APPLICATIONS OF CLOSE COUPLING ALGORITHMS TO ELECTRON-ATOM, ELECTRON-MOLECULE, AND ATOM-MOLECULE SCATTERING

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Abstract. We discuss some of the details of our implementation of the

Numerov and R matrix propagation methods for close coupling calculations.

We discuss some of the successes and problems we have had applying these

and other methods in various applications, and we present some execution

times for runs we made to compare various methods.

I. Introduction

In this contribution, we summarize the procedures we currently use to solve close coupling equations for electron-atom, electron-molecule, and atom-molecule collisions, and we discuss some of our relevant past experiences in applying various numerical approaches to close coupling calculations. To facilitate comparison of these methods we also present some timing information which we gathered for this workshop. The numerical methods we compare here are the Numerov method,[1-11] the piecewise analytic method of Gordon with linear reference potential,[12-16] the integral equations algorithm of Sams and Kouri,[17-23] and the R matrix propagation method of Light and Walker with piecewise constant reference potential.[24-29]

In section II we introduce all four methods and discuss in detail our implementation of the Numerov[8] and R matrix propagation[29] methods. In section III we discuss applications of all four methods to elastic and vibrationally and rotationally inelastic electron scattering by N_2 using anisotropic model potentials. Section IV gives applications to electronically inelastic electron scattering by H. Sections V and VI discuss vibrationally and rotationally inelastic atom-diatom scattering, respectively.

II. Discussion of methods

A. Introduction. For this workshop we have compiled some comments on our experiences with close coupling calculations of electron-molecule, electron-atom, and atom-molecule scattering. In this section we provide a detailed description of our implementation of the Numerov and R matrix propagation methods. We also briefly introduce the codes which we used to apply the piecewise analytic method and the Sams-Kouri method, and we comment on our timing studies and on our use of adiabatic basis functions.

B. Numerov method. We have found the Numerov method to be convenient and reliable for many problems. Since the method is easy to apply, the computer program is relatively transparent and easy to modify and simple checks of convergence with respect to numerical parameters can be made.

The Numerov method is a hybrid finite difference method applicable to any set of second-order linear differential equations containing no first derivatives. It is a sixth-order method, i.e., if h denotes the stepsize and $f(r)$ denotes the exact solution of

$$\frac{d^2 f(r)}{dr^2} = D(r) f(r) \tag{1}$$

then the leading term in the truncation error per step is $\frac{h^6}{240} \frac{d^6 f}{dr^6}\Big|_{r=r^*}$ where r^* is some (generally unknown) point in the interval.[4,30] Blatt[4] has suggested that the Numerov method is "the method of choice for the integration of (1) because it is the highest-order method which is at the same time a three-point method." However, the cumulative error in the Numerov method is of order h^4, which is the same order as the Runge-Kutta method which has an h^5 truncation error per step.[31,32]

Lester[33] has pointed out a minor disadvantage of the Numerov
method, namely it requires different algorithms for doubling and halving
the stepsize, respectively. For this reason, Lester chose the deVogelaere
method,[34] which is a variable stepsize method and requires only a single
algorithm for changing the stepsize. Allison[5] compared the regular Numerov,
iterative Numerov, and deVogelaere methods for a test case[36] involving rota-
tional excitation in an atom-rigid-rotator collision, and he found the iter-
ative Numerov method to be the fastest for a given precision. His tests
are significant in that they were run on the same computer using computer
codes written by the same author thereby eliminating two of the major varia-
bles usually existing in such comparisons. He also compared his Numerov
program to Gordon's program[35] using the piecewise analytic method for the
same test case, and he found for calculations of similar precision that the
execution times were comparable for problems having as many as nine channels.
Our program is based mainly on the work of Allison.[5] Further development of
the method has been carried out by Johnson who calls the resulting algorithm
the renormalized Numerov method.[34] As compared to the original matrix Numerov
method, Johnson makes two transformations. The first eliminates one matrix
multiplication and is identical to a transformation used by Allison. The
method obtained after this transformation is called the regular Numerov
method. Johnson's second tranformation is to define a ratio matrix
($\underset{\sim}{Y}_{n+1}\ \underset{\sim}{Y}_n^{-1}$ is the notation used below). This does not change the amount of
computation per step, but it does eliminate the need for stablizing trans-
formations. As discussed below, our program uses stablizing transformations
but our experience has been that these have not required a great amount of
computational effort. In the following general review of the numerical

techniques, we use Allison's equations wherever possible, but we change the notation somewhat to conform more closely with the notation used elsewhere in this report.

The set of N coupled second order differential equations to be solved are

$$\frac{d^2}{dr^2} \underset{\sim}{f}(r) - \underset{\sim}{D}(r) \underset{\sim}{f}(r) = \underset{\sim}{0} \tag{2}$$

with

$$D_{ij}(r) = - \left[k_i^2 - \frac{\ell_i(\ell_i + 1)}{r^2} \right] \delta_{ij} + (2\mu/\hbar^2) v_{ij}(r) \tag{3}$$

We use the convention that $\underset{\sim}{A}$ denotes a matrix with elements A_{ij}. (The columns of $\underset{\sim}{A}$ are denoted $\underline{A}$.) Equation (2) is solved subject to the boundary conditions

$$\underset{\sim}{f}(0) = \underset{\sim}{0} \tag{4}$$

and

$$\underset{\sim}{f}(r) \underset{r \to \infty}{\sim} \underset{\sim}{S}(r)\underset{\sim}{P} + \underset{\sim}{C}(r)\underset{\sim}{Q} \tag{5}$$

where, for the case of all channels asymptotically open,

$$S_{ij}(r) \underset{r \to \infty}{\sim} k_i^{-\frac{1}{2}} \delta_{ij} \sin(k_i r - \tfrac{1}{2}\ell_i \pi) \tag{6}$$

and

$$C_{ij}(r) \underset{r \to \infty}{\sim} k_i^{-\frac{1}{2}} \delta_{ij} \cos(k_i r - \tfrac{1}{2}\ell_i \pi) \tag{7}$$

A subblock $\underset{\sim}{R}$ of the reactance matrix is then given as[37]

$$\underset{\sim}{R} = \underset{\sim}{Q}\underset{\sim}{P}^{-1} \tag{8}$$

This method of asymptotic analysis is easily generalized to the case where some channels are closed.

It is interesting to note that $\underset{\sim}{f}(r)$ is not unique, i.e., for any non-singular matrix $\underset{\sim}{G}$, $\underset{\sim}{f}(r)\underset{\sim}{G}$ satisfies the eqs. (2), (4), and (5) if $\underset{\sim}{f}(r)$ does. However, $\underset{\sim}{R}$ is given in terms of the $\underset{\sim}{f}(r)\underset{\sim}{G}$ solution as

$$\underset{\sim}{\hat{R}} = (\underset{\sim}{Q}\underset{\sim}{G})(\underset{\sim}{P}\underset{\sim}{G})^{-1} = \underset{\sim}{Q}\underset{\sim}{G}\underset{\sim}{G}^{-1}\underset{\sim}{P}^{-1} = \underset{\sim}{Q}\underset{\sim}{P}^{-1} \tag{9}$$

and is the same as for the $\underset{\sim}{f}(r)$ solution. Since $\underset{\sim}{P}^{-1}$ is required, the columns of $\underset{\sim}{f}(r)$ must be linearly independent. Furthermore, any set of N linearly independent linear combinations of the columns of $\underset{\sim}{f}(r)$ is an equally valid set of solution vectors satisfying (2), (4), and (5).

We use the notation $\underset{\sim}{x}_n \equiv \underset{\sim}{x}(r_n)$ where $\underset{\sim}{x}$ is any matrix and r_n is a grid point, and we let the stepsize between grid points be $h \equiv r_{n+1} - r_n$. At a given point, the approximate solution $\underset{\sim}{f}_{n+1}$ to (2) is calculated from $\underset{\sim}{D}(r)$ evaluated at the equally spaced points r_{n+1}, r_n, and r_{n-1}, respectively, and from $\underset{\sim}{f}_n$ and $\underset{\sim}{f}_{n-1}$ as

$$(\underset{\sim}{I} - \frac{h^2}{12}\underset{\sim}{D}_{n+1})\underset{\sim}{f}_{n+1} = (2\underset{\sim}{I} + \frac{10}{12}h^2\underset{\sim}{D}_n)\underset{\sim}{f}_n - (\underset{\sim}{I} - \frac{h^2}{12}\underset{\sim}{D}_{n-1})\underset{\sim}{f}_{n-1} \tag{10}$$

Let

$$\underset{\sim}{F} = -\frac{h^2}{12}\underset{\sim}{D} \tag{11}$$

and

$$\underset{\sim}{Y}_{n+1} = (\underset{\sim}{I} + \underset{\sim}{F}_{n+1})\underset{\sim}{f}_{n+1} \tag{12}$$

Then (10) may be rewritten as

$$\underset{\sim}{Y}_{n+1} = 2\underset{\sim}{Y}_n - 12\underset{\sim}{F}_n\underset{\sim}{f}_n - \underset{\sim}{Y}_{n-1} \tag{13}$$

with

$$\underset{\sim}{f}_{n+1} = (\underset{\sim}{I} + \underset{\sim}{F}_{n+1})^{-1}\underset{\sim}{Y}_{n+1} \tag{14}$$

We refer to (13) and (14) together as the "regular" Numerov method.

In an attempt to speed up the calculation of $(I + F_{n+1})^{-1}$ Allison proposed the following iterative method of calculating f_{n+1}. Let $d(r)$ and $\Delta(r)$ be defined to have elements given by

$$d_{ij}(r) = F_{ii}(r)\, \delta_{ij} \tag{15}$$

and

$$\Delta_{ij}(r) = -(h^2/12) \sum_{\substack{k=1 \\ k \neq j}}^{N} V_{ik}(r)\, f_{kj}(r) \tag{16}$$

so

$$F(r)\, f(r) = d(r)\, f(r) - \Delta(r) \tag{17}$$

Putting (17) at r_n into (13) yields

$$Y_{n+1} = 2Y_n + 12(\Delta_n - d_n f_n) - Y_{n-1} \tag{18}$$

and putting (17) at r_{n+1} into (12) and solving for f_{n+1} yields formally

$$f_{n+1} = (I + d_{n+1})^{-1} \left[Y_{n+1} + \Delta_{n+1} \right] \tag{19}$$

Since $d(r)$ is a diagonal matrix the evaluation of $(I + d_{n+1})^{-1}$ is trivial. But Δ_{n+1} on the right-side of (19) depends on f_{n+1} so Allison proposed using Gauss-Seidel iteration[38] to converge (19) at the current grid point before using (18) for the next grid point, i.e.,

$$T_{n+1} = \lim_{m \to \infty} T_{n+1}^{(m)} \tag{20}$$

for $T(r) = f(r)$ or $\Delta(r)$.

The Gauss-Seidel iteration procedure is a method for finding the solution x to the system of linear algebraic equations

$$\underset{\sim}{A}\underset{\sim}{x} = \underset{\sim}{b} \tag{21}$$

where $\underset{\sim}{A}$, $\underset{\sim}{x}$, and $\underset{\sim}{b}$ are $N \times N$ matrices. First one makes the replacement

$$\underset{\sim}{A} = \underset{\sim}{W} - \underset{\sim}{U} - \underset{\sim}{L} \tag{22}$$

where $\underset{\sim}{W}$ is a diagonal matrix, $\underset{\sim}{U}$ is a strictly upper triangular matrix, and $\underset{\sim}{L}$ is a strictly lower triangular matrix. Putting (22) into (21) and re-arranging yields

$$\underset{\sim}{x} = \underset{\sim}{W}^{-1}\underset{\sim}{U}\underset{\sim}{x} + \underset{\sim}{W}^{-1}\underset{\sim}{L}\underset{\sim}{x} + \underset{\sim}{W}^{-1}\underset{\sim}{b} \tag{23}$$

This motivates the Gauss-Seidel iteration procedure for solving (21);

$$\underset{\sim}{x}^{(m+1)} = \underset{\sim}{W}^{-1}\underset{\sim}{U}\underset{\sim}{x}^{(m)} + \underset{\sim}{W}^{-1}\underset{\sim}{L}\underset{\sim}{x}^{(m+1)} + \underset{\sim}{W}^{-1}\underset{\sim}{b} \tag{24}$$

Varga has shown[38a] that (24) will converge if and only if $\underset{\sim}{A}$ is a positive definite matrix. One way of insuring[38b] that $\underset{\sim}{A}$ is a positive definite matrix is for it to be strictly diagonally dominant, i.e.,

$$|A_{ii}| > \sum_{\substack{j=1 \\ j \neq 1}}^{N} |A_{ij}| , \quad i = 1,2,\ldots,N \tag{25}$$

If the option to try Gauss-Seidel iteration is chosen for a given step, our program checks (25) and uses the regular Numerov instead if it is not satisfied.

Comparing (12) with (21) and (19) with (23) shows that $\underset{\sim}{A} = \underset{\sim}{I} + \underset{\sim}{F}_{n+1}$, $\underset{\sim}{x} = \underset{\sim}{f}_{n+1}$, $\underset{\sim}{b} = \underset{\sim}{Y}_{n+1}$, $\underset{\sim}{W} = \underset{\sim}{I} + \underset{\sim}{d}_{n+1}$, and $(\underset{\sim}{U} + \underset{\sim}{L})\underset{\sim}{x} = \underset{\sim}{\Delta}_{n+1}$. Recalling (16) and putting these assignments into (24) yields the following Gauss-Seidel iteration procedure

$$\left(\underset{\sim}{f}_{n+1}^{(m+1)} \right)_{ij} = [1 + (\underset{\sim}{d}_{n+1})_{ii}]^{-1} [(\underset{\sim}{Y}_{n+1})_{ij} + \left(\underset{\sim}{\Delta}_{n+1}^{(m)} \right)_{ij}] \tag{26}$$

$$\left(\Delta_{\sim n+1}^{(m)}\right)_{ij} = -(h^2/12) \; [\; \sum_{k<i} (V_{\sim n+1})_{ik} \left(f_{\sim n+1}^{(m+1)}\right)_{kj} + \sum_{k>i} (V_{\sim n+1})_{ik} \left(f_{\sim n+1}^{(m)}\right)_{kj} \;] \quad (27)$$

Allison doesn't describe what to use for $f_{\sim n+1}^{(0)}$ in (27). We let

$$f_{\sim n+1}^{(0)} = f_{\sim n} \qquad\qquad\qquad (28)$$

Then using (27) the first row of $\Delta_{\sim n+1}^{(0)}$ can be calculated and put into (26) to calculate the first row of $f_{\sim n+1}^{(1)}$ which together with (28) can be used in (27) to calculate the second row of $\Delta_{\sim n+1}^{(0)}$ and so on, i.e., row k of $\Delta_{\sim n+1}^{(m)}$ only requires $f_{\sim n+1}^{(m)}$ and the first $(k-1)$ rows of $f_{\sim n+1}^{(m+1)}$ and row k of $f_{\sim n+1}^{(m+1)}$ requires only row k of $\Delta_{\sim n+1}^{(m)}$. Provided $(I + F_{\sim n+1})$ is positive definite, equations (28), (26), and (27) are used in the above manner until

$$\frac{1}{N} \left[\sum_{i=1}^{N} \sum_{j=1}^{N} \left| \left(f_{\sim n+1}^{(m+1)}\right)_{ij} - \left(f_{\sim n+1}^{(m)}\right)_{ij} \right|^2 \right]^{\frac{1}{2}} < EPS \qquad (29)$$

where EPS is an input variable. Then putting $f_{\sim n+1} = f_{\sim n+1}^{(m+1)}$ into (16), $\Delta_{\sim n+1}$ is evaluated and $Y(r)$ is evaluated at the next grid point using (18). We refer to the above procedure as the "iterative" Numerov method.

The program has three options regarding the use of the regular and iterative Numerov methods. In the first mode of operation, only the regular Numerov method will be used. In the second, the regular Numerov method is used until an r value is reached at which the iterative Numerov method becomes faster. The time comparison between the two methods is made after the first integration step and every KCKth step until the iterative Numerov method becomes faster. KCK is an input variable. In the third mode only the iterative Numerov method should be used. If the matrix $(I + F_{\sim n+1})$ does not satisfy (25) for some r, the regular Numerov method is used for that r

independent of the choice of mode. For modes two and three the program has an input variable NCONV. NCONV is the maximum number of Gauss-Seidel iterations made at a mesh point. If convergence is not achieved in NCONV iterations, the regular Numerov method is used to find f(r) at that mesh point. If convergence is not reached in NCONV iterations but the time used is less than used by the regular Numerov method the program automatically increases NCONV. Usually we set EPS = 10^{-4} and NCONV = 200. As stressed by Allison,[5] the efficiency of the iterative Numerov method is largely dependent on one's ability to vary the value of the convergence criterion, consistent with obtaining the desired accuracy. Allison used a convergence criterion he called ε and found that $\varepsilon = 10^{-2}$ was sufficient for his calculations. Since we use the reasonably safe value EPS = 10^{-4} for our convergence criterion, we need not check so carefully for convergence with respect to EPS, but our efficiency is not optimized. To obtain the best possible timings one should vary EPS to obtain the value just sufficient for the desired precision.

Next we consider the method used to change the stepsize h. Blatt[4] has suggested a method for applications to single differential equations for determining when h can be doubled or should be halved. A generalization of his error criterion to coupled differential equations has been included in our program. The criterion we use for the variable-stepsize runs used to gather timing information for the present report is to require h be small enough that

$$REPS(r) < 64\delta \tag{30}$$

where δ is an input variable and the estimated relative error per step is

$$REPS(r) = 7.2\left(\frac{h^2}{12}\max_i \left| D_{ii}(r)\right|\right)^3 \tag{31}$$

In practice we double the stepsize if $REPS(r_n) < \delta$ and we half it if $REPS(r_n) > 64\delta$. There is also a provision for restricting the maximum stepsize h_{max} and the stepsize is not doubled if h exceeds $\frac{1}{2}h_{max}$. Although (31) is based on Blatt's error analysis, an essentially equivalent result can be obtained by the following argument. To obtain reasonable accuracy one would expect to require a certain number of steps per deBroglie wavelength, i.e.,

$$h \leq \delta' \min_i \lambda_i \tag{32}$$

where λ_i is the deBroglie wavelength in channel i and δ' is the reciprocal of the number of steps per deBroglie wavelength. Using (3) and a corresponding criterion for locally closed channels we rewrite (32) as

$$h \leq (const.)\delta'(\max_i \left|D_{ii}\right|)^{-\frac{1}{2}} \tag{33}$$

For comparison we use (31) to rewrite (30) as

$$h \leq (const.')\,\delta^{\frac{1}{6}}(\max_i \left|D_{ii}\right|)^{-\frac{1}{2}} \tag{34}$$

The effect of (33) is the same as the effect of (34), but the constant has a different name.

Because the stepsize is not changed with $\delta < REPS(r) < 64\delta$, and because the stepsize is only changed by factors of 2, the actual stepsize used at a given r depends on the initial stepsize h_0 as well as on r. The program can also operate in a fixed-stepsize mode, or used fixed stepsizes at small r and variable stepsizes at large r.

Doubling the stepsize is straightforward. It merely requires using the values of $\underset{\sim}{f}(r)$ and $\underset{\sim}{D}(r)$ at r_n and r_{n-2} instead of r_n and r_{n-1} and using $2h$ instead of h in (10) to calculate $\underset{\sim}{f}_{n+2}$ instead of $\underset{\sim}{f}_{n+1}$.

However, when the stepsize should be halved, $\underset{\sim}{f}(r)$ has not been calculated at·a half step back and, until it is, the integration cannot proceed using half the current stepsize h. The method[4] used to calculate $\underset{\sim}{f}(r)$ at $r' = r_n - \dfrac{h}{2}$ from h, $\underset{\sim}{f}_n$, $\underset{\sim}{D}_n$, $\underset{\sim}{f}_{n-1}$, and $\underset{\sim}{D}_{n-1}$ is as follows. Let $h' = \dfrac{h}{2}$, i.e., half the current stepsize, let $r_{n+1} = r_{n-1} + 2h' = r_{n-1} + h$, i.e., the old r_n becomes the new r_{n+1} and the old $\underset{\sim}{f}_n$ and $\underset{\sim}{D}_n$ become the new $\underset{\sim}{f}_{n+1}$ and $\underset{\sim}{D}_{n+1}$, respectively, and the new $r_n = r_{n-1} + h' = r'$. Using this new grid, $\underset{\sim}{f}(r') = \underset{\sim}{f}_n$ can be found from (10) and $\underset{\sim}{D}_n = \underset{\sim}{D}(r')$ as

$$\underset{\sim}{f}_n = (\underset{\sim}{I} + \tfrac{10}{12}h'^2\underset{\sim}{D}_n)^{-1}\left[(\underset{\sim}{I} - \tfrac{h'^2}{12}\underset{\sim}{D}_{n+1})\underset{\sim}{f}_{n+1} + (\underset{\sim}{I} - \tfrac{h'^2}{12}\underset{\sim}{D}_{n-1})\underset{\sim}{f}_{n-1}\right] \qquad (35)$$

after which the integration can proceed as before but with h' replacing h in all equations.

Now we consider the procedure for starting the propagation of the solution vectors. If the elements of $\underset{\sim}{V}(r)$ have no singularities of order two or higher at the origin, then for small r the solutions of (2) that satisfy (4) are given by

$$f_{ij}(r) \underset{r\to 0}{\sim} c_{ij}r^{\ell_i+1} \qquad (36)$$

Since, as explained in the previous subsection, we need merely obtain any linearly independent set of N solutions of the coupled equations we may let $c_{ij} = c_{ii}\delta_{ij}$. For electron-molecule and electron-atom scattering the program calculates the initial grid point r_0 by solving

$$r_0^{\ell_{min}+1} = \text{UTEST} \tag{37}$$

where UTEST is a small number, usually 10^{-12} atomic units, which is an input variable of the program, and

$$\ell_{min} = \min_i \{\ell_i\}_{i=1}^N \tag{38}$$

For atom-molecule scattering we set r_0 to a value sufficiently small so that all channels are strongly closed. In either case the results should be invariant to decreasing UTEST or r_0. Since the Numerov method is a 3-point method, it requires $\underline{f}(r)$ at r_0 and $r_1 = r_0 + h_0$ to get started. As discussed above, the calculation of a subblock of the reactance matrix requires that the column vectors of the solution matrix be linearly independent. Therefore the program starts the solution with a linearly independent set of column vectors as

$$\underline{f}_0 = \underline{0} \tag{39}$$

and

$$\underline{f}_1 = \underline{I} \tag{40}$$

Starting the solution with a set of linearly independent column vectors does not insure that the computed solution vectors will remain linearly independent until (5) is valid. For example, if the local kinetic energy in the ith channel [which is proportional to $-D_{ii}(r)$] is negative, the ith row of $\underline{f}(r)$ will grow exponentially as the integration proceeds and the linear independence of the column vectors will be lost. If this problem occurs one must perform stabilizing transformations, i.e., one must periodically replace the columns of $\underline{f}(r)$ by linear combinations of the columns

to insure linear independence is not lost. There is of course more than one way to do this. Riley's method,[39] consisting of periodic reorthogonal-ization of the columns of $\underset{\sim}{f}(r)$, is particularly easy to apply and was chosen for our program. An alternative method has been presented by Gordon.[12] Riley's method consists of defining a transformed solution $\underset{\sim}{f}^t(r)$ in terms of the solution $\underset{\sim}{f}(r)$ as

$$\underset{\sim}{f}_k^t = \underset{\sim}{f}_k \underset{\sim}{f}_n^{-1} \qquad k = n, n-1, n-2, \ldots, 0 \tag{41}$$

with $\underset{\sim}{f}^t(r)$ replacing $\underset{\sim}{f}(r)$ in all equations using $\underset{\sim}{f}(r)$. The transformation is applied only when at least one of the $D_{ii}(r)$ is positive. The number of integration steps taken between successive applications of (41) in such regions is set by an input parameter, NLINDP, of the program. If NLINDP is set too large, the subblock $\underset{\sim}{R}^J$ of the reactance matrix calculated in the asymptotic region is not symmetric. For a typical case, we find it sufficient to reorthogonalize at every 20th step for which the local kinetic energy in any channel is negative. Riley's method of stablization may also be used as part of a procedure for eliminating closed channels at large r so that the number of channels propagated may be reduced to those that are open asymptotically.[14]

As mentioned above, the solution to (2) is matched in the asymptotic region using (5) to a linear combination of matching functions $\underset{\sim}{S}(r)$ and $\underset{\sim}{C}(r)$. The program uses either of two sets of matching functions as des-cribed next.

If the elements of $\underset{\sim}{V}(r)$ all go to zero at large r faster than r^{-2}, then beyond some large value r' of r the quantity $\underset{\sim}{\ell}^2 r^{-2}$ will dominate $\underset{\sim}{V}(r)$

to such an extent that $\underline{V}(r)$ can be dropped from (3). This reduces (2) to the N^2 uncoupled second order differential equations

$$\frac{d^2}{dr^2} f_{ij}(r) - \frac{\ell_i(\ell_i+1)}{r^2} f_{ij}(r) + k_i^2 f_{ij}(r) = 0 \tag{42}$$

with $1 \le i \le N$, $1 \le j \le N$, and $r > r'$. The solution to (42) is just a linear combination of regular and irregular Ricatti-Bessel functions $j_{\ell_i}(k_i r)$ and $n_{\ell_i}(k_i r)$, respectively, for $i = 1,2,\ldots,N$, where the Ricatti-Bessel functions are defined in terms of spherical Bessel functions of the first kind and second kind[40] by

$$j_\ell(x) = x\, j_\ell(x) \tag{43}$$

$$n_\ell(x) = x\, n_\ell(x) \tag{44}$$

(Reference 40 uses $y_n(z)$ in denoting the spherical Bessel function of the second kind.) For large r[41]

$$k_i r j_{\ell_i}(k_i r) \underset{r\to\infty}{\sim} \sin(k_i r - \tfrac{1}{2}\ell_i\pi) \tag{45}$$

and

$$k_i r n_{\ell_i}(k_i r) \underset{r\to\infty}{\sim} -\cos(k_i r - \tfrac{1}{2}\ell_i\pi) \tag{46}$$

Comparing (6) and (7) with (45) and (46) yields

$$S_{ij}(r) = k_i^{-\frac{1}{2}}\delta_{ij} j_{\ell_i}(k_i r) \tag{47}$$

and

$$C_{ij}(r) = -k_i^{-\frac{1}{2}}\delta_{ij} n_{\ell_i}(k_i r) \tag{48}$$

as one set of matching functions.

However, if some elements of $\underset{\sim}{V}(r)$ go to zero at large r as r^{-2}, r^{-3}, or r^{-4} (as is the case for electron-molecule scattering with realistic effective potentials), then the r' for which (42) is valid is generally very large and the use of (47) and (48) requires numerical integration of (2) over a very large region which is expensive. Therefore, Burke and Schey[42] and Burke, McVicar, and Smith[43] (BMS) have derived asymptotic solutions to (2) computed from the long-range part of the potential and a computer program for using the BMS solutions as matching functions has been described in detail by Norcross.[44] For open channels, the matching functions are written in terms of asymptotic series as

$$S_{ij}(r) = k_i^{-\frac{1}{2}}[\alpha_{ij}(r) \sin \phi_i(r) + \beta_{ij}(r) \cos \phi_i(r)] \tag{49}$$

and

$$C_{ij}(r) = k_i^{-\frac{1}{2}}[\alpha_{ij}(r) \cos \phi_i(r) - \beta_{ij}(r) \sin \phi_i(r)] \tag{50}$$

where

$$\phi_i(r) = k_i r - \tfrac{1}{2} \ell_i \pi \tag{51}$$

and

$$\gamma_{ij}(r) = \sum_{p=0}^{P_i} \gamma_{ij}^p \, r^{-p} \tag{52}$$

for $\gamma = \alpha$ or β where P_i is determined as described below and

$$\alpha_{ij}^0 = \delta_{ij} \qquad \text{and} \qquad \beta_{ij}^0 = 0 \tag{53}$$

The remaining coefficients γ_{ij} are determined by the following procedure. The function $\underset{\sim}{V}(r)$ in (2) and (3) is replaced by its long range form

$$V_{ij}(r) \underset{r \to \infty}{\sim} \sum_{m=1}^{M} c_{ij}^{(m)} r^{-m-1} \tag{54}$$

and substituting the $\underset{\sim}{S}(r)$ of (49) or the $\underset{\sim}{C}(r)$ of (50) into (2) for $\underset{\sim}{f}(r)$ yields recursion relations among the coefficients of like powers of r^{-1}. The recursion relations have two different forms, one for when $k_i = k_j$ and the other for when $k_i \neq k_j$. The latter form depends on $(k_i^2 - k_j^2)^{-1}$ and becomes numerically unstable as k_i^2 approaches k_j^2 so a test is made using the input parameter n_1 to decide which form to use. Only if $|k_i^2 - k_j^2| > n_1 k_i^2$ is the latter form used. As compared to Norcross' version[44] we made one additional change in the recursion relation for the case of degenerate energies, i.e., if $|k_i^2 - k_j^2| < n_1 k_i^2$ we approximated both k_i and k_j by their arithmetic mean rather than replacing them both by k_i as Norcross did. From these relations the remaining values of γ_{ij}^p can be calculated. It is well known that the best approximation which can be obtained from an asymptotic series is obtained by summing up to the smallest term and retaining half that term. In this spirit we replace (52) by

$$\gamma_{ij}(r) = \sum_{p=0}^{P_i} \gamma_{ij}^p r^{-p} - \tfrac{1}{2}\gamma_{ij}^{P_i} r^{-P_i} \tag{55}$$

(This is another change from the procedure used by Norcross.) The value of P_i is determined for each channel $i = 1,2,\ldots,N$ using the input parameter τ as follows. For a given p and i, the maximum absolute value of $\alpha_{ij}^p r^{-p}$ or $\beta_{ij}^p r^{-p}$ is set equal to τ and solved for r. The solution is called $r(i,p)$. This is done for each $p \geq 1$ in increasing order of p until $p = p'$ where p' is the smallest p for which $r(i,p+1) > r(i,p)$ or until p is the maximum value P_{max} allowed by the program. If the former, then P_i is set equal to p' and $r(i,P_i)$ is the minimum value of r for which (52) may be used with the smallest term being less than or equal to τ for the ith channel.

(It is interesting to note that Norcross[44] always uses $P_i \geq 4$ in his program.)

If $r(i,p) < r(i,p-1)$ for all $p \leq P_{max}$ then P_i is set equal to P_{max} and $r(i,P_i)$ is set to the value of r for which the maximum absolute value of $\alpha_{ij}^{P_{max}} r^{-P_{max}}$ or $\beta_{ij}^{P_{max}} r^{-P_{max}}$ is equal to 10^{-14}.

An estimate of where (5) with (49) and (50) becomes valid is then made as the maximum of the $r(i,P_i)$ values for the various channels i and the value of r for which (54) is valid.

The above method can also be generalized to include closed channels.[44]

The choice between matching to Ricatti-Bessel functions or BMS functions is controlled by an input variable MMAX. Assuming one has reached an r for which the asymptotic form (5) is valid, the program matches $\underset{\sim}{f}(r)$ to either matching functions (47) and (48) or (49) and (50) at two grid points r_n and r_{n+1}. After rearranging terms, this yields

$$(\underset{\sim}{C}_{n+1} - \underset{\sim}{S}_{n+1}\underset{\sim}{S}_n^{-1}\underset{\sim}{C}_n)\underset{\sim}{Q} = \underset{\sim}{f}_{n+1} - \underset{\sim}{S}_{n+1}\underset{\sim}{S}_n^{-1}\underset{\sim}{f}_n \tag{56}$$

which is solved for the approximate Q, called $\underset{\sim}{Q}_n$, and two approximate $\underset{\sim}{P}$ matrices, called $\underset{\sim}{P}_n$ and $\underset{\sim}{P}_{n+1}$, are then found using

$$\underset{\sim}{P}_k = \underset{\sim}{S}_k^{-1}(\underset{\sim}{f}_k - \underset{\sim}{C}_k\underset{\sim}{Q}_n) \qquad k = n, n+1 \tag{57}$$

If

$$\text{norm}(\underset{\sim}{P}_{n+1} - \underset{\sim}{P}_n) < STEST \tag{58}$$

where STEST is an input variable and the norm of a matrix is defined as

$$\text{norm} \underset{\sim}{A} = \frac{1}{N} \left(\sum_{i=1}^{N} \sum_{j=1}^{N} |A_{ij}|^2 \right)^{\frac{1}{2}} \tag{59}$$

then $\underset{\sim}{R}$ is calculated from $\underset{\sim}{P}_n$ and $\underset{\sim}{Q}_n$ as

$$\underset{\sim}{P}_n^T \underset{\sim}{R} = \underset{\sim}{Q}_n^T \qquad\qquad (60)$$

In deriving (60) we use the fact[45] that $\underset{\sim}{R} = \underset{\sim}{R}^T$.

<u>C. R matrix propagation method.</u> The version of the R matrix propagation method we use is our own adaptation[25,26,28,29] to inelastic scattering problems of the method Light and Walker[24] developed for reactive scattering problems. The R matrix propagation method has also been adapted to inelastic scattering problems by Stechel <u>et al.</u>,[27] but their procedures differ from ours in several respects.

In the R matrix propagation method the range of the translation coordinate r is subdivided into many sectors. In sector (i) the total wave function $\Psi(\vec{z},r)$ is expanded in a "primitive" basis of N orthonormal functions $X_n(\vec{z})$, here assumed to be the same in every sector, and a set of N close coupling equations in the primitive representation is derived for each of the 2N linearly independent translational wave functions $\underline{f}(r)$. We use the convention that $\underline{A}$ denotes a column vector with component A_i and $\underset{\sim}{A}$ denotes a matrix each of whose columns is an $\underline{A}$. These equations have the form (2). An "adiabatic" basis for sector (i) is found by diagonalizing $\underset{\sim}{D}_C^{(i)}$, the interaction matrix at the center of sector (i). The wave function is expanded in P of the adiabatic-basis functions $Z_n^{(i)}(\vec{z})$, and a set of P close coupling equations in the adiabatic representation is obtained for each of the 2P linearly independent translational wave functions $\underline{g}^{(i)}(r)$. The basis functions $X_n(\vec{z})$ and $Z_n^{(i)}(\vec{z})$ are related by a transformation matrix $\underset{\sim}{T}^{(i)}$. Similarly, $\underset{\sim}{T}^{(i)}$ is used to relate the translational wave functions $f_n(r)$ and $g_n^{(i)}(r)$ to each other. The adiabatic-representation translational

wave functions and their derivatives are propagated through sector (i) by a propagation matrix $\underset{\sim}{P}^{(i)}(E)$. Then the requirement that $\Psi(\vec{z},r)$ and $\Psi'(\vec{z},r)$, where an apostrophe denotes a derivative, be continuous at the boundary between sectors (i) and (i+1) is used to obtain sector matching conditions. To express the continuity between the wave function in the adiabatic representation in sector (i) and the wave function in the adiabatic representation in sector (i+1), the transformation matrix $\underset{\sim}{T}^{(i)}$ is used to transform from the adiabatic representation to the primitive representation in sector (i), and the matrix $\underset{\sim}{T}^{(i+1)^{T}}$ is used to transform from the primitive representation in sector (i+1) to the adiabatic representation in sector (i+1). The combined effects of these two steps is expressed in terms of a transformation matrix $\underset{\sim}{T}(i,i+1)$ which relates the adiabatic representation in sector (i) to that in sector (i+1). The propagator $\underset{\sim}{P}^{(i+1)}$ is then used to propagate the adiabatic-representation translational wave functions $\underset{\sim}{g}^{(i+1)}(r)$ and their derivatives through sector (i+1), $\underset{\sim}{T}(i+1,i+2)$ is used to transform to the adiabatic representation in sector (i+2), and so forth. In this way the translational wave functions and their derivatives could be propagated from the strong-interaction region through each sector and across sector boundaries. Rather than propagate the wave function and its derivative though, we propagate the global R matrix $\underset{\sim}{R}^{(i)}$, which relates the matrices $\underset{\sim}{g}^{(1)}[r_{L}^{(1)}]$ and $\underset{\sim}{g}^{(i)}[r_{R}^{(1)}]$ of 2P linearly independent wave functions at the left side of the first sector and at the right side of sector (i) to their derivatives at these locations. In each sector this global R matrix $\underset{\sim}{R}^{(i)}$ is computed from $\underset{\sim}{R}^{(i-1)}$ and the sector R matrix $\underset{\sim}{r}^{(i)}$, which relates the adiabatic-basis translational wave functions at the right sides of sectors (i-1) and (i) to their derivatives at these locations. In turn the sector R matrix is obtained from the

transformation matrix $T(i-1,i)$ and the propagator $P^{(i)}$ In this way we propagate the global R matrix from sector to sector until we obtain the global R matrix in the last sector. This relates the matrix of linearly independent physical wave functions in the strong-interaction or small-r region and in the large-r asymptotic region to the matrix of their derivatives. Small-r and large-r boundary conditions on the wave functions and their derivatives are then imposed in such a way that the reactance matrix R can be obtained in terms of known quantities.

The sector-by-sector propagation is essentially the same as in reference 24. The $2P \times 2P$ sector propagator $P^{(i)}$ is defined by

$$G_L^{(i)} = P^{(i)} G_R^{(i)} \tag{61}$$

where each column of the $2P \times 2P$ matrix $G^{(i)}(r)$ is defined by

$$G^{(i)}(r) = \begin{bmatrix} g^{(i)}(r) \\ g'^{(i)}(r) \end{bmatrix} \tag{62}$$

where $g^{(i)}(r)$ is one of the 2P linearly independent P-component solution vectors. Here and in the following equations subscripts R, L, and C denote quantities evaluated at the right-hand and left-hand sector boundaries and the center of the sector, respectively, e.g., $g_L^{(i)} = g^{(i)}[r_L^{(i)}]$. The matrix $P^{(i)}$ is partitioned into four $P \times P$ submatrices

$$P^{(i)} = \begin{bmatrix} P_1^{(i)} & P_2^{(i)} \\ P_3^{(i)} & P_4^{(i)} \end{bmatrix} \tag{63}$$

$\underset{\sim}{P}^{(i)}$ is computed by diagonalizing $\underset{\sim C}{D}^{(i)}$ and assuming that the eigenvalues of $\underset{\sim}{D}$ are independent of r within a sector.[24] This assumption would be true if the interaction potential were constant throughout the sector. The sector R matrix $\underset{\sim}{r}^{(i)}$ is the matrix which relates the wave functions $\underset{\sim R}{g}^{(i-1)}$ and $\underset{\sim R}{g}^{(i)}$ evaluated at the right-hand side of sectors (i-1) and (i) to their derivatives. It is defined by

$$\underset{\sim}{r}^{(i)} = \begin{pmatrix} \underset{\sim 1}{r}^{(i)} & \underset{\sim 2}{r}^{(i)} \\ \underset{\sim 3}{r}^{(i)} & \underset{\sim 4}{r}^{(i)} \end{pmatrix} \tag{64}$$

where

$$\begin{bmatrix} \underset{\sim R}{g}^{(i-1)} \\ \underset{\sim R}{g}^{(i)} \end{bmatrix} = \begin{bmatrix} \underset{\sim 1}{r}^{(i)} & \underset{\sim 2}{r}^{(i)} \\ \underset{\sim 3}{r}^{(i)} & \underset{\sim 4}{r}^{(i)} \end{bmatrix} \begin{bmatrix} \underset{R}{g}'^{(i-1)} \\ -\underset{\sim R}{g}'^{(i)} \end{bmatrix} \tag{65}$$

The equations for the sector R matrices are

$$\underset{\sim 1}{r}^{(i)} = \underset{\sim}{T}(i-1,i)\, \underset{\sim 1}{P}^{(i)}\, \underset{\sim 3}{P}^{(i)^{-1}}\, \underset{\sim}{T}(i-1,i)^{-1} \tag{66}$$

$$\underset{\sim 2}{r}^{(i)} = \underset{\sim}{T}(i-1,i)\, \underset{\sim 3}{P}^{(i)^{-1}} \tag{67}$$

$$\underset{\sim 3}{r}^{(i)} = \underset{\sim 3}{P}^{(i)^{-1}}\, \underset{\sim}{T}(i-1,i)^{-1} \tag{68}$$

$$\underset{\sim 4}{r}^{(i)} = \underset{\sim 3}{P}^{(i)^{-1}}\, \underset{\sim 4}{P}^{(i)} \tag{69}$$

The global R matrix $\underset{\sim}{R}^{(i)}$ spanning the configuration space from the first sector to sector (i) is defined by

$$\underset{\sim}{R}^{(i)} = \begin{pmatrix} \underset{\sim 1}{R}^{(i)} & \underset{\sim 2}{R}^{(i)} \\ \underset{\sim 3}{R}^{(i)} & \underset{\sim 4}{R}^{(i)} \end{pmatrix} \tag{70}$$

$$
\begin{bmatrix} g_L^{(1)} \\ g_R^{(i)} \end{bmatrix} = \begin{bmatrix} R_1^{(i)} & R_2^{(i)} \\ R_3^{(i)} & R_4^{(i)} \end{bmatrix} \begin{bmatrix} g_L^{'(1)} \\ -g_R^{'(i)} \end{bmatrix}
\tag{71}
$$

$R^{(i)}$ is propagated from the first sector to the asymptotic region in which the scattering matrix elements and other physically interesting quantites are calculated.

A real symmetric global R matrix $R^{(i)}$ insures a symmetric reactance matrix and hence a unitary scattering matrix. If $R^{(i-1)}$ and $r^{(i)}$ are symmetric matrices, then $R^{(i)}$ is symmetric. But

$$
R_1^{(1)} = P_1^{(1)} P_3^{(1)-1}
\tag{72}
$$

$$
R_2^{(1)} = R_3^{(1)} = P_3^{(1)^{-1}}
\tag{73}
$$

$$
R_4^{(1)} = P_3^{(1)^{-1}} P_4^{(1)}
\tag{74}
$$

so that $R^{(1)}$ is symmetric. The sector R matrix $r^{(i)}$ is symmetric if the transformation matrix $T(i-1,i)$ is orthogonal. The transformation matrix is orthogonal if and only if the number P of propagated adiabatic channels equals the number N of primitive basis functions. Thus the scattering matrix is automatically unitary if and only if $P = N$.[29] It has been suggested[24,27] that in order to insure a symmetric $R^{(i)}$ the matrix $T(i-1,i)^{-1}$ be replaced by $T(i-1,i)^{T}$. This also may afford computational advantages. When $P = N$, this is not an approximation. However, for contracted basis sets, i.e., when $P < N$, $T(i-1,i)$ is not orthogonal. For contracted bases replacing $T(i-1,i)^{-1}$ by $T(i-1,i)^{T}$ in each sector changes the results unless of course the calculations are converged with respect to P and N. For

unconverged calculations we generally obtained more accurate answers by using the inverse and symmetrizing the reactance matrix than by using the transpose. For this reason we have used the inverse for our final production runs; however, the choice in general is still somewhat ambiguous. Both choices should converge to the correct limit as P and N are increased. Since, when P ≠ N, using the inverse does not automatically produce a symmetric reactance matrix and hence a unitary scattering matrix, we symmetrized our reactance matrix by taking an arithmetic mean with its transpose.

We obtain the reactance matrix $\underset{\sim}{R}$ from the global R matrix equation by imposing asymptotic scattering boundary conditions on the adiabatic wave functions in the following way. The P × 2P solution matrix $\underset{\sim}{g}^{(c)}(r)$ in the adiabatic representation in sector (c) consists of 2P linearly independent vectors of order P. Because the solutions are linearly independent, the P × P matrix $\underset{\sim}{\phi}^{(c)}(r)$, each column of which is a scattering vector, i.e., one of P linearly independent linear combinations of the former set of vectors which satisfies correct small-r and large-r boundary conditions, satisfies the global R matrix equations for sector (c). Using (71), one can show that

$$
\begin{bmatrix} \underset{\sim}{\phi}_L^{(1)} \\ \\ \underset{\sim}{\phi}_R^{(c)} \end{bmatrix} = \begin{bmatrix} \underset{\sim}{R}_1^{(c)} & \underset{\sim}{R}_2^{(c)} \\ \\ \underset{\sim}{R}_3^{(c)} & \underset{\sim}{R}_4^{(c)} \end{bmatrix} \begin{bmatrix} \underset{\sim}{\phi}_L'^{(1)} \\ \\ -\underset{\sim}{\phi}_R'^{(c)} \end{bmatrix} \tag{75}
$$

where $\underset{\sim}{\phi}_{mn}^{(i)}(r)$ is the m-th component of the n-th scattering vector and the P × P matrices $\underset{\sim}{\phi}_L^{(1)}$ and $\underset{\sim}{\phi}_R^{(c)}$ consist of the P linearly independent scattering vectors evaluated at the left side of the first sector and the right side of sector (c), respectively. $\underset{\sim}{R}_1^{(c)}$, $\underset{\sim}{R}_2^{(c)}$, $\underset{\sim}{R}_3^{(c)}$, and $\underset{\sim}{R}_4^{(c)}$ are the P × P submatrices of the 2P × 2P global R matrix $\underset{\sim}{R}^{(c)}$ which spans

the configuration space from the left side of the first sector to the right side of sector (c). To obtain R we substitute scattering boundary conditions for $\phi_{\sim L}^{(1)}$ and $\phi_{\sim R}^{(c)}$ and their derivatives into (75).

To use (75) to extract the reactance matrix we first require expressions for $\phi_{\sim L}^{(1)}$ and $\phi_{\sim L}'^{(1)}$. Since only P of the 2P linearly independent solutions $g^{(i)}(r)$ satisfy physical boundary conditions in the strong interaction region, we include in our analysis of (75) only the P functions which provide physical solutions in the small-r region.

For channels which are closed at $r = r_L^{(1)}$ we use the following exponential functions for the wave functions

$$\left(\phi_{\sim L}^{(1)}\right)_{mn} = d_{mn} \exp\left[\left|\kappa_m\left(r_L^{(1)}\right)\right| r_L^{(1)}\right] \qquad \text{m closed} \qquad (76)$$

$$\left(\phi_{\sim L}'^{(1)}\right)_{mn} = d_{mn}\left|\kappa_m\left(r_L^{(1)}\right)\right| \exp\left[\left|\kappa_m\left(r_L^{(1)}\right)\right| r_L^{(1)}\right] \qquad (77)$$

where $\kappa_m\left(r_L^{(1)}\right)$ is the local wave number in the m-th channel calculated at $r_L^{(1)}$ and the coefficients d_{mn} are unknowns. All channels with nonzero orbital angular momentum are closed at the origin. For channels which are open in the small-r region the boundary conditions on the wave functions can be written

$$\left(\phi_{\sim L}^{(1)}\right)_{mn} = e_{mn} \sin\left[\left|\kappa_m\left(r_L^{(1)}\right)\right| r_L^{(1)}\right] \qquad \text{m open} \qquad (78)$$

$$\left(\phi_{\sim L}'^{(1)}\right)_{mn} = e_{mn}\left|\kappa_m\left(r_L^{(1)}\right)\right| \cos\left[\left|\kappa_m\left(r_L^{(1)}\right)\right| r_L^{(1)}\right] \qquad (79)$$

where the coefficients e_{mn} are not known. To facilitate the calculations we cast (76)-(77) and (78)-(79) in the same form, so that for both open and closed channels the boundary conditions we use at $r = r_L^{(1)}$ are

$$\underset{\sim}{\Phi}_L^{(1)} = \underset{\sim}{C} \qquad (80)$$

$$\underset{\sim}{\Phi'}_L^{(1)} = \underset{\sim}{x}^{(1)} \underset{\sim}{C} \qquad (81)$$

where

$$x_{mn}^{(1)}(E) = \delta_{mn} \begin{cases} |\kappa_m(r_L^{(1)})| \cos\left[|\kappa_m(r_L^{(1)})|r_L^{(1)}\right] \Big/ \sin\left[|\kappa_m(r_L^{(1)})|r_L^{(1)}\right] & m \text{ open} \\[3mm] |\kappa_m(r_L^{(1)})| & m \text{ closed} \end{cases} \qquad (82)$$

and the coefficients C_{mn} are unknowns.

At large r the close coupling equation becomes

$$\left\{ \frac{d^2}{dr^2} - [\lambda_{mm}^{(c)}(r)]^2 \right\} g_m^{(c)}(r) = 0 \qquad (83)$$

where $[\underset{\sim}{\lambda}^{(c)}(r)]^2$ is a diagonal matrix, the elements of which at the center $r = r_C^{(c)}$ of sector (c) are the eigenvalues of the interaction matrix $\underset{\sim}{D}_C^{(c)}$.

For the discussion of the large-r boundary conditions we find it useful to introduce the following notation. We define the asymptotic interaction matrix $\underset{\sim}{D}^a$ by

$$\lim_{r \to \infty} \underset{\sim}{D}(r) = \underset{\sim}{D}^a \qquad (84)$$

We denote the diagonal matrix of the eigenvalues of $\underset{\sim}{D}^a$ by $[\underset{\sim}{\lambda}^a]^2$, where the square of the diagonal matrix of the asymptotic channel wave numbers is given by

$$[\underset{\sim}{k}]^2 = -[\underset{\sim}{\lambda}^a]^2 \qquad (85)$$

Once the real potential has vanished and the r dependence of $\underset{\sim}{D}(r)$ is dominated

by the centrifugal potential, the eigenvalues of the interaction matrix in sector (c) are given by

$$[\lambda_{mm}^{(c)}(r)]^2 = \lambda_{mm}^{a^2} + \frac{\ell_m(\ell_m+1)\hbar^2}{2\mu r^2} \tag{86}$$

In the large-r region P^0 of the P channels are open, and the channels are ordered in such a way that channel m corresponds to an open channel for $1 \leq m \leq P^0$ and to a closed channel for $P^0 < m \leq P$. In the large-r asymptotic region the boundary conditions for closed-channel wave functions are expressed as linear combinations of exponentially increasing and decreasing functions

$$\left[\underset{\sim}{\phi}_R^{(c)}\right]_{mn} = \delta_{mn} b \exp\left[|k_m| r_R^{(c)}\right] + a_{mn}^{(c)} \exp\left[-|k_m| r_R^{(c)}\right] \quad P^0 < m \leq P \tag{87}$$

$$\left[\underset{\sim}{\phi}_R^{\prime(c)}\right]_{mn} = \delta_{mn} b |k_m| \exp\left[|k_m| r_R^{(c)}\right] - a_{mn}^{(c)} |k_m| \exp\left[-|k_m| r_R^{(c)}\right] \tag{88}$$

where b is an unknown coefficient of the exponentially increasing component of the $P - P^0$ closed-channel wave functions.

For the large-r boundary conditions on the open-channel wave functions in sector (c) we use

$$\left[\underset{\sim}{\phi}_R^{(c)}\right]_{mn} = \delta_{mn} j_{\ell_m}\left(k_m r_R^{(c)}\right) - a_{mn}^{(c)} n_{\ell_m}\left(k_m r_R^{(c)}\right) \quad 1 \leq m \leq P^0 \tag{89}$$

$$\left[\underset{\sim}{\phi}_R^{\prime(c)}\right]_{mn} = k_m\left[\delta_{mn} j'_{\ell_m}\left(k_m r_R^{(c)}\right) - a_{mn}^{(c)} n'_{\ell_m}\left(k_m r_R^{(c)}\right)\right] \quad 1 \leq m \leq P^0 \tag{90}$$

where the Ricatti-Bessel functions are defined in terms of spherical Bessel functions by (43) and (44). The elements of the reactance matrix are related to the open-channel amplitudes $a_{mn}^{(c)}$ by

$$R_{mn} = |k_m|^{\frac{1}{2}} a_{mn}^{(c)} |k_n|^{-\frac{1}{2}} \qquad \begin{array}{l} 1 \leq m \leq P^0 \\ 1 \leq n \leq P^0 \end{array} \qquad (91)$$

The large-r boundary conditions on the adiabatic wave functions can be written concisely in matrix notation as

$$\underset{\sim R}{\Phi}^{(c)} = \underset{\sim}{B}^{(c)} \underset{\sim}{\Delta} + \underset{\sim}{F}^{(c)} \underset{\sim}{a}^{(c)} \qquad (92)$$

$$\underset{\sim R}{\Phi}'^{(c)} = \underset{\sim}{G}^{(c)} \underset{\sim}{\Delta} - \underset{\sim}{H}^{(c)} \underset{\sim}{a}^{(c)} \qquad (93)$$

where

$$B_{mn}^{(c)} = \delta_{mn} \begin{cases} j_{\ell_m}\left(k_m r_R^{(c)}\right) & 1 \leq m \leq P^0 \\[2ex] \exp\left(|k_m| r_R^{(c)}\right) & P^0 < m \leq P \end{cases} \qquad (94)$$

$$F_{mn}^{(c)} = \delta_{mn} \begin{cases} -n_{\ell_m}\left(k_m r_R^{(c)}\right) & 1 \leq m \leq P^0 \\[2ex] \exp\left(-|k_m| r_R^{(c)}\right) & P^0 < m \leq P \end{cases} \qquad (95)$$

$$G_{mn}^{(c)} = \delta_{mn} \begin{cases} k_m j'_{\ell_m}\left(k_m r_R^{(c)}\right) & 1 \leq m \leq P^0 \\[2ex] |k_m| \exp\left(|k_m| r_R^{(c)}\right) & P^0 < m \leq P \end{cases} \qquad (96)$$

$$H_{mn}^{(c)} = \delta_{mn} \begin{cases} k_m n'_{\ell_m}\left(k_m r_R^{(c)}\right) & 1 \leq m \leq P^0 \\[2ex] |k_m| \exp\left(-|k_m| r_R^{(c)}\right) & P^0 < m \leq P \end{cases} \qquad (97)$$

$$\Delta_{mn} = \delta_{mn} \begin{cases} 1 & 1 \leq m \leq P^0 \\[2ex] b & P^0 < m \leq P \end{cases} \qquad (98)$$

and

$$\underset{\sim}{R} = [\underset{\sim}{k}^{00}]^{\frac{1}{2}} \underset{\sim}{a}^{(c)00}(E) [\underset{\sim}{k}^{00}]^{-\frac{1}{2}} \qquad (99)$$

where the superscript 00 is used to denote the $P^0 \times P^0$ submatrix which links open channels to open channels.

Substituting (80), (81), (92), and (93) into (75) yields

$$
\begin{bmatrix} \underset{\sim}{C} \\ \underset{\sim}{B}^{(c)}\underset{\sim}{\Delta} + \underset{\sim}{F}^{(c)}\underset{\sim}{a}^{(c)} \end{bmatrix} = \begin{bmatrix} \underset{\sim 1}{R}^{(c)} & \underset{\sim 2}{R}^{(c)} \\ \underset{\sim 3}{R}^{(c)} & \underset{\sim 4}{R}^{(c)} \end{bmatrix} \begin{bmatrix} \underset{\sim}{x}^{(1)}\underset{\sim}{C} \\ -\underset{\sim}{G}^{(c)}\underset{\sim}{\Delta} + \underset{\sim}{H}^{(c)}\underset{\sim}{a}^{(c)} \end{bmatrix} \tag{100}
$$

Solving for the $P \times P$ matrix $\underset{\sim}{a}^{(c)}$ gives

$$
\underset{\sim}{a}^{(c)} = [-\underset{\sim}{F}^{(c)} + \underset{\sim}{M}^{(c)}\underset{\sim}{H}^{(c)}]^{-1} [\underset{\sim}{B}^{(c)} + \underset{\sim}{M}^{(c)}\underset{\sim}{G}^{(c)}]\underset{\sim}{\Delta} \tag{101}
$$

where

$$
\underset{\sim}{M}^{(c)} = \underset{\sim 4}{R}^{(c)} + \underset{\sim 3}{R}^{(c)}\underset{\sim}{x}^{(1)} [\underset{\sim}{1} - \underset{\sim 1}{R}^{(c)}\underset{\sim}{x}^{(1)}]^{-1} \underset{\sim 2}{R}^{(c)} \tag{102}
$$

Therefore, the matrix $\underset{\sim}{a}^{(c)}$ from which we calculate $\underset{\sim}{R}$ is independent of $\underset{\sim}{C}$, the matrix of coefficients giving the appropriate linear combinations of functions at $r = r_L^{(1)}$. Further $\underset{\sim}{a}^{(c)00}$, the only portion of $\underset{\sim}{a}^{(c)}$ which we used to obtain $\underset{\sim}{R}$, is independent of the last $P - P^0$ columns of $\underset{\sim}{\Delta}$ and consequently is independent of b, the coefficient of the exponentially increasing component of the closed-channel wave functions in sector (c). In the computer code b is set equal to zero and $B_{mn}^{(c)}$ and $G_{mn}^{(c)}$ are set equal to zero for $P^0 < m \leq P$.

When all channels are closed in the small-r region one finds[29]

$$
\underset{\sim 2}{R}^{(1)} \overset{\sim}{=} \underset{\sim}{0} \tag{103}
$$

and

$$
\underset{\sim 3}{R}^{(1)} \overset{\sim}{=} \underset{\sim}{0} \tag{104}
$$

if sector (1) is located deep enough into the classically forbidden region. In such a case $R_2^{(i)}$ and $R_3^{(i)}$ remain small in all subsequent sectors and in particular

$$R_2^{(c)} \overset{\sim}{=} \underset{\sim}{0} \qquad (105)$$

and

$$R_3^{(c)} \overset{\sim}{=} \underset{\sim}{0} \qquad (106)$$

In such a case (102) becomes

$$\underset{\sim}{M}^{(c)} = R_4^{(c)} \qquad (107)$$

Consequently the determination of the reactance matrix from (99) and (101) becomes independent of $R_1^{(c)}$, $R_2^{(c)}$, and $R_3^{(c)}$. Furthermore the propagation equation[24] for $R_4^{(i)}$ is independent of $R_1^{(i-1)}$, $R_2^{(i-1)}$, and $R_3^{(i-1)}$. Thus when all channels are closed at small r we propagate only $R_4^{(i)}$ to save computer time.

Although the asymptotic analysis just presented allows for the inclusion of channels which are closed for large r, the presence of strongly closed channels in the asymptotic analysis sometimes gives rise to numerical difficulties. To eliminate these, the program has two options which can be used to simplify the asymptotic analysis. One option is used to eliminate closed channels from the propagation at large r. We have shown that if all elements of the last row and column, corresponding to the most strongly closed channel of $r_2^{(i)}$ are small, the last channel is uncoupled from the remaining channels and may be dropped from propagation without degrading the accuracy of the results.[29] We have implemented this option in the following way. In the large-r region, if the number P of channels propagated

in sector (i) is greater than the number of open channels, the program

checks whether

$$\left| \left(r_2^{(i)} \right)_{iP} \right| \leq \text{EPSRED} \qquad\qquad i = 1,2,\ldots,P \qquad\qquad (108)$$

and

$$\left| \left(r_2^{(i)} \right)_{Pi} \right| \leq \text{EPSRED} \qquad\qquad i = 1,2,\ldots,P \qquad\qquad (109)$$

In these equations, channel P is the most strongly closed propagated channel,

and EPSRED is an input variable. If this criterion is satisfied, channel

P is dropped from propagation and only the remaining P − 1 channels are

propagated in sector (i+1). As we have implemented this option, at most

one channel is dropped from propagation in any sector. We have also im-

plemented a second method to avoid numerical difficulties associated with

including in the asymptotic analysis channels which are strongly closed

for large r. In this method we eliminate those closed channels from the

asymptotic analysis even if they have been included in the propagation.

The option as we have coded it in our programs is appropriate when the

asymptotic analysis is based on only the R_4 part of the global R matrix.

The procedure we use for deciding whether a closed channel can be eliminated

from the asymptotic analysis is the following. In the large-r region,

if the number of channels propagated is greater than the number P^0 of

channels open asymptotically, the program compares the off-diagonal elements

of $R_4^{(i)}$ for channel P, the most strongly closed propagated channel, to

EPSDR, an input variable. If

$$\left| \left(R_4^{(i)} \right)_{iP} \right| \leq \text{EPSDR} \qquad\qquad i = 1,2,\ldots,(P-1) \qquad\qquad (110)$$

and

$$\left| \left(R_4^{(i)} \right)_{Pi} \right| \leq \text{EPSDR} \qquad\qquad i = 1, 2, \ldots, (P-1) \qquad\qquad (111)$$

then the number of channels P' to be included in the asymptotic analysis is set to $P' = P - 1$. This procedure is repeated for subsequent closed channels until an element for $\underset{\sim}{R}_4^{(i)}$ for some closed channel fails the test of (110) and (111) or until all closed channels have been eliminated and $P' = P^0$.

The stepsize $h^{(i)}$ for sector (i) is defined by

$$h^{(i)} = r_R^{(i)} - r_L^{(i)} \qquad\qquad (112)$$

We set $r_L^{(1)}$, $h^{(1)}$, and $h^{(2)}$ by input variables, and we check that they are sufficiently small that the calculations are converged with respect to them. If one or more channels is open at the origin, then $r_L^{(1)}$ should be close to zero. The determination of the stepsizes for subsequent sectors is crucial to the efficiency of the method. A reasonable stepsize criterion can be obtained for $i > 2$ by requiring that the effect of the lowest-order neglected term in the propagator[46] be small. We simplified this argument to make it computationally more convenient and arrived at the following algorithm which is used by the code for $i \geq 2$:

$$h^{(i+1)} = \min \left\{ \begin{array}{l} \varepsilon^{(i)} \left[\dfrac{1}{m} \sum_{j=1}^{m} \left(\dfrac{dD_{jj}^{(i)}}{dr} \right)^2 \right]^{-1/6} \\[20pt] h_{max} \end{array} \right. \qquad\qquad (113)$$

where h_{max} is an input variable, m is the largest value of P to be used in a given run, and the derivative is estimated by a backward difference. The error-control parameter is determined as follows. The range of r is divided into three subranges in each of which $\varepsilon^{(i)}$ is constant, i.e., independent of (i). The values of $\varepsilon^{(i)}$ for a given run are set by input variables, EPSA, EPSB, and EPSC. The calculations must be tested for convergence with respect to decreasing all three values. For most applications it has been sufficient to set all values of $\varepsilon^{(i)}$ equal to each other.

One of the advantages of the piecewise analytic method and the R matrix propagation method is that if calculations are required at several energies with the same potential, calculations at the second and subsequent energy can be performed more rapidly by saving certain information generated in the first calculation. We have not made much use of this feature for electron-molecule scattering because we use energy-dependent potentials to include exchange effects (see, e.g., references 10, 11, and 25 and references therein). However, even for this type of problem, this feature might be useful at higher energies or for large orbital angular momenta where exchange effects can sometimes be neglected. For atom-molecule scattering this feature is very useful, and the dramatic reduction in execution time of R matrix propagation calculations for subsequent energies as compared with the calculation at the first energy is discussed in section V.

Because we are interested in making close coupling calculations more efficient, we also want to demonstrate the success we have had in reducing the size of the close coupling calculations by using adiabatic basis functions in the context of R matrix propagation calculations. We have found for

electron-molecule and atom-molecule scattering calculations that we could generally obtain similar or better accuracy with an adiabatic basis of the same or even significantly smaller propagation dimension P than with a conventional $N = P$ basis. As discussed above we construct a P-function adiabatic basis for sector (i) by diagonalizing the $N \times N$ interaction matrix at the center of sector (i) and taking its P lowest-energy eigenfunctions.

D. Piecewise analytic method. The piecewise analytic method of Gordon is described elsewhere.[12,13] We have used two different programs for calculations with this method. One was obtained originally from Quantum Chemistry Program Exchange[35] (QCPE) and was modified in various ways by two of us (M.A.B. and D.G.T.). The second program was written by Wagner.[14]

E. Integral equations algorithm. For our calculations using the integral equations algorithm we used the computer code of Morrison, Lane, and Collins, which is described in detail by them.[20-22] The integral equations method was first presented by Sams and Kouri.[17] The applications presented here have used a trapezoidal rule quadrature scheme. An important feature of the integral-equations formalism for electron scattering problems is the recent development of an efficient means of including non-local Hartree-Fock exchange operators without increasing the size of the solution matrix over the local-potential case.[47] This feature will not be explored here since the examples presented for electron-molecule scattering involve local, energy-dependent potentials. Another important feature is the truncation procedure by which the number of coupled channels is decreased at a "truncation radius"; this can yield substantial savings of computer time.[21,22,48]

F. **Timing comparisons.** It is very difficult to make precise timing comparisons for several reasons. The most obvious reason is that one method may be programmed more efficiently than another, or a given compiler may produce more efficient code for one method than another. Another difficulty is that one seldom completely optimizes all the numerical parameters for a given application. It is usually more efficient for production runs to set some or all numerical parameters at safe values which produce more accurate results than are really required for parts of the calculation or even for the final cross sections. A related problem is the efficiency of utility codes, e.g., our R matrix propagation code uses the EISPACK subprogram RSP for matrix diagonalization and University of Minnesota codes for solution of sets of linear equations. Another problem, less significant than those mentioned above, is that the computer time even for an identical run may vary 10% or more depending on the time of day and overall computer load. A question which has no unique answer but depends on the application is how to define accuracy or precision. For the present report we have made special runs designed to approximately determine the minimum computing time required to achieve a given precision for some test cases. By precision we refer to all accuracy criteria except convergence with respect to N and P, i.e., we mean accuracy of the numerical solution for given basis-set sizes. [Recall that N is the order of the close coupling equation (2) and P is the number of channels propagated; for all the methods considered here except R matrix propagation, P = N.] Bearing in mind the above caveats, one should not attempt to draw conclusions based on the fine details of the computer times presented in this report. Some overall trends

and general magnitudes are however meaningful and interesting. All com-
puter times given in this report are execution times, excluding compilation.
All source codes, except for the University of Minnesota linear equation
solver used in both our Numerov and R matrix propagation codes, were written
in FORTRAN. For purposes of rough comparison to calculations performed
on other computers, Table 1 gives approximate conversion factors.

III. Electron-molecule scattering

We have applied all four methods introduced in section II to electron

scattering by N_2. We consider two classes of problems: (A) vibrational-

rotational close coupling and (B) rotational close coupling with the rigid

rotator approximation.

A. Vibrational-rotational close coupling. The first method we attempted

to apply to electron-molecule scattering was the piecewise analytic method.

We used our modified version of the QCPE program. Although we had limited

success with this method, we found that it was inadequate to complete some

of the applications we attempted. These applications[9] involved vibrational-

rotational close coupling calculations for electron scattering by N_2 at

energies of 5-45 eV. Two difficulties we encountered were: (i) we were

unable to calculate accurate small transition probabilities, especially

those associated with vibrational transitions, with reasonable stepsizes;

(ii) for some problems the results were not converged even with impractically

small stepsizes, e.g., 5×10^{-6} a_0. The first difficulty we tentatively as-

sociate with the fact that the piecewise analytic solution used is correct

for a diagonal linear reference potential, but although the transformation

method used diagonalizes the potential at the center of each sector, it does

not diagonalize the derivative of the potential. Thus the transformed poten-

tial through linear terms is not diagonal in a sector. This or some other as-

pect of the method causes it to be poorly suited for the accurate calculation

of small S matrix elements. In considering difficulty (ii), we note that the

success and efficiency of a sophisticated variable-stepsize integrator is

highly dependent on the reliability of the stepsize algorithm. In the

present case, however, during the course of the solution, the predicted

stepsize sometimes became exceedingly small, e.g., 10^{-12} a_0. It was suggested to us that we just substitute a very small minimum stepsize, e.g., 10^{-3} a_0, and continue to propagate until the stepsize algorithm again predicted stepsizes larger than the minimum. Since the piecewise analytic method requires more expense per step than less sophisticated methods like the Numerov method, its efficiency requires that the stepsizes be fairly large. Nevertheless we tried the minimum stepsize procedure and were disappointed to find some applications where the results were not converged with respect to minimum stepsize even at 5×10^{-6} a_0. The difficulty of calculating small vibrational transition amplitudes by the piecewise analytic method has also been noted elsewhere.[49]

The second method we applied to electron-molecule vibrational-rotational close coupling was the Numerov method.[8,9] We found this method to be accurate and reliable for all cases attempted, even those for which the piecewise analytic method was unacceptable.

B. Rotational close coupling with the rigid rotator approximation.
We now consider the electron-N_2 rotational close coupling problem studied in reference 26. In that study the diatom is treated as a rigid rotator with the equilibrium internuclear distance (2.068 a_0), and the rotational close coupling problem is formulated in the laboratory frame using the total angular momentum representation of Arthurs and Dalgarno.[50] Only the ground electronic state is included explicitly, and effects of electronic-charge-cloud polarization and of electron exchange are included by means of an effective potential.[10] The anisotropic electron-molecule interaction potential is expanded as

$$V(r,\chi) = \sum_{\lambda} V_{\lambda}(r) P_{\lambda}(\cos \chi) \tag{114}$$

where χ is the colatitude of the scattering electron with respect to the internuclear axis. The individual terms $V_{\lambda}(r)$ are represented by spline functions that have a cusp at one half the internuclear distance, i.e., at $r = 1.034\ a_0$. Both our Numerov and our R matrix propagation codes have special provisions for choice of stepsize in the vicinity of the cusp. For the Numerov calculations reported here we did not use this provision; we just ignored the cusp. For the R matrix propagation calculations we shortened the sector before the cusp to put a sector boundary at the cusp.

The calculations of reference 26 used the R matrix propagation scheme, and we attempted to obtain three-significant-figure precision in the elastic and inelastic transition probabilities. In a separate study[10] we had found that $j_{max} = 6$ was required for convergence of the $J = 5$, even-j partial cross sections at 30 eV impact energy where j and J are rotational and total angular momentum quantum numbers in the Arthurs-Dalgarno scheme. A conventional basis for this j_{max} and J consists of 15 channels. The next smaller conventional basis ($j_{max} = 4$) and the ℓ-dominant[51] basis both contain 9 functions. In reference 26 we compared calculations with various conventional, ℓ-dominant, and adiabatic bases. In Table 2 we give for comparison some representative results. These examples show the general result that the ℓ-dominant basis provides significantly more accurate results for elastic and inelastic scattering from the ground rotational state than the conventional basis of the same dimension, but that a 9-function adiabatic basis (consisting of the 9 lowest energy eigenfunctions obtained by taking linear combinations of the 15 total angular momentum eigenfunctions of the

primitive basis in each sector) is considerably more accurate than either
of these. In fact, for transitions between excited rotational states even
a 6-function adiabatic basis provides better agreement with the converged
results than either of the two 9-function diabatic bases.

For the $N = 15$, $P = 15$ and $N = 15$, $P = 9$ cases we have used trace
statements to make a detailed study of how much computer time is spent in
each subprogram. We then related the computer time spent in each sub-
program to the computer time spent on various parts of the calculation.
The results of this timing study are shown in Table 3. For the computer
runs upon which Table 3 is based, we used a single-energy, single-basis-
set version of our code which used no disk reads or writes during the cal-
culation. Dimensions for arrays in common blocks were set to accomodate
a maximum of 15 channels and 3000 sectors. The field length required for
this to run was 101500 (base 8) words. We propagated only $\underset{\sim}{R}_4$ and we used
the tranpose rather than the inverse of $\underset{\sim}{T}$. We set all $\varepsilon^{(i)} = 0.07$. Results
of the same accuracy can be obtained more efficiently by dividing the
propagation range into three or four intervals and optimizing $\varepsilon^{(i)}$ separately
in each. This extra optimization was employed for some production runs[26]
but not for the timing comparison reported here. We placed the center of
the first sector at 0.03 a_0 and used 5×10^{-6} a_0 for the first two stepsizes.
The stepsize algorithm yields $h^{(3)} = 4.4 \times 10^{-4}$ a_0. The 15/15 run required
250 steps to reach 1 a_0 where $h^{(i)} = 0.014$ a_0, 50 more steps to reach 2 a_0
where $h^{(i)} = 0.031$ a_0, and 45 more steps to reach 4 a_0, where $h^{(i)} = 0.058$ a_0.
The final asymptotic analysis was performed at 101.6 a_0 by which point the
stepsize had increased monotonically to 1.4 a_0. The first 486 of the sectors
are located at $r < 30$ a_0. Multiplying the first three entries in Table 3

by 486/572 gives an estimate of 65 sec for the execution time of a calculation which would quit at 30 a_0. A similar correction to 30 a_0 yields 47 sec for the 15/9 calculation. One should keep in mind that the time required for the calculation of $\underline{D}$ is highly dependent on the complexity of the interaction potential and the efficiency of the potential subprogram.

The most striking result in Table 3 is that most of the computer time is involved in diagonalizing $\underline{D}$. The propagation of the $\underline{R}_4$ matrix accounts for only 32% of the time in the 15/15 run and only 13% of the time in the 15/9 run. Thus, increasing the efficiency of this step by even a factor of two would result in savings of only 16% and 6% in the two runs, respectively.

For the 15/15 case, decreasing $\varepsilon^{(i)}$ to 0.05 and moving the asymptotic analysis to 120.8 a_0 to check the accuracy required 867 sectors and 109.5 sec computer time. Most partial cross sections calculated in this run agreed to ±1 in the third significant figure with those for the run described above.

For comparison with these calculations we ran the Numerov code with the same potential and a similar potential subprogram for the same impact energy and J = 5. We also used the same compiler (MNF) and the same computer (the CDC Cyber 74). Trial calculations showed that one can obtain about three significant figures of precision by performing the asymptotic analysis at 30 a_0 with Ricatti-Bessel functions. Similar accuracy can be obtained at 10 a_0 using BMS functions, but with our computer program the overall cost for the present case is greater with BMS functions because of the cost of computing the BMS functions. The BMS functions are less expensive for cases with a smaller number of channels. We made several runs designed

to discover the most efficient procedure for solving the 15-channel test problem performing the asymptotic analysis at 30 a_0 using Ricatti-Bessel functions. All these runs began the propagation at 10^{-6} a_0 with $h_0 = 0.0005$ a_0. We used h_0 for the first ten steps. First we used the regular Numerov method with $h_{max} = 0.064$ a_0 and various δ to determine the δ required for three significant figures of accuracy. This yielded $\delta = 10^{-4}$ a_0, 547 steps, and a computer time of 33 sec. With the same numerical parameters the iterative Numerov method with EPS = 10^{-4} required 48 sec. With the same values of h_0, h_{max}, and δ, we ran the option which tests the iterative against the regular Numerov method every 25 steps. With EPS = 10^{-4}, the iterative Numerov method was found to be slower at all distances for this test case; this run also required 33 sec. In the runs just discussed the maximum stepsize of 0.064 a_0 was reached at r = 0.70 a_0. We removed the maximum stepsize criterion and again searched for the δ which yields about three significant figures of accuracy. For most partial cross sections this could be achieved with $\delta = 10^{-6}$ or 10^{-5}. Using KCK = 25 and EPS = 10^{-4}, these two calculations required 357 and 268 steps and 28 and 19 sec, respectively. These times may be compared with 65 sec for the R matrix propagation code on the same compiler and same computer.

Then the Numerov calculation with KCK = 25 and $\delta = 10^{-6}$ was rerun with the FTN compiler with optimization levels OPT = 1 and OPT = 2; the execution times decreased to 24 sec and 15 sec, respectively. Retaining KCK = 25, $\delta = 10^{-6}$, and OPT = 2, we increased EPS to 10^{-2}; the regular Numerov method was still faster at every check. For some other electron-molecule scattering calculations we have found that the iterative Numerov method is relatively more efficient at large r and large J.

The dimensions in the Numerov program were set for 15 channels and the field length required to execute was 114500 (octal) words. For 15-channel calculations on the He-HF system considered below the field length required is only 105700 (octal) words. The difference is accounted for by the large number of spline coefficients in the electron-N_2 interaction potential.

It is difficult to compare the computation times for the calculations of reference 23 using the integral equations algorithm to those reported here as obtained with the other programs. The integral equations algorithm has been used for calculations in the body-frame formalism,[21-23] whereas the other calculations discussed in this section use the Arthurs-Dalgarno formalism.[50] The input for the integral equations program consists of the $V_\lambda(r)$ values on the integration mesh, whereas the input for the Numerov and R matrix propagation programs consists of spline fits to the $V_\lambda(r)$. This means that the stepsizes for the integral equations calculations are input variables. For a typical run in reference 23, the stepsize for the first twenty steps was 0.001 a_0, followed by 298 steps with h = 0.01 a_0, 152 steps with h = 0.1 a_0, and 100 steps with h = 0.2 a_0, for a total of 570 ending at 38.2 a_0. Table 4 shows typical computation times for various numbers of channels. These calculations are for Σ_g symmetry at E = 13.6 eV with λ_{max} = 28. No truncation of the number of coupled channels was employed, i.e., the truncation radius is infinite. Thus all N channels were propagated at all distances as in the Numerov calculations and the R matrix propagation calculations with P = N.

The potential used for the R matrix propagation and Numerov test cases is called potential i in reference 10. The results presented above were

presented at the NRCC Workshop in June, 1979. We have also submitted a set of $V_\lambda(r)$ for this potential to L. Thomas who prepared a potential subprogram based on this potential for the Workshop participants as a test case for further study.

IV. Electron-atom scattering

Electron-hydrogen atom scattering provides an interesting test case for close coupling codes.[41a] It is a prototype for electronically inelastic electron-atom scattering in general, but it has the advantage that the interaction potential matrix is known analytically. The interaction potential for electron-atom scattering is qualitatively different from the interaction potential for the other test problems considered in this report in that it tends to $-\infty$ at the origin. The same limit occurs for electron scattering from molecules like CO_2, which has a nucleus at the origin.[52] For comparison of computation times for electron-atom scattering we consider a 2-channel problem: 1s-2s close coupling without exchange and with total angular momentum zero.

To use the piecewise analytic method for electron-hydrogen atom scattering, we had to modify the QCPE program to allow for starting channels which are open at the origin. For various 3- and 4-channel examples, reasonably precise results could be obtained by starting at about 10^{-5} a_0 and using a stepsize error criterion of 10^{-5} or 10^{-6}. Using the FT3 compiler and a CDC 6600 computer, precise results for the 1s-2s s-wave test case required about 1.6 sec. This corresponds to about 1.5 sec on the CDC Cyber 74. In general it was difficult, as compared to using our Numerov program, to test and obtain convergence with respect to the starting point and the stepsize error criterion.

The R matrix propagation method, propagating $\underset{\sim}{R}_1$, $\underset{\sim}{R}_2$, $\underset{\sim}{R}_3$, and $\underset{\sim}{R}_4$, was applied to the test case and the numerical parameters were adjusted so that the partial cross sections were precise to ± 1 in the third significant figure. This yielded $\varepsilon^{(i)} = 0.05$. The calculation was well

converged at sector 166 at 17.5 a_0. The stepsize became very large at large r, and two more steps brought the calculation to the final sector centered at 25.1 a_0. The computation time, using the MNF compiler and the Cyber 74 computer, was 0.6 sec.

To compare the efficiency of the computer codes we applied the variable-stepsize regular Numerov method with Ricatti-Bessel function boundary conditions to the same problem, again using the MNF compiler and the Cyber 74 computer. Asymptotic analysis was performed at 25 a_0 where it was converged with respect to further propagation to 5 significant figures. We used h = 5×10^{-4} a_0 for the first ten steps. Subsequent stepsizes were determined by increasing δ in successive runs until we obtained only three significant figures of precision in the partial cross sections. This required $\delta = 10^{-6}$ and a computation time of 0.42 sec. In this run the stepsize doubled every step from the eleventh until it reached 0.128 a_0. It then increased to its final value, 0.256 a_0 at 0.52 a_0. The calculation required 116 steps. We repeated the calculation using the option to check every 11th step whether the regular or iterative Numerov method is faster. With EPS = 10^{-4}, the iterative Numerov method became faster at r = 18.2 a_0. This whole calculation required 0.44 sec. The iterative Numerov method is relatively more efficient for cases with centrifugal barriers.

To check the sensitivity to compiler we reran the most efficient of the above calculations with a code compiled on the FTN compiler with optimization levels OPT = 1 and 2. The computer time increased from 0.42 sec to 0.44 and 0.43 sec, respectively.

A class of methods which has been widely applied to electron-atom scattering, and to a lesser extent to electron-molecule scattering, is

the algebraic variational method and related techniques involving expansion of the translational wave function in a basis set.[53-59] In these methods the potential is generally represented in a basis set rather than as a function of the radial coordinate. These methods can often be used to solve the same problems as are attacked by close coupling codes like the ones discussed here which rely on numerical integration of coupled differential equations. However, they become relatively more efficient and more useful when nonlocal exchange potentials are included.

Using our original algebraic variational program[60] with the FUN compiler on the CDC 6600 computer, a typical run on the 2-channel test problem of this section required 26 sec (equivalent to about 24 sec on the CDC Cyber 74). This run involved 15 and 10 uncontracted basis functions for the expansion of the translational wave functions in the 1s and 2s channels respectively. This time can be speeded up by using more efficient procedures for evaluation of the integrals over basis functions. Unfortunately a computer time is not available using our more efficient integrals packages[61,62] on this test problem. The computer time can also be decreased by using contracted basis functions.[63]

V.   Vibrationally inelastic atom-diatom scattering

For atom-molecule scattering the interaction potential is independent. of energy.   When the R matrix propagation method is used to study systems with energy-independent interaction potentials, great savings of computer time can be made since calculations with the same number N of primitive basis functions can be carried out for several energies with the time-consuming diagonalization of the interaction matrix $\underset{\sim}{D}$ carried out only once.[24]   The calculation at the first energy is called a reference-mode calculation.   In a reference mode calculation, $\underset{\sim}{D}$ is calculated and dia-gonalized in every sector, the eigenvalues are stored on the disk, and the transformation matrix $\underset{\sim}{T}$ is calculated and stored on the disk.   If $\underset{\sim}{T}^{-1}$ is to be used, it too is computed and stored on the disk.   Calculations at additional energies may be carried out in a propagation-mode.   Additionally, to test convergence with respect to P the propagation-mode can also be used to run calculations at the same energy but with successively smaller values of P.

We here report a detailed study of the timing requirements of the many-energy, many-basis version of our R matrix propagation program for a test problem.   The test problem is collinear scattering of He by H_2 with a harmonic oscillator potential for H_2 and an exponential repulsive inter-action potential.   The Hamiltonian is the same as used in two published studies[64,65] and corresponds to m = 2/3 and α = 0.314 in the unitless notation of reference 65.   We considered total energies of $8\hbar\omega$ and 7.75 $\hbar\omega$ and used harmonic oscillator eigenfunctions for the primitive basis.   We used the many-energy, many-basis version of our computer program to run a series of nineteen calculations with various values of N and P in the

range 7-15. By printing out the computation times in various subprograms
we were able to approximately distribute the computation times into four
categories: setup, calculation and diagonalization of $\underset{\sim}{D}$, propagation, and
asymptotic analysis. We then fit each category of computation time (in
sec) to an empirical function of N or P. The total computation time (in
sec) is called t, and the functions for the four categories are called s,
d, p, and a respectively. For a reference-mode calculation we obtained

$$t \overset{\sim}{=} s_1 + d(N) + p_1(P) + a \tag{115}$$

where

$$s_1 \overset{\sim}{=} 0.5 \tag{116}$$

$$d(N) \overset{\sim}{=} 1.13 \times 10^{-3} N^3 + 0.031 N^2 \tag{117}$$

$$p_1(P) \overset{\sim}{=} 0.029 P^2 \tag{118}$$

and

$$a \overset{\sim}{=} 0.5 \tag{119}$$

For a propagation-mode calculation we obtained

$$t \overset{\sim}{=} s_2 + p_2(P) + a \tag{120}$$

where

$$s_2 \overset{\sim}{=} 0.3 \tag{121}$$

$$p_2(P) \overset{\sim}{=} 0.021 P^2 (1 + 0.008P) \tag{122}$$

and a is as before. The functional forms in (117), (118), and (122) have
not been fit exactly; they are chosen strictly to provide a simple empirical
fit over the range of N and P examined. In principle other powers of N and

P should appear. Using these functions we can generate the sample computation times in Table 5.

For the runs used to generate equations (115)-(122), we propagated only R_4 and we used the inverse of T. We also made runs in which we used the transpose of T; for our program there was little difference in the execution time as compared to using the inverse. We determined that $\varepsilon^{(i)} = 0.15$ and $r_L^{(1)} = 1.195$ a_0 were just sufficient to get 2% accuracy for all transition probabilities and 3-significant-figure accuracy for those greater than 10^{-5}. We found that placing the center of the last sector at $r_R^{(c)} \geq 6$ a_0 was sufficient to ensure that our results were converged with respect to increasing the range of the propagation. To achieve this convergence for all the runs and to use a fixed number of sectors to simplify the interpretation of the computation times, we used 150 sectors for all the runs and propagated to 7-24 a_0, depending on N and P; however, the stepsize becomes large at large r (for the last few steps $h^{(i)} = h_{max} = 3$ a_0), and r = 6 a_0 is not reached earlier than the 142nd sector. Typical values for the centers of the sectors and the stepsizes are $r_c^{(i)} = 1.40$, 1.67, and 2.54 a_0 and $h^{(i)} = 0.0096$, 010122, and 0.0261 a_0 for i = 25, 50, and 100, respectively.

Table 5 shows that calculations at second and subsequent energies are faster by factors of about 3-5 than calculations at the initial energy. These savings are also achieved when a series of P values is run to test convergence.

In Tables 6 and 7 we give representative transition probabilities $P_{vv'} = |S_{vv'}|^2$ calculated for the simple model of vibrationally inelastic

collinear atom-molecule scattering described above.[29] For energies cor-
responding to $4\hbar\omega$ and $8\hbar\omega$ we see that an adiabatic basis of propagation
dimension P can give significantly more accurate results than a conven-
tional basis of the same dimension. For example, at $E = 8\hbar\omega$ converged
results for all but transitions involving the highest open channel, $v' = 7$,
can be obtained with a 9-function conventional basis which includes har-
monic oscillator eigenfunctions corresponding to $v = 0-8$. In contrast
the transition probabilities obtained by calculations using the 8-function
conventional basis which includes only the open channels can have large
errors. E.g., as shown in Table 7, the $N = 8$, $P = 8$ calculations of P_{25},
P_{46}, and P_{06} have errors of 12%, 47%, and more than a factor of two, re-
spectively. The $N = 9$, $P = 8$ adiabatic basis, however, gives all but 3
transition probabilities (P_{34}, P_{57}, and P_{67}) to within 1%. Thus we see
for this example, that when the results differ, adiabatic bases yield con-
siderably more accurate results than conventional bases of the same or
frequently even larger propagation dimension P. This is an important
result. To obtain the adiabatic basis extra effort must be expended to
diagonalize the $N \times N$ interaction matrix $\underset{\sim C}{D}^{(i)}$ in each sector. However,
when the interaction potential is independent of energy, as it is for the
present problem, the adiabatic basis functions in each sector are also
independent of energy. Consequently, as we have seen above, significant
computational savings can result from obtaining the adiabatic basis in a
reference-mode calculation and using it for several energies in propagation-
mode calculations.

Table 5 shows that most of the computer time in a reference-mode cal-
culation is spent calculating and diagonalizing $\underset{\sim}{D}$. Since the interaction

potential is very simple for this test case, the diagonalization step is the slow one. One idea for a method to reduce the time required to evaluate the eigenvalues and eigenvectors of $\underset{\sim}{D}$ is to calculate and diagonalize $\underset{\sim}{D}$ on a coarse grid, fit the eigenvalues and eigenvectors to spline functions, and use the spline functions for a propagation-mode calculation on a finer grid. One would have to converge the calculation with respect to the spline grid as well as the propagation grid. We tried this for the case N = 8, P = 8 with the unconverged coarse grid being about ten times coarser than the propagation grid. We used the storage-efficient but computer-time inefficient version of our spline subprograms. The computer time was 7.4 sec (compare 5.5 sec in Table 5). Since the spline version of the program was not at all optimized, this test indicates that this kind of idea deserves further consideration. Another possible way to speed up the diagonalization step is to use an iterative method for the diagonalization. The diagonalization at the previous step would be used to start the iteration.

The piecewise analytic method has also been used for this test problem. We used the program written by Wagner[14] for this purpose. Compiling this on the MNF compiler and running it on the CDC 6600 computer required 9.1 sec computer time (corresponding to about 8.4 sec on the Cyber 74) to obtain slightly less than three-significant-figure accuracy for a basis with 8 channels; at the energy considered 5 channels were open, and no transition probabilities were less than 10^{-4}. The piecewise analytic method, like the R matrix propagation method, has the advantage that additional calculations at subsequent energies can be performed with reduced cost.

VI. Rotationally Inelastic Atom-Diatom Scattering

We have applied three different methods to rotationally inelastic scattering of an atom by a rigid rotator using the Arthurs-Dalgarno[50] scheme Consider first He-HF scattering with the interaction potential of Collins and Lane.[20,28,66] For a test case we study scattering at total angular momentum J = 12 and impact energy 0.05 eV using a conventional 10-function basis with j_{max} = 3. Using the R matrix propagation scheme (propagating only $\underset{\sim}{R}_4$) we found that propagating from 3.5 a_0 to 20 a_0 was sufficient to give 1% precision for the real and imaginary parts of all S matrix elements greater than 10^{-2} and three-significant-figure precision for partial cross sections from the ground state. We used the same $\varepsilon^{(i)}$ for every sector and increased it till we just retained this accuracy. This required $\varepsilon^{(i)}$ = 0.3, and took 4.8 sec execution time for a program compiled on the MNF compiler and run on the Cyber 74 computer. Using the same compiler and computer, we repeated the calculation with the regular Numerov method, starting at 3.5 a_0 and applying Ricatti-Bessel function boundary conditions at 24 a_0. Using fixed stepsizes, we found that we could satisfy the criteria given above with h = 0.064 a_0. This calculation required 15 sec computer time. We repeated this calculation using the FTN compiler with optimization level OPT = 2, and the execution time decreased to 10 sec. We then tried the variable-stepsize algorithm and obtained comparable accuracy for $\delta = 7 \times 10^{-8}$; in this run the stepsize increased to 0.064 a_0 at r = 4.50 a_0 and remained at this value; the execution time was still 10 sec with the FTN compiler and optimization level OPT = 2. Based on Allison's experience[5] one would assume that the execution could be improved by using the iterative Numerov method with a carefully chosen value of EPS.

One advantage of the R matrix propagation method for this problem is that, since the interaction potential is independent of energy, one can perform calculations at additional energies at a reduced cost. Further, by judicious use of contraction, i.e., $P < N$, one can often obtain good accuracy without propagating the full number of functions required in the primitive basis set.[28] To illustrate this we give in Table 8 some representative rotational excitation cross sections for $E = 0.05$ eV for $J = 4$ and 12.[28-29] As shown here, we found that in all cases adiabatic bases of propagation dimension P gave more accurate results than conventional calculations of the same dimension except where accidental cancellation of errors occurred. In Table 8 we see that a 10-function conventional basis including channels with $j \leq j_{max} = 3$ gives converged results for both total angular momenta. In contrast the next smaller conventional basis, the 6-function $j_{max} = 2$ basis, gives errors of 15% and 66% in $\sigma_{0 \to 1}^4$ and $\sigma_{0 \to 2}^4$, respectively, and 12% and 48% in $\sigma_{0 \to 1}^{12}$ and $\sigma_{0 \to 2}^{12}$. However, the $N = 10$, $P = 6$ adiabatic basis yields all four cross sections with an accuracy of 9%. In Table 9 we show that the significant increase in accuracy obtained when an adiabatic basis is used instead of a conventional basis is not predicated on a fortuitous cancellation of errors. For this example, the $j_{max} = 2$ basis gives errors of almost a factor of 2 for each partial cross section, while the 6-function adiabatic basis yields all three partial cross sections within 6%.

The piecewise analytic method has been widely used for atom-rigid-rotator collisions, although even for this problem the difficulty of obtaining very precise answers has been noted.[5] We applied the piecewise analytic method to the 16-channel problem of Johnson et al.[67] Using the

numerical parameters of the QCPE test data, the FUN compiler, and the CDC 6600 computer, we obtained less than three significant figures of precision in 12 sec for a first-energy calculation. This corresponds to about 11 sec on the CDC Cyber 74 computer. This problem required propagating from 0.73 a_0 to 6.5 a_0. For comparison, the R matrix propagation method for the He-HF problem discussed above, with $\varepsilon^{(i)} = 0.3$ and propagating from 3.5 to 20.0 a_0, required 10.3 and 8.4 sec computer time on the CDC Cyber 74 computer for $N = 15$, $P = 15$ and $N = 15$, $P = 10$ problems, respectively, for first-energy calculations.

VII. Summary

We have presented some details of our implementation of the Numerov and R matrix propagation methods for inelastic close coupling calculations. We have found that these methods are convenient and reliable for electron-atom, electron-molecule, and atom-molecule collisions involving rotationally, vibrationally, and electronically inelastic scattering where the close coupling equations take the form of coupled differential equations. We have shown that the computer time requirements of these two methods as well as the piecewise analytic method and the integral equations method are similar for a variety of inelastic close coupling calculations. The ultimate choice among these methods should therefore often be based on other considerations, such as ease of programming in the Numerov method or of using adiabatic basis sets in the R matrix propagation method. Both these methods have favorable properties for checking convergence with respect to numerical parameters in calculations performed on a production basis.

VIII. Acknowledgements

1. B. Numerov, Publ. Observatoire Central Astrophys. Russ. $\underline{2}$, 188 (1933).

2. R. W. Hamming, <u>Numerical Methods for Scientists and Engineers</u> (McGraw-Hill, New York, 1962), p. 215.

3. L. L. Barnes, N. F. Lane, and C. C. Lin, Phys. Rev. $\underline{137}$, A388 (1965).

4. J. M. Blatt, J. Comput. Phys. $\underline{1}$, 382 (1967).

5. A. C. Allison, Ph.D. thesis, University of Glasgow, Glasgow, Scotland, 1967; A. C. Allison, J. Comput. Phys. $\underline{6}$, 378 (1970).

6. N. F. Lane and S. Geltman, Phys. Rev. $\underline{160}$, 53 (1967).

7. R. J. W. Henry and E. S. Chang, Phys. Rev. A $\underline{5}$, 276 (1972).

8. M. A. Brandt, M.S. thesis, University of Minnesota, Minneapolis, 1975.

9. M. A. Brandt, D. G. Truhlar, and F. A. Van-Catledge, J. Chem. Phys. $\underline{64}$, 4957 (1976); D. G. Truhlar, M. A. Brandt, A. Chutjian, S. K. Srivastava, and S. Trajmar, J. Chem. Phys. $\underline{65}$, 5335 (1976); D. G. Truhlar, M. A. Brandt, A. Chutjian, S. K. Srivastava, and S. Trajmar, J. Chem. Phys. $\underline{65}$, 2962 (1976).

10. K. Onda and D. G. Truhlar, J. Chem. Phys. $\underline{69}$, 1361 (1978), $\underline{70}$, 1681 (1979).

11. K. Onda and D. G. Truhlar, to be published.

12. R. G. Gordon, J. Chem. Phys. $\underline{51}$, 14 (1969).

13. R. G. Gordon, Methods Comput. Phys. $\underline{10}$, 81 (1971).

14. A. F. Wagner and V. McKoy, J. Chem. Phys. $\underline{58}$, 2604 (1973), $\underline{58}$, 5561 (1973).

15. M. H. Alexander, J. Comput. Phys. $\underline{20}$, 248 (1976).

16. R. J. Gordon, J. Chem. Phys. $\underline{67}$, 5923 (1977).

17. W. N. Sams and D. J. Kouri, J. Chem. Phys. $\underline{51}$, 4809 (1969), $\underline{51}$, 4815 (1969).

18. R. A. White and E. F. Hayes, J. Chem. Phys. $\underline{57}$, 2895 (1972), Chem. Phys. Lett. $\underline{14}$, 98 (1972).

19. J. T. Adams, R. L. Smith, and E. F. Hayes, J. Chem. Phys. $\underline{61}$, 2193 (1974).

20. L. A. Collins, Ph.D. Thesis, Rice University, Houston, Texas, 1975.

21. M. A. Morrison, Ph. D. thesis, Rice University, Houston, Texas, 1976.

22. M. A. Morrison, L. A. Collins, and N. F. Lane, Chem. Phys. Lett. 42, 356 (1976), M. A. Morrison, N. F. Lane, and L. A. Collins, Phys. Rev. A 15, 2186 (1977).

23. J. R. Rumble and D. G. Truhlar, J. Chem. Phys. 70, 4101 (1979).

24. J. C. Light and R. B. Walker, J. Chem. Phys. 65, 4272 (1976).

25. D. G. Truhlar and N. A. Mullaney, J. Chem. Phys. 68, 1574 (1978).

26. N. A. Mullaney and D. G. Truhlar, Chem. Phys. Lett. 58, 512 (1978).

27. E. B. Stechel, R. B. Walker, and J. C. Light, J. Chem. Phys. 69, 3518 (1978).

28. N. A. Mullaney and D. G. Truhlar, Chem. Phys. 39, 91 (1979).

29. N. Mullaney Harvey, Ph.D. thesis, University of Minnesota, Minneapolis, 1979.

30. J. W. Cooley, Math. Comp. 15, 363 (1961).

31. I. H. Sloan, J. Comp. Phys. 2, 414 (1968).

32. B. R. Johnson, J. Chem. Phys. 69, 4678 (1978).

33. W. A. Lester, Jr., J. Comput. Phys. 3, 322 (1968); W. A. Lester, Jr., University of Wisconsin Theoretical Chemistry Institute Technical Report WIS-TCI-285, Madison, 1968.

34. R. deVogelaere, J. Research Natl. Bur. Std. 54, 119 (1955); R. deVogelaere, Z. Angew. Math. Phys. 8, 151 (1957).

35. R. G. Gordon, program entitled "Coupled Channel Scattering Matrices", program no. 187 described in Quantum Chemistry Program Exchange Catalog and Procedures, Vol. 10 (Indiana University Chemistry Department, Bloomington, Indiana, 1974), p. 67.

36. W. A. Lester, Jr. and R. B. Bernstein, Chem. Phys. Lett. 1, 207 (1967), erratum: 1, 347 (1967).

37. N. F. Mott and H. W. S. Massey, The Theory of Atomic Collisions, third edition (Oxford University Press, London, 1965), pp. 388ff.

38. R. S. Varga, Matrix Iterative Analysis (Prentice-Hall, New Jersey, 1962), p. 56; (a) p. 78; (b) p. 23.

39. M. E. Riley and A. Kuppermann, Chem. Phys. Lett. 1, 537 (1968); M. E. Riley, Ph.D. thesis, California Institute of Technology, Pasadena, 1968.

40. *Handbook of Mathematical Functions*, M. Abramowitz and I. A. Stegun, eds. (U.S. Dept. of Commerce, Natl. Bur. Standards Appl. Math Series 55, Washington, D.C., 1964), p. 437.

41. K. Smith, *The Calculation of Atomic Collision Processes* (Wiley-Interscience, New York, 1971), p. 15, (a) p. 96.

42. P. G. Burke and H. M. Schey, Phys. Rev. 126, 147 (1962).

43. P. G. Burke, D. D. McVicar, and K. Smith, Proc. Phys. Soc. (London) 83, 397 (1964).

44. D. W. Norcross, Comput. Phys. Commun. 1, 88 (1969). This program has been revised in A. T. Chivers, Comput. Phys. Commun. 5, 416 (1973).

45. D. G. Truhlar, C. A. Mead, and M. A. Brandt, Advan. Chem. Phys. 33, 295 (1975).

46. J. C. Light, Methods. Comp. Phys. 10, 111 (1971).

47. L. A. Collins, W. D. Robb, and M. A. Morrison, J. Phys. B 11, L777 (1978).

48. M. A. Morrison, in *Electron- and Photon-Molecule Collisions*, edited by V. McKoy, T. N. Rescigno, and B. I. Schneider (Plenum, New York), in press.

49. S. Green, J. Chem. Phys. 70, 4686 (1979).

50. A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc., Lond., Ser. A 256, 540 (1960).

51. A. E. dePristo and M. H. Alexander, J. Chem. Phys. 63, 3552, 5327 (1975).

52. K. Onda and D. G. Truhlar, J. Phys. B 12, 283 (1979).

53. F. E. Harris and H. H. Michels, Methods. Comp. Phys. 10, 143 (1971).

54. D. G. Truhlar, J. Abdallah, Jr., and R. L. Smith, Advan. Chem. Phys. 25, 211 (1974).

55. P. G. Burke and W. D. Robb, Advan. At. Molec. Phys. 11, 143 (1975).

56. R. K. Nesbet, Advan. Quantum Chem. 9, 215 (1975).

57. J. Callaway, Phys. Reports 45, 89 (1978).

58. B. I. Schneider, in *Electronic and Atomic Collisions*, edited by G. Watel (North Holland, Amsterdam, 1978), p. 259.

59. A. Fliflet and V. McKoy, Phys. Rev. A 18, 2107 (1978).

60.   R. L. Smith and D. G. Truhlar, Phys. Lett. A 39, 35 (1972).

61.   R. L. Smith and D. G. Truhlar, Comput. Phys. Commun. 5, 80 (1973),
       erratum: 8, 333 (1974).

62.   J. Abdallah, Jr. and D. G. Truhlar, Comput. Phys. Commun. 9, 327 (1975).

63.   J. Abdallah, Jr. and D. G. Truhlar, J. Chem. Phys. 61, 30 (1976).

64.   A. P. Clark and A. S. Dickinson, J. Phys. B 6, 164 (1973).

65.   J. W. Duff and D. G. Truhlar, Chem. Phys. 9, 243 (1975).

66.   L. A. Collins and N. F. Lane, Phys. Rev. A 14, 1358 (1976).

67.   B. R. Johnson, D. Secrest, W. A. Lester, Jr., and R. B. Bernstein,
       Chem. Phys. Lett. 1, 396 (1967).

Table 1. Approximate conversion factors for computer time

Computer	Factor relative to CDC Cyber 74
CDC 6400	0.35[a]
CDC 6600	0.92
CDC 7600	6.0
IBM 360/75	0.6
IBM 370/168	1.4
IBM 360/91	2.8
IBM 370/195	6.0
Univac 1108	0.4

[a]For example, to convert a computation time obtained with the CDC 6400 computer to an expected computation time on the CDC Cyber 74, multiply by 0.35.

Table 2. Sums of transition probabilities for transitions from the ground state $(j,\ell) = (0,5)$ and from the second rotationally excited state[a] as a function of basis for $e-N_2$, $J = 5$ scattering at 30 eV.[b]

description of basis	conventional	conventional	ℓ-dominant	adiabatic	adiabatic
N/P	15/15	9/9	9/9	15/9	15/6
j'			$\sum_{\ell'} P_{05j'\ell'}$		
2	2.92(-3)[c]	3.16(-3)	2.70(-3)	2.97(-3)	
4	5.36(-4)	2.39(-4)	4.40(-4)	5.63(-4)	
6	1.99(-4)		1.42(-4)	2.11(-4)	
j'			$\sum_{\ell'} P_{23j'\ell'}$		
4	2.46(-1)	1.04(-1)	2.28(-1)	2.48(-1)	2.47(-1)
6	1.07(-1)		8.08(-2)	1.11(-1)	1.10(-1)

[a] These are dominated by transitions from $(j,\ell) = (2,3)$ channel

[b] See reference 26

[c] The number in parentheses denotes the power of ten by which the entry should be multiplied.

Table 3. Timing study using the R matrix propagation method
for two runs on the electron-N_2 scattering problem
of reference 26.

Function	computation time (sec)[a]	
	N/P = 15[b]	N/P = 15/9[c]
Calculation of $\underset{\sim}{D}$	9.1	8.8
Diagonalization of D	40.7	39.9
R matrix propagation	24.1	7.5
Asymptotic analysis	0.6	0.8
Miscellaneous	1.5	1.4
Total	76.0	58.5

	computing time (as a percentage of 76.0 sec)	
Calculation of $\underset{\sim}{D}$	12	12
Diagonalization of $\underset{\sim}{D}$	54	52
R matrix propagation	32	10
Asymptotic analysis	1	1
Miscellaneous	2	2
Total	100	77

[a] MNF compiler, Cyber 74 computer.

[b] 572 sectors

[c] 561 sectors

Table 4.   Computation times (in sec) for body-frame
close coupling calculations on electron-N_2
scattering using the integral equations
program.

N^a	CDC 7600[b]	Cyber 74[c]
14	12.2	61
9	7.0	35
8	6.3	31.5
7	5.5	27.5

[a] number of coupled channels

[b] NCAR FORTRAN compiler

[c] converted using Table 1

Table 5. Computation times (in sec) generated by equations
(113)-(120) for He + H_2.[a]

N	P	Reference mode	Propagation mode
		Calculation and diagonalization of $\underset{\sim}{D}$	
14	14	9.2	0.0
	11	9.2	0.0
	8	9.2	0.0
11	11	5.3	0.0
	8	5.3	0.0
8	8	2.6	0.0
		Propagation	
14	14	5.7	4.6
	11	3.5	2.8
	8	1.9	1.4
11	11	3.5	2.8
	8	1.9	1.4
8	8	1.9	1.4
		Total	
14	14	15.9	5.4
	11	13.7	3.6
	8	12.1	2.2
11	11	9.8	3.6
	8	7.2	2.2
8	8	5.5	2.2

[a]MNF compiler, Cyber 74 computer

Table 6. Transition probabilities $P_{vv'} = |S_{vv'}|^2$ for the model He-H$_2$ system[a] at $E = 4\hbar\omega$.[b]

description of basis		$v_{max} = 5$	$v_{max} = 3$	adiabatic
N/P		6/6	4/4	6/4
v	v'			
0	1	1.33(-1)[c]	1.30(-1)	1.33(-1)
0	2	2.04(-3)	1.65(-3)	2.04(-3)
0	3	4.97(-7)	4.56(-7)	4.9(-7)
1	2	5.51(-1)	4.61(-2)	5.51(-1)
1	3	3.09(-5)	1.11(-5)	3.3(-5)
2	3	2.11(-3)	7.76(-5)	2.2(-3)

[a]The system is described in references 64 and 65

[b]The results are from reference 29

[c]The number in parentheses denotes the power of ten by which the entry should be multiplied

Table 7. Transition probabilities $R_{vv'} = |S_{vv'}|^2$ for the model He-H$_2$ system[a] at $E = 8\hbar\omega$.[b]

description of basis		$v_{max} = 8$	$v_{max} = 7$	adiabatic
N/P		9/9	8/8	9/8
v	v'			
0	6	1.77(-6)[c]	4.03(-6)	1.77(-6)
1	4	7.33(-2)	6.98(-2)	7.33(-2)
1	6	3.31(-5)	5.15(-5)	3.32(-5)
2	5	2.58(-2)	2.26(-2)	2.58(-2)
4	6	1.90(-2)	1.11(-2)	1.90(-2)

[a]The system is described in references 64 and 65

[b]The results are from reference 29

[c]The number in parentheses denotes the power of ten by which the entry should be multiplied

Table 8. Rotational excitation cross sections $\sigma^J_{0 \to j}$, (a_0^2) for transitions from the ground rotational state for He-HF at $E = 0.05$ eV.[a]

description of basis	$j_{max} = 4$	$j_{max} = 3$	$j_{max} = 2$	adiabatic
N/P	15/15	10/10	6/6	10/6
j'		$J = 4$		
1	2.06(-1)[b]	2.03(-1)	2.36(-1)	2.25(-1)
2	9.75(-2)	9.57(-2)	1.62(-1)	9.55(-2)
3	2.70(-2)	2.86(-2)		
j'		$J = 12$		
1	4.83(-1)	4.82(-1)	5.42(-1)	4.94(-1)
2	1.74(-1)	1.75(-1)	2.58(-1)	1.59(-1)
3	3.38(-2)	3.56(-2)		

[a]See references 28 and 29

[b]The number in parentheses denotes the power of ten by which the entry should be multiplied

Table 9. Partial cross sections $\sigma^{4}_{04 \to 2\ell'}$ (a^{2}_{0}) for He–HF for

J = 4 and E = 0.05 eV.[a]

description of basis	$j_{max} = 4$	$j_{max} = 2$	adiabatic
N/P	15/15	6/6	10/6
ℓ'			
2	2.88(−2)[b]	4.82(−2)	2.72(−2)
4	4.57(−2)	4.26(−2)	2.49(−2)
6	4.30(−2)	7.07(−2)	4.34(−2)

[a]See references 28 and 29

[b]The number in parentheses denotes the power of ten by which
the entry should be multiplied

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