JOURNAL OF COMPUTATIONAL PHYSICS 20, 248–250 (1976)

Stable Solutions of the Close-Coupled Equations for Ro-Vibrationally Inelastic Collisions*

In the quantum-mechanical study of inelastic collisions between atoms and diatomic molecules, one must solve a set of coupled second-order ordinary differential equations, commonly called the close-coupled (CC) equations [1]. In matrix notation these are:

$$\left[\frac{d^2}{dR^2}\mathbf{1} + \mathbf{k}^2 - \mathbf{V}(R)\right]\mathbf{u}(R) = 0 \tag{1}$$

where $\mathbf{V}(R)$ is the Hermitian matrix of the coupling potential plus the centrifugal varrier and $\mathbf{k}^2$ is the diagonal wavevector matrix. Gordon [2–4] has developed a widely used program for the efficient numerical solution of these equations. Some recent work [5, 6] has suggested that this program may be poorly suited for the determination of vibrationally inelastic cross sections at low collision energies whenever the suare magnitude of the relevant S-matrix elements drops below $\sim 1 \cdot 10^{-6}$. Typically, nonvanishing fluctuations in the S-matrix appear as one increases the number of channels or, alternatively, as one decreases the input tolerance parameters. For example, extensive calculations on the He–H_2 system [6] indicate that S-matrix elements of square magnitude $1 \cdot 10^{-7}$ can be determined only to within $\pm 20\%$ and those of square magnitude $\lesssim 1 \cdot 10^{-8}$ can become lost in computational "noise." This problem occurs only when closed channels are included [6]. As we will discuss in this note, these difficulties do *not* arise from an inherent instability in either the algorithm [2] or program [3], and can be easily eliminated.

The Gordon algorithm is based on propagating the solutions to the CC equations outward through a series of intervals. For the He–H_2 system [6] $\sim$200 intervals are required for the accurate determination of ro-vibrationally inelastic cross sections of $\sim 10^{-6}$ Å^2. Since, for coupled equations, the error is roughly proportional to the cube of the step size [3], doubling the number of intervals theoretically results in an order of magnitude increase in accuracy. Within each interval the solutions, $\mathbf{u}(R)$, are subjected to a unitary transformation which is chosen to

* Research supported by the Computer Science Center of the University of Maryland; the Office of Naval Research, Contract N00014-67-0239-0023-02; and the Research Corporation.

diagonalize the sum of the wavevector and potential matrices at the midpoint of the interval, R_m. Expanding the potential matrix $\mathbf{V}(R)$ in a power series about R_m, one can write the transformed CC equations as

$$\left[\frac{d^2}{dR^2}\mathbf{1} + \mathbf{f} - \mathbf{G}(R - R_m) + \cdots\right]\mathbf{v}(R) = 0 \tag{2}$$

where $\mathbf{f}$ is the (diagonal) transform of $\mathbf{k}^2 - \mathbf{V}(R_m)$ and $\mathbf{G}$ is the transform of the first derivative of $\mathbf{V}(R)$. By neglecting the off-diagonal elements of $\mathbf{G}$ as well as higher derivatives of $\mathbf{V}(R)$, these equations can be uncoupled and the solutions expressed in terms of Airy functions. For the nth channel one has

$$v_n(R) = A_n Ai[\alpha_n(R + \beta_n)] + B_n Bi[\alpha_n(R + \beta_n)] \tag{3}$$

where $\alpha_n = (G_{nn})^{1/3}$ and $\beta_n = -(f_{nn}/G_{nn} + R_m)$. The coefficients A_n and B_n are determined by solution-matching at the boundary of the previous interval.

The first-order corrections to the uncoupling approximation are related to integrals involving the various uncoupled solutions [2]. Since general analytic expressions for these integrals do not exist, the program performs an "average α" calculation replacing the true solutions by

$$v_n \simeq \bar{v}_n(R) = \bar{A}_n Ai[\bar{\alpha}(R + \beta_n)] + \bar{B}_n Bi[\bar{\alpha}(R + \beta_n)] \tag{4}$$

where $\bar{\alpha}$ represents an average value for all channels and the new expansion coefficients are determined by matching $\bar{v}_n(R)$ to $v_n(R)$ at the right-hand endpoint of the interval. The maximum values of $\bar{A}_n$ and $\bar{B}_n$ are also used to set thresholds for the neglect of small correction terms to the uncoupled solutions.

In regions where the potential is slowly varying, the Airy functions for vibrationally closed channels exhibit extreme exponential behavior, creating the possibility of instabilities due to numerical overflow and underflow. As discussed by Gordon [3], these can easily be avoided in the propagation of the uncoupled solutions $v_n(R)$. However, problems do arise in the evaluation of the first-order corrections, where, for the closed channel components, the $\bar{A}_n$ and $\bar{B}_n$ expansion coefficients can become enormously large. This is a direct consequence of replacing the correct α_n for each channel by an averaged value. As a result, the numerical thresholds mentioned above become too high, leading to an artificial neglect of important correction terms arising from the off-diagonal elements of the G-matrix [Eq. (2)]. Since the largest of the correction terms is used to determine the size of the next interval, the program is induced into taking steps which are too large, thereby losing the desired accuracy in the solutions and, ultimately, in the S-matrix. The use of double-precision arithmetic is hardly effective in controlling this problem.

The way out of this dilemma is to use simpler, constant-potential [3] solutions to evaluate the perturbation integrals whenever the maximum Airy function argument exceeds a critical value, while retaining the correct linear slope (Airy function) zeroth-order solutions. This procedure is already incorporated in the Gordon program [4, statement 81, subroutine STEP]; however, branching occurs for an argument of 22, which is too high to avoid the difficulties discussed in the preceding paragraph. We have found it necessary to use a value of 7.5; so statement 81 of STEP should be changed to read:

IF (TEST.GT.7.5) GO TO 20. The accuracy of the computed first-order corrections can be further insured by setting the tolerance parameter TOLLO considerably smaller than the main tolerance parameter TOLHI [4]. These changes result in only a small increase ($\lesssim 10\,\%$) in the total number of integration steps and, consequently, the computation time, yet lead to stability in the calculation of ro-vibrationally inelastic S-matrix elements of square magnitude 10^{-10} or less. The modified program has been carefully tested [7] for accuracy against a totally different scattering program based on the deVogelaere algorithm [1].

References

1. W. A. Lester, Jr., *Meth. Comput. Phys.* **10** (1971), 211.
2. R. G. Gordon, *J. Chem. Phys.* **51** (1969), 14.
3. R. G. Gordon, *Meth. Comput. Phys.* **10** (1971), 81.
4. R. G. Gordon, Program 187, Quantum Chemistry Program Exchange (QCPE), Indiana University, Bloomington, In.
5. H. Rabitz and G. Zarur, *J. Chem. Phys.* **61** (1974), 5076; A. W. Raczkowski and W. H. Miller, *J. Chem. Phys.* **61** (1974), 5413; J. Schaefer and W. A. Lester, Jr., *J. Chem. Phys.* **62** (1975), 1913.
6. M. H. Alexander, *J. Chem. Phys.* **61** (1974), 5167; also unpublished work.
7. M. H. Alexander and P. McGuire, *J. Chem. Phys.* **64** (1976), in press.

Received: July 21, 1975

Millard H. Alexander

Department of Chemistry
University of Maryland
College Park, Maryland 20742