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An Efficient Method for Computing NMR Spectral Densities Involving Kohlrausch/Williams–Watts Decay Function

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An Efficient Method for Computing NMR Spectral Densities Involving Kohlrausch/Williams–Watts Decay Function

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Abstract

Motivation. The relaxation behavior of dielectrics in time dependent external electric and magnetic fields plays an important role in the determination and understanding of chemical structures. For example, NMR often requires the evaluation of spectral densities to determine relaxation parameters. Traditionally, spectral densities are represented by semi–infinite integrals with oscillatory integrands. Special algorithms are needed to compute these accurately, and this affects evaluation of all related properties. A new procedure is presented in this paper for the fast and accurate calculation of the spectral densities that involve the Kohlrausch/Williams–Watts decay function. Comparisons with previously published benchmarks show that our procedure is numerically stable and can be used safely for a wide range of parameters.

Method. NMR spectral densities obtained using the Kohlrausch/Williams–Watts decay function is usually represented by a semi–infinite integral containing an oscillating integrand. For certain values of the parameters, these oscillations for certain parameters are very strong and pose challenging difficulties from a practical point of view since classical integration techniques are usually unable to interpolate accurately the integrand. In this investigation, we propose to evaluate the spectral densities of interest by means of an infinite series which is obtained from the initial integral representation. However, based on two theoretical results, our series are shown to converge logarithmically which makes direct summation techniques extremely costly. To circumvent this difficulty we apply Wynn's epsilon algorithm to accelerate the convergence of the infinite series hence allowing an efficient numerical procedure to be obtained.

Results. Thorough comparisons with previously published data by Dishon *et al*. (*J. Res*. *Natl*. *Bur*. *Stand*. **1985**, *90*, 27–39) are carried. Selected numerical data are presented in several tables showing the agreement of our calculations with those in the literature. In addition, the result of a large scale comparison is provided as a gray level image in which the axes represent typical values of some parameters (used in practice) while the gray level provides the number of exact digits.

Conclusions. It is shown that the procedure developed in this paper allows spectral densities to be accurately computed accurately. Thorough comparisons with previous work show the stability of the numerical approach. In addition, the proposed algorithm is very general and is therefore useable for a wide range of parameters that are needed in practice.

Keywords. Kohlraush/Williams–Watts decay function; NMR spectral densities; oscillating integrands; logarithmic convergence; convergence accelerators; epsilon algorithm.

Dedicated on the occasion of the 75th birthday to Professor Lemont B. Kier.

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1 INTRODUCTION

In the past few years, numerous papers in which Kohlrausch/Williams–Watts, abbreviated to KWW, decay function was used to model experimental data [1–4] have reinforced the status of this function as a valuable tool for experimentalists. When the literature is examined, one finds that generally speaking, KWW function is often used in connection with modeling relaxation phenomena. And because the latter occurs in many areas of engineering and applied sciences, *e.g*. dielectrics, nuclear magnetic resonance, polymer dynamics, semi–conductors, KWW function became one of the most commonly used models for fitting experimental data, hence allowing experimentalists to extract relaxation parameters. In a recent review paper by Anderssen *et al*. [5], the properties of KWW function were extensively discussed and a few applications related to visco–elasticity and polymer dynamics were presented.

The spectral density, $J(\omega)$, arises in the field of NMR and dielectrics in connection with relaxation phenomena. In this paper we develop a new procedure geared towards an efficient evaluation of $J(\omega)$ in which the correlation term is approximated by the so–called KWW decay function also known as the stretched exponential. This adds to the arsenal of tools available in the literature, namely the numerical algorithm of Weiss *et al*. [7]. In the original work of Weiss *et al*., the authors expanded the integral of interest as an infinite series whose summation was then accelerated by means of the so–called Aitken Δ^2 non–linear sequence transformation [8]. The Aitken transformation is certainly a good starting point when dealing with convergence acceleration of infinite series but in the past decades tremendous progress was made in this field [8–10] which led to numerical procedures far better than Aitken's. It must be emphasized that one such procedure, also known to be amongst the most versatile and general purpose, was obtained by Wynn who referred to it as the epsilon (ε) algorithm [11]. Incidentally, Aitken's Δ^2 procedure can be obtained as a special case of Wynn's.

2 MATHEMATICAL PRELIMINARIES

When dealing with NMR experimental data, one is usually required to compute few parameters characterizing the relaxation of the sample under study. Quantum mechanically, such parameters can be computed using a numerical procedure involving a quantity known as the spectral density [12],

$$\mathrm{j}(\omega) = \int_0^{+\infty} G(t)\exp(i\omega t)\,dt = J(\omega) - iK(\omega) \tag{1}$$

where $G(t)$ is the auto–correlation function. In the context of a macroscopic study of the spin relaxation behavior of a sample material subjected to a time varying magnetic field, experience has shown that the KWW function $\phi(t) = \exp[-(t/\tau)^{\alpha}]$ is probably the most adequate analytical form

allowing a good description of the correlation. As a consequence, replacing the correlation function $G(t)$ in Eq. (1) by $\phi(t)$ yields,

$$j(\omega) = \tau \left[Q_\alpha(z) - V_\alpha(z) \right] \tag{2}$$

where $z = \omega\tau$ and:

$$\begin{aligned} Q_\alpha(z) &= \int_0^{+\infty} \exp(-u^\alpha)\, \cos(zu)\, du \\ V_\alpha(z) &= \int_0^{+\infty} \exp(-u^\alpha)\, \sin(zu)\, du \end{aligned} \tag{3}$$

Note, that the above definitions of $Q_\alpha(z)$ and $V_\alpha(z)$ were previously derived by Dishon *et al*. [6]. In what follows, we focus on the function $Q_\alpha(z)$, also known as the Lévy law density [5]. Of course, the procedure developed for $Q_\alpha(z)$, can equally be applied to $V_\alpha(z)$ without any further modifications.

2.1 Evaluation by Means of Infinite Series Expansion

The difficulty in computing the functions $Q_\alpha(z)$ and $V_\alpha(z)$ stems from the fact that the integrands are highly oscillatory for large values of *z*. Consequently, classical numerical integration techniques, such as Gauss–Laguerre or a combination of Gauss–Legendre and Gauss–Laguerre, are likely to fail since the interpolation polynomials cannot fully capture the extreme oscillatory nature of the integrand. To circumvent this shortcoming, we first start by expanding the function $Q_\alpha(z)$ as infinite series. However, instead of expanding some (or all) terms occurring in the integrand as in Ref. [7], we rather express the integration range as a sequence of adjacent and finite sub–intervals. The upper and lower boundaries of each of these sub–intervals are chosen to be consecutive roots of the function $\cos(zu)$. After some straightforward algebra we can finally write,

$$Q_\alpha(z) = \int_0^{+\infty} \exp(-u^\alpha) \cos(zu)\, du = \left[\int_0^{\pi/2} + \sum_{n=0}^{\infty} \int_{(2n+1)\pi/(2z)}^{(2n+3)\pi/(2z)} \right] \exp(-u^\alpha) \cos(zu)\, du \tag{4}$$

In previous work Weiss *et al*. [7] proposed a series expansion of $Q_\alpha(z)$, obtained by expanding the exponential term and integrating term by term. The resulting infinite series written as,

$$Q_\alpha(z) = \frac{1}{\pi} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\Gamma[1+n\alpha]}{n!\, z^{1+n\alpha}} \sin\left(n \frac{\alpha\pi}{2} \right) \text{ with } 0 \le \alpha \le 1 \tag{5}$$

converges for values of $0 \le \alpha \le 1$. In the above expansion, because the parameter *z* appears in the denominator, the numerical algorithm based on Eq. (5) is likely to suffer from numerical instabilities for small values of the *z*. To circumvent this difficulty the authors proposed another series expansion, which although formally divergent is semi–convergent in practice and very useful for small values of *z*,

$$Q_\alpha(z) = \frac{1}{\pi\alpha}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{\Gamma[(2n-1)/\alpha]}{(2n-2)!}z^{2(n-1)} \tag{6}$$

The aim of the present work is to obtain a numerical algorithm that unifies the evaluation of the function $Q_\alpha(z)$ and this regardless of the magnitude of the parameters α and *z*. Indeed, from Eq. (4) it can be seen readily that the same formulation can be used for any set of parameters $\alpha > 0$ and *z*. To make the far right side of Eq. (4) slightly simpler, we introduce a new variable $x = u - n\pi/(2z)$ allowing the expansion of $Q_\alpha(z)$ to be re–written as:

$$Q_\alpha(z) = \int_0^{\pi/2}\exp\left(-u^\alpha\right)\cos(zu)\,du + \underbrace{\sum_{n=0}^{\infty}(-1)^n\int_{\pi/(2z)}^{3\pi/(2z)}\exp\left[-\left(x+n\frac{\pi}{2z}\right)^\alpha\right]\cos(zx)\,dx}_{U_{2n}(z)-U_{2n+1}(z)} \tag{7}$$

As can be seen, the infinite summation in the above expansion can be expressed as a difference of two subsequences $U_{2n}(z)$ and $U_{2n+1}(z)$ of positive terms. For numerical stability (and especially when the terms to be summed are small), it is advisable to evaluate $U_{2n}(z)$ and $U_{2n+1}(z)$ separately before performing the subtraction leading to the numerical value of $Q_\alpha(z)$. Since efficiency is the focus of this work, it is important to analyze the convergence of the series given in Eq. (7) in order to provide a theoretical ground justifying the necessity of using a convergence accelerator.

To shed some light on this issue, let's start by recapping two principal results regarding the convergence of a sequence of numbers,

(1) Let *S* be a sequence such that $\lim_{n\to\infty}\frac{S_{n+1}-s}{S_n-s} = \rho$, where $S_n = \sum_{k=0}^{n}a_k$ stands for the n^{th} partial sum of the sequence whose limit is *s*. According to Wimp [9], the series converges linearly if $|\rho| < 1$ and logarithmically if $\rho = 1$. From a practical point of view, a linearly converging series can generally be evaluated using a brute force algorithm in which terms of the series are added until a pre–defined accuracy threshold is reached. Although, this is not necessarily the best procedure to perform the summation, the computational time required by this procedure may nonetheless be within reasonable bounds. However, in the case of logarithmically converging series, it is extremely hard, if possible in practice, for brute force procedures to achieve acceptable accuracy. Perhaps the most widely cited example in this category is the Riemann function $\varsigma(1)$ that after summing a million terms yields 14.3927, giving a false sense of convergence. Of course, based on theoretical considerations, the function $\varsigma(1)$ is known to diverge. As a consequence, for such extremely slow diverging (or converging) series, convergence accelerators become one of the most useful, if not necessary, tools for carrying out the summation efficiently.

(2) For practical purposes, the definition above cannot be applied straightforwardly to determine the type of convergence of the sequence *S* since it requires the knowledge of the limit *s*. Luckily

numerous theorems are available that simplify the experimental work. These include two theorems due to Clark, Gray and Adams [14] that state the following,

Theorem 1 [Clark, Gray and Adams] [14]

Let $R_n = a_{n+1}/a_n$. *If* a_n *is of constant sign and*,

$$\lim_{n\to\infty} S_n = s \text{ and } \lim_{n\to\infty} R_n = R \text{ then } \lim_{n\to\infty} \frac{s - S_{n+1}}{s - S_n} = R$$

More explicitly,

$$\lim_{n\to\infty} \frac{\sum_{k=n+2}^{\infty} a_k}{\sum_{k=n+1}^{\infty} a_k} = \lim_{n\to\infty} \frac{a_{n+1}}{a_n}$$

Theorem 2 [Clark, Gray and Adams] [14]

Let $R_n = a_{n+1}/a_n$ *and* $a_n = (-1)^n c_n$, *where* $c_n > c_{n+1} > 0$.

If $\lim_{n\to\infty} R_n = R \neq -1$ *then* $\lim_{n\to\infty} \frac{s - S_{n+1}}{s - S_n} = R$.

Moreover, if $R = -1$ *and* $\lim_{n\to\infty} \frac{1 + R_{n+1}}{1 + R_n} = 1$, *then the above result holds*.

Since the infinite expansion in Eq. (7) fits the description of the sequence considered in Theorem 2, *i.e.* $a_n = (-1)^n c_n$, let us show that the terms c_n satisfy the condition $c_n > c_{n+1} > 0$. In fact, this is true since over the range $[\pi/(2z), 3\pi/(2z)]$,

(1) The integrand $-\exp\left\{-\left[x + n\pi/(2z)\right]^{\alpha}\right\}\cos(zx)$ is always positive and greater than 0.

(2) The function $-\exp\left\{-\left[x + n_1\pi/(2z)\right]^{\alpha}\right\}\cos(zx) > -\exp\left\{-\left[x + n_2\pi/(2z)\right]^{\alpha}\right\}\cos(zx)$ for any n_1 and n_2 such that $n_1 < n_2$.

This clearly proves that the first two conditions of Theorem 2 are fully satisfied. Note that for the rest of the proof, we do not necessarily need to include the negative sign in the asymptotic expansions since what matters is the ratio of the terms of the expansion.

In order to apply the results of Theorem 2 to the series expansion given by Eq. (7), we proceed to obtain the general asymptotic expression of the integral over $[\pi/(2z), 3\pi/(2z)]$ which will be referred to as $I_n(\alpha, z)$. Using the approximation $(1+\varepsilon)^{\alpha} \approx 1 + \alpha\varepsilon$, for small values of ε, we can finally write,

$$I_n(\alpha, z) \sim (-1)^n \exp\left[-\left(n\frac{\pi}{2z}\right)^{\alpha}\right] \int_{\pi/(2z)}^{3\pi/(2z)} \exp\left[-\alpha\left(n\frac{\pi}{2z}\right)^{\alpha-1} x\right] \cos(zx)\, dx \tag{8}$$

where the notation $f(n) \sim g(n)$ means that $g(n)$ is equivalent to $f(n)$ for large values of the parameter n. Performing the integration (using a simple integration by part) we obtain the following,

$$I_n(\alpha, z) \sim \frac{(-1)^n z}{z^2 + \left\{\alpha\left[(n\pi)/(2z)\right]^{\alpha-1}\right\}} \exp\left[-\left(\frac{n\pi}{2z}\right)^{\alpha-1} \frac{\alpha\pi + n\pi}{2z}\right] \left\{1 + \exp\left[-\frac{\alpha\pi}{z}\left(\frac{n\pi}{2z}\right)^{\alpha-1}\right]\right\} \tag{9}$$

At this point, let us compute the ratio $R_n = I_{n+1}(\alpha, z)/I_n(\alpha, z)$ as needed by Theorem 2. In fact, when the above expression is examined, one can notice that two separate cases, corresponding to $\alpha < 1$ and $\alpha > 1$, need to be studied. The case for which $\alpha = 1$ is not considered in the following analysis since the integral in Eq. (4) can be evaluated analytically. For the computation of $\lim_{n\to\infty} R_n$, it can easily be shown that the limits of two terms is constant regardless of the value of α,

$$\lim_{n\to\infty} \frac{z^2 + \left\{\alpha\left[(n\pi)/(2z)\right]^{\alpha-1}\right\}^2}{z^2 + \left\{\alpha\left[(n+1)\pi/(2z)\right]^{\alpha-1}\right\}^2} = 1 \text{ and } \lim_{n\to\infty} \frac{1 + \exp\left\{-(\alpha\pi)/z\left[(n+1)\pi/(2z)\right]^{\alpha-1}\right\}}{1 + \exp\left\{-(\alpha z)/\pi\left[(n\pi)/(2z)\right]^{\alpha-1}\right\}} = 1 \tag{10}$$

During the calculation of the limit of R_n, as required by Theorem 2, the terms given above can be ignored, hence leaving only the following,

$$\lim_{n\to\infty} R_n = \lim_{n\to\infty} -\frac{\exp\left\{-\left[(n+1)\pi/(2z)\right]^{\alpha-1}\left(\alpha\pi + (n+1)\pi\right)/(2z)\right\}}{\exp\left\{-\left[(n\pi)/(2z)\right]^{\alpha-1}\left(\alpha\pi + n\pi\right)/(2z)\right\}} = \lim_{n\to\infty} -\exp\left\{-\alpha\left[\pi/(2z)\right]^{\alpha} n^{\alpha-1}\right\} \tag{11}$$

Clearly, for $\alpha > 1$, $\lim_{n\to\infty} R_n = 0$ which according to Theorem 2 and the introductory remarks given above (after Eq. (7)), proves that the series given in Eq. (7) converges linearly. However, for $\alpha < 1$, we have $\lim_{n\to\infty} R_n = -1$. In this case, Theorem 2 states that extra work is required in order to make a final decision. Starting from Eq. (8) the ratio R_n can be written asymptotically as following:

$$R_n \sim -\frac{1 + \left[\frac{\alpha}{z}\left(\frac{n\pi}{2z}\right)^{\alpha-1}\right]^2}{1 + \left[\frac{\alpha}{z}\left(\frac{(n+1)\pi}{2z}\right)\right]^2} \sim -\left\{1 - \left[\frac{\alpha}{z}\left(\frac{(n+1)\pi}{2z}\right)^{\alpha-1}\right]^2 + \left[\frac{\alpha}{z}\left(\frac{n\pi}{2z}\right)^{\alpha-1}\right]^2\right\} \tag{12}$$

Using the above asymptotic expansion we can calculate the limit:

$$\lim_{n\to\infty} \frac{1 + R_{n+1}}{1 + R_n} = \lim_{n\to\infty} \frac{(n+2)^{\alpha-1} - (n+1)^{\alpha-1}}{(n+1)^{\alpha-1} - n^{\alpha-1}} = \lim_{n\to\infty}\left(1 + \frac{1}{n}\right)^{\alpha-1} \frac{1 + \left[1 + 1/(n+1)\right]^{\alpha-1} - 1}{\left[1 + 1/n\right]^{\alpha-1} - 1} \tag{13}$$

The rightmost ratio occurring in the above equation can be shown to be asymptotically equivalent to $n/(n+1)$. Therefore, we can write:

$$\lim_{n\to\infty}\frac{1+R_{n+1}}{1+R_n}=\lim_{n\to\infty}\left(1+\frac{1}{n}\right)^{\alpha-1}\frac{n}{n+1}=1 \tag{14}$$

The calculated limit fits the requirement of the second part of Theorem 2. As a consequence, we can conclude that for $\alpha<1$ the infinite series in Eq. (7) has a logarithmic convergence and this constitute a compelling reason for using a convergence accelerator to speed up the summation process.

The approach developed above can also be applied to prove, based on Theorem 1, that the subsequences $U_{2n}(z)$ and $U_{2n+1}(z)$ converge linearly for $\alpha>1$ and logarithmically when $\alpha<1$. In other words, for $\alpha<1$ the convergence of both series $U_{2n}(z)$ and $U_{2n+1}(z)$ is expected to increasingly deteriorate as α moves away from 1 towards 0.

3 RESULTS AND DISCUSSION

At this point, it worth emphasizing that the series expansion given by Eq. (5), originally obtained by Weiss *et al*. [7], becomes highly unstable for intermediate values of α and z approaching 0. A visual illustration of this difficulty is provided by Figure 1 in which we have plotted the values of z below which Eq. (5) becomes numerically inaccurate.

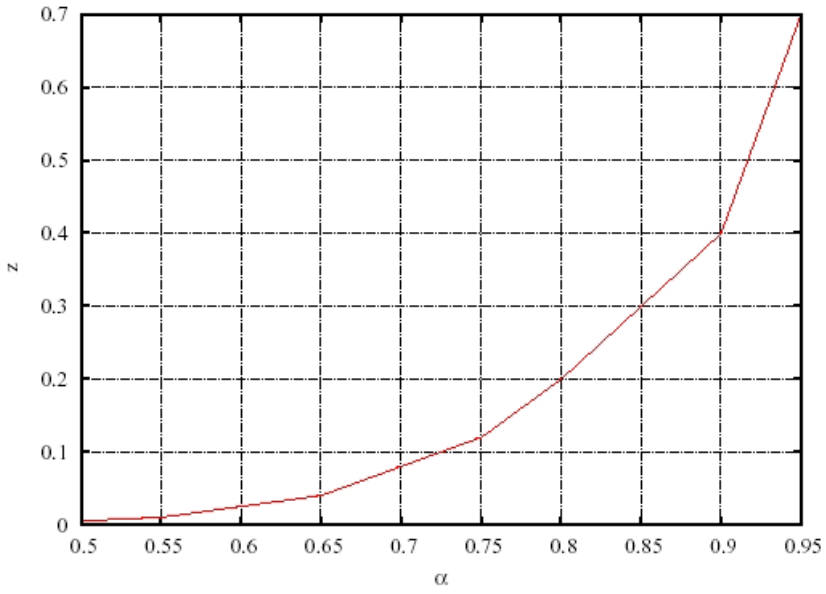

Figure 1. Smallest value of z at which a quadruple precision representation of the series (5) becomes numerically stable.

It is important to understand that such inaccuracies result from the fact that some of the terms in Eq. (5) are so large that their representation (even in quadruple precision) becomes very questionable. This is illustrated in Table 1 in which we have listed some values showing the increase in magnitude of the terms of Eq. (5) as a function of the parameters α and z.

Table 1. Selected terms from the series (5) for special values of αand *z*. Numbers in parentheses denote powers of 10.

n	α = 0.7, *z* = 0.1	α = 0.8, *z* = 0.1	α = 0.9, *z* = 0.1
1	4.057627075040309969 40(01)	5.589011352788976600 70(01)	7.545521677919876812 70(01)
11	–1.215723869178177232 10(05)	3.484567047375188324 30(07)	8.933296491273003871 80(08)
21	–5.037129524314571291 90(07)	2.359443653668298210 50(12)	–1.388270012549948185 50(17)
31	1.224611811605898353 00(09)	5.927316372458492404 70(16)	–3.296408725157005567 10(23)
41	4.282551694579877411 10(10)	7.721660096596656932 90(20)	2.246887954430890749 20(31)
51	–1.856871294827447248 10(11)	6.145937036869243847 40(24)	3.003016258594140437 80(37)
61	–1.715629524299658915 40(12)	3.296550217498929247 10(28)	–1.313424811420387027 30(45)
71	2.511056368542558904 80(12)	1.272046835838128230 50(32)	–1.222258963477049016 00(51)
81	9.265102065052494328 90(12)	3.700049006077481968 60(35)	3.936646468050226904 00(58)
91	–6.122386201782772519 30(12)	8.402490445738473360 10(38)	2.810363674131329632 80(64)
101	–1.119953719335382485 70(13)	1.530976882969659757 70(42)	–7.163965664806301146 30(71)

To make things worse, the values of $Q_\alpha(z)$ as given by Eq. (5) require subtracting such large terms making the summation procedure highly unstable in some cases. Maple, Mathematica and other symbolic algebra systems support unrestricted precision arithmetic that provides numerical tables for use as benchmarks. The precision that is needed in the body of the calculation of the functions $Q_\alpha(z)$ and $V_\alpha(z)$ can be very high. Indeed, using $Q_{0.9}(z)$, computed by means of the series (5), as a case study, we have gathered in Table 2 the parameters illustrating the need for an extended precision. Successive columns contain,

(1) *z*, the value of the argument in $Q_{0.9}(z)$

(2) P, the precision that was specified in Maple for the calculation of intermediate results.

(3) N, the number of terms that were summed before convergence is achieved (for the first four cases).

(4) $T_{\max}$, the largest term involved in the computation of $Q_{0.9}(z)$ by means of the series expansion (5).

Table 2. Number of exact digits requested from Maple for an accurate evaluation of $Q_{0.9}(z)$ using Eq. (5). Numbers in parentheses denote powers of 10.

z	P	N	$T_{\max}$
0.50	20	667	7.715800997343615152 20(08)
0.45	40	1387	3.627640414261301573 68(22)
0.40	80	4147	3.615564321087058410 37(64)
0.35	300	13498	8.158179187339814585 25(213)
0.30	500	44527	2.097852177449689589 74(855)

The last line in Table 2 shows that even after summing 44527 terms, represented accurately using an extremely extended accuracy (500–digits), it was impossible to obtain the exact value of $Q_{0.9}(0.3)$. Indeed, in the fourth column it can clearly be seen that the largest term involved in the summation process requires (in the worst case, *i.e.* if there is no repeating sequence) 855 digits to be accurately represented.

Clearly, as *z* decreases towards 0, the precision provided by Maple must be increased to ensure a

proper representation of the terms of the series, hence allowing an accurate of $Q_{0.9}(z)$. However, extending the number of exact digits comes with a substantial penalty in terms of computational time which can go from few minutes to hours in some cases. To circumvent, the abovementioned difficulties, Weiss *et al* introduced a semi–convergent series (6) useful for computing the values of $Q_\alpha(z)$ and $V_\alpha(z)$ for small values of z.

An interesting alternative to the series presented in Ref. [7] is our series expansion (7) the use of which leads to a unified algorithm (working for arbitrary values of z and $\alpha > 0$) that can be used for the evaluation of $Q_\alpha(z)$ and $V_\alpha(z)$. For numerical efficiency and since we have shown above that the auxiliary series of interest including $U_{2n}(z)$ and $U_{2n+1}(z)$ converge logarithmically as α gets closer to 0. In such particular cases a direct summation becomes too costly and this becomes a compelling reason to rely on convergence accelerating technique to speed up the numerical procedure. Note, that in their previous work, Weiss *et al*. used the Euler transformation to enhance the convergence of summation procedure based on Eq. (6). In this respect, it should be mentioned that although the findings of the authors confirm the practical usefulness of the Euler transformation, the pattern of the terms of the series (6) is not very regular (*i.e*., strictly monotonic or oscillating). This fact is of importance, since generally speaking convergence accelerators perform better on monotonous or oscillating series for which a good deal of results is available in the literature [13,15].

Accordingly, there may be some advantage in using the series proposed in this work. Indeed, it was found that for $\alpha \in (0,1]$ and $0.001 \le z \le 2500$, the application of the Wynn's ε algorithm to the first 20 partial sums of the auxiliary series $U_{2n}(z)$ and $U_{2n+1}(z)$ (as defined in Eq. (7)) yields (at least) an accuracy comparable to the benchmarks published in [1], *i.e*. 6 digit precision.

Table 3. Accuracy of the series (7) developed in this work as compared to the values in Ref. [1]. Numbers in parentheses denote powers of 10.

z	$Q_{0.5}(z)$ [a]	$Q_{0.5}(z)$ [b]	$Q_{0.7}(z)$ [a]	$Q_{0.7}(z)$ [b]	$Q_{1.0}(z)$ [a]	$Q_{1.0}(z)$ [b]
0.001	0.636582	0.636582	0.402922	0.402922	0.318310	0.318310
0.002	0.636467	0.636467	0.402916	0.402916	0.318309	0.318309
0.003	0.636277	0.636277	0.402906	0.402906	0.318307	0.318307
0.004	0.636011	0.636011	0.402893	0.402893	0.318305	0.318305
0.005	0.635671	0.635671	0.402875	0.402875	0.318302	0.318302
0.1	0.476436	0.476436	0.384759	0.384759	0.315158	0.315158
0.5	0.170762	0.170762	0.220440	0.220440	0.254648	0.254648
1	0.861071(–1)	0.861071(–1)	0.117027	0.117027	0.159155	0.159155
5	0.123487(–1)	0.123487(–1)	0.133356(–1)	0.133356(–1)	0.122427(–1)	0.122427(–1)
10	0.487226(–2)	0.487226(–1)	0.449934(–2)	0.449934(–2)	0.315158(–2)	0.315158(–2)
50	0.503342(–3)	0.503342(–3)	0.319872(–3)	0.319871(–3)	0.127273(–3)	0.127273(–3)
100	0.184054(–3)	0.184054(–3)	0.100049(–3)	0.100049(–3)	0.318278(–4)	0.318278(–4)
500	0.172135(–4)	0.172135(–4)	0.659746(–5)	0.657745(–5)	0.127323(–5)	0.127323(–5)
1000	0.615026(–5)	0.615025(–5)	0.203692(–5)	0.203692(–5)	0.318310(–6)	0.318310(–6)
2500	0.157046(–5)	0.157046(–5)	0.430026(–6)	0.430026(–6)	0.509296(–7)	0.509296(–7)

[a] Values obtained after applying Wynn's ε algorithm to the first 20 sums calculated using Eq. (7).
[b] Benchmark values extracted from the tables in Ref. [1].

A sample of the results illustrating the accuracy and the usefulness of the approach described above are gathered in Table 3. A larger scale comparison is also provided in Figure 2 in which we represented the accuracy (number of digits achieved by expansion in Eq. (7)) as a gray scale image. The (X, Y) coordinates of each pixel in Figure 2 correspond to a pair of values (α, z) as selected by Dishon *et al*. [6]. For this particular experiment, we have limited our comparisons to the values of α such that $0 < \alpha \le 1$ which is the range that is mostly used in practice.

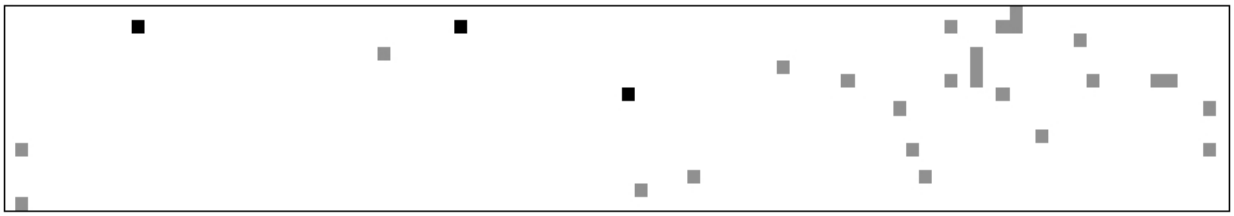

Figure 2. Comparison of our values with those of Dishon *et al*. in Ref. [6]. The values of the parameters α and *z* corresponding to the X and Y axes are such that: $0 < \alpha \le 1$ and $0.001 \le z \le 2500$ (c.f. Ref. [1]). White areas correspond to exact matches (6 digits), gray and dark pixels to 5 and 4 digits respectively.

Although in most practical cases the value of the exponent lies within $(0,1]$, it is of importance, at least from a mathematical perspective, to address the case where $\alpha > 1$. Note that for $\alpha = 1$, the functions $Q_\alpha(z)$ and $V_\alpha(z)$ can be evaluated by means of their closed analytical formulae, easily obtainable using integration by part,

$$Q_1(z) = \frac{1}{\pi(1+z^2)}$$
$$V_1(z) = \frac{z}{\pi(1+z^2)} \tag{15}$$

As for $\alpha > 1$, the approach presented above still applies. However, in this case, because the integrand $\exp\left[-(x+n\pi/z)^\alpha\right]\cos(zx)$ has a single peak within the range $\left(\pi/(2z),\ 3\pi/(2z)\right)$ which becomes sharper as n increases, it is crucial to use a reliable algorithm to compute the partial sums. In this respect, it was found that for $\alpha > 2$, some numerical instabilities occur as soon as $z > 10$. To understand the origin of this problem, we remind that our procedure is built as a two–component algorithm: evaluation of the partial sums which is carried out using a Gauss–Legendre Gauss numerical quadrature followed by the application of the convergence accelerator. To isolate the faulty component, we have thoroughly experimented with the case in which $\alpha = 2$ and $z = 25$. Using Maple (with a 50–digit internal accuracy), we have generated the first 20 partial sums of $U_{2n}(25)$ and $U_{2n+1}(25)$ required by the Wynn's ε algorithm. When proceeding as described, we were able to reproduce the result of Dishon *et al*. [6]. Clearly, it is the evaluation of the partial sums that were at the origin of the numerical instabilities and this is mainly due to the presence of a sharp peak in the integrand that makes low order Gauss–Legendre quadrature unable to capture accurately the shape of the integrand. To circumvent this difficulty we have selected an adaptive integration scheme. This algorithm proceeds by adjusting the number of points to be used during the

interpolation step based on the value of the derivative. As a consequence, in fast varying regions (as is the case in the close vicinity of the sharp peak), the magnitude of derivative increases drastically which hints the algorithm to use more points.

4 CONCLUSIONS

In this work, we have proposed an efficient numerical procedure that could be used to evaluate the NMR spectral densities using the KWW decay function. Using the integral representation of the quantities of interest as a starting point we derived a series representation which was shown to converge logarithmically. Because of this, use of convergence accelerating techniques is crucial. It was shown that our numerical values by applying Wynn's ε algorithm applied to the first 20 partial sums of the series in (7) are in agreement with those published in the literature. Our procedure provides a unified approach for the computation of the spectral densities regardless of the magnitude of the parameters. This is novel. This work can be viewed as an improvement to the procedure proposed by Weiss *et al*. [7] who had to use different series based on the parameters.

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