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Citation: The Journal of Chemical Physics **77**, 4431 (1982); doi: 10.1063/1.444445
View online: http://dx.doi.org/10.1063/1.444445
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Solution of vibrational excitation problems with constant step size Magnus propagators: Convergence, perturbation analysis, and approximate decoupling

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(Received 6 October 1981; accepted 16 November 1981)

Constant step size Magnus propagators are used to integrate the Secrest–Johnson vibrational excitation problem with parameters given by Stechel, Walker, and Light. Calculations are done for a six channel basis for $E = 6$ and 8 and for a 30 channel basis for $E = 60$. For all the calculations the error scales as the fourth power of the step size for small steps. This indicates a significant cancellation between the errors in the Magnus propagation and the assumed diagonalization of the potential over each interval. The error grows rapidly when the step size is such that at least one channel is propagated by near half a wavelength. The errors in the $E = 6$ calculation are compared with those for the log derivative, renormalized Numerov, R matrix propagation methods, and a quadratic approximate potential method. The constant step size Magnus method is superior to the other methods for this vibrational excitation problem. A perturbation analysis is presented to show why accurate calculations are possible with large nonclassical steps, since we have used steps much larger than those usually recommended for use with the Magnus propagator. Finally, a perturbative calculation of the transform that diagonlizes the potential matrix is described. The perturbative transform is rapidly calculated, and gives excellent results for diagonalizations at large distances.

I. INTRODUCTION

Over the past 15 years there has been considerable interest in quantum mechanical calculations of inelastic and reactive collision processes. For inelastic processes the practical work in quantum calculations consists of solving a system of coupled linear second order differential equations. A review of many of the methods that have been used to solve such systems has been published recently by Secrest.[1] Widely used methods can be classified as approximate solution or approximate potential, and each of the methods has its own proponents. Although there is general agreement in the literature that there is no method that is ideal for all problems, it is still interesting to ask which of various methods is optimum for a given problem. In this paper we consider carefully the solution of the coupled equations that describe the excitation of an oscillator in a collinear collision. This quantum mechanical problem was first accurately solved by Secrest and Johnson,[2] and we study here the vibrational excitation problem defined by Stechel, Walker, and Light[3] (SWL). We solve these equations by means of the Magnus propagator method[4] with *constant* step size over the integration range. We find that this constant step and potential method is superior to the log derivative,[5,6] renormalized Numerov,[4] and variable-step R matrix propagation[3] methods. Our simple Magnus method is also superior to an approximate potential method that fits the quasiadiabatic potential to a quadratic function.[7] We also find that surprisingly large steps may be used in the nonclassical region. The best method for solving quantum problems is necessary to know in order to compare the effort of a quantum method, with semiclassical approaches.

This paper is divided into five major sections. Section II describes our implementation of the Magnus method in some detail. We give useful formulas for the first step propagation, and a simple way to avoid numerical overflow.

In Sec. III we use the constant step Magnus propagator method on the six channel SWL problem with $E = 6$ and 8, and on a 30 channel problem with $E = 60$. For all of the problems, for sufficiently large numbers of intervals the error for the integration is proportional to h^4. All the calculations exhibit a marked increase in error when the step size is large enough to allow propagation of a channel by half a de Broglie wavelength. This rapid increase in error is further evidence for the "magic π" instability discovered by Mitchell and Anderson.[8] For the $E = 30$ calculation interesting structure in the inelastic probabilities reflects the number of maxima in the probability function for the initial oscillator displacement.

In Sec. IV the Richardson extrapolation[9] of our calculations is considered. We find that the convergence of the method is of a simple form.

In Sec. V a perturbation treatment of the nonclassical propagator is presented. The analysis shows that large step sizes can be used in the nonclassical region! This result clearly shows that workers in the past have used needlessly small step sizes in the nonclassical region and near the turning point.

Finally, in Sec. VI a perturbative calculation of the matrices that diagonalize the Hamiltonian is presented. The calculation of the approximate transformation matrices only takes M^2 multiplication for a M channel problem. At large collision distances where the perturbative method is valid, the transformation matrices can be computed much more rapidly than with usual numerical methods that take several M^3 operations. A method is also presented here to potentially shorten the work involved in transforming the wave function and its derivative between intervals.

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II. EFFICIENT USE OF MAGNUS PROPAGATOR METHOD

We first outline the use of the Magnus propagator method to solve the coupled Schrödinger equation

$$[\mathbf{1}(d^2/dr^2) + \mathbf{1}k^2 - \mathbf{U}(r)]\Psi = 0 \ , \tag{1}$$

where k^2 is the reduced collision energy, $\mathbf{1}$ is the identity matrix, and $\mathbf{U}$ is the reduced potential energy matrix. Much of the following discussion has been published by Light and co-workers in various places,[4,10–12] but we have found Eqs. (6) and (7) and the use of constant step sizes after the first step to be particularly useful for efficient Magnus calculations.

The range of the variable r after the first step of length h_1 is divided into intervals of length h. In the ith interval from r_1 to r_2 the wave function Ψ and potential $\mathbf{U}(r)$ are transformed into the basis that diagonalizes $\mathbf{U}(r)$ at the midpoint of the interval $\bar{r} = (r_1 + r_2)/2$. In this new basis the potential and wave function are

$$\begin{aligned} \mathbf{H}(r) &= \mathbf{T}_i^T \mathbf{U}(r) \mathbf{T}_i \ , \\ \Phi(r) &= \mathbf{T}_i^T \Psi(r) \ , \end{aligned} \tag{2}$$

where $\mathbf{T}_i$ is an orthogonal matrix and $\mathbf{T}_i^T$ is its transpose. Within the interval the potential $H(r)$ is replaced with its value at $\bar{r}$

$$\mathbf{H}^0 = \mathbf{H}(\bar{r}) \ .$$

As a result of this approximation, Eq. (1) becomes a set of uncoupled equations inside the interval

$$\left(\mathbf{1}\frac{d^2}{dr^2} + \mathbf{1}k^2 - \mathbf{H}^0\right)\Phi = 0 \ . \tag{3}$$

The propagators are defined in the usual manner as

$$\begin{bmatrix} \Phi(r_2) \\ \Phi'(r_2) \end{bmatrix} = \begin{bmatrix} C1 & C2 \\ C3 & C4 \end{bmatrix} \begin{bmatrix} \Phi(r_1) \\ \Phi'(r_1) \end{bmatrix} \ . \tag{4}$$

The propagators $C1$, $C2$, $C3$, $C4$ are diagonal M by M matrices, and for H^0 assumed constant we can easily obtain the Magnus propagators. Defining

$$X_m \equiv |k^2 - H^0_{mm}|^{1/2} \ ,$$

the propagators are

$$\begin{aligned} C1_{mm} &= C4_{mm} = \cos[X_m(r_2 - r_1)] \ , \\ C2_{mm} &= X_m^{-1} \sin[X_m(r_2 - r_1)] \quad \text{for } k^2 > H^0_{mm} \ , \\ C3_{mm} &= -X_m \sin[X_m(r_2 - r_1)] \ , \\ C1_{mm} &= C4_{mm} = \cosh[X_m(r_2 - r_1)] \ , \\ C2_{mm} &= X_m^{-1} \sinh[X_m(r_2 - r_1)] \ , \quad \text{for } k^2 < H^0_{mm} \ , \\ C3_{mm} &= X_m \sinh[X_m(r_2 - r_1)] \ . \end{aligned} \tag{5}$$

We now consider important details for the efficient use of the method. We will find it convenient to define the quasiadiabatic log derivative matrix, $D(r)$ as

$$\mathbf{D}(r) \equiv \Phi'(r)\Phi^{-1}(r) \ .$$

This matrix is the inverse of the $\mathbf{R}$ matrix of Light and Walker,[10] and the following discussion can be easily modified to give expressions in terms of the $\mathbf{R}$ matrix.

The first interval is subject to the boundary conditions at the starting radius r_0

$$\begin{aligned} \Psi(r_0) &= \mathbf{0} \ , \\ \Psi'(r_0) &= \mathbf{1} \ , \end{aligned}$$

where $\mathbf{0}$ is the zero matrix and $\mathbf{1}$ is the unit matrix. For this choice of boundary conditions the elements of the wave function and log derivative matrices at the end of the first interval are simply

$$[\Phi(r_2)]_{ij} = \delta_{ij} \ , \tag{6}$$

and

$$[\mathbf{D}_0(r_2)]_{ij} = X_i \delta_{ij} / \tanh(X_i h_1) \ .$$

We note that at the end of an interval, the quasiadiabatic wave function corresponding to $\mathbf{D}$ is always the identity matrix. The explicit treatment of the first interval is recommended because it allows the use of a large first step without encountering numerical overflow.

Now for subsequent intervals we must calculate $\mathbf{T}_{i+1}^T \mathbf{T}_i$,

$$\Phi_{i+1}(r_1) = \mathbf{T}_{i+1}^T \mathbf{T}_i \ ,$$

and

$$\Phi'_{i+1}(r_1) = [\mathbf{T}_{i+1}^T \mathbf{T}_i] \mathbf{D}_i(r_2) \ .$$

Once the $\mathbf{T}_{i+1}^T \mathbf{T}_i$ matrices are calculated and stored, only one matrix multiplication is necessary to form the new quasiadiabatic wave function for the $i+1$ interval. Now $\Phi_{i+1}(r_2)$ and $\Phi'_{i+1}(r_2)$ are calculated with Eq. (4) and the log derivative matrix $\mathbf{D}_{i+1}(r_2)$ is easily obtained with a linear equation solver.

The propagation is continued to the final value of r where the $\mathbf{S}$ matrix is evaluated with standard techniques.[13,14]

The procedure works well as long as the elements of $\Phi_{i+1}(r_2)$ and $\Phi'_{i+1}(r_2)$ are kept within the numerical range of the computer. Deep inside the nonclassical region, we have found it convenient when working with large step sizes to subdivide the interval in the transformed basis. The algorithm we use is to find the channel j with the largest value of $|k^2 - U(\bar{r})|^{1/2}$ and to propagate with several subintervals of length h/N where

$$N = \text{int}[X_j h/50] + 1 \ . \tag{7}$$

The log derivative matrix is calculated after each subinterval and is used for the next subinterval. The subdivision allows the elements of Φ and Φ' to grow by maximum factors of 5×10^{21} in an interval.

Finally, our experience with the problems treated in this paper is that the most efficient Magnus method uses constant integration steps. This conclusion is a marked departure from the existing literature on such calculations. It appears that the errors in approximating the quasiadiabatic potentials as constants and in using discontinuous rotations of the basis tend to optimally cancel when constant steps are used. Our attempts at using variable steps have always yielded larger errors for the same number of intervals used in a constant step calculation. However, we stress that we have shown the superiority of the constant step size Magnus method only for the SWL problem.

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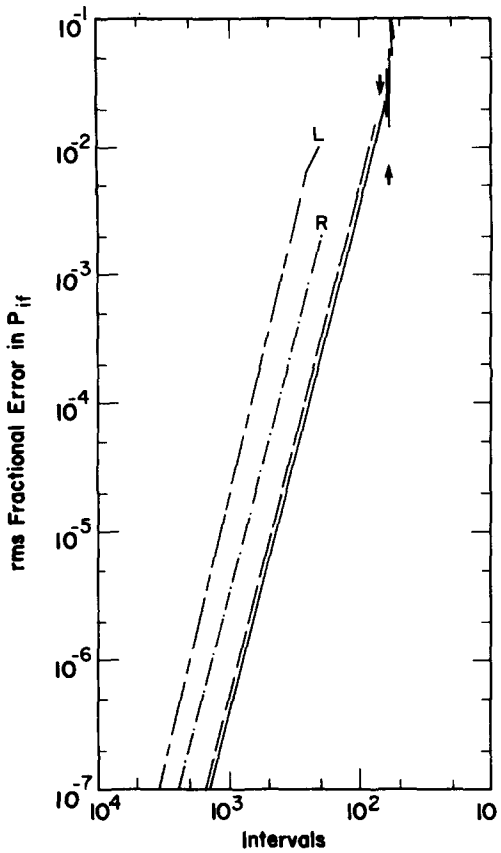

FIG. 1. The lines represent the rms fractional error [Eq. (A1)] for the six channel vibrational excitation problem vs the number of propagation intervals. The solid line is for the constant step Magnus propagator at $E=6$, and the dashed is for $E=8$. The dot–dash line is the error of the renormalized Numerov method (Ref. 6) for $E=6$, and the long–short dashed line is the error of the log derivative method (Ref. 6). The two arrows represent the number of intervals that yields $kh=\pi$. The arrow pointing upward is for $E=6$, and the arrow pointing downward is for $E=8$. The errors are referred to a first Richardson extrapolation of calculations with 25 600 and 12 800 intervals.

III. TEST CALCULATIONS

The method discussed in Sec. III is now applied to the solution of the Secrest–Johnson[2] collinear vibrational excitation problem. The Schrödinger equation for this problem is

$$\left[-\frac{1}{2m}\frac{\partial^2}{\partial x^2}-\frac{1}{2}\frac{\partial^2}{\partial y^2}+\tfrac{1}{2}y^2+V(x-y)-\frac{E}{2}\right]\Psi=0\ ,$$

where the interaction potential is

$$V(x-y)=A\exp[-\alpha(x-y)]\ .$$

Recently accurate transition probabilities have been obtained by Stechel, Walker, and Light[3] for the parameters: $m=\frac{2}{3}$, $A=41\,000$, and $\alpha=0.3$ for $E=6$ and 8. They use a six channel expansion of the wave function and an integration range of $0\le x\le 100$. We have used these same parameters in some of the following calculations. The problem has three closed channels for $E=6$ and two for $E=8$.

We have used constant interval sizes ($h=100/N$, where N is the number of intervals) for most of the calculations. Constant interval sizes are the simplest choice, and if such a choice works it is likely to be efficient. The calculations are done with DEC 11/780 UNIX Fortran 77 using 8 byte arithmetic.

The convergence of the calculations is shown in Fig. 1 where the definition of rms fractional error is given in Appendix A. We note that there is uniform monotonic convergence $0(h^4)$ for sufficiently large numbers of intervals. For smaller numbers of intervals the method exhibits an apparent instability and more or less random probabilities are found. The results become inaccurate when propagations of near one-half a de Broglie wavelength are attempted. (Note arrows in Fig. 1.) For $E=6$ and 8 the number of intervals that correspond to less than half a wavelength of the most classical channel are 59 and 69. Monotonic convergence is found for $N=66$ and 77 in the calculations. A complete analysis of the magic π instability is presented by Mitchell and Anderson.[8] We show that the magnitude of the error in the Magnus propagator abruptly changes when the product $X_m h$ approaches π. The error is only proportional to a small term ϵ^2 for smaller step sizes but is proportional to ϵ for $X_m h$ near π!

We note that excellent accuracy can be obtained with a rather small number of steps. In fact the accuracy of the results quoted by Stechel, Walker, and Light is obtained with only 700 intervals. SWL used 4500 intervals in their calculations. Much of the extra effort done by SWL is spent doing small variable steps in the region of maximum coupling. We find in our work that variable steps are not necessary.

The error for $E=6$ and for $h=1$ introduced with a large first step is shown in Fig. 2. We see that a very good calculation is possible by using a first step of 27. The wave function is much too small for smaller r to have any effect on the final calculation of the **S** matrix. However, we would expect that smaller first steps would be necessary for higher collision energies. To help establish a criterion for general estimation of the first step, we have calculated the squares in Fig. 2. They are drawn at the midpoint of various intervals and they are determined by the expression

$$Y(r+\tfrac{1}{2})=\exp\left[\frac{3}{4}\int_r^{r_s}X_s(r')dr'\right]\ , \tag{8}$$

where X_s is determined as in Eqs. (5) by the smallest eigenvalue of $\mathbf{U}(r)$, and r_s is the turning point for this channel. The quantity defined by Eq. (8) is clearly related to the form of the semiclassical expression for a wave function determined by $H^0_{ss}(r)$.

The six channel calculation clearly works well, and to further illustrate the efficiency of constant step size Magnus calculations we have integrated a 30 channel, $E=60$ problem using the SWL potential with equal steps from 0 to 100. At this energy all 30 channels are open, and although the system is unphysical, it provides convincing evidence for the stability of the method. Some of the transition probabilities are exhibited in Figs. 3 and 4. The probabilities range from a minimum of 2.86

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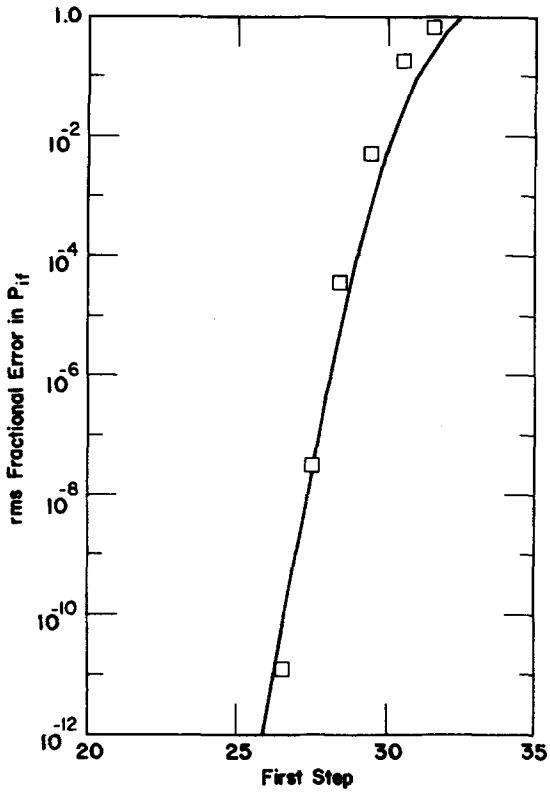

FIG. 2. The line represents the rms fractional error for the six channel problem vs the size of the first integration step. The squares are given by Eq. (8). Errors are referred to a calculation with $h_1 = h = 1$.

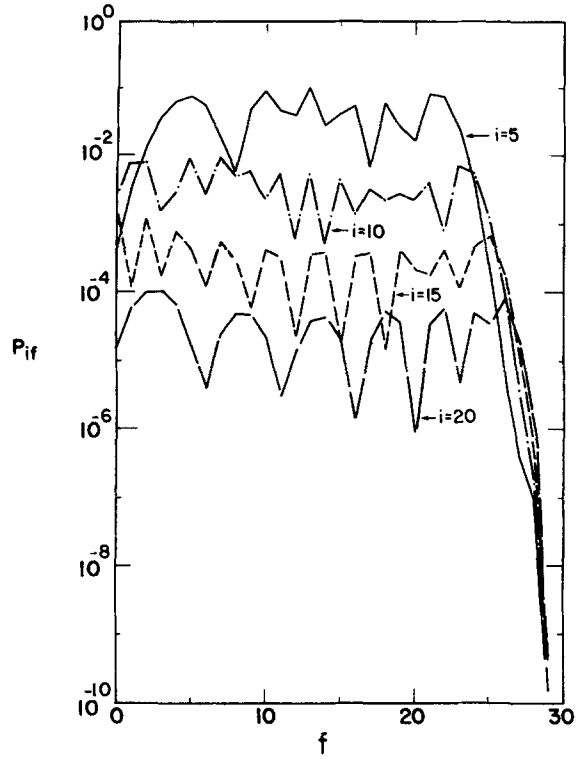

FIG. 4. Same as Fig. 3, but for initial oscillator states $i = 5$ (solid line), $i = 10$ (dot–dash line), $i = 15$ (short dash line), and $i = 20$ (long dash line). The plotted probabilities are the two probabilities multiplied by the following factors for display clarity: 1 for $i = 5$, 0.1 for $i = 10$, 0.01 for $i = 15$, and 0.001 for $i = 20$.

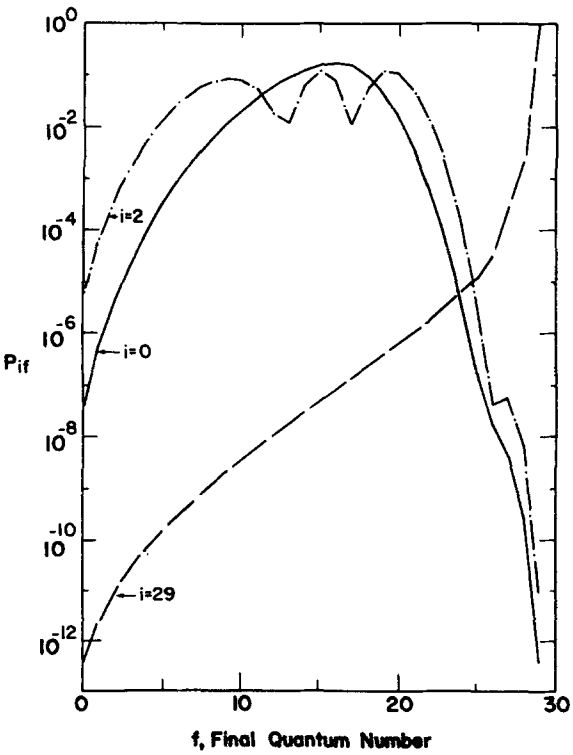

FIG. 3. Inelastic transition probabilities for the 30 channel, $E = 60$ calculation are plotted against the final quantum number f of the oscillator. The solid line is the excitation for initial oscillator state $i = 0$. The dot–dash line is for initial oscillator state $i = 2$. The dashed line is for initial oscillator state $i = 29$.

$\times 10^{-13}$ for $0 \rightarrow 29$ or $29 \rightarrow 0$ to a maximum of 0.172 for $0 \rightarrow 16$ or $16 \rightarrow 0$.

The transition probabilities also exhibit interesting structure. For example although P_{0f} exhibits only a single maximum at $f = 16$, P_{2f} exhibits three maxima at $f = 9$, 15, and 19. P_{5f} exhibits six maxima and P_{10f} exhibits 11 resolved maxima. Fewer maxima are found for larger initial quantum numbers. The results show that there are $i + 1$ maxima for $i \leq 10$. Since the probabilities are known at only 30 possible values of f, it is not likely to resolve more than 11 or 12 maxima. Hence, the trend toward $i + 1$ peaks is lost and broader maxima structure are found for $i > 10$.

The maxima are very pronounced, and this is clear when the logarithmic nature of the scale in Figs. 3 and 4 is noted. The simplest explanation of the structure of the P_{if} for $i \leq 10$ is that the transition probabilities from a given initial state are sensitive to the displacement of the oscillator. The probability of finding an oscillator (quantum number i) with a given displacement exhibits $i + 1$ maxima.

The convergence of the 30 channel Magnus propagator method for $E = 60$ is shown in Fig. 5. Again $0(h^4)$ convergence is found, and the error grows rapidly in the vicinity of the magic π. A rms fractional error of 10^{-3} is found with only 250 intervals. The importance of the rms fractional error is that it shows that even the tran-

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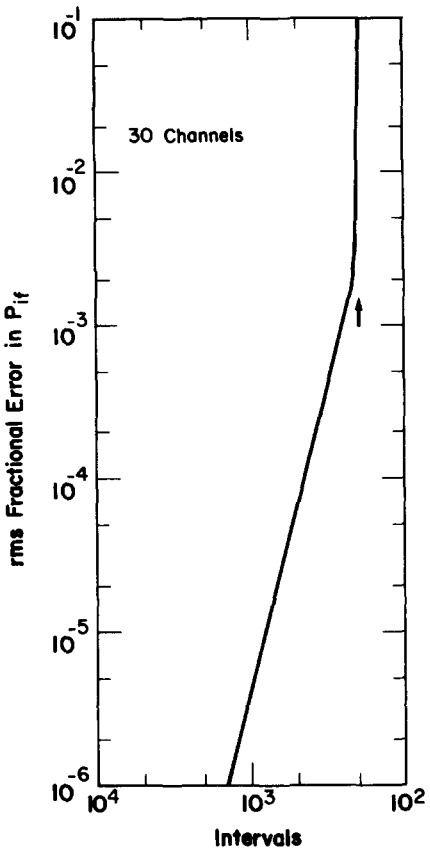

FIG. 5. The solid line represents the rms fractional error for the 30 channel problem vs the number of propagation intervals. The arrow represents the number of intervals that yield $kh=\pi$. The errors are referred to a first Richardson extrapolation of calculations with 800 and 400 intervals.

sition probabilities of size 2.86×10^{-13} are determined to better than 3% with 250 intervals with the maximum error estimate of Appendix A. The actual error in $P_{0,29}$ is 0.3%. The R matrix is symmetric and the S matrix is unitary to more than 13 decimal places.

IV. RICHARDSON EXTRAPOLATION

We have exploited the uniform $0(h^4)$ convergence of the results to use a Richardson extrapolation[9] of probabilities calculated with N and $2N$ intervals to obtain a much more accurate result. Mitchell and Anderson[8] have completely described the method and have found it as useful in scattering calculations as Johnson[15] has found it for bound state calculations.

We note here that for the Secrest–Johnson problem a probability P^N obtained with N intervals is given for sufficiently large N ( ) as

$$P^N = P^* + \frac{a}{N^4} + \frac{b}{N^6} + \frac{c}{N^8} .$$

Hence, if the terms involving b and c are ignored, the first Richardson extrapolation gives

$$P^* \simeq \frac{2^4 P^{2N} - P^N}{2^4 - 1} .$$

The results of the first Richardson extrapolation can be used to then eliminate the N^{-6} term with a second extrapolation. A third extrapolation on the results of the second will eliminate the N^{-8} term.

Table I illustrates the effectiveness of the method at $E=6$ for P_{02}. We note that the third Richardson extrapolation of calculations with 100, 200, 400, and 800 intervals has about the same accuracy as an unextrapolated calculation with 25 600 intervals! In terms of total work the 800 interval third Richardson result is roughly comparable to a single calculation with 1500 intervals.

Although no one in their right mind is likely to want probabilities for a physical system to one part in 10^{12}, we present the Richardson extrapolation to this accuracy to illustrate the remarkable stability and lack of round-off error in the Magnus method.

V. PERTURBATION ANALYSIS OF THE NONCLASSICAL MAGNUS PROPAGATOR

The results of the model calculations of Sec. III indicate that highly accurate calculations are possible when

TABLE I. Richardson extrapolation on P_{02} for $E=6$.[a]

N	No extrapolation	1st	2nd	3rd
100	0.501 166 572 372			
200	0.503 768 350 323	0.503 941 802 186		
400	0.503 936 256 227	0.503 947 449 954	0.503 947 539 601	
800	0.503 946 821 640	0.503 947 526 001	0.503 947 527 208	0.503 947 527 159
1 600	0.503 947 483 052	0.503 947 527 146	0.503 947 527 164	0.503 947 527 164
3 200	0.503 947 524 407	0.503 946 527 164	0.503 947 527 164	0.503 947 527 164
6 400	0.503 947 526 992	0.503 946 527 164	0.503 947 527 164	0.503 947 527 164
12 800	0.503 947 527 153	0.503 947 527 164	0.503 947 527 164	0.503 947 527 164
25 600	0.503 947 527 164	0.503 947 527 165	0.503 947 527 165	0.503 947 527 165

[a]Probabilities calculated with ending radius of 100. The entries in the table are $P_{02}\times10^5$. The true P_{02} for the SWL potential differs slightly from the accurate values shown. An accurate calculation with an ending radius of 150 gives

$$P_{01}=0.221\,093\,172\,087\times10^{-1},\quad P_{02}=0.503\,947\,554\,932\times10^{-5},\quad P_{12}=0.898\,031\,229\,026\times10^{-3}.$$

This longer integration for P_{02} differs by 2.7768×10^{-13} from the most accurate entries in the body of the table.

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large step sizes are used in the nonclassical region. This result has been overlooked by previous workers,[3,4] who determine step sizes for the Magnus method by requiring that the first correction term in the Magnus series must be small compared to the constant potential term. We will now show with perturbation theory that the higher order terms tend to cancel to make error estimates based on the first correction term needlessly conservative.

We consider the one dimensional Schrödinger equation

$$\frac{d^2\psi}{dr^2} + [k^2 - U(r)]\psi = 0 \ . \tag{9}$$

We also restrict our attention to nonclassical regions of r. Within an interval of the variable r from r_1 to r_2 the two by two propagator matrix C is defined by the relation

$$\Psi(r_2) = C\Psi(r_1) \ , \tag{10}$$

where in this section

$$\Psi(r) = \begin{bmatrix} \psi(r) \\ \psi'(r) \end{bmatrix} \ .$$

The constant potential approximation computes an approximate propagator C_0 that becomes equivalent to the exact propagator C as the interval length h approaches zero. Expanding the potential $U(r)$ in a Taylor series about the midpoint of the interval $\bar{r}$

$$U(r) = U(\bar{r}) + (r - \bar{r})U'(\bar{r}) + \cdots \ .$$

Defining $U^0 \equiv U(\bar{r})$ and replacing the exact potential with U^0 we obtain

$$\frac{d^2\psi_0}{dr^2} - q^2\psi_0 = 0 \ , \tag{11}$$

where q is the effective wave number

$$q \equiv [U^0 - k^2]^{1/2} \ . \tag{12}$$

The Magnus propagator C_0 is equal to the exact propagator C when the potential is constant. When the potential is not constant Ψ_0 and C_0 are zeroth-order approximations to the corresponding exact quantities. The wave function ψ may be written as a combination of the zeroth-order wave function ψ_0 and a correction term ψ_p

$$\psi = \psi_0 + \psi_p \ .$$

The function ψ_p is a solution of the inhomogeneous equation

$$\frac{d^2\psi_p}{dr^2} - q^2\psi_p = [U(r) - U^0](\psi_0 + \psi_p) \ . \tag{13}$$

A first-order estimate ψ_1 of ψ_p is found by assuming that ψ_0 is much greater than ψ_p in Eq. (13) and considering only the linear deviation from the constant approximation to the true potential. Thus, the first-order correction ψ_1 is a solution of

$$\frac{d^2\psi_1(r)}{dr^2} - q^2\psi_1(r) = U'(r - \bar{r})\{\cosh[q(r - r_1)]\psi_0(r_1) + q^{-1}\sinh[q(r - r_1)]\psi_0'(r_1)\} \tag{14}$$

in the nonclassical region. The boundary conditions are $\psi_1(r_1) = \psi_1'(r_1) = 0$ and we assume $\Psi_0(r_1) = \Psi(r_1)$. With Laplace transforms the solution of the perturbation Eq. (13) is found to be

$$\begin{aligned} \psi_1(r_2) &= -\epsilon\psi(r_1) \ , \\ \psi_1'(r_2) &= \epsilon\psi'(r_1) \ , \end{aligned} \tag{15}$$

where the perturbation ϵ is

$$\epsilon = [U'(\bar{r})/4q^3][(qh)\cosh(qh) - \sinh(qh)] \ . \tag{16}$$

The perturbation Eqs. (15) for $\psi_1(r_2)$ and $\psi_1'(r_2)$ may be combined with the Magnus propagator C_0 to obtain an equation for the perturbation propagator C_1 that is correct to first order

$$\Psi(r_2) \approx C_1\Psi(r_1) \ , \tag{17}$$

where

$$C_1 = \begin{bmatrix} \cosh(qh) - \epsilon & q^{-1}\sinh(qh) \\ q\sinh(qh) & \cosh(qh) + \epsilon \end{bmatrix} \ . \tag{18}$$

Propagator C_1 differs from C_0 only by $\pm\epsilon$ in the diagonal terms.

We apply the propagator defined by Eq. (18) to the stabilized wave function that we write as

$$\begin{bmatrix} \psi(r_1) \\ \psi'(r_1) \end{bmatrix} = \begin{bmatrix} 1 \\ D(r_1) \end{bmatrix} \ . \tag{19}$$

The zeroth-order estimate of $D(r_2)$ is now $D_0(r_2)$ and $D(r_2)$ is the log derivative correct to first order. By neglecting ϵ in Eq. (18), it is easy to show that

$$D_0(r_2) = \frac{q[\tanh(qh) + D(r_1)]}{1 + D(r_1)\tanh(qh)} \ . \tag{20}$$

For large qh,

$$D_0(r_2) = q \ .$$

Now we can calculate the fractional error in $D_0(r_2)$ as

$$\delta = [D(r_2) - D_0(r_2)]/D_0(r_2) \ . \tag{21}$$

For small h, a Taylor series expansion gives

$$\delta \simeq \frac{U'(\bar{r})h^3}{6} \ . \tag{22}$$

This expression is equivalent to the error introduced by the first correction term in the Magnus series. For large h, the error depends on $U'(\bar{r})$, h, q, and $D(r_1)$. However, the messy expression for δ is well approximated for small and large x as

$$\delta = \frac{U'h}{q^2}\frac{x - 1 + (x + 1)\exp(-2x)}{4x} \ , \tag{23}$$

where $x = qh$. We see that δ is proportional to $\Delta V/[U(\bar{r}) - E]$, where ΔV is the change in the potential over the interval and E is the kinetic energy of the one dimensional system. The expression in brackets approaches 0.25 for large x.

To show that the error for large steps will be small for the systems considered in this paper we assume that: $U(r) = U^0\exp(-\alpha r)$ so that since $U(\bar{r}) = q^2 + k^2$, $U'(\bar{r}) = -\alpha(q^2 + k^2)$. For $\bar{r}$ sufficiently far in the nonclassical region, $q^2 \gg k^2$ so we conclude that a useful approxima-

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tion to $U'(\bar{r})$ is $-\alpha q^2$. Hence, Eq. (23) predicts that

$$\delta = \frac{-\alpha h}{4}$$

for large qh. Since $\alpha = 0.3$ for the SWL potential, we find a *noncumulative* error of -0.075 for $h=1$. This error is not serious, and it is clear that large step sizes can be used in the nonclassical region! The error predicted by Eq. (22) is $-\alpha q^2 h^3/6$, which would require that the quantity q^2h^3 must be equal to 1.5 to yield an error of -0.075. Clearly, needlessly small h are predicted for large q when errors are calculated with Eq. (22).

The error in $D_0(r_2)$ for intervals near the classical turning point needs special attention. The errors for such intervals may be quite large. We consider an interval with its center at the turning point. Now $q=0$ and

$$D_0(r_2) = \frac{D(r_1)}{1+D(r_1)h} .$$

A first order perturbation analysis like the preceding for $q=0$ gives the relative error at the turning point as

$$\delta = \frac{\sigma[2+D(r_1)h]}{1+D(r_1)h-\sigma} , \tag{24}$$

where $\sigma = U'(\bar{r})h^3/12$. Now

$$U'(\bar{r}) = -\alpha k^2 .$$

For $h=1$, $\alpha=0.3$, $k=1.82$, we have δ in the range -0.076 to 0.153 depending on whether $D(r_1)$ is large or small. These values for δ are expected to give a reasonable calculation. As we have noted previously the error in constant approximate potential methods appears to grow rapidly when qh is near π. For purely repulsive potentials this is equivalent to $kh=\pi$. Although we have ascribed this magic π instability to propagation in the classical region, it is necessary to consider the possibility that propagation near the turning point may explain the instability, or at least prevent the calculation from converging for values of $h<\pi/k$.

For $kh=\pi$, the expected relative error for $D(r_1)\approx k$ is simply

$$\delta = \frac{\sigma(2+\pi)}{1+\pi-\sigma} , \quad \text{where } \sigma = \frac{-\alpha\pi^3}{12k} . \tag{25}$$

For $\alpha=0.3$ and $k=1.82$ this error is -0.48. This error is large enough to prevent an accurate calculation for $h=1.73$. This large error for $kh=\pi$ may explain why the SWL calculations for $E=6$ do not start to have monotonic convergence until $h=1.51$. The error for a turning point interval, however, cannot explain the magic π finding for the Olson–Smith[16] calculation of Mitchell and Anderson because there $k=178$, $\alpha=1.475$, and Eq. (25) predicts an error of only -0.0264 for $kh=\pi$. For the $E=60$ vibrational excitation problem $k=7.7$, and the error is -0.113.

We have compared the error estimates of Eq. (24) with exact results using linear, quadratic, or cubic approximations[17] to the potential, and Eq. (24) always gives useful estimates of the error.

Although we have considered in detail only exponential interactions in this section, the error estimates for power law potentials are similar, and in general we expect that large nonclassical steps can be used in coupled channel problems.

Our perturbation analysis treats only the error in the propagation over the quasiadiabatic basis. For coupled channel problems, the rotation of the basis between intervals may be a significant source of error. Consideration of the basis rotation has been built into the step size algorithm of SWL.[3] However, our experience in using constant steps in the integration of curve crossing problems[8,17,18] shows that the magic π instability[8] is much more significant in determining the error than the rapid rotation of the basis in the vicinity of a curve crossing. Furthermore, we have done some variable step size integrations for the SWL problem, and we have always found larger errors in variable step calculations than for the same number of intervals in constant step calculations. Apparently constant steps allow optimum cancellation of the errors in the quasiadiabatic basis and the rotation of the basis between intervals. For example, SWL calculations with step size h for $x>40$ and $h/2$ for $x\leq 40$ have an error about 100 times larger than a constant step of h calculation. (Care is taken to use an even number of $h/2$ intervals so that the end point is always the same.)

VI. APPROXIMATE DECOUPLING METHODS

In the usual implementation of approximate potential methods the **U** matrix is accurately diagonalized by means of Givens, Householder, or Jacobi methods. These methods obtain the eigenvalues and eigenvectors of **U**, but they are time consuming because they require several M^3 operations. Although the diagonalizations are not required for subsequent energies, the time spent in doing the first energy can be very large. We now describe a scheme to greatly shorten the first energy time and which can potentially reduce the transformation at subsequent energies.

The method calculates the transformation matrix **T** by first-order perturbation theory. To this order it is easy to show that the elements of **T** for nondegenerate diagonal elements of **U** are

$$T_{ij} = \begin{cases} 1 , & i=j \\ U_{ij}/(U_{jj}-U_{ii}), & i\neq j \end{cases} . \tag{26}$$

This transformational matrix will be valid whenever a nondiagonal element of **U** is small compared to the difference of the corresponding diagonal elements. This condition is met for large x in the SWL problem. To this approximation the eigenvalues of **U** are simply the diagonal elements of **U**. These eigenvalues are accurate to $O[U_{ij}^2/(U_{jj}-U_{ii})]$ and the off diagonal elements of T^TT have magnitudes of $O[U_{ij}^2/(U_{jj}-U_{ii})^2]$. Hence, we expect the error in this approximation will scale like the square of nondiagonal elements of **U**. For nondiagonal elements of **U** that vary as $\exp(-\alpha r)$, the error should vary as $\exp(-2\alpha r)$. This error rapidly becomes insignificant.

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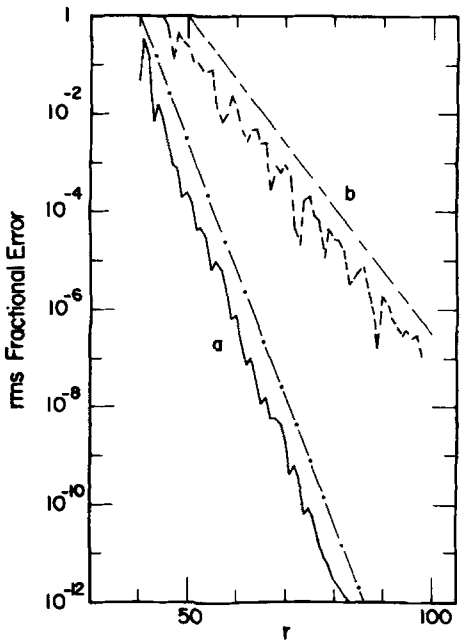

FIG. 6. The rms fractional error vs the radius, r, at which approximate transformation matrices are used. The solid line is for using the perturbative transformation [Eq. (26)] and the short dashed line is for using the identity matrix for transformations. The dot–dash and short–long dash lines are guide lines discussed in the text. The reference for error calculation is the same as for Fig. 2.

Figure 6 shows the effectiveness of the perturbation transformation. The bumpy lines of steeper slope is the error for calculations where Householder diagonalization is used for $x \leq r$ and the perturbative transformation is used for $r < x = 100$. The accompanying straight line (dot–dash) is $\exp[-0.6(r-40)]$, and shows that since the nondiagonal elements in the SWL potential have $\alpha = 0.3$ the error in the perturbation method varies as expected. The less steep bumpy line shows the error in a calculation that uses identity transformation matrices for $r < x = 100$ and the diagonal elements of $\mathbf{U}$ as eigenvalues. The straight line (short–long dash) in this case is $\exp[-0.3(r-50)]$, and shows that the use of zeroth-order transformation matrices has an error that is $O(U_{ij})$. It is interesting to note that the error in stopping the calculation at r is almost identical to the identity transformation errors. Figure 6 shows that an excellent integration is possible by using the perturbative transformations with r as small as 50. The ending radius for stopping an exact diagonalization integration must be at least 72 for the same accuracy.

The perturbative calculation of T involves only M^2 operations, so for a large problem it is very much faster than "exact" diagonalizations. However, in general, the use of the perturbative transformation will still require $2M^3$ or $2\frac{1}{3}M^3$ operations during each interval for each energy. The smaller operation count assumes no stabilization in an interval and the larger count assumes a stabilization by means of a linear equation solver. Obviously, it would be wonderful if a way can be found to substantially reduce the transformation effort. The perturbation calculation can often lead to greatly reduced transformation operations.

For many problems a large fraction of the $\mathbf{U}$ matrix elements are zero. For some of these problems like the calculation of intramultiplet mixing cross sections,[18] the zeros allow block diagonalization and the reduction of a $2M$ channel problem into two M channel problems. For operation counts that scale cubically the transformation and stabilization times are descreased by a factor of 4. Computer storage is also reduced by a factor of 4. However, for other problems a large fraction of $\mathbf{U}$ may be zero, but block diagonalization is not possible. For this situation the perturbation calculation of $\mathbf{T}$ may be very useful, when the product $\mathbf{T}_k^T\mathbf{T}_{k-1}$ has elements approximated as

$$(T_k^T T_{k-1})_{ij} = \begin{cases} 1 & , \ i=j \\ \dfrac{U_{ij}^{(k)}}{U_{ii}^{(k)} - U_{jj}^{(k)}} - \dfrac{U_{ij}^{(k-1)}}{U_{ii}^{(k-1)} - U_{jj}^{(k-1)}} & , \ i \neq j \end{cases} . \quad (27)$$

Now there can be no more nonzero, nondiagonal elements of $\mathbf{T}_k^T\mathbf{T}_{k-1}$ than there are nonzero, nondiagonal elements of $\mathbf{U}$. If all the channels are classical in two adjacent intervals substantial savings in computer time and memory are possible. Up to a factor of ~2 can be realized when stabilizations with general matrix methods are necessary. A greater savings may be found when sparse matrix methods can be used for stabilization.

The simple perturbative approach given here is only useful when the diagonal elements of $\mathbf{U}$ are nondegenerate. We are presently working on extensions of these ideas when degeneracy exists.

VII. DISCUSSION

We have found that the constant step size Magnus propagation method works very well for vibrational excitation problems. It is interesting, however, to compare its accuracy and computational effort with other methods. First, we can compare with results for Johnson's log derivative[5,6] and renormalized Numerov[6] methods because he has published[6] results for the SWL potential at $E=6$. We have converted his errors to our measure and the rms fractional errors are shown in Fig. 1. Both of the methods also exhibit $0(h^4)$ convergence, but the errors for a given number of intervals are 60 times the constant step Magnus error for the log derivative method, and 8.4 times the Magnus error for the renormalized Numerov method. Since the error scales as h^4, to get the same accuracy one must use 270, 170, and 100 intervals for the log derivative, renormalized Numerov, and constant step Magnus to get the same accuracy. The computational effort involved with the log derivative and renormalized Numerov methods is quite small for a problem with a large number of channels M and a simple potential matrix. We estimate that the number of multiplications per step is $7/4\ M^3$ and $5/2\ M^3$ for the two methods. After the first energy the Magnus method requires only $7/3\ M^3$ multiplications per step. Hence, it needs slightly less multiplications than the renormalized Numerov method, and slightly more

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than the log derivative method. We can define the effectiveness of an integration method as one divided by the product of the number of intervals and the number of multiplications per interval needed to achieve a given accuracy. With this definition and for the Magnus efficiency assigned efficiency equal to 1, the log derivative method has efficiency of 0.48, and the renormalized Numerov has efficiency at 0.56. The Magnus method for subsequent energies needs approximately 1/2 the effort needed by the log derivative method. Since we have found that subsequent energy Magnus calculations take only 1/3 as much time as the first energy, the Magnus method will be better than the log derivative method for a calculation done at more than one energy.

We can also compare the error in the constant step Magnus method with the R matrix propagation method of Stechel, Walker, and Light.[3] Their method is essentially a variable step size Magnus method. To compare our results with SWL, we have computed the rms errors for our calculation using Eq. (30) of their paper. A few errors for our work that can be compared with the errors in Figs. 3 and 4 of SWL are 4.2×10^{-5} for 100 intervals, 2.7×10^{-6} for 200 intervals, and 1.7×10^{-7} for 400 intervals. Only the first of these errors will fit on their Fig. 4. However, the reader can easily verify that the minimum SWL error for 100 intervals is 50 times the constant Magnus propagator error. If the maximum SWL error is assumed to be safe, their method requires 1000 intervals to get the same accuracy as the constant Magnus method with 100 intervals. Hence, the R matrix propagator method has a relative efficiency of 0.1 for subsequent energy calculations.

The oscillatory dependence of SWL error on the number of intervals in their Fig. 3 is probably due to having varying numbers of intervals that exhibit the magic π instability. It is certain that at least some SWL intervals have $kh > \pi$ when their step size algorithm is used with a small total number of intervals. This would also explain why the magnitude of the oscillations appears to damp out for large numbers of intervals in their Fig. 4. However, the basically larger error with the variable step method appears to be due to nonoptimum cancellation of errors in the quasiadiabatic propagation and in the rotation of the basis between intervals when variable steps are used. We have tried variable steps while maintaining $qh < \pi$, and we always find larger errors for the same number of intervals.

Additional evidence for cancellation of errors in the Secrest–Johnson problem is the fact that we find $0(h^4)$ convergence. From the perturbation analysis of this paper and of Mitchell and Anderson,[8] the error in each step of the Magnus method is $0(h^3)$. Since the number of steps scales as h^{-1}, the global error for the Magnus method should be $0(h^2)$. This convergence is found for the single and two state problems studied by Mitchell and Anderson. Since the error in the rotation of the basis should also scale as $0(h^2)$, the overall convergence of the Magnus method should converge as $0(h^2)$. However the $0(h^4)$ convergence for the SWL problem, shows that the $0(h^2)$ terms in the propagation and basis rotation errors exactly cancel. The presence of the cancellation for the Magnus method, implies that linear or quadratic approximations to the quasiadiabatic potential should result in $0(h^2)$ error.

This poorer convergence is actually found in the quadratic propagator results of DeVries and George.[7] They solve the $E=6$ SWL problem with an integration range of $10 \le x \le 90$. We have determined accurate probabilities of $P_{01}=2.21093\times10^{-2}$, $P_{02}=5.03947\times10^{-6}$, and $P_{12}=8.98031\times10^{-4}$ for an integration ending at $x=90$. The reader can easily calculate with these values the errors in the DeVries and George results. A log–log plot of this error versus the number of intervals quickly shows that their quadratic approximate potential results converge as $0(h^2)$! Their Magnus results for $N>60$ converge as $0(h^4)$ as we find in this work. It appears that a linear[13,14,19] or quadratic[7,20,21] approximate potential method will be inferior to the Magnus method for Secrest–Johnson vibrational excitation.

The transition probabilities that we find for the $E=60$ calculation are interesting. Assuming that the results are not an artifact of using no closed channels, the results suggest an interesting experiment. If the vibrational transition of a molecule are measured for monoenergetic collisions with an atom, then the structure of the transition probabilities will basically display the initial vibrational state of the molecule. Perhaps the experiment could be done with photon excitation of I_2, collisions with a beam of He, and optical detection of the vibrational transitions. The success of the experiment will depend on the three dimensional nature of actual collisions not affecting the collinear results found here. However, the photo-selection can be used to emphasize collinear collisions. The wave function display may also be found in the "half-collisions" of photodissociation.[22]

The perturbation results of Sec. V show that large steps are possible in the nonclassical region. The truth of this discussion is additionally supported by the superiority of the constant step Magnus method over the log derivative method. The log derivative method has been generally recognized until now as the best method for nonclassical propagation. It would be interesting to compare the Magnus and log derivative methods for propagation of the equations just up to the radius where each asymptotically open channel leaves the nonclassical region.

The perturbative decoupling scheme of Sec. VI is important, because it greatly reduces the work at the first energy. We have found that typically subsequent energies take only 1/3 the time as the first energy when Householder diagonalization is used. With the perturbation calculation of T, the subsequent energies take only about 0.7 as much time as the first energy. The first energy calculation will be as fast as subsequent energies when the ideas in the last part of Sec. VII are appropriate.

The combination of the possibility of large initial steps and perturbative transformations at large r can result in very fast calculations at the first energy. If a calculation with rms error of 3×10^{-3} is desired at

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$E=6$, initial step length of 29 can be used, and perturbative transformations can be used for $r>50$. Hence, only 21 intervals with $h=1$ need to use accurate diagonalization.

The possibility of using perturbative transformations with large numbers of zero elements must be explored in future work. Although the vibrational excitation problem studied in this work does not have zero elements in Sec. V, many channel curve crossing models may have significant numbers of zero elements.

Finally, although constant steps and the simple Magnus propagators appear optimal for the SWL problem, there may be problems where variable steps and higher order propagators are more efficient. We have found that variable steps do not improve the error for a given number of steps for the Olson–Smith problem, but perhaps they will help in problems like rotational excitation. We are presently investigating this possibility.

ACKNOWLEDGMENTS

We wish to acknowledge the contributions to this research by the Macsyma program conceived by the Mathlab Group at M.I.T. The VAX implementation used in this work was supported in part by the U. S. Department of Energy, Contract DE-AM03-765F00034, Project Agreement DE-AS03-79ER10358. (University of California, Berkeley.)

APPENDIX A: ERROR FORMULAS

The rms fractional error σ of the inelastic transition probabilities is calculated with the equation

$$\sigma=(n^2-n)^{-1}\left[\sum_{i\neq j}^{n}(1-P_{ij}/P_{ij}^{*})^2\right]^{1/2}, \tag{A1}$$

where P_i^* is the reference value, and n is the number of open channels.

The significance of the σ values plotted in Figs. 1, 2, 5, and 6 is that the largest possible fractional error of a transition probability must have a magnitude less than $(n^2-n)^{1/2}\sigma$. This upper limit to the error assumes that the other n^2-n-1 inelastic transition probabilities have no error! Hence, for the $E=6$, 8, 60 calculations the maximum possible fractional errors are 2.4σ, 3.5σ, and 29.5σ.

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