

Note

Stiffness of the Master Equation for Low-Temperature Reaction Rates

When the master equation is used to describe a chemical reaction taking place at very low temperature, severe cancellation problems are encountered in calculating the eigenvalue corresponding to the reaction rate. A computational strategy which overcomes this difficulty is presented.

1. INTRODUCTION

The difficulty of finding the smallest eigenvalue (corresponding to the reaction rate) of the master equation by standard numerical methods has been described in detail elsewhere [1]. An extreme example of this problem arises in the calculation of the rate of recombination of hydrogen atoms at 77°K. The most reliable method for doing this [2] is to calculate the rate constant k_d for dissociation of H_2 at 77°K and then to obtain the required recombination rate constant k_r from the rate quotient law, i.e., $k_r = K_c^{-1}k_d$, where K_c is the equilibrium constant for the reaction at that temperature. To find k_d , it is necessary to solve for the smallest eigenvalue of a reaction matrix which is of order about 170: its eigenvalues generally span the range from about 10^3s^{-1} (vibrational relaxation rate) to about $10^{13}s^{-1}$ (a predissociation rate), but the smallest one, $\gamma_0 = k_d$ is about $1.2 \times 10^{-301}s^{-1}$ at this temperature [2].

There are two distinct numerical problems here. First, many computing machines can handle only rather small ranges of exponent, e.g., $10^{\pm 38}$ on DEC machines, $10^{\pm 78}$ on IBM machines, and so on; this difficulty is relatively easy to overcome by separating the number from its exponent, and by processing them separately where necessary in the calculation. The more fundamental problem is that of the word length of the machine, i.e., the number of significant figures available in its arithmetic instructions; as a consequence, conventional eigenvalue routines generally only give the smallest eigenvalue to about the same number of significant figures as if the sum of all the other eigenvalues had been subtracted from the trace. Our failure to solve this problem satisfactorily by using standard methods, e.g., Householder reduction followed by bisection or QR, Rayleigh Quotient iteration, inverse iteration, is documented in detail elsewhere [3, 4]; typically, if the temperature was chosen to be 2000°K, where $\gamma_0 \approx 5 \times 10^{-2}s^{-1}$, only two significant decimal places could be achieved when using double-length arithmetic on an IBM machine (i.e., about 16 significant figures per operation).

We discuss first some of the convergence properties of approximations to γ_0 , the

eigenvalue of smallest numerical magnitude of a symmetric reaction matrix written in the form $[A + D]$, where A describes the internal relaxation processes and D is a diagonal matrix representing the reaction steps. Matrix A is symmetric, and has one zero eigenvalue by construction, with the corresponding eigenvector related to the Boltzmann equilibrium population distribution; the nonzero elements of D occur only in positions which project onto elements of this vector having exceedingly small numerical magnitude. We then suggest a strategy for use in practical reaction rate calculations, and demonstrate that it is effective by application to a realistic problem.

2. APPROXIMATIONS TO γ_0

Some methods were developed in [5] to approximate the lowest eigenvalue of a matrix L expressible in the form $[\mu(1 - p_0) + C]$ with $C \geq 0$ and μ being a constant; here, $p_0 = S_0(S_0, \cdot)$, where (\cdot, \cdot) denotes the scalar product, and S_0 is the eigenvector of A corresponding to its zero eigenvalue. In the following, we show that most of the results are valid even when $L = [A + D]$, $A, D \geq 0$, $AS_0 = 0$. In order to avoid unnecessary complications in the exposition, we assume that γ_0 is simple.

Consider the eigenvalue equation

$$[A + D - \gamma_0]\psi = 0. \quad (1)$$

With an arbitrary $\alpha > 0$, (1) is equivalent to

$$[A + D + \alpha p_0 - \gamma_0]\psi = \alpha p_0 \psi. \quad (2)$$

Let $\sigma_0(L)$, $\sigma_1(L)$ denote the lowest and the next lowest eigenvalue of L . Since $\sigma_0(A + \alpha p_0) = \alpha$ one has that $\sigma_0(A + D + \alpha p_0) \geq \alpha$. Thus, for large enough α , $\sigma_0(A + D + \alpha p_0) > \gamma_0$, implying that $(u, [A + D + \alpha p_0 - \gamma_0]u) > 0$ for each u . Letting $u = \psi$, we have that $(\psi, p_0 \psi) > 0$, yielding also that $(S_0, \psi) \neq 0$. Since $[A + D + \xi p_0]$ is continuous in ξ , it has a continuous (normalised) eigenvector $v(\xi)$ such that $v(\xi) \rightarrow_{\xi \rightarrow 0} \psi$, where we take ψ to be normalised also. It follows from the Hellmann-Feynman theorem that

$$\sigma_0(A + D + \alpha p_0) = \gamma_0 + \int_0^\alpha d\xi (v(\xi), p_0 v(\xi)) \geq \gamma_0.$$

Since $(v(0), p_0 v(0)) = (\psi, p_0 \psi) > 0$ and $v(\xi)$ is continuous, however, the integral is strictly positive, yielding that $\sigma_0(A + D + \alpha p_0) > \gamma_0$ for each $\alpha > 0$. Consequently, $[A + D + \alpha p_0 - \gamma_0]^{-1}$ exists. Using further the fact that $(S_0, \psi) \neq 0$, (2) reduces to $\phi(\gamma_0) = 1$, where

$$\phi(x) = \alpha (S_0, [A + D + \alpha p_0 - x]^{-1} S_0). \quad (3)$$

It is clear that $\phi(x)$ is a well-defined positive function on $(-\infty, \sigma_0(A + D + \alpha p_0))$ with $\phi(-\infty) = 0$ and all of its derivatives are positive. It follows, as in [5], that γ_0

is the unique solution of $\phi(x) = 1$ which can be approximated monotonically from above by Newton's method. To be precise, let $x_{m+1} = x_m + (1 - \phi(x_m))/\phi'(x_m)$, $m = 0, 1, 2, \dots$, with $x_0 < \sigma_0(A + D + ap_0)$ such that $x_1 < \sigma_0(A + D + ap_0)$; then $x_m \downarrow \gamma_0$; here, the prime denotes the derivative.

Now, let $\bar{\phi}(x)$, $\chi(x)$ be defined by

$$\bar{\phi}(x) = \alpha - (\alpha - x)\phi(x) = \alpha(S_0, [A + D + ap_0 - x]^{-1} DS_0) \tag{4}$$

and

$$\chi(x) = \frac{\bar{\phi}(x)}{\phi(x)} = \frac{\alpha - (\alpha - x)\phi(x)}{\phi(x)} = \frac{(\alpha - x)\bar{\phi}(x)}{\alpha - \bar{\phi}(x)}. \tag{5}$$

It is obvious that $\phi(x) = 1$ if and only if $\bar{\phi}(x) = x$ and $\chi(x) = x$; i.e., γ_0 is the unique fixed point of $\bar{\phi}(x)$ and $\chi(x)$ in the interval of their definition. In the following, we show that $\chi(x)$ is independent of α .

If B is an invertible matrix and β is a constant, then

$$\begin{aligned} (S_0, [B - \beta p_0]^{-1} S_0) &= (S_0, B^{-1}[1 - \beta p_0 B^{-1}]^{-1} S_0) \\ &= (S_0, B^{-1} S_0) / (1 - \beta(S_0, B^{-1} S_0)) \end{aligned}$$

whenever the terms make sense. Setting $B = [A + D + ap_0 - x]$ and $\beta = (\alpha - x)$, we have that

$$\frac{1}{\chi(x)} = \frac{(S_0, [A + D + ap_0 - x]^{-1} S_0)}{1 - (\alpha - x)(S_0, [A + D + ap_0 - x]^{-1} S_0)} = (S_0, [A + D - (1 - p_0)x]^{-1} S_0). \tag{6}$$

It follows from (6) that $\chi(x)$ is a differentiable decreasing function of x . It is also clear that $\chi(x) > 0$ for each $x \leq \gamma_0$; thus, it is positive for each $x < \xi_0$ with some $\xi_0 > \gamma_0$, defined by $\chi(\xi_0) = 0$. This is sufficient to establish the following result [6]: let $x_{m+1} = \chi(x_m)$ with $x_0 \leq 0$, $x_m < \xi_0$, $m = 0, 1, 2, \dots$; then $x_{2m} \uparrow y_1 \leq \gamma_0 \leq y_2 \downarrow x_{2m+1}$. The condition $x_m < \xi_0$ is equivalent to $\chi(x_{m+1}) > 0$. If $\chi'(x) < 1$ on (x_0, ξ_0) , then $y_1 = y_2 = \gamma_0$. An alternative method, the min. max. method which was described in [5], enables one to obtain converging upper and lower bounds to γ_0 even when $\chi'(x) \geq 1$.

The results to this point are valid with an arbitrary p_0 such that $(\psi, p_0 \psi) > 0$ and, in fact, for the special case where A is tridiagonal (e.g., for the so-called step-ladder model in unimolecular reaction theory), p_0 can simply be taken as $S(S, \)$, where S is the vector $1, 0, 0, \dots$

We now consider the iterative sequence generated by $\bar{\phi}(x)$, i.e., $\{x_m\}$ defined by $x_{m+1} = \bar{\phi}(x_m)$ with x_0 such that $x_m < \sigma_0(A + D + ap_0)$. It is a standard result, again, that if $\bar{\phi}'(x) < 1$ on the interval containing $\{x_m\}$, then $x_m \rightarrow \gamma_0$ [7]. Since

$$|\bar{\phi}'(x)| = |\alpha(S_0, [A + D + ap_0 - x]^{-2} DS_0)| \leq \alpha \|DS_0\| / (\alpha - x)^2,$$

$|\bar{\phi}'(x)|$ can be made arbitrarily small by increasing α ; here $\|\cdot\|$ denotes the norm. Therefore, one can always obtain a convergent $\{x_m\}$. Furthermore, convenient bounds on $|\gamma_0 - x_m|$ are available in terms of $|\bar{\phi}'(x_m)|$ [7]; however, here we show that if $0 < \alpha < \sigma_1(A)$, then $x_m \uparrow \gamma_0$.

It is clear from (4), using $AS_0 = 0$, that

$$\bar{\phi}(x) = \alpha(S_0, [A + D + \alpha p_0 - x]^{-1} PS_0),$$

where $P = [A + D - (1 - p_0)\alpha]$. Now, $(S_0, PS_0) = (S_0, DS_0) \geq 0$ and for any u orthogonal to S_0 , $(u, Pu) = (u, [A + D - \alpha]u) \geq [\sigma_1(A) - \alpha](u, u)$; this is sufficient to conclude that $P \geq 0$ [5]. Hence $P^{1/2} \geq 0$ is well defined and commutes with $[A + D + \alpha p_0]$, which results in

$$\bar{\phi}(x) = \alpha(P^{1/2}S_0, [A + D + \alpha p_0 - x]^{-1} P^{1/2}S_0). \quad (7)$$

From (7) it follows that $\bar{\phi}'(x) \geq 0$, which is sufficient to imply that $x_m \uparrow \gamma_0$ provided that $x_0 \leq \gamma_0$ [5].

It is pertinent to remark here that Newton's method may also be used to approximate the fixed points of $\bar{\phi}(x)$ and $\chi(x)$, i.e., γ_0 [5].

3. THE COMPUTATIONAL METHOD

Since γ_0 is pathologically small, we can safely choose the first approximation $x_0 = 0$. Equation (4) may then be written

$$\bar{\phi}(0) = \alpha(S_0, [A + D + \alpha p_0]^{-1} DS_0) = (S_0, f), \quad (8)$$

where

$$f = \alpha[A + D + \alpha p_0]^{-1} DS_0, \quad (9)$$

i.e.,

$$[A + D + \alpha p_0]f = \alpha DS_0. \quad (10)$$

Forming the scalar product of S_0 with (10), we have

$$(S_0, [A + D + \alpha p_0]f) = (S_0, Df) + \alpha(S_0, f) = \alpha(S_0, DS_0), \quad (11)$$

where we have used the fact that S_0 is the normalised eigenvector of A corresponding to a zero eigenvalue. From (8) and (11), we then get

$$\bar{\phi}(0) = (S_0, f) = (S_0, DS_0) - (S_0, Df)/\alpha. \quad (12)$$

This we have shown to be a lower bound to γ_0 , and the corresponding upper bound, from (5), is $\bar{\phi}(0)/(1 - \bar{\phi}(0)/\alpha)$; in the example we give below, where $\alpha = 1$ and

$\gamma_0 \approx 10^{-50}$, the upper and lower bounds are computationally indistinguishable. The power of this method depends upon the fact that we have reduced the eigenvalue problem to an inversion, and that the inversion, Eq. (9), is stable.

4. A SIMPLE EXAMPLE

A model calculation was performed on the unimolecular dissociation of CO_2 at 500°K . The energy-level spectrum was divided into 40 equally spaced grains, with 30 of them below the reaction threshold, and appropriate values were assigned to the elements of A and D [6]; the elements of A are proportional to the pressure p , but those of D are fixed. With the numerical values assumed, 39 of the eigenvalues of A spanned the range $1.3p \times 10^5$ to $6.6p \times 10^9 \text{s}^{-1}$, where p is the pressure in Torr; the remaining one is of course identically zero, with an eigenvector S_0 whose elements are $\tilde{n}_i^{1/2}$, where \tilde{n}_i is the Boltzmann population in grain i at 500°K [6]. We chose to experiment with the value of $\alpha = 1$ and a pressure range $10^{-5} \leq p \leq 10^{20}$ Torr: thus α was always less than $\sigma_1(A)$, whence $\bar{\phi}(0)$ is always a lower bound; note that the (i, j) th element of p_0 is simply $\tilde{n}_i^{1/2}\tilde{n}_j^{1/2}$. In the range $10^{-5} \leq p \leq 10^{-3}$ Torr, our calculated rate constant was strictly second order, with a numerical value of $3.024p \times 10^{-46} \text{s}^{-1}$, whereas in the range $10^8 \leq p \leq 10^{10}$ Torr, the rate constant was strictly constant at $8.960 \times 10^{-45} \text{s}^{-1}$. These limiting values are known to be correct, since they can be deduced analytically from the general properties of the theory of unimolecular reactions [6]. Moreover, throughout the pressure range $10^{-5} \leq p \leq 10^{10}$ Torr, $\bar{\phi}(0)$ exhibited the correct fall-off behaviour and no difficulty was experienced in calculating the rate constant at any of these pressures.

Some problems may be encountered at extremes of pressure. For example, at $p = 10^{20}$ Torr and $\alpha = 1$, the elements of αp_0 become insignificant compared with the elements of A and the inversion of $[A + D]$ fails: however, the correct high-pressure rate constant is recovered if α is increased to, say, 10^{10} , since the inversion is now stabilised by the presence of a significant αp_0 term; note that at these high pressures, a value of α of 10^{10} is still less than $\sigma_1(A)$. On the other hand, at extremely low pressures, the elements of A will become insignificant compared with those of D , and a solution can only be obtained if sufficient computer word length is available; however, this problem does not usually arise in chemical kinetic calculations. Finally, we should point out that if the computing system or compiler available is one which counts underflows and terminates the execution of the program if "too many" underflows occur, then it is necessary to intercept these interrupts in the inversion routine: we have found the Choleski square root method [8] very convenient in this respect for the calculation of f in Eq. (9). The number of underflows encountered is large, and depends upon the value of α that is chosen; however, we explored the behaviour of $\bar{\phi}(0)$ obtained from a fixed matrix $[A + D]$ by choosing widely differing values of α , and found that the result was unaffected to at least 5 significant figures as the number of suppressed underflows was varied.

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REFERENCES

1. H. O. PRITCHARD, *Specialist Periodical Rep., React. Kinet.* **1** (1975), 243.
2. A. W. YAU AND H. O. PRITCHARD, *J. Phys. Chem.* **83** (1979), 134.
3. D. L. S. MCELWAIN, Ph. D. Thesis, York University, Toronto, 1970.
4. T. ASHTON, Ph. D. Thesis, York University, Toronto, 1972.
5. S. R. VATSYA, *J. Phys. A*, in press.
6. S. R. VATSYA AND H. O. PRITCHARD, *Proc. Roy. Soc. London Ser. A* **375** (1981), 409.
7. P. HENRICI, "Elements of Numerical Analysis," Wiley, New York, 1964.
8. V. N. FADDEVA, "Computational Methods of Linear Algebra," Dover, New York, 1959.

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H. O. PRITCHARD AND S. R. VATSYA

*Centre for Research in Experimental Space Science,
York University, Downsview, Ontario, Canada M3J 1P3*