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A Highly Convergent Perturbative Method for the Solution of Systems of Coupled Equations Arising from the Schrödinger Equation

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A new method is here proposed for the solution of systems of coupled equations arising from the Schrödinger equation. It is essentially a perturbative method lying upon piecewise constant reference potential. Its algorithm includes the zeroth-order solutions plus corrections from the first two orders of the perturbation theory. The local truncation error and the accumulated error are proportional to h^7 and h^6, respectively. A typical experimental example is also reported. This shows that our method is faster by an order of magnitude than the methods of Numerov and of de Vogelaere while the number of steps required is smaller by an order of magnitude.

1. INTRODUCTION

A new method for solving systems of coupled differential equations arising from the Schrödinger equation is here developed. Our method is essentially a perturbative method based upon piecewise constant reference potential. Thus it preserves the general advantages of the perturbative methods such as the possibility of obtaining accurate solutions at coarse partitions as well as the capability of being used safely in case of higher energies. It also preserves the specific advantage of the perturbative methods based upon piecewise constant potential of yielding stable results at narrow partitions, a property discussed at large in Refs. [1, 2] for the case of single equations.

The algorithm includes the zeroth-order solution plus corrections from the first two orders of the perturbation theory. Its local truncation error and accumulated error behave as h^7 and h^6, respectively. For comparison, recall that for the methods of Numerov [3], de Vogelaere [4], and Gordon [5, 6], the two errors behave as h^6 and h^4, as h^5 and h^4, and as h^3 and h^2, respectively. There are no such investigations for the perturbative methods of Rosenthal and Gordon [7] and Andresen [8], but there are reasons to believe that their errors are proportional to h^5 and h^4, and to h^3 and h^2, respectively.

2. BASIC LEMMA

We consider for moment the following Cauchy problem in a single step:

$$y'' + (EI - V^{\text{orig}}(\delta))\, y = 0, \qquad \delta \in [0, h], \qquad y(0) = y_0\,, \qquad y'(0) = y_0'\,, \quad (2.1)$$

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where the energy E is a scalar, I is the $N \times N$ unit matrix, $V^{\text{orig}}(\delta)$ is an $N \times N$ matrix of functions, $y(\delta)$, y_0 and y_0' are column vectors with N elements.

To solve it we introduce a reference potential $V^{\text{ref}}(\delta)$, i.e., a potential so that the system

$$y^{\text{ref}''} + (EI - V^{\text{ref}}(\delta))\, y^{\text{ref}} = 0, \qquad \delta \in [0, h], \tag{2.2}$$

admits analytic solutions. Let the $N \times N$ matrices $u^{\text{ref}}(\delta)$ and $v^{\text{ref}}(\delta)$ be two sets of linear independent solutions of this system, with the initial conditions

$$u_{ij}^{\text{ref}}(0) = v_{ij}^{\text{ref}}(0) = u_{ij}^{\text{ref}'}(0) = v_{ij}^{\text{ref}'}(0) = 0 \qquad \text{for} \quad i \neq j, \tag{2.3a}$$

$$u_{ii}^{\text{ref}}(0) = v_{ii}^{\text{ref}'}(0) = 1, \qquad u_{ii}^{\text{ref}'}(0) = v_{ii}^{\text{ref}}(0) = 0, \qquad i = 1, 2, \ldots, N. \tag{2.3b}$$

The solution of Eq. (2.2) with the initial conditions $y^{\text{ref}}(0) = y_0$, $y^{\text{ref}'}(0) = y_0'$ then reads

$$y^{\text{ref}}(\delta) = u^{\text{ref}}(\delta)\, y_0 + v^{\text{ref}}(\delta)\, y_0'. \tag{2.4}$$

The reference equation (2.2) is used to obtain the solution of the original equation (2.1) by means of the perturbation theory. If the potentials V^{orig} and V^{ref} are close together the perturbation theory converges and the actual recipe for constructing the solution of Eq. (2.1) is given by the following

LEMMA. *The solution of Eq.* (2.1) *reads*

$$y(\delta) = u(\delta)\, y_0 + v(\delta)\, y_0', \tag{2.5}$$

where u and v are given by series with respect to the perturbation

$$\Delta V = V^{\text{orig}}(\delta) - V^{\text{ref}}(\delta), \tag{2.6}$$

i.e.,

$$u(\delta) = u^{\text{ref}}(\delta) + u^1(\delta) + u^2(\delta) + \cdots, \tag{2.7a}$$

$$v(\delta) = v^{\text{ref}}(\delta) + v^1(\delta) + v^2(\delta) + \cdots. \tag{2.7b}$$

The $N \times N$ matrices of functions u^k and v^k are the solutions of the systems

$$u^{k''} = (V^{\text{ref}}(\delta) - EI)\, u^k + \Delta V u^{k-1}, \qquad k = 1, 2, \ldots, \tag{2.8a}$$

$$v^{k''} = (V^{\text{ref}}(\delta) - EI)\, v^k + \Delta V v^{k-1}, \qquad k = 1, 2, \ldots, \tag{2.8b}$$

with vanishing initial conditions,

$$u^k(0) = v^k(0) = u^{k'}(0) = v^{k'}(0) = 0 \tag{2.9}$$

and $u^0 = u^{\text{ref}}$, $v^0 = v^{\text{ref}}$.

This lemma is exactly the Rayleigh–Ritz approach for the *initial-value* problem. Its proof is straightforward and can be made without difficulty. In fact, write $V^{\text{orig}} = V^{\text{ref}} + \lambda \Delta V$, and search for u and v as series in powers of the coupling constant λ,

$$u(\delta) = \sum_{k=0}^{\infty} \lambda^k u^k(\delta), \qquad v(\delta) = \sum_{k=0}^{\infty} \lambda^k v^k(\delta). \tag{2.10}$$

Next, introduce (2.5) with (2.10) into Eq. (2.1) and rearrange the terms in powers of λ,

$$\begin{aligned} &\lambda^0[(u^{0''} - (V^{\text{ref}} - EI)\, u^0)\, y_0 + (v^{0''} - (V^{\text{ref}} - EI)\, v^0)\, y_0'] \\ &+ \sum_{k=1}^{\infty} \lambda^k \{[u^{k''} - (V^{\text{ref}} - EI)\, u^k - \Delta V\, u^{k-1}]\, y_0 \\ &+ [v^{k''} - (V^{\text{ref}} - EI)\, v^k - \Delta V\, v^{k-1}]\, y_0'\} = 0. \end{aligned}$$

This equation must be satisfied for any values of λ, k, y_0, and y_0'. Then the coefficients of $\lambda^0 y_0$ and $\lambda^0 y_0'$ should be zero,

$$u^{0''} = (V^{\text{ref}} - EI)\, u^0, \qquad v^{0''} = (V^{\text{ref}} - EI)\, v^0,$$

while the coefficients of $\lambda^k y_0$ and of $\lambda^k y_0'$ for $k \neq 0$ are just Eqs. (2.8a) and (2.8b). Moreover, if we identify u^0 and v^0 as u^{ref} and v^{ref}, respectively, the initial conditions for u^k and v^k should be taken simply as zero, thus leading to Eq. (2.9). Q.E.D.

It is appropriate to mention that the way to calculate the perturbative corrections by means of this lemma is different from that used before in connection with perturbative numerical methods. For instance, Gordon [5, 6] also starts with the reference equation (2.2) but the exact solution of Eq. (2.1) is written as

$$y(\delta) = u^{\text{ref}}(\delta)\, A(\delta) + v^{\text{ref}}(\delta)\, B(\delta), \tag{2.11}$$

i.e., the perturbation theory is applied to the coefficients A and B. While both approaches are theoretically equivalent, the one given by this lemma appears to be more convenient. In fact, when used with some skill, it proves more handy and transparent. Second, the formulas of the perturbative corrections in u and v are definitely less sensitive with respect to the cancellation of like terms than those of the corrections in A and B. These points will be detailed in various discussions below.

3. The Algorithm

We consider the system of N coupled equations (arising from the Schrödinger equation)

$$\Psi''(x) + (EI - V(x))\, \Psi(x) = 0, \qquad x \in [a, b], \tag{3.1}$$

with the initial conditions $\Psi(a) = \Psi_a$, $\Psi'(a) = \Psi'_a$, where Ψ_a and Ψ'_a are known column vectors with N elements. The potential matrix $\mathscr{V}(x)$ is supposed to be a real $N \times N$ symmetric matrix and each element $\mathscr{V}_{ij}(x)$ is a well-behaved function. (The numerical treatment of Eq. (3.1) in the vicinity of the origin in the case when $\mathscr{V}_{ij}(x)$ contains singular terms proportional to x^{-2} and to x^{-1} is described in Ref. [9].)

A partition of $[a, b]$ is introduced,

$$x_0 = a, x_1, x_2, \ldots, x_n = b,$$

so that one is left with the Cauchy problem in each individual interval; the initial conditions are the values computed at RHS of the previous interval.

To fix the ideas take the current interval $[x_p, x_{p+1} = x_p + h]$, introduce the inner variable $\delta = x - x_p$, $0 \leqslant \delta \leqslant h$, and denote $v(\delta) = \mathscr{V}(x_p + \delta)$, $\psi(\delta) = \Psi(x_p + \delta)$. Equation (3.1) now reads

$$\psi''(\delta) + (EI - v(\delta))\,\psi(\delta) = 0, \quad \delta \in [0, h], \quad \psi(0) = \Psi(x_p), \quad \psi'(0) = \Psi'(x_p). \tag{3.2}$$

Construction of the Reference Potential

The perturbation procedure for solving Eq. (3.2) gains in efficiency if the reference potential is taken as close as possible to $v(\delta)$ and, in addition, if it is a diagonal matrix. The last requirement suggests a change of representation of Eq. (3.2) such that, in the new basis, the system becomes as uncoupled as possible. (Such a procedure was also used in Refs. [5–8].) We do this as follows. First, we approximate $v(\delta)$ by a parabola:

$$v(\delta) \to \tilde{v}(\delta) = \bar{v} + \tilde{v}^1\left(\delta - \frac{h}{2}\right) + \tilde{v}^2\left(\delta^2 - \frac{h^2}{3}\right). \tag{3.3}$$

The best fit is obtained by use of formulas (A4) of Ref. [10], for each element v_{ij} All three matrices, $\bar{v}$, $\tilde{v}^1$, and $\tilde{v}^2$, will be symmetric, as was the original $v(\delta)$, from which they were derived. In particular this is true for $\bar{v}$, which represents the approximation of the potential function matrix elements by constants. Thus a unitary matrix U always exists which brings $\bar{v}$ to a diagonal matrix $\bar{V}$ and therefore it generates a basis in which the system becomes almost uncoupled. In this basis the system reads

$$y'' + (EI - V(\delta))\,y(\delta) = 0, \qquad \delta \in [0, h], \qquad y(0) = y_0, \qquad y'(0) = y'_0, \tag{3.4}$$

with $y(\delta) = U^T\psi(\delta)$ (U^T is the transposed of U) and

$$V(\delta) = \bar{V} + V^1\left(\delta - \frac{h}{2}\right) + V^2\left(\delta^2 - \frac{h^2}{3}\right), \quad \bar{V} = U^T\bar{v}U, \quad V^s = U^T\tilde{v}^sU, \quad s = 1, 2. \tag{3.5}$$

Equation (3.4) can be solved as shown in the previous section with the following identifications: $V^{\text{orig}} \equiv V(\delta)$, $V^{\text{ref}} \equiv \bar{V}$, and

$$\Delta V \equiv V^1\left(\delta - \frac{h}{2}\right) + V^2\left(\delta^2 - \frac{h^2}{3}\right). \tag{3.6}$$

Zeroth-Order Solution

By its very construction the reference potential $\bar{V}$ is a diagonal matrix. Thus the linear independent solutions of the reference equation are also diagonal matrices. They read:

$$u_{ij}^{\text{ref}}(\delta) = \delta_{ij}\xi(F_i, \delta), \qquad v_{ij}^{\text{ref}}(\delta) = \delta_{ij}\eta(F_i, \delta), \tag{3.7}$$

where $F_i \equiv \bar{V}_{ii} - E$. The functions ξ and η are defined in the Appendix, Eqs. (A1) and (A2).

Perturbative Corrections (General Scheme)

Formulas of the first-order corrections for a constant reference potential evaluated on the basis of representation (2.11) are given in [6]. Here we use the more natural representation, Eq. (2.5). As explained in [2], the latter also ensures higher computational accuracy.

The basic observation for our scheme, which is valid in *any* order k of the perturbation theory, is that the pair ξ, η remain closed on differentiation with respect to δ; see Eqs. (A15). This suggests that the solutions of Eqs. (2.8a) and (2.8b) can be sought as linear combinations of this set; for instance,

$$u_{ij}^k(\delta) = \sum_{l=1}^{N} [a_{ij;l}^k(\delta)\,\xi(F_l, \delta) + b_{ij;l}^k(\delta)\,\eta(F_l, \delta)]. \tag{3.8}$$

To find the coefficients a^k and b^k we insert (3.8) in (2.8a) and, for fixed i, j, and k, obtain the following inhomogeneous system of $2N$ linear differential equations:

$$\begin{aligned} a_{ij;l}^{k''} + 2b_{ij;l}^{k'} + (F_l - F_i)\,a_{ij;l}^k &= \sum_{s=1}^{N} \Delta V_{is} a_{sj;l}^{k-1}, \\ b_{ij;l}^{k''} + 2F_l a_{ij;l}^{k'} + (F_l - F_i)\,b_{ij;l}^k &= \sum_{s=1}^{N} \Delta V_{is} b_{sj;l}^{k-1}, \qquad l = 1, 2, \ldots, N, \end{aligned} \tag{3.9a}$$

with the initial conditions (at $\delta = 0$)

$$\sum_{l=1}^{N} a_{ij;l}^k = 0, \qquad \sum_{l=1}^{N} a_{ij;l}^{k'} + \sum_{l=1}^{N} b_{ij;l}^k = 0. \tag{3.9b}$$

The system (3.9a), (3.9b) admits a unique solution of polynomial form provided the inhomogeneous term in each equation of the system is also a polynomial in δ. To see this, use is made of the observation that the coefficients in the LHS of Eq. (3.9a) are simple numbers, *not* functions of δ. Thus a particular solution of polynomial form

can be found at once and this is unique except for the free terms in $a^k_{ij;i}$ and $b^k_{ij;i}$ (note that their coefficients in Eq. (3.9a) are zero). These two constants are finally adjusted according to the initial conditions.

Therefore, as long as ΔV and the coefficients of the zeroth-order solutions are polynomials in δ (and this is actually the case; see Eq. (3.6) and note that $a^0_{sj;l} = \delta_{sj}\delta_{jl}$ and $b^0_{sj,l} = 0$, as resulting from the first of Eqs. (3.7)) the perturbative corrections can be evaluated analytically in *any* order k of the perturbation theory. As for the practical problem of how many of them should actually be taken to obtain an *optimal* algorithm, this is settled by computational arguments, as seen below.

First-Order Correction

The solution of the Cauchy problem, Eq. (3.4), is given by the transfer matrix algorithm

$$\begin{pmatrix} y(\delta) \\ y'(\delta) \end{pmatrix} = \begin{pmatrix} u(\delta) & v(\delta) \\ u'(\delta) & v'(\delta) \end{pmatrix} \begin{pmatrix} y(0) \\ y'(0) \end{pmatrix}. \tag{3.10}$$

This is a condensed form for Eq. (2.5) and its derivative with respect to δ. The latter must be also included since we need both $y(\delta)$ and $y'(\delta)$, which, evaluated at $\delta = h$, yield the initial conditions on the next interval.

From the first of Eqs. (3.7) it is found that $a^0_{ij;l} = \delta_{ij}\delta_{jl}$ and $b^0_{ij;l} = 0$ and therefore $u^1_{ij}(\delta)$ will consist of a sum of only four nonvanishing terms, viz.:

$$u^1_{ij}(\delta) = a^1_{ij;i}\xi(F_i, \delta) + a^1_{ij;j}\xi(F_j, \delta) + b^1_{ij;i}\eta(F_i, \delta) + b^1_{ij;j}\eta(F_j, \delta). \tag{3.11}$$

Accordingly, the system (3.9a), (3.9b) also consists of only four equations. The solutions are

$$a^1_{ij;i} = \left[\frac{1}{2}hV^1_{ij} - V^2_{ij}\left(-\frac{h^2}{3} - 2D + 8F_jD^2\right)\right] D, \tag{3.12a}$$

$$b^1_{ij;i} = V^1_{ij}(F_i + F_j)\, D^2, \tag{3.12b}$$

$$a^1_{ij;j} = \left[V^1_{ij}\left(\delta - \frac{h}{2}\right) + V^2_{ij}\left(\delta^2 - \frac{h^2}{3} - 2D + 8F_jD^2\right)\right] D, \tag{3.12c}$$

$$b^1_{ij;j} = -2D^2F_j(V^1_{ij} + 2V^2_{ij}D\delta), \tag{3.12d}$$

where $D = (F_j - F_i)^{-1}$. Equations (3.11) and (3.12a)–(3.12d) give the analytic expression of u^1_{ij} at any $\delta \in [0, h]$. However, we are mainly interested in the value of u^1_{ij} at $\delta = h$. This is

$$\begin{aligned} u^1_{ij}(h) = {} & D^2V^1_{ij}\left[\Delta\frac{h}{2}\xi_i + (\Delta + 2F_i)\,\eta_i + \frac{h}{2}\Delta\xi_j - 2(\Delta + F_i)\,\eta_j\right] \\ & + D^3V^2_{ij}\left[-\left(-\frac{h^2}{3}\Delta^2 + 6\Delta + 8F_i\right)\xi_i + \left(\frac{2}{3}h^2\Delta^2 + 6\Delta + 8F_i\right)\xi_j \right. \\ & \left. - 4\Delta(\Delta + F_i)\,h\eta_j\right]. \end{aligned} \tag{3.13}$$

Here $\Delta = D^{-1} = F_j - F_i$ and the label i on the auxiliary functions ξ and η stands for the pair (F_i, h).

When F_i and F_i are close together, the computation of Eq. (3.13) becomes difficult due to the heavy cancellation of the like terms. To cure this Taylor series are taken, in powers of Δ, for the functions ξ_j and η_j (see Eqs. (A16)–(A17)); they lead to the following formula, valid for small Δ:

$$\begin{aligned} u_{ij}^1(h) = \frac{1}{4}\Big\{ & V_{ij}^1\Big[-\zeta_i + \frac{1}{2}\Delta\left(\rho_i + \frac{1}{6}h^2\zeta_i\right) - \frac{1}{16}(-\varphi_i + h^2\rho_i)\Delta^2 \\ & - \frac{1}{16}\left(\tau_i + \frac{3}{20}h^2\varphi_i\right)\Delta^3 - \frac{1}{96}(\chi_i - h^2\tau_i)\Delta^4\Big] \\ & + V_{ij}^2 h\Big[-\zeta_i + \frac{1}{4}\left(3\rho_i + \frac{h^2}{3}\zeta_i\right)\Delta \\ & + \frac{1}{5}\left(\frac{9}{16}\varphi_i - \frac{h^2}{3}\rho_i\right)\Delta^2 - \frac{1}{96}(12\tau_i + h^2\varphi_i)\Delta^3\Big]\Big\}. \end{aligned} \tag{3.14}$$

The same procedure can be repeated for $v_{ij}^{1'}$, $u_{ij}^{1'}$, and $v_{ij}^{1'}$. Their formulas at $\delta = h$ read:

$$\begin{aligned} v_{ij}^1(h) = {} & D^2V_{ij}^1\Big[2\xi_i + \frac{h}{2}\Delta\eta_i - 2\xi_j + \frac{h}{2}\Delta\eta_j\Big] \\ & + D^3V_{ij}^2\Big[-\left(-\frac{h^2}{3}\Delta^2 + 2\Delta + 8F_i\right)\eta_i - 4\Delta h\,\xi_j \\ & + \left(\frac{2h^2}{3}\Delta^2 + 6\Delta + 8F_i\right)\eta_j\Big], \end{aligned} \tag{3.15}$$

$$\begin{aligned} u_{ij}^{1'}(h) = {} & D^2V_{ij}^1\Big[(\Delta + 2F_i)\,\xi_i + \frac{h}{2}\Delta F_i\,\eta_i - (\Delta + 2F_i)\,\xi_j + \frac{h}{2}\Delta(\Delta + F_i)\,\eta_j\Big] \\ & + D^3V_{ij}^2\Big[-F_i\left(-\frac{h^2}{3}\Delta^2 + 6\Delta + 8F_i\right)\eta_i - 2\Delta(\Delta + 2F_i)\,h\xi_j \\ & + (\Delta + F_i)\left(\frac{2h^2}{3}\Delta^2 + 2\Delta + 8F_i\right)\eta_j\Big], \end{aligned} \tag{3.16}$$

$$\begin{aligned} v_{ij}^{1'}(h) = {} & D^2V_{ij}^1\Big[\frac{h}{2}\Delta\xi_i + 2F_i\eta_i + \frac{h}{2}\Delta\xi_j - (\Delta + 2F_i)\,\eta_j\Big] \\ & + D^3V_{ij}^2\Big[-\left(-\frac{h^2}{3}\Delta^2 + 2\Delta + 8F_i\right)\xi_i \\ & + \left(\frac{2h^2}{3}\Delta^2 + 2\Delta + 8F_i\right)\xi_j - 2\Delta(\Delta + 2F_i)\,h\eta_j\Big]. \end{aligned} \tag{3.17}$$

The case $F_j \to F_i$ can be equally accommodated by means of Eqs. (A16)–(A17). As for the accuracy, we find that the dimensionless parameter

$$X = |\,\Delta\,|\,h^2$$

represents a good descriptor. For various values of X we compared the results given by the exact expressions with the ones given by their Taylor counterparts and found that the best correspondence (it is actually of about five coinciding figures) takes place for $1.7 \leqslant X \leqslant 2$, no matter what the individual values of F_i, F_j, and h are. Consequently, the threshold value of $X_t = 1.8$ was assumed for all subsequent computations. Note in passing that our five-figure accuracy compares very favorable with the one reported by Gordon [6], who observed that cases occurred in which the very signs of the computed corrections were altered due to heavy cancellation of like terms.

The computational effort to evaluate the four matrices $u^1(h)$, $v^1(h)$, $u^{1\prime}(h)$, and $v^{1\prime}(h)$ is approximately $60N^2\tau$, where τ is the time required to carry out one floating point multiply + one addition + one references main storage. To give a scale for this τ note that the time to compute the product of two $N \times N$ matrices is $N^3\tau$.

Second-Order Correction

The computational effort to evaluate the second-order correction is proportional to $N^3\tau$ so that its inclusion will be efficient only if the constant of proportionality is a small number. Unfortunately this is not the case for the exact expressions of u^2, v^2, $u^{2\prime}$, and $v^{2\prime}$. (Our qualitative estimates indicate that the effort would be of at least $300N^3\tau$.) Thus we are forced to look for approximations which lead to expressions which are less time-consuming and this is done in the following.

We start with the observation that each second-order propagator is quadratic in the weights of the perturbation, viz.:

$$u_{ij}^2(h) = \sum_{s=1}^{N} (V_{is}^1 V_{sj}^1 \alpha_{ij}^s(h) + V_{is}^1 V_{sj}^2 \beta_{ij}^s(h) + V_{is}^2 V_{sj}^1 \gamma_{ij}^s(h) + V_{is}^2 V_{sj}^2 \theta_{ij}^s(h)). \quad (3.18)$$

Clearly, each of the $4N$ coefficients $\alpha_{ij}^s(h)$, $\beta_{ij}^s(h)$, $\gamma_{ij}^s(h)$, and $\theta_{ij}^s(h)$ ($s = 1, 2, \ldots, N$ and fixed i and j) is, for fixed h, an analytic function of F_i, F_j, and F_s. Therefore we can use its Taylor expansion around the three-dimensional point (F_s, F_s, F_s). For instance, $\alpha_{ij}^s(h)$ reads:

$$\begin{aligned} \alpha_{ij}^s(h) &\equiv \alpha(F_i, F_j, F_s; h) \\ &= \alpha(F_s, F_s, F_s; h) + (F_i - F_s) \frac{\partial \alpha}{\partial F_i}\bigg|_{F_i=F_s} + (F_j - F_s) \frac{\partial \alpha}{\partial F_j}\bigg|_{F_j=F_s} + \cdots. \end{aligned} \quad (3.19)$$

The leading term represents just the second-order *diagonal* contribution. Its expression is already known: it is the coefficient of V_1^2 in the perturbative scheme for single equations (see Appendix of Ref. [10]),

$$\alpha_{ss}^s(h) \equiv \alpha(F_s, F_s, F_s; h) = (1/32)\, h\rho_s. \quad (3.20)$$

(The label s in the function ρ stands for the pair (F_s, h).) The error generated when only this term is retained in Eq. (3.19) can be found easily by dimensional arguments. It can be shown that $[\partial\alpha/\partial F] = [\alpha][F^{-1}] = [\alpha][h^2]$, i.e., the relative error is propor-

tional to h^2. As the coefficient $\alpha_{ss}^s(h)$ is itself a sixth-order function in h, the absolute error when only this is retained in Eq. (3.19) is obviously proportional to h^8.

The inspection of the leading terms of the other coefficients in Eq. (3.18) and of the similar coefficients in the expressions of v^2, $u^{2'}$, and $v^{2'}$ show that they are of the fifth order in h, at least. Therefore the approximations of these coefficients by their diagonal counterparts are correct within $O(h^7)$, at least.

A more realistic and also simple approximation is the one which averages over the three involved diagonal contributions, viz.:

$$\alpha_{ij}^s(h) = \frac{1}{3}(\alpha_{ss}^s(h) + \alpha_{jj}^j(h) + \alpha_{ii}^i(h)) = \frac{1}{96}h(\rho_s + \rho_j + \rho_i). \tag{3.21}$$

The relative error is also proportional to h^2 but its coefficient should be numerically smaller than in the direct approximation (3.20).

Further simplification is suggested by the fact that the leading terms of the coefficients of V^{1^2}, V^1V^2, V^2V^1, and V^{2^2} are proportional to h^6, h^7, h^7, and h^8, respectively, in u^2 and $v^{2'}$; to h^7, h^8, h^8, and h^9 in v^2; but to only h^5, h^6, h^6 and h^7 in $u^{2'}$. For the last case, however, it can be shown that the coefficients of V^{12}, hV^1V^2, and hV^2V^1 are equal within $O(h^7)$. Thus the use of the approximate linear perturbation

$$\Delta V^{\text{approx}} = V^{1\text{approx}}(\delta - h/2), \qquad V^{1\text{approx}} = V^1 + hV^2, \tag{3.22}$$

instead of its exact expression, Eq. (3.6), is sufficient to compute second-order propagators with absolute errors of $O(h^7)$, at least. Moreover, this choice generates *equal* coefficients for u^2 and $v^{2'}$, and this is another helpful factor in decreasing the computational effort.

In conclusion, the formulas of the approximate second-order propagators are

$$u_{ij}^2(h) = \frac{1}{96}h\sum_{s=1}^{N} V_{is}^{1\text{approx}}(\rho_s + \rho_i + \rho_j)\, V_{sj}^{1\text{approx}}, \tag{3.23a}$$

$$v_{ij}^2(h) = \frac{1}{96}\sum_{s=1}^{N} V_{is}^{1\text{approx}}(\varphi_s + \varphi_i + \varphi_j)\, V_{sj}^{1\text{approx}}, \tag{3.23b}$$

$$u_{ij}^{2'}(h) = \frac{1}{96}\sum_{s=1}^{N} V_{is}^{1\text{approx}}(\mu_s + \mu_i + \mu_j)\, V_{sj}^{1\text{approx}}$$

$$(\mu_k = 7\rho_k - \tfrac{1}{3}h^2\zeta_k\,,\ k = i, j, s), \tag{3.23c}$$

$$v_{ij}^{2'}(h) = u_{ij}^2(h). \tag{3.23d}$$

If formulas (3.23a)–(3.23d) are computed simultaneously (namely, compute $V_{is}^{1\text{approx}} \times V_{sj}^{1\text{approx}}$ once and then use its value in all of them), the computational effort is of only $4.5N^3\tau$. For systems of 10 or 20 equations this is about as large as for the first-order propagators.

To summarize, our algorithm computes each propagator of the one-step transfer matrix, Eq. (3.10), as the sum of the contributions from the zeroth, Eqs. (3.7); first, Eqs. (3.13), (3.15), (3.16), (3.17); and second order, Eqs. (3.23a)–(3.23d), of the perturbation theory. The leading term of its truncation error is proportional to h^7.

4. Choosing Step Sizes

We follow here the procedure given in [10] for single equations. However, since the formulas reported there are too long to be computed quickly in case of systems, our main task is now to compress them into forms which, while preserving enough accuracy, need only a small amount of computational effort.

There are two main sources of error in each step. The first comes from the approximation of the original potential by a parabola. It consists of two main kinds of contributions:

(i) energy-dependent contribution

$$\mathscr{E} = \frac{1}{5 \times 7!} h^7 \left| (\bar{V} - EI)\left(V_3 + \frac{1}{2} hV_4\right)\right|, \tag{4.1}$$

see Eq. (2.12a) of [10], and

(ii) energy-independent contributions

$$\epsilon_1 = \frac{1}{20 \times 7!} h^7 \left| (V^1 + hV^2)\left(V_3 + \frac{1}{2} hV_4\right) + \left(V_3 + \frac{1}{2} hV_4\right)(V^1 + hV^2)\right|, \quad \epsilon_2 = \frac{1}{2} h\epsilon_1, \tag{4.2}$$

which approximate Eqs. (2.8a)–(2.8d) of [10].

The second major source is the limited number of orders of the perturbation theory incorporated into our algorithm to solve the system with parabolic matrix potential. Its importance is measured by the contributions from the nonincluded orders. In fact, two of them are dominant:

(i) third-order contribution

$$\epsilon_3 = \frac{1}{9!} h^9 |(V^1 + hV^2)|^3, \tag{4.3}$$

which approximates Eqs. (2.7a)–(2.7d) of Ref. [10], and

(ii) remaining terms from the second order,

$$\epsilon_4 = \frac{15}{4 \times 7!} h^7 |(V^1 + hV^2)^2 \bar{V} + \bar{V}(V^1 + hV^2)^2 - 2(V^1 + hV^2)\bar{V}(V^1 + hV^2)|. \tag{4.4}$$

Equation (4.4) takes into account the fact that only parts from the second-order correction were actually retained in our algorithm. This ϵ_4 has no analog in Ref. [10].

The five contributions, namely, $\mathscr{E}$, ϵ_1, ϵ_2, ϵ_3, and ϵ_4, are sufficient to furnish reliable rules for choosing step sizes. Their computation is quite fast since they were systematized so as to contain operations with only three essential matrices, viz., $\bar{V}$, $V_3 + \frac{1}{2}hV_4$, and $V^1 + hV^2$. The step size consistent with some preset level ϵ for the *local* error is the solution of the equation

$$\lambda(h) = \epsilon, \tag{4.5a}$$

where

$$\lambda(h) = \sup_{i,j} \{(\epsilon_{1_{ij}} + \epsilon_{2_{ij}} + \epsilon_{3_{ij}} + \epsilon_{4_{ij}}), \mathscr{E}_{ij}\}, \qquad i, j = 1, 2,..., N. \tag{4.5b}$$

In the case when the preset quantity is not ϵ but the level of the propagated error, call it TOLV, an extra computation is necessary to calculate the corresponding local level ϵ; this is achieved by means of the equation

$$\epsilon = [(b - a)\tilde{C}]^{-1}\,\mathrm{TOLV}^{7/6}, \tag{4.6}$$

as also explained in [10]. One should note here that generally too small values for the step sizes result from this procedure and this is the direct consequence of the fact that the procedure, as described above, makes use of only *upper bounds* for errors. However, as verified in practice, the simple replacement of Eq. (4.6) by the more relaxed one, $\epsilon = \mathrm{TOLV}^{7/6}$, usually compensates for this effect and so it is used in our program.

5. Numerical Results

We consider here the systems of coupled equations corresponding to the rotational excitation of a diatomic molecule by neutral particle impact; see [3, 4] and references therein. Specifically, we solve the same problem Allison solved in [3], which leads to systems of 4, 9, and 16 equations. We give detailed results for the middle case, $N = 9$. Our method (3) is compared with the matrix Numerov (1) and de Vogelaere (2) schemes. (The last two methods were also used in Ref. [3].) Our analysis is broader than Allison's, in the sense that we do not restrict the investigation only to the accuracy in $|S|^2$, as he did, but also extend it to Re S and Im S.

For all three methods the initial point for integration was fixed at 0.75. Three different partitions are used for methods 1 and 2:

(a) 60 steps at $h = 0.015$ followed by 140 steps at $h_1 = 0.03$, which result in $r_f = 5.85$,

(b) 100 steps at $h = 0.007$ followed by 350 steps at $h_1 = 0.014$, i.e., $r_f = 6.35$, as used by Allison, and

(c) 140 steps at $h = 0.005$ followed by 490 steps at $h_1 = 0.01$, i.e., $r_f = 6.35$. For our method the final point is always $r_f = 6.35$ and the step sizes are adjusted automatically in terms of the preset global accuracy TOLV, as explained in the previous section.

The computations were carried out in single-precision arithmetic on two computers: an IBM 370/135 at the Institute of Physics and Nuclear Engineering in Bucharest, and a CDC 6500 at the Joint Institute for Nuclear Research at Dubna. The word length for the first computer is about seven decimal places in the mantissa. For the second computer it is about fourteen decimal places. The results computed on the CDC with method 3 at TOLV $= 10^{-6}$ were taken as reference.

In Table I the maximum deviations of the computed Re S, Im S, and $|S|^2$ from the reference data, for instance,

$$\max |\Delta \operatorname{Re} S| \equiv \sup_{i,j=1,2,\ldots,N} |\operatorname{Re} S_{ij}^{\text{ref}} - \operatorname{Re} S_{ij}^{\text{comput}}|,$$

are presented, as well as the corresponding CPU times. For method 3 the first number in the CPU time column represents the actual time for integration. The second number, in parentheses, represents the preliminary time, i.e., the time consumed to generate the partition consistent with the preset TOLV. Clearly, only the first time is further consumed for each repeated integration of the system at different energies.

The comparison of the results obtained from the two computers reveals the influence of the accumulation of the round-off errors. One sees that for methods 1 and 2 it is so severe on the IBM computer that these methods are not able to produce even one exact figure in the S-matrix elements. In contrast, it is impressively smaller in the case of method 3. In fact, on the IBM this yields results which are accurate within one unit at the third decimal place in Re S and Im S and within one unit at the fourth place in $|S|^2$.

If the accuracies are compared for Re S and Im S on one hand, and for $|S|^2$ on the other, a major difference is revealed between the classical methods and the present method. For the former ones the results for $|S|^2$ are by two orders of magnitude more accurate than for Re S and Im S. (This is actually normal simply because these methods are sensitive to the oscillating behavior of the wavefunctions, and also because the matrices Re S and Im S are merely descriptors of these oscillations. In contrast, $|S|^2$ depends mainly on the wavefunction *amplitudes*.) For the present method the three errors are approximately equal.

As for the practical efficiency one sees that for similar accuracies the number of steps required and the computing time are definitely smaller (by an order of magnitude or so) for the present method.

One can thus conclude that this method exhibits advantages which may be well appropriate to treat numerically many physical problems. The program is available from the author on request.

TABLE I

Experimental Results, Obtained on Two Computers, from Two Usual Methods (Numerov and de Vogelaere) and from the Method Presented in This Paper for the System of Ref. [3] with $N = 9$ Equations

	Partition[a] TOLV[b]	Total number of steps	max $\lvert \Delta \mathrm{Re}\, S \rvert$ (10^{-4} units)	max $\lvert \Delta \mathrm{Im}\, S \rvert$ (10^{-4} units)	max $\lvert \Delta \lvert S \rvert^2 \rvert$ (10^{-4} units)	CPU time (seconds)
IBM 370/135						
Matrix Numerov	(a)	200	>10,000	>10,000	>10,000	150
	(b)	450	>10,000	>10,000	>10,000	316
	(c)	630	>10,000	>10,000	>10,000	446
De Vogelaere	(a)	200	>10,000	>10,000	>10,000	101
	(b)	450	>10,000	>10,000	>10,000	212
	(c)	630	>10,000	>10,000	>10,000	295
This method	10^{-2}	21	27	27	2	20.3 (79.8)
	10^{-3}	30	10	11	1	28.3 (107.4)
	10^{-4}	44	10	11	0.5	41.3 (156.2)
CDC 6500						
Matrix Numerov	(a)	200	4,495	4,437	50	44.1
	(b)	450	228	224	2	93.0
	(c)	630	50	51	0.5	131.2
De Vogelaere	(a)	200	5,702	5,951	130	29.7
	(b)	450	364	359	3	62.4
	(c)	630	103	101	1	86.8
This method	10^{-2}	21	27	26	2	5.2 (24.3)
	10^{-3}	30	2.5	2.9	1.4	7.5 (34.9)
	10^{-4}	44	0.34	0.35	0.46	11.4 (51.6)
	10^{-5}	64	0.04	0.04	0.02	17.5 (73.9)

[a] Matrix Numerov and de Vogelaere schemes.
[b] This method.

APPENDIX

In this paper we use the following basic functions (see also the Appendix of [10]):

$$\begin{aligned}\xi(F,\delta) \equiv (\exp(F^{1/2}\delta) + \exp(-F^{1/2}\delta))/2 &= \cos(|F|^{1/2}\delta) \quad \text{for} \quad F \leqslant 0,\\ &= \cosh(F^{1/2}\delta) \quad \text{for} \quad F > 0;\end{aligned} \tag{A1}$$

$$\begin{aligned}\eta(F,\delta) \equiv (\exp(F^{1/2}\delta) - \exp(-F^{1/2}\delta))/2F^{1/2} &= \sin(|F|^{1/2}\delta)/|F|^{1/2} \quad \text{for} \quad F < 0,\\ &= \delta \quad \text{for} \quad F = 0,\\ &= \sinh(F^{1/2}\delta)/F^{1/2} \quad \text{for} \quad F > 0;\end{aligned} \tag{A2}$$

$$\zeta(F,\delta) \equiv (\delta\xi(F,\delta) - \eta(F,\delta))/F; \tag{A3}$$

$$\rho(F,\delta) \equiv (-(\delta^2/3)\,\eta(F,\delta) + \zeta(F,\delta))/F; \tag{A4}$$

$$\varphi(F,\delta) \equiv -(5\rho(F,\delta) + \tfrac{1}{3}\delta^2\zeta(F,\delta))/F; \tag{A5}$$

$$\tau(F,\delta) \equiv (7\varphi(F,\delta) - \delta^2\rho(F,\delta))/(10F); \tag{A6}$$

$$\chi(F,\delta) \equiv -(\tfrac{9}{2}\tau(F,\delta) + \tfrac{1}{20}\delta^2\varphi(F,\delta))/F. \tag{A7}$$

Their series expansions in powers of $Z \equiv F\delta^2$ read:

$$\xi(F,\delta) = \sum_{q=0}^{\infty} \frac{1}{(2q)!} Z^q, \tag{A8}$$

$$\eta(F,\delta) = \delta \sum_{q=0}^{\infty} \frac{1}{(2q+1)!} Z^q, \tag{A9}$$

$$\zeta(F,\delta) = 2\delta^3 \sum_{q=0}^{\infty} \frac{q+1}{(2q+3)!} Z^q, \tag{A10}$$

$$\rho(F,\delta) = -\frac{4}{3}\delta^5 \sum_{q=0}^{\infty} \frac{(q+1)(q+2)}{(2q+5)!} Z^q, \tag{A11}$$

$$\varphi(F,\delta) = -\frac{8}{3}\delta^7 \sum_{q=0}^{\infty} \frac{(q+1)(q+2)(q+3)}{(2q+7)!} Z^q, \tag{A12}$$

$$\tau(F,\delta) = \frac{8}{15}\delta^9 \sum_{q=0}^{\infty} \frac{(q+1)(q+2)(q+3)(q+4)}{(2q+9)!} Z^q, \tag{A13}$$

$$\chi(F,\delta) = \frac{8}{15}\delta^{11} \sum_{q=0}^{\infty} \frac{(q+1)(q+2)(q+3)(q+4)(q+5)}{(2q+11)!} Z^q. \tag{A14}$$

In practical computations Eqs. (A1)–(A7) should be used for $|Z| > Z_{\text{threshold}}$, while for $|Z| \leqslant Z_{\text{threshold}}$ the series expansions should accordingly be used. In the latter case seven terms in ξ should be retained; six in η; five in ζ, ρ, and φ; and four in τ and χ, to obtain nine exact figures for $Z_{\text{threshold}} = 1$ and fifteen exact figures for $Z_{\text{threshold}} = 0.06$.

These functions obey the following differential relationships:

Differentation with respect to δ:

$$\frac{\partial \xi}{\partial \delta} = F\eta, \quad \frac{\partial \eta}{\partial \delta} = \xi, \quad \frac{\partial \zeta}{\partial \delta} = \delta\eta, \quad \frac{\partial \rho}{\partial \delta} = -\frac{1}{3}\delta\zeta,$$
$$\frac{\partial \tau}{\partial \delta} = \delta\rho, \quad \frac{\partial \tau}{\partial \delta} = -\frac{1}{10}\delta\varphi, \quad \frac{\partial \chi}{\partial \delta} = \frac{1}{2}\delta\tau. \tag{A15}$$

Differentiation with respect to F:

$$\frac{\partial^{k+1}\xi}{\partial F^{k+1}} = \frac{\delta}{2}\frac{\partial^k \eta}{\partial F^k}, \tag{A16}$$

$$\frac{\partial \eta}{\partial F} = \frac{1}{2}\zeta, \quad \frac{\partial^2 \eta}{\partial F^2} = -\frac{3}{4}\rho, \quad \frac{\partial^3 \eta}{\partial F^3} = -\frac{3}{8}\varphi, \quad \frac{\partial^4 \eta}{\partial F^4} = \frac{15}{8}\tau, \quad \frac{\partial^5 \eta}{\partial F^5} = \frac{15}{8}\chi. \tag{A17}$$

Formulas (A16) and (A17) allow us to write the Taylor expansions of $\xi(F + \Delta, \delta)$ and $\eta(F + \Delta, \delta)$ in terms of the basic functions of arguments F and δ; such expansions are useful, among other things, to eliminate the indeterminacy for $\Delta \to 0$ in formulas (3.13), (3.15), (3.16), and (3.17).

Note added in proof. In the meantime, several improvements have implemented our method. They refer mainly to the procedures of choosing step sizes and of computing second-order corrections. With the newer version, the accuracies mentioned in Table I are obtained with a reduction of about one half for both number of steps and CPU times.

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