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Multi-exponential unimolecular rate formulae

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Summary. We derive analytic expressions for the upper and lower bounds to the rate constant of a unimolecular reaction, which is treated as a competition between decay of reactive states and an arbitrary number of collisional relaxation processes all with different rate constants. The unimolecular rate is identified with the eigenvalue of smallest numerical magnitude. An analytic approximation to the corresponding eigenvector is also derived. Behaviour of the low-pressure rate constant is investigated and an analytic expression, in terms of the populations and the rates connecting them, is derived for the collision efficiency parameter β_c. It is shown that there is a direct relationship between the limiting low-pressure rate and the reactive fraction of molecules only in the special case where all unreactive molecules are connected by a pure exponential collisional relaxation.

Key words: Unimolecular fall-off — Multi-exponential decay — Collision efficiency

1. Introduction

It is usual to treat the thermal unimolecular reaction problem as one in which there is a competition between the decay of reactive states and a single collisional relaxation process of rate ω, and to write the rate constant in the steady-state

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form

$$k_{\text{uni}} = \frac{\omega}{Q(T)} \int_0^\infty \frac{\varrho(E) k(E)\, e^{-E/RT}}{\omega + k(E)}\, dE \tag{1}$$

where $Q(T)$ is the partition function of the molecule at the temperature T, $\varrho(E)$ is the density of states at energy E, and $k(E)$ is the specific rate constant for reaction at that energy. Because our approach is a matrix one [1], we prefer to rewrite Eq. (1) in its equivalent discrete form

$$k_{\text{uni}} = \mu \sum_r \frac{\tilde{\beta}_r d_r}{\mu + d_r} \tag{2}$$

where $\tilde{\beta}_r$ is the equilibrium population in grain r, d_r is the decay rate constant for that grain, and $\mu \equiv \omega$. Equation (2) is often used in practical calculations rather than (1).

This steady-state approach suffers from a number of serious deficiencies and inconsistencies, including the following:

1. Because no account is taken of the structure of the collisional relaxation process, all states below the reaction threshold are in a thermal equilibrium with each other, which corresponds to the reaction temperature.

2. No account is taken of the cascading quality of the relaxation above the reaction threshold, which is so often demonstrated by chemical activation studies.

3. In a shock-wave heating experiment, the incubation time for reaction at the high-pressure limit is identified with the inverse of the deactivation rate (i.e. $1/\omega$), whereas it should correlate with the vibrational relaxation time, which is sometimes several orders of magnitude longer; also, at the low-pressure limit, a nonsensical result is obtained.

These problems, and others associated with competing pairs of reactions, are discussed at length elsewhere [2]. The results given below will permit a resolution of all of these difficulties.

Some years ago, we proposed a form of relaxation matrix M which was a superposition of strong-collision matrices [3], such that the whole system was connected by an exponential relaxation of rate μ_0. Above a certain threshold, all states were coupled with a rate $(\mu_0 + \mu_1)$; above the next threshold, with a rate $(\mu_0 + \mu_1 + \mu_2)$; and so on. The form of this matrix is depicted in more detail in Fig. 1 of [3], and also in the numerical example given later in this paper; it corresponds to the pattern generally believed to be appropriate for small molecules: that the relaxation rate increases monotonically with increasing energy of excitation. It was shown in the earlier paper that the eigenvalues of the rank n matrix M were given by $\lambda_j = \sum_{i=0}^{j} \mu_i$, and solutions were found for the (upper and lower bounds of the) eigenvalue of the reaction matrix $(M + D)$, where D is a diagonal matrix of the d_r, for $j = 1$. We now derive a solution for any value of j, and illustrate its use with a numerical example; also, in the Appendix, we derive an expression for the low-pressure limiting rate, which leads to a compact formula for the collision efficiency parameter β_c.

To be precise, let J_0 be the identity matrix, which will be denoted by 1 also; and let J_j, $j = 1, 2, \ldots, N$, be the identity projections on the proper subspaces of the original n-vector space. The range of J_j contains, properly, that of J_{j+1} for each j, implying that $J_jJ_k = J_kJ_j = J_k$ for $k \geqslant j$. The matrix M is then defined by

$$M = \sum_{j=0}^{N} \mu_j(J_j - p_j) \tag{3}$$

where $p_j = J_jS_0(J_jS_0, \ )/(S_0, J_jS_0)$. Here, $(\ , \ )$ denotes the usual scalar product and S_0 is the n-vector with elements $\tilde{n}_i^{1/2}$, where $\tilde{n}_i \neq 0$ is the equilibrium population of state i. The l_2-norm will be denoted by $\| \ \|$. The rate constant is the smallest eigenvalue of the matrix $(M + D)$, where D is the diagonal matrix of decay rates such that $(J_0 - J_1)D$ has at least one entry equal to zero.

2. Preliminaries

In this section, we collect some results that will be used to obtain approximations to the rate constant, its limiting value, and a corresponding eigenvector.

Lemma 1. *Let $\gamma_0 < \mu$ be the lowest eigenvalue of a real symmetric matrix $[\mu(1 - p_0) + C]$ with $C \geqslant 0$, $\mu > 0$. Then*

$$\psi_0 = \psi(\gamma_0) = \mu(\mu - \gamma_0 + C)^{-1}S_0$$

is the corresponding eigenvector normalised so that $(S_0, \psi_0) = 1$.

Proof. [4], Sect. 2.

Let the functions $\phi(x)$, $\bar{\phi}(x)$, and $\chi(x)$ for x in the open interval $(-\infty, \mu)$ be defined as follows:

$$\phi(x) = \mu(S_0, [\mu - x + C]^{-1}S_0) \tag{4}$$

$$\begin{aligned}\bar{\phi}(x) &= \mu(S_0, [\mu - x + C]^{-1}CS_0) \\ &= \mu - (\mu - x)\phi(x),\end{aligned} \tag{5}$$

$$\chi(x) = \frac{\bar{\phi}(x)}{\phi(x)} \tag{6}$$

Lemma 2. *With symbols as in Lemma 1, γ_0 is the unique solution of $\phi(x) = 1$, $\bar{\phi}(x) = x$ and $\chi(x) = x$.*

Proof. [4], Lemma 1.

The fixed-point characterisation of γ_0 stated in Lemma 2, together with some properties of the functions $\bar{\phi}(x)$ and $\chi(x)$ enable one to produce converging lower and upper bounds to γ_0. These bounds may be produced by an iterative method or by Newton's method. We state the relevant result as

Lemma 3. *Let $x_0 \leqslant \gamma_0$ and $x_{m+1} = \bar{\phi}(x_m)$, $m = 0, 1, 2, \ldots$; then $x_m \uparrow \gamma_0$ and $\chi(x_m) \downarrow \gamma_0$.*

Proof. For the first part, see [4], Theorem 1(i). The second part is a consequence of the property of $\chi(x)$ stated in Corollary 1 of the same reference.

Lemma 4. *Let* $x_m \underset{m\to\infty}{\longrightarrow} \gamma_0$; *then* $\|\psi(x_m) - \psi_0\| \underset{m\to\infty}{\longrightarrow} 0$.

Proof. Since $(\mu - \gamma_0 + C)^{-1}$ is bounded and $x_m \to \gamma_0$ as $m \to \infty$, $(\mu - x_m + C)^{-1}$ is uniformly bounded for m greater than some m_0. Hence

$$\begin{aligned}&\|(\mu - x_m + C)^{-1} - (\mu - \gamma_0 + C)^{-1}\| \\ &\quad \leqslant |x_m - \gamma_0|\, \|(\mu - x_m + C)^{-1}\|\, \|(\mu - \gamma_0 + C)^{-1}\| \underset{m\to\infty}{\longrightarrow} 0.\end{aligned}$$

Consequently

$$\begin{aligned}\|\psi(x_m) - \psi_0\| &= \|[(\mu - x_m + C)^{-1} - (\mu - \gamma_0 + C)^{-1}]S_0\| \\ &\leqslant \|(\mu - x_m + C)^{-1} - (\mu - \gamma_0 + C)^{-1}\|\, \|S_0\| \underset{m\to\infty}{\longrightarrow} 0.\end{aligned}$$

The results of Lemma 3 and Lemma 4 reduce the problem of approximating γ_0 and ψ_0 to that of computing $\psi(x)$. It will be shown later that $\psi(x)$ may be computed by using the following recursive scheme developed recently to invert a perturbed matrix [5].

Define a sequence of matrices A_k for $k = 0, 1, 2, \ldots, N$ by

$$A_k = A_0 + \sum_{j=1}^{k} \chi_j(\chi'_j, \quad) \tag{7}$$

where $\{\chi_j\}$, $\{\chi'_j\}$ are sets of linearly independent n-vectors. We state the main result as

Lemma 5. *Let* A_k *and* A_{k+1} *be invertible for some* k. *Then* A_{k+1}^{-1} *is given by*

$$A_{k+1}^{-1} = A_k^{-1} - \frac{A_k^{-1}\chi_{k+1}(\chi'_{k+1}, A_k^{-1} \quad)}{1 + (\chi'_{k+1}, A_k^{-1}\chi_{k+1})}$$

Proof. See [5], Sect. 2.

3. Approximations to γ_0 and ψ_0

In the following, we use the results of Sect. 2 to obtain approximations to the lowest eigenvalue of the matrix $(M + D)$ which will be denoted by γ_0, and a corresponding eigenvector denoted by ψ_0. It was shown earlier [3] that $\gamma_0 \leqslant \mu_0$. A stronger result is shown to hold in Lemma 8 below. The matrix $(M + D)$ may be written as

$$(M + D) = \mu_0(1 - p_0) + \tilde{C}$$

where $\tilde{C} = \sum_{j=1}^{N} \mu_j(J_j - p_j) + D \geqslant 0$. Thus the conditions of Lemma 1 are satisfied by setting $\mu = \mu_0$ and $C = \tilde{C}$.

In order to use the above results we need $\psi(x)$ which, in this case, is given by

$$\begin{aligned}\psi(x) &= \mu_0\left[\mu_0 - x + D + \sum_{j=1}^{N} \mu_j(J_j - p_j)\right]^{-1} S_0 \\ &= \mu_0\left[B_0 - \sum_{j=1}^{N} \mu_j p_j\right]^{-1} S_0 \\ &= \mu_0 B_N^{-1} S_0 \end{aligned} \tag{8}$$

where

$$B_0 = \left[D - x + \sum_{j=0}^{N} \mu_j J_j\right]$$

and

$$B_k = B_0 - \sum_{j=1}^{k} \bar{\mu}_j \phi_j(\phi_j, \quad), \qquad k = 1, 2, \ldots, N;$$

with

$$\phi_j = J_{N-j+1} S_0 \quad \text{and} \quad \bar{\mu}_j = \frac{\mu_{N-j+1}}{\|\phi_j\|^2}.$$

Thus $\psi(x)$ may be computed by the scheme given in Lemma 5 if B_k is invertible for $k = 0, 1, \ldots, N$; this we establish in Lemma 6.

Lemma 6. *With B_k defined as above, B_k^{-1} exists as a positive matrix for each k, and x in $(-\infty, \mu_0)$.*

Proof. It follows from definitions that

$$B_N = (\mu_0 - x + \tilde{C}) > 0 \quad \text{for } x < \mu_0,$$

and $B_k \geqslant B_{k+1}$, $k = 0, 1, \ldots, (N-1)$, and for each x. Hence $B_k > 0$ for each $x < \mu_0$ and $k = 0$ to N. This implies the result.

The result of Lemma 5 may now be used to obtain B_{k+1}^{-1} in terms of B_k^{-1}. This enables one to compute B_k^{-1} for $k = 1, 2, \ldots$, provided that B_0^{-1} is known. B_0^{-1} is given by the following lemma.

Lemma 7. *With B_0 as above,*

$$B_0^{-1} = \sum_{j=0}^{N} (D_j - x + \lambda_j)^{-1} I_j = \sum_{j=0}^{N} \sigma_j^0 I_j$$

where $I_j = J_{j+1} - J_j$, $j = 0, 1, \ldots, (N-1)$, and $I_N = J_N$; $\lambda_j = \sum_{k=0}^{j} \mu_k$ and $D_j = DI_j = I_j D$.

Proof. See [3], Sect. 3.

In Theorem 1 we obtain $B_l^{-1}\phi_k$ instead of $B_N^{-1}\phi_{N+1} = \psi(x)/\mu_0$, which, in addition to yielding $\psi(x)$, will form the basis of several other results.

Theorem 1. *With symbols as above*

$$B_l^{-1}\phi_k = \sum_{j=N-k+1}^{N} \sigma_j^l I_j S_0, \qquad l = 0, 1, \ldots, N, \quad k = l+1, \ldots, (N+1);$$

with σ_j^l *being the diagonal matrices defined by*

$$\sigma_j^l = \sigma_j^0, \qquad j = (N-k+1), \ldots, (N-l);$$

$$\sigma_j^l = \frac{\sigma_j^{l-1}}{1-\bar{\mu}_l \eta_l}, \qquad j = (N-l+1), \ldots, N;$$

where

$$\eta_l = (\phi_l, B_{l-1}^{-1}\phi_l) = \sum_{m=N-l+1}^{N} (S_0, \sigma_m^{l-1} I_m S_0),$$

and $\{\sigma_j^0\}$ *is as defined in Lemma 7.*

Proof. It follows from Lemma 7 that

$$B_0^{-1}\phi_k = \sum_{j=0}^{N} (D_j - x + \lambda_j)^{-1} I_j J_{N-k+1} S_0$$

$$= \sum_{j=N-k+1}^{N} \sigma_j^0 I_j S_0, \qquad k = 1, 2, \ldots, (N+1).$$

Thus the result is true for $l = 0$. Assume it to hold for some l. From Lemma 5 and Lemma 6, we have

$$B_{l+1}^{-1}\phi_k = B_l^{-1}\phi_k + \bar{\mu}_{l+1} B_l^{-1}\phi_{l+1} \frac{(\phi_{l+1}, B_l^{-1}\phi_k)}{1-\bar{\mu}_{l+1}\eta_{l+1}}$$

$$= \sum_{j=N-k+1}^{N} \sigma_j^l I_j S_0 + \bar{\mu}_{l+1} \frac{(\phi_{l+1}, B_l^{-1}\phi_k)}{1-\bar{\mu}_{l+1}\eta_{l+1}} \sum_{j=N-l}^{N} \sigma_j^l I_j S_0$$

$$= \sum_{j=N-k+1}^{N} \sigma_j^{l+1} I_j S_0, \qquad k = l+2, \ldots, (N+1).$$

Here we have used the induction assumption and have set

$$\sigma_j^{l+1} = \sigma_j^l = \sigma_j^0, \qquad j = (N-k+1), \ldots, (N-l-1);$$

and

$$\sigma_j^{l+1} = \sigma_j^l \left[1 + \bar{\mu}_{l+1} \frac{(\phi_{l+1}, B_l^{-1}\phi_k)}{1-\bar{\mu}_{l+1}\eta_{l+1}} \right], \qquad j = (N-l), \ldots, N.$$

Now,

$$(\phi_{l+1}, B_l^{-1}\phi_k) = (\phi_k, B_l^{-1}\phi_{l+1})$$

$$= \sum_{j=N-l}^{N} (J_{N-k+1} S_0, \sigma_j^l I_j S_0)$$

$$= \sum_{j=N-l}^{N} (S_0, \sigma_j^l I_j S_0)$$

$$= \eta_{l+1}$$

since the sets of diagonal matrices $\{J_j\}$, $\{I_j\}$ and $\{\sigma_j^l\}$ all commute. In addition since $k \geqslant l+1$, $j \geqslant N-l$, one has that $J_{N-k+1} I_j = I_j$. Consequently

$$\sigma_j^{l+1} = \frac{\sigma_j^l}{1 - \bar{\mu}_{l+1}\eta_{l+1}}, \qquad j = (N-l), \ldots, N.$$

The result now follows by induction.

In view of the result of Theorem 1, $\psi(x)$, $\phi(x)$ and $\bar{\phi}(x)$ are given by

$$\begin{aligned} \psi(x) &= \mu_0 \sum_{j=0}^{N} \sigma_j^N I_j S_0, \\ \phi(x) &= \mu_0 \sum_{j=0}^{N} (S_0, \sigma_j^N I_j S_0), \\ \bar{\phi}(x) &= \mu_0 \sum_{j=0}^{N} (DS_0, \sigma_j^N I_j S_0). \end{aligned} \tag{9}$$

Furthermore, the σ_j^N are generated recursively starting with σ_j^0, yielding

$$\sigma_j^N = \frac{\sigma_j^0}{\prod_{k=1}^{j} \tilde{\eta}_{N-k+1}} = \frac{\sigma_j^0}{\zeta_j}, \qquad j = 0, 1, \ldots, N; \tag{10}$$

where $\tilde{\eta}_j = (1 - \bar{\mu}_j \eta_j)$. We have adopted the convention that, for $j = 0$, the product in the denominator is equal to one. Substitution for σ_j^N in (9) yields the following representations for $\psi(x)$, $\phi(x)$ and $\bar{\phi}(x)$.

Proposition 1. *With symbols as above*

(i) $$\psi(x) = \mu_0 \sum_{j=0}^{N} \frac{\sigma_j^0}{\zeta_j} I_j S_0,$$

(ii) $$\phi(x) = \mu_0 \sum_{j=0}^{N} \frac{(S_0, \sigma_j^0 I_j S_0)}{\zeta_j},$$

(iii) $$\bar{\phi}(x) = \mu_0 \sum_{j=0}^{N} \frac{(D_j S_0, \sigma_j^0 S_0)}{\zeta_j}.$$

The set $\{\eta_j\}$ is needed to compute $\{\zeta_j\}$, $j = 1, \ldots, N$. In Theorem 2 we obtain a recursive procedure to evaluate $\{\eta_j\}$. This also provides a more convenient scheme to compute $\phi(x)$, $\bar{\phi}(x)$ and $\chi(x)$.

Theorem 2. *Let η_l be as above, with $\eta_0 = 0$. Then*

$$\eta_{l+1} = (I_{N-l} S_0, \sigma_{N-l}^0 S_0) + \frac{\eta_l}{\tilde{\eta}_l}, \qquad l = 0, 1, \ldots, N;$$

yielding

$$\begin{aligned} \phi(x) &= \mu_0 \eta_{N+1}, \\ \bar{\phi}(x) &= \mu_0 - \mu_0(\mu_0 - x)\eta_{N+1}, \\ \chi(x) &= \frac{1}{\eta_{N+1}} - (\mu_0 - x). \end{aligned}$$

Proof. From Theorem 1, we have

$$\eta_{N+1} = (\phi_{l+1}, B_l^{-1}\phi_{l+1}) = \sum_{j=N-l}^{N} (J_{N-l}S_0, \sigma_j^l I_j S_0)$$

$$= \sum_{j=N-l}^{N} (S_0, \sigma_j^l I_j S_0)$$

$$= (I_{N-l}S_0, \sigma_{N-l}^l S_0) + \sum_{j=N-l+1}^{N} (I_j S_0, \sigma_j^l S_0)$$

$$= (I_{N-l}S_0, \sigma_{N-l}^0 S_0) + \frac{1}{\tilde{\eta}_l} \sum_{j=N-l+1}^{N} (I_j S_0, \sigma_j^{l-1} S_0)$$

$$= (I_{N-l}S_0, \sigma_{N-l}^0 S_0) + \frac{\eta_l}{\tilde{\eta}_l}$$

The result is thus transparent for $l \geqslant 1$; for $l = 0$, the second term is absent and the result holds by virtue of the choice $\eta_0 = 0$. The expressions for $\phi(x)$, $\bar{\phi}(x)$ and $\chi(x)$ follow from their definitions.

While $\bar{\phi}(x)$ may be evaluated from η_{N+1} as given in Theorem 2, it may also be computed by alternative recursive procedures, as follows:

Theorem 3. *Let* $\xi_{l+1} = (D\phi_{l+1}, B_l^{-1}\phi_{l+1})$ *with* $\xi_0 = 0$. *Then*

$$\xi_{l+1} = (D_{N-l}S_0, \sigma_{N-l}^0 S_0) + \frac{\xi_l}{\tilde{\eta}_l}$$

$$= (D_{N-l}S_0, \sigma_{N-l}^0 S_0) + \frac{\xi_l}{1 - \dfrac{\bar{\mu}_l}{\mu_0 - x}\left[\left(1 - \sum_{j=l}^{N} \mu_{N-j+1}\right)\|J_{N-l+1}S_0\|^2 - \xi_l\right]}$$

$$l = 0, 1, \ldots, N;$$

yielding $\bar{\phi}(x) = \mu_0 \xi_{N+1}$.

Proof. The first of the equalities follows from manipulations similar to those of Theorem 2. For the second, we use the relation

$$(\mu_0 - x)(\mu_0 - x + C')^{-1} = 1 - (\mu_0 - x + C')^{-1} C'$$

with

$$C' = D + \sum_{j=1}^{N} \mu_j J_j - \sum_{j=1}^{l} \bar{\mu}_j \phi_j(\phi_j, \quad)$$

which yields

$$(\mu_0 - x)\eta_{l+1} = \left(1 - \sum_{j=l+1}^{N} \mu_{N-j+1}\right)\|J_{N-l+1}S_0\|^2 - \xi_{l+1}.$$

The expression for $\bar{\phi}(x)$ is implied by definitions.

The recursive relations obtained in Lemma 8 and Lemma 9 enable one to develop continued fraction expansions for various quantities involving η_l and ξ_l. For convenience, we illustrate this for $\tilde{\eta}_l$.

By rearranging the equality of Theorem 2, we have

$$\tilde{\eta}_{l+1} = \alpha_{l+1} - \frac{\beta_{l+1}}{\tilde{\eta}_l}, \qquad l = 1, 2, \ldots, N; \tag{11}$$

where

$$\beta_{l+1} = \bar{\mu}_{l+1}/\bar{\mu}_l$$

and

$$\alpha_{l+1} = 1 + \beta_{l+1} - \bar{\mu}_{l+1}(I_{N-l}S_0, \sigma^0_{N-l}S_0).$$

It follows that

$$\tilde{\eta}_{l+1} = \alpha_{l+1} - \cfrac{\beta_{l+1}}{\alpha_l - \cfrac{\beta_l}{\alpha_{l-1} - \ddots - \cfrac{\beta_3}{\alpha_2 - \cfrac{\beta_2}{\tilde{\eta}_1}}}}$$

and

$$\tilde{\eta}_1 = 1 - \frac{\mu_N}{\|I_N S_0\|^2}(I_N S_0, (D_N - x + \lambda_N)^{-1} S_0).$$

Theorem 2, Theorem 3, and Proposition 1 in conjunction with Lemma 1 and Lemma 3 enable one to approximate γ_0 and ψ_0 with an arbitrary degree of accuracy; in most cases of interest, $\bar{\phi}(0)$ and $\chi(0)$ are close enough to be satisfactory. Whilst a rough estimate of ψ_0 is provided by $\psi(0)$, approximations with comparative accuracy are given by $\psi(\bar{\phi}(0))$ and $\psi(\chi(0))$; $\|\psi(\bar{\phi}(0)) - \psi(\chi(0))\|$ also provides a measure of accuracy.

4. Numerical implementation

Consider the energy-level spectrum of the molecule to be divided into groups of equilibrium population $\tilde{\beta}_j$ normalised so that $\sum_j \tilde{\beta}_j = 1$. This division is such that all states within group j are coupled with a relaxation rate λ_j, and the groups are ordered in such a way that $\lambda_{j+1} > \lambda_j$ since all of the $\mu_j > 0$. Within each group of states j, there are subgroups with equilibrium population $\tilde{n}_m$ having rate constants for decay to product d_m, where d_m can have any positive value, including zero; the only restriction is that there shall be at least some states of population $\tilde{n}_0$ within the domain of λ_0 and having $d_0 = 0$.

In order to be able to write the final expression for the rate constant in a compact form, we define the following notation:

j	0		1			2	3		4			5		...
	λ_0		λ_1			λ_2	λ_3		λ_4			λ_5		...
	μ_0		μ_1			μ_2	μ_3		μ_4			μ_5		...
	$\tilde{\beta}_0$		$\tilde{\beta}_1$			$\tilde{\beta}_2$	$\tilde{\beta}_3$		$\tilde{\beta}_4$			$\tilde{\beta}_5$		...
m	0	1	2	3	4	5	6	7	8	9	10	11	12	...
	$\tilde{n}_0$	$\tilde{n}_1$	$\tilde{n}_2$	$\tilde{n}_3$	$\tilde{n}_4$	$\tilde{n}_5$	$\tilde{n}_6$	$\tilde{n}_7$	$\tilde{n}_8$	$\tilde{n}_9$	$\tilde{n}_{10}$	$\tilde{n}_{11}$	$\tilde{n}_{12}$	...
	$d_0 = 0$	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	...
n_j	$n_0 = 1$		$n_1 = 4$			$n_2 = 5$	$n_3 = 7$		$n_4 = 10$			$n_5 = 12$		...

(a) λ_j is the relaxation rate for group j;
(b) μ_j is the incremental relaxation rate for group j;
(c) $\tilde{\beta}_j$ is the equilibrium population in group j;
(d) $\tilde{n}_m$ is the population in subgroup m;
(e) d_m is the decay rate for all molecules in subgroup m.

Most of this notation is self-explanatory. The index n_j is used to select the appropriate subgroup properties from the total list; we also define $n_{-1} = -1$. Notice that by introducing the population $\tilde{n}_m$ as distinct from the $\tilde{\beta}_j$ or the $\tilde{\beta}_r$ of Eq. (2), we retain the freedom for a domain within one relaxational environment to be subdivided into components with different characteristics (e.g. reactive or unreactive or decaying to separate products, and so on).

We now make a comparison of the results of the various methods described above for evaluating the unimolecular rate as a function of pressure for a particular model reaction, that of the thermal dissociation of N_2O at 2000°K which was described more fully elsewhere [6]. The energy-level spectrum was divided up into groups of width 1 kcal · mol^{-1} ($\sim$350 cm^{-1}), for $0 \leqslant E \leqslant 95$ kcal · mol^{-1}, and the reaction threshold was taken to be at 59 kcal · mol^{-1}. Below the threshold, all grains were taken to be unreactive, i.e. $d_m = 0$, but above threshold, each grain was divided into two components with the bulk of the population being unreactive and a small fraction having a non-zero value of d_m—the non-randomisation case for that model. Thus, in the above defining table, subgroups $m = 0$ to 58 were unreactive, and subgroups 59 to 130 (now two per 1 kcal · mol^{-1} group) were alternately reactive and unreactive, with the appropriate values of the population $\tilde{n}_m$ and decay rate d_m calculated as described before. This was then overlaid with an arbitrarily chosen relaxation pattern λ_j: divisions were made initially every 10 kcal · mol^{-1}, with the lowest group having $\lambda_0 = 2.5 \times 10^3$ Torr^{-1} s^{-1}, which is the experimental vibrational relaxation rate for this temperature, and the topmost group below threshold having $\lambda_j = 3 \times 10^6$ Torr^{-1} s^{-1}, which is the apparent deactivation rate. After a slight iteration to cause the limiting low-pressure rate constant to

Table 1. Distribution of populations, reaction rates and relaxation patterns for a model calculation of the thermal dissociation of N_2O at 2000°K

j	Energy band kcal · mol^{-1}	λ_j Torr^{-1} s^{-1}	m	$\tilde{n}_m$	d_m s^{-1}
0	0–10	2.5×10^3	0	0.343	0
1	10–20	3.0×10^3	1	0.428	0
2	20–48	4.0×10^3	2	0.226	0
3	48–56	4.5×10^5	3	2.00×10^{-3}	0
4	56–59	3.0×10^6	4	2.53×10^{-4}	0
5	59–70	3.5×10^6	5	2.88×10^{-4}	0
5			6	3.25×10^{-7}	2.60×10^{10}
6	70–75	4.0×10^6	7	2.36×10^{-5}	0
6			8	3.25×10^{-7}	5.63×10^{10}
7	75–80	5.0×10^6	9	8.53×10^{-6}	0
7			10	3.00×10^{-7}	7.27×10^{10}
8	80–85	6.0×10^6	11	2.99×10^{-6}	0
8			12	2.21×10^{-7}	8.05×10^{10}
9	85–90	7.0×10^6	13	1.01×10^{-6}	0
9			14	1.43×10^{-7}	8.33×10^{10}
9	90–95		15	3.27×10^{-7}	0
9			16	8.24×10^{-8}	8.36×10^{10}

Total fraction of molecules above E_{crit} (59.0 kcal · mol^{-1}) = 3.262×10^{-4}; $k_0 = 4.0$ Torr^{-1} s^{-1}; $k_\infty = 8.5 \times 10^4$ s^{-1}. Notice that the original 131 values of m (corresponding to a 1 kcal · mol^{-1} grain width) have been collapsed into only 17: where, for a given j, there are several sub-grains all having $d_m = 0$, this contraction has no effect on the rate; where the $d_m \neq 0$, the lumping together of sub-grains for a given j into larger ones has a marginal effect on the fallen-off rate in this case, because the d_m vary only weakly with E

agree with the observed value of 4.0 Torr^{-1} s^{-1}, the λ_j relaxation pattern was as shown in Table 1. This is not a unique pattern, but it *does* require a relatively fast relaxation to extend a considerably (10 kcal · mol^{-1}) below reaction threshold if the low-pressure rate constant is to be recovered.

With this assumed model, we are now in a position to make a fair comparison between the various methods we have derived for the calculation of the rate constant. We have available, of course, the direct numerical calculation of the eigenvalue and eigenvector by standard procedures (Householder, bisection and QR) [7]. We have from Theorem 2 the quantity $\phi(x)$ from which the upper bound $\chi(x)$ and lower bound $\bar{\phi}(x)$ can be deduced and, as is well known, under most circumstances the zeroth approximation is all that is needed to achieve acceptable accuracy. The relationship between these quantities is [3]

$$\bar{\phi}(0) = \mu_0[1 - \phi(0)] \leqslant \gamma_0 \leqslant \mu_0[1 - \phi(0)]/\phi(0) = \chi(0). \tag{12}$$

Thus, the calculation of η_{N+1}, as defined in Theorem 2, is all that is needed to implement Eq. (12) completely. Alternatively, η_{N+1} may be calculated by the continued fraction method via $\tilde{\eta}_{N+1}$, Eq. (11); these two methods yield virtually identical results, and the choice between them is open. Unfortunately, with the

kinds of numbers often encountered in unimolecular rate calculations (populations in the 10^{-6}–10^{-10} range, and d_m in the 10^{7}–$10^{10}\ s^{-1}$ range), Eq. (12) is subject to some cancellation problems in obtaining $\bar{\phi}(0)$ and $\chi(0)$ from $\phi(0)$ at or near the high-pressure limit—particularly so for $\bar{\phi}(0)$, the lower bound. Thus, we present an alternative analytic formula for the lower bound $\bar{\phi}(0)$ in which the subtraction implicit in (12) is done analytically rather than numerically by using Proposition 1(iii), *viz.*

$$\bar{\phi}(0) = \mu_0 \sum_{j=0}^{N} \frac{\sum_{m=n_{j-1}+1}^{n_j} \frac{\tilde{n}_m d_m}{\lambda_j + d_m}}{\prod_{k=1}^{j} (1 - \bar{\mu}_{N-k+1}\eta_{N-k+1})} \tag{13}$$

where

$$\lambda_j = \sum_{i=0}^{j} \mu_i, \qquad \bar{\mu}_j = \frac{\mu_{N-j+1}}{\|\phi_j\|^2}, \qquad \phi_j = J_{N-j+1} S_0,$$

$$\eta_l = (I_{N-l+1} S_0, \gamma^0_{N-l+1} S_0) + \frac{\eta_{l-1}}{1 - \bar{\mu}_{l-1}\eta_{l-1}},$$

with

$$\gamma_j^0 = \sum_{m=n_{j-1}+1}^{n_j} \frac{\tilde{n}_m}{\lambda_j + d_m} \quad \text{and} \quad \prod_{k=1}^{0} = 1.$$

This formula is attractive in the sense that it is much less subject to cancellation problems (ordinary Fortran Real*8 precision is ample in most cases); it is, of course, the lower bound, and the corresponding upper bound is easily found

Table 2. Comparison of lower and upper bounds with numeric eigenvalues for the thermal dissociation of N_2O at 2000°K, using the model described in Table 1; incubation times are also shown, they are to be compared with a vibrational relaxation time of $\tau_{rel} = 4.0 \times 10^{-4}\ \text{Torr}^{-1}\ s^{-1}$, *viz.* 4.0×10^{-2} s at 10^{-2} Torr, 4.0×10^{-14} s at 10^{10} Torr

Pressure Torr	Lower bound $\bar{\phi}(0)$ s^{-1}	Numeric eigenvalue s^{-1}	Upper bound $\chi(0)$ s^{-1}	τ_{inc} s
10^{-2}	$3.99596232 \times 10^{-2}$	$4.00079628 \times 10^{-2}$	$4.00235964 \times 10^{-2}$	3.021×10^{-2}
10^{-1}	$3.99594443 \times 10^{-1}$	$4.00077835 \times 10^{-1}$	$4.00234169 \times 10^{-1}$	3.021×10^{-3}
10^{0}	3.99576554×10^{0}	4.00059909×10^{0}	4.00216222×10^{0}	3.021×10^{-4}
10^{1}	3.99397759×10^{1}	3.99880752×10^{1}	4.00036854×10^{1}	3.021×10^{-5}
10^{2}	3.97619757×10^{2}	3.98099146×10^{2}	3.98253170×10^{2}	3.026×10^{-6}
10^{3}	3.80770055×10^{3}	3.81215647×10^{3}	3.81350883×10^{3}	3.067×10^{-7}
10^{4}	2.69616147×10^{4}	2.69859283×10^{4}	2.69907233×10^{4}	3.339×10^{-8}
10^{5}	6.99240110×10^{4}	6.99427397×10^{4}	6.99435740×10^{4}	3.828×10^{-9}
10^{6}	8.33311541×10^{4}	8.33339177×10^{4}	8.33339319×10^{4}	3.979×10^{-10}
10^{7}	8.49631429×10^{4}	8.49634315×10^{4}	8.49634317×10^{4}	3.997×10^{-11}
10^{8}	8.51298969×10^{4}	8.51299259×10^{4}	8.51299259×10^{4}	3.999×10^{-12}
10^{9}	8.51466087×10^{4}	8.51466116×10^{4}	8.51466116×10^{4}	3.999×10^{-13}
10^{10}	8.51482802×10^{4}	8.51482805×10^{4}	8.51482805×10^{4}	3.999×10^{-14}

Table 3. Selection of algorithm structures

```
ubar(0) = zero[a]
ubar(Nmu + 1) = rmu(0)
phisq(Nmu + 1) = one
do j = Nmu,1, −1
    phisq(j) = phisq(j + 1)
    do k = n(Nmu − j − 1) + 1,n(Nmu − j)
        phisq(j) = phisq(j) − tilde_n(k)[b]
    enddo
    ubar(j) = rmu(Nmu − j + 1)/phisq(j)[c]
enddo

do j = 0,Nmu
    gamma0(j) = zero
    top(j) = zero
    do k = n(j − 1) + 1,n(j)
        sigma0(k) = tilde_n(k)/(rlamda(j) + d(k))
        gamma0(j) = gamma0(j) + sigma0(k)
        top(j) = top(j) + sigma0(k)*d(k)[d]
    enddo
enddo

eta(0) = zero
do j = 1,Nmu + 1
    eta(j) = gamma0(Nmu − j + 1) + eta(j − 1)/(one − ubar(j − 1)*eta(j − 1))
enddo

prod(0) = one
do k = 1,Nmu
    prod(k) = prod(k − 1)*(one − ubar(Nmu − k + 1)*eta(Nmu − k + 1))
enddo

do j = 0,Nmu[e]
    do k = n(j − 1) + 1,n(j)
        vector(k) = sigma0(k)*rmu(0)/(prod(j)*S0(k))
    enddo
enddo

ph0bar = zero[f]
do j = 1,Nmu
    ph0bar = ph0bar + top(j)/prod(j)
enddo
ph0bar = ph0bar*rmu(0)

chi0 = (one − rmu(0)*eta(Nmu + 1))/eta(Nmu + 1)[g]

tilde_eta(1) = one − ubar(1)*eta(1)[h]
do l = 1,Nmu
    beta(l + 1) = ubar(l + 1)/ubar(l)
    alpha(l + 1) = one + beta(l + 1) − ubar(l + 1)*gamma0(Nmu − l)
    tilde_eta(l + 1) = alpha(l + 1) − beta(l + 1)/tilde_eta(l)
enddo
eta(Nmu + 1) = (one − tilde_eta(Nmu + 1))/ubar(Nmu + 1)
```

[a] ubar(0) defined but numerical value not needed
[b] Note: phisq not function of pressure
[c] Note: ubar = const × pressure
[d] top(0) is not used
[e] To calculate eigenvector
[f] To calculate $\tilde{\phi}(0)$ by Eq. (13)
[g] To calculate $\chi(0)$ by Theorem 3 and Eq. (12)
[h] To calculate η_{N+1} by continued fraction

from Eq. (12). Moreover, it reduces *by inspection* to Eq. (2) for the traditional one-μ case.

In Table 2, we give three columns of eigenvalues calculated by these methods for this model reaction, and it is seen that the results are well-behaved in the sense that the inequality (12) always holds. Also, it can be seen that the separation between the lower and upper bounds is quite small, even at the lowest pressures, and that there is no need to go to the trouble of iterating beyond $\bar{\phi}(0)$ and $\chi(0)$.

A corresponding eigenvector $\psi(0)$ is also available through Proposition 1(i), from which it is possible to calculate the steady-state distribution and the incubation time [8]. It was found that, even for this relatively high-temperature reaction, all elements of the numerical vector and $\psi(0)$ usually agreed to five significant figures and, of course, this calculation of $\psi(0)$ is orders of magnitude faster than that for the numerical procedure. This agreement reflects itself in the fact that the incubation times calculated by the two methods differed only by about 1% at the low pressures, and converged towards each other, and towards τ_{rel}, as $p \to \infty$; in practice, induction times are very sensitive to errors in the vector ψ_0: thus, only one calculation of τ_{inc} is compared with τ_{rel} in Table 2.

These procedures can be programmed very compactly, and a specimen algorithm is shown in Table 3 demonstrating a selection of the methods described in this paper.

5. Behaviour at the low-pressure limit

The derivations of the results discussed in this section are to be found in the Appendix to this paper. Corollary 2 presented there provides the pair of bounds

$$\mu_0 \|I^D S_0\|^2 \leqslant \gamma_0 \leqslant \mu_0(1-\epsilon), \tag{14}$$

accurate to first order in μ_0, which are instructive in understanding the relationship between the vibrational relaxation rate and the low-pressure rate constant; here $\epsilon = \tilde{n}_0$, the total fractional population that lies within the range of d_0 and therefore remains in equilibrium with the heat bath during reaction under fall-off conditions. Thus, the low-pressure rate is bounded by the product of the vibrational relaxation rate with, on the one side the total reactive population, and on the other side, the total non-ground-state population. For our particular model calculation at 2000°K, the population difference $(1-\tilde{n}_0)$ is 0.66, the reactive fraction is about 1.3×10^{-6}, and with $\mu_0 = 2.5 \times 10^3\ \text{Torr}^{-1}\ \text{s}^{-1}$, this inequality becomes $3.2 \times 10^{-3} \leqslant 4.0 \leqslant 1.6 \times 10^3$, all in units of $\text{Torr}^{-1}\ \text{s}^{-1}$. On the other hand, if one makes the standard RRKM assumption that all states above the threshold are reactive, the value of $\|I^D S_0\|^2$ increases by a factor of about 65 to 8.3×10^{-5}, but there is only a 2.5-fold increase in the rate: the inequality (14) now reads $0.21 \leqslant 9.93 \leqslant 1.6 \times 10^3$ ($\text{Torr}^{-1}\ \text{s}^{-1}$). The point to appreciate here is that the low-pressure rate is only weakly dependent on the numerical magnitude of $\|I^D S_0\|^2 (\equiv \sum' \tilde{n}_m)$ — except in the special case when the total unreactive population is coupled with a single relaxation rate $\lambda_0 = \mu_0$

(Corollary 3). Such a situation is encountered in the usual one-μ approximation, when the upper and lower bounds in (14) coalesce; however, it can happen whenever the range of J_1 lies entirely within the range of D.

The limiting low-pressure rate constant has played an important rôle in weak-collision unimolecular reaction rate theory, and it has been used together with the result of Corollary 3 to define a "collision efficiency β_c" on the assumption that

$$k_{\text{uni},0} \equiv \mu_0 \gamma_0^0 = \beta_c Z \| I^D S_0 \|^2 \tag{15}$$

where Z is the collision rate and $\| I^D S_0 \|^2 \equiv \sum' \tilde{n}_m$ is the total population above reaction threshold. For the general case, much tighter bounds than Eq. (14) are available in Theorem 4 although, as noted above and illustrated in Table 2, the range between $\bar{\phi}(0)$ and $\chi(0)$ is the greatest at the low-pressure limit. Nevertheless, for most purposes $\bar{\phi}(0)$ is an adequate approximation and, either from Eq. (13) or Theorem 4(i), we can write the low-pressure limiting rate in the form

$$\bar{\phi}(0) = \mu_0 \sum_{j=0}^{N} \frac{\| I_j^D S_0 \|^2}{\prod_{k=1}^{j} \tilde{\eta}_{N-k+1}^0(0)} + \mathcal{O}(\mu_0^2) \tag{16}$$

where, from Lemma 9(iii), $\tilde{\eta}_0^0(0) = 1$, $\beta_1^0 = 0$, and

$$\tilde{\eta}_{N-k+1}^0(0) = 1 + \frac{\mu_k}{\lambda_k} \frac{(S_0, [I_k^D - I_k] S_0)}{\| J_k S_0 \|^2} + \beta_{N-k+1}^0 \left(1 - \frac{1}{\tilde{\eta}_{N-k}^0(0)} \right),$$

$$\beta_{N-k+1}^0 = \frac{\mu_k \| J_{k+1} S_0 \|^2}{\mu_{k+1} \| J_k S_0 \|^2}.$$

Equation (16) is independent of the d_m as it should be [9]. Thus, we can write

$$\beta_c = \frac{\mu_0}{Z \| I^D S_0 \|^2} \sum_{j=0}^{N} \frac{\| I_j^D S_0 \|^2}{\prod_{k=1}^{j} \tilde{\eta}_{N-k+1}^0(0)} \tag{17}$$

but because of its recursive nature, it is only possible to find simple expressions for β_c or the limiting low-pressure rate when the structure of the collisional relaxation is approximated by only a few values of μ, see, e.g., [10]. However, both analytic and numerical evidence indicates that γ_0^0 is very weakly determined by the value of $\| I^D S_0 \|^2$, as was already known for one solvable weak-collision case, the tridiagonal one [11], and for the analogous diatomic dissociation case [12].

6. Discussion

Our original aim when we introduced the relaxation matrix M in 1981 was to provide a general way of dealing with weak-collision systems [3], in which the collisional relaxation could not be described by a single rate μ_0. In this paper, we have provided the apparatus to deal with a generalised N-μ relaxation–reaction

system. Analytic converging bounds on the rate constant have been derived and, in fact, the zeroth approximation is usually sufficient, giving a close pair of bounds and an acceptable eigenvector. In the way we have illustrated it, we have taken a small molecule and assumed (reasonably) that its relaxation rates increase with increasing energy; it is therefore obvious that if the index j is allowed to correlate with energy, and the transition rates among states at different energies are known, these equations provide a complete solution for the rate constant at all pressures. The corresponding eigenvector will allow us to compute the non-equilibrium steady-state population during the reaction and the incubation time. The restrictions of the existing theory, namely the need to neglect cascading above reaction threshold; that all states below threshold must be in equilibrium with each other (since we may use as many λ_j as we like simply to span the unreactive range); and the induction time in a shock-wave experiment must be the same as the collisional deactivation rate ω are removed. In fact, the incubation time now correlates with the vibrational relaxation time, as it should.

However, Eq. (13) and its equivalents are a *general* solution to the unimolecular thermal rate problem in the sense that *all* relaxation matrices A may be reduced by a similarity transformation to the matrix M of Eq. (3). This is easily shown, as follows. Let the two matrices A and M have the same set of eigenvalues, and write the diagonalised forms as A^d and M^d. Then there exists a transformation matrix Ω_A (comprising the normalised eigenvectors of A), such that $\Omega_A^{-1} A \Omega_A = A^d$ with $\Omega_A^{-1} = \Omega_A^T$. Similarly, $\Omega_M^{-1} M \Omega_M = M^d = A^d$ with $\Omega_M^{-1} = \Omega_M^T$. Hence, $\Omega_M A^d \Omega_M^T = M = \Omega_M \Omega_A^T A \Omega_A \Omega_M^T$, i.e. there always exists a matrix $\Omega_A \Omega_M^T$ that will transform A to M. Thus, Eq. (13) and its equivalents contain all of the permissible functionality of the thermal rate of a unimolecular reaction, even for cases where it may not be possible to write down, by inspection, the appropriate form of the relaxation matrix M.

Since we are approaching a time when measurements are yielding relaxation rates among states or groups of states, it may soon become possible to construct a table of properties (i.e. the λ_j and their ranges) such as that shown in Sect. 4, whence the full solution to the rate problem would be at hand, including properties that can only be calculated through a knowledge of the eigenvector. This is therefore a considerable advance upon the existing situation where steady-state methods are commonly used to describe the competition between reaction and relaxation in unimolecular reaction processes.

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Appendix: Limiting behaviour of γ_0

In this Appendix we study the behaviour of γ_0 as $\mu_j \to 0$ for each j. In particular, we develop procedures to determine

$$\gamma_0^0 = \lim_{\mu_0 \to 0} \frac{\gamma_0}{\mu_0}$$

which are similar to those for determining γ_0; it will be assumed that

$$\frac{\mu_j}{\mu_0} \underset{\mu_0 \to 0}{\longrightarrow} \nu_j = \text{const.} \quad \text{for all } j \geqslant 0.$$

Let $x = \mu_0 y$. As x varies over $(-\infty, \mu_0)$, y varies over the open interval $(-\infty, 1)$. It is clear that

$$\gamma_0^0 = \lim_{\mu_0 \to 0} \frac{\bar{\phi}(\gamma_0)}{\mu_0} = \lim_{\mu_0 \to 0} \frac{\chi(\gamma_0)}{\mu_0}.$$

Thus γ_0^0 may be characteristed as the fixed point of $\bar{\phi}^0(y)$ and $\chi^0(y)$ where

$$\bar{\phi}^0(y) = \lim_{\mu_0 \to 0} \frac{\bar{\phi}(x)}{\mu_0} \tag{18}$$

and

$$\chi^0(y) = \lim_{\mu_0 \to 0} \frac{\chi(x)}{\mu_0}. \tag{19}$$

It should be remarked that $\bar{\phi}^0(\gamma_0^0) = \chi^0(\gamma_0^0)$ differs from $\bar{\phi}(\gamma_0)/\mu_0 = \chi(\gamma_0)/\mu_0$ by terms of $\mathcal{O}(\mu_0)$. The functions $\bar{\phi}^0(y)$ and $\chi^0(y)$ are extensions of $\bar{\phi}^0(\gamma_0^0)$ and $\chi^0(\gamma_0^0)$ respectively, as defined by Eqs. (18) and (19). This is sufficient to determine γ_0^0 provided that $\gamma_0^0 < 1$. Since $0 \leqslant \gamma_0 < \mu_0$, we have that $0 \leqslant \gamma_0^0 \leqslant 1$. In Lemma 8 we improve the upper bound to enable us to make use of Eqs. (18) and (19). The identity projection on the range of D_j will be denoted by I_j^D for each j and that on the range of D by I^D, i.e. $I^D = \sum_{j=0}^{N} I_j^D$.

Lemma 8. *Let γ_0^0 be as above. Then we have*

$$0 \leqslant \gamma_0^0 \leqslant 1 - (S_0, (I_0 - I_0^D)S_0) = 1 - \epsilon.$$

Proof. Since γ_0 is the lowest eigenvalue of $(M + D)$, γ_0/μ_0 is the lowest eigenvalue of

$$\frac{1}{\mu_0}(M + D) = \left[(1 - p_0) + \sum_{j=1}^{N} \frac{\mu_j}{\mu_0}(J_j - p_j) + \frac{1}{\mu_0} D\right].$$

Consequently

$$\frac{\gamma_0}{\mu_0} \leqslant \frac{1}{\mu_0} \frac{(\theta, (M + D)\theta)}{(\theta, \theta)}$$

with any non-zero vector θ. We have used the fact that $(1/\mu_0)(M + D)$ is self-adjoint. Let θ vary over the range of $(I_0 - I_0^D)$, which, by assumption, has at least one non-zero vector. For each such θ, $D\theta = 0$ and $J_j\theta = p_j\theta = 0$ for $j = 1, 2, \ldots, N$. Hence

$$\frac{\gamma_0}{\mu_0} \leqslant \min_{\theta} \frac{(\theta, (1 - p_0)\theta)}{(\theta, \theta)} \leqslant 1 - \max_{\theta} \frac{(\theta, p_0\theta)}{(\theta, \theta)} = 1 - \delta$$

where min and max are taken as θ varies over the range of $(I_0 - I_0^D)$. It is clear that

$$\delta = \max_{\theta} \frac{(\theta, (I_0 - I_0^D)p_0(I_0 - I_0^D)\theta)}{(\theta, \theta)}$$

and hence δ is the largest eigenvalue of

$$(I_0 - I_0^D)p_0(I_0 - I_0^D) = \epsilon \frac{(I_0 - I_0^D)p_0(I_0 - I_0^D)}{\epsilon} = \epsilon q.$$

Since q is an orthoprojection, it has precisely two eigenvalues, namely zero and one. Hence $\delta = \epsilon$. The result follows by taking the limit as $\mu_0 \to 0$ and observing that ϵ is independent of μ_0.

It will be shown that $\bar{\phi}^0(y)$ and $\chi^0(y)$ are determined by the limits of $D_j\sigma_j^0(\mu_0 y)$, $\mu_0\sigma_j^0(\mu_0 y)I_j$ and $\tilde{\eta}_j(\mu_0 y)$ for each j as $\mu_0 \to 0$ which we determine in Lemma 9.

Lemma 9. *Let the symbols be as above and y in $(-\infty, 1)$. Then*

(i) $$\lim_{\mu_0 \to 0} D_j\sigma_j^0(\mu_0 y) = I_j^D, \qquad j = 0, 1, \ldots, N;$$

(ii) $$\lim_{\mu_0 \to 0} \mu_0\sigma_j^0(\mu_0 y)I_j = \frac{(I_j^D - I_j)}{y - \sum_{k=0}^{j} \nu_k}, \qquad j = 0, 1, \ldots, N;$$

(iii) $$\tilde{\eta}_{j+1}^0(y) = \lim_{\mu_0 \to 0} \tilde{\eta}_{j+1}(\mu_0 y)$$

$$= 1 - \frac{\nu_{N-j}}{\|J_{N-j}S_0\|^2} \frac{(S_0, [I_{N-j}^D - I_{N-j}]S_0)}{y - \sum_{k=0}^{N-j} \nu_k} + \beta_{j+1}^0 \left(1 - \frac{1}{\tilde{\eta}_j^0(y)}\right), \qquad j = 0, 1, \ldots, N;$$

where

$$\beta_{j+1}^0 = \lim_{\mu_0 \to 0} \frac{\bar{\mu}_{j+1}}{\bar{\mu}_j} = \frac{\mu_{N-j}}{\mu_{N-j+1}} \frac{\|J_{N-j+1}S_0\|^2}{\|J_{N-j}S_0\|^2}, \qquad j = 1, \ldots, N;$$

with β_1^0 being arbitrary and $\tilde{\eta}_0^0(y) = 1$.

Remark. It will be convenient to set $\beta_1^0 = 0$ or to determine $\tilde{\eta}_{j+1}^0(y)$ recursively starting with $\tilde{\eta}_1^0(y)$ rather than $\tilde{\eta}_0^0(y)$.

Proof. (i) It follows from Lemma 7 that

$$D_j\sigma_j^0(\mu_0 y) = (D_j - \mu_0 y + \lambda_j)^{-1}D_j.$$

Since $\mu_0 y$ and λ_j tend to zero with μ_0, and D_j is invertible on its range, we have

$$\lim_{\mu_0 \to 0} D_j\sigma_j^0(\mu_0 y) = I_j^D.$$

(ii) Again, from the definition

$$\mu_0\sigma_j^0(\mu_0 y)I_j = \mu_0(D_j - \mu_0 y + \lambda_j)^{-1}I_j.$$

By the same argument as in (i)

$$\mu_0(D_j - \mu_0 y + \lambda_j)^{-1} I_j^D \xrightarrow[\mu_0 \to 0]{} 0.$$

Consequently

$$\lim_{\mu_0 \to 0} \mu_0 \sigma_j^0(\mu_0 y) I_j = \lim_{\mu_0 \to 0} \frac{\mu_0}{\mu_0 y - \lambda_j}(I_j^D - I_j) = \frac{(I_j^D - I_j)}{y - \sum_{k=0}^{j} \nu_k}.$$

(iii) From (11), we have

$$\tilde{\eta}_{j+1}^0(y) = 1 + \beta_{j+1}^0\left(1 - \frac{1}{\tilde{\eta}_j^0(y)}\right) - \frac{\nu_{N-j}}{\|J_{N-j} S_0\|^2} \lim_{\mu_0 \to 0} (I_{N-j} S_0, \mu_0 \sigma_{N-j}^0(\mu_0 y) S_0).$$

The result follows from (ii). Values for β_1^0 and $\tilde{\eta}_0^0$ are specified to include $\tilde{\eta}_1^0$ in the range of the definition.

Lemma 9 contains sufficient information to derive defining equations for $\bar{\phi}^0(y)$ and $\chi^0(y)$, which we do in Theorem 4.

Theorem 4. *Let the symbols be as above. Then*

(i)
$$\bar{\phi}^0(y) = \sum_{j=0}^{N} \frac{\|I_j^D S_0\|^2}{\prod_{k=1}^{j} \tilde{\eta}_{N-k+1}^0(y)},$$

(ii)
$$\bar{\phi}^0(y) = \xi_{N+1}^0(y)$$

where

$$\xi_{j+1}^0(y) = \lim_{\mu_0 \to 0} \xi_{j+1}(\mu_0 y) = \|I_{N-j}^D S_0\|^2 + \frac{\xi_j^0(y)}{\tilde{\eta}_j^0(y)}$$

$$= \|I_{N-j}^D S_0\|^2 + \frac{\xi_j^0(y)}{1 - \frac{\bar{\mu}_j^0}{1-y}[\|J_{N-j+1} S_0\|^2 - \xi_j^0(y)]}, \quad j = 0, 1, \ldots, N;$$

with $\bar{\mu}_j^0 = \lim_{\mu_0 \to 0}(\bar{\mu}_j/\mu_0)$ *and* $J_{N+1} = 0$, $\xi_0^0 = 0$.

(iii)
$$\bar{\phi}^0(y) = 1 - (1-y)(1 - \tilde{\eta}_{N+1}^0(y)) = y + (1-y)\tilde{\eta}_{N+1}^0(y),$$

(iv)
$$\chi^0(y) = y + \frac{1}{1 - \tilde{\eta}_{N+1}^0(y)} - 1.$$

Here $\tilde{\eta}_{N+1}^0(y)$ is as in Lemma 9(iii).

Proof.
(i) Follows from Proposition 1(iii) and Lemma 9(i).
(ii) Both of the equalities follow from Theorem 3 and Lemma 9(i).
(iii) Follows from Theorem 2 and Eq. (18).
(iv) Follows from Theorem 2 and Eq. (19).

Instead of deriving expressions for $\bar{\phi}^0(y)$ and $\chi^0(y)$ in Theorem 4, one may obtain $\bar{\phi}^0(\gamma_0^0)$ and $\chi^0(\gamma_0^0)$. The extensions $\bar{\phi}^0(y)$ and $\chi^0(y)$ are then obtained by

replacing γ_0^0 on the right-hand side by y. The result is the same as given in Theorem 4.

Let $0 \leqslant x_0 \leqslant \gamma_0$ and $y_0 = \lim_{\mu_0 \to 0} (x_0/\mu_0)$. Then since

$$\frac{x_0}{\mu_0} \leqslant \frac{\bar{\phi}(x_0)}{\mu_0} \leqslant \frac{\gamma_0}{\mu_0} \leqslant \frac{\chi(x_0)}{\mu_0},$$

we have

$$y_0 \leqslant \bar{\phi}^0(y_0) \leqslant \gamma_0^0 \leqslant \chi^0(y_0). \tag{20}$$

Conversely, with $y_0 \leqslant \gamma_0^0$, one may obtain $x_0(\mu_0)$ such that $y_0 = \lim_{\mu_0 \to 0} (x_0/\mu_0)$ and $0 \leqslant x_0 \leqslant \gamma_0$ in a small neighbourhood of $\mu_0 = 0$. Hence (20) holds for an arbitrary $y_0 \leqslant \gamma_0^0$. Thus Theorem 4 provides procedures to produce lower and upper bounds to γ_0^0. However, the convergence of the iterative procedure, which is similar to that of Lemma 3, is not obvious. Properties of $\tilde{\eta}_j^0(y)$ obtained in Lemma 10 and Lemma 11 will be sufficient to deduce this and some other results.

Lemma 10. *With $\tilde{\eta}_j^0(\gamma_0^0)$ as in Lemma 9(iii), we have*

$$0 \leqslant \tilde{\eta}_j^0(\gamma_0^0) \leqslant 1, \qquad j = 0, 1, \ldots, (N+1).$$

Proof. The result follows from the definition if

$$0 \leqslant \tilde{\eta}_j(\gamma_0) \leqslant 1, \qquad j = 0, 1, \ldots, (N+1),$$

which we show below.

Values of $\tilde{\eta}_0(\gamma_0)$ and $\tilde{\eta}_{N+1}(\gamma_0)$ are exactly known, equal to one and zero respectively. Thus one may restrict $j = 1, 2, \ldots, N$. By definition

$$\eta_j(\gamma_0) = (\phi_j, B_{j-1}^{-1}(\gamma_0)\phi_j), \qquad j = 1, 2, \ldots, N;$$

and $B_{j-1} > 0$ from Lemma 6, since $\gamma_0 < \mu_0$. Hence $\eta_j(\gamma_0) \geqslant 0$ implying that $\bar{\mu}_j \eta_j \geqslant 0$, i.e. $\tilde{\eta}_j(\gamma_0) \leqslant 1$.

It is straightforward to check that

$$\|J_{N-j+1} S_0\|^2 \tilde{\eta}_j(\gamma_0) = (J_{N-j+1} S_0, [1 - \mu_{N-j+1}(\mu_{N-j+1} + Q)^{-1}] J_{N-j+1} S_0)$$

where

$$Q = \mu_0 - \gamma_0 + D + \sum_{k=1}^{j-1} \mu_{N-k+1}(J_{N-k+1} - p_{N-k+1}) + \sum_{k=j+1}^{N} \mu_{N-k+1} J_{N-k+1} \geqslant 0.$$

Hence

$$\|J_{N-j+1} S_0\|^2 \tilde{\eta}_j(\gamma_0) = (J_{N-j+1} S_0, Q^{1/2}(\mu_{N-j+1} + Q)^{-1} Q^{1/2} J_{N-j+1} S_0) \geqslant 0,$$

i.e. $\tilde{\eta}_j(\gamma_0) \geqslant 0$.

Remark. Whilst the lower bound on $\tilde{\eta}_j^0$ is zero, it will not be reached whenever it appears in a denominator, for all such quantities are well-defined.

Lemma 11. *Let* $\tilde{\eta}^0_{N+1}(y)$ *be defined in Lemma* 9(*iii*) *for* y *in* $(-\infty, 1)$; *then*

$$\frac{d}{dy}\tilde{\eta}^0_{N+1}(y) \leqslant 0.$$

Proof. The result will be established if $(d/dy)\tilde{\eta}^0_j(y) \leqslant 0$ for $j = 0, 1, \ldots, (N+1)$. This is clearly true for $j = 0$. Let it be true for some j. It follows from Lemma 9(iii) that

$$\frac{d}{dy}\tilde{\eta}^0_{j+1}(y) = \beta^0_{j+1}\frac{1}{(\tilde{\eta}^0_j(y))^2}\frac{d}{dy}\tilde{\eta}^0_j(y) + \frac{\nu_{N-j}}{\|J_{N-j}S_0\|^2}\frac{(S_0, [I^D_{N-j} - I_{N-j}]S_0)}{\left(y - \sum_{k=0}^{N-j}\nu_k\right)^2} \leqslant 0$$

for $\beta^0_{j+1} \geqslant 0$, $\nu_{N-j} \geqslant 0$ and $I^D_{N-j} \leqslant I_{N-j}$. The result follows by induction.

Non-negativity and monotonicity of $\tilde{\eta}^0_j(y)$ imply the same for $\xi^0_j(y)$ and hence for $\bar{\phi}^0(y)$:

Lemma 12. *Let* $\bar{\phi}^0(y)$ *be as in Theorem* 4, *then for each* $y < 1$,

(i) $\bar{\phi}^0(y) \geqslant 0$ (ii) $\dfrac{d\bar{\phi}^0(y)}{dy} \geqslant 0.$

Proof. Consider the representation of $\bar{\phi}^0(y)$ given in Theorem 4(ii). It will be sufficient to prove the result for $\xi^0_j(y)$ for each j.
(i) For $j = 0$, it is clearly true. Let $\xi^0_j(y) \geqslant 0$ for some j. Then $\xi^0_{j+1}(y) \geqslant 0$ from Lemma 10. By induction $\xi^0_j(y) \geqslant 0$ for each j.
(ii) Again, for $j = 0$ the result is true. Assume it to hold for some j. Then

$$\frac{d\xi^0_{j+1}(y)}{dy} = \frac{1}{\tilde{\eta}^0_j(y)}\frac{d\xi^0_j(y)}{dy} - \frac{\xi^0_j(y)}{(\tilde{\eta}^0_j(y))^2}\frac{d\tilde{\eta}^0_j(y)}{dy} \geqslant 0$$

as a consequence of (i) and Lemma 11.

Lemma 12 provides a procedure to approximate γ^0_0 from below.

Corollary 1. *Let* $y_0 \leqslant \gamma^0_0$ *and* $y_{m+1} = \bar{\phi}^0(y_m)$, $m = 0, 1, \ldots,$; *then* $y_m \uparrow \gamma^0_0 \downarrow \chi^0(y_m)$.

Proof. In view of Lemma 12, the result follows by the same argument as used to deduce the result of Lemma 3. Use is also made of (20).

In view of Corollary 1, converging lower and upper bounds to γ^0_0 may be produced iteratively starting with some $y_0 \leqslant \gamma^0_0$. A convenient value of y_0 is equal to zero. Although $\bar{\phi}(0)$ and $\chi(0)$ provide satisfactory bounds to γ_0, $\bar{\phi}^0(0)$ and $\chi^0(0)$ are not expected to be that close. More satisfactory values will be obtained by using the lower bound of Corollary 2 instead of zero.

Corollary 2. *With* γ^0_0 *and* I^D_j *as above, we have*

$$\|I^D S_0\|^2 \leqslant \gamma^0_0 \leqslant 1 - \epsilon$$

with $\epsilon > 0$.

Proof. The upper bound was established in Lemma 8. The lower bound follows from Theorem 4(i), Eq. (18) and Lemma 10 as they imply that

$$0 \leqslant \prod_{k=1}^{j} \tilde{\eta}^0_{N-k+1}(\gamma^0_0) \leqslant 1 \quad \text{for } j = 0, 1, \ldots, N.$$

In view of Corollary 1 and Corollary 2 we have

Proposition 2. *With the symbols as above*

$$0 \leqslant \bar{\phi}^0(0) \leqslant \bar{\phi}^0(\|I^D S_0\|^2) \leqslant \gamma^0_0 \leqslant \chi^0(\|I^D S_0\|^2) \leqslant \chi^0(0).$$

Proof. The fact that $0 \leqslant \bar{\phi}^0(0)$ follows form the non-negativity of $\bar{\phi}(x)$; $\bar{\phi}^0(0) \leqslant \bar{\phi}^0(\|I^D S_0\|^2) \leqslant \gamma^0_0$ follows from Lemma 11, Corollary 2 and the fact that $\bar{\phi}^0(\gamma^0_0) = \gamma^0_0$. The inequality $\gamma^0_0 \leqslant \chi^0(\|I^D S_0\|^2)$ follows from (19) by setting $y_0 = \|I^D S_0\|^2$. The last inequality is obtained exactly as in (19) using the fact that $\chi(x)$ is a non-increasing function on $(-\infty, \mu_0)$.

For some special cases, γ^0_0 may be obtained exactly:

Corollary 3. *Let* $I^D_j = I_j$ *for* $j = 1, 2, \ldots, N$; *then*

$$\gamma^0_0 = \|I^D S_0\|^2.$$

Proof. Under the assumption, one has that

$$I^D = 1 - (I_0 - I^D_0)$$

and the result follows from Corollary 2.

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