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ABSTRACT

Binary reaction problems occur in various circumstances in chemical kinetics, reaction plasma, stellar evolution, and nucleosynthesis.

These processes are governed by equations of the type

$$\underline{n}' = B\,\underline{n}\,\underline{n}\ . \qquad (1)$$

Assuming that the tensor B is symmetric and constant in some time interval Δt, we show that the solution to Eq. (1) is

$$\underline{n}(t) = [I - A(t_0)\,\Delta t]^{-1}\,\underline{n}(t_0)\ , \qquad (2)$$

where $\underline{n}(t_0)$ are the given initial densities and the matrix $A(t)$ is given by $A(t) = B\,\underline{n}(t)$.

Evaluation of the norm conditions for known approximate solutions to Eq. (1) indicates that the proposed solution method will always be as fast as, or faster than, the first-order methods.

I. INTRODUCTION

Binary or quadratic reaction problems occur in a variety of circumstances including chemical combustion processes,[1] reacting plasmas,[2] the analysis of the major burning stages in stellar evolution,[3,4] and nucleosynthesis.[5,6]

The usual analyses are limited to solutions of the equilibrium equations $(\partial n/\partial t \approx 0)$ or to dynamic (or transient) solutions involving only small changes from the initial conditions.

In this report, we exhibit a solution method that is applicable over a wider time region, being restricted only by the assumption that the reaction rate may be adequately approximated as constant in time.

II. BINARY REACTION EQUATIONS.

The binary reaction equations can be written in the form[1-5] $(dn_i/dt = n_i')$

$$\frac{dn_i(t)}{dt} = B_i^{jk}\, n_j(t)\, n_k(t) \ \text{for}\ t_0 < t < t_1, \qquad (1)$$

where the densities at time t, $n_i(t)$, are to be solved in terms of the initial conditions of the components $(i = 1,2,\ldots,N)$, $n_i(t_0)$. The indices i,j,k range over the number of reactants. The reaction rate tensor, B_i^{jk}, is assumed to be symmetric in the upper indices, $B_i^{jk} = B_i^{kj}$. The summation convention on repeated indices is understood.

For this study, we assume that B_i^{jk} is constant in time over the interval $[t_0, t_1]$. Variations in B_i^{jk} owing to density, temperature, or energy dependence[1-5] are assumed to be representable by suitably averaged quantities in the interval $[t_0, t_1]$.

III. SOLUTION REPRESENTATION

The Taylor series representation of Eq. (1) at time $t + \Delta t$ may be written as

$$n_i(t + \Delta t) = \sum_{\ell=0}^{\infty} \frac{[n_i(t)\ \Delta t]^{\ell}}{\ell!} \qquad (2)$$

In principle, we need only evaluate all the derivatives of Eq. (1). If we terminate Eq. (2) at $\ell = 1$ we obtain the first-order approximation given by

$$n_i(t + \Delta t) = n_i(t) + n_i'(t)\ \Delta t$$

$$= n_i(t) + B_i^{jk}\ (t) n_j(t)\ n_k(t)\ \Delta t \quad . \qquad (3)$$

This approximation, or its variants, has been used in the past as a suitable solution representation of Eq. (1). For sufficiently small Δt, Eq. (3) is a valid solution representation.

In obtaining a general solution to Eq. (1), we begin by defining a time-dependent matrix A(t), having elements given by

$$A_i^k\ (t) \equiv B_i^{jk}\ n_i(t) \ . \qquad (4)$$

Then, in vector notation, $[\underline{n}(t) \equiv n_i(t)]$, Eq. (1) is

$$\underline{n}'(t) = A(t)\ \underline{n}(t) \ , \qquad (5)$$

where, of course, A(t) depends explicitly on $\underline{n}(t)$ and implicitly upon t.

To determine the coefficients in the Taylor series of Eq. (2), we differentiate Eq. (5) to obtain

$$\underline{n}''(t) = A'(t)\ \underline{n}(t) + A(t)\ \underline{n}'(t) \quad . \qquad (6)$$

On the other hand, differentiating Eq. (1) and using the symmetry of B_i^{jk} $(= B_i^{kj})$, we have

$$n_i''(t) = B_i^{jk}\ n_j\ n_k' + B_i^{jk}\ n_j'\ n_k$$

$$= 2\ B_i^{jk}\ B_j^{\ell m}\ n_k\ n_\ell\ n_m \quad . \qquad (7)$$

Applying the Eq. (4) definition of A(t) to Eq. (7) yields

$$n_i''(t) = 2\ B_i^{jk}\ n_k\ B_j^{\ell m}\ n_m\ n_\ell$$

$$= 2\ A_i^j(t)\ A_j^\ell\ (t)\ n_\ell \quad , \qquad (8)$$

or, in vector notation,

$$\underline{n}''(t) = 2A^2\ \underline{n} \quad . \qquad (9)$$

Comparison of Eqs. (9) and (6) yields the operator result

$$A'(t) = A^2(t) \quad . \qquad (10)$$

Performing successive differentiations, we obtain

$$\underline{n}^{(\ell)}(t) = \ell!\ A^\ell(t)\ \underline{n}(t) \quad . \qquad (11)$$

For $\ell = 1$ and 2, Eq. (11) is true; see Eqs. (1) and (9). Assume that Eq. (11) is true for ℓ. Differentiating Eq. (11) and using Eqs. (7) and (10), we find

$$\underline{n}^{(\ell+1)}(t) = \ell!\,[\ell A^{\ell-1}(t)\ A'(t)\underline{n}(t) + A(t)\ \underline{n}'(t)]$$

$$= \ell!\,[\ell A^{\ell-1}(t)\ A^2(t)\ \underline{n}(t) + A^{\ell+1}(t)\ \underline{n}(t)]$$

$$= (\ell + 1)!\ A^{\ell+1}(t)\ \underline{n}(t) \ . \qquad (12)$$

Hence, if Eq. (11) is true for ℓ it is also true for $\ell + 1$. By transfinite induction, it is therefore true for all ℓ.

Substituting Eq. (11) into the Taylor series of Eq. (2), we find

$$\underline{n}(t + \Delta t) = \sum_{\ell=0}^{\infty} A^\ell(t)\ (\Delta t)^\ell\ \underline{n}(t) \qquad (13a)$$

$$= [I - A(t)\ \Delta t]^{-1}\ \underline{n}(t) \ , \qquad (13b)$$

provided that the norm $\|\ A(t)\Delta t\ \| < 1$, which is a necessary and sufficient condition for the series to converge.[7] Thus, if Eq. (13a) converges, it converges to the inverse given by Eq. (13b).

By very similar manipulations, we can find the Taylor series expansion of A(t), because

$$A(t + \Delta t) \equiv \sum_{\ell=0}^{\infty} \left.\frac{A^{(\ell)}(\tau)}{\ell!}\right|_{\tau = t} (\Delta t)^\ell$$

$$= \sum_{\ell=0}^{\infty} A^\ell(t)\ (\Delta t)^\ell$$

$$= [I - A(t)\ \Delta t]^{-1}\ A(t) \ , \qquad (14)$$

where we have used the operator result

$$A^{(\ell)}(t) = \ell!\ A^\ell(t) \qquad (15)$$

which is proven analogously to Eq. (11).

Thus, for the reaction rate tensor, B_i^{jk}, not an explicit function of t, the solution to Eq. (1) is given by

$$A(t_0) = B\ \underline{n}(t_0) \qquad (16)$$

$$\underline{n}(t) = [I - A(t_0)\ (t - t_0)]^{-1}\ \underline{n}\ (t_0) \ . \qquad (17)$$

The verification that Eqs. (16) and (17) solve Eq. (1) is straightforward. Multiplying Eq. (17) by $[I - A(t_0)\ (t - t_0)\ (t - t_0)]$ and differentiating, we obtain

$$[I - A(t_0)\ (t - t_0)]\underline{n}'(t) = A(t_0)\ \underline{n}\ (t)\ . \quad (18)$$

Multiplying Eq. (13) by $[I - A(t_0)\ (t - t_0)]^{-1}$ and using Eq. (14) yields

$$\begin{aligned} \underline{n}'(t) &= [I - A(t_0)\ (t - t_0)]^{-1}\ A(t_0)\ \underline{n}(t) \\ &= A(t)\ \underline{n}(t)\ . \end{aligned} \quad (19)$$

Thus for binary reaction problems we may use either Eqs. (16) and (17) or the Taylor series representation given by Eq. (13a). In all instances, however, we must guarantee that the norm of $M(t,t_0)$,

$$||M(t,t_0)|| = ||A(t_0)\ (t - t_0)|| < 1\ , \quad (20)$$

is satisfied for the convergence of the series to the solution.

IV. COMPARISION OF EXACT AND APPROXIMATE SOLUTIONS

Comparison of the K^{th} approximate to the "exact" solution can be made as follows. The K^{th} approximate is given by

$$\underline{n}_K(t) \equiv \sum_{\ell=0}^{K} M^{\ell}\ \underline{n}\ (t_0)\ . \quad (21)$$

The "exact" solution is given by

$$\underline{n}(t) = \sum_{\ell=0}^{\infty} M^{\ell} n(t_0) = (I - M)^{-1}\underline{n}(t_0)\ . \quad (22)$$

Define the norm of $A(t_0)$ as

$$a = ||\ A(t_0)||\ . \quad (23)$$

Then, using Eq. (20) with $\Delta t = t - t_0$ gives

$$||M(t,\ t_0)\ || = ||\ A(t_0)\ \Delta t\ || = a\ \Delta t < 1\ . \quad (24)$$

Equation (21) for the K^{th} approximate can be rewritten as

$$\underline{n}_K(t) = (I - M)^{-1}\ (I - M^{K+1})\ \underline{n}\ (t_0)\ . \quad (25)$$

If we wish to adjust Δt and, hence, M so that the K^{th} approximate differs from the "exact" solution $n(t)$ by less than ε, we must require that

$$||M^{K+1}|| = ||M||^{K+1} = (a\Delta t)^{K+1} < \varepsilon\ . \quad (26)$$

Using Eq. (26), we can calculate the number (K) of terms in the approximate solution Eq. (21) required to represent the exact solution to order ε;

$$K + 1 = [\ell n(\varepsilon)/\ell n\ (a\Delta t)]\ , \quad (27)$$

where, in this instance, the brackets [ ] indicate the greatest integer. This result is summarized in Table I for representative ε and $a\Delta t$ values.

TABLE I

K+1 TERMS FOR ε ACCURACY OF APPROXIMATE SOLUTION

$a\Delta t \setminus \varepsilon$	10^{-5}	10^{-4}	10^{-3}	10^{-2}
10^{-4}	2	1	1	1
10^{-3}	2	2	1	1
10^{-2}	3	2	2	1
10^{-1}	5	4	3	2

Similarily, we may compare the relative computational effort involved in the various order approximations compared to the K^{th} approximate.

A standard technique used for some first-order solutions is to adjust Δt to maintain a certain fractional density change, or

$$\underline{n}(t) - \underline{n}(t_0) \leq \varepsilon\ \underline{n}(t_0)\ . \quad (28)$$

Equation (28) is equivalent to requiring that

$$a\Delta t_0 = \varepsilon\ , \quad (29)$$

where a is defined by Eq. (23) and Δt_0 denotes the time step for this technique.

Using the norm given in Eq. (26) for $K = 1$, on the other hand, we find that for first-order methods we should require

$$(a\Delta t_1)^2 = \varepsilon\ , \quad (30)$$

and for Kth order approximate

$$(s\Delta t)^{K+1} = \varepsilon \, . \qquad (31)$$

Therefore, the relative time steps are given by

$$\frac{\Delta t_0}{\Delta t} = \varepsilon^{\frac{K}{K+1}} \qquad (32)$$

and

$$\frac{\Delta t_1}{\Delta t} = \varepsilon^{\frac{1}{2}\,\frac{K-1}{K+1}} \qquad (33)$$

The number of terms K required to make the Kth approximate agree with the exact solution to $\varepsilon = 10^{-n}$ is determined from Eq. (27), given $s\Delta t$. For the same s, we display the relative time step ratio of Δt_0 or Δt_1 to the Kth approximate, Δt, in Tables II and III.

TABLE II

RELATIVE TIME STEPS $\Delta t_0/\Delta t$ (EQ. 32) FOR $\varepsilon = 10^{-n}$ AND K DETERMINED FROM EQ. (27)

K/n	1	2	3	4	5
1	0.316	10^{-1}	3.16×10^{-2}	10^{-2}	3.16×10^{-3}
2	0.215	4.6×10^{-2}	10^{-2}	2.15×10^{-3}	4.64×10^{-4}
3	0.178	3.1×10^{-2}	5.62×10^{-3}	10^{-3}	1.78×10^{-4}
4	0.158	2.5×10^{-2}	3.97×10^{-3}	6.31×10^{-4}	10^{-4}
5	0.147	2.15×10^{-2}	3.16×10^{-3}	4.64×10^{-4}	6.81×10^{-5}

TABLE III

RELATIVE TIME STEPS $\Delta t_1/\Delta t$ (EQ. 33) FOR $\varepsilon = 10^{-n}$ AND K DETERMINED BY EQ. (27).

K/n	1	2	3	4	5
1	1	1	1	1	1
2	0.681	0.464	0.316	0.215	0.147
3	0.562	0.316	0.178	0.1	0.056
4	0.501	0.251	0.126	0.063	0.032
5	0.464	0.215	0.1	0.046	0.022

Finally we estimate the ratio, f, of the number of operations involved in forming the 1st and Kth order solutions with N components. The initial formation of $A(t_0)$ will involve $\approx \frac{1}{2} N^3$ operations in both instances. In addition, each of the K approximates beyond the first will involve an additional $N^2 + N = N(N+1)$ operations. Thus,

$$f = \frac{1}{1 + \frac{2(K-1)\,(N+1)}{N^2}} \qquad (34)$$

will be approximate speed reduction factor of the computation of the Kth approximate compared to the 1st. The factor f is displayed in Table IV for representative values of K and N.

TABLE IV

SPEED REDUCTION FACTOR f FOR VARIOUS K AND N

K/n	2	4	6	8	10
1	1	1	1	1	1
2	0.4	0.62	0.72	0.78	0.9
3	0.25	0.46	0.56	0.64	0.69
4	0.18	0.35	0.46	0.54	0.60
5	0.14	0.29	0.39	0.47	0.53

Defining $\lambda_1 = \frac{1}{f}\frac{\Delta t_0}{\Delta t}$ and comparing Tables II and IV, we note that $\lambda_1 < 1$ for all $N \geq 2$ and all $K \geq 1$. Further, defining $\lambda_2 = \frac{1}{f}\frac{\Delta t_1}{\Delta t}$ and comparing Tables III and IV, we conclude that $\lambda_2 < 1$ for $N > 2$ and all n, and $\lambda_2 < 1$ for $n > 2$ and all $N \geq 2$. This implies that, except for a small number of components and high inaccuracy, the proposed Kth approximate method is more efficient and faster in overall execution than first-order schemes. This is dramatically emphasized if $\varepsilon \leq 10^{-3}$ and $N \approx 4$ to 6 components for which we see that the Kth approximate method is approximately 30 to 120 times faster than the fractional change method Eq. (29) and approximately 1 to 30 times faster than the first-order method.

V. CONCLUSIONS

We have derived an exact solution to the pure binary reaction problem for a time interval in which the reaction rate is independent of time.

This solution is compared to various approximate techniques. It is shown to be as fast or faster than the lower order approximations for the same accuracy, even though more computation is involved. This is due primarily to the dynamic determination of the approximation order from the required accuracy and normed reaction matrix. In comparison, the lower order or fractional change methods fix the approximation and lower the time step to satisfy the accuracy conditions.

This new solution method automatically reduces to the lowest K^{th} order approximation (including first order) commensurate with the accuracy specified.

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