary point.) A direct consequence of this property is

$$\omega(x'', x') = \Omega(x'', y)\omega(y, x') + \omega(x'', y), \tag{69}$$

for any $y \in [x', x'']$. In the limit of $y \to x''$, one verifies simply that $\omega(y, x')$ satisfies equation (66)

$$D\omega(x, x') = Y, \qquad \omega(x', x') = 0. \tag{70}$$

(Here y is renamed to x). Moreover, the property $\Omega(x', x'') = \Omega^{-1}(x'', x')$ is implied.

From the Lagrange identity (equation (27)) applied to $D(=D^\dagger)$, the following symmetry relation results for Ω

$$\Omega^{\mathrm{T}}(x'', x')J(x'')\Omega(x'', x') = J(x'). \tag{71}$$

So, in the case of

$$J = \begin{pmatrix} 0 & I \\ \ge I & 0 \end{pmatrix},$$

Ω is a symplectic matrix. Definite advantages may be taken of this property of the standard propagator in designing algorithms for solving the coupled equations. Therefore it is useful to have equation (66) converted to a form

$$\check{D}\check{X} = \check{Y}, \tag{72}$$

$$\check{D} = (T^{-1})^{\mathrm{T}}DT^{-1} = \check{J}\frac{\mathrm{d}}{\mathrm{d}x} + \check{M}, \tag{72\,a}$$

$$\check{X} = TX = \begin{pmatrix} \check{\psi} \\ \check{\lambda} \end{pmatrix}, \qquad \check{Y} = (T^{-1})^{\mathrm{T}}Y, \tag{72\,b}$$

which involves self-adjoint operator $\check{D}$ with

$$\check{J} = \begin{pmatrix} 0 & I \\ \ge I & 0 \end{pmatrix}.$$

This forms of $\check{J}$ can be obtained by means of the following transformations T

$$T = T_1 T_2, \quad \text{with } T_1 = \begin{pmatrix} t_1 & 0 \\ 0 & t_1 \end{pmatrix}, \quad \text{and } T_2 = \begin{pmatrix} I & 0 \\ t_2 & I \end{pmatrix}, \tag{73}$$

by setting $\mathbf{t}_1 = \mathbf{j}^{1/2}$ and $\mathbf{t}_2 = \frac{1}{2}\mathbf{j}^{-1}\mathbf{j}_0 + \mathbf{j}^{-1/2}\mathbf{s}\mathbf{j}^{+1/2}$, where $\mathbf{s}$ is a symmetric matrix. Choosing $\mathbf{s}$ appropriately, one can get also the following symmetric form for the matrix $\check{M}$

$$\check{M} = \begin{pmatrix} \mathbf{w} & \mathbf{c} \\ \mathbf{c}^{\mathrm{T}} & \mathbf{I} \end{pmatrix}, \qquad \text{with } \mathbf{w} = \mathbf{w}^{\mathrm{T}}, \qquad \text{and } \mathbf{c} = -\mathbf{c}^{\mathrm{T}}. \tag{74}$$

For example, in order to convert the operator $_{(F)}D$ of equation (64) to the desired form $_{(F)}\check{D}$ one should use the transformation T with $\mathbf{t}_1 = \mathscr{S}^{1/2}$ and $\mathbf{t}_2 = \frac{1}{2}\mathscr{S}^{-1}(\mathscr{F} + \mathscr{S}^{(1)})$, obtaining the following expressions for $\mathbf{w}$ and $\mathbf{c}$

$$\begin{aligned}
\mathbf{w} &= \mathscr{S}^{-1/2}[\mathscr{W} - \tfrac{1}{4}(\mathscr{F} - \mathscr{S}^{(1)})\mathscr{S}^{-1}(\mathscr{F} + \mathscr{S}^{(1)})]\mathscr{S}^{-1/2}, \\
\mathbf{c} &= \tfrac{1}{2}\mathscr{S}^{-1/2}\left[\mathscr{F} + \left(\frac{\mathrm{d}}{\mathrm{d}x}\mathscr{S}^{1/2}\right)\mathscr{S}^{1/2} - \mathscr{S}^{1/2}\frac{\mathrm{d}}{\mathrm{d}x}\mathscr{S}^{1/2}\right]\mathscr{S}^{-1/2}.
\end{aligned} \tag{75}$$

(Note, the matrices $\mathscr{A}^{(1)}$, $\mathscr{C}^{(1)}$, and $\mathscr{S}^{(2)}$ do not appear here.)

Obviously, the second-order matrix differential equation for the function $\check{\psi}$, obtained after elimination of $\check{\lambda}$ in equation (72), involves the first derivative coupling term $2\mathbf{c}\,\mathrm{d}\check{\psi}/\mathrm{d}x$. This term is eliminated by converting the operator $\check{D}$ to the form

$$D_{\bar{x}} = (T_{\bar{x}}^{-1})^{\mathrm{T}}\check{D}T_{\bar{x}}^{-1} = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ >\mathbf{I} & \mathbf{0} \end{pmatrix}\frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} \mathbf{w}_{\bar{x}} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}, \tag{76}$$

where

$$\mathbf{w}_{\bar{x}}(x) = \mathbf{t}^{\mathrm{T}}(x; \bar{x})\mathbf{w}(x)\mathbf{t}(x; \bar{x}).$$

The transformation $T_{\bar{x}}$ used to this end has the structure of T_1 with $\mathbf{t}_1 \equiv \mathbf{t}^{\mathrm{T}}(x; \bar{x})$, where $\mathbf{t}(x; \bar{x})$ is the orthogonal matrix which satisfies the equations (Smith 1969, Baer et al. 1980)

$$\left(\mathbf{I}\frac{\mathrm{d}}{\mathrm{d}x} + \mathbf{c}\right)\mathbf{t}(x; \bar{x}) = 0, \qquad \mathbf{t}(\bar{x}; \bar{x}) = \mathbf{I}. \tag{77}$$

In what follows, the operators $D_{\bar{x}}$ and $\check{D}$ with

$$\check{J} = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{pmatrix},$$

and $\check{M}$ given by equation (74) will be called respectively, diabatic and non-diabatic forms (representations) of the operator D.

The transformation $D \to \check{D}$ defined in equation (72 a) implies the following relation between the respective standard propagators

$$\Omega(x'', x') = T^{-1}(x'')\check{\Omega}(x'', x')T(x'). \tag{78}$$

Let us proceed now to a reformulation of the above relations in terms of the propagator L

$$\underset{2N \times 2N}{L} = \begin{pmatrix} \mathbf{L}_1 & \mathbf{L}_2 \\ \mathbf{L}_3 & \mathbf{L}_4 \end{pmatrix},$$

which is defined (Mrugała and Secrest 1983a) through the following operation on the blocks of the standard propagator Ω

$$L(x', x'') = \hat{L}[\Omega(x'', x')], \tag{79}$$

$$\hat{L}\left[\begin{pmatrix} \Omega_1 & \Omega_2 \\ \Omega_3 & \Omega_4 \end{pmatrix}\right] = \begin{pmatrix} -\Omega_2^{-1}\Omega_1 & \Omega_2^{-1} \\ \Omega_3 - \Omega_4\Omega_2^{-1}\Omega_1 & \Omega_4\Omega_2^{-1} \end{pmatrix}, \tag{79a}$$

provided $\det \Omega_2(x'', x') \neq 0$. Useful properties of the operation $\hat{L}$ are

$(a) \quad \hat{L}[\Gamma] = \Gamma, \quad$ where $\Gamma = \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix}, \quad (b) \quad \hat{L}(\hat{L}[\Omega]) = \Omega,$ \hfill (80)

$(c) \quad \hat{L}[\Gamma\Omega\Gamma] = (\hat{L}[\Omega])^{-1}, \quad\quad\quad (d) \quad \hat{L}[\Omega^{-1}]\Gamma\hat{L}[\Omega]\Gamma.$

First of all, one gets the following form of the relation (67) for propagating solutions

$$X(x) = \begin{pmatrix} \psi(x) \\ \lambda(x) \end{pmatrix},$$

of equation (66)

$$\begin{pmatrix} \lambda(a) \\ \lambda(b) \end{pmatrix} = L(a, b) \begin{pmatrix} \psi(a) \\ \psi(b) \end{pmatrix} + l(a, b), \tag{81}$$

where

$$l(a, b) = \begin{pmatrix} \mathbf{Q}(a, b) \\ \mathbf{P}(a, b) \end{pmatrix} = \hat{L}_1[\Omega(b, a)]\omega(b, a), \tag{81a}$$

and $\hat{L}[\Omega]$ denotes

$$\hat{L}_1[\Omega] = \begin{pmatrix} -\Omega_2^{-1} & 0 \\ -\Omega_4\Omega_2^{-1} & I \end{pmatrix}. \tag{81b}$$

Further on, using equation (80d) one determines immediately how the propagator L behaves under reversal of the direction of propagation. The symmetry relation satisfied by the fundamental matrix Ω, equation (71), translates into the following relation for the matrix L

$$L(x', x'') = \begin{pmatrix} \mathbf{j}^{-1}(x') & 0 \\ 0 & \mathbf{j}^{-1}(x'') \end{pmatrix} \left[\begin{pmatrix} -\mathbf{j}_0(x') & 0 \\ 0 & > \mathbf{j}_0(x'') \end{pmatrix} \right.$$

$$\left. + \begin{pmatrix} -I & 0 \\ 0 & I \end{pmatrix} L^{\mathrm{T}}(x', x'') \begin{pmatrix} -\mathbf{j}(x') & 0 \\ 0 & \mathbf{j}(x'') \end{pmatrix} \right]. \tag{82}$$

It becomes clear now that the advantage of having equations (63) and (66) in the form with

$$\mathbf{J} = \begin{pmatrix} \mathbf{j}_0 & \mathbf{j} \\ -\mathbf{j} & 0 \end{pmatrix} = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix},$$

lies in that the L propagator is a symmetric matrix in this case (the sign in the respective relation for the off-diagonal blocks, $\mathbf{L}_3 = -\mathbf{L}_2^{\mathrm{T}}$ is not mentioned).

Concerning the symmetry of the propagators, let us stress again that the above relation is valid only when equation (25) involves a self-adjoint operator $\mathscr{D}$. If $\mathscr{D} \neq \mathscr{D}^\dagger$ (as in the majority of cases of operators resulting from the CCA schemes and also in the case of the operator $\bar{\bar{\mathscr{D}}}$ involved in the unsymmetrized Fock coupled equations, see

equation (60)), then also the operator D of equation (63) is not self-adjoint, usually because the coefficient matrix M no longer satisfies the condition stated in equations (63). In such cases, the relations (71) and (82) should involve, in place of the propagators Ω^{T} and L^{T}, transposes of the respective propagators for adjoint equations, $_t\Omega^{\mathrm{T}}$ and $_+L^{\mathrm{T}}$. Though it may be proper to assume that locally, i.e. in small intervals $[x', x'']$, the propagators $_+\Omega(x'', x')$ and $_+L(x', x'')$ do not differ much from the propagators $\Omega(x'', x')$ and $L(x', x'')$, respectively, (the derivation of the algorithm given by Stechel *et al.* (1979) for equations involving a non-self-adjoint $\overline{\overline{\mathscr{D}}}$-type operator actually relies on such an assumption) this certainly is not always true globally, i.e. for the propagators over the entire range $[x_0, x_\infty]$.

The counterpart of the relation (68) for the matrix L, obtained also by a straightforward exploitation of the involutional property (80 *b*) of the operation $\hat{L}$, is

$$L(x', x'') = \hat{L}\{\hat{L}[L(y, x'')]\hat{L}[L(x', y)]\}. \tag{83}$$

Written explicitly, it gives the recurrence relations (Mrugała and Secrest 1983a) for 'addition' of the blocks of the L propagators acting within two adjacent intervals $[x', y]$ and $[y, x'']$. Let us list here only the basic relation—for the block $\mathbf{L_4}$

$$\mathbf{L_4}(x', x'') = \mathbf{L_4}(y, x'') + \mathbf{L_3}(y, x'')\mathbf{l}(x', y, x'')\mathbf{L_2}(y, x''),$$
$$\mathbf{l}(x', y, x'') = [\mathbf{L_4}(x', y) - \mathbf{L_1}(y, x'')]^{-1}. \tag{83 a}$$

The respective recurrence relations for the blocks of the matrix

$$\mathbf{l} = \begin{pmatrix} \mathbf{Q} \\ \mathbf{P} \end{pmatrix},$$

have been published by Mrugała (1985). That for $\mathbf{P}$ reads

$$\mathbf{P}(x', x'') = \mathbf{P}(y, x'') - \mathbf{L_3}(y, x'')\mathbf{l}(x', y, x'')[\mathbf{P}(x', y) - \mathbf{Q}(y, x'')]. \tag{84}$$

In the limit of $y \to x''$, the differential equations with respect to the imbedding parameter—here y—results from the above recurrence relations for the blocks of the matrices $L(x', y)$ and $l(x', y)$ (see Section 4); the nonlinear equation—for the block $\mathbf{L_4}$—reads

$$\frac{\mathrm{d}}{\mathrm{d}y}\mathbf{L_4}(x', y) = \mathbf{A_3}(y) + \mathbf{A_4}(y)\mathbf{L_4}(x', y) - \mathbf{L_4}(x', y)[\mathbf{A_1}(y) + \mathbf{A_4}(y)\mathbf{L_4}(x', y)].$$

$\mathbf{A}_i$ denote blocks of the matrix $A = -J^{-1}M$. These differential equations (listed in full by Mrugała and Secrest (1983a), see also Mrugała (1980)), together with the initial conditions $L(x', x') (= \lim_{\varepsilon \to 0} \hat{L}[\Omega(x' + \varepsilon, x')])$,

$$L(x', x') = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \begin{pmatrix} -\mathbf{I} & \mathbf{I} \\ -\mathbf{I} & \mathbf{I} \end{pmatrix} \mathbf{A}_2^{-1}(x'), \tag{85}$$

and $l(x', x')$, are counterparts of the linear initial value problems connected with the 'addition' relations (68) and (69) for the matrices Ω and ω, i.e., of equations (65) and (70), respectively.

Whereas the standard propagator Ω and the matrix ω are defined through the initial value problems (65) and (70), respectively, the propagator L and the matrix l

appear to be directly related to the following two-point boundary value problems involving the same differential operator D

$$DX^\alpha_{x'x''}(x) = \delta_{\alpha,0}Y, \quad \text{for } \alpha = +, -, 0, \quad \text{with } X^\alpha_{x'x''} = \begin{pmatrix} \psi^\alpha_{x'x''}(x) \\ \lambda^\alpha_{x'x''}(x) \end{pmatrix}, \quad (86)$$

and

$$\psi^\pm_{x'x''}(x') = \begin{cases} \mathbf{I} \\ \mathbf{0} \end{cases}, \quad \psi^\pm_{x'x''}(x'') = \begin{cases} \mathbf{0} \\ \mathbf{I} \end{cases}, \quad (86\,a)$$

$$\psi^0_{x'x''}(x') = \psi^0_{x'x''}(x'') = \mathbf{0}. \quad (86\,b)$$

Indeed, applying the propagation relation (81) to the solutions of these problems one gets

$$\begin{pmatrix} \mathbf{L}_1(x',x'') & \mathbf{L}_2(x',x'') \\ \mathbf{L}_3(x',x'') & \mathbf{L}_4(x',x'') \end{pmatrix} = \begin{pmatrix} \lambda^+_{x'x''}(x') & \lambda^-_{x'x''}(x') \\ \lambda^+_{x'x''}(x'') & \lambda^-_{x'x''}(x'') \end{pmatrix},$$

and

$$\mathbf{Q}(x',x'') = \lambda^0_{x'x''}(x'), \quad \mathbf{P}(x',x'') = \lambda^0_{x'x''}(x''). \quad (87)$$

The connection with the above boundary value problems could have been taken, of course, as the feature defining the matrices L and l instead of the definitions given in equations (79) and (81 a).

Obviously, there is a close relation between the propagator $L(x', x'')$ and the matrix Green function $G_{x'x''}(x, y)$ for the operator D

$$DG_{x'x''}(x, y) = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix} \delta(x - y), \quad (88)$$

which satisfies the conditions

$$\mathbf{G}^1_{x'x''}(x', y) = \mathbf{G}^1_{x'x''}(x'', y) = \mathbf{0}. \quad (88\,a)$$

$\mathbf{G}^i_{x'x''}$ with $i = 1, 2, 3, 4$ denote $N \times N$ blocks of $G_{x'x''}$

$$G = \begin{pmatrix} \mathbf{G}^1 & \mathbf{G}^2 \\ \mathbf{G}^3 & \mathbf{G}^4 \end{pmatrix}.$$

The relation can be easily derived from the expression for $G_{x'x''}$ in terms of the solutions $X^\pm_{x'x''}$ of the problems (86, 86 a)

$$G_{x'x''}(x, y) = \begin{cases} X^-_{x'x''}(x)(W^{-1})^{\mathrm{T}}[X^+_{x'x''}(y)]^{\mathrm{T}}, & \text{for } x < y, \\ X^+_{x'x''}(x)W^{-1}[X^-_{x'x''}(y)]^{\mathrm{T}}, & \text{for } x > y, \end{cases} \quad (89)$$

where

$$W = \mathbf{W}_{n=1}(X^-_{x'x''}, X^+_{x'x''}) = [X^-_{x'x''}(x)]^{\mathrm{T}}J(x)X^+_{x'x''}(x) \equiv \text{const},$$

(see equation (27 a)). Namely, using equation (87) one gets

$$L(x', x'') = \lim_{\varepsilon \to 0} \begin{bmatrix} \mathbf{G}^4_{x'x''}(x'+\varepsilon, x') & \mathbf{G}^4_{x'x''}(x', x'') \\ \mathbf{G}^4_{x'x''}(x'', x') & \mathbf{G}^4_{x'x''}(x''-\varepsilon, x'') \end{bmatrix} \begin{bmatrix} -\mathbf{j}(x') & \mathbf{0} \\ \mathbf{0} & \mathbf{j}(x'') \end{bmatrix}. \quad (90)$$

Moreover, from the expression for the solution $X^0_{x'x''}$ in terms of Green function $G_{x'x''}$, $X^0_{x'x''} = G_{x'x''} Y$ (written abbreviatedly), the following formula results for the matrix

$$l = \begin{pmatrix} \mathbf{Q} \\ \mathbf{P} \end{pmatrix},$$

$$l(x', x'') = \begin{bmatrix} -\mathbf{j}^{-1}(x') & \mathbf{0} \\ \mathbf{0} & \mathbf{j}^{-1}(x'') \end{bmatrix} \begin{bmatrix} (X^+_{x'x''}|Y) \\ (X^-_{x'x''}|Y) \end{bmatrix}. \tag{91}$$

$(|)$ denotes here the same scalar product as defined in equation (24) but with the range of integration confined to the interval $[x', x'']$. Use has been made in equations (89) and (91) of the self-adjointness property of D. If D were not self-adjoint, but with the coefficient matrix J still in the form $(63\,c, d)$, the formula (91) would involve, instead of the functions $X^\pm_{x'x''}$, the solutions $_+X^\pm_{x'x''}$ of equations $(86, 86\,a)$ with the operator $D^\dagger$ standing in place of D.

For determining the propagator $L(x', x'')$, it is convenient to have the boundary value problems $(86, 86\,a)$ converted to appropriate integral equations

$$X^\alpha_{x'x''}(x) = {}_{\mathrm{ref}}X^\alpha_{x'x''}(x) - \int_{x'}^{x''} {}_{\mathrm{ref}}G_{x'x''}(x, y) {}^{\mathrm{res}}M(y) X^\alpha_{x'x''}(y)\, \mathrm{d}y, \qquad \text{for } \alpha = +, -. \tag{92}$$

Such equations involve solutions $_{\mathrm{ref}}X^\alpha_{x'x''}$ of analogous problems with a reference operator $_{\mathrm{ref}}D(= {}_{\mathrm{ref}}D^\dagger)$

$${}_{\mathrm{ref}}D = J\frac{\mathrm{d}}{\mathrm{d}x} + {}_{\mathrm{ref}}M, \tag{93}$$

and the respective Green function $_{\mathrm{ref}}G_{x'x''}$ for the reference operator and the residual operator $^{\mathrm{res}}M$, $^{\mathrm{res}}M = M - {}_{\mathrm{ref}}M$. Obviously, it is of practical value that the reference operator $_{\mathrm{ref}}D$ be such that the corresponding $_{\mathrm{ref}}L$ part of L is easily obtainable and has a simple form. Thus, it is worth noting that for D's in the diabatic representation, equation (76), the operator $_{\mathrm{ref}}D$ may be chosen in the form

$${}_{\mathrm{ref}}D = \begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{I} & \mathbf{0} \end{pmatrix} \frac{\mathrm{d}}{\mathrm{d}x} + \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}, \tag{94}$$

giving $_{\mathrm{ref}}L$ as simple as

$${}_{\mathrm{ref}}L(x', x'') = \frac{1}{x'' - x'} \begin{pmatrix} -\mathbf{I} & \mathbf{I} \\ -\mathbf{I} & \mathbf{I} \end{pmatrix}. \tag{94\,a}$$

This choice was made in the derivation of the original log–derivative algorithm (see Section 5.2) and has been one of the factors determining the particular simplicity of this algorithm.

Since practical aspects have just come into consideration this is a good moment for a comparison of the L-matrix formalism with formalisms based on other invariant imbedding type propagators. The R-matrix propagator may be introduced through the relation

$$\begin{pmatrix} \psi(a) \\ \psi(b) \end{pmatrix} = R(a, b) \begin{pmatrix} \lambda(a) \\ \lambda(b) \end{pmatrix} + r(a, b), \tag{95}$$

which comes, just as equation (81) for the matrix L, from a simple rearrangement of the standard relation (67). Provided $\det \Omega_3(b, a) \neq 0$, one defines (see equations (79 a), (80 a), and (81 b))

$$R(a, b) = \hat{L}[\Gamma \Omega(b, a) \Gamma], \tag{95 a}$$

$$r(a, b) = \hat{L}_1[\Gamma \Omega(b, a) \Gamma] \Gamma \omega(b, a). \tag{95 b}$$

The propagator actually used in the method of Light and co-workers (see Section 4) is

$$R \begin{pmatrix} -\mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix},$$

the minus sign serves only to emphasize the connection of the method with the **R**-matrix theory of Wigner and Eisenbud (see, Lane and Thomas (1958)).

Another rearrangement of the relation (67), originally proposed by Denman (1971)

$$\begin{pmatrix} \psi(b) \\ \lambda(a) \end{pmatrix} = U(a, b) \begin{pmatrix} \psi(a) \\ \lambda(b) \end{pmatrix} + u(a, b),$$

and possible if only $\det \Omega_4(b, a) \neq 0$, introduces the propagator (see equations (80 a), (81 b))

$$U(a, b) = \hat{U}[\Omega(b, a)], \tag{96 a}$$

and the matrix

$$u(a, b) = \hat{U}_1[\Omega(b, a)] \Gamma \omega(b, a), \tag{96 b}$$

where

$$\hat{U} = \Gamma \hat{L} \Gamma, \quad \text{and} \quad \hat{U}_1 = \Gamma \hat{L}_1 \Gamma.$$

Blocks of the propagator U are most directly related to the matrices of transmission and reflection coefficients generated in the amplitude density function method and to the S-matrix propagator used in the method of Manz and co-workers (see again Section 4). The connection of the propagators R and U with the propagator L (over intervals for which these propagators simultaneously exist) is given by the formula

$$L = R^{-1} = \Gamma \hat{L}(U), \tag{97}$$

and the matrices r, u, and l, necessary for inhomogeneous equations, are connected as follows

$$l = -R^{-1}r = \Gamma \hat{L}_1[U]u. \tag{97 a}$$

In order to assess the usefulness of the three propagators in the construction of algorithms one has to compare the initial value problems associated with these propagators. Concerning discrete forms of the problem, i.e. the respective recurrence relations, the following two facts should be noted: (i) the structure of the relation for the matrix R is the same as that shown in equation (83) for the matrix L, i.e.

$$R(x', x'') = \hat{L}\{\hat{L}[R(y, x'')]\hat{L}[R(x', y)]\}. \tag{98}$$

Identical structures have also the respective relations for the matrices r and l; (ii) the relation for the matrix U

$$U(x', x'') = \hat{U}\{\hat{U}[U(y, x'')]\hat{U}[U(x', y)]\}, \tag{99}$$

is more complex since it involves more matrix multiplications than equation (83 *a*) when written explicitly for the respective blocks of *U*. The limiting continuous, i.e. differential equation, forms of the recurrence relations are for all the three propagators practically the same. The blocks of the coefficient matrices $A(= -J^{-1}M)$ and $B(=J^{-1}Y)$ occurring in the equations for the matrices *L* and *l* have only to be renumbered appropriately in order to make these equations valid for the matrices *R* and *r* or *U* and *u*. More essential are some differences that occur between the initial conditions to the particular equations. While the condition (85) and the respective condition for the matrix *R* (looking similar, i.e. A_3 appears in place of A_2) are rather awkward to start numerical integration of differential equations, the condition for the matrix *U* is as simple and convenient as

$$U(x', x') = \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}.$$

Obviously, the same initial conditions have to be used in order to start the recurrence process with the respective relation, equation (83), (98), or (99). In this case, however, the infiniteness of the matrices $L(x', x)$ and $R(x', x)$ poses no practical difficulty (see Section 5.2). Thus, the propagator **U** might be preferable to the two others only if the respective initial value problems were to be solved in their differential equation forms. The use of the recurrence relations however, opens, more possibilities in the construction of algorithms as there is much more freedom in the sectorization of a given integration interval and a variety of procedures may be tried for the evaluation of required sector propagators. In view of the fact (i) stated above, differences in the determination of the respective sector propagators may only lead to a discrimination of the *L*-matrix and *R*-matrix propagators in practice. In this context, it is worth noting that the simple reference operator (94) would not be acceptable if boundary value problems appropriate for the matrix *R*, i.e. equation (86) with the conditions

$$\lambda^{\pm}_{x'x''}(x') = \begin{cases} \mathbf{I} \\ \mathbf{0} \end{cases}, \qquad \lambda^{\pm}_{x'x''}(x'') = \begin{cases} \mathbf{0} \\ \mathbf{I} \end{cases},$$

were to be solved instead of the problems (86, 86 *a*). Indeed, the standard propagator (see equation (65)) for equation with $_{ref}D$ in the form (94)

$$_{ref}\Omega(x'', x') = \begin{pmatrix} \mathbf{I} & (x'' - x')\mathbf{I} \\ \mathbf{0} & \mathbf{I} \end{pmatrix},$$

cannot be rearranged to the *R*-matrix with the formula (95 *a*). Thus, despite of the simple connection between the *R* and *L* propagators (equation (99)) and the identical structure of the respective recurrence relations it would not be possible to construct an approximate-solution type algorithm as simple as the original log–derivative algorithm if the propagator *R* were employed instead of *L*.

In connection with the transition amplitudes for half-collision and for collision mediated processes, defined in equations (14, 15), the following integrals are considered within the *L*-matrix formalism (Mrugała 1989)

$$\mathbf{J}^{\alpha}_{x'x''} = (\psi^{\alpha}_{x'x''}|\phi), \qquad \text{for } \alpha = +, -, \tag{100}$$

$$J^{0}_{x'x''} = (\psi^{0}_{x'x''}|\bar{\phi}), \tag{101}$$

where ϕ and $\bar{\phi}$ are $N \times 1$ matrices of given functions. Obviously, the integrals $\mathbf{J}^{\alpha}_{x'x''}$ with $\alpha = +, -$ are directly related to the quantities $\mathbf{Q}(x', x'')$ and $\mathbf{P}(x', x'')$ if the inhomogeneity in equation (66) is

$$Y = \begin{pmatrix} \phi \\ 0 \end{pmatrix},$$

$$J^{-}_{x'x''} = \mathbf{j}(x'')\mathbf{P}(x', x''), \qquad J^{+}_{x'x''} = -\mathbf{j}(x')\mathbf{Q}(x', x''). \tag{102}$$

So, the recurrence relation (84) can be applied for accumulation of the $\mathbf{J}^{-}$ integrals evaluated over subsequent intervals of the integration range. Analogous relation for the integral $\mathbf{J}^{0}_{x'x''}$ can be derived by exploiting the following linear superposition relations for the solutions of the problems $(86, 86\,b)$ on intervals $[x', x'']$, $[x', y]$, and $[y, x'']$, $(x' \leqslant y \leqslant x'')$

$$\psi^{\alpha}_{x'x''}(x) = (\delta_{\alpha, +} + \delta_{\alpha, 0})\psi^{\alpha}_{x'y}(x) + \psi^{-}_{x'y}(x)\psi^{\alpha}_{x'x''}(y), \qquad \text{for } x \in [x', y], \tag{103\,a}$$

$$\psi^{\alpha}_{x'x''}(x) = (\delta_{\alpha, -} + \delta_{\alpha, 0})\psi^{\alpha}_{yx''}(x) + \psi^{+}_{yx''}(x)\psi^{\alpha}_{x'x''}(y),$$
$$\text{for } x \in [y, x''] \qquad \text{and } \alpha = +, -, 0, \tag{103\,b}$$

and the following connections between the functions $\psi^{\alpha}_{x'x''}(y)$ and the propagator L, the matrices $\mathbf{Q}$ and $\mathbf{P}$ for the intervals $[x', y]$ and $[y, x'']$

$$\psi^{\alpha}_{x'x''}(y) = \mathbf{l}(x', y, x'') \begin{cases} [-\mathbf{L}_{3}(x', y)], & \text{for } \alpha = +, \\ \mathbf{L}_{2}(y, x''), & \text{for } \alpha = -, \\ [-\mathbf{P}(x', y) + \mathbf{Q}(y, x'')], & \text{for } \alpha = 0, \end{cases} \tag{104}$$

(see equation $(83\,a)$ for the definition of $\mathbf{l}$). The relation reads

$$J^{0}_{x'x''} = J^{0}_{x'y} + J^{0}_{yx''} - [\mathbf{P}(x', y) - \mathbf{Q}(y, x'')]^{\mathrm{T}}\mathbf{l}^{\mathrm{T}}(x', y, x'')[\bar{\mathbf{J}}^{-}_{x'y} + \bar{\mathbf{J}}^{+}_{yx''}]. \tag{105}$$

Overbar denotes that the respective integral is obtained after replacing ϕ with $\bar{\phi}$ in equation (100).

Obviously, a number of other integrals involving solutions of the basic boundary value problems $(86, 86\,b)$ may be considered and treated in a way analogous to that presented above (see Mrugała 1990). Here, let us comment only on the following integrals

$$\mathbf{J}^{\alpha, \beta}_{x'x''} = (\psi^{\alpha}_{x'x''}|\kappa\psi^{\beta}_{x'x''}), \qquad \text{for } \alpha, \beta = +, -, \tag{106}$$

where κ denotes an $N \times N$ matrix of given functions of x. These integrals arise generally when the L-matrix formalism is applied to the determination of free–free type transition amplitudes. The Born and the distorted-wave Born approximants to the scattering matrices are typical examples of such amplitudes. In terms of integrals of the type (106), one can also express the derivatives with respect to energy of the blocks of the L propagator which are the quantities actually needed for determination of the energy derivatives of the scattering matrices (see equation (112)). To make this evident, the following two facts should be noted. Firstly, as in the case of the integrals $\mathbf{J}^{\alpha}_{x'x''}$ for $\alpha = +, -$, which were shown above (equations (102), (87)) to be related to the solution $X^{0}_{x'x''}$ of equation (86) with the inhomogeneity term

$$Y = \begin{pmatrix} \phi \\ 0 \end{pmatrix},$$

the integrals $J_{x'x''}^{\alpha,\beta}$ can be related to analogous solutions of equation (86) with inhomogeneity terms

$$Y^\beta = \begin{pmatrix} \kappa & 0 \\ 0 & 0 \end{pmatrix} X_{x'x''}^\beta, \qquad \text{for } \beta = +, -. \tag{107}$$

Denoting these solutions as

$$X_{x'x''}^{0(\beta)}(x) = \begin{pmatrix} \psi_{x'x''}^{0(\beta)}(x) \\ \lambda_{x'x''}^{0(\beta)}(x) \end{pmatrix},$$

with $\beta = +, -$, and the matrices $\lambda_{x'x''}^{0(\beta)}(x')$ and $\lambda_{x'x''}^{0(\beta)}(x'')$ as $\mathbf{Q}^\beta(x',x'')$ and $\mathbf{P}^\beta(x',x'')$, respectively, one gets

$$\mathbf{J}_{x'x''}^{-,\beta} = \mathbf{j}(x'')\mathbf{P}^\beta(x',x''), \qquad \mathbf{J}_{x'x''}^{+,\beta} = -\mathbf{j}(x')\mathbf{Q}^\beta(x',x''), \qquad \text{for } \beta = +, -. \tag{108}$$

Secondly, differentiating equations (86, 86 a) with respect to the energy E and taking into account that the operator D depends on E only through the coefficient matrix $\mathbf{a}_0$ (see equation (63 e)) one realizes that the functions $(\mathrm{d}/\mathrm{d}E)X_{x'x''}^{\pm}(x)$ are examples of the solutions $X_{x'x''}^{0(\pm)}(x)$ of equation (86) with the inhomogeneities $Y^\pm$ involving the matrix $\kappa = (\mathrm{d}/\mathrm{d}E)\mathbf{a}_0$. In consequence, the following equality holds in this case

$$\frac{\mathrm{d}}{\mathrm{d}E}L(x',x'') = \begin{pmatrix} \mathbf{Q}^+(x',x'') & \mathbf{Q}^-(x',x'') \\ \mathbf{P}^+(x',x'') & \mathbf{P}^-(x',x'') \end{pmatrix}. \tag{109}$$

Necessary recurrence relations for accumulation of the $\mathbf{J}^{\alpha,\beta}$ integrals over subsequent sectors $[x',y]$ and $[y,x'']$ result, of course, from applying the relations (103 a, 104) to the functions $\psi_{x'x''}^\alpha(x)$ and $\psi_{x'x''}^\beta(x)$ for $\alpha, \beta = +, -$. Being aware of the connections (108) and (109) one can obtain the same result also by differentiating with respect to E the relation (83) for the respective blocks of the matrix $L(x',x'')$ and by exploiting the symmetry, equation (82).

It is not difficult to establish how the L-matrix propagator and the quantities related to it are affected by the transformations performed on the coupled equations in equations (72 a, b). Namely, exploiting the form of the corresponding transformations on the standard propagator, equation (78), and defining $\check{L}(x',x'') = \hat{L}[\check{\Omega}(x'',x')]$ (see equations (79, 79 a)), one finds out that the following relation holds when the transformation $\mathbf{T}$ has the form $\mathbf{T}_1$ (see equation (73))

$$L(x',x'') = \begin{pmatrix} \mathbf{t}_1^{-1}(x') & 0 \\ 0 & \mathbf{t}_1^{-1}(x'') \end{pmatrix} \check{L}(x',x'') \begin{pmatrix} \mathbf{t}_1(x') & 0 \\ 0 & \mathbf{t}_1(x'') \end{pmatrix}, \tag{110}$$

and the following in the cases of T being in the T_2 form

$$L(x',x'') = \begin{pmatrix} -\mathbf{t}_2(x') & 0 \\ 0 & -\mathbf{t}_2(x'') \end{pmatrix} + \check{L}(x',x''). \tag{111}$$

Concerning the matrix

$$l = \begin{pmatrix} \mathbf{Q} \\ \mathbf{P} \end{pmatrix},$$

one finds out that it is not affected by transformations of the T_2 type, i.e. $l(x',x'') = \check{l}(x',x'')$, and that the relations appropriate in the $T = T_1$ cases read

$$\mathbf{Q}(x',x'') = \mathbf{t}_1^{-1}(x')\check{\mathbf{Q}}(x',x''), \qquad \mathbf{P}(x',x'') = \mathbf{t}_1^{-1}(x'')\check{\mathbf{P}}(x',x''). \tag{110 a}$$

The corresponding transformations on the J integrals can be found easily on the basis of the respective relations which take place in the $T = T_1$ and $T = T_2$ cases between the solutions of the problems $(86, 86\,b)$, $X^\alpha_{x'x''}$ for $\alpha = +, -, 0$ (or $X^{0(\beta)}_{x'x''}$ for $\beta = +, -$), and the solutions $\check{X}^\alpha_{x'x''}$ (or $\check{X}^{0(\beta)}_{x'x''}$) of the problems with the transformed operator $\check{D}$ (see equation $(72\,a)$) and with the transformed inhomogeneity terms

$$\check{Y} = (T^{-1})^\mathrm{T} \begin{pmatrix} \boldsymbol{\phi} \\ \mathbf{0} \end{pmatrix} \qquad \left(\text{or } \check{Y}^\beta = (T^{-1})^\mathrm{T} \begin{pmatrix} \boldsymbol{\kappa} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} T^{-1} \check{X}^\beta_{x'x''} \right).$$

One notices, for example, that the integrals $\mathbf{J}^+$ and $\mathbf{J}^-$ transform like the matrices $\mathbf{Q}$ and $\mathbf{P}$, respectively, except for the fact that counterparts of equations $(110\,a)$ for these integrals involve matrices $\mathbf{t}_1^\mathrm{T}$ in place of $\mathbf{t}_1^{-1}$.

Finally, a comment is in order on the role of the three forms of first-order differential equations, introduced at the beginning of this Section, in solving the equivalent second-order matrix differential equation (25). The basic is the form (63) in which $\lambda \equiv \psi^{(1)}$. For this equation, the forth block of the L propagator, $\mathbf{L}_4(x', x)$, has the meaning of the log–derivative matrix of any set of N linearly independent solutions

$$\psi(x),$$
$$N \times N$$

which vanish at the point x', i.e. $\mathbf{L}_4(x', x) = \psi^{(1)}(x)[\psi(x)]^{-1}$ when $\psi(x') = \mathbf{0}$. Knowledge of the log–derivative matrix for the interval $[x', x''] = [x_0, x_\infty]$ suffices for evaluation of the matrix $\mathbf{K}$ when the scattering boundary conditions are imposed as described in Section 3 (where the scattering coordinate was assumed to have the property of hyperradius. In the reaction coordinate formulations, the boundary conditions are imposed in a way requiring determination of all blocks of the propagator; see, e.g., Light and Walker 1976b). The following formula for $\mathbf{K}$ results from the conditions $(37\,a)$ and $(37\,b)$ (assuming $\mathbf{g}^a(x_\infty) = \mathbf{S}^{aa}(x_\infty) = \mathbf{I}^a$)

$$\mathbf{K} = [\dot{\boldsymbol{n}} - (\check{\mathbf{L}}_4 + \mathbf{d})\boldsymbol{n}]^{-1}[\dot{\boldsymbol{m}} - (\check{\mathbf{L}}_4 + \mathbf{d})\boldsymbol{m}], \tag{112}$$

where

$$\check{\mathbf{L}}_4 = \mathbf{L}_4 + \mathbf{A} + \mathbf{C}. \tag{112\,a}$$

In the case of the coupled equations in the Fock scheme derived in the previous section (equations $(61, 62\,a, b)$)

$$\mathbf{d}(x_\infty) = -\frac{5}{2x_\infty}\mathbf{I}, \qquad \text{and} \quad \check{\mathbf{L}}_4(x_0, x_\infty) = \mathbf{L}_4(x_0, x_\infty) + \mathscr{C}(x_\infty). \tag{113}$$

Having determined the matrix $\mathbf{K}$ and the solution $\psi^-_{x_0 x_\infty}(x)$ at points x within the interval $[x_0, x_\infty]$ one can easily evaluate the corresponding (standing wave) scattering function (see equations $(37\,a)$ and $(62\,a)$) within this interval

$$\psi(x) = \begin{bmatrix} \psi^{\alpha\alpha}(x) & \psi^{\alpha\beta}(x) & \psi^{\alpha\gamma}(x) \\ \psi^{\beta\alpha}(x) & \psi^{\beta\beta}(x) & \psi^{\beta\gamma}(x) \\ \psi^{\gamma\alpha}(x) & \psi^{\gamma\beta}(x) & \psi^{\gamma\gamma}(x) \end{bmatrix} = \psi^-_{x_0 x_\infty}(x)[\boldsymbol{m}(x_\infty) - \boldsymbol{n}(x_\infty)\mathbf{K}]. \tag{114}$$
$$N \times N_{\mathrm{op}}$$

In order to calculate the transition amplitudes $\mathbf{K}^b$ and K^{bb} for the collision related processes (see equations (14) and (15)) one has to evaluate, in addition to the log–

derivative matrix, the integrals $J^-_{x_0 x_\infty}$ and $\bar{J}^-_{x_0 x_\infty}$ with $\phi \equiv \phi^b$ and $\bar{\phi} \equiv \phi^{\bar{b}}$, respectively, and the integral $J^0_{x_0 x_\infty}$

$$K^b = -[\dot{n} - (\check{L}_4 + d)n]^{-1}J^-,$$ (115)

$$\frac{\hbar^2}{2\mu} K^{\bar{b}b} = J^0 - J^{-T}[(\check{L}_4 + d - \dot{n}n^{-1})^{-1}]^T J^-.$$ (116)

It should be remembered, of course, that $J^0, J^-, \bar{J}^-$, and L_4 refer to the interval $[x_0, x_\infty]$ and all the other matrices occurring in the above formulas are evaluated at the point x_∞.

As already mentioned, the log–derivative matrix and, in general, the propagator L connected with the basic form of equation (63) are not symmetric matrices. So, if this propagator were employed to generate numerical solutions of the coupled equations, not much could be practically profited from self-adjointness of these equations. The two other forms of equation (63) introduced, the diabatic and the non-diabatic ones, do have the property of being connected with symmetric L propagators. Actually, the matrix $\hat{L}_4(x_0, x_\infty)$ defined in equation (112 a) is the fourth block of the propagator $\check{L}(x_0, x_\infty)$ for the non-diabatic equation (72) and, in particular, for the equation with the operator $_{(F)}\check{D}$ (see equations (64), (72 a), (74), (75), and (113) and the relations (110) and (111) where, in the case of the Fock equations, $t_1(x'' = x_\infty) = I$ and $t_2(x_\infty) = \frac{1}{2}\mathscr{F}(x_\infty) = \mathscr{C}(x_\infty)$).

The non-diabatic form of equation (63) (equations (72), (72 a), (74)) is closer than the diabatic form (equation (76)) to the original formulation of the coupled equations (equation (25)) in the sense that $\check{\psi} \equiv \psi$ if $a_2 \equiv I$. Essential properties of the basis originally chosen, e.g. its ability to describe the change of bonding between atoms in the course of reaction (especially when natural reaction coordinates are used), remain unaffected. This may sometimes facilitate interpretation of solutions of the coupled equations, giving an insight into the reaction mechanism, but more important seem to be some practical implications. Namely, in serial calculations, for one system at many collision energies, there is a possibility of saving computational time (at lower energies) by contracting the basis length and by reusing an appropriate part of energy-independent information stored in previous calculations (Walker and Light 1976b, Parker *et al.* 1980, Thomas *et al.* 1981). A much smaller amount of information can be reused after basis contraction if the coupled equations are converted to diabatic form (Mrugała 1987).

On the other hand, there are some inconveniences associated with numerical treatment of the coupled equations in a non-diabatic form. The simplest and most efficient of the discretization schemes of second-order differential equations, such as the Numerov scheme, are neither directly applicable nor easily adaptable to situations when first derivative coupling terms are present. Therefore direct discretization of coupled equations in non-diabatic representations was rarely attempted in designing codes for scattering calculations (see the review by Garrett and Truhlar (1981) and Nguyen-Dang *et al.* (1989) for the latest attempt). It is becoming a popular practice now (see, for example, Bačic *et al.* (1990)) to replace the non-diabatic form of the coupled equations with a quasi-diabatic one, called also locally diabatic (Kupperman 1981) or diabatic-by-sector (Lepetit *et al.* 1986a, b). This means representing the non-diabatic operator $\check{D}$ (equations (72 a), (74)) by a sequence of diabatic operators $\{D_{\bar{x}_p}\}_{p=1}^M$ (see equation (76))

$$\check{D}(x) = \sum_{p=1}^M [T_{\bar{x}_p}(x)]^T D_{\bar{x}_p}(x) T_{\bar{x}_p}(x) \Theta(x - \bar{x}_p - h_p) \Theta(\bar{x}_p + h_p - x),$$ (117)

with $\bar{x}_p$ for $p = 1, \ldots, M$ being midpoints of a set of M sectors $[\bar{x}_p - h_p, \bar{x}_p + h_p]$ which cover the entire integration range $[x_0, x_\infty]$, i.e. $\bar{x}_p = \bar{x}_{p-1} + h_{p-1} + h_p$, $x_0 = x_1 - h_1$, and $x_\infty = x_M$; Θ denotes the step function: $\Theta(x) = 1$ (0) for $x > 0$ ($x \leqslant 0$).

5.2. *The generalized log–derivative algorithms*

In this subsection, the algorithms will be presented which have been constructed on the basis of the relations given in the previous subsection for solving the boundary-value problems (86, 86 b) in the diabatic representation, i.e., with $D = D_{\bar{x}}$ (see equation (76)), and in the quasi-diabatic representation, i.e., with $D = \breve{D}$ (see equation (72), (74)) and $\breve{D}$ being represented in the form (117). The inhomogeneity term will have in both cases the form

$$Y = \begin{pmatrix} \phi \\ 0 \end{pmatrix},$$

(or the form (108) when the integrals (106) will be dealt with). The algorithms will be for evaluation of the propagator $L(x', x'')$, of the integrals $J^-_{x'x''}(= \mathbf{P}(x', x''))$, $J^{-\,-}_{x'x''}$ ($= \mathbf{P}^-(x', x'')$), and $J^0_{x'x''}$, and of the functions $\psi^-_{x'x''}(x)$ and $\psi^0_{x'x''}(x)$ at points x inside the interval $[x', x'']$ which may be any part of the integration range. It is convenient to describe first the algorithms designed.

5.2.1. *For equations in the diabatic representation*

Let $[x', x'']$ be the entire interval $[x_0, x_\infty]$ and let this interval be divided into M sectors or into $2M$ half-sectors of length h with x_i for $i = 1, 2, \ldots, 2M$ being the endpoints of these half-sectors, i.e., $x_i = x_{i-1} + h$ and $x_{2M} = x_\infty$. In the derivation of the algorithms, the recurrence relations (83), (84), (105), (103 a)–(104), and the respective relation for $J^{-\,-}$, not listed in the present paper (see, Mrugała (1990)), were applied to some discrete counterparts of the L propagator, of the J-integrals, and of the functions ψ^α, $\alpha = +, -, 0$, defined for the half-sectors. These quantities appear in the result of discretization of the problems (86)–(86 b) with the procedure which was originally established (Mrugała and Secrest 1983a) to rederive the log–derivative algorithm of Johnson (1973) and later exploited and modified to generalize and to improve this algorithm (Mrugała 1983, 1985, 1989, 1990, Mrugała and Secrest 1983b, Manolopoulos 1986, 1988, Alexander *et al.* 1987, 1989a, b). The procedure involves:

(i) conversion of (the diabatic form of) the problems (86)–(86 b) defined on the sectors $[p] = [x_{2p-2}, x_{2p}]$ for $p = 1, 2, \ldots, M$ to integral equations for the functions $\psi^\alpha_{[p]}(x)$ with $\alpha = +, -, 0$ (see equation (92)). This is done with the aid of appropriate Green functions $\mathbf{G}_{[p]}(=_{\text{ref}}\mathbf{G}^1_{[p]})$ determined either for the operator $\mathscr{D}_{\text{ref}} = \mathbf{I}(d^2/dx^2)$ (which is equivalent to the operator $_{\text{ref}}D$ of equation (94)) or for the operators $\mathscr{D}^p_{\text{ref}} = \mathbf{I}(d^2/dx^2) + (\mathbf{k}^p)^2$ with $(\mathbf{k}^p)^2 = \mathbf{w}^p_{\text{ref}} = \text{diag } \mathbf{w}_{\bar{x}}(x_{2p-1})$ and $p = 1, \ldots, M$.

(ii) discretization of the integral equations by means of the Simpson formula modified to integrands having discontinuous first derivatives (Secrest and Johnson 1966). The error of this formula, when applied to the integral

$$\int_{\bar{y}-h}^{\bar{y}+h} f(y)\,dy,$$

with f having also the third derivative discontinuous, reads

$$R = -\frac{h^4}{72} \lim_{\varepsilon \to 0_+} (f^{(3)}(\bar{y}+\varepsilon) - f^{(3)}(\bar{y}-\varepsilon)) - \frac{h^5}{90} f^{(4)}(\xi), \tag{118}$$

where $\xi \in [\bar{y}-h, \bar{y}+h]$.

(iii) specification of boundary-value problems for functions $F^\alpha_{2p-2,2p}(x_k)$, $\alpha = +$, $-, 0$, $p = 1, \ldots, M$, defined on three points x_k, with $k = 2p-2,\ 2p-1,\ 2p$

$$F^\alpha_{2p-2,2p}(x_k) = (\mathbf{q}^p_k)^{-1}\psi^\alpha_{2p-2,2p}(x_k) - \delta_{\alpha,0}\gamma_k\phi(x_k),\qquad (119)$$

where

$$\mathbf{q}^p_k = (\mathbf{I} + \gamma_k\mathbf{w}^p_k)^{-1},\qquad \mathbf{w}^p_k = \mathbf{w}_{\bar{x}}(x_k) - \mathbf{w}^p_{\text{ref}},\qquad (119\,a)$$

$\mathbf{w}_k = \mathbf{w}_{\bar{x}}(x_k)$, $\gamma_k = (h^2/6)(0)$ for k odd (even), and $\psi^\alpha_{2p-2,2p}(x_k) \cong \psi^\alpha_{x_{2p-2}x_{2p}}(x_k)$ with '$\cong$' meaning approximation due to the discretization.

(iv) adaptation of the L matrix formalism to the discrete problems for the functions $F^\alpha_{2p-2,2p}$. This leads to specification of analogous problems for functions $F^\alpha_{l-1,l}(x_k)$, $l = 1, \ldots, 2M$, defined on two points x_k, with $k = l-1, l$. In terms of derivatives (denoted here with over-dots) of these functions, are defined: the half-sector counterparts of the matrix L

$$L_{l-1,l} = \begin{pmatrix} \mathbf{L}^1_{l-1,l} & \mathbf{L}^2_{l-1,l} \\ \mathbf{L}^3_{l-1,l} & \mathbf{L}^4_{l-1,l} \end{pmatrix},$$

e.g., $\mathbf{L}^4_{l-1,l} = \dot{\mathbf{F}}^-_{l-1,l}(x_l)$ (see equation (87)), the half-sector $\mathbf{P}$ matrices, $\mathbf{P}_{l-1,l} = \dot{\mathbf{F}}^0_{l-1,l}(x_l)$, and $\mathbf{Q}$ matrices, $\mathbf{Q}_{l-1,l} = \dot{\mathbf{F}}^0_{l-1,l}(x_{l-1})$. Analogously to the latter quantities, the half-sector counterparts of the matrices $\mathbf{P}^\beta$ and $\mathbf{Q}^\beta$ for $\beta = +, -$ are also defined, i.e., $\mathbf{P}^\beta_{l-1,l} = \dot{\mathbf{F}}^{0(\beta)}_{l-1,l}(x_l)$ and $\mathbf{Q}^\beta_{l-1,l} = \dot{\mathbf{F}}^{0(\beta)}_{l-1,l}(x_{l-1})$, where the superscript '$0(\beta)$' means that the inhomogeneity term ϕ has been replaced with $\kappa\psi^\beta_{x'x''}$ in the respective equations for $\mathbf{F}^0_{l-1,l}$. The following expressions have been derived for these quantities

$$h L_{l-1,l} = \begin{bmatrix} -(\mathbf{l}^p - h\mathbf{S}^p_{l-1}) & \mathbf{s}^p \\ -\mathbf{s}^p & \mathbf{l}^p - h\mathbf{S}^p_l \end{bmatrix},\qquad (120)$$

$$\mathbf{P}_{l-1,l} = \omega_l\mathbf{q}^p_l\phi_l,\qquad\qquad \mathbf{Q}_{l-1,l} = -\omega_{l-1}\mathbf{q}^p_{l-1}\phi_{l-1},\qquad (120\,a)$$

$$\mathbf{P}^-_{l-1,l} = \omega_l\mathbf{q}^p_l\kappa_l\mathbf{q}^p_l,\qquad\qquad \mathbf{Q}^-_{l-1,l} = 0,$$

$$\mathbf{Q}^+_{l-1,l} = -\omega_{l-1}\mathbf{q}^p_{l-1}\kappa_{l-1}\mathbf{q}^p_{l-1},\qquad \mathbf{P}^+_{l-1,l} = 0,$$

$$\text{for } l = 2p-1, 2p \qquad \text{and } p = 1, \ldots, M,\qquad (120\,b)$$

where

$$\mathbf{S}^p_k = \omega_k\mathbf{q}^p_k\mathbf{w}^p_k,\qquad \text{for } k = 2p-2, 2p-1, 2p,\qquad (120\,c)$$

$$\mathbf{s}^p = h|\mathbf{k}^p|/\sin(h|\mathbf{k}^p|),$$

$$\mathbf{l}^p = h|\mathbf{k}^p|\cot(h|\mathbf{k}^p|)\qquad \text{if } (\mathbf{k}^p)^2_{i,i} > 0;\qquad (120\,d)$$

respective hyperbolic functions appear in the latter formulas if $(\mathbf{k}^p)^2_{i,i} < 0$; $\omega_l = (2h/3)\ (h/3)$ for odd (even) l; $\phi_l = \phi(x_l)$, and $\kappa_l = \kappa(x_l)$.

By definition, the functions $F^\alpha_{l-1,l}(x_k)$ satisfy the same conditions at the boundaries of the half-sectors as the functions $\psi^\alpha_{x'x''}(x)$ do at the boundaries of the interval $[x', x'']$ (see equations $(86\,a, b)$). In this sense, these functions may be considered to be the proper half-sector counterparts of the functions $\psi^\alpha_{x'x''}$. It is useful to introduce also the following 'unproper' half-sector functions

$$\psi^\alpha_{l-1,l}(x_k) = \mathbf{q}^p_k[F^\alpha_{l-1,l}(x_k) + \delta_{\alpha,0}\gamma_k\phi_k],$$

for $k = l-1, l, l = 2p-1, 2p$ and $p = 1, \ldots, M$, in terms of which the half-sector J^0 integral can be simply defined

$$J^0_{l-1,l} = \sum_{k=l-1}^{l} \omega_k [\psi^0_{l-1,l}(x_k)]^T \bar{\phi}(x_k) = \sum_{k=l-1}^{l} \omega_k \gamma_k \phi_k^T q_k^p \bar{\phi}_k,$$

$$\text{for } l = 2p-1, 2p \qquad \text{and } p = 1, \ldots, M. \qquad (120\,e)$$

The respective integrals $\mathbf{J}^+_{l-1,l}$, $\mathbf{J}^-_{l-1,l}$, $\mathbf{J}^{+,\beta}_{l-1,l}$, and $\mathbf{J}^{-,\beta}_{l-1,l}$ for $\beta = +, -$, can be defined analogously and, as expected, the expressions resulting for them are the same as those given above for the matrices $-\mathbf{Q}_{l-1,l}$, $\mathbf{P}_{l-1,l}$, $-\mathbf{Q}^\beta_{l-1,l}$, and $\mathbf{P}^\beta_{l-1,l}$, respectively.

Besides the expressions for the half-sector L propagators and J integrals one needs also values of these quantities for intervals of zero length (see equation (85)) $(\mathbf{L}^i_{0,0})^{-1} = \mathbf{0}$ for $i = 1, 2, 3, 4$, $\mathbf{P}_{0,0} = \mathbf{0}$, $\mathbf{P}^-_{0,0} = \mathbf{0}$, and $J^0_{0,0} = 0$. The results of 'adding' to these zero-length values the matrices $\mathbf{L}^{(i)}_{k-1,k}$, $\mathbf{P}_{k-1,k}$, $\mathbf{P}^-_{k-1,k}$, and $J^0_{k-1,k}$ for $k = 1, \ldots, l$ according to the appropriate recurrence relations will be denoted as $\mathbf{L}^i_{0,l}$, $\mathbf{P}_{0,l}$, $\mathbf{P}^-_{0,l}$, and $J^0_{0,l}$, respectively. For even values of l

$$\mathbf{L}^i_{0,l} \cong \mathbf{L}_i(x_0, x_l) \quad \text{for } i = 1, 2, 3, 4, \qquad \mathbf{P}_{0,l} \cong \mathbf{P}(x_0, x_l)(= \mathbf{J}^-_{x_0 x_l}),$$

$$\mathbf{P}^-_{0,l} \cong \mathbf{P}^-(x_0, x_l)(= \mathbf{J}^{-,-}_{x_0 x_l}), \qquad \text{and} \qquad J^0_{0,l} \cong J^0_{x_0 x_l}.$$

To adapt the linear superposition relations (103 a)–(104) to the discretized problems and, eventually, to evaluate the functions $\psi^-_{x_0 x_{2M}}(x)$ and $\psi^0_{x_0 x_{2M}}(x)$ at internal grid points, one has two choices (see Section 4):

(iv)′   that consistent with the (classical) invariant imbedding technique—to fix x' at x_0 and x at given grid point x_k, where $0 < k < 2M$, and then, setting y and x'' to subsequent points x_{l-1} and x_l for $l = k+1, \ldots, 2M$, to obtain the following recurrence relations

$$\mathbf{F}^\alpha_{0,l}(x_k) = \delta_{\alpha,0} \mathbf{F}^0_{0,l-1}(x_k) + \mathbf{F}^-_{0,l-1}(x_k) \mathbf{E}^\alpha_{l-1}, \qquad \text{for } \alpha = -, 0, \qquad (121)$$

where $\mathbf{E}^\alpha_{l-1} = \mathbf{F}^\alpha_{0,l}(x_{l-1})$ and

$$\mathbf{E}^\alpha_{l-1} = (\mathbf{L}^4_{0,l-1} - \mathbf{L}^1_{l-1,l})^{-1} \begin{cases} \mathbf{L}^2_{l-1,l}, & \text{for } \alpha = -, \\ (-\mathbf{P}_{0,l-1} + \mathbf{Q}_{l-1,l}), & \text{for } \alpha = 0, \end{cases} \qquad (121\,a)$$

which should be used with the initial values $\mathbf{F}^-_{0,k}(x_k) = \mathbf{I}$ and $\mathbf{F}^0_{0,k}(x_k) = \mathbf{0}$. For even values of l, $\mathbf{F}^\alpha_{0,l}(x_k)$ give approximate values $\psi^\alpha_{0,l}$ of the functions $\psi^\alpha_{x_0 x_l}$ at the point x_k through the relation $\psi^\alpha_{0,l}(x_k) = q_k^p [\mathbf{F}^\alpha_{0,l}(x_k) + \delta_{\alpha,0} \gamma_k \phi(x_k)]$, where $p = (k/2)((k+1)/2)$ for even (odd) k.

(iv)″   the way of the Ricatti transformation type—to fix the points x' and x'' at x_0 and x_{2M}, respectively, and then, setting $x = x_l$ and $y = x_{l+1}$ for $l = 2M-1$, $2M-2, \ldots, 1$, to use the relations

$$\mathbf{F}^\alpha_{0,2M}(x_l) = \delta_{\alpha,0} \mathbf{E}^0_l + \mathbf{E}^-_l \mathbf{F}^\alpha_{0,2M}(x_{l+1}), \qquad \text{for } \alpha = -, 0, \qquad (122)$$

with the appropriate initial conditions posed at the point x_{2M}.

Depending on whether the functions are required only at single or at all grid points, the choices (iv)′ or (iv)″ may appear more advantageous. Only algorithms employing the former way will be explicitly written below.

To simplify the final algorithms for all the quantities of interest, the following working quantities have been introduced

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

$$\mathbf{p}_l = h(\mathbf{P}_{0,l} - \mathbf{Q}_{l,l+1}), \quad \mathbf{u}_l = h(\mathbf{P}_{0,l}^- - \mathbf{Q}_{l,l+1}^-), \quad \mathbf{j}_l = h(\mathbf{J}_{0,l}^0 + \mathbf{J}_{l,l+1}^0), \quad \text{for } l = 2p-1,$$

$$\mathbf{p}_l = h(\mathbf{P}_{0,l} + \omega_l \phi_l), \quad \mathbf{u}_l = h(\mathbf{P}_{0,l}^- + \omega_l \kappa_l), \quad \mathbf{j}_l = h\mathbf{J}_{0,l}^0, \quad \text{for } l = 2p,$$

$$\text{and } p = 1, 2, \ldots, M,$$

$$\mathbf{F}_l = \mathbf{F}_{0,l}^-(x_k), \quad \text{and } \mathbf{f}_l = \mathbf{F}_{0,l}^0(x_k), \quad \text{for } l = k, k+1, \ldots, 2M.$$

The algorithms are:

(a i) for the log–derivative matrix $\mathbf{L}_{0,2M}^4$

$$\mathbf{z}_0 = c\mathbf{I}, \quad \text{where } c \gg 1,$$

$$\left.\begin{array}{l} \mathbf{z}_{l-1} = \check{\mathbf{z}}_{l-1} + \mathbf{a}^p, \\[2mm] \mathbf{z}_l = 2\mathbf{I}^p - 8\mathbf{I} + \mathbf{g}_l^p - \mathbf{s}^p \mathbf{z}_{l-1}^{-1} \mathbf{s}^p, \end{array}\right\} \quad \text{for } l = 2p-1,$$

$$\check{\mathbf{z}}_l = \mathbf{a}^p - \frac{2h^2}{3}\mathbf{w}_l - \mathbf{s}^p \mathbf{z}_{l-1}^{-1} \mathbf{s}^p, \quad \text{for } l = 2p,$$

where

$$\mathbf{a}^p = \mathbf{I}^p + \frac{h^2}{3}\mathbf{w}_{\text{ref}}^p, \quad \mathbf{g}_l^p = 8\mathbf{q}_l^p, \quad p = 1, 2, \ldots, M,$$

$$\mathbf{L}_{0,2M}^4 = \frac{1}{h}\left(\check{\mathbf{z}}_{2M} + \frac{h^2}{3}\mathbf{w}_{2M}\right).$$

(a ii) for the matrix $\mathbf{P}_{0,2M}(=\mathbf{J}_{0,2M}^-)$

$$\mathbf{p}_0 = \frac{h^2}{3}\phi_0,$$

$$\mathbf{p}_l = \mathbf{s}^p \mathbf{z}_{l-1}^{-1} \mathbf{p}_{l-1} + \begin{cases} \dfrac{h^2}{6}\mathbf{g}_l^p \phi_l, & \text{for } l = 2p-1, \\[4mm] \dfrac{2h^2}{3}\phi_l, & \text{for } l = 2p, \end{cases} \qquad p = 1, 2, \ldots, M,$$

$$\mathbf{P}_{0,2M} = \frac{1}{h}\left(\mathbf{p}_{2M} - \frac{h^2}{3}\phi_{2M}\right),$$

(Analogous formulae for the matrix $\bar{\mathbf{P}}_{0,2M}(=\mathbf{J}_{0,2M}^-)$ involve the matrices $\bar{\phi}_l$ in place of ϕ_l. The associated working quantity will be denoted by $\bar{\mathbf{p}}_l$ below.)

(a iii) for the integral $J_{0,2M}^0$

$$j_0 = 0,$$

$$j_l = j_{l-1} - \mathbf{p}_{l-1}^{\mathrm{T}} \mathbf{z}_{l-1}^{-1} \bar{\mathbf{p}}_{l-1} + \begin{cases} \dfrac{h^4}{36}\phi_l^{\mathrm{T}} \mathbf{g}_l^p \bar{\phi}_l, & \text{for } l = 2p-1, \\[4mm] 0 & \text{for } l = 2p, \end{cases} \qquad p = 1, 2, \ldots, M,$$

$$J_{0,2M}^0 = \frac{1}{h}j_{2M}.$$

(a iv) for the matrix $\mathbf{P}_{0,2M}^{-}(=\mathbf{J}_{0,2M}^{-\prime-})$

$$\mathbf{u}_0 = \frac{h^2}{3}\boldsymbol{\kappa}_0,$$

$$\mathbf{u}_l = \mathbf{s}^p\mathbf{z}_{l-1}^{-1}\mathbf{u}_{l-1}\mathbf{z}_{l-1}^{-1}\mathbf{s}^p + \begin{cases} \dfrac{h^2}{48}\mathbf{g}_l^p\boldsymbol{\kappa}_l\mathbf{g}_l^p, & \text{for } l=2p-1, \\[2mm] & \qquad\qquad p=1,2,\dots,M, \\[2mm] \dfrac{2h^2}{3}\boldsymbol{\kappa}_l, & \text{for } l=2p, \end{cases}$$

$$\mathbf{P}_{0,2M}^{-} = \frac{1}{h}\left(\mathbf{u}_{2M} - \frac{h^2}{3}\boldsymbol{\kappa}_{2M}\right).$$

(a v) for the function $\psi_{0,2M}^{-}(x_k)$ at point x_k which may be the midpoint, $k=2\bar{p}-1$, or the endpoint, $k=2\bar{p}$, of $\bar{p}$th sector, where $1\leqslant\bar{p}\leqslant M$

$$\mathbf{F}_k = \mathbf{I},$$

$$\mathbf{F}_l = \mathbf{F}_{l-1}\mathbf{z}_{l-1}^{-1}\mathbf{s}^p, \qquad \text{for } l=2p-1,2p \qquad \text{and } p=\bar{p},\bar{p}+1,\dots,M,$$

$$\psi_{0,2M}^{-}(x_k) = \begin{cases} \frac{1}{8}\mathbf{g}_k^{\bar{p}}\mathbf{F}_{2M}, & \text{if } k=2\bar{p}-1, \\[1mm] \mathbf{F}_{2M} & \text{if } k=2\bar{p}. \end{cases}$$

(a vi) for the function $\psi_{0,2M}^{0}(x_k)$

$$\mathbf{f}_k = 0,$$

$$\mathbf{f}_l = \mathbf{f}_{l-1} - \mathbf{F}_{l-1}\mathbf{z}_{l-1}^{-1}\mathbf{p}_{l-1}, \qquad \text{for } l=k+1,k+2,\dots,2M,$$

$$\psi_{0,2M}^{0}(x_k) = \begin{cases} \frac{1}{8}\mathbf{g}_k^{\bar{p}}\left(\mathbf{f}_{2M}+\dfrac{h^2}{6}\boldsymbol{\phi}_k\right), & \text{if } k=2\bar{p}-1, \\[2mm] \mathbf{f}_{2M}, & \text{if } k=2\bar{p}. \end{cases}$$

Before commenting further on the above, let us present the algorithms

5.2.2. *For equations in the quasi-diabatic representation*

In the construction of the quasi-diabatic representation of the coupled equations according to the formula (117), the points $\bar{x}_p$ were chosen to be the midpoints of the sectors $[x_{2p-2}, x_{2p}]$, i.e., $\bar{x}_p = x_{2p-1}$ and $h_p = h$ for $p=1,2,\dots,M$. Within each sector, the original non-diabatic equations were converted to the diabatic representation and then discretized with the procedure described above, giving two sets of the respective half-sector quantities. Let us denote them here as $\check{L}_{l-1,l}$, $\check{Q}_{l-1,l}$, $\check{P}_{l-1,l}$, $\check{Q}_{l-1,l}^{\pm}$, $\check{P}_{l-1,l}^{\pm}$, for $l=2p-1$, $2p$ and $p=1,\dots,M$.

Appropriate expressions for these quantities can be obtained by replacing in equations (119 a)–(120 d): $\mathbf{w}_k^p\to\check{\mathbf{w}}_k^p=\check{\mathbf{w}}_k-\mathbf{w}_{\text{ref}}^p$, $\boldsymbol{\phi}_k\to\check{\boldsymbol{\phi}}_k$, and $\boldsymbol{\kappa}_k\to\check{\boldsymbol{\kappa}}_k$, where $\check{\mathbf{w}}_k=\mathbf{t}_{k,2p-1}^{\mathsf{T}}\mathbf{w}_k\mathbf{t}_{k,2p-1}$ with $\mathbf{w}_k=\mathbf{w}(x_k)$, $\check{\boldsymbol{\phi}}_k=\mathbf{t}_{k,2p-1}^{\mathsf{T}}\boldsymbol{\phi}_k$, and $\check{\boldsymbol{\kappa}}_k=\mathbf{t}_{k,2p-1}^{\mathsf{T}}\boldsymbol{\kappa}_k\mathbf{t}_{k,2p-1}$, for $k=2p-2,2p-1,2p$. $\mathbf{t}_{k,2p-1}$ denote numerical values of the matrices $\mathbf{t}(x_k;x_{2p-1})$ which occur in the transformations $T_{x_{2p-1}}(x_k)$ for $k=2p-2$, $2p-1$, $2p$, defined in equations (76)–(77). Obviously, $\mathbf{t}_{k,k}=\mathbf{I}$ and $\mathbf{t}_{k,j}=\mathbf{t}_{j,k}^{\mathsf{T}}$. The reference potentials are: $\mathbf{w}_{\text{ref}}^p=\operatorname{diag}\check{\mathbf{w}}_{2p-1}=\operatorname{diag}\mathbf{w}_{2p-1}$ for $p=1,2,\dots,M$. Before insertion into the recurrence relations, the matrices $\check{L}_{l-1,l}$, $\check{P}_{l-1,l}$, $\check{Q}_{l-1,l}$, $\check{P}_{l-1,l}^{\pm}$, and $\check{Q}_{l-1,l}^{\pm}$ were converted back to the non-diabatic representation using the formulas (110) and (110 a) with $\mathbf{t}_1(x)\to\mathbf{t}^{\mathsf{T}}(x;x_l)$

in the first halves of sectors, i.e. for $l = 2p - 1$, and with $\mathbf{t}_1(x) \rightarrow \mathbf{t}^{\mathrm{T}}(x; x_{l-1})$ in the second halves, i.e. for $l = 2p$, where $p = 1, 2, \ldots, M$. The result is

$$hL_{l-1,l} = \begin{pmatrix} -\mathbf{t}_{l-1,l}\mathbf{a}^p\mathbf{t}_{l-1,l}^{\mathrm{T}} & \mathbf{t}_{l-1,l}\mathbf{s}^p \\ -\mathbf{s}^p\mathbf{t}_{l-1,l}^{\mathrm{T}} & \mathbf{l}^p \end{pmatrix} + h\begin{pmatrix} \mathbf{S}_{l-1} & 0 \\ 0 & -\mathbf{S}_l^p \end{pmatrix} \qquad \text{for } l = 2p - 1,$$

$$hL_{l-1,l} = \begin{pmatrix} -\mathbf{l}^p & \mathbf{s}^p\mathbf{t}_{l-1,l} \\ -\mathbf{t}_{l-1,l}^{\mathrm{T}}\mathbf{s}^p & \mathbf{t}_{l-1,l}^{\mathrm{T}}\mathbf{a}^p\mathbf{t}_{l-1,l} \end{pmatrix} + h\begin{pmatrix} \mathbf{S}_{l-1}^p & 0 \\ 0 & -\mathbf{S}_l \end{pmatrix} \qquad \text{for } l = 2p. \tag{123}$$

Apart from the replacement of $\mathbf{w}_{\bar{x}}$ with the matrix $\mathbf{w}$ coming from the non-diabatic equations, equations (72) and (74), the matrices $\mathbf{a}^p$ and $\mathbf{S}_{2p-1}^p$ denote here the same quantities as defined in the diabatic case (see equations (120 c), (119 a) and the formulae (a i)). $\mathbf{S}_k = \omega_k \mathbf{w}_k$ for $k = 2p - 2, 2p$. The conversion of the matrices $\check{\mathbf{P}}_{l-1,l}$, $\check{\mathbf{Q}}_{l-1,l}$, $\check{\mathbf{P}}_{l-1,l}^{\pm}$, and $\check{\mathbf{Q}}_{l-1,l}^{\pm}$ to the non-diabatic representation gives the expressions (120 a, b) for the respective matrices $\mathbf{P}_{l-1,l}$, $\mathbf{Q}_{l-1,l}$, $\mathbf{P}_{l-1,l}^{\pm}$, and $\mathbf{Q}_{l-1,l}^{\pm}$. Using working quantities defined as in the diabatic case, one obtains the final algorithms:

(b i) for the matrix $\mathbf{L}_{0,2M}^4$. The initial formula–for $\check{z}_0$—and the last—giving $\mathbf{L}_{0,2M}^4$—are, of course, the same as in the algorithm (a i). The others read

$$\left.\begin{array}{l} z_{l-1} = \check{z}_{l-1} + \mathbf{t}_{l-1,l}\mathbf{a}^p\mathbf{t}_{l-1,l}^{\mathrm{T}}, \\ z_l = 2\mathbf{l}^p - 8\mathbf{I} + \mathbf{g}_l^p - \mathbf{s}^p\mathbf{t}_{l-1,l}^{\mathrm{T}}z_{l-1}^{-1}\mathbf{t}_{l-1,l}\mathbf{s}^p, \end{array}\right\} \qquad \text{for } l = 2p - 1,$$

$$\check{z}_l = -\frac{2h^2}{3}\mathbf{w}_l + \mathbf{t}_{l-1,l}^{\mathrm{T}}(\mathbf{a}^p - \mathbf{s}^p z_{l-1}^{-1}\mathbf{s}^p)\mathbf{t}_{l-1,l}, \qquad \text{for } l = 2p,$$

$$p = 1, 2, \ldots, M.$$

(b ii) for the matrix $\mathbf{P}_{0,2M} = \mathbf{J}_{0,2M}^-$. The first term in the formula for $\mathbf{p}_l$ in the algorithm (a ii) is modified to $\mathbf{s}^p\mathbf{t}_{l-1,l}^{\mathrm{T}}z_{l-1}^{-1}\mathbf{p}_{l-1}$ for $l = 2p - 1$ and to $\mathbf{t}_{l-1,l}^{\mathrm{T}}\mathbf{s}^p z_{l-1}^{-1}\mathbf{p}_{l-1}$, for $l = 2p$. (Compare the off-diagonal blocks of $L_{l-1,l}$ in equations (123) and in equations (120).)

Similar differences in comparison with the algorithms (a iv) and (a v) occur in the respective formulae (b iv) for the matrix $\mathbf{P}_{0,2M}^-$ and (b v) for the function $\psi_{0,2M}^-(x_k)$. The appropriate formulae (b iii) for the integral $J_{0,2M}^0$, and (b vi) for the function $\psi_{0,2M}^0(x_k)$ look the same as in the diabatic case.

Obviously, all the formulae (b i)–(b vi) reduce to the diabatic formulas (a i)–(a vi) when $\mathbf{t}_{l-1,l} = \mathbf{I}$ for $l = 1, \ldots, 2M$, i.e., when $\mathbf{c} \equiv 0$ in equation (74).

The point of concern in the construction of the above algorithms was to make them especially efficient in handling self-adjoint coupled equations. Thus, it is in order to stress that the basic working quantity—the matrix z_l which has to be inverted at every step l for $l = 1, 2, \ldots, 2M$—is a symmetric matrix. The approximate log–derivative matrices generated with the algorithms (a i) or (b i) satisfy strictly the respective symmetry relation (82).

Obviously, the above algorithms may be applied also to (non-self-adjoint) equations which involve non-symmetric matrices $\mathbf{w}_{\bar{x}}$ or $\mathbf{w}$ (see equations (74) and (76)), e.g., to the coupled equations in the CCA schemes. It should be noted, however, that the matrices $\mathbf{P}_{0,2M}$ generated with the formulae (a ii) or (b ii) in such cases will be equal to the integrals $_{\dagger}\mathbf{J}_{0,2M}^-$

$$_{\dagger}\mathbf{J}_{0,2M}^- = \sum_{k=0}^{2M} \omega_k [_{\dagger}\psi_{0,2M}^-(x_k)]^{\mathrm{T}}\phi(x_k),$$

involving respective solutions $_\dagger\psi^-_{0,2M}(x)$ of the equations with transposed matrices $\mathbf{w}_{\bar{x}}$ or $\mathbf{w}$. (An analogous remark concerns the matrices $\mathbf{P}^-_{0,2M}$ generated with the formulae (a iv) or (b iv).) The sign of transposition has to be added to the matrices $\mathbf{z}^{-1}_{l-1}$ and $\mathbf{g}^p_l$ standing in the formulae (a ii) and (b ii) in order to make them work as generators of the integral $\mathbf{J}^-_{0,2M}(=_\dagger\mathbf{P}_{0,2M})$. Moreover, it should be remembered in the non-symmetric cases that of the two quantities $\mathbf{p}_{l-1}$ and $\bar{\mathbf{p}}_{l-1}$ occurring in the formulae (a iii) the former is related to the matrix $\mathbf{P}_{0,l-1}$ whereas the latter to the integral $\bar{\mathbf{J}}^-_{0,l-1}$.

Considering the character of the discretization procedure used in the derivation, one should classify the presented algorithms as hybrid approximate-solution approximate-potential ones (Manolopoulos 1986). It should be remembered here that in the purely approximate-potential approach the reference potentials are always chosen to give adequate approximations to the entire potential coupling matrix within particular sectors. The construction involves transformations to a locally adiabatic representation via diagonalizations of the coupling matrix at the midpoints of sectors. In the purely approximate-solution approach in turn, no reference potentials are used. Thus, setting $\mathbf{w}^p_{\text{ref}}=\mathbf{0}$ and $\mathbf{s}^p=\mathbf{l}^p=\mathbf{I}$ for $p=1,\ldots,M$ in the formulae (a i)–(a vi) and (b i)–(b vi) one obtains purely approximate-solution versions of these algorithms. The difference between the two versions becomes visible in behaviour of errors of the quantities calculated when the energy E used in calculation is increased (considered here are problems where E enters only the diagonal elements of the respective matrices $\mathbf{w}_{\bar{x}}$ or $\mathbf{w}$). The errors of the results generated by the purely approximate-solution algorithms reveal a rapid cubic growth with energy. Still, efficiency of these algorithms, even at not quite low energies, is very high. This is due to the remarkable simplicity of the formulae of the purely approximate-solution version. In the hybrid algorithms, the energy is included into the reference potentials and much of the energy dependence of the final results is accounted for exactly through the matrices $\mathbf{s}^p$ and $\mathbf{l}^p$ (equation (120 d)). The growth of errors with energy is considerably reduced, becoming close to linear (Mrugała 1989).

A detailed comparison of the algorithm (a i) with its purely approximate-solution counterpart, i.e. with the original log–derivative of Johnson (1973), was presented by Manolopoulos (1986, 1988) on some standard inelastic scattering tests problems. Applications of this algorithm to reactive scattering calculations were reported by Manolopoulos and Wyatt (1989) and recently by Lepetit and Launay (1991). Further tests of the formulae (a i) and, first of all, of the formulae (a ii) and (a iii) in the hybrid and in the non-hybrid versions were provided by Mrugała (1988, 1989) in application to half-collision calculations concerning photodissociation of H_2. The algorithm (a i)–(a iii) was tried also in application to atom–diatom reactive scattering, namely, in solving variationally the BKLT equations (see Section 2) for the collinear $H+H_2\rightarrow H_2+H$ reaction (Mrugała 1990). It was demonstrated, in particular, that all the matrix elements occurring in the Schwinger variational expression for the reactance matrix, also those involving Green functions could be evaluated without storing a large amount of intermediate results such as the 'half-integrated Green functions' (Schwenke *et al.* 1988, 1989). A 'half-integrated Green function' in the L-matrix formalism is, of course, the function $\psi^0_{x'x''}(x)$ (see equations (86), (86 b)). Direct determination of such functions becomes necessary, e.g. in evaluation of some matrix elements (involving non-local potentials) which arise in the Newton variational method (Newton 1982) when it is applied to reactive scattering (Schwenke *et al.* 1988). It would be interesting to test in this context the algorithm (a vi) or its version based on the Riccati transformations (122).

The algorithm (a iv) for evaluation of the free–free type integrals $J^{-'-}_{x'x''}$ (or of the matrix $P^-(x', x'')$) was published by Mrugała (1990) as a modification of the purely approximate-solution version of this algorithm derived earlier (Mrugała 1985). As follows from the comment given in Section 5.1, see equations (106)–(109), the formulae (a iv) (and also (b iv)) are directly applicable to evaluation of the energy derivative of the log–derivative matrix, i.e. $J^{-'-}_{0,2M} \cong (d/dE)L_4(x_0, x_{2M})$ when $\kappa = (d/dE)w_{\tilde{x}}$ (or $\kappa = (d/dE)w$ in the non-diabatic case). Concerning this particular application, it is worth stressing that the approximations to the log–derivative matrix and its energy derivative, $L^4_{0,2M}$ and $J^{-'-}_{0,2M}$, strictly satisfy the relation

$$\frac{d}{dE}(L^4_{0,2M}) = J^{-'-}_{0,2M}, \qquad (124)$$

if they are obtained with the purely approximate-solution versions of the algorithms (a i) and (a iv), respectively, (or (b i) and (b iv)). In other words, the formulae (a iv) in the approximate-solution version follow in this case from differentiation of the formulae (a i) (in the same version, of course). This is the means of adaptation of the original algorithm of Johnson to the direct evaluation of energy derivatives which was suggested recently by Darakjian and Hayes (1990). The algorithm was implemented successfully (Darakjian *et al.* 1991) to 3D calculations of resonances in the He $+ H^+ \rightarrow HeH^+ + H$ reaction. Concerning application of the hybrid algorithms (a iv) or (b iv) to the evaluation of $(d/dE)L^4$, one should stress that these algorithms are much simpler than the ones one would get by differentiating with respect to E the formulae (a i) or (b i). This simplicity is achieved at the expense of assuring only approximately the relation (124) between the quantities generated. Nevertheless the overall accuracy of the energy derivatives of the log–derivative matrix generated with these algorithms can improve considerably in comparison with the accuracy yielded by the respective purely approximate-solution algorithms. An illustration of that is provided in Section 5.2 (see also Mrugała (1990)).

The extension of the log–derivative algorithm to determination of scattering wave functions (the formulae (a v)) was originally suggested by Alexander *et al.* 1989a, b). It has been tested so far on some model curve-crossing problems (Alexander *et al.* 1989b) and applied to analysis of some spin-changing transitions in atomic collisions (Alexander and Pouilly 1989a).

The algorithm for generating the L matrix in the non-diabatic representation—the formulae (b i) plus appropriate formulas for the blocks $L^3(= -L^2)^T$ and L^1, not listed explicitly but easily obtainable from equations (123) and (83)—is a simplified version of the algorithm proposed previously (Mrugała and Secrest 1983b) and tested on collinear reactive scattering problems (Mrugała 1987, Mrugała and Römelt 1987) against the R-matrix propagation (Light and Walker 1976b, Zvijac and Light 1976, Bondi *et al.* 1982) and against the S-matrix propagation (Manz 1974, Hauke *et al.* 1980, Römelt 1980, 1982) methods. By implementing that approximate-solution algorithm into the R-matrix code of Walker (1978) an improvement in efficiency of (Mrugała 1987). That algorithm was exploited also in the L-matrix propagation code constructed especially for the treatment of collinear reactions in Delves' coordinates (Mrugała and Römelt 1987). Fast convergence with respect to accuracy control parameters in this code was exploited in performing lifetime analysis of vibrational resonances in ABA-type molecules (Bisseling *et al.* 1987). The present algorithm (b i) is much simpler than the previous one due to the use of the half-sector propagators instead of the sector propagators. So, the performance of the L-matrix method

demonstrated in the previous investigations would be even better if the present version were employed.

Besides being exploited in the derivation of the above algorithms, the recurrence relations of the *L*-matrix formalism were used also to modify some existing purely approximate-potential methods. The linear reference potential method of Gordon (1969, 1971); (see also Alexander and Gordon (1971)) has been reformulated to a stable scheme (Alexander and Manolopoulos 1987) and a new hybrid code using this reformulated algorithm and the approximate-solution log–derivative algorithm in different regions of the integration range has been constructed (Alexander 1987).

Reformulation of the *R*-matrix propagation method of Light and Walker (1976b) in terms of the matrix *L* was demonstrated to give a completely equivalent computational scheme (Mrugała 1987) (which is consistent with the conclusions of the comparison of the *R*-matrix and *L*-matrix formalisms presented in Section 5.1).

5.3. *A comparison with other invariant imbedding algorithms*

5.3.1. *With the R-matrix propagation algorithms*

As already mentioned, any difference in performance between the generalized log–derivative algorithms and the *R*-matrix propagation algorithms may stem only from the use in their derivations of different approaches to approximate the respective sector-propagators. So, the detailed comparisons (Manolopoulos 1986, 1988, Mrugała 1987) could only confirm to a lesser or larger extent the conclusion of the 1981 study by Thomas *et al.* on complementarity of the approximate solution and of the approximate-potential approaches with respect to their usefulness in scattering calculations.

It remains to be mentioned that besides the basic algorithm for determination of the matrix *R* itself there is the well-established and commonly used extension of the *R*-matrix propagation method for evaluation of the first-order transition amplitudes (equation (14)) for photodissociation of triatomic molecules (Kulander and Light 1980, Schneider and Taylor 1982); so, the formulae (*a* ii) (or (*b* ii)) of the generalized log–derivative method together with the formula (115) can be considered and exploited as an approximate-solution complement to this *R*-matrix algorithm (see Manolopoulos 1988). It should be mentioned also that the first attempt to design an invariant imbedding approximate-solution algorithm for determination of the first-order amplitudes was undertaken by Singer *et al.* (1982). With respect to efficiency, however, their method (consisting of applying the standard Runge–Kutta procedure to some initial value problems formulated for the amplitudes in differential equation form) cannot complete with the generalized log–derivative algorithm.

A way of extending the established scattering methods, and the *R*-matrix propagation method in the first place, to determination of second-order transition amplitudes (equation (15)) was indicated by Singer *et al.* (1987). Judging by the degree of complexity of the algorithms derived by these authors, the generalization of the log–derivative algorithm—the formulae (*a* iii) plus equation (116)—is believed to offer a more efficient way of evaluation of these amplitudes.

The most recent extension of the *R*-matrix propagation method, proposed by Walker and Hayes (1988), is to direct evaluation of energy derivatives of the *R* matrix (eventually, of the S matrix). This extension does not seem, however, to be fully satisfactory, partly because of the approach taken to its derivation. The differentiation with respect to energy of the formulas of the basic algorithm for the matrix *R* yields quite a complicated result when the transformations to locally adiabatic representation

are also energy dependent in these formulae. The complication would be less severe if an approach analogous to that presented in Section 5.1 were taken, i.e. if boundary value problems appropriate for the matrix R were differentiated with respect to E before applying any discretization procedure to them. Still, it remains to be tested as to what extent (if at all) purely approximate-potential algorithms may be more efficient than the hybrid algorithms, $(a\,iv)$, $(b\,iv)$, or $(c\,iv)$ (see the next subsection), in evaluation of the energy derivatives or, more generally, of free–free type transition amplitudes.

No extensions of the R-matrix propagation method to determination of the functions exist to be compared with the formulae $(a\,v)$ and $(a\,vi)$.

It is certainly much more interesting to learn how the log–derivative algorithms compare with other algorithms of the same category, in particular.

5.3.2. *With renormalized Numerov algorithms*

Under this heading, a number of invariant imbedding algorithms will be considered which have been derived on the basis of the following two-step discretization scheme of second-order differential equation $f^{(2)} + wf = 0$ (see e.g. Henrici (1964))

$$f(x+h) + af(x) + f(x-h) = b_0 f^{(2)}(x+h) + b_1 f^{(2)}(x) + b_0 f^{(2)}(x-h) + R. \quad (125)$$

In the original Numerov scheme, the coefficients a, b_0, and b_1 are $a = -2$, $b_0 = h^2/12$, and $b_1 = h^2 - 2b_0$, and the expression resulting for the local discretization error is

$$R = -\tfrac{1}{240} h^6 f^{(6)}(\xi), \quad (126)$$

where $\xi \in [x-h, x+h]$. Obviously, $R = 0$ for $f(x) = 1$, x, x^2, x^3, x^4, x^5. In the scheme modified by Raptis and Allison (1978), the zero error is assured for the functions $f(x) = 1, x, x^2, x^3, \exp[\pm(\omega_{ref})^{1/2}x]$, where ω_{ref} denotes a constant which approximates $w(x)$ within at least a single sector $[x-h, x+h]$. Appropriate sets of formulas for the coefficients a, b_0, and b_1 have also been derived to make the scheme (125) exact for the functions $f(x) = 1, x, \exp[\pm(\omega_{ref})^{1/2}x], x\exp[\pm(\omega_{ref})^{1/2}x]$ (Ixaru and Rizea 1980) and for the functions $f(x) = \exp[\pm(\omega_{ref})^{1/2}x], x\exp[\pm(\omega_{ref})^{1/2}x], x^2\exp[\pm(\omega_{ref})^{1/2}x]$ (Ixaru and Rizea 1987). The former case will be referred to as the IR scheme. Correspondingly, the abbreviations N and RA will be used to denote the schemes of Numerov and of Raptis and Allison.

For the first derivative of $f(x)$, the following formula has been derived (see, Johnson 1978a) which may be used together with the scheme (125) in the N and RA versions

$$2hf^{(1)}(x) \cong f(x+h) - f(x-h) - \frac{h^2}{12}[f^{(2)}(x+h) - f^{(2)}(x-h)], \quad (127)$$

The following boundary-value problems for three-point matrix difference equations result from applying the scheme (125) to the systems of coupled second-order differential equations for the functions $\psi^{\alpha}_{x'x''}(x)$ with $\alpha = -, 0$ in the diabatic representation, (equations (86)–(86 b) with $D = D_{\bar{x}}$)

$$\mathbf{U}^{\alpha}_{0,2M}(x_{k+1}) - \mathbf{Q}_k\mathbf{U}^{\alpha}_{0,2M}(x_k) + \mathbf{U}^{\alpha}_{0,2M}(x_{k-1})$$

$$= \delta_{\alpha,0}(\mathbf{b}_0\boldsymbol{\phi}_{k+1} + \mathbf{b}_1\boldsymbol{\phi}_k + \mathbf{b}_0\boldsymbol{\phi}_{k-1}), \quad \text{for } \alpha = -, 0, \quad (128)$$

$$\mathbf{U}^{-}_{0,2M}(x_0) = \mathbf{0}, \qquad \mathbf{U}^{-}_{0,2M}(x_{2M}) = \mathbf{I}; \qquad \mathbf{U}^{0}_{0,2M}(x_0) = \mathbf{U}^{0}_{0,2M}(x_{2M}) = \mathbf{0},$$

where

$$\mathbf{Q}_k = -(\mathbf{a} + \mathbf{b}_1 \mathbf{w}_k)(\mathbf{I} + \mathbf{b}_0 \mathbf{w}_k)^{-1},$$

$$\mathbf{w}_k = \mathbf{w}_{\bar{x}}(x_k), \qquad \boldsymbol{\phi}_k = \boldsymbol{\phi}(x_k),$$

$$x_k = x_0 + kh, \qquad x_0 = x', \qquad x_{2M} = x'',$$

$\mathbf{a}$, $\mathbf{b}_0$, and $\mathbf{b}_1$ denote here diagonal matrices built from the coefficients a, b_0, and b_1, respectively. In the case of the N scheme, $\mathbf{a} = a\mathbf{I}$, $\mathbf{b}_0 = b_0\mathbf{I}$, and $\mathbf{b}_1 = b_1\mathbf{I}$. In the cases of the RA and IR schemes, the matrices are obtained by replacing the reference value ω_{ref} in the respective formulas for a, b_0, and b_1 with a diagonal matrix $\mathbf{w}_{\text{ref}}$. Here, $\mathbf{w}_{\text{ref}}$ will be chosen in exactly the same way as in the log–derivative algorithms, i.e. $\mathbf{w}_{\text{ref}} = \mathbf{w}_{\text{ref}}^p = \mathbf{w}_{\bar{x}}(x_{2p-1})$ within the sector $p = [x_{2p-2}, x_{2p}]$ for $p = 1, 2, \ldots, M$. (Thus, new coefficients $\mathbf{a}$, $\mathbf{b}_0$, and $\mathbf{b}_1$ have to be evaluated for every sector, i.e. at every second step.) The solutions $\mathbf{U}_{0,2M}^\alpha(x_k)$ with $\alpha = -, 0$ give approximate values of the functions $\boldsymbol{\psi}_{x_0 x_{2M}}^\alpha(x_k)$ through the following formula

$$\boldsymbol{\psi}_{x_0 x_{2M}}^\alpha(x_k) \cong \boldsymbol{\psi}_{0,2M}^\alpha(x_k) = (\mathbf{I} + \mathbf{b}_0 \mathbf{w}_k)^{-1} \mathbf{U}_{0,2M}^\alpha(x_k)(\mathbf{I} + \delta_{\alpha,-} \mathbf{b}_0 \mathbf{w}_{2M}).$$

The corresponding approximation $\mathbf{L}_{0,2M}^4$ to the log–derivative matrix $\mathbf{L}_{x_0 x_{2M}}^4$ (if required) may be evaluated by applying equation (127) to the function $\boldsymbol{\psi}_{x_0 x_{2M}}^-(x_{2M})$.

Application of the invariant imbedding technique to the problems (128) defined on the interval $[x_0, x_{2M}]$ requires that these problems be related to the analogous problems defined on the intervals $[x_0, x_l]$ for $l = 1, \ldots, 2M-1$. Let $\mathbf{U}_{0,l}^\alpha(x_k)$ with $0 \leqslant k \leqslant l$ and $l = 1, \ldots, 2M-1$ denote solutions of these problems. Actually, the relations between the solutions $\mathbf{U}_{0,l}^\alpha$ and $\mathbf{U}_{0,l-1}^\alpha$ for $\alpha = -, 0$ are the same as in the case of the functions $\mathbf{F}_{0,l}^\alpha$ introduced in the derivation of the log–derivative algorithms (equation (121)), i.e.

$$\mathbf{U}_{0,l}^\alpha(x_k) = \delta_{\alpha,0} \mathbf{U}_{0,l-1}^0(x_k) + \mathbf{U}_{0,l-1}^-(x_k) \mathbf{U}_{0,l}^\alpha(x_{l-1}),$$

$$\text{for } \alpha = -, 0, \qquad \text{and } k \leqslant l. \quad (129)$$

Using these relations, one can easily derive the corresponding recurrence relations for the following quantities

$$\mathbf{R}_l = \mathbf{U}_{0,l+1}^-(x_l), \qquad \mathbf{r}_l = \mathbf{U}_{0,l+1}^0(x_l),$$

$$\mathbf{J}_l^\alpha = \sum_{k=0}^{l} \bar{\omega}_k [(\mathbf{I} + \mathbf{b}_0 \mathbf{w}_k)^{-1} \mathbf{U}_{0,l}^\alpha(x_k)]^{\mathrm{T}} \boldsymbol{\phi}_k, \qquad \text{for } \alpha = -, 0,$$

$$\mathbf{J}_l^{-'-} = \sum_{k=0}^{l} \bar{\omega}_k [(\mathbf{I} + \mathbf{b}_0 \mathbf{w}_k)^{-1} \mathbf{U}_{0,l}^-(x_k)]^{\mathrm{T}} \boldsymbol{\kappa}_k (\mathbf{I} + \mathbf{b}_0 \mathbf{w}_k)^{-1} \mathbf{U}_{0,l}^-(x_k),$$

where $\bar{\omega}_k$ are the weights of the ordinary Simpson quadrature formula

$$\bar{\omega}_0 = \bar{\omega}_{2M} = \frac{h}{3}, \qquad \text{and } \bar{\omega}_k = \frac{4h}{3}\left(\frac{2h}{3}\right) \qquad \text{for } k \text{ odd (even)}.$$

These relations are the basic constitutents of the following algorithms:

(*c* i) for the matrix $\mathbf{R}_{2M}$ (or $\mathbf{L}_{0,2M}^4$);

$$\mathbf{R}_0 = \mathbf{0},$$

$$\mathbf{R}_l = (\mathbf{Q}_l - \mathbf{R}_{l-1})^{-1},$$

where

$$\mathbf{Q}_l = -\mathbf{b}_1 \mathbf{b}_0^{-1} + \mathbf{c} \mathbf{q}_l,$$

$$\mathbf{q}_l = (\mathbf{b}_0 + \mathbf{b}_0 \mathbf{w}_l \mathbf{b}_0)^{-1},$$

$$\mathbf{c} = \mathbf{b}_1 - \mathbf{b}_0 \mathbf{a} \qquad (= h^2 \mathbf{I} \text{ for the N and RA schemes})$$

$$\text{for } l = 1, 2, \dots, 2M,$$

$$\left[\mathbf{L}_{0,2M}^4 = \frac{1}{h} (\mathbf{p}_{2M+1} \mathbf{R}_{2M}^{-1} - \mathbf{p}_{2M-1} \mathbf{R}_{2M-1}) \mathbf{q}_{2M}^{-1} \mathbf{b}_0^{-1}, \right.$$

$$\left. \text{where } \mathbf{p}_l = (\tfrac{1}{2} \mathbf{b}_0 + \mathbf{d} \mathbf{w}_l \mathbf{b}_0) \mathbf{q}_l, \qquad \text{for } l = 2M \pm 1, \qquad \mathbf{d} = \frac{h^2}{12} \mathbf{I} \right].$$

(c ii) for the integral $\mathbf{J}_{0,2M}^-$;

$$\mathbf{J}_0^- = 0,$$

$$\mathbf{J}_l^- = \mathbf{R}_{l-1}^\mathrm{T} \mathbf{J}_{l-1}^- + \bar{\omega}_l (\mathbf{b}_0 \mathbf{q}_l)^\mathrm{T} \boldsymbol{\phi}_l, \qquad \text{for } l = 1, 2, \dots, 2M,$$

$$\mathbf{J}_{0,2M}^- = \mathbf{b}_0^{-1} (\mathbf{q}_{2M}^{-1})^\mathrm{T} \mathbf{J}_{2M}^-,$$

(c iii) for the integral $J_{0,2M}^0$;

$$\mathbf{r}_{-1} = 0, \qquad J_0^0 = 0,$$

$$\mathbf{r}_{l-1} = \mathbf{R}_{l-1} (\mathbf{r}_{l-2} - \mathbf{b}_0 \boldsymbol{\phi}_l - \mathbf{b}_1 \boldsymbol{\phi}_{l-1} - \mathbf{b}_0 \boldsymbol{\phi}_{l-2}),$$

$$J_l^0 = \mathbf{r}_{l-1}^\mathrm{T} \mathbf{J}_{l-1}^- + J_{l-1}^0, \qquad \text{for } l = 1, 2, \dots, 2M,$$

$$J_{0,2M}^0 = J_{2M}^0,$$

(c iv) for the integral $\mathbf{J}_{0,2M}^{-'-}$;

$$\mathbf{J}_0^{-'-} = 0,$$

$$\mathbf{J}_l^{-'-} = \mathbf{R}_{l-1}^\mathrm{T} J_{l-1}^{-'-} \mathbf{R}_{l-1} + \bar{\omega}_l (\mathbf{b}_0 \mathbf{q}_l)^\mathrm{T}{}_\kappa{}_l \mathbf{b}_0 \mathbf{q}_l, \qquad \text{for } l = 1, 2, \dots, 2M,$$

$$\mathbf{J}_{0,2M}^{-'-} = (\mathbf{q}_{2M}^{-1} \mathbf{b}_0^{-1})^\mathrm{T} \mathbf{J}_{2M}^{-'-} \mathbf{q}_{2M}^{-1} \mathbf{b}_0^{-1}.$$

(c v) for the function $\psi_{0,2M}^-(x_k)$ at a grid point $x_k 1 \leqslant k \leqslant 2M - 1$; (working quantity $\mathbf{U}_l = \mathbf{U}_{0,l}^-(x_k)$, for $l = k, k+1, \dots, 2M$ is used)

$$\mathbf{U}_k = \mathbf{I},$$

$$\mathbf{U}_l = \mathbf{U}_{l-1} \mathbf{R}_{l-1}, \qquad \text{for } l = k+1, k+2, \dots, 2M,$$

$$\psi_{0,2M}^-(x_k) = \mathbf{b}_0 \mathbf{q}_k \mathbf{U}_{2M} \mathbf{q}_{2M}^{-1} \mathbf{b}_0^{-1}.$$

The formulae (c i) and (c v) with the coefficients $\mathbf{a}$, $\mathbf{b}_0$, and $\mathbf{b}_1$ of the N scheme are essentially the formulae of the renormalized Numerov method proposed by Johnson (1978a, b). The only difference is that the basic working quantity used by Johnson is the inverse of the matrix $\mathbf{R}_l$ used here.

There are evident similarities between the above formulae of the renormalized Numerov method and the formulae (a i)–(a v) of the generalized log–derivative method. They result not only from the fact that in construction of both methods the same technique, i.e. invariant imbedding, was employed to impose the boundary conditions but also from the common features of the procedures used to discretize the original, differential or integral, equations. In both methods, three-point schemes are used.

Obviously, the Numerov (N) scheme falls into the category of the purely approximate-solution approaches. The modified schemes—RA and IR—correspond clearly to the hybrid approximate-solution approximate-potential approach described in the previous subsection. The accumulated discretization errors in both the Numerov and the log–derivative methods are proportional to h^4. There are, of course, differences in the proportionality constants between the different versions of these methods. In particular, the dependence on energy of these factors in the N, RA, and in the IR versions of the Numerov method is cubic, quadratic and linear, respectively, (Ixaru and Rizea 1987) and, as mentioned previously, it is cubic and linear, respectively, in the nonhybrid and in the hybrid log–derivative algorithms.

Some quantitative information on relative accuracy of the non-hybrid and hybrid versions of the log–derivative and of the Numerov methods is provided in tables 1 and 2. The test problem is the s-wave scattering in the Woods–Saxon potential and the results reported concern determination of energies at which the phase shift (modulo π) crosses $\pi/2$ (table 1) and determination of resonance energies (table 2 A) and time delays (table 2 B) via evaluation and analysis of the lifetime matrix (the collision time delay function, in the single channel case). In the latter calculations, the formulae (a iv) of the

Table 1. s-wave scattering in Woods–Saxon potential.† Absolute errors,‡ $E^{\text{ref}}_{\pi/2} - E_{\pi/2}$, of results by the non-hybrid and hybrid versions of the log–derivative and Numerov algorithms.

$E^{\text{ref}}_{\pi/2}$	h	Non-hybrid		Hybrid		
		log–der	N§	log–der	RA§	IR§
53·588872	$\frac{1}{16}$		−230727	−206	267	−41
	$\frac{1}{32}$	−37860	−14110	−12	8	−1
	$\frac{1}{64}$	−2342	−879	<1	<1	<1
163·215341	$\frac{1}{16}$		−9106839	−633	4481	−137
	$\frac{1}{32}$	−1329226	−479227	−30	134	−4
	$\frac{1}{64}$	−79039	−29500	−2	5	<1
341·495874	$\frac{1}{16}$			−2032	36308	−411
	$\frac{1}{32}$		−7536068	−65	1030	−12
	$\frac{1}{64}$	−1185616	−436825	−4	32	<1
989·701916	$\frac{1}{16}$			3580	1052006	−3933
	$\frac{1}{32}$			−253	23419	−51
	$\frac{1}{64}$			−11	689	−1
	$\frac{1}{128}$	−4417705	−1637376	<1	23	

† Test problem of Ixaru and Rizea (1980, 1987):

$$\left[\frac{d^2}{dx^2} + E - V(x)\right]\psi(x) = 0, \qquad V(x) = u_0/(1+t) + u_1 t/(1+t)^2,$$

$$t = \exp\left[(x - x_0)/a_0\right], \qquad u_1 = -u_0/a_0, \qquad u_0 = -50, \qquad a_0 = 0\cdot6, \qquad x_0 = 7;$$

the integration range $[x', x''] = [0, 15]$. Determined are the values of E at which the phase shift (modulo π) crosses $\pi/2$.

‡ Given in 10^{-6} units.

§ N—the original Numerov scheme. RA and IR denote the schemes modified by Raptis and Allison and by Ixaru and Rizea, respectively. In the notation of Ixaru and Rizea (1987), IR corresponds to the S_2 scheme. The coefficients a, b_0, and b_1 were calculated at every second step according to the formulas listed by Ixaru (1980).

Table 2.   s-wave resonances in Woods–Saxon potential.† Errors of results calculated with the non-hybrid and hybrid versions of the log–derivative and Numerov algorithms.

(A). Absolute errors of resonance energies,‡ $E_{res}^{ref} - E_{res}$.

	E_{res}^{ref}	h	Non-hybrid		Hybrid	
			log–der	N§	log–der	RA§
(1)	6·1080391	$\frac{1}{32}$	16813(−7)‖	6276(−7)	345(−7)	69(−7)
		$\frac{1}{64}$	1045(−7)	392(−7)	22(−7)	4(−7)
(2)	12·805501	$\frac{1}{32}$	2337(−6)	872(−6)	41(−6)	8(−6)
		$\frac{1}{64}$	145(−6)	54(−6)	2(−6)	<1(−6)
(3)	19.782826	$\frac{1}{32}$	3166(−6)	1181(−6)	48(−6)	8(−6)
(4)	26·99595	$\frac{1}{32}$	419(−5)	156(−5)	6(−5)	1(−5)
(5)	34·4097	$\frac{1}{32}$	54(−4)	20(−4)	<1(−4)	<1(−4)
(6)	42·0668	$\frac{1}{32}$	71(−4)	26(−4)	1(−4)	<1(−4)
(7)	50·1044	$\frac{1}{32}$	89(−4)	36(−4)	<1(−4)	2(−4)
(8)	58·6331	$\frac{1}{32}$	130(−4)	38(−4)	⟨1(−4)	7(−4)
(9)	67·6729	$\frac{1}{32}$	124(−4)	99(−4)	1(−4)	21(−4)

(B). Relative errors of time delays at resonance energies,‡
$$[\tau(E_{res})/\tau(E_{res}^{ref}) - 1]/h^4.$$

	$\tau(E_{res}^{ref})$		Non-hybrid		Hybrid	
			log–der	N§	log–der	RA§
(1)	0·46645743	(4)‖	6·9(2)	2·6(2)	−3·7(1)	4·7(0)
(2)	0·64178458	(3)	7·3(2)	2·8(2)	−3·6(1)	1·3(1)
(3)	0·12122577	(3)	8·4(2)	3·1(2)	−3·3(1)	1·6(1)
(4)	0·27408724	(2)	9·7(2)	3·7(2)	−2·8(1)	3·3(1)
(5)	0·71720718	(1)	1·1(3)	4·7(2)	−2·3(1)	8·3(1)
(6)	0·21373143	(1)	1·5(3)	5·0(2)	−1·9(1)	4·5(1)
(7)	0·68367511	(0)	1·9(3)	·9·3(2)	−1·9(1)	3·7(2)
(8)	0·19751232	(0)	4·7(3)	1·5(3)	−5·2(0)	5·5(2)
(9)	0·16540420	(−1)	2·8(4)	2·2(4)	−2·2(2)	1·7(4)

† The parameters of the problem are as listed in table 1 except $a_0 = 0·2$ here.
‡ The resonance energies, E_{res}, are determined as positions of positive value maxima of the collision time delay function $\tau(E)$

$$\tau(E) = 2\frac{d}{dE}\delta(E) = (1 + K^2)^{-1}\frac{d}{dE}K,$$

where δ is the phase shift and $K = tg(\delta)$ is the single channel K matrix.
§ See table 1.
‖ The numbers in parentheses denote powers of 10.

log–derivative method and (c iv) of the Numerov method were employed to direct evaluation of the energy derivatives of the log–derivative matrix (see Section 5.1).

The observation to be made on the purely approximate-solution versions of both methods is that the (global) errors of the log–derivative results are larger than the errors of the results by the Numerov (N) algorithm by a factor which is pretty close (in all cases in table 1 and in the majority of cases in table 2) to the ratio of the coefficients 1/90 and 1/240 standing in the respective expressions for the local discretization errors (compare equations (118) and (126)). The same was seen in the test provided by Johnson (1978a) which concerned determination of bound state energies in a Morse potential. Actually, the observation has been confirmed in calculations on many problems, among them also on problems involving coupled equations and requiring evaluation of integrals of J^-- and J^0-type (Mrugała 1989). Despite this practical evidence, however, one should not take the factor of 240/90 as a strict measure of relative accuracy of the renormalized Numerov and the log–derivative algorithms. There may be situations where the term caused by discontinuity of the third derivative of the integrand in the expression for error of the modified Simpson formula, equation (118), will intervene more significantly in the global error of results generated by the log–derivative algorithm. To complete the comparison, one should also mention that despite their simpler appearance the formulas of the renormalized Numerov algorithm involve a larger number of operations per step than the formulas of the log–derivative algorithm. For example, two matrix inversions per step (half-sector) are required in evaluation of the matrix $\mathbf{R}_{2M}$ (or $\mathbf{L}^4_{0,2M}$) according to the formulae (c i) whereas only one and one half (i.e. two per sector) matrix inversions are involved in evaluation of the log–derivative matrix according to the formulas (a i). Two more matrix multiplications per step occur in the formulae (c iv) than in (a iv). Thus, with the only reservation that accuracy of functions generated by the log–derivative algorithm at unevenly numbered grid points may not be quite the same as the accuracy at even points, one can estimate efficiency of this algorithm, strictly of the non-hybrid version, as being comparable with efficiency of the Numerov (N) algorithm.

Concerning comparison of the hybrid versions of the methods, table 1 seems to support the theoretical finding of the rate of growth of errors with energy being the same in the log–derivative and in the Numerov–IR algorithms. In absolute values, the errors in the latter algorithm are smaller than in the former. The RA version appears in table 1 to be less accurate than the log–derivative algorithm. Table 2 shows, however, that at low energies also this version of the Numerov method may perform better than the hybrid log–derivative algorithm. Similar observations were made in other tests, on simple two channel problems.

Unfortunately, the tests of the hybrid log–derivative algorithms versus the hybrid Numerov related algorithms performed so far, including the ones reported in tables 1 and 2, do not suffice to draw any conclusions on the relative efficiency of these algorithms, especially in multichannel calculations. As a contribution to possible future investigations on this matter, let us note that the basic working quantity of the renormalized Numerov method, the matrix $\mathbf{R}_l$, ceases to be a symmetric matrix in the IR version. This is because in this version (see Ixaru (1980)) the diagonal coefficient matrix $\mathbf{c}$ involved in the formulae (c i) is not just a constant multiplied by the unit matrix and it does not necessarily commute with the matrix $\mathbf{q}_l$.

Acknowledgment

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