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Eigenvalue Methods in Unimolecular Rate Calculations

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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. Two available methods to overcome this cancellation problem are examined, and it is shown that one of them, the Nesbet procedure, can fail if the master equation relaxation matrix is improperly normalized, or when some time-saving computational approximations are used.

Introduction

The cancellation problem in computing small rate constants via master equation eigenvalue methods is well known.[1] In the case of a unimolecular reaction rate constant, the standard contemporary procedure is to use the Nesbet method[2,3a] in order to determine the eigenvalue. Generally, this approach is very reliable but, from time to time, verbal reports allude to “difficulties in calculating small eigenvalues” in unimolecular rate constant calculations.[4,5]

Herein, we describe an extensive testing of the Nesbet method as it is applied in unimolecular reaction theory and demonstrate two conditions under which it may fail. To do this, the results from a newly written Nesbet algorithm are compared with those from two other methods, as described in more detail below.

Basic Formulation

With the energy-level spectrum of the molecule divided into consecutive grains of equilibrium population $\tilde{n}_i$ at the temperature T in question, the master equation for the system can be cast in matrix form[6a,b]

$$\mathrm{d}n(t)/\mathrm{d}t = [Q - D]n(t) \tag{1}$$

where the vector $n(t)$ contains the individual populations n_i at time t, normalized to unity; the elements of the diagonal matrix D are the decay rate constants d_i for the respective grains, being only nonzero above the reaction threshold; and the elements of Q, q_{ij}, represent the rates of collisional transfer from states i to states j.

In the absence of reaction, conservation of reactant is ensured by[6a]

$$[Q]_{ij} = [(1 - \delta_{ij})q_{ji} - \delta_{ij}\sum_k (1 - \delta_{ik})q_{ik}] \tag{2}$$

i.e., q_{ii} is minus the sum of all the other elements in the ith column. Also, since the collisional transfer rates obey detailed balancing,

$$q_{ij}\tilde{n}_i = q_{ji}\tilde{n}_j \tag{3}$$

Let E be a (diagonal) matrix with elements $[e]_{ij} = \tilde{n}_j\delta_{ij}$, whence the transformation $-E^{-1/2}[Q - D]E^{1/2}$ yields a positive definite symmetric matrix $[A + D]$ and in which A itself is positive semi-definite, i.e., 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 $(S_0)_j = \tilde{n}_j^{1/2}$.

Finally, the smallest eigenvalue, γ_0, of $[A + D]$ is the required rate constant[6b] and is equal to the scalar product[6c] $(S_0,D\Psi_0)$ where (,) denotes a scalar product and Ψ_0 is the eigenvector of $[A + D]$ corresponding to γ_0.

Perturbation Solutions

When the rate constant is pathologically small, the reactive population distribution $n_i = (S_0)_i(\Psi_0)_i$ is very close to that at equilibrium, and so the eigenvector Ψ_0 is very little different from S_0. Hence, perturbation methods should be effective.

First, we summarize the use of the Nesbet method.[2,3a] This is an iterative procedure which starts with a guessed value for the eigenvalue λ_0 and a plausible eigenvector c_0 (properly normalized such that $(S_0,c_0) = 1$) and which converges smoothly toward the correct smallest eigenvalue γ_0 of the matrix, i.e., k_{uni}, no matter how small this rate constant may be. In the numerical examples described below, we will always begin at the highest pressure with $\lambda_0 = k_\infty$ and $c_0 = S_0$ and then work downward in pressure, using the preceding γ_0 and Ψ_0 as the starting values for the next case; this tends to minimize the number of iterations needed in the calculation of a complete falloff curve.

For short, denote the matrix $[A + D]$ by B and construct the vector

$$s_i = \sum_j B_{ij}(c_0)_{j,0} - (\lambda_0)_0(c_0)_{i,0} \tag{4}$$

from which an improved, but unnormalized, vector

$$(c_0)_{i,1} = (c_0)_{i,0} + \frac{s_i}{(\lambda_0)_0 - B_{ii}} \tag{5}$$

is formed. It is normalized by $(S_0, (c_0)_1) = 1$ and the next $(\lambda_0)_1$ is calculated as $(S_0, D(c_0)_1)$. These new $(c_0)_1$ and $(\lambda_0)_1$ are put back into eq 4 and the process repeated until $(\lambda_0)_{n-1}$ and $(\lambda_0)_n$ differ by less than the required tolerance, whence $(\lambda_0)_n$ is taken to be $\gamma_0 = k_{\mathrm{uni}}$ and the properly normalized $(c_0)_n$ is taken to be Ψ_0.

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A quite different perturbation method[7] is less well known and is restated briefly here. We define a function

$$\bar{\phi}(0) = \alpha(S_0, [A + D + \alpha p_0]^{-1} DS_0) = (S_0, f) \qquad (6)$$

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

$$f = \alpha[A + D + \alpha p_0]^{-1} DS_0 \qquad (7)$$

i.e.,

$$[A + D + \alpha p_0]f = \alpha DS_0 \qquad (8)$$

Forming the scalar product of S_0 with eq 8, we have

$$(S_0, [A + D + \alpha p_0]f) = (S_0, Df) + \alpha(S_0, f) = \alpha(S_0, DS_0) \quad (9)$$

From eqs 6 and 9, we then get

$$\bar{\phi}(0) = (S_0, f) = (S_0, DS_0) - (S_0, Df)/\alpha = k_\infty - (S_0, Df)/\alpha \qquad (10)$$

which has been shown[7] to be a lower bound to γ_0, and with a corresponding upper bound given by $\bar{\phi}(0)/(1 - \bar{\phi}(0)/\alpha)$. The function of the constant α in these equations is to stabilize the inversion in eq 7 to obtain f, if needed.

In applying these algorithms to the test reaction below, they will be referred to as the Nesbet and inversion methods, respectively. Where possible, standard matrix routines[8] were used, but others of local origin, including the newly written Nesbet procedure, were incorporated where necessary.

The Model Reaction

The test reaction was taken to be the isomerization of $CH_3NC \rightarrow CH_3CN$. Given the molecular constants, the density of states $\rho(E)$ was tabulated at 1 kcal mol^{-1} intervals by using standard methods;[6d] 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 $k(E)$ was tabulated as the inverse Laplace transform of the Arrhenius rate law.[6e] The first 32 grains were collapsed into 8 equally spaced widths, yielding a test matrix of dimension 40, which was a convenient size with which to expose the failings of the Nesbet method, if and when they occur.

For each test temperature T, the grain populations were calculated and a ΔE_{down} exponential transition probability[3b] matrix Q was constructed, and thence A by symmetrization. The corresponding *reaction* matrix $[A + D]$ was formed from the *relaxation* matrix A by addition of the diagonal matrix D whose elements are the grained specific rate constants $k(E)$. All calculations were performed in FORTRAN real*8 arithmetic, over a standard pressure range $10^{-3} \leq P/\text{Torr} \leq 10^6$, unless otherwise stated.

Most of the tests described below were for a temperature of 503 K, and the $k(E)$ function was adjusted by a fraction of a percent so that the calculated k_∞ was exactly 9×10^{-4} s^{-1}.

Numerical Results

At first, a simple comparison was made between eigenvalues obtained from the Nesbet and the standard Householder methods, with apparently successful results. However, at the low pressures, the corresponding eigenvectors differed significantly, it being deduced from what follows that those generated by the Householder and QL procedures[8] were of poor quality in these cases.

The accuracy of the Nesbet algorithm was then tested extensively in a different manner. The matrix A can be transformed into another matrix M having the same set of eigenvalues,[9] but for which there exists an analytical solution[10] for the smallest eigenvalue *and* eigenvector of $[M + D]$. Over the complete range of pressures, the Nesbet eigenvalue agreed with the analytical solution to the number (7) of significant figures requested. Within this range, the absolute difference in any of the 40 eigenvector elements never exceeded 5×10^{-11}; in more detail, at 10^6 Torr, the fractional difference in the elements ranged from $\sim 10^{-15}$ for the largest elements to $\sim 10^{-3}$ for the smallest; on the other hand, at 10^{-3} Torr, the fractional differences ranged from $\sim 10^{-10}$ to $\sim 10^{-8}$. Remembering that the Nesbet eigenvalue itself was not completely converged and that the analytic solution is merely a first approximation, this result can be considered as conclusive.

The capacity of this Nesbet procedure to recover small eigenvalues was tested by successively reducing the temperature, so as to produce very small rate constants. At 100 K, it correctly recovered rate constants from $\sim 7.8 \times 10^{-72}$ to $\sim 3.9 \times 10^{-75}$ s^{-1} over the trial pressure range, usually within 3 or 4 iterations to achieve 7-figure accuracy. However, at 75 K, with rate constants between $\sim 3.1 \times 10^{-100}$ to $\sim 1.6 \times 10^{-103}$ s^{-1}, convergence to within 7-figure accuracy could not be achieved in fewer than 10 000 iterations, although 6-figure accuracy was readily achievable. Finally, at 50 K, where the computed rate constants lie within the range $\sim 4.6 \times 10^{-157}$ to $\sim 2.4 \times 10^{-160}$ s^{-1}, the Nesbet method gave nonsensical results. Depending upon the pressure, the trace of $[A + D]$ lies between $\sim 10^{11}$ and $\sim 10^{15}$ s^{-1}, for rounding errors roughly beween $\sim 10^{-4}$ and $\sim 10^0$ s^{-1} in real*8 arithmetic.

These results were confirmed by using the inversion method: for these very low rate constants, the upper and lower bounds were identical, not only with each other but with the Nesbet results as well. Moreover, the inversion method easily yielded an acceptable set of results for the 50 K test just mentioned, in which γ_0 is some 10^{-170} of the magnitude of the dominant matrix elements.

Tests were also conducted up to $T = 1000$ K, and for variables within the ranges $10^{-6} \leq P/\text{Torr} \leq 10^{15}$, $100 \leq \Delta E_{\text{down}}/\text{cm}^{-1} \leq 2000$; these limits on T, P, and ΔE_{down} are far-removed from the values expected in practice for typical reactions (and in the latter case, the choice of ΔE_{down} to be smaller than the grain size of 350 cm^{-1} would tend to exacerbate the numerical difficulties), but both methods perform equally well throughout, and a selection of typical results is given in the top half of Table 1.

Hence, the ability of either method to handle eigenvalues very many orders of magnitude smaller than would ever be encountered in practice over a wide range of parameters is not in doubt, and if there are hidden difficulties, they must reside elsewhere in the algorithms that are used by unimolecular reaction kineticists. Also, this validation of the inversion method opens the possibility (see below) of extension to multiwell problems with multiple eigenvalues.

The Nesbet Method in Failure Mode

A chance programming error (highlighted in the deposited material) revealed that the Nesbet method can fail disastrously even though no other obvious signs of trouble are apparent. The standard normalization procedure[3c] for the original Q matrix became compromised: the conservation eq 2 no longer held

TABLE 1: Unimolecular Rate Constants, $10^4 \times (k_{uni}/s^{-1})$, Calculated by the Nesbet Method, the Lower (LB) and Upper (UB) Bounds from the Inversion Method, and the Exact Solution, for the Model Calculation of the Isomerization of CH_3NC with $\Delta E_{down} = 400$ cm^{-1} at T = 503 K, as a Function of Pressure P

P/Torr	exact[a]	LB	UB	Nesbet	n_{iter}[b]
		standard normalization			
10^6	8.9990	8.9909	8.9990	8.9990	28
10^5	8.9871	8.9790	8.9871	8.9871	37
10^4	8.8768	8.8690	8.8768	8.8768	49
10^3	8.1265	8.1199	8.1265	8.1265	63
10^2	5.6009	5.5978	5.6009	5.6009	72
10^1	2.1798	2.1793	2.1798	2.1798	73
		improper normalization			
10^6	−ve	9.0003	9.0084	1.73×10^{11}	1475
10^5	−ve	9.0003	9.0084	7.84×10^{10}	736
10^4	−ve	8.6669	8.6744	1.02×10^{1}	220
10^3	8.0180	7.9684	7.9748	8.2463	64
10^2	5.6008	5.5656	5.5687	5.6023	72
10^1	2.1798	2.1760	2.1765	2.1798	73

[a] Exact solution is by the Householder method in quadruple-precision (real*16) arithmetic. [b] n_{iter} is the number of iterations required for convergence of the Nesbet procedure to 1 part in 10^7.

precisely, although the resulting A matrix remained perfectly symmetric, with the results shown for the $\Delta E_{down} = 400$ cm^{-1} case in the lower half of Table 1. Below atmospheric pressure, where one would normally study this reaction, the results are close enough to the correct ones as to not arouse immediate suspicion. However, at higher pressures, the Householder and Nesbet methods fail catastrophically but, remarkably, the inversion method continues to report fairly sensible rate constants. This curious situation is analyzed below.

For $\Delta E_{down} = 1000$ cm^{-1} and unit collision rate, the matrix A has 39 eigenvalues ranging from 0.90 to 0.15 s^{-1}, and one at -7.6×10^{-15} s^{-1}, a not-unreasonable approximation to zero when using real*8 arithmetic in FORTRAN. However, the corresponding eigenvector, $S_0^{\ddagger}$, is not S_0: it begins to diverge after about the 10th element, and by the last one, $S_0^{\ddagger}$ is significantly in error, viz. 6×10^{-10} instead of 2×10^{-10}. Moreover, $k_{\infty}^{\ddagger} = (S_0, DS_0^{\ddagger}) = 9.190 \times 10^{-4}$ s^{-1} instead of 9×10^{-4} s^{-1}, because the elements of the vector $S_0^{\ddagger}$ are too large in the range where D is nonzero. In fact, the Nesbet solution is very slightly too large throughout the whole pressure range due to this imperfection in $S_0^{\ddagger}$. But when the calculation is repeated using quadruple precision (real*16) arithmetic, it is found that the last eigenvalue is *not* zero, but -7.4×10^{-15} s^{-1}, and the corresponding eigenvector is the same as was found by using real*8 arithmetic. Hence, the smallest eigenvalue of A is not identically zero as required by the conservation condition, but has a real value which compromises the quality of the corresponding eigenvector.

For $\Delta E_{down} = 400$ cm^{-1}, however, the changes are more bizarre: there is still an eigenvalue close to zero, -7.4×10^{-16} s^{-1}, but all of the eigenvector elements for the states above threshold are now negative. These changes account for the exact rate constants also becoming negative at the higher pressures, when the A matrix dominates over D, in column 2 of Table 1. On the other hand, the Nesbet procedure fails to find the correct, although negative, solution at all. The reason is that it is trying to calculate the eigenvalue as the scalar product $(S_0, D\Psi_0)$ instead of $(S_0^{\ddagger}, D\Psi_0)$: S_0 is inconsistent with the relaxation part of the defective reaction matrix $[A + D]$ and so, after a relatively large number of iterations, it arrives at an meaningless answer.

A surprising result is that the inversion method provides a pair of bounds that are very close to the expected eigenvalue at all pressures. Presumably, the mismatch between S_0 and $S_0^{\ddagger}$ is almost damped out by the presence of the powerful αp_0 term in eq 6.

Also, not shown here but available from the deposited material, if the diagonal elements of the improper relaxation matrix Q are adjusted arbitraily to conform exactly with the conservation condition (eq 2), all methods agree: the Nesbet procedure converges rapidly and the inversion method upper bound is always in agreement with the exact value.

Incorrect normalization is unlikely to occur and to remain undetected for long. What the above analysis does show, however, is that if there is an inconsistency between the true eigenvector that the Nesbet method is trying to achieve and the one that it is constrained to find, then it can fail. Such a constraint may arise in one variant of the reduced matrix approximation, as used, for example, in the well-known suite of algorithms provided by Gilbert and Smith.[3d] Here, it is assumed that in the falloff region, all states of energy less than half of the critical value maintain their equilibrium populations. This means that all the corresponding elements of Ψ_0 are the same as those of S_0, apart from a minuscule change in the normalization. In a typical calculation using these programs on the CH_3NC isomerization reaction at 503 K and 1 Torr pressure, with $\Delta E_{down} = 1000$ cm^{-1}, the error in Ψ_0 at the halfway point is about 2×10^{-8}, and this causes no problem.

However, if the energy transfer pattern among the lower levels is weak and they do not maintain their equlbrium populations during the reaction, the Nesbet method can get into difficulties if this particular form of reduced matrix constraint is applied. In the model calculation, we fix the first five elements of the trial $(c_0)_j$, $j = 0, ..., n$ to be the same as those of S_0, the equilibrium eigenvector; this corresponds to states lying below 20 kcal mol^{-1}, just about half of the assumed critical energy of 39 kcal mol^{-1}. With $\Delta E_{down} = 1000$ cm^{-1}, the procedure behaves normally, but if ΔE_{down} is reduced to 100 cm^{-1}, problems arise. Now, convergence can take up to 10 times as long, and the eigenvalues are are degraded slightly. However, if the number of constrained levels is raised to six or seven, then the eigenvalues at low-pressure assume an error of more than an order of magnitude.

Conclusion

From these observations, we can conclude that the Nesbet method has no difficulty in computing *exceedingly small* rate constants reliably, but when an inconsistency exists between S_0 and A, or between $[A + D]$ and Ψ_0, its performance can be degraded. In particular, use of this form of the reduced matrix approximation is almost always benign, but very occasionally, depending upon the reaction parameters, it may noticeably delay the convergence of the Nesbet procedure or even yield spurious results. Given the power of modern computing machines, it is probably best to abandon the use of this approximation, or at least provide the choice to use it or not.

General Comments

First, a note about the difference in the properties of the solutions of $[M + D]$ and of $[A + D]$: the two falloff curves for the methyl isocyanide reaction are virtually exactly superimposable, as they should be because the shape of the falloff is determined principally by the dispersion of the values of $\rho(E)k(E)$ over the reactive energy range,[6h] and this is unchanged. On the other hand, the two low-pressure limiting rates are different because in M, stepwise relaxation rates are arbitrarily assigned at the grain boundaries, thus altering the original physical picture of the *relaxation* process and making the truncated M quite different from the truncated A matrix;[11] hence, the method of Gilbert and Ross[11] must be used to establish the second-order limit whence the analytic curve can be moved into coincidence. It should be added, though, that the transformation back from the eigenvector of $[M + D]$ to that of $[A + D]$ can often be quite ill-conditioned.

The inversion method has both advantages and disadvantages: Its use is limited to "small" eigenvalues, but that is not a problem in this context, nor does it provide an eigenvector needed to examine population distributions in the falloff range,[6f] or to calculate incubation times.[6g] However, given a reliable eigenvalue, it will usually not be difficult to find the corresponding eigenvector by any one of a variety of methods.[12]

A more serious disadvantage is that inversion procedures often become problematic for large matrices. In these examples, I have used conventional Choleski square-root[13] or *LU* decomposition[8] methods, but modern procedures based on conjugate-residual and conjugate-gradient methods[14a] can reduce the problem very significantly to the inversion of a rank $[\dim(D)+2]$ matrix.[14b] However, one has to wonder whether the huge matrices, of the order of a thousand or so, often used in unimolecular master equation calculations, are really necessary? Given the crude approximations usually employed in unimolecular reaction theory (harmonic oscillators, rigid rotors, formulaic energy transfer models, etc.), a reduction by an order of magnitude in size would probably not be noticeable and may make the inversion method reasonably competitive with the Nesbet method in most unimolecular reaction applications.

On the other hand, the inversion method has three advantages. One that it is slightly more robust than the Nesbet method in finding very small eigenvalues, and is somewhat more fault-tolerant. Another is that its instruction count, depending upon the method of inversion used, is more-or-less fixed, whereas convergence of the Nesbet procedure can (for some combinations of kinetic and structural parameters) be exceedingly slow—sometimes in excess of 10 000 iterations in the model examples described here; the cause and remedy for this slow convergence remain to be investigated.

But most important, both it and the analytic method described above can be extended to multiwell systems in a straightforward manner; this is because both procedures are derived from the same fundamental theory.[15a] All that is needed in order to find, for example, the second eigenvalue in such a system is the second eigenvector of the unperturbed relaxation matrix A, which will not often present much, if any, numerical difficulty. Of the two, the inversion method is to be preferred because of its greater simplicity. A detailed description of these techniques available elsewhere.[15]

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Supporting Information Available: An extensively documented set of FORTRAN algorithms and input data with which to demonstrate these points is available free of charge via the Internet at http://pubs.acs.org.

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