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Eigenvalue Methods for Unimolecular Rate Calculations with Several Products

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When the calculation of a unimolecular reaction rate constant is cast in the form of a master equation eigenvalue problem, the magnitude of that rate is often smaller than the rounding error of the trace of the corresponding reaction matrix. Here, a previously published procedure (Pritchard, H. O. *J. Phys. Chem. A* **2004**, *108*, 5249–5252) for solving this problem is extended to the case of more than one reaction product. An Appendix notes the occurrence of avoided crossings between eigenvalues of the master equation in reversible, in mixed reversible–irreversible, and in multiwell unimolecular reaction calculations.

Introduction

In a recent publication,¹ a robust inversion method² was tested for the calculation of the eigenvalue corresponding to the reaction rate constant of an irreversible unimolecular reaction under conditions where standard linear algebra methods fail due to numerical cancellation. During the processing of that paper, a Reviewer asked whether the method could be extended to the determination of more than one eigenvalue for processes with more than one product. The question was answered, rather hastily, in the affirmative based on the fact that similar procedures³ had already been used to calculate the energies of the $1s^2$ and $1s2s\ ^1S$ states of the helium atom to a very high degree of precision.⁴ On further examination, it appears, as described briefly in Appendix 1, that it is not possible to cast the multiproduct irreversible unimolecular reaction problem in a form where each individual rate constant is given by its own distinct eigenvalue.

Basic Formulation

As usual, we consider an energy-level spectrum of the molecule divided into consecutive grains of equilibrium population \tilde{n}_i at the temperature T in question. Without repeating the basic formulation given previously,¹ the master equation for the system can be cast in the form of a positive definite symmetric matrix $[A + D]$, in which A is a simple transform of the matrix Q of collisional energy-transfer probabilities; A itself is positive semidefinite, that is, it has one eigenvalue which is identically zero, and the remainder are all positive. Crucially, the eigenvector S_0 corresponding to the zero eigenvalue has elements $(S_0)_j = \tilde{n}_j^{1/2}$.

Then, the smallest eigenvalue, γ_0 , of $[A + D]$ (where D is a diagonal matrix containing the rate constants for the individual decay processes) is the required rate constant and is equal to the scalar product $(S_0, D\Psi_0)$, where $(,)$ denotes a scalar product and Ψ_0 is the eigenvector of $[A + D]$ corresponding to γ_0 .

We now wish to decompose D into $D = D_1 + D_2 + \dots$, whence the solutions for the individual rate constants γ_0^i , $i = 1, 2, \dots$, are

$$\gamma_0^{1,2,\dots} = (S_0, D_1\Psi_0), (S_0, D_2\Psi_0), \dots \quad (1)$$

This result is straightforward except for the fact that even in quite mundane situations, acceptable results cannot be obtained when using double-precision (Fortran real*8) arithmetic due to cancellation; compare the examples in Figure 1 of Appendix 1.

Computing machines supporting quadruple-precision (Fortran real*16) arithmetic are not widely available; on the other hand, multiple-precision emulation is available for Unix/Linux-type machines,⁵ but the procedures are more cumbersome, and execution is slower. For these reasons, we now present a simple extension of the previous cancellation-resistant eigenvalue procedure¹ to the solution of eq 1.

As before,¹ the test reaction was the isomerization of MeNC \rightarrow MeCN. Given the molecular constants, the density of states $\rho(E)$ was tabulated at 1 kcal mol^{−1} intervals by using standard methods;^{6a} also, from the reaction threshold at 39 kcal mol^{−1} up to the cutoff at 65 kcal mol^{−1} and with the same grain width, the specific rate constant $k(E) \equiv D_1$ was tabulated as the inverse Laplace transform of the Arrhenius rate law.^{6b} The dimension of the test matrix was then 65.

This isomerization does, in fact, have a minor side reaction (<1%), giving CH₄ and HCN,⁷ but its kinetic parameters are not known. Trial $k(E)$ functions for the D_2 component were chosen either to start at the same threshold as that of D_1 but with reduced numerical values or with the same numerical form as that in D_1 but commencing at a higher threshold.

For the test temperature T , the grain populations were calculated, and a ΔE_{down} exponential transition probability⁸ matrix Q was constructed and, thence, A by symmetrization. The corresponding reaction matrix $[A + D]$ was formed from the relaxation matrix A for the given pressure by addition of the diagonal matrix $D = D_1 + D_2$ as described in eq 1. All calculations were performed in Fortran real*8 arithmetic and verified in real*16 arithmetic over a standard pressure range of $10^{-3} \leq P/\text{Torr} \leq 10^6$, unless otherwise stated.

Calculation of the Eigenvalue γ_0 . For completeness, an outline of the original method^{1,2} is reproduced here. We define a function

$$\bar{\phi}(0) = \alpha(S_0, [A + D + \alpha p_0]^{-1} D S_0) = (S_0, f) \quad (2)$$

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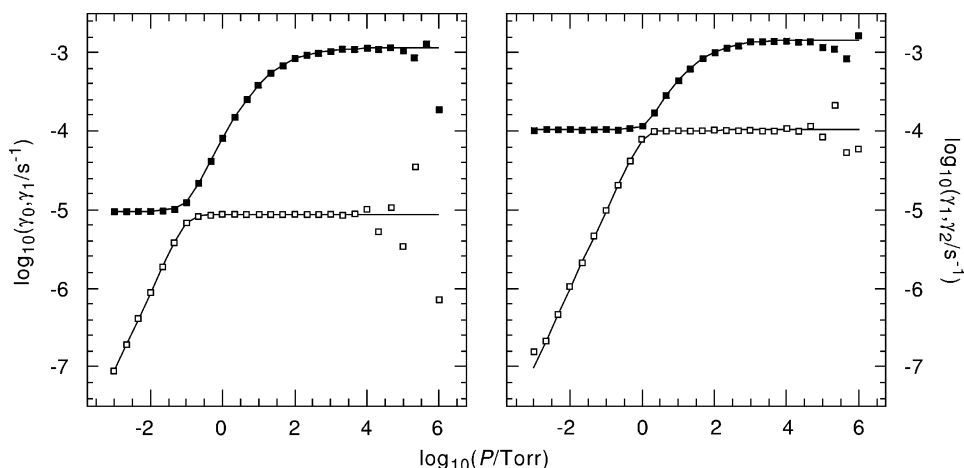


Figure 1. Left-hand panel: two smallest eigenvalues of $[A' + D_2]$; right-hand panel: two smallest nonzero eigenvalues of $[A'']$. Full lines are calculated by the Householder/QL method in quadruple-precision (Fortran real*16) arithmetic; the points are by the same instruction set but in double-precision (Fortran real*8) arithmetic. These calculations are seriously compromised by cancellation errors in real*8 arithmetic, even to the extent that reordering the instructions within the assembly and symmetrization of the relevant matrices can give markedly different answers; many of the low-pressure points in the right-hand panel are correct to only 2 significant figures in real*8 arithmetic.

where α is a positive constant (usually chosen to be 1), p_0 is the operator $S_0(S_0, \cdot)$, and

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

that is

$$[A + D + \alpha p_0]f = \alpha D S_0 \quad (4)$$

Forming the scalar product of S_0 with eq 4, we have

$$(S_0, [A + D + \alpha p_0]f) = (S_0, Df) + \alpha(S_0, f) = \alpha(S_0, D S_0) \quad (5)$$

where we have used the fact that S_0 is the normalized eigenvector of A corresponding to its zero eigenvalue. From eqs 2 and 5, we then get

$$\bar{\phi}(0) = (S_0, f) = (S_0, D S_0) - (S_0, Df)/\alpha = k_\infty - (S_0, Df)/\alpha \quad (6)$$

which has been shown² to be a lower bound to γ_0 , with a corresponding upper bound given by $\chi(0) = \bar{\phi}(0)/(1 - \bar{\phi}(0)/\alpha)$. The function of the constant α in these equations is to stabilize the inversion in eq 3 to obtain f , if needed.

Calculation of the Eigenvector Ψ_0 . We wish to solve the equation

$$[A + D - \gamma_0]\Psi_0 = 0 \quad (7)$$

for the eigenvector Ψ_0 . With an arbitrary $\alpha > 0$, this is equivalent to²

$$[A + D + \alpha p_0 - \gamma_0]\Psi_0 = \alpha p_0 \Psi_0 = \alpha S_0 \quad (8)$$

since $(S_0, \Psi_0) = 1$ by normalization, and it follows that the eigenvector

$$\Psi_0 = \alpha[A + D + \alpha p_0 - \gamma_0]^{-1} S_0 \quad (9)$$

In what follows, the eigenvalue γ_0 will be taken as the upper bound from the inversion calculation, it always being a much

closer approximation to the exact eigenvalue;¹ also, as noted previously,^{1,2} we have found the Choleski square root method⁹ to be a simple and stable procedure for calculating these inverses.

Results and Discussion

Numerical comparison of the eigenvectors of $[A + D]$ calculated by eq 9 in real*8 arithmetic and those calculated by standard linear algebra procedures (Householder/QL)¹⁰ in real*16 arithmetic showed exact agreement to better than 6 significant figures for all 65 elements at all pressures in the range $10^{-3} \leq P/\text{Torr} \leq 10^2$ but degenerated gradually to 3 or 4 significant figures at 10^6 Torr. (Several tables demonstrating comparisons between sets of eigenvalues and between sets of eigenvectors are available in the Supporting Information associated with this paper.) This, then, renders calculation of the partial rates of individual products by eq 1 a simple matter at all pressures of practical interest.

The present procedures reduce the standard unimolecular reaction eigenvalue problem of solving the reaction matrix $[A + D]$ to a noniterative one, involving just two matrix inversions, one of $[A + D + \alpha p_0]$ to get the eigenvalue γ_0 and then of $[A + D + \alpha p_0 - \gamma_0]$ to get the eigenvector. It does not matter that the matrix $[A + D]$ may be ill-conditioned because its inversion is stabilized by the extra αp_0 term, and should an instability occur in the inversion, it can be countered by giving α a different value.

The previous caveats^{1,2} concerning the use of very large matrices in some unimolecular calculations, or of inversion under extremes of pressure, still stand; however, Appendix 2 suggests a possible approach to a solution, at least for the case of two competing reactions.

Appendix 1: Nondissipative Formulations

As an alternative to the usual dissipative formulation, the master equation can also be cast in conservative form.¹¹ One variant, model (iii) of ref 12, has a single lumped product P with equilibrium constant $K_{\text{eq}} = [P]_{\text{eq}}/[R]_{\text{eq}}$ connected reversibly to all of the above-threshold reactant R states. The elements d_i of D are unfolded out of $[A + D]$ to form the last row and column of a new reaction matrix A' . This leaves the main body

of A' the same as that of the original A ; the diagonal elements are then adjusted to fulfill the conservation condition^{6c} because of the presence of the new row and column, following which, the last row and column are brought into symmetry by using detailed balancing.

The matrix A' is now positive semidefinite, with a zero eigenvalue γ'_0 and a corresponding eigenvector S'_0 having all of the usual properties; the next eigenvalue γ'_1 is the relaxation rate for the system and, in real*16 arithmetic, is exactly $\gamma_0(1 + K_{eq})/K_{eq}$, as required by standard theory.^{12,13}

It now seems logical to represent the main reaction D_1 in this fashion and to graft on to it a second, smaller irreversible component by forming the matrix $[A' + D_2]$ just in the same manner as $[A + D]$ was formed from A before. However, the result is an avoided crossing, as shown in the left-hand panel of Figure 1. Assuming that this behavior was due to some, as yet, unexplained symmetry violation, the D_2 was unfolded out of the diagonal by connection to a second product species P' to form a conservative reaction matrix A'' , but (for a different pair of D_1, D_2) a similar result is shown in the right-hand panel of Figure 1.

These avoided crossings have the interesting property that as the pressure is reduced, they propagate leftwards upon encountering each of the internal relaxation eigenvalues^{6d} γ'_i , $i > 1$, or γ''_i , $i > 2$. At each crossing, the horizontal line experiences a small upward displacement until the last one occurs at around 10^{-12} Torr; the differences between the high- and low-pressure limits for this eigenvalue are small, 1–10% depending upon the values of D_1 and D_2 , and are independent of the form of the collisional probability matrix for a given D_1, D_2 .

Avoided crossings, in the context of unimolecular reaction calculations, do not appear to have been mentioned before, although there is probable evidence for their existence in the recent work of Blitz, Hughes, Pilling, and Robertson,¹⁴ possibly in their Figure 6d–e but more clearly in Figure 7a–c. However, they still were able to calculate acceptable rate constants “from a mixture ... of eigenvalues”—language consistent with avoided crossing phenomena.

These calculations were likewise compromised by cancellation problems, and multiple-precision arithmetic was needed to complete them. In view of current interest in these multiwell problems, the following is a brief outline of extension to multiple eigenvalues.

The generalization of eq 8 for any eigenvalue γ_j is

$$[A + D + \alpha p - \gamma_j]u_j = \alpha p u_j = \alpha u(u, u_j) \quad (10)$$

where $p = u(u,)$ and u is an arbitrary vector with u such that $(u, u_j) \neq 0$. It can be shown that

$$\phi(\gamma_j) = \alpha(u, [A + D + \alpha p - \gamma_j]^{-1}u) = 1 \quad (11)$$

defines the eigenvalues γ_j of $[A + D]$ for all j , the corresponding eigenvectors being

$$u_j = \alpha[A + D + \alpha p - \gamma_j]^{-1}u \quad (12)$$

with normalization $(u, u_j) = 1$.

Equation 11 can be reduced to a fixed-point equation

$$\begin{aligned} \bar{\phi}(\gamma) &= \alpha - (\alpha - \gamma)\phi(\gamma) \\ &= \alpha(u, [A + D + \alpha p - \gamma]^{-1}[A + D]u) = \gamma \end{aligned} \quad (13)$$

which becomes eq 2 if $u = S_0$ because $AS_0 = 0$. Both $\phi(x)$ and $\bar{\phi}(x)$ are equal to zero at $x = -\infty$ and rise toward ∞ as x approaches the lowest eigenvalue of $[A + D + \alpha p]$. Following this singularity, the functions resume at $-\infty$ and reach ∞ again in the vicinity of the next eigenvalue, and so on. Each pair of singularities brackets an eigenvalue of $[A + D]$, all of them encompassing the set for which $(u, u_j) \neq 0$. For each $j = 0, 1, 2, \dots, J$, if $(u, u_j) \neq 0$, then the first $(J + 1)$ eigenvalues are singularities. However, their location either by iteration or by Newton's method can prove difficult as there is an inflection at each crossing of zero, but bisection can be used.

A second method that avoids the need to use bisection is that given in the work mentioned previously on the singlet states of He.^{4,15}

Appendix 2: Falloff Shape Correlations

The present methods can still fail in extreme cases,^{1,2} but solutions to eq 1, acceptable for approximate numerical modeling, may still be possible. As noted previously, given a relaxation matrix M having the same eigenvalues as A , the reaction matrix $[M + D]$ can be solved analytically for the rate constant and eigenvector,¹⁶ and the shape of the falloff curve for $[M + D]$ is very similar to that for $[A + D]$, although the low-pressure limits are different.¹

The low-pressure limiting rate for $[A + D]$ is easily established as the smallest eigenvalue of the matrix A truncated at threshold;^{17,18} neither calculation of this eigenvalue nor those of A itself usually presents any problem. Having then recalculated the falloff curve for $[M + D]$ with a pressure shift bringing its limits into coincidence with those of $[A + D]$, the eigenvector can be used in eq 1 to give an estimate for the dominant reaction D_1 ; the rates will be close to the true values at both pressure limits and usually within $\sim \pm 10\%$ in midrange. The same is not true, however, for the minor reaction as the magnitudes of the vector elements of $[M + D]$ at low pressures decline too slowly with increasing energy, causing the falloff to be too shallow; thus, some method of locating the low-pressure limit for the second reaction is needed.

This may be possible because the multiproduct rates for the strong-collision matrix^{6e} $[\mu(1 - p_0) + D]$ are already known analytically,¹⁹ and those for $[M + D]$ can be calculated numerically, yielding the following low-pressure equalities

$$\lim_{\mu \rightarrow 0} \frac{\gamma_{ap,1}}{\gamma_{ap,2}} = \lim_{p \rightarrow 0} \frac{(S_0, D_1 \Phi_0)}{(S_0, D_2 \Phi_0)} = \lim_{p \rightarrow 0} \frac{(S_0, D_1 \Phi'_0)}{(S_0, D_2 \Phi'_0)}$$

where $\gamma_{ap,1}$, $\gamma_{ap,2}$ are the strong-collision rates for the two reactions in question, Φ_0 is the eigenvector corresponding to γ_0 of $[M + D]$ and Φ'_0 refers to a different $[M + D]$ derived from a different A . This is equivalent to saying that for a given pair D_1, D_2 , the pressure shifts at the low-pressure limit between the two reactions for any $[M + D]$ matrix are the same as that for the strong-collision case with the same D_1, D_2 . These correlations, however, do not extend to $[A + D]$, but an analysis of these equivalences, together with an estimate of the shape broadening factor,²⁰ may resolve the issue.

Acknowledgment. I wish to thank Dr. Raj Vatsya for many valuable comments and for permission to use, in Appendix 1, unpublished results from his forthcoming monograph on variational and perturbation methods.

Supporting Information Available: An extensively documented set of Fortran algorithms and input data with which to

demonstrate these points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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