JOURNAL OF COMPUTATIONAL PHYSICS 14, 391–419 (1974)

Stability Concepts in the Numerical Solution of Classical Atomic and Molecular Scattering Problems*

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Received August 20, 1973

Stability concepts arising in the numerical solution of ordinary differential equations are reviewed in order to analyze their role in the classical solution of atomic and molecular scattering problems. Treatment of dynamically stable systems is shown to require consideration of the integrator's absolute stability range while treatment of dynamically unstable systems primarily requires the use of stable integrators with small truncation errors. The stability properties of a variety of model scattering problems are considered and restrictions due to absolute stability requirements are related to characteristic frequencies of the system. Dynamic instability due to long range attractive interactions as well as in collinear $H + H_2$ collisions is also discussed. The time dependent eigenvalues of the stability matrix are given for several atom — harmonic oscillator and collinear $H + H_2$ sample trajectories.

INTRODUCTION

Over the past decade, the classical trajectory technique has been firmly established as a useful tool for studying reactive scattering in chemical systems [1]. In addition, classical trajectory techniques have also been used to study a variety of other molecular processes, such as rotational and vibrational energy transfer [2], equilibrium behavior of large systems [3], and molecular scattering off surfaces [4]. Until recently, these studies were primarily in the hands of trajectory "experts," but the technique now appears sufficiently well developed and informative to show signs of becoming part of the tools of the trade for many chemical physicists. Furthermore, recent developments in semiclassical scattering theory [5] indicate that classical dynamics may be useful for the study of quantum as well as classical effects in atomic and molecular scattering. Thus, one can expect to see more studies involving classical trajectory techniques in the near future.

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* Supported in part by grants from the National Science Foundation, GP7907X, GP-31224.

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Despite these developments, little effort has been made to design integrators specifically suited to molecular dynamics problems or to utilize recently developed integration techniques; such efforts require facility with stability concepts which are often unfamiliar to the "molecular dynamicist." Thus, for example, the majority of studies have been carried out using classical Runge–Kutta methods [6]; only recently have more efficient predictor–corrector methods been employed [7].

This paper deals with numerical methods for integrating Hamilton's equations. Our purpose is to clarify the role of absolute, relative and dynamic stability in the practical solution of molecular scattering problems. Section I provides an introduction to these stability concepts. It is specifically designed to provide a much needed summary of the fundamentals of numerical methods for ordinary differential equations. Particular emphasis is placed on the relationship between the stability matrix and the choice of integration technique. In Section 2 the theory is placed in the context of solving Hamilton's equations for atomic and molecular systems and the behavior of the eigenvalues of the stability matrix for several model dynamic systems is discussed.

1. STEPWISE SOLUTION TO COUPLED SETS OF ORDINARY DIFFERENTIAL EQUATIONS [8]

A. Introduction

Consider the initial value problem described by an autonomous system of ordinary differential equations

$$\begin{aligned} d\mathbf{y}/dt &= \mathbf{f}(\mathbf{y}(t)), \\ \mathbf{y}(t_0) &= \mathbf{y}_0, \end{aligned} \tag{1}$$

where $\mathbf{y}$ is k dimensional vector. An example is Hamilton's equations for an n particle dynamical system with Hamiltonian H of the form

$$H = \sum_{i=1}^{r} p_i^2/2m_i + V(q_1, ..., q_r), \tag{2}$$

where $r = 3n$, p_i are the momenta conjugate to the coordinates q_i, m_i are generalized masses, and V is the potential energy. Classically, the time evolution of the system is described by Hamilton's equations [9],

$$\begin{aligned} dq_i/dt &= \partial H/\partial p_i = p_i/m_i \\ dp_i/dt &= -\partial H/\partial q_i = -\partial V/\partial q_i, \end{aligned} \qquad (i = 1, ..., r), \tag{3}$$

where t is the time.

With the initial values of q_i, p_i at time t_0, Eq. (3) forms a system of the type encompassed by Eq. (1). We assume that these equations satisfy the conditions necessary to admit a solution, and that the right hand side of Eq. (3) has as many derivatives as required to satisfy the conditions of theorems leading to the results discussed below.[1]

Knowing $\mathbf{y}$ at time $t_{n-1} = t_0 + (n-1)h$ we might try to obtain $\mathbf{y}$ at some time $t_n = t_{n-1} + h$ via

$$\mathbf{y}(t_n) = \mathbf{y}(t_{n-1}) + h\mathbf{g}(t_{n-1}, \mathbf{y}(t_{n-1}), h), \tag{4}$$

where $h\mathbf{g}(t_{n-1}, \mathbf{y}(t_{n-1}), h)$ approximates the change in $\mathbf{y}$, given exactly by Eq. (1), between times t_n and t_{n-1}. We denote a solution to Eq. (1) at time t_n, obtained by an algorithm such as Eq. (4), by $\mathbf{y}(t_n)$; the exact solution will be denoted by $\mathbf{z}(t_n)$. Successive application of Eq. (4), starting with the given initial condition $\mathbf{y}(t_0) = \mathbf{y}_0$, results in the tabulation of $\mathbf{y}$ at equally spaced values of the independent variable t. Equation (4) describes the general class of one step methods.

If, for example, $\mathbf{g}(t_{n-1}, \mathbf{y}(t_{n-1}), h)$ is taken to be

$$\mathbf{g}(t_{n-1}, \mathbf{y}(t_{n-1}), h) = \left.\frac{d\mathbf{y}}{dt}\right|_{t_{n-1}} + \frac{1}{2}\left.\frac{d^2\mathbf{y}}{dt^2}\right|_{t_{n-1}} h + \cdots + \frac{1}{j!}\left.\frac{d^{(j)}\mathbf{y}}{dt^{(j)}}\right|_{t_{n-1}} h^{j-1}, \tag{5}$$

Eq. (4) is a truncated Taylor series expansion for $\mathbf{y}(t_n)$ about t_{n-1}.

In both one step methods and multistep methods discussed in Section 1D below, one defines the truncation error as the local error made in approximating the change of the dependent variable from time t_{n-1} to t_n. In the case of Eq. (4) with $\mathbf{g}$ given by Eq. (5) it is on the order of $(d^{(j+1)}\mathbf{y}/dt^{(j+1)})|_{t_{n-1}} h^{j+1}/(j+1)!$. A method with a truncation error of the order h^{m+1} is said to be a method of order m. Other errors which enter into the calculated $\mathbf{y}(t_n)$ result from roundoff and other numerical errors introduced in the computation of functions contributing to the right side of Eq. (4). Furthermore, in the nth application of Eq. (4), to calculate $\mathbf{y}(t_n)$ from $\mathbf{y}(t_{n-1})$, we pass on the error accumulated from all preceding steps. Thus, in utilizing methods of the form of Eq. (4), or of any step dependent method, we are concerned not only with the magnitude of the error incurred at each step, but also with the extent to which this error is propagated.

Any numerical method proposed to approximate the solution to Eq. (1) should satisfy two conditions [8]:

(a) In the limit of small enough step size h we can obtain, via application of the method, a numerical solution which is as close to the true solution as desired. A method which satisfies this criterion is said to be *convergent*.

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[1] It is generally assumed that the physical nature of the problem assures that these conditions are satisfied. The necessary requirements are outlined in most texts on ordinary differential equations.

(b) A step size $h_0 > 0$ should exist for each differential equation, such that a fixed change in the initial conditions produces a bounded change in the numerical solution for all $0 < h \leqslant h_0$. A method satisfying this criterion is said to be *stable*.

These are necessary (but not sufficient) conditions for the *usefulness* of a particular method in practice. They essentially guarantee that the method can provide as accurate a solution as desired, and that the method does not amplify the effects of changes in the initial conditions. These are not, however, practical conditions since a method may only satisfy conditions (a) and (b) with an infinitesimal (and hence nonuseful) step size. In practice a finite step size must be used and we want the method to satisfy practical analogues of these requirements, i.e., that (a) by reducing the step size to a still useable value we can obtain a solution with tolerable error, and that (b) for the range of useful step sizes, the method does not amplify changes in the initial conditions.

B. Absolute Stability

The concept of absolute stability is introduced in an effort to obtain a practical criterion for error propagation in a particular numerical method. One considers a special case of Eq. (1), the single differential equation

$$\frac{dy}{dt} = \lambda y, \qquad y(t_0) = y_0 \tag{6}$$

with λ a complex number. We ask how an error, introduced at time t_{n-1} propagates to t_n *for a particular method.* For one step methods, the region of the λh complex plane in which errors introduced at time t_{n-1} do not amplify in the step to t_n defines the region of absolute stability for the particular method. As an example, consider Euler's method (i.e., $\mathbf{g}(t_{n-1}, \mathbf{y}(t_{n-1}), h) = d\mathbf{y}/dt\,|_{t_{n-1}}$ in Eq. (4)) giving

$$\begin{aligned} y(t_n) &= y(t_{n-1}) + \left.\frac{dy}{dt}\right|_{t_{n-1}} h \\ &= y(t_{n-1})(1 + \lambda h). \end{aligned} \tag{7}$$

Assurance that an error introduced at time t_{n-1} is not amplified in the step to t_n requires

$$|\, 1 + \lambda h \,| < 1; \tag{8}$$

i.e., that λh be confined to the unit circle about $(-1, 0)$ in the complex λh plane. This then is the region of absolute stability for the Euler method. Clearly, different methods have different regions of absolute stability. In practical applications we want to vary h so that $h\lambda$ remains in the region of absolute stability, thus reducing local error propagation.

Although Eq. (6) is used to define the region of absolute stability, the region so obtained is useful for other differential equations as well. Consider the system of differential equations given by Eq. (1). If the exact solution of the system at t_n is $\mathbf{z}(t_n)$ and the computed solution is $\mathbf{y}(t_n)$, the error $\mathbf{e}(t_n)$ at time t_n is given by [10]

$$\mathbf{e}(t_n) = \mathbf{z}(t_n) - \mathbf{y}(t_n)$$

and

$$\frac{d\mathbf{e}(t_n)}{dt} = \frac{d\mathbf{z}(t_n)}{dt} - \frac{d\mathbf{y}(t_n)}{dt} = \mathbf{f}(\mathbf{y}(t_n) + \mathbf{e}(t_n)) - \mathbf{f}(\mathbf{y}(t_n)). \tag{9}$$

Assuming that $\mathbf{f}$ is well behaved in the region of $\mathbf{z}(t_n)$ and $\mathbf{y}(t_n)$ we have, for the components of $\mathbf{e}(t_n)$, by the mean value theorem,

$$\frac{d}{dt}\begin{bmatrix} e_1(t_n) \\ \vdots \\ e_k(t_n) \end{bmatrix} = \begin{bmatrix} \frac{\partial f_1}{\partial y_1} & \frac{\partial f_1}{\partial y_2} & \cdots & \frac{\partial f_1}{\partial y_k} \\ \vdots & & & \vdots \\ \frac{\partial f_k}{\partial y_1} & \frac{\partial f_k}{\partial y_2} & \cdots & \frac{\partial f_k}{\partial y_k} \end{bmatrix} \begin{bmatrix} e_1(t_n) \\ \vdots \\ e_k(t_n) \end{bmatrix}, \tag{10}$$

where the matrix $(\partial\mathbf{f}/\partial\mathbf{y})$ (the stability matrix) is evaluated at the mean value, which lies between $\mathbf{y}(t_n) + \mathbf{e}(t_n)$ and $\mathbf{y}(t_n)$. Equation (10) demonstrates that $(\partial\mathbf{f}/\partial\mathbf{y})$ provides an indication of local error propagation, for a system of differential equations. When applied to Eq. (3) this matrix provides a connecting link between local error propagation in the numerical solution of Hamilton's equations and physical properties of the system under consideration. This is considered in greater detail in Sections 1F and 2 below.

Analogy with the discussions above regarding Eq. (7) suggests that $h\lambda_i$, where λ_i are the eigenvalues[2] of $(\partial\mathbf{f}/\partial\mathbf{y})$, should be confined to the region of absolute stability to reduce error propagation. This is indeed the recommended procedure [8] although rigorous results regarding stability regions have primarily been established for coupled sets of *linear* differential equations. Nonlinear equations are usually treated by first subjecting them to linearization; i.e., Eq. (1) is expanded about $\mathbf{y}(t_n)$ to yield

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(\mathbf{y}(t_n)) + \left.\frac{\partial\mathbf{f}}{\partial\mathbf{y}}\right|_{\mathbf{y}(t_n)} (\mathbf{y} - \mathbf{y}(t_n)) + O(h^2).$$

[2] The stability matrix will be diagonalizable if all its eigenvalues are distinct. If the eigenvalues are not distinct then the proof is somewhat more complicated but the same result is obtained. (See Ref. [10].)

Thus, discussions based on the eigenvalues of $\partial\mathbf{f}/\partial\mathbf{y}$ for nonlinear systems are not rigorous but do provide a qualitative guide to local error propagation [8b, Section 3.5].

In practice we can approximate $\partial\mathbf{f}/\partial\mathbf{y}$ or λ_i at the mean value by the value at $\mathbf{y}(t_n)$ if $\partial\mathbf{f}/\partial\mathbf{y}$ or λ_i vary sufficiently slowly. As discussed below (Section 2), for problems in classical molecular dynamics, λ_i can be positive or vary considerably over the course of a trajectory so that it may not be possible to choose or vary h so that it always lies in the region of absolute stability for a given integration method.

C. Higher Order One Step Methods

Euler's method [Eq. (7)] is the simplest application of the Taylor series. Expressions involving higher order terms in the Taylor series result in smaller truncation errors but are computationally slow and tedious due to the need for the higher derivatives. To avoid the evaluation of these derivatives Runge–Kutta methods may be used, methods in which the evaluation of each successive higher derivative is replaced by an evaluation of the function $\mathbf{f}(\mathbf{y})$ at intermediate points in the interval $[t_{n-1}, t_n]$.

Consider for example the second order Taylor series method (the notation used is for one differential equation but is valid for its vectorial analog)

$$y(t_n) = y(t_{n-1}) + \left.\frac{dy}{dt}\right|_{t_{n-1}} h + \frac{1}{2}\left.\frac{d^2y}{dt^2}\right|_{t_{n-1}} h^2. \tag{11}$$

The leading term in the truncation error is of order $(d^3y/dt^3)|_{t_{n-1}}\, h^3/6$. We wish to replace Eq. (11) by

$$\begin{aligned} y(t_n) &= y(t_{n-1}) + \beta h f[y(t_{n-1}), t_{n-1}] + \gamma h f(X, t_{n-1} + \eta h), \\ X &= y(t_{n-1}) + \alpha h f[y(t_{n-1}), t_{n-1}], \end{aligned} \tag{12}$$

where β, γ, η, and α are unknown parameters. Expanding $f(X, t_n + \eta h)$ in a Taylor series, substituting into Eq. (12) and equating powers of h and h^2 in the resulting equation with those in Eq. (11), gives the conditions $\alpha = \eta = 1/(2\gamma)$ and $\beta + \gamma = 1$; that is, three equations in four unknowns. The free parameter may be used to minimize the truncation error (of order h^3), the roundoff propagation, etc., each choice resulting in a different second order method. Higher order Runge–Kutta methods are developed in a similar fashion.[3] As in the above example, their derivation leaves several free parameters which are useful for minimizing

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[3] In high order methods care must be taken to insure that the derivation is valid for systems of equations as well as a single differential equation. (See Ref. [13].)

truncation error, roundoff error, and error propagation. The fourth order Runge–Kutta method, extensively used to obtain solutions to chemical dynamics problems, has the form [11]

$$\mathbf{y}(t_n) = \mathbf{y}(t_{n-1}) + \sum_{i=1}^{4} a_i \mathbf{k}_i , \tag{13}$$

where a_i are constants and $\mathbf{k}_i$ are $\mathbf{f}$ evaluations at various points in the interval $[t_n , t_{n-1}]$. Its region of absolute stability, obtained by applying Eq. (13) to $y' = \lambda y$, is given by

$$\left| \sum_{n=0}^{4} \frac{h^n \lambda^n}{n!} \right| < 1 \tag{14}$$

and is shown in Fig. 1a. The region is considerably larger than that of the Euler method discussed above.

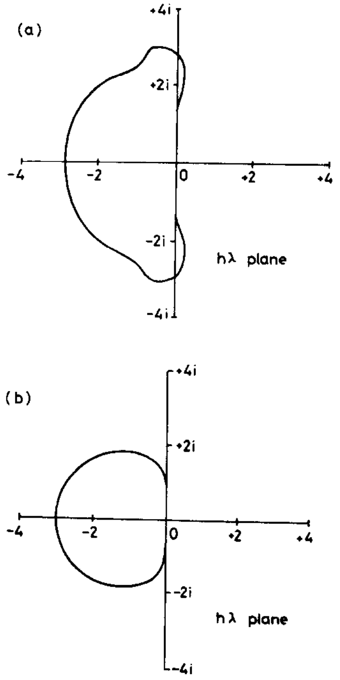

FIG. 1. Absolute stability region for (a) the fourth order Runge–Kutta method and (b) the fourth order Adams–Moulton method.

Runge–Kutta methods have several features which make them useful. The algorithms are simple and possess large regions of absolute stability. They are stable and convergent [12], being simply related to the Taylor series expansion. Furthermore, $\mathbf{y}(t_n)$ is evaluated using values at t_{n-1} only, thus if step size changes become necessary, either to modulate the truncation error or to comply with absolute stability requirements, they may be introduced at any point during the course of the integration. The methods have, however, several undesirable features. First, in order to attain a kth order method, $k \leqslant 4$, $\mathbf{f}(\mathbf{y})$ must be evaluated k times. For $k > 4$ at least $k + 1$ evaluations must be made [13, 14]. If $\mathbf{f}(\mathbf{y})$ is time consuming to evaluate, as it often is in a realistic trajectory calculation, this can be a serious restriction. Furthermore, it is difficult to reliably estimate the local truncation error at time t_n in order to ascertain whether a step size change is required. Modified Runge–Kutta methods which include local truncation error estimates such as the Runge–Kutta–Merson method [15] often require additional evaluations of $\mathbf{f}(\mathbf{y})$ although there are some exceptions [16].

An additional drawback of Runge–Kutta methods, from the viewpoint of computing time, is that they are inefficient. They are based on an interpolation from $\mathbf{y}(t_{n-1})$ to $\mathbf{y}(t_n)$ using evaluations of $\mathbf{f}(\mathbf{y}(t))$ in the interval $[t_{n-1}, t_n]$, i.e., a forward interpolation from t_{n-1}. Thus, although $\mathbf{y}(t_i)$ and $\mathbf{f}(\mathbf{y}(t_i))$ $i = 0,..., n - 1$, have already been evaluated they are not utilized in the step from t_{n-1} to t_n. Methods utilizing these values are referred to as multistep methods and can provide accurate solutions with fewer function evaluations.

D. Multistep Methods and Stability

Multistep methods are conceptually different from one step methods in that the system of differential equations is replaced by a set of linear difference equations which provide a means of obtaining $\mathbf{y}(t_n)$ from the set of values $\mathbf{y}(t_{n-i})$, $i = 1,..., k$ and $\mathbf{f}(\mathbf{y}(t_{n-i}))$, $i = 0,..., k$. They are designed to give $\mathbf{y}(t_n)$ exactly if $\mathbf{y}(t)$ is a polynomial in t of some predetermined order and in this respect are similar to quadrature methods for the integral evaluation [17]. In replacing the system of differential equations by a set of difference equations, one introduces difficulties related to the stability of the method, as discussed below.

The general multistep method may be derived as follows [18]; Equation (1) is rewritten as

$$\mathbf{y}(t_n) = \mathbf{y}(t_{n-1}) + \int_{t_{n-1}}^{t_n} \mathbf{f}(\mathbf{y}(t))\, dt, \tag{15}$$

and $\mathbf{f}(\mathbf{y}(t))$ is approximated by an interpolating polynomial in t with coefficients containing previously known values of $\mathbf{f}$, i.e., $\mathbf{f}(\mathbf{y}(t_{n-1}))$, $\mathbf{f}(\mathbf{y}(t_{n-2}))$....

The integral in Eq. (15) is then easily evaluated giving

$$\mathbf{y}(t_n) = \mathbf{y}(t_{n-1}) + h \sum_{i=0}^{k} \beta_i \mathbf{f}(\mathbf{y}(t_{n-i})), \tag{16}$$

where $h = (t_n - t_{n-1}) = (t_{n-1} - t_{n-2}) = \cdots = (t_{n-k+1} - t_{n-k})$, and β_i are constants characteristic of the interpolating polynomial. This equation provides an approximation to $\mathbf{y}(t_n)$ using values of $\mathbf{y}(t_{n-1})$ and $\mathbf{f}(\mathbf{y}(t_{n-i}))$, $i = 0, \ldots, k$.

Alternatively, $d\mathbf{y}/dt$ can be approximated using a finite difference

$$d\mathbf{y}/dt\,|_{t_n} = \frac{1}{h} \sum_{i=0}^{k} \alpha_i \mathbf{y}(t_{n-i}) = \mathbf{f}[\mathbf{y}(t_n)].$$

Rearranging gives

$$\mathbf{y}(t_n) = -\frac{1}{\alpha_0}\left[\sum_{i=1}^{k} \alpha_i \mathbf{y}(t_{n-i})\right] + \frac{h}{\alpha_0} \mathbf{f}(\mathbf{y}(t_n)), \tag{17}$$

where α_i are constants characteristic of the particular finite difference approximation. Equation (17) gives $\mathbf{y}(t_n)$ in terms of $\mathbf{f}(\mathbf{y}(t_n))$ and $\mathbf{y}(t_{n-1})$, $i = 1, \ldots, k$.

Combining Eqs. (16) and (17) gives the general k-step integration method

$$a_0 \mathbf{y}(t_n) = \sum_{i=1}^{k} a_i \mathbf{y}(t_{n-i}) + h \sum_{i=0}^{k} b_i \mathbf{f}(\mathbf{y}(t_{n-i})), \tag{18}$$

where a_i, b_i are combinations of α_i and β_i.

Although Eq. (18) has been derived by assuming a particular choice of the interpolating polynomial to obtain (16) and finite difference approximation to obtain (17), an alternative approach is possible. We can regard Eq. (18) as a general interpolation formula for $y(t_n)$ and choose a_i, b_i so that Eq. (18) is exact for $y = 1, t, t^2, \ldots, t^p$; the linear form of (18) insures that it is also exact for any $y(t)$ of the form $\sum_{i=0}^{p} C_i t^i$. The method is then of order p with a truncation error for any general $\mathbf{y}(t)$, of $D[d^{(p+1)}\,\mathbf{y}/dt^{(p+1)}]\,h^{p+1}$, with D given in terms of a_i, b_i. With $2k + 2$ constants in Eq. (18), less one for normalization, an interpolating polynomial can be constructed resulting in an integration method of order $2k$. Having obtained the constants a_i, b_i, it is necessary to ascertain whether the method is convergent and stable. It is unfortunately not; in general one cannot construct a stable integration method based on Eq. (18) which is of order greater than $k + 2$ [19]. This result will be discussed in greater detail below.

If, in Eq. (18), $b_0 = 0$, then evaluation of $\mathbf{y}(t_n)$ makes use of the values $\mathbf{y}(t_{n-i})$ and $\mathbf{f}(\mathbf{y}(t_{n-i}))$ for $i = 1, \ldots, k$, and the method is said to be explicit. If $b_0 \neq 0$, then Eq. (18) is a nonlinear equation for $\mathbf{y}(t_n)$ and the method is said to be implicit.

The advantages of methods based on Eq. (18) over one step methods are obvious. In explicit methods ($b_0 = 0$) a step from t_{n-1} to t_n requires only one evaluation of **f**, at $\mathbf{y}(t_{n-1})$, and we can obtain this with a truncation error as small as $O(h^{k+3})$. This provides a considerable saving in computer time over the one step methods where the truncation error is related to the number of function evaluations. Starting at t_0 with $\mathbf{y}(t_0)$ and $\mathbf{f}(\mathbf{y}(t_0))$ known does require the use of a one step method to accumulate k values of **y** and **f**, but this is only a minor inconvenience. A major disadvantage of the k-step method, however, is that step size changes require restarting with a one step method or the inclusion of an auxiliary interpolation procedure. Nevertheless, the multistep methods are usually more efficient than the one step methods.

In one step methods the nature of the Taylor series, and the simple connection between the Taylor Series and the Runge–Kutta method results in methods which are stable and convergent. We have already implied that this is not the case for the multistep methods. To demonstrate the difficulties involved in establishing a stable multistep method we consider a modification of the example due to Hamming [17]. For $k = 3$ and a single differential equation (the argument can be generalized to a system of equations), Eq. (18) becomes, with a_0 absorbed into the other coefficients,

$$y_n - a_1 y_{n-1} - a_2 y_{n-2} - a_3 y_{n-3} = F_n(y),$$

where

$$y_n = y(t_n) \qquad \text{and} \qquad F_n(y) = h \sum_{i=0}^{3} b_i f(y(t_{n-i})).$$

If z_n is the exact solution to the differential equation at t_n, then

$$z_n - a_1 z_{n-1} - a_2 z_{n-2} - a_3 z_{n-3} = F_n(z) + \epsilon_n, \tag{19}$$

where $F_n(z) = h \sum_{i=0}^{3} b_i f(z(t_{n-i}))$. The quantity ϵ_n is nonzero since the true solution to the differential equation does not satisfy the difference equation. The equation for the error $e_n = z_n - y_n$ at time t_n, is then

$$e_n - a_1 e_{n-1} - a_2 e_{n-2} - a_3 e_{n-3} = F_n(z) - F_n(y) + \epsilon_n. \tag{20}$$

The solution to Eq. (20) is a combination of the general solution to the homogeneous difference equation

$$e_n - a_1 e_{n-1} - a_2 e_{n-2} - a_3 e_{n-3} = 0 \tag{21}$$

and a particular solution to Eq. (20). Note that the solution to Eq. (21) may be regarded as the solution of Eq. (20) in the limit of h and $\epsilon_n \to 0$ since $F_n(z)$ and $F_n(y)$ are proportional to h.

The solution to Eq. (21) is obtained by assuming that $e_n = (\rho)^n$. Equation (21) then becomes

$$\rho^3 - a_1\rho^2 - a_2\rho - a_3 = 0, \tag{22}$$

with the general solution

$$e_n = C_1\rho_1{}^n + C_2\rho_2{}^n + C_3\rho_3{}^n, \tag{23}$$

if ρ_1, ρ_2, ρ_3, the roots of Eq. (22), are distinct. C_i are constants dependent on the initial conditions associated with Eq. (20). In general one root, say ρ_1 (the principal root) will equal 1 and corresponds to the behavior of the solution itself. ρ_2 and ρ_3, however, result from the use of y_{n-1} and y_{n-2} in the approximation to the differential equation and are explicit functions of the coefficients a_i. If $| \rho_2 | > 1$ or $| \rho_3 | > 1$ then these terms will dominate the growth of the error and the method would be unstable. To insure that these extraneous roots do not cause the error to grow faster than the solution, a_1, a_2, a_3 must be chosen so that $| \rho_2 |$ and $| \rho_3 |$ are $\leqslant 1$. (ρ_2 or ρ_3 may not equal one since if one does (say ρ_2) the solution to Eq. (22) is $e_n = C_1\rho_1{}^n + C_2 n\rho_2{}^n + C_3\rho_3{}^n$ and once again the extraneous roots dominate the error growth.)

It is worthwhile emphasizing that this result has been obtained in the limit $h \to 0$ and is therefore a stability property of the integrator, independent of the step size h (unlike absolute stability discussed above). Unstable methods must therefore be avoided since variation of h during the calculation cannot correct this difficulty. In general, methods proposed after 1960 explicitly consider stability requirements.[4]

Extension of this type of argument to the k-step method [19] shows that a method is stable if the roots ρ_i of the equation

$$a_0\rho^k - \sum_{i=1}^{k} a_i\rho^{k-i} = 0 \tag{24}$$

are inside or on the unit circle and the roots on the unit circle are distinct. It is this type of condition which leads to the restrictions that stable methods based on Eq. (18) can be at most of order $k + 2$.

As in the case of the one step methods it is necessary to consider finite step sizes, our concern being directed towards insuring that the extraneous roots, for nonzero h, are damped out for large n. This requirement establishes the region of absolute stability in the λh plane. Thus, we consider Eq. (20) with finite h for the differential equation $dy/dt = f = \lambda y$, giving

$$e_n(1 - h\lambda b_0) - e_{n-1}(a_1 + h\lambda b_1) - e_{n-2}(a_2 + h\lambda b_2) - e_{n-3}(a_3 + h\lambda b_3) = \epsilon_n\,. \tag{25}$$

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[4] Recent texts, such as that of Gear [8] and J. W. Daniel and R. E. Moore [18], discuss the stability properties of many older integrators.

The homogeneous difference equation associated with Eq. (25) has the solution $e_n = C_1\rho_1{}^n + C_2\rho_2{}^n + C_3\rho_3{}^n$ where ρ_i are the roots (assumed distinct) of the equation

$$\lambda h(b_0\rho^3 + b_1\rho^2 + b_2\rho + b_3) = \rho^3 - a_1\rho^2 - a_2\rho - a_3\,. \tag{26}$$

The roots are functions of λh and depend on the coefficients a_i, b_j with the principal root ρ_1 behaving like $e^{\lambda hn}$. The region of absolute stability of the method is that region of the λh plane where $|\,\rho_i(\lambda h)| \leqslant 1$.

As an example, consider the fourth order Adams–Moulton method; that is, $a_1 = 1$, $a_2 = a_3 = 0$, $24b_0 = 9$, $24b_1 = 19$, $24b_2 = -5$, $24\mathrm{b}_3 = 1$. The method is stable, since Eq. (22) becomes $\rho^3 - \rho^2 = 0$, with the solution $\rho_1 = 1$, $\rho_2 = \rho_3 = 0$, i.e. all the roots are in, or simple on, the unit circle. The region of absolute stability, obtained from Eq. (26), is shown in Fig. 1b.[5]

Explicit methods based on Eq. (18) provide a simple and direct method of numerically approximating the solution to Eq. (1). In practice, however, implicit methods, which involve the solution of a nonlinear equation for $\mathbf{y}(t_n)$, are more prevelant. Implicit methods are preferred since (a) the region of absolute stability for an implicit method is significantly larger than the region of absolute stability for an explicit method of the same order; (b) the truncation error of the implicit method is generally smaller than for the explicit method; (c) solution of the nonlinear equation in the implicit method by the predictor–corrector method, as described below, allows for an estimate of the local truncation error incurred at each step. The latter can be particularly useful in scattering problems, where the behavior of the system, and consequently the required step size, can differ considerably in the region where the particles are incoming or outgoing and in the region of the strong interaction.

E. *Predictor–Corrector Methods*

In utilizing implicit methods, one must evaluate $\mathbf{f}(\mathbf{y}(t_n))$ when $\mathbf{y}(t_n)$ is yet unknown. Predictor–corrector methods accomplish this task by evaluating an approximate value (the predicted value) of $\mathbf{y}(t_n)$, denoted $\mathbf{y}^*(t_n)$, using an explicit formula (the predictor) and then approximating $\mathbf{f}(\mathbf{y}(t_n))$ by $\mathbf{f}(\mathbf{y}^*(t_n))$ in the implicit formula (the corrector) to obtain $\mathbf{y}(t_n)$ (the corrected value). If $\mathbf{y}(t_n)$ is not sufficiently accurate, it can be regarded as a new predicted value and the corrector reapplied. Not sufficiently emphasized, however, is that this iterative procedure will converge only for a restricted range, dependent on the particular predictor–corrector scheme, of $h\lambda$.

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[5] In this discussion we have neglected the concept of convergence introduced in Section 1B above. The relationship between stability; convergence and Eq. (24) is discussed in detail in [8a] and [21].

The general predictor–corrector scheme is thus based on successive applications of a pair of equations in the form (see Eq. (18))

$$\begin{aligned} \mathbf{y}^*(t_n) &= \frac{1}{a_0}\Big[\sum_{i=1}^{k} a_i\mathbf{y}(t_{n-i}) + h\sum_{i=1}^{k} b_i\mathbf{f}_{n-i}\Big] \\ \mathbf{y}(t_n) &= \frac{1}{c_0}\Big[\sum_{i=1}^{k'} c_i\mathbf{y}(t_{n-i}) + hd_0\mathbf{f}(y^*(t_n)) + \sum_{i=1}^{k'} d_i\mathbf{f}_{n-i}\Big], \end{aligned} \tag{27}$$

where $\mathbf{f}_{n-i} = \mathbf{f}(\mathbf{y}(t_{n-i}))$. Application of this method with one iteration of the corrector requires two evaluations of **f** per step. Since each successive application of the corrector requires an additional **f** evaluation, iteration of the corrector can be very time consuming. Thus, in practice, the corrector is normally applied only once, the step size being made smaller if the resultant $\mathbf{y}(t_n)$ is not sufficiently accurate.[6]

If the predictor is a method of order m with truncation error $\sigma^* \sim O(h^{m+1})$ and the corrector is of order n with truncation error $\sigma \sim O(h^{n+1})$, then the truncation error τ of the predictor-corrector method with the corrector applied once is [21]

$$\tau = \sigma + hd_0\, \partial f/\partial y\, \sigma^* \sim O(h^{n+1}) + O(h^{m+2}), \tag{28}$$

where $\partial f/\partial y$ is a mean value. Thus the order of the predictor-corrector method is $\min[n, m+1]$. For a system of differential equations, Eq. (28) holds with τ, σ, σ^* as vectors and with $\partial f/\partial y$ replaced by the stability matrix.

Normally, the stability properties of the predictor–corrector method are similar to those of the corrector, thus one can get a significant improvement in the range of absolute stability over that obtained for the predictor alone. In practice, the most useful aspect of predictor-corrector methods, however, is that $\Delta_n^{(i)} = |\, y^{*(i)}(t_n) - y^{(i)}(t_n)|$ can provide an estimate to the truncation error occurring in the nth step, where $y^{(i)}$ is the ith component of **y**. Step size changes are made when $\Delta_n^{(i)}$ becomes larger or smaller than given tolerances. Thus, unlike the one step methods where error monitoring is difficult, the monitoring of local errors in these schemes is relatively simple. The actual change of step from h_{old} to h_{new} may be carried out in one of several ways. An obvious but time consuming method is to restart at that point with a one step method. Alternatively, an interpolating polynomial [22] using stored values of **y** and **f** separated by h_{old} may be used to obtain those **y** and **f** values separated by h_{new} required to apply the predictor–corrector scheme with the new step size. It is important to insure that the truncation error of the interpolation formulae are of equal or higher order than the truncation error of the method itself. Otherwise the interpolation routine will restrict the

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[6] This is the approach advocated, for example, by Hamming [17]. More recent developments tend to imply that two applications of the corrector may be more efficient [8b, 20].

accuracy of the method.[7] Step size changes by the interpolation method are usually carried out by either halving or doubling the step, due to the relative ease of these operations. It is necessary, however, to accumulate a certain number of steps of the same size before the step size change can be made. In the case of high order predictor-corrector schemes this requirement becomes very restrictive, the accumulation of a large number of steps being required before the step can be changed. Furthermore, higher order methods tend to have smaller ranges of absolute stability. Thus, higher order methods need not necessarily be more efficient than lower order schemes.

Permitting only halving or doubling, as opposed to arbitrary step size changes, can result in a considerable loss of efficiency. Recently developed variable-mesh methods [18, 24] are designed to overcome this difficulty and increase integrator efficiency; e.g. a reduction of computing time by a factor of two for atom-rigid rotor collisions has recently been attributed to the use of a variable mesh Nordsieck method [25].

Finally we note that a variety of methods, such as extrapolation [26a], variable order [26b], variable coefficient difference equations [26c] and hybrid [26d] methods have been developed and have, as yet, attracted little attention in trajectory studies. Consideration of such methods seems warranted at this time.

F. *Relative and Dynamic Stability*

We have considered two notations of stability—stability of the method, which is a requirement in the limit of $h \to 0$, and absolute stability which relates to finite h. There are two additional interrelated stability concepts which must also be discussed.

Relative Stability. Consider Eq. (6), which has the solution $y(t) = y_0 e^{\lambda t}$, where $y_0 = y(t_0)$. In the examples given above (e.g. the Runge–Kutta, Euler or fourth order Adams–Moulton methods) the region of absolute stability does not include $\mathrm{Re}(\lambda) > 0$. Thus if $\mathrm{Re}(\lambda) > 0$ it is not possible to vary h in order to force λh into the region of absolute stability for any of these methods. Intuitively, the reason for this is clear. The difference equation has a principal root which behaves like the actual solution, i.e., like $e^{\lambda h n}$ for $h \neq 0$ and 1 if $h = 0$. Thus at least one term in e_n will propagate like the solution to the equation, in this case exponentially, and for $\mathrm{Re}(\lambda) > 0$ it is not possible to obtain an h such that the error is not amplified at each step. Nevertheless the equation can be integrated since our primary interest is not to obtain a final error of small magnitude, but rather to obtain an error which is an acceptable fraction of the final solution. Thus, if both the error and solution

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[7] An example is the Nordsieck method [23a]. For an analysis of Nordsieck's step size changing routine see [23b].

grow as $e^{\lambda t}$, $\lambda > 0$ the final solution may still be acceptable. Since the principal root, for finite h, behaves like the actual solution, we can assure that the growth of [redacted] than the principal root. This is said to be the region of *relative* stability.

It is clear that although the principal root behaves like the solution, the extent to which it actually does so depends upon the accuracy, i.e., the size of the truncation error, of the method. As Gear indicates [8a], in practice the accuracy of the solution for cases where $\text{Re}(\lambda) > 0$, is not usually limited by the relative stability criterion. Rather, for methods with extraneous roots to Eq. (24) well within the unit circle, the limiting factor is the requirement to reduce h to sufficiently small size so that the behavior of the principal root accurately reflects the behavior of the true solution. Hence, in practice, if $\text{Re}(\lambda) > 0$, we will want to utilize a method with small truncation error having extraneous roots (for $h = 0$) well within the unit circle, and to carry out the integration with a small step size.

The relative stability criteria may be extended to systems of linear equations. The case of general nonlinear systems of differential equations appears to be considerably more complex [8, 24].

Dynamic Stability. The final notion of stability relates not to the method of integration, but rather to the behavior of the differential equation. For the single differential equation $dy/dt = \lambda y$ if $\text{Re}(\lambda) > 0$ the differential equation is said to be unstable, whereas if the $\text{Re}(\lambda) < 0$ the differential equation is said to be stable. For the system of differential equations $d\mathbf{y}/dt = \mathbf{f}$ stability is defined in terms of the real part of the eigenvalues λ_i of the stability matrix $(\partial f_i/\partial y_j)$. If these eigenvalues are distinct and $\text{Re}(\lambda_i) < 0$ for all the roots, then the system is said to be stable. Since this approach is closely allied to the stability theory of dynamic systems [27] we shall refer to this as *dynamic stability*.[8]

Relative, absolute and dynamic stability are thus coupled in the following sense. If the system of equations displays *dynamic instability* then the relevant notion for their numerical solution is *relative stability*. Alternately, if the system of differential equations is *dynamically stable*, then the relevant notion for their numerical solution is *absolute stability*.[9] The behavior of λ_i, the eigenvalues of the stability matrix, during the time evolution of a dynamic system are seen to provide an indication of the type of integrator most suited to the particular problem.

[8] For a brief introduction to dynamic stability, as well as a review of its recent applications in nonequilibrium thermodynamics. (See Ref. [28].)

[9] We call the attention of the reader to the unfortunate lack of convention in the literature since 1960 regarding stability terminology. Ofttimes authors refer to each of these simply as stability. (As an example of the difficulties one encounters the reader is invited to reread the last paragraph in the text, replacing the words "absolute stability," "relative stability," "dynamic stability," and "stability" by the word "stability.")

2. The Stability Matrix in Classical Atomic and Molecular Scattering

In this section we consider the stability matrix for model scattering problems in order to gain insight into the behavior of λ_i and the relationship between the various stabilities and the physical properties of the system. Examining these model systems allows us to ascertain the extent to which absolute and relative stability criteria enter when solving Hamilton's equations with realistic potentials.

A. *Form of the Stability Matrix*

Hamilton's equations of motion for Hamiltonia of the form given by Eq. (2), are given in Eq. (3). In terms of mass weighted cartesian coordinates

$$\xi_i = m_i q_i \quad (i = 1,\ldots, r)$$

Eq. (3) becomes,

$$\frac{d}{dt}\begin{bmatrix} \xi_1 \\ \vdots \\ \xi_r \\ p_1 \\ \vdots \\ p_r \end{bmatrix} = \begin{bmatrix} p_1 \\ \vdots \\ p_r \\ -m_1 \partial V/\partial \xi_1 \\ \vdots \\ -m_r \partial V/\partial \xi_r \end{bmatrix}, \tag{29}$$

Identifying $\mathbf{y} = (\xi_1 ,\ldots, \xi_r , p_1 ,\ldots, p_r)$ and $\mathbf{f} = (p_1 ,\ldots, p_r , -m_1\, \partial V/\partial \xi_1 ,\ldots, -m_r\, (\partial V/\partial \xi_r))$, the stability matrix $(\partial f_i/\partial y_j)$, defined in Eq. (10), is given by

$$\left(\frac{\partial f_i}{\partial y_j}\right)$$

$$= \begin{bmatrix} \partial p_1/\partial \xi_1 & \cdots & \partial p_1/\partial \xi_r & \partial p_1/\partial p_1 & \cdots & \partial p_1/\partial p_r \\ \vdots & & \vdots & \vdots & & \vdots \\ \partial p_r/\partial \xi_1 & \cdots & \partial p_r/\partial \xi_r & \partial p_r/\partial p_1 & \cdots & \partial p_r/\partial p_r \\ \frac{\partial}{\partial \xi_1}\left[-m_1 \frac{\partial V}{\partial \xi_1}\right] & \cdots & \frac{\partial}{\partial \xi_r}\left[-m_1 \frac{\partial V}{\partial \xi_1}\right] & \frac{\partial}{\partial p_1}\left[-m_1 \frac{\partial V}{\partial \xi_1}\right] & \cdots & \frac{\partial}{\partial p_r}\left[-m_1 \frac{\partial V}{\partial \xi_1}\right] \\ \vdots & & \vdots & \vdots & & \vdots \\ \frac{\partial}{\partial \xi_1}\left[-m_r \frac{\partial V}{\partial \xi_r}\right] & \cdots & \frac{\partial}{\partial \xi_r}\left[-m_r \frac{\partial V}{\partial \xi_r}\right] & \frac{\partial}{\partial p_1}\left[-m_r \frac{\partial V}{\partial \xi_r}\right] & \cdots & \frac{\partial}{\partial p_r}\left[-m_r \frac{\partial V}{\partial \xi_r}\right] \end{bmatrix} \tag{30}$$

$$= \left[\begin{array}{c:c} 0 & I \\ \hdashline A & 0 \end{array}\right],$$

where 0 is an $r \times r$ matrix of zeroes, I is an $r \times r$ unit matrix and A is an $r \times r$ matrix with elements $A_{ij} = -m_i\, \partial^2 V/\partial\xi_i\, \partial\xi_j = -(1/m_j)\, \partial^2 V/\partial q_i\, \partial q_j$.

The eigenvalues λ of the stability matrix satisfy the equation

$$\det \left[\begin{array}{c|c} -\lambda I & I \\ \hline A & -\lambda I \end{array}\right] = 0$$

or

$$\det \left[\begin{array}{c|c} 0 & I \\ \hline A - \lambda^2 I & 0 \end{array}\right] = 0. \tag{31}$$

The roots λ^2 of this polynomial are the same as those of the determinantal equation

$$\det(B - \lambda^2 I) = 0, \tag{32}$$

where B is a symmetric matrix with elements $B_{ij} = -(m_i m_j)^{-1/2}\, \partial^2 V/\partial q_i\, \partial q_j$. Thus the eigenvalues of the $2r \times 2r$ stability matrix for Hamilton's equations occur in pairs $(\lambda, -\lambda)$ and are given by the solution to an $r \times r$ determinantal equation (32). This reduction in dimensionality results from the independence of the momenta p_i and coordinates q_i, as well as the p_i independence of the potential V.

Several general features are obvious from the form of Eq. (32). The eigenvalues are explicitly determined by the masses and potential appearing in the Hamiltonian. The available energy and momenta implicitly influence the eigenvalues by determining the region of coordinate space in which Eq. (32) is to be solved. Furthermore, free translation, which is not associated with any potential will contribute eigenvalues which are zero. In addition, since B is symmetric, λ^2 must be real; i.e., λ is either real or pure imaginary. Since the eigenvalues come in pairs if $\mathrm{Re}(\lambda_i) \neq 0$ then for every exponentially increasing component there is also an exponentially decreasing component.

Equation (32) provides a useful form from which the eigenvalues of the stability matrix may be obtained. In order to gain insight into the meaning of the eigenvalues for physical systems of interest, we consider some model scattering problems below. These model problems are chosen to emphasize some of the essential features of the more complicated three dimensional many body scattering problem.

B. *Model Problems*

i. *Translational–Vibrational Energy Transfer*

We consider the well known problem of the collision of a particle A with an harmonic oscillator *B-C*, the particles being constrained to move along a line.

The Hamiltonain is given by [29]

$$H = \frac{1}{2\mu_1} p_x^2 + \frac{1}{2\mu_2} p_y^2 + V(x, y), \tag{33}$$

where

$$V(x, y) = \tfrac{1}{2}K(y - y_0)^2 + De^{-(x-\gamma y)/L} \tag{34}$$

and

$$\begin{aligned} \gamma &= m_C/(m_B + m_C), \\ \mu_1 &= m_A(m_B + m_C)/(m_A + m_B + m_C), \\ \mu_2 &= m_B m_C/(m_B + m_C). \end{aligned}$$

The coordinate x is the distance between A and the center of mass of BC and y is the $B - C$ distance. The quantities p_x and p_y are the associated conjugate momenta. The masses of A, B and C are m_A, m_B and m_C, K and y_0 are the oscillator force constant and equilibrium distance, respectively. It has been assumed that a repulsive exponential potential of strength D and range L acts between particles A and B. With $P = [De^{-(x-\gamma y)/L}]/L^2$ and $F = (K + P\gamma^2)$, the characteristic equation (32) for this system is

$$\begin{vmatrix} -P/\mu_1 - \Lambda & P\gamma/(\mu_1\mu_2)^{1/2} \\ P\gamma/(\mu_1\mu_2)^{1/2} & -F/\mu_2 - \Lambda \end{vmatrix} = 0, \tag{35}$$

with the solution

$$\lambda^2 = \Lambda = -\frac{1}{2}\left[\frac{P}{\mu_1} + \frac{F}{\mu_2}\right] \pm \left[\frac{1}{4}\left(\frac{P^2}{\mu_1^2} + \frac{F^2}{\mu_2^2}\right) - \frac{PK}{2\mu_1\mu_2} + \frac{P^2\gamma^2}{2\mu_1\mu_2}\right]^{1/2}. \tag{36}$$

To illustrate the physics, we consider two limits of this expression. If the repulsive potential is short range (small L) or weak (small D), or if x is large, then $P \to 0$ and the motion corresponds to essentially free translation of particle A and harmonic oscillation of the pair $B - C$. Equation (36) becomes

$$\lambda^2 = \Lambda = -\frac{1}{2\mu_2}K \pm \frac{1}{2\mu_2}K$$

or

$$\begin{aligned} \lambda_1 &= \lambda_2 = 0, \\ \lambda_3 &= -\lambda_4 = i(K/\mu_2)^{1/2} = 2\pi i/\tau, \end{aligned} \tag{37}$$

where τ is the vibrational period of the harmonic oscillator. The roots λ_1, λ_2 correspond to free translation and λ_3, λ_4 correspond to the unperturbed vibrational motion.

For the oscillator eigenvalues, the restriction that $h\lambda$ lie inside a region in the $h\lambda$ plane is analogous to the condition that the step size h be restricted to less than a particular fraction of the vibrational period. If $| h\lambda | = s$ defines the limit of the absolute stability region for a particular integration method, then h must be less than $s\tau/2\pi$ to prevent error propagation. Thus, for example, for Nordsieck's method [23], where $s = 0.38$, $h < 0.06\tau$ is required to avoid error amplification. In the fourth order Runge–Kutta case, however, $s \sim 2.5$ (see Fig. 1a), hence $h < 0.40\tau$ while the 5th order Adams–Moulton method, with $s \sim 1$ (see [8, Fig. 8.2], requires h to be less than $\sim 0.16\tau$. For anharmonic oscillators these provide first estimates for the range of h applicable with a given integration method. Furthermore, these estimates provide a sample case where absolute stability requirements of a predictor–corrector method (e.g., the Nordsieck method) requiring only two function evaluations per step may force the step size to be so small that it becomes less efficient than the fourth order Runge–Kutta method which requires four function evaluations per step.

In the second limit, that of unperturbed $A - B$ relative motion, (i.e., $K = 0$ and $m_B \gg m_C$) we have $\gamma \to 0, \mu_2 \to m_C, \mu_1 \to m_A m_B/(m_A + m_B)$. The two nonzero roots of Eq. (36) are

$$\lambda_3 = -\lambda_4 = i\left(\frac{D}{\mu_1 L^2}\, e^{-x/L}\right)^{1/2}. \tag{38}$$

Thus, long range potentials (large L), light reduced masses (μ_1 small) or strong potentials (large D) can result in large values of $| \lambda |$ at small x.

In both these limits, Eqs. (37) and (38), the eigenvalues are pure imaginary, i.e., the motion is dynamically stable. Indeed one may easily show that the atom–oscillator system described by Eqs. (33) and (34) is dynamically stable throughout the course of the trajectory, independent of initial conditions. To see this we note that Λ in Eq. (36) can be real and positive only if $PK < 0$, which is not a physically meaningful regime.

The dynamics of vibrational energy transfer for this system has been studied in great detail by Kelley and Wolfsberg [30]. To ascertain the behavior of the eigenvalues of the stability matrix during collision we have repeated their calculations, λ being obtained from Eq. (36) at fixed time intervals. The results shown in Fig. 2 are typical of those obtained. Here $| \lambda_t |$ and $| \lambda_v |$ are the absolute values of the (pure [redacted] the trajectory. Both the $| \lambda_t |$ and $| \lambda_v |$ curves show little structure, with a single peak seen in the region of small intermolecular distances. In some unusual cases, corresponding to multiple collisions [30], $| \lambda_t |$ is bimodal. Large energy transfers were frequently found to be associated with max $| \lambda_t | \cong 2\pi/\tau$, where τ is the unperturbed oscillator frequency. For fixed masses and force constant the maxi-

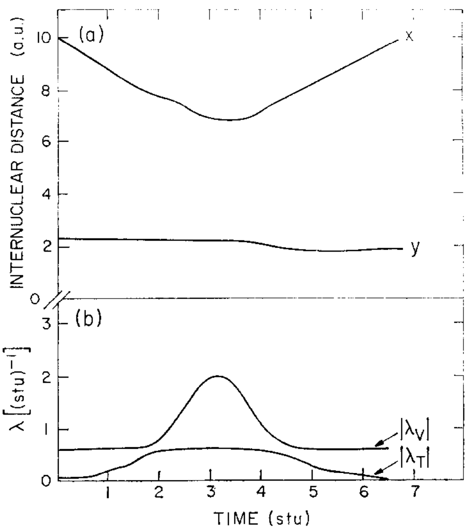

FIG. 2. Sample oscillator-atom trajectory with weak energy transfer; the oscillator is initially nonvibrating; (a) coordinates and (b) stability matrix eigenvalues as a function of time. Solid lines for $|\lambda_v|$ and $|\lambda_t|$ indicate pure imaginary values. The standard time unit (STU) is 0.56×10^{-14} sec.

mum value of $|\lambda_t|$ and $|\lambda_v|$ increases with increasing collision energy, although $|\lambda_t|$ never exceeded $2\pi/\tau$. The largest eigenvalue observed in these studies was $\lambda = 9.839\,STU^{-1}$ ($1.756 \times 10^{15}\,\text{sec}^{-1}$) which, with the Wolfsberg–Kelly stepsize $h = 0.01785\,STU$(1×10^{-16} sec), gives $\lambda h = 0.1756$, a value well within the absolute stability region of the fourth order Runge–Rutta method used. Numerical studies on several sets of trajectories indicate that the stepsize is limited by truncation errors rather than by stability considerations.

ii. *Long Range Attractive Interactions*

For the unbound motion of a particle in a potential well the situation is quite different from that described above. Introducing a long range attractive potential of the form $-C/x^N$, $C > 0$, between A and B, the potential V (Eq. (34)) becomes

$$V(x, y) = \tfrac{1}{2}K(y - y_0)^2 + De^{-(x-\gamma y)/L} - C/x^N. \qquad (39)$$

In the limit of unperturbed $A - B$ motion we are considering unbound motion in the potential well

$$V(x) = De^{-x/L} - C/x^N,$$

and the nonzero eigenvalues of the stability matrix are given by

$$\lambda = \pm i \left(\frac{1}{\mu_1} \left\{ \frac{D}{L^2} e^{-x/L} - \frac{N(N+1)\,C}{x^{N+2}} \right\} \right)^{1/2}. \tag{40}$$

For large x, if $N(N+1)\,C/x^{N+2} > (De^{-x/L})/L^2$, λ is real, the positive λ indicating an unstable dynamic situation. For smaller x, where $D/L^2e^{-x/L} > N(N+1)\,C/x^{N+2}$ the eigenvalues are pure imaginary. Thus, as A approaches B the system passes through a region of positive $\mathrm{Re}(\lambda)$ and errors introduced at this stage will tend to amplify as a result of the instability of the system.

The result is made more general by noting that two nonoverlapping atoms or molecules with centers of mass separated by a distance x interact via a potential which may be described by the multipole expansion [31]. This expansion is comprised of terms of the form C_N/x^N, where C_N depends on the instantaneous orientation of the system. For orientations where the C_N is negative and other interaction terms are small we can obtain positive real λ for motion along x and hence expect error propagation. The magnitude of λ, however, depends upon the precise nature of the interaction.

As discussed in Section *IF*, regions in coordinate space with $\mathrm{Re}(\lambda) > 0$ must be integrated with accurate integration methods having roots to Eq. (24) well inside the unit circle. Although trajectories passing through regions where $\mathrm{Re}(\lambda) > 0$ may be difficult to integrate, accurate solutions can be obtained if sufficient care is taken.

To determine the extent to which a long range attraction alters the behavior of the atom-oscillator system discussed above we have considered several of the atom-oscillator systems of Kelley and Wolfsberg augmented by a coulombic $-1/x$ interaction. [i.e., $C = 1, N = 1$ in Eq. (39)]. The results show that at large x, λ_t is real and small ($\sim 0.18\,STU^{-1}$) and becomes imaginary while still in the region where λ_v is at its unperturbed value. The change in the maximum of $|\lambda_v|$, due to the coulombic term, is only 10 %. The implications of this result are that error propagation due to dynamic instability at long range resulting from attractive interactions is probably serious only if the system remains in the unstable region for extended time periods or, naturally, if the integration is inaccurately carried out in this region.

iii. *Small Vibrations About A Potential Minimum*

We consider N particles interacting through a potential V which displays a minimum at coordinates Q_{i0}. Such systems arise in classical trajectory studies of unimolecular decomposition [32] $A \rightarrow B + C$ and in bimolecular reactions displaying a bound intermediate complex $A + B \rightleftarrows [A - B] \rightarrow C + D$ [33]. In the energy range where the motion consists of small vibrations about the potential minimum, the Hamiltonian H may be approximated by [34]

$$H = \sum_{i=1}^{3N} P_i^2/2m_i + \tfrac{1}{2}\sum_{i,j}^{3N} (\partial^2 V/\partial Q_i \partial Q_j)_0\, Q_i Q_j\,, \tag{41}$$

where Q_i are the cartesian displacements from the potential minimum, and where the subscript 0 indicates that $(\partial^2 V/\partial Q_i\, \partial Q_j)$ is to be evaluated at the potential minimum. P_i are the momenta conjugate to the coordinates Q_i. The characteristic equation (32) becomes

$$\det(B - \Lambda I) = 0,$$

where

$$B_{ij} = -(m_i m_j)^{-1/2}\, (\partial^2 V/\partial Q_i\, \partial Q_j)_0$$

or

$$\det(F - \Lambda' I) = 0, \tag{42}$$

where $F_{ij} = -B_{ij}$ and $\Lambda' = -\Lambda$.

Equation (42) is identical to the secular equation defining the normal modes of the N particle system [34], with the kth normal mode frequency given by $(\Lambda_k')^{1/2}/2\pi$. Defining $\tau_k = 2\pi/(\Lambda_k')^{1/2}$ as the period associated with the kth normal mode, the eigenvalues of the stability matrix are given by

$$\lambda_k = \pm(\Lambda_k)^{1/2} = \pm i(\Lambda_k')^{1/2} = \pm i 2\pi/\tau_k\,, \tag{43}$$

i.e., if there are n normal modes there are two n roots which come in pairs. The restriction on $h\lambda_k$ to insure absolute stability, i.e., $h < s\tau_k/2\pi$ where s is a property of the particular integration method, is seen to restrict h to values less than some fraction of the smallest normal mode period of the system. This is a natural extension of the result obtained above for a single oscillator, but is valid, of course, only in the region where the small vibrations Hamiltonian (Eq. (41)) is applicable.

iv. *Collinear Reactive $H + H_2$*

As a final example we consider the reactive collision of H and H_2 with the atoms restricted to lie along a line. This system which is regarded as a model for simple chemical reactions has been the subject of extensive investigation [35]. The Hamiltonian is given by Eq. (33); x and y coordinates are defined as above. The potential $V(x, y)$ is taken to be the realistic Porter–Karplus (PK) potential surface [36] and is shown in Fig. 3. Characteristic features are a saddle point of 0.396eV at $x = 2.55$a.u., $y = 1.70$a.u., and symmetric troughs which describe the incident and outgoing H_2 diatomics. The diatomic equilibrium intermolecular distance is at 1.40a.u. Reactive scattering occurs along a path of initially decreasing x (oscillating y) and proceeds along a path at ~ 60° angle with respect to the x axis. Nonreactive scattering results when the trajectory is reflected back along the incident path.

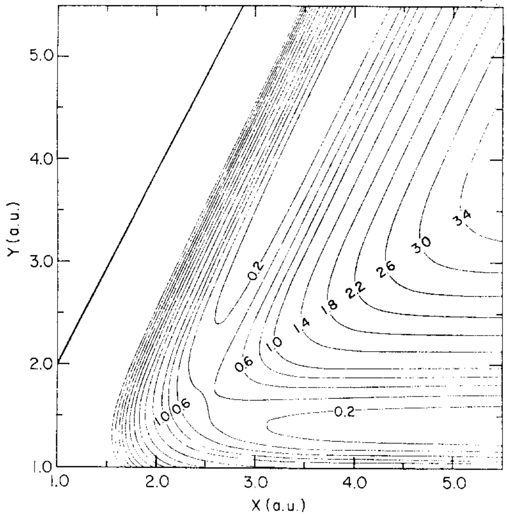

FIG. 3. Energy contours for the Porter-Karplus potential surface for collinear $H + H_2$ [36]. Contours are spaced 0.2 eV apart for energies less than 1.0 eV and are spaced by 0.4 eV for energies greater than 1.0 eV. Regions to the left of the diagonal line in the upper left- of the figure are classically inaccessible for the approach of A to the B end of the B–C diatomic.

Contour diagrams of the two stability matrix eigenvalues are shown in Figs. 4 and 5. The eigenvalue $|\lambda_T|$ (Fig. 4) initially corresponds to translational motion and asymptotically (large x) approaches zero. The second eigenvalue $|\lambda_v|$ (Fig. 5), initially corresponds to vibrational motion of an unperturbed H_2 molecule. In both cases small x or y values are seen to lie in stable regions, whereas large x and y values correspond to a dynamically unstable region. The region of dynamic instability for $|\lambda_T|$ begins at a much smaller x and y value than that for $|\lambda_v|$. In addition, the maximum unstable $|\lambda_T|$ is four times that of $|\lambda_v|$. An incoming H_2 molecule in its lowest vibrational state, will oscillate about $y = 1.40$a.u. and will, for x smaller than ~2.9a.u., pass in and out of the $|\lambda_T|$ region of dynamic instability. A reactive or nonreactive path, at low energies is not expected, however to cross into the region of $|\lambda_v|$ instability.

Sample reactive and nonreactive trajectories for ground state H_2 with 0.483 eV translational energy are shown in Figs. 6 and 7. As expected, $|\lambda_v|$ remains pure imaginary and $|\lambda_T|$ shows oscillations, between dynamic stability and instability, during the close collision. The sharp peakes in $|\lambda_T|$ are a consequence of the rapid

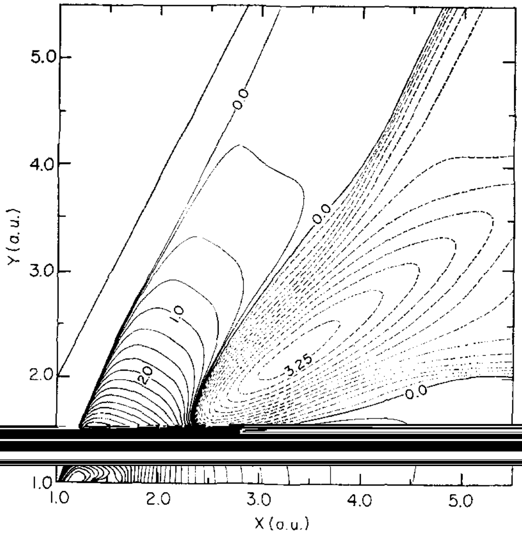

FIG. 4. Absolute value of the first eigenvalue (λ_T) for the *PK* surface (Fig. 3) ————, imaginary values, – – – – – – –, real values. Contours are spaced 0.25 STU^{-1} apart.

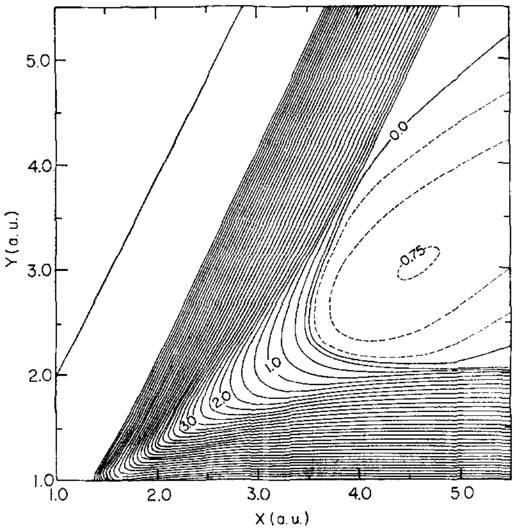

FIG. 5. Absolute value of the second eigenvalue (λ_v) for the *PK* surface (Fig. 3). Notation as in Fig. 4.

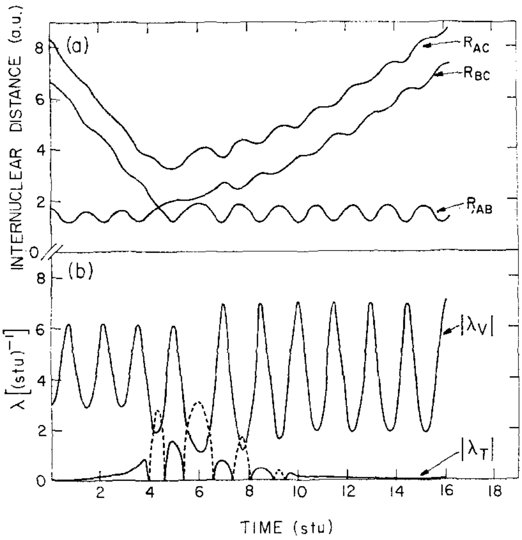

FIG. 6. Sample reactive $H + H_2$ trajectory; (a) coordinates and (b) eigenvalues of the stability matrix, as a function of time. In (b); ————, imaginary values, - - - - - - -, real values. In (a); $R_{AC} = x + y/2$, $R_{BC} = y$, $R_{AB} = x - y/2$.

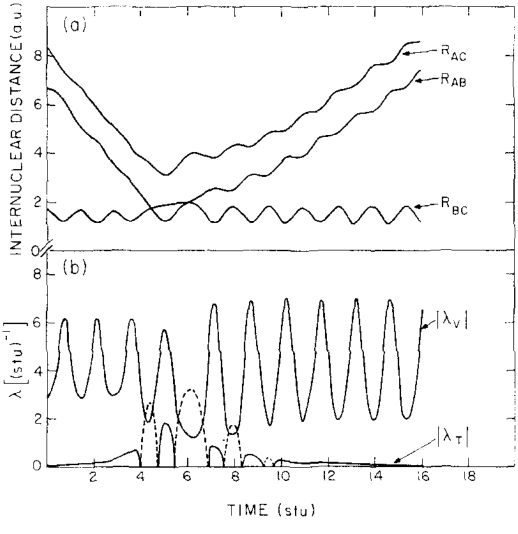

FIG. 7. Sample nonreactive $H + H_2$ trajectory. Notation as in Fig. 6.

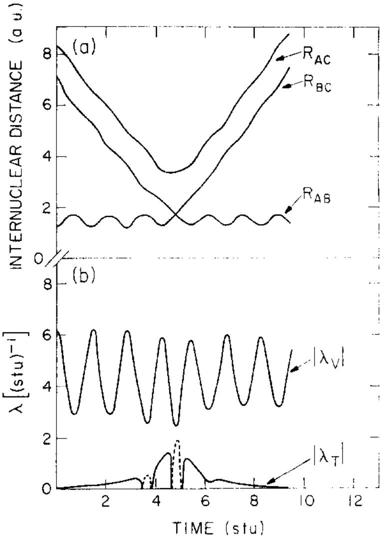

FIG. 8. Shorter sample reactive $H + H_2$ trajectory. Notation as in Fig. 6.

changes in the magnitude and nature of the eigenvalue contours in the region near the saddle point. No apparent difference in the behavior of $|\lambda_v|$ or $|\lambda_T|$ is seen between the reactive and nonreactive trajectories. In addition, the increase in magnitude of $|\lambda_v|$ in the outgoing path is primarily a consequence of vibrational energy transfer into the product H_2 molecule. A somewhat shorter reactive trajectory, more characteristic of those seen in three dimensional calculations[10] [1b], is shown in Fig. 8. Here $|\lambda_T|$ shows only one sharp unstable peak in the region of the close collision. In summary, the system is dynamically stable (in the x, y coordinate system) during the majority of the collision. In the region of close collision, however, error propagation will tend to be large as a consequence of the dynamic instability of the system. The fact that the time spent in the dynamically unstable region is relatively short suggests that excessive difficulty in numerical integration, due to dynamically unstable behavior is not an attribute of the low energy $H + H_2$ system.

CONCLUDING REMARKS

We have considered the general relationship between desirable properties of an integration algorithm and the behavior of the stability matrix [Eq. (10)] for a given

[10] To my knowledge, no one has previously noted that collinear nonreactive $H + H_2$ collisions tend to take place more slowly than collinear reactive collisions. This behavior is not seen for three dimensional collisions and is the subject of more extensive investigations.

system of interest. In addition, we have demonstrated the nature of the stability matrix eigenvalues for a few model problems. Such considerations can lead to more efficient and accurate solutions to problems of chemical interest, either through numerical methods specifically tailored to the problem of interest or via suggestions for alternate coordinate systems in which dynamic instabilities are encountered less frequently. In addition, the relationships between the characteristic frequencies of the system and the absolute stability range of the integrator (Eqs. (37) and (43)), derived via the stability matrix, can aid in the choice of proper stepsizes. Thus far, little attempt has been made to exploit the behavior of the stability matrix. It would seem advantageous to further investigate this matrix particularly for dynamic problems which display strong dependence on initial conditions. Such systems include the formation and dissociation of collision complexes in bimolecular collisions [33], oscillator systems displaying Kolmogorov-Arnold–Moser instability [37] and a variety of models of biological interest [28]. For the notoriously unstable *n*-body gravitational problem [38] some work in this direction has already begun [39].

ACKNOWLEDGMENTS

I should like to thank Professor M. Karplus for encouragement and support during the course of this work. I am also indebted to Dr. W. Neilson for enlightening discussions and to Professor G. Fix for his helpful comments on an early version of the manuscript.

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