NON-EXPONENTIAL TIME BEHAVIOR OF ELECTRON TRANSFER IN AN INHOMOGENEOUS POLAR MEDIUM

W. NADLER and R.A. MARCUS

Arthur Amos Noyes Laboratory of Chemical Physics [1], *California Institute of Techology, Pasadena, CA 91125, USA*

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An analysis is made of electron transfer (ET) in a polar medium described by a distribution of dielectric relaxation times, for the case that intramolecular contributions to the ET are negligible. The *generalized moment expansion* is used for an approximate multi-exponential description of the non-exponential time behavior of the ET. As an example, ET in glycerol-like solvents is considered, treated by the spatially inhomogeneous model for dielectric relaxation. For this model the ET rate at long times is found to vary as τ_0^{-1}, τ_0 being a dielectric relaxation time parameter, in contrast with a fractional dependence at short times.

1. Introduction

Recent experimental [1–10] and theoretical [11–27] results have established that ET in polar solvents can depend strongly on the dielectric relaxation of the surrounding medium. When intramolecular contributions to the ET are negligible, and the dielectric relaxation of the solvent around the donor–acceptor complex is characterized by a single dielectric relaxation time τ (Debye solvent) [#1], the time behavior of the ET process is *single exponential* [19,21]. This time behavior holds approximately even in case the barrier of the reaction is small. For the single-exponential time behavior an ET transfer rate constant can be defined unambiguously and is given by

$$\frac{1}{k_{\mathrm{ET}}(\tau)}=\frac{1}{k_{\mathrm{e}}}+I\tau\,, \qquad (1)$$

where τ is the longitudinal dielectric relaxation time of the solvent. I is a numerical factor depending on the free energy barrier ΔG^* of the reaction [19,21],

$$I=\ln 2+2\int_0^1 \mathrm{d}x\,\frac{\exp[(1-x^2)\beta\Delta G^*]-1}{1-x^2}$$
$$\approx\sqrt{\pi/\beta\Delta G^*}\,\exp(\beta\Delta G^*)\,,\quad \text{for}\ \beta\Delta G^*\ \text{large}\,. \qquad (2)$$

β is the scaled inverse temperature, $\beta=(k_{\mathrm{B}}T)^{-1}$, and the free energy barrier ΔG^* is related to the standard free energy ΔG^0 of the reaction by $\Delta G^*=(\Delta G^0-\lambda_0)^2/4\lambda_0$, λ_0 being the reorganization energy of the solvent [19,21]. The rate constant k_{e} in eq. (1) is the equilibrated ET rate constant,

$$k_{\mathrm{e}}=\nu_{\mathrm{q}}\exp(-\beta\Delta G^*)\,, \qquad (3)$$

and refers to adiabatic as well as non-adiabatic processes [11]. The functional form of the prefactor ν_{q} in eq. (3) depends on the adiabaticity of the reaction [18,19]. Experimentally, the observed rate constant k_{ET} will be k_{e} in the limit of fast dielectric relaxation of the solvent.

For ET processes with non-vanishing intramolecular contributions the time behavior of the fraction $Q(t)$ of non-reacted donors can deviate strongly from a single-exponential form [19,21]. This behavior is also expected for ET in a medium inhomogeneous with respect to the dielectric relaxation times [22], even in the absence of intramolecular contribu-

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[#1] We note, however, that there is recent theoretical and experimental evidence that, although the bulk dielectric properties of a solvent have Debye form, the local dielectric relaxation in the vicinity of an ion can be more complicated; see, e.g., refs. [24–26], and references therein.

tions [#2]. In such a situation the unambiguous definition of a (time-independent) ET rate constant is no longer possible. Instead, for a comparison of theoretical results with experiment the full complexity of the time behavior of $Q(t)$ should be taken into account in this case.

Recently, McGuire and McLendon [9] have reported results on intermolecular ET in solid glycerol which indicated a fractional power-law dependence of the ET rate on the dielectric relaxation time, $k_{\mathrm{ET}} \propto \tau^{-0.6}$. The analysis of their experiment is somewhat indirect since they observed ET between randomly distributed donors and acceptors, i.e. they saw a superposition of many different ET processes, and inferred a time-independent ET rate constant from their time-resolved data under the assumption of a single-exponential behavior for each individual process. The dielectric behavior of glycerol deviates strongly from a Debye form [28], and the deviation has been considered as deriving from an underlying microscopic spatial inhomogeneity in the dielectric relaxation times [22,29]. Rips and Jortner [22] have shown that under this assumption the short-time rate constant $k_s = -(\mathrm{d}/\mathrm{d}t)Q(t=0)$ exhibits a fractional power-law dependence, the exponent being equal to the exponent governing the distribution of relaxation times, as in eq. (8) below, having a value of about 0.6 for glycerol. One expects that the full time behavior of $Q(t)$ would be strongly non-exponential. Subsequently, Heitele et al. [10] reported time-resolved measurements of intramolecular ET in propylene glycol, having dielectric properties similar to glycerol, which showed a strong deviation from a single-exponential behavior. The short-time rate constant inferred from their observed $Q(t)$ again showed the fractional power-law dependence on τ with an exponent of about 0.6.

This successful description of the short-time behavior of ET in glycerol-like solvents raises the question of the time range of the validity of a static model using a distribution of dielectric relaxation times. Apart from providing a further check of that hypothesis on the origin of the dielectric behavior of glycerol-like solvents, an analysis of the full range of time-resolved data on ET, particularly near the glass transition, would also provide interesting information concerning the glassy properties of these media. For example, the temperature dependence of the time range for the validity of the inhomogeneous medium approximation could give information about the freezing out of dynamical degrees of freedom near the glass transition. It should also be noted that the nature of the *microscopic processes* giving rise to the Davidson–Cole behavior of the dielectric spectrum and to other relaxation processes with similar properties in glycerol and glycerol-like solvents has apparently not yet been resolved [#3]. The time behavior of ET is related to this question because of the coupling of ET to the dielectric relaxation.

In the following we wish to provide some theoretical tools for a further analysis of time-resolved measurements. An algorithm is given, based on the generalized moment expansion method [31], for the approximate description of the non-exponential time behavior of ET in an inhomogeneous medium, and is applied to the particular case of glycerol-like solvents. In this Letter we restrict our attention to the case of ET with a vanishing intramolecular contribution, where the local time behavior of the reaction can be described by eq. (1). The more complex case of including a contribution from the intramolecular degrees of freedom will be treated in a later publication [32].

2. Theory

The time behavior of a reaction process is usually monitored by observing the fraction $Q(t)$ of the unreacted species at time t. In the case of ET, for example, $Q(t)$ is the fraction of unreacted donor–acceptor complexes. In a spatially inhomogeneous medium, each donor–acceptor has a local solvent environment with a relaxation time τ, with a probability distribution $g(\tau)$ for the latter. The time behavior of a local reaction process is described by a function $Q(t|\tau)$ that depends on the actual microscopic environment through the parameter τ. The macroscopically observed time behavior is obtained by

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[#2] For a spatially homogeneous medium multiple relacation times have been treated in an electron transfer context in ref. [27].

[#3] For a discussion of different points of view and of experimental results, see, e.g., ref. [30].

averaging the local function $Q(t|\tau)$ over the distribution $g(\tau)$, i.e.

$$Q(t)=\langle Q(t|\tau)\rangle_\tau=\int \mathrm{d}\tau\, g(\tau)\, Q(t|\tau)\,. \tag{4}$$

Even when $Q(t|\tau)$ is single-exponential eq. (4) cannot be evaluated analytically, in general, and $Q(t)$ is expected to be strongly non-exponential. However, provided the *generalized moments* [31], i.e. the short-time moments $(n\geqslant 0)$

$$\mu_n=(-1)^n \left.\frac{\mathrm{d}^n}{\mathrm{d}t^n}\right|_{t=0} Q(t) \tag{5a}$$

and the long-time moments $(n>0)$

$$\mu_{-n}=\frac{1}{(n-1)!}\int_0^\infty \mathrm{d}t\, t^{n-1} Q(t) \tag{5b}$$

are finite (and non-zero), and can be calculated analytically or numerically, one can determine a multi-exponential approximation

$$Q(t)\approx q_N(t)=\sum_{i=1}^{N} b_i \exp(-\lambda_i t) \tag{6}$$

to the non-exponential function $Q(t)$ [33] [#4]. The parameters b_i and λ_i in the N-exponential approximation eq. (6) are determined from the requirement that $q_N(t)$ reproduces N short-time moments (5a) and N long-time moments (5b), as in ref. [31]. An actual algorithm to determine these parameters from the moments μ_{-N} to μ_{N-1} is provided in the present appendix. The degree N necessary for a sufficient approximation is determined by comparing approximations of successive degree. If the plot of $q_{N+1}(t)$ does not change visibly from $q_N(t)$, the approximation is presumed to be converged. In our experience, the convergence is relatively rapid because of the construction of $q_N(t)$ as an interpolation between short-time and long-time behavior.

We assume in the following that for ET in an inhomogeneous medium the local function $Q(t|\tau)$ is given by a single exponential with rate constant $k_{\mathrm{ET}}(\tau)$, eq. (1). In this case the generalized moments can be determined easily to be averages of powers of the rate constant with respect to $g(\tau)$, i.e.

$$\mu_n=\langle [k_{\mathrm{ET}}(\tau)]^n\rangle_\tau\,, \quad \text{for all } n\,. \tag{7}$$

3. Example: ET in glycerol-like solvents

In glycerol, propylene glycol, and other solvents the data on the frequency dependence of the dielectric constant (Davidson–Cole spectrum [28]) can be described in one view by assuming there exists a distribution of dielectric relaxation times [29]

$$g_{\mathrm{DC}}(\tau)=\frac{\sin(\pi\beta)}{\pi\tau}\left(\frac{\tau}{\tau_0-\tau}\right)^{\beta}, \quad \text{for } \tau\leqslant\tau_0\,, \tag{8}$$

with $g_{\mathrm{DC}}(\tau)$ being zero for $\tau>\tau_0$, the exponent β having a value of about 0.6 in the case of glycerol, and of about 0.66 in the case of propylene glycol. Using this distribution of relaxation times the generalized moments can be calculated readily from eq. (7), with the result

$$\mu_n=(k_{\mathrm{e}})^n F(n,\beta;1;-A)\,, \tag{9}$$

where F is the hypergeometric function [34] and

$$A=Ik_{\mathrm{e}}\tau_0\,, \tag{10}$$

with I given by eq. (2).

For negative values of n the function F is given by polynomials in A,

$$F(-n,\beta;1;-A)=\sum_{\nu=0}^{n}\binom{n}{\nu}(\beta)_\nu\frac{A^\nu}{\nu!}\quad (n>0)\,, \tag{11}$$

where $\binom{n}{\nu}$ is a binomial coefficient and $(\beta)_\nu$ is Pochhammers symbol [34],

$$(\beta)_\nu=\beta(\beta+1)...(\beta+\nu-1)\,,$$

with $(\beta)_0=1$. For positive values of n the functional form of F in eq. (9) can be determined by successively using Gauss' recurrence relations [34],

$$F(n+1,\beta;1;-A)=\frac{1}{n(1+A)}$$
$$\times\{[n(2+A)-(1+\beta A)]F(n,\beta;1;-A)$$
$$-(n-1)F(n-1,\beta;1;-A)\}\,, \tag{12a}$$

[#4] This approach applies to pseudo-first-order reactions with an exponential long-time behavior. In case of an algebraic long-time tail $Q(t)\propto t^{-\alpha}$ for $t\to\infty$, like, e.g., as in case of second-order reactions, a modified treatment can be given. The situation of ET donors and acceptors not forming isolated complexes and donors not in excess of acceptors would be such a case. However, we do not wish to introduce unnecessary complications here.

with

$$F(0,\beta;1;-A)=1 \tag{12b}$$

and

$$F(1,\beta;1;-A)=(1+A)^{-\beta} \tag{12c}$$

as starting values. Specifically, the lowest-order short- and long-time moments are

$$\mu_1=k_e(1+A)^{-\beta}\ , \tag{13a}$$

$$\mu_0=1\ , \tag{13b}$$

$$\mu_{-1}=k_e^{-1}(1+\beta A)\ , \tag{13c}$$

$$\mu_{-2}=k_e^{-2}[1+2\beta A+\tfrac{1}{2}\beta(\beta+1)A^2]\ . \tag{13d}$$

For $A<1$ the time behavior of $Q(t)$ is approximately single exponential with a relaxation time given by μ_{-1}. This result can also be seen from the fact that all moments can be approximated, correctly up to first order in A, by $\mu_n\approx(k_e)^n(1+\beta A)^n$, which has the functional dependence on n expected from a single-exponential behavior of $Q(t)$. The non-exponential behavior becomes pronounced for $A\gg 1$. In fig. 1 the results for the non-exponential time behavior of $Q(t)$ using the method of section 2 are shown for $A=10$ and for $A=100$. The value of β used was 0.6. The multi-exponential approximation was considered converged for $N=3$ and $N=5$, respectively.

For comparison, and in order to demonstrate the deviation from a single-exponential behavior, we have included in fig. 1 several one-exponential approximations. The short-time approximation

$$q_s(t)=\exp(-k_s t)\ , \tag{14a}$$

with

$$k_s=\mu_1 \tag{14b}$$

is equivalent to the approximate description already discussed by Rips and Jortner [22]. Fig. 1 shows that this approximation is useful at sufficiently short times. Its range of validity, which decreases with increasing values of A, i.e. for increasing τ_0, can become quite small at large A, as is demonstrated in fig. 1b. The long-time approximation

$$q_b(t)=q_b(0)\exp(-t/\tau_b)\ , \tag{15a}$$

with

$$\tau_b=\mu_{-2}/\mu_{-1} \tag{15b}$$

and

$$q_b(0)=(\mu_{-1})^2/\mu_{-2} \tag{15c}$$

reproduces the first two long-time moments (5b) of the exact function $Q(t)$. As fig. 1 shows, it provides a reasonable approximation of the exact $Q(t)$ for $k_e t\gtrsim\frac{1}{3}A$. In the mean (or linear) relaxation time approximation

$$q_a(t)=\exp(-t/\tau_a)\ , \tag{16}$$

the time constant τ_a is given by the first long-time

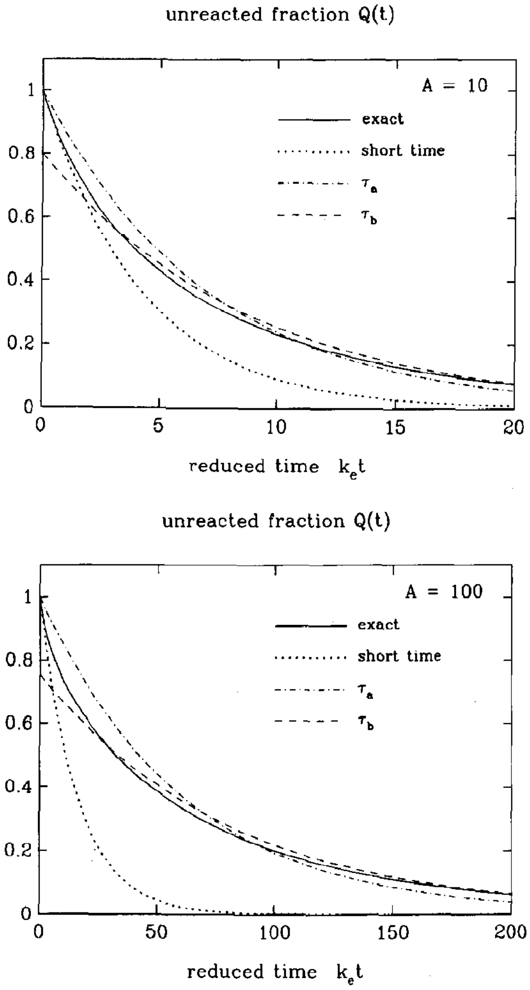

Fig. 1. Surviving fraction $Q(t)$ versus time for $A=10$ (upper) and $A=100$ (lower); the Davidson–Cole exponent is $\beta=0.6$; (dotted) short-time approximation, eqs. (14); (dashed) long-time approximation, eqs. (15); (dash-dotted) mean relaxation time approximation, eq. (16).

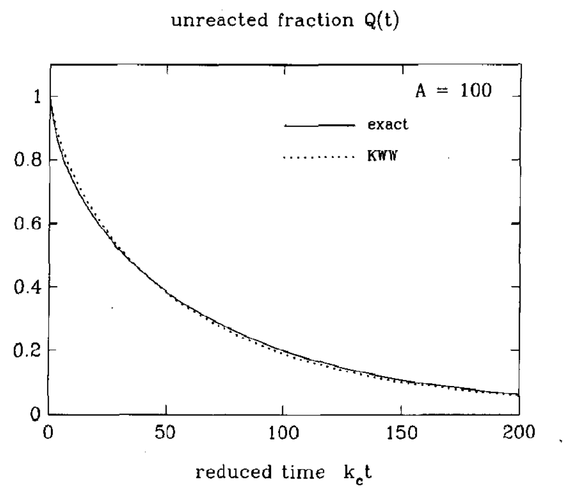

Fig. 2. Comparison of exact $Q(t)$ with Kohlrausch–Williams–Watts function, eq. (17); $A=100$.

moment μ_{-1}. The mean relaxation time τ_a is frequently employed as a first approximation of the time scale of the relaxation and, therefore, of the inverse of the average rate constant. Fig. 1 shows that, other than for short times, τ_a is a much better estimate than the short-time rate constant k_s at large values of A. However, the long-time approximation eq. (15) is still superior to eq. (16) as an approximate description of the decay of $Q(t)$ for $k_e t \gtrsim \frac{1}{2}A$.

A common approximation of relaxation processes in glassy systems is the stretched exponential function [30]

$$q_K(t) = \exp[-(t/\tau_K)^{\alpha_K}]\,, \qquad (17)$$

sometimes also called the Kohlrausch or Williams–Watts function. A modification of the generalized moment scheme [35] can be used to determine an optimized stretched exponential description of $Q(t)$. The parameters α_K and τ_K are given as solutions of the coupled equations

$$\mu_{-1} = \frac{\tau_K \Gamma(1/\alpha_K)}{\alpha_K}\,, \quad \mu_{-2} = \frac{(\tau_K)^2 \Gamma(2/\alpha_K)}{\alpha_K}\,, \qquad (18)$$

where Γ is the gamma function [34]. For large values of A ($A \gtrsim 100$) these parameters are $\alpha_K = 0.78$ and $\tau_K = 0.65\tau_b$. In fig. 2, eq. (17) is compared with the exact function for $A = 100$. It is evident that $Q(t)$ deviates somewhat from a stretched exponential form. However, eq. (17) is seen to provide a reasonable first approximation of the exact behavior over the full time range.

4. Discussion

We have presented above an analysis of the non-exponential time behavior of ET in glycerol-like solvents, under the assumption that the dielectric relaxation in this medium can be described by an intrinsic spatial inhomogeneity. Some conclusions that can be inferred from the above results are commented on below.

First, however, we comment on the significance of the important parameter A, defined in eq. (10). As the form of eq. (1) indicates, $1/I\tau$ is a solvent-dynamics-controlled rate constant, when the solvent dielectric relaxation time is τ (cf. also refs. [19,21]). The smallest value of the latter for the present inhomogeneous distribution of τ values is $1/I\tau_0$, since $\tau_0 \geqslant \tau$ in eq. (8). Thus, A is the ratio of k_e to this smallest solvent-controlled rate constant $1/I\tau_0$.

The short-time description of Rips and Jortner, useful at sufficiently short times, is seen to be applicable only for a small time range (relative to the time scale of the overall decay) when the parameter A is large, i.e. when the dielectric relaxation becomes slow. This result is particularly relevant near the glass transition, since τ_0 becomes large in this regime. Laser excitation of a reaction is frequently employed nowadays to study time-resolved reaction dynamics, and a successful deconvolution from the shape of the laser pulse is needed to extract the detailed very-short-time behavior.

We note that the non-exponential character of the decay of $Q(t)$ is present mainly in the very-short-time range. As seen in fig. 1, the long-time approximation eq. (15) is a reasonable approximation for $k_e t \gtrsim \frac{1}{2}A$. τ_b can therefore be regarded as the inverse of a valid long-time ET rate constant, and may be the dominant contribution to a multi-exponential fit to experimental data.

The short-time rate constant k_s shows a fractional power-law dependence on τ_0 for slow dielectric relaxation, $k_s \propto \tau_0^{-\beta}$, as discussed by Rips and Jortner [22]. In contrast, a different behavior holds for the long-time relaxation times τ_a and τ_b, as seen from eqs. (13), (15), and (16), in the case of the spatially inhomogeneous model for the solvent. Both relaxation times depend linearly on τ_0, i.e. $\tau_{a,b} \propto \tau_0$, for τ_0 large. It may also be noted from eqs. (13), (15), and (16) that the ratio of τ_a and τ_b assumes a constant value in the limit of very slow dielectric relaxation, i.e. for $A \to \infty$. This constant is given by

$$\frac{\tau_a}{\tau_b} \to \frac{2\beta}{\beta+1} \tag{19}$$

and has a value of about 3/4 for glycerol ($\beta \approx 0.6$). The single-exponential value of τ_a/τ_b would be unity. The result that $\tau_{a,b} \propto \tau_0$, for large τ_0, is not surprising: At long reaction times, the donor–acceptor complexes that are in a solvent environment with the shorter τ values in the distribution in eq. (8) have largely reacted, leaving as survivors mainly complexes whose solvent environment tends to have τ values near the peak at τ_0 in the distribution, τ_0 being the largest relaxation time in eq.(8).

Comparison of the theoretically predicted long- and very-short-time behavior of ET with experimental data may serve to determine whether the static description using a distribution of relaxation times [28,29] is appropriate for glycerol-like solvents, or whether a more dynamical model is necessary. Indeed, in a more dynamical model $\tau_{a,b}$ may no longer be proportional to τ_0 at large τ_0.

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Appendix

The algorithm to determine the parameters b_i and λ_i of the multi-exponential approximation eq. (6) from the moments μ_{-N} to μ_{N-1} presented below is the one given in ref. [31]. However, we repeat it here for the sake of completeness and easier accessibility.

The rates λ_i of the approximation eq. (6) are the eigenvalues of the *Frobenius matrix*

$$\mathbf{F} = \begin{pmatrix} 0 & 0 & \cdots & 0 & \gamma_0 \\ 1 & 0 & \cdots & 0 & \gamma_1 \\ 0 & 1 & \cdots & 0 & \gamma_2 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & \gamma_{N-1} \end{pmatrix}, \tag{A1}$$

a special form of an upper Hessenberg matrix [36]. Due to the specific from of $\mathbf{F}$, these eigenvalues can be determined, alternatively to numerical diagonalization, by determining the roots of the related polynomial in λ,

$$P_N(\lambda) = \lambda^N - \gamma_{N-1}\lambda^{N-1} - \ldots - \gamma_1\lambda - \gamma_0\,. \tag{A2}$$

The γ_i in $\mathbf{F}$ are the elements of a vector γ which is the solution of the linear equation

$$\mathbf{A}\gamma = \boldsymbol{a}_N, \tag{A3}$$

where the matrix $\mathbf{A}$ is given by ($i, j = 0, \ldots, N-1$)

$$(\mathbf{A})_{ij} = \mu_{-N+i+j}\,, \tag{A4}$$

and the vectors $\boldsymbol{a}_j$ by ($i = 0, \ldots, N-1; j = 0, \ldots, N$)

$$(\boldsymbol{a}_j)_i = \mu_{-N+i+j}\,. \tag{A5}$$

The amplitudes b_i of the exponentials in eq. (6) are given by

$$b_i = \frac{(\boldsymbol{a}' \cdot \boldsymbol{f}_i)(\boldsymbol{a} \cdot \boldsymbol{f}_i)}{(\boldsymbol{f}_i \cdot \mathbf{A}\boldsymbol{f}_i)}\,, \tag{A6}$$

where $\boldsymbol{f}_i$ is the (right) eigenvector of the matrix $\mathbf{F}$ for the eigenvalue λ_i. Because of the simple form of $\mathbf{F}$ the eigenvectors can be determined directly from the eigenvalues, i.e.

$$(\boldsymbol{f}_i)_0 = \gamma_0/\lambda_i, \tag{A7a}$$

$$(\boldsymbol{f}_i)_j = [(\boldsymbol{f}_i)_{j-1} + \gamma_j]/\lambda_i\,, \quad j > 0\,. \tag{A7b}$$

The vectors $\boldsymbol{a}$ and $\boldsymbol{a}'$ in eq. (A5) are particular vectors $\boldsymbol{a}_j$ given for even N by

$$\boldsymbol{a} = \boldsymbol{a}' = \boldsymbol{a}_{N/2}\,, \tag{A8a}$$

and for odd N by

$$\boldsymbol{a} = \boldsymbol{a}_{(N-1)/2}\,, \quad \boldsymbol{a}' = \boldsymbol{a}_{(N+1)/2}\,. \tag{A8b}$$

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