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Numerical Integration of an Inhomogeneous Boundary Value Problem

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A numerical method is developped for the integration of stiff inhomogeneous coupled ordinary differential equations. It is shown how to compute integrals with integrands containing the solution of the differential equations. The method is stable and avoids storing of large amounts of intermediate results. The present method can also be applied to problems involving solutions of homogeneous coupled equations.

1. INTRODUCTION

In recent years many new numerical methods have been developed to deal with sets of coupled ordinary, linear and homogeneous differential equations describing various physical problems. In particular the problem of bound states described by a set of differential equations was investigated in several [1–5] papers and methods that are used can be roughly divided into two groups: methods related to the invariant imbedding technique and leading to systems of nonlinear equations [4–6] and methods [1–3] related to the Gram–Schmidt orthogonalization procedure [7].

Depending on the detailed nature of the studied problem one can argue in favor of either the invariant imbedding or the Gram–Schmidt orthogonalization method but in principle either method may be used to solve homogeneous sets of differential equations. However, these methods can not be directly applied to inhomogeneous linear boundary value problems as are encountered when a perturbation is applied to a coupled-channel problem and the perturbation theory is used to deal with the perturbation. In particular an inhomogeneous problem arises in one of the approaches to the nonadiabatic theory of diatomic molecules [8].

The origin of difficulties in the numerical integration of an inhomogeneous set is the same as in the case of homogeneous equations: some of the solutions of the corresponding homogeneous equations grow very fast and in consequence they swamp completely the desired solution of the inhomogeneous set.

To overcome, at least partly, this difficulty is the aim of the present work. It has been started in connection with the nonadiabatic theory of diatomic molecules [8] and therefore reference is made to diatomic molecules in Section 2 when we give a sketch of the derivation of the general form of the inhomogeneous equations. The method of integration of this set is presented in Section 3.

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2. Specification of the Considered Equations

Although the present investigation was started in connection with the nonadiabatic corrections to the energy of diatomic molecules, the numerical difficulties that we would like to discuss are not restricted to this particular problem. However, it is practically impossible to design an efficient numerical method without making some assumptions about the orders of magnitude of the coefficients in the equations. Therefore we give below the relevant equations for a molecule to specify the orders of magnitude that we are interested in.

Let μ be the reduced mass of the two nuclei and r the scalar internuclear distance. If the remaining coordinates in the center of mass system are denoted by x, the nonrelativistic hamiltonian of the molecule can be written as (see, e.g., [9])

$$H = -\frac{1}{2\mu r}\frac{\partial^2}{\partial r^2} r + H_m(x; r), \tag{1}$$

where the operator $H_m(x; r)$ commutes with r. The explicit form of H_m can be found in [9] but we will not need it here.

Approximate solutions of the Schrödinger equation with H given by (1),

$$(H - E)\psi = 0 \tag{2}$$

are often sought in the form of a finite expansion

$$\psi = r^{-1} \sum_{i=1}^{N} \varphi_i(x; r)\, \chi_i(r), \tag{3}$$

where $\varphi_i(x; r)$ is a given basis set which we will assume to be real and orthonormal for all r:

$$\int \varphi_i(x; r)\, \varphi_k(x; r)\, dx = \delta_{ik}. \tag{4}$$

A substitution of (3) into (2) leads to the coupled equations for the column vector $\chi = (\chi_1, \chi_2, \ldots, \chi_N)^T$:

$$\left\{\frac{d^2}{dr^2} + B\frac{d}{dr} + \lambda_0 - V\right\} \chi = 0, \tag{5}$$

where $\lambda_0 = 2\mu E$ and B and V are r-dependent $N \times N$ matrices with elements

$$\begin{aligned} B_{ik} &= 2\int \varphi_i \frac{\partial}{\partial r} \varphi_k\, dx, \\ V_{ik} &= \int \varphi_i \left[2\mu H_m \varphi_k - \frac{\partial^2}{\partial r^2}\varphi_k\right] dx \end{aligned} \tag{6}$$

and by A^T we denote the matrix transposed to A. For bound states χ must vanish at the origin, $r=0$, and at some large $r_{\max}$.

Suppose now that we have a perturbed problem with the hamiltonian $\tilde{H}=H+H'$. The correction to the wavefunction, ψ', satisfies the familiar first order equation of the perturbation theory

$$(H-E)\psi' = -(H'-E')\psi \tag{7}$$

with E' being the first-order correction to the energy. If we expand ψ' rather than ψ in the form of Eq. (3) we get the inhomogeneous coupled set:

$$\left\{\frac{d^2}{dr^2}+B\frac{d}{dr}+\lambda_0-V\right\}\chi=\phi \tag{8}$$

with the boundary conditions at $r=0$ and $r=r_{\max}$:

$$\chi(0)=0, \qquad \chi(r_{\max})=0. \tag{9}$$

The right-hand side in (8) is a column vector with the components

$$\phi_i(r)=2\mu\int r\varphi_i[H'-E']\psi\,dx \tag{10}$$

and the second-order energy correction is given by

$$E''=\int \psi' H'\psi\,dx\,dr=-(2\mu)^{-1}\cdot\lambda'',$$

where

$$\lambda''=\int \chi^T\cdot\phi\,dr. \tag{11}$$

In the molecular bound state problems we have usually (in atomic units)

$$r_{\max}\sim 10, \qquad \mu\gtrsim 1000, \qquad \|B\|\sim 1, \qquad (2\mu)^{-1}\|\lambda_0-V\|\approx 0.1-0.5$$

with $\|\cdot\|$ being a matrix norm.

In principle one could attempt to solve (8) by using, e.g., the imbedding technique [6]. However, this would result in first order equations and in consequence one would have to use a very small integration step, h, to satisfy the necessary condition

$$h\cdot\|\lambda_0-V\|<1. \tag{12}$$

With μ exceeding 10^3, Eq. (12) leads to $h\sim 10^{-3}$. Thus the integration of the first order equations in the interval $0\leqslant r\leqslant 10$ would require as much as 10^4 integration steps. Therefore we will not transform (8) to a first order set. Instead we will

transform Eq. (8) to remove the first derivatives. Obviously, this can be done by a linear transformation

$$\chi = S \cdot f, \tag{13}$$

where the $N \times N$ matrix S satisfies the differential equation

$$2 \cdot dS/dr + B \cdot S = 0 \tag{14}$$

with the initial condition

$$S(r_0) = I. \tag{15}$$

In (15) I denotes the identity transformation and r_0 is arbitrary but fixed.

Since B is skew symmetric, $B^T = -B$, it follows: $S^T S = I$. For a hermitian hamiltonian, Eq. (1), Eqs. (5) are self adjoined, i.e.,

$$V^T = V + dB/dr. \tag{16}$$

Using Eqs. (13)–(16) we get the equations for the vector f:

$$d^2f/dr^2 + Q \cdot f = g \tag{17}$$

with

$$g = S^T \cdot \phi \tag{18}$$

and

$$Q = -\tfrac{1}{2} S^T \{V + V^T - \tfrac{1}{2} B^T B - \lambda_0\} S. \tag{19}$$

The second order correction, Eq. (11), reads now

$$\lambda'' = \int f^T g \, dr, \tag{20}$$

and the equivalent of Eq. (12) is

$$h^2 \cdot \|Q\| < 1 \tag{21}$$

which reduces significantly the number of integration steps required by Eq. (12).

Clearly, to get Q, Eq. (19), we have to solve Eq. (14). However, since $\|B\| \sim 1$ and S is orthogonal, numerical integration of Eq. (14) creates no problems and can be performed by any standard method. If the dimension is small, Eq. (14) can be integrated and S stored. For larger sets it is more convenient to perform the integration of Eqs. (14) and (17) simultaneously and with the same step size h.

Unfortunately, Eq. (17) has all the inherent instabilities that are typical for Eqs. (5) and (8). For that reason Eq. (17) cannot be integrated in a straightforward manner. We will discuss this point in some detail in the next section.

3. The Method of Numerical Integration

Let us consider the boundary value problem

$$d^2f/dr^2 + Q \cdot f = g, \tag{22}$$

$$f(0) = f(r_{\max}) = 0 \tag{23}$$

with f and g being N-dimensional column vectors and Q a real, symmetric matrix. By F^{out} we will denote a $N \times N$ matrix whose columns represent N linearly independent solutions of the corresponding homogeneous equations

$$d^2F/dr^2 + Q \cdot F = 0 \tag{24}$$

satisfying

$$F(0) = 0. \tag{25}$$

The solutions of Eq. (24) satisfying

$$F(r_{\max}) = 0 \tag{26}$$

will be denoted by F^{in}.

Similarly, f^{out} and f^{in} are solutions of Eq. (22) satisfying $f^{\text{out}}(0) = 0$, and $f^{\text{in}}(r_{\max}) = 0$. The solution of (22), (23) is now

$$f = f^{\text{out}} + F^{\text{out}}c = f^{\text{in}} + F^{\text{in}}d, \tag{27}$$

where c and d are constant vectors that can be in principle easily determined, e.g., by using Eq. (27) twice, for two different values of r, and solving the resulting linear equations. However, it is a well-known fact that for stiff equations the solutions forming F becomes practically linearly dependent and f becomes proportional to a fast growing solution of the homogeneous equations, when one proceeds with the integration of Eqs. (24) and (22), respectively. In such a case Eq. (27) does not hold and it is difficult to determine f. Fortunately, the difficulties arising from the linear dependencies in F can be overcome by using some sort of an orthogonalization process whenever F threatens to become linearly dependent [1, 7] and thus assuring the linear independence of the solutions. This, however, does not suffice if one lost the small inhomogeneous solution in f^{out} and f^{in} because it was swamped by large homogeneous solutions. Therefore one should try to subtract from f, in the course of integration, linear combinations of the homogeneous solutions in order to keep $\|f\|$ possibly small. Below we apply this idea to get an algorithm for the solution of Eqs. (22)–(23).

To begin, let us convert Eqs. (22) and (24) into a discrete problem by using the Numerov method (see [3, 10]). For a given number of $n+1$ grid points we write $h = r_{\max}/n$ and $r_k = k \cdot h$ $(k = 0, 1, \ldots, n)$.

Defining

$$T_k = -\frac{h^2}{12} Q(r_k),$$
$$G_k = \frac{h^2}{12} g(r_k), \tag{28}$$

we get the following recurrence relations for $f_j = f(r_j)$, $F_j = F(r_j)$:

$$Y_{j+1} - U_j Y_j + Y_{j-1} = G_{j+1} + 10G_j + G_{j-1}, \tag{29}$$
$$Y_0 = Y_n = 0, \tag{30}$$
$$Z_{j+1} - U_j Z_j + Z_{j-1} = 0, \tag{31}$$

where

$$Y_j = (I - T_j) f_j, \tag{32}$$
$$Z_j = (I - T_j) F_j, \tag{33}$$
$$U_j = (2 \cdot I + 10 \cdot T_j) \cdot (I - T_j)^{-1}. \tag{34}$$

Let Z_j^1 be a solution of Eq. (31) satisfying

$$Z_0^1 = 0, \qquad Z_1^1 = I. \tag{35}$$

We define now

$$Z_j^s = Z_j^1 (Z_s^1)^{-1}, \qquad s > 0, \quad j = 0, 1, ..., \tag{36}$$

i.e., Z_j^s is a solution of Eq. (31) with the boundary conditions

$$Z_0^s = 0, \qquad Z_s^s = I. \tag{37}$$

If Y_j is any solution of Eq. (29) satisfying $Y_0 = 0$, and c a constant vector,

$$\bar{Y}_j(c) = Y_j - Z_j^1 c \tag{38}$$

is also a solution and satisfies $\bar{Y}_0 = 0$. We will use the notation

$$Y_j^k = \bar{Y}_j(c_0), \tag{39}$$

where c_0 is a vector that minimizes

$$\delta = (\bar{Y}_k)^T \bar{Y}_k + (\bar{Y}_{k-1})^T \bar{Y}_{k-1}. \tag{40}$$

Note that in view of $Z_0 = 0$, Eq. (40) leads to $Y_1^1 = 0$.

It follows from the above definitions that the vectors that form Z_j^s are orthogonal for $j = s$, and so they are certainly linearly independent for indices j close to s. At the same time Y_j^s is small.

To avoid the problem of testing Z_j^s for the linear independence of columns, it is advantageous to change the independent basis by going over from Z_j^s to Z_j^{s+1} after each integration step. Thus we can proceed as follows: Suppose Eq. (29) and (31) have been solved for $j \leqslant k$ and we have Y_j^k and Z_j^k. Now, computing Z_{j+1}^k from Eq. (31), we get for $j \leqslant k+1$:

$$Z_j^{k+1} = Z_j^k (Z_{k+1}^k)^{-1}. \tag{41}$$

It follows from Eq. (37)

$$Z_{k+1}^k = Z_{k+1}^1 (Z_k^1)^{-1} = R_k, \tag{42}$$

where R_k is the ratio matrix introduced recently by Johnson [3]. Thus Eq. (41) now reads

$$Z_j^{k+1} = Z_j^k \cdot R_k^{-1}. \tag{43}$$

Equation (29) yields Y_j^k for $j = k+1$ and the new vector is

$$Y_j^{k+1} = Y_j^k - Z_j^{k+1} c^k \tag{44}$$

with c^k satisfying according to Eq. (40):

$$(R_k + R_k^{-1}) c^k = Y_k^k + R_k Y_{k+1}^k. \tag{45}$$

In (45) use has been made of (37) and of the symmetry of R_k [3].

So far we have constructed the outward solutions related through Eqs. (32), (33) to f^{out} and F^{out} appearing in Eq. (27). The inward solutions, $\hat{Y}_j^k$ and $\hat{Z}_j^k$ can be constructed in a similar manner if we start from

$$\hat{Y}_n = \hat{Y}_{n-1} = 0, \qquad \hat{F}_n = 0 \qquad \text{and} \qquad \hat{F}_{n-1} = I,$$

and use (29) and (31) for decreasing indices. Instead of Eqs. (42)–(45) we get for the inward solutions:

$$\hat{Z}_{k-1}^k = \hat{Z}_{k-1}^{n-1} (\hat{Z}_k^{n-1})^{-1} = \hat{R}_k, \tag{46}$$

$$\hat{Z}_j^{k-1} = \hat{Z}_j^k \hat{R}_k^{-1}, \tag{47}$$

$$\hat{Y}_j^{k-1} = \hat{Y}_j^k - \hat{Z}_j^{k-1} \cdot d^k \tag{48}$$

with d^k satisfying:

$$(\hat{R}_k + \hat{R}_k^{-1}) d^k = \hat{Y}_k^k + \hat{R}_k \hat{Y}_{k-1}^k. \tag{49}$$

Now, having both the outward solution, Y_j^m, for $0 \leqslant j \leqslant m+1$ and the inward solution $\hat{Y}_j^{m+1}$ for $m \leqslant j \leqslant n$, we can use Eq. (27) to match them.

In analogy with Eq. (27) we write

$$Y_j = Y_j^m - Z_j^{m+1} c = \hat{Y}_j^{m+1} - \hat{Z}_j^m d \tag{50}$$

and for $j = m$ and $j = m+1$ we get, respectively,

$$Y_m^m - R_m^{-1} c = \hat{Y}_m^{m+1} - d, \tag{51}$$

$$Y_{m+1}^m - c = \hat{Y}_{m+1}^{m+1} - \hat{R}_{m+1}^{-1} \cdot d, \tag{52}$$

i.e.,

$$c = Y_{m+1}^m - Y_{m+1}^{m+1} + R_{m+1}^{-1} \cdot d, \tag{53}$$

and d is given by

$$(R_m - \hat{R}_{m+1}^{-1}) d = Y_{m+1}^m - \hat{Y}_{m+1}^{m+1} - R_m (Y_m^m - \hat{Y}_m^{m+1}). \tag{54}$$

If the matrix $R_m - \hat{R}_{m+1}^{-1}$ is nonsingular, we get from Eqs. (54), (53), and (50) a unique solution Y_j. If the matrix is singular, the homogeneous problem corresponding to (29), (30) has [3] a nontrivial solution Yo_j and in consequence Y_j is not unique, similarly as is the case with the differential equations (22).

It is clear from definitions (36) and (42) that

$$\begin{aligned} Z_j^k &= R_{j-1} R_{j-2} \cdots R_k \qquad \text{for} \quad j > k, \\ &= R_j^{-1} R_{j+1}^{-1} \cdots R_{k-1}^{-1} \qquad \text{for} \quad j < k \end{aligned} \tag{55}$$

and similar relations hold for $\hat{Z}_j^k$. Hence it suffices to compute Y_j^k, $\hat{Y}_j^k$ and the ratio matrices R_j, $\hat{R}_j$ to solve our problem. As was shown by Johnson [3], these matrices can be obtained conveniently from the equations:

$$R_k = U_k - R_{k-1}^{-1}, \qquad R_0^{-1} = 0 \tag{56}$$

and

$$\hat{R}_k = U_k - \hat{R}_{k+1}^{-1}, \qquad \hat{R}_n^{-1} = 0. \tag{57}$$

Although the method that we outlined above can be used for a step-by-step integration without the danger of instabilities connected with the initial rapid growth of the solutions, the computation of the wavefunction, for large systems, is still a practical problem, similarly as in the case of homogeneous equations. For relatively weakly bound states, as, e.g., those considered by Dunker and Gordon [2], one can—by using repeatedly our formulas (43)–(49)—compute the proper initial values Y_1 and $\hat{Y}_{n-1}$ and then obtain Y_j from Eq. (29) in analogy with [2]. However, for stiff problems this method must fail because of inherent instabilities.

An other possibility is to compute and store the matrices R_j and $\hat{R}_k$ and construct the solution with the aid of Eqs. (46)–(55). This method is stable and was successfully used by Johnson [3] for homogeneous equations. However, it has the disadvantage that it requires a very large amount of storage to store the $n \times N^2$ numbers forming the ratio matrices. Therefore it can not very well be used even for moderately large systems. Fortunately, in most cases in practice we need the solutions of Eqs. (22)–(23) only to compute integrals of the form

$$\int f^T \cdot \bar{P}\, dr = h \cdot J_1 \tag{58}$$

or

$$\int f^T \bar{A} f\, dr = h \cdot J_2, \tag{59}$$

where the vector $\bar{P}$ and the symmetric matrix $\bar{A}$ are given functions of r. An example of Eq. (58) is the second order energy, Eq. (20).

Below we present a stable computational scheme for the evaluation of (58)–(59) that does not require storing of the ratio matrices.

If we use the trapezoidal rule we get in view of the boundary conditions, Eq. (30), the expressions

$$J_1 = \sum_{j=1}^{n-1} (Y_j)^T P_j, \tag{60}$$

$$J_2 = \sum_{j=1}^{n-1} (Y_j)^T A_j Y_j, \tag{61}$$

where we have used the notation

$$\begin{aligned} P_j &= (I - T_j)^{-1} \bar{P}_j, \\ A_j &= (I - T_j)^{-1} \bar{A}_j (I - T_j)^{-1}. \end{aligned} \tag{62}$$

To compute J_1 we define the auxiliary quantities

$$M_s = \sum_{j=1}^{s} (Z_j^{s+1})^T P_j, \tag{63}$$

$$E_s = \sum_{j=1}^{s} (Y_j^s)^T P_j \tag{64}$$

and for the evaluation of J_2

$$N_s = \sum_{j=1}^{s} (Z_j^{s+1})^T A_j Z_j^{s+1}, \tag{65}$$

$$L_s = \sum_{j=1}^{s} (Y_j^s)^T A_j Y_j^s, \tag{66}$$

$$K_s = \sum_{j=1}^{s} (Z_j^{s+1})^T A_j Y_j^s. \tag{67}$$

Obviously, E_s and L_s are scalars, M_s and K_s vectors and N_s a matrix.

By making use of Eq. (44) we get the following recurrence relations

$$M_{s+1} = R_{s+1}^{-1}(M_s + P_{s+1}), \tag{68}$$

$$E_{s+1} = E_s - (c^s)^T M_s + (Y_{s+1}^{s+1})^T P_{s+1}, \tag{69}$$

$$N_{s+1} = R_{s+1}^{-1}(N_s + A_{s+1}) R_{s+1}^{-1}, \tag{70}$$

$$L_{s+1} = L_s - (c^s)^T K_s - (K_s)^T c^s + (c^s)^T N_s c^s + (Y_{s+1}^{s+1})^T A_{s+1} Y_{s+1}^{s+1}, \tag{71}$$

$$K_{s+1} = R_{s+1}^{-1}(K_s - N_s c^s + A_{s+1} Y_{s+1}^{s+1}). \tag{72}$$

Thus, starting with $E_0 = L_0 = 0$, $M_0 = K_0 = 0$ and $N_0 = 0$ and using (68)–(72) simultaneously with the step-by-step integration described above we get at the matching point M_m, E_m, N_m, K_m and L_m.

If we define

$$\hat{M}_s = \sum_{j=s}^{n-1} (\hat{Z}_j^{s-1})^T P_j \tag{73}$$

and similarly $\hat{E}_s, \hat{N}_s, \hat{L}_s$ and $\hat{K}_s$, we get for the inward integration formulas quite analogous to Eqs. (68)–(72)

$$\hat{M}_{s-1} = \hat{R}_{s-1}^{-1}(\hat{M}_s + P_{s-1}), \tag{74}$$

$$\hat{E}_{s-1} = \hat{E}_s - (d^s)^T \hat{M}_s + (\hat{Y}_{s-1}^{s-1})^T P_{s-1}, \tag{75}$$

$$\hat{N}_{s-1} = \hat{R}_{s-1}^{-1}(\hat{N}_s + A_{s-1}) R_{s-1}^{-1}, \tag{76}$$

$$\hat{L}_{s-1} = \hat{L}_s - (d^s)^T \hat{K}_s - (\hat{K}_s)^T d^s + (d^s)^T \hat{N}_s d^s + (\hat{Y}_{s-1}^{s-1})^T A_{s-1} \hat{Y}_{s-1}^{s-1}, \tag{77}$$

$$\hat{K}_{s-1} = \hat{R}_{s-1}^{-1}(\hat{K}_s - \hat{N}_s d^s + A_{s-1} \hat{Y}_{s-1}^{s-1}), \tag{78}$$

where d^s is defined by (49).

Now using (50) we write with c and d given by (53)–(54)

$$\begin{aligned} J_1 &= \sum_{j=1}^{m} (Y_j^m - Z_j^{m+1} c)^T P_j + \sum_{j=m+1}^{n-1} (\hat{Y}_j^{m+1} - \hat{Z}_j^m d)^T P_j \\ &= E_m - c^T M_m + \hat{E}_{m+1} - d^T \hat{M}_{m+1} \end{aligned} \tag{79}$$

and

$$J_2 = L_m + c^T N_m c - c^T K_m - (K_m)^T c + \hat{L}_{m+1} + d^T \hat{N}_{m+1} d - d^T \hat{K}_{m+1} - (\hat{K}_{m+1})^T d. \tag{80}$$

This completes the evaluation of the integrals (58), (59). In particular, if we set in (58) $\bar{P}(r) = g(r)$, we get the energy correction, Eq. (20), $\lambda'' = h \cdot J_1$.

It is worth noting that our method of simultaneous integration of the differential equations and evaluation of the necessary integrals can be easily applied to the case of homogeneous equations. If one uses Johnson's method [3] for the homogeneous equations, one can easily get integrals involving the wavefunction. The necessary formulas are obtained from Eqs. (60)–(80) if one sets $Y_i^k = \hat{Y}_j^s = 0$. Clearly, to get proper normalization it is necessary to compute also the equivalent of N_s, $\hat{N}_k$ with $\bar{A} = I$.

4. Numerical Example and Conclusions

As an illustration of the present method a two-dimensional problem

$$\begin{aligned} L(r)y &= g(r), \\ y(a) &= y(b) = 0 \end{aligned} \tag{81}$$

with

$$L(r) = -(2\mu)^{-1} d/dr^2 + V - E \tag{82}$$

was solved and the integral

$$J = \int_a^b y \cdot g \, dr \tag{83}$$

was computed with the aid of the formulas given in the preceding section.

In (82) V is a symmetrix 2×2 matrix with elements

$$V_{11} = -0.66 - 0.035 \times \{1 - \exp(-r + 2)\}^2, \tag{84}$$

$$V_{22} = -0.72 - 0.095 \times \{1 - \exp[-0.7(r - 3)]\}^2, \tag{85}$$

$$V_{12} = 0.0005 \exp[-5.8(r - 3.125)^2] \tag{86}$$

and the right-hand side in (81) was given as

$$g(r) = L(r)\, y_0(r) \tag{87}$$

with

$$y_0 = \begin{pmatrix} 1 \\ 2 \end{pmatrix} \exp[-5(r-3)^2]. \tag{88}$$

The remaining constants were: $\mu = 1000$, $a = 0$ and $b = 7$. Equation (81) was solved and J computed by the present method for several different values of E chosen in such a way that the lowest value used was below the lowest eigenvalue of $Ly = 0$ and the highest E used was well above the asymptotic values of V for large r. Thus the lowest E corresponds to a situation where the solution of the homogeneous problem grows very fast and one could expect numerical instabilities. On the other hand, for high E the solutions of $Ly = 0$ oscillate relatively fast which again could lead to numerical problems.

The results obtained with different integration steps, h, are given in Table I together with the exact results. It is seen that even for a relatively large integration step $h = 0.07$ the results are accurate to within 10^{-7} and they rapidly converge to the exact results when h decreases.

The method was also tested for stability on a real, HD^+ molecule, problem [11]. Several sets of up to 21 coupled second order equations of the form (8) were solved and second order energies of the form (11) computed. Different step sizes, h, and integration intervals $[a, b]$ were used, and the position of the matching point of the outward and inward solutions was varied but no instabilities were encountered. It is believed, therefore, that the present method is accurate and also relatively efficient

TABLE I

Results Obtained for the Integral J

	E		
h	−0.6	−0.625	−0.65
0.07	−0.28330654	−0.21324415	−0.14318176
0.04	−0.28330678	−0.21324439	−0.14318200
0.02	−0.28330681	−0.21324442	−0.14318203
0.01	−0.28330681	−0.21324442	−0.14318203
0.005	−0.28330681	−0.21324442	−0.14318203
exact	−0.283306807	−0.213244417	−0.143182027
	−0.675	−0.7	−0.725
0.07	−0.073119372	−0.0030569818	0.067005408
0.04	−0.073119609	−0.0030572184	0.067005172
0.02	−0.073119635	−0.0030572447	0.067005145
0.01	−0.073119637	−0.0030572464	0.067005144
0.005	−0.073119637	−0.0030572465	0.067005144
exact	−0.0731196366	−0.00305724646	0.0670051438

and it may be useful for solving various linear inhomogeneous problems. Also, as was pointed out in the preceding section, the method can be used to get integrals involving solutions of stiff homogeneous equations.

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REFERENCES

1. R. G. GORDON, *J. Chem. Phys.* **51** (1969), 14.
2. A. M. DUNKER AND R. G. GORDON, *J. Chem. Phys.* **64** (1976), 4984.
3. B. R. JOHNSON, *J. Chem. Phys.* **69** (1978), 4678.
4. M. R. SCOTT, *J. Comput. Phys.* **12** (1973), 334.
5. D. M. SLOAN, *J. Comput. Phys.* **24** (1977), 320.
6. J. CASTI AND R. KALABA, "Imbedding Methods in Applied Mathematics," Adison–Wesley, Reading, Mass., 1973.
7. R. E. BELLMAN AND R. E. KALABA, "Modern Analytic and Computational Methods in Science and Mathematics," Section 21, American Elsevier, New York, 1965.
8. L. WOLNIEWICZ, *Canad. J. Phys.* **53** (1975), 1207.
9. R. T. PACK AND J. O. HIRSCHFELDER, *J. Chem. Phys.* **52** (1970), 521.
10. D. R. HARTREE, "The Calculation of Atomic Structures," Wiley, New York, 1957.
11. L. WOLNIEWICZ AND J. D. POLL, *J. Chem. Phys.*, in press.