

Extrapolation Methods for Improving the Convergence of Oligomer Calculations to the Infinite Chain Limit of *Quasi*-Onedimensional Stereoregular Polymers

ERNST JOACHIM WENIGER

Institut für Physikalische und Theoretische Chemie
Universität Regensburg, D-93040 Regensburg, Germany
Joachim.Weniger@chemie.uni-regensburg.de

BERNARD KIRTMAN

Department of Chemistry and Biochemistry
University of California, Santa Barbara, CA 93106-9510, U.S.A.
kirtman@chem.ucsb.edu

Submitted to the Special Issue

“Numerical Methods in Physics, Chemistry and Engineering”
of *Computers & Mathematics with Applications*

Guest Editors: T.E. Simos, G. Avdelas, and J. Vigo-Aguiar

12 April 2000

Abstract — *Quasi*-onedimensional stereoregular polymers as for example polyacetylene are currently of considerable interest, both experimentally as well as theoretically. There are basically two different approaches for doing electronic structure calculations: One method, the so-called crystal orbital method, uses periodic boundary conditions and is essentially based on concepts of solid state theory. The other method is essentially a quantum chemical method since it approximates the polymer by oligomers consisting of a finite number of monomer units, i.e., by molecules of finite size. In this way, the highly developed technology of quantum chemical molecular programs can be used. Unfortunately, oligomers of finite size are not necessarily able to model those features of a polymer which crucially depend of its in principle infinite extension. However, in such a case extrapolation techniques can be extremely helpful. For example, one can perform electronic structure calculations for a sequence of oligomers with an increasing number of monomer units. In the next step, one then can try to determine the limit of this sequence for an oligomer of infinite length with the help of suitable extrapolation methods. Several different extrapolation methods are discussed which are able to accomplish an extrapolation of energies and properties of oligomers to the infinite chain limit. Calculations for the ground state energy of polyacetylene are presented which demonstrate the practical usefulness of extrapolation methods.

Keywords — Quantum chemical oligomer calculations, quasi-onedimensional stereoregular polymers, extrapolation methods, sequence transformations.

1 Introduction

The classic example of a *quasi*-onedimensional stereoregular polymer is polyacetylene, which can be generated by translating the repeat unit $-(CH=CH)-$. Conjugated polymers such as polyacetylene are currently of great technological interest because of potential applications in a wide variety of optical and optoelectronic devices based on their conducting, photophysical, and nonlinear optical properties [1,2]. Moreover, the keen interest in polyacetylene especially is documented by the fact that there even exists a monograph with the title *Polyacetylene* [3].

Numerous properties involving the electronic structure of these polymers are not yet understood in a completely satisfactory way. Consequently, these polymers are not only very interesting

from a technological point of view but are also quite challenging from a basic science point of view.

There are two approaches to *ab initio* molecular electronic structure calculations. One may be described as the wavefunction approach and the other as the density approach (also known as density functional theory). The starting point for the wavefunction approach is an effective independent particle treatment of the Schrödinger equation named after Hartree [4] and Fock [5]. In the density approach one uses an equation of similar general form due to Kohn and Sham [6] but, in principle, the electron interactions are fully taken into account. The solution of either equation is a set of one-electron functions, called orbitals, that can be used to construct the multi-electron wavefunction (Hartree-Fock) or the electron density (Kohn-Sham). In either case the orbitals are expanded in terms of finite linear combination of analytic basis functions (nowadays usually Gaussians).

The Hartree-Fock approach combined with analytic basis functions leads to the so-called Roothaan equations [7], which can be written in the form of a generalized matrix eigenvalue problem. For meaningful results it is necessary for the number of basis functions and, hence, the dimension of the Roothaan equations to exceed the number of electrons. This imposes obvious restrictions on the size of the oligomers used to model a polymer, which can be handled by *ab initio* programs based on the highly developed computational techniques of molecular quantum chemistry (see for instance [8, 9]).

If, however, the polymer under consideration is a stereoregular *quasi*-onedimensional polymer like polyacetylene, it is nevertheless possible to compute energies or properties on the basis of quantum mechanics. There are two fundamentally different computational approaches – the *crystal orbital* approach and the *finite oligomer* method – that have complementary advantages and disadvantages.

The crystal orbital approach, which is for example discussed in monographs by Pisani, Dovesi, and Roetti [10], Ladik [11], and André, Delhalle, and Brédas [12] or in review articles by André [13], Kertész [14], and Ladik [15], treats polymers as solids and uses the concepts and techniques of solid state physics such as translational symmetry and cyclic boundary conditions (see for example [16, 17]). This leads to band structure, or crystal orbital, calculations whose complexity is limited by the number of interacting neighboring unit cells. Such calculations have the undeniable advantage that one only has to consider these interactions for a representative unit cell since all unit cells are identical. This is a major simplification over a molecular-type calculation where the unit cells are translationally inequivalent. Thus, the crystal orbital approach is in principle well suited for describing those features of a polymer which crucially depend on its in principle infinite extension.

Nevertheless, there are still some open problems with crystal orbital calculations. For example, convergence problems in the Hartree-Fock iterations and the proper handling of long range Coulomb interactions can be problematic [18]. Moreover, it is very difficult to take into account the effect of nonperiodic perturbations such as the interaction with an electric field. The term in the polarization response, which is linear in the interacting electric field, determines the polarizability of the polymer, whereas the nonlinear terms determine the hyperpolarizabilities. The nonlinear response is connected with properties such as second harmonic generation, optical rectification, and the intensity dependent refractive index (see for example [19]) which are of considerable interest in materials science these days. Despite many years of effort going back to the 1940's and substantial recent progress [20–25], it is fair to say that an incontrovertible crystal orbital method [26, 27] has yet to be presented, even at a simplified Hartree-Fock level where just the average - rather than the instantaneous - interelectronic repulsion is taken into account.

Another problem of the crystal orbital approach is that the explicit incorporation of electronic correlation is difficult. In the Hartree-Fock approximation the instantaneous interaction between electrons is replaced by an orbital-averaged interaction. The error due to making this approximation is known as the electron correlation error (see for example [28–30]). For some properties, such as the energy per unit cell, this error is quite small on a percentage basis. Nonetheless, correlation is very important because it can easily be the deciding factor between alternative structural conformations. For other properties, such as hyperpolarizabilities, the correlation error may be as large as 800 % [31].

The density method includes electron correlation but the one-electron potential, which simultaneously takes into account both electron exchange (Pauli Principle) and correlation, must be approximated. In practice, the approximations used are local in nature – they involve the density, its gradient and, possibly, the Laplacian at each point. For that reason [32] the method fails to predict electrical properties (dipole moment, linear polarizability, hyperpolarizabilities) [33,34] of spatially extended systems. One can expect that the same will be true of other properties of spatially extended systems, such as the mechanical force constants describing the interaction between different unit cells, but that has not been checked as yet.

Because of the problems mentioned above, a different approach – the *finite oligomer* method – has gained popularity in the middle to the late 1980's: Stereoregular *quasi*-onedimensional polymers are approximated by molecules of finite length [35–42]. In the case of polyacetylene, this means that the polymer $(\text{CH}=\text{CH})_\infty$ is approximated by an oligomer $\text{H}-(\text{CH}=\text{CH})_N-\text{H}$, where N is a finite integer. The oligomer approach offers many advantages. The *ab initio* treatment of electron correlation using any of the techniques available in standard molecular *ab initio* programs is straightforward. Moreover, the same is true for the calculation of hyperpolarizabilities, which has yet to be successfully implemented within the framework of crystal orbital theory even at the Hartree-Fock level. Molecular-type calculations using finite oligomers have been done not only at the Hartree-Fock level, but have also incorporated electron correlation by many-body perturbation theory [31,43–45]. As a result, it has become known that the role of electron correlation can be exceptionally significant for this problem. The same may be said regarding the importance of the vibrational contribution to the hyperpolarizability [46,47] that arises because the electronic response depends upon the nuclear positions. In addition, studies have been undertaken to determine the effect of interactions in the solid state with other polymer chains [48,49] and with dopants [50–52] that either accept or donate electrons. All of these investigations are readily feasible because of the availability of quantum chemistry computer codes developed for ordinary finite molecules.

However, the finite oligomer approach of course also has some shortcomings which may lead to numerical problems. The basic problem of the approximation of a *quasi*-linear stereoregular polymer A_∞ by an oligomer $\text{X}-\text{A}_N-\text{Y}$, whose terminal free valences are saturated by suitably terminal groups X and Y (usually hydrogen atoms), is the choice of the number N of repeat units A. Of course, N should be small enough to permit an accurate quantum chemical calculation of the oligomer. However, N should also be large enough in order to provide a sufficiently realistic representation of those features of the polymer that result from its in principle infinite extension.

Obviously, these two requirements tend to be contradictory which implies that finite oligomer calculations can suffer badly from slow convergence to the infinite chain limit. This is where extrapolation methods come into play: Instead of calculating the intensive energy $E(N)$ or more generally for an intensive property $P(N)$ of a single oligomer $\text{X}-\text{A}_N-\text{Y}$, one can perform calculations for a sequence of oligomers $\text{X}-\text{A}_N-\text{Y}$ with $N = 1, 2, \dots, N_{\text{max}}$. The sequences $E(1), E(2), \dots, E(N_{\text{max}})$ and $P(1), P(2), \dots, P(N_{\text{max}})$ can then be extrapolated to the infinite chain limits $E(\infty)$ and $P(\infty)$, respectively.

Many different approaches for doing the extrapolations are possible. In this article, we want to use sequence transformations for that purpose. Numerical techniques for the acceleration of convergence or the summation of divergent series are as old as calculus. According to Knopp [53, p. 249], the first series transformation was published by Stirling [54] already in 1730, and in 1755 Euler [55] published the series transformation which now bears his name. In rudimentary form, convergence acceleration methods are even older. Brezinski [56, pp. 90 - 91] mentioned that in 1654 Huygens used a linear extrapolation scheme which is a special case of what we now call Richardson extrapolation [57] for obtaining better approximations to π , and that in 1674 Seki Kowa, the probably most famous Japanese mathematician of that period, tried to accomplish this with the help of the so-called Δ^2 process, which is usually attributed to Aitken [58]. Further details on the historical development of extrapolation methods can be found in an article by Brezinski [59].

The modern theory of sequence transformations begins with two articles by Shanks [60] and Wynn [61]. Shanks introduced a sequence transformation which in the case of a power series produces Padé approximants [62], and Wynn showed that this transformation can be computed conveniently by a nonlinear recursive scheme called the epsilon algorithm. These two articles appeared at a time when the first computers became publicly available. The subsequent revolution created a great demand for powerful numerical tools, and the two articles by Shanks and Wynn, which offered solutions to practical problems, had an enormous impact: They stimulated research not only on Padé approximants [62] but also on other sequence transformations, as documented by the large number of monographs [63–72] and review articles [73, 74] which appeared in the last years twenty years or so. Moreover, there is not only a lot of research on sequence transformations and their properties, but the number of articles which describe applications also increases steadily (see for example the list of references in [75]).

Sequence transformations have already been used for the extrapolation of oligomer calculations. Initially, they were applied to ground state energies [40, 42], but more recently, they have also been employed for the computation of static and dynamic linear polarizabilities [76]. It is the intention of this article to provide a sufficiently detailed discussion of those sequence transformations that are suited for the extrapolation of oligomer calculations to the infinite limits. As discussed later in more detail, sequence transformations try to accomplish an improvement of convergence by detecting and utilizing regularities of the input data. For that purpose, they have to access the information stored in the later digits of the input data. However, in the case of oligomer calculations, the input data are produced by molecular *ab initio* programs which are huge packages of FORTRAN code (more than 100 000 lines of code). Normally, these programs operate in FORTRAN DOUBLE PRECISION which corresponds to an accuracy of 14 - 16 decimal digits (depending on the compiler). Unfortunately, this does not mean that their results have this accuracy. Numerous internal approximations plus the inevitable rounding errors reduce the accuracy of the results. This alone is not necessarily a problem. However, the complexity of the calculations, which are performed in such a molecular program, makes it impossible to obtain an estimate of the errors by standard mathematical approaches, and the only realistic alternative are mathematical experiments. Consequently, the emphasis of this manuscript will not be so much on powerful sequence transformations but rather on sequence transformations which produce reliable results under the restrictions that are typical of oligomer calculations.

In Section (2), we give a short discussion of use the Euler Maclaurin formula for the evaluation of infinite series and show that sequence transformations also try to eliminate the truncations errors, albeit by purely numerical means. In Sections (3) and (4), we discuss sequence transformations that are able to accelerate either linear or logarithmic convergence. In Section (5), we show that oligomer calculations for the ground state energy of polyacetylene can be extrapolated

effectively to the infinite chain limit by sequence transformations, and finally in Section (6) there is a short summary.

2 The Euler-Maclaurin Formula and Sequence Transformations

A model example of a slowly convergent series is the Dirichlet series for the Riemann zeta function:

$$\zeta(z) = \sum_{\nu=0}^{\infty} (\nu+1)^{-z}. \quad (2.1)$$

This series converges provided that $\text{Re}(z) > 1$. However, it is notorious for extremely slow convergence if $\text{Re}(z)$ is only slightly larger than 1.

The Euler-Maclaurin formula, which is treated in most books on asymptotics (see for instance [77, pp. 279 - 295]), makes it possible to evaluate $\zeta(z)$ even if the convergence of the Dirichlet series is extremely slow. Let us consider an infinite series $\sum_{\nu=0}^{\infty} f(\nu)$, and let us assume that its terms $f(\nu)$ are *smooth* and *slowly varying* functions of the index ν . Then, the integral

$$\int_M^N f(x) dx \quad (2.2)$$

with $M, N \in \mathbb{Z}$ can provide a good approximation to the sum

$$\frac{1}{2}f(M) + f(M+1) + \dots + f(N-1) + \frac{1}{2}f(N) \quad (2.3)$$

and vice versa. To see this, one only has to approximate the integrand by step functions.

In the years between 1730 and 1740, Euler and Maclaurin derived independently correction terms, which ultimately yielded what we now call the Euler-Maclaurin formula:

$$\begin{aligned} \sum_{\nu=M}^N f(\nu) &= \int_M^N f(x) dx + \frac{1}{2} [f(M) + f(N)] \\ &\quad + \sum_{j=1}^k \frac{B_{2j}}{(2j)!} \left[f^{(2j-1)}(N) - f^{(2j-1)}(M) \right] + R_k(f), \end{aligned} \quad (2.4a)$$

$$R_k(f) = -\frac{1}{(2k)!} \int_M^N B_{2k}(x - \llbracket x \rrbracket) f^{(2k)}(x) dx. \quad (2.4b)$$

Here, $\llbracket x \rrbracket$ is the integral part of x , $B_k(x)$ is a Bernoulli polynomial, and $B_m = B_m(0)$ is a Bernoulli number.

If we set $M = n+1$ and $N = \infty$, the leading terms of the Euler-Maclaurin formula provides rapidly convergent approximations to the truncation error $\sum_{\nu=n+1}^{\infty} f(\nu)$, provided that f is smooth and a slowly varying function of the index ν . Of course, it is also necessary that the integral as well as derivatives of f with respect to ν can be computed.

The terms $(\nu+1)^{-z}$ of the Dirichlet series (2.1) are obviously smooth functions of the index ν and they can be differentiated and integrated easily. Thus, we can apply the Euler-Maclaurin

formula (2.4) with $M = n + 1$ and $N = \infty$ to the truncation error of the Dirichlet series:

$$\begin{aligned} \sum_{\nu=n+1}^{\infty} (\nu+1)^{-z} &= \frac{(n+2)^{1-z}}{z-1} + \frac{1}{2} (n+2)^{-z} \\ &\quad + \sum_{j=1}^k \frac{(z)_{2j-1} B_{2j}}{(2j)!} (n+2)^{-z-2j+1} + R_k(n, z), \end{aligned} \quad (2.5a)$$

$$R_k(n, z) = -\frac{(z)_{2k}}{(2k)!} \int_{n+1}^{\infty} \frac{B_{2k}(x - \llbracket x \rrbracket)}{(1+x)^{z+2k}} dx. \quad (2.5b)$$

Here, $(z)_m = z(z+1)\cdots(z+m-1) = \Gamma(z+m)/\Gamma(z)$ is a Pochhammer symbol.

The expansion (2.5) for the truncation error of the Dirichlet series (2.1) for $\zeta(z)$ is only asymptotic as $n \rightarrow \infty$. Nevertheless, it is numerically extremely useful for sufficiently large values of n , as shown by the following simple example:

$$\zeta(z) \approx \sum_{\nu=0}^n (\nu+1)^{-z} + \frac{(n+2)^{1-z}}{z-1} + \frac{1}{2} (n+2)^{-z} + \sum_{j=1}^3 \frac{(z)_{2j-1} B_{2j}}{(2j)!} (n+2)^{-z-2j+1}. \quad (2.6)$$

If we now choose $n = 20$ and $z = 1.01$, we obtain

$$\sum_{\nu=0}^n (\nu+1)^{-z} = 3.599\,497\,439\,829\,47, \quad (2.7a)$$

$$\frac{(n+2)^{1-z}}{z-1} = 96.956\,241\,819\,2202, \quad (2.7b)$$

$$\frac{1}{2(n+2)^z} = 0.220\,355\,095\,043\,682 \times 10^{-1}, \quad (2.7c)$$

$$\frac{(z)_1 B_2}{2!(n+2)^{z+1}} = 0.168\,605\,034\,844\,029 \times 10^{-3}, \quad (2.7d)$$

$$\frac{(z)_3 B_4}{4!(n+2)^{z+3}} = -0.351\,266\,295\,216\,895 \times 10^{-7}, \quad (2.7e)$$

$$\frac{(z)_5 B_6}{10!(n+2)^{z+5}} = 0.347\,155\,401\,295\,600 \times 10^{-10}. \quad (2.7f)$$

The sum of these 6 terms, which is 100.577 943 338 497, agrees completely with the “exact” result $\zeta(1.01) = 100.577\,943\,338\,497$ obtained by the computer algebra system Maple.

This numerical example shows that a suitable truncation of the Euler-Maclaurin formula (2.4) provides an excellent approximation to the truncation error $\sum_{\nu=n+1}^{\infty} (\nu+1)^{-z}$. Here, it should be taken into account that it is practically impossible to compute $\zeta(1.01)$ with sufficient accuracy by adding up the terms of the Dirichlet series (2.1) successively. We would need $n \approx 10^{600}$ to obtain $(n+2)^{1-z}/(z-1) = 10^{-4}$ for the leading term on the right-hand side of Eq. (2.4), which corresponds to the integral (2.2). Thus, 10^{600} terms of the Dirichlet series (2.1) with $z = 1.01$ would lead to an accuracy of only 6 decimal places in the final result.

In view of these excellent results, it looks like an obvious idea to try to use the Euler-Maclaurin formula also in the case of other slowly convergent series. Unfortunately, this is not always possible. The Euler-Maclaurin formula requires that the terms of the series can be differentiated and integrated with respect to the index. This is only possible if the terms have a sufficiently simple analytic structure, which excludes most cases of interest. Moreover, the Euler-Maclaurin formula cannot be applied in the case of alternating or divergent series since their terms are neither smooth nor slowly varying functions of the index.

However, the probably worst drawback of the Euler-Maclaurin formula is that it is an *analytic* convergence acceleration method. This means that it cannot be applied if only the numerical

values of the terms of a series are known. This is quite unfortunate since convergence acceleration techniques are often badly needed in situations in which apart from a few numerical data very little is known.

These facts give rise to the obvious question whether the Euler-Maclaurin formula can be generalized in such a way that approximations to the truncations errors of sequences and series can be constructed under less restrictive conditions.

Principal tools to overcome convergence problems are *sequence transformations* which can accomplish something even if no explicit analytical expression for the truncation error is available. Here, it should be noted that Padé approximants, which have become the standard tool to overcome convergence problems with power series, are special sequence transformations since the partial sums of a power series are transformed into a doubly indexed sequence of rational functions [62].

Let us assume that we have a sequence $\{s_n\}_{n=0}^{\infty}$ which converges to some limit $s = s_{\infty}$. Then, its elements can be partitioned into the limit s and a remainder r_n according to

$$s_n = s + r_n, \quad n \in \mathbb{N}_0. \quad (2.8)$$

A *sequence transformation* \mathcal{T} is a rule which transforms a sequence $\{s_n\}_{n=0}^{\infty}$ into some other sequence $\{s'_n\}_{n=0}^{\infty}$:

$$\mathcal{T} : \{s_n\}_{n=0}^{\infty} \longmapsto \{s'_n\}_{n=0}^{\infty}. \quad (2.9)$$

A sequence transformation is only useful for our purposes if the transformed sequence $\{s'_n\}_{n=0}^{\infty}$ converges to the same limit $s = s_{\infty}$ as the original sequence $\{s_n\}_{n=0}^{\infty}$. If this is true, then the elements of the transformed sequence can also be partitioned into the limit s and a transformed remainder r'_n according to

$$s'_n = s + r'_n, \quad n \in \mathbb{N}_0. \quad (2.10)$$

With the exception of some more or less trivial model problems, the transformed remainders r'_n will be different from zero for all *finite* values of the index n . Thus, it looks as if nothing substantial is gained by applying a sequence transformation. However, the new remainders can have much better numerical properties than the original remainders.

Accordingly, a sequence transformation is said to *accelerate convergence* if the transformed remainders $\{r'_n\}_{n=0}^{\infty}$ vanish more rapidly than the original remainders $\{r_n\}_{n=0}^{\infty}$ according to

$$\lim_{n \rightarrow \infty} \frac{r'_n}{r_n} = \lim_{n \rightarrow \infty} \frac{s'_n - s}{s_n - s} = 0. \quad (2.11)$$

In the case of some sequence transformations, it is actually possible to compute the transformed remainders $\{r'_n\}_{n=0}^{\infty}$ recursively if the numerical values of the original remainders $\{r_n\}_{n=0}^{\infty}$ are known [78].

Thus, a sequence transformation tries to construct an approximation to the actual remainder r_n and to eliminate it from s_n . This yields a new sequence $\{s'_n\}_{n=0}^{\infty}$ with hopefully superior numerical properties. In this context, we are confronted with the practical problem of constructing approximations to the actual remainders if we do not know explicit analytical expressions for them. However, even if we know explicit expressions, this normally does not help. For example, if the input data are the partial sums

$$s_n = \sum_{k=0}^n a_k, \quad (2.12)$$

of an infinite series, then the remainders are given by

$$r_n = - \sum_{k=n+1}^{\infty} a_k. \quad (2.13)$$

We automatically have an explicit expression for the remainders if we have an explicit analytical expression for the terms a_k . However, this does not help. The computation of r_n via the infinite series (2.13) is normally not easier than the direct computation of the infinite series by adding up the terms successively. Consequently, the straightforward computation of the remainders of an infinite series is normally either not possible or not feasible, and we must use *indirect* approaches to obtain suitable approximations to the remainders.

If we want to use a sequence transformation to speed up convergence, the minimal information, which we need to have, is a *finite* string of numerical values of input data, for example the sequence elements $s_n, s_{n+1}, \dots, s_{n+k}$ with $k, n \in \mathbb{N}_0$. This alone is, however, not enough for the construction of an approximation to the *unknown* truncation error, in particular since there can be an in principle unlimited variety of different types of remainders. Consequently, it should be obvious that a *universal* algorithm for the determination and elimination of completely arbitrary unknown remainders $\{r_n\}_{n=0}^{\infty}$ cannot exist. Delahaye and Germain-Bonne [79, 80] were able to proof this rigorously.

Fortunately, in most cases at least some *structural* and *asymptotic* information about the dependence of the remainders r_n on the index n is available, or – if this is not the case – some more or less plausible assumptions can be made. We will show in the next sections how powerful sequence transformations can be constructed on the basis of simple assumptions. For example, let us assume that the elements of a sequence $\{s_n\}_{n=0}^{\infty}$ can be expressed by the following series expansion:

$$s_n = s + \sum_{j=0}^{\infty} c_j \varphi_j(n), \quad n \in \mathbb{N}_0. \quad (2.14)$$

Here, the coefficients c_j are assumed to be unknown, whereas the functions $\varphi_j(n)$ are assumed to be known, but otherwise they are essentially arbitrary.

A numerical algorithm can only involve a finite number of arithmetic operations. Consequently, a *complete numerical* determination of the remainder $r_n = \sum_{j=0}^{\infty} c_j \varphi_j(n)$ is impossible since this would require the determination of an infinite number of unknown coefficients c_j . So, the best we can hope for is the determination of a finite number of unknown coefficients c_j . If, however, the functions $\varphi_j(n)$ decrease with increasing index j , we achieve an acceleration of convergence by eliminating the first k terms in the infinite series on the right-hand side of (2.14), which yields the transformed sequence

$$s'_n = s + \sum_{\kappa=0}^{\infty} c'_{k+\kappa} \varphi_{k+\kappa}(n), \quad n \in \mathbb{N}_0. \quad (2.15)$$

For example, if the functions $\varphi_j(n)$ do not only decrease with increasing index, but are an *asymptotic sequence* according to

$$\varphi_{j+1}(n) = o(\varphi_j(n)), \quad n \in \mathbb{N}_0, \quad (2.16)$$

then s_n is according to (2.14) of order $O(\varphi_0(n))$ as $n \rightarrow \infty$, whereas s'_n is according to (2.15) of order $O(\varphi_k(n))$, which for sufficiently large values of k leads to a substantial improvement of convergence.

The elimination of the leading k terms on the right-hand side of (2.14) can be accomplished with the help of a sequence transformation which is exact for the *model sequence*

$$\tilde{s}_n = \tilde{s} + \sum_{j=0}^{k-1} \tilde{c}_j \varphi_j(n). \quad (2.17)$$

The elements of this model sequence contain $k+1$ unknowns, the limit \tilde{s} and the k coefficients $\tilde{c}_0, \tilde{c}_1, \dots, \tilde{c}_{k-1}$. Since all unknowns occur *linearly*, it follows from Cramer's rule that a sequence transformation can be constructed which is given as the ratio of two determinants, and which can determine the limit \tilde{s} in (2.17) if the numerical values of $k+1$ sequence elements $\tilde{s}_n, \tilde{s}_{n+1}, \dots, \tilde{s}_{n+k}$ are available. An admittedly complicated recursive scheme for this general sequence transformation, which is determined completely as soon as the functions $\varphi_j(n)$ are specified, was derived independently by Schneider [81], Brezinski [82], and Håvie [83].

Thus, model sequences $\tilde{s}_n = \tilde{s} + \tilde{r}_n$ with remainders \tilde{r}_n containing a finite number of terms as in (2.17) are very useful for the construction of sequence transformations that are special cases of the general sequence transformation mentioned above. If the remainders $\{\tilde{r}_n\}_{n=0}^{\infty}$ of the model sequence $\{\tilde{s}_n\}_{n=0}^{\infty}$ provide sufficiently accurate approximations to the remainders $\{r_n\}_{n=0}^{\infty}$ of the sequence $\{s_n\}_{n=0}^{\infty}$ to be transformed, then it can be hoped that a sequence transformation, which is exact for the model sequence $\{\tilde{s}_n\}_{n=0}^{\infty}$, will be able to accelerate the convergence of $\{s_n\}_{n=0}^{\infty}$ to its limit s . More detailed discussions of this construction principle as well as many examples can be found in [66, 74].

Before we explicitly construct sequence transformations with the help of model sequences of the type of (2.17), let us first mention that in the literature on sequence transformations, simple asymptotic conditions are used to classify the type of convergence of a sequence. For example, many practically relevant sequences $\{s_n\}_{n=0}^{\infty}$ converging to some limit s can be characterized by the asymptotic condition

$$\lim_{n \rightarrow \infty} \frac{s_{n+1} - s}{s_n - s} = \rho, \quad (2.18)$$

which closely resembles the ratio test in the theory of infinite series. If $|\rho| < 1$, the sequence is called *linearly* convergent, and if $\rho = 1$, it is called *logarithmically* convergent.

3 Aitken Extrapolation and Wynn's Epsilon Algorithm

Let us assume that the remainders of the elements of a sequence $\{s_n\}_{n=0}^{\infty}$ consist of a single exponential term:

$$s_n = s + c\lambda^n, \quad c \neq 0, \quad |\lambda| \neq 1, \quad n \in \mathbb{N}_0. \quad (3.1)$$

For $n \rightarrow \infty$, this sequence obviously converges to its limit s if $0 < |\lambda| < 1$, and it diverges away from its generalized limit s if $|\lambda| > 1$. Thus, if this sequence converges, it converges linearly according to (2.18). Moreover, this model sequence contains the partial sums $\sum_{\nu=0}^n (-z)^\nu = [1 - (-z)^{n+1}]/[1 + z]$ of the geometric series as special cases.

If we consider s , c , and λ in (3.1) as unknowns of the linear system $s_{n+j} = s + c\lambda^{n+j}$ with $j = 0, 1, 2$, then we can easily construct a sequence transformation, which is able to determine the (generalized) limit s of the model sequence (3.1) from the numerical values of three consecutive sequence elements s_n, s_{n+1} and s_{n+2} . A short calculation shows that

$$\mathcal{A}_1^{(n)} = s_n - \frac{[\Delta s_n]^2}{\Delta^2 s_n}, \quad n \in \mathbb{N}_0, \quad (3.2)$$

is able to determine the limit s of the model sequence (3.1) according to $\mathcal{A}_1^{(n)} = s$. The forward difference operator Δ in (3.2) is defined by its action on a function $g = g(n)$:

$$\Delta g(n) = g(n+1) - g(n). \quad (3.3)$$

The Δ^2 formula (3.2) is certainly one of the oldest sequence transformations. It is usually attributed to Aitken [58], but it is actually much older. As already mentioned in Section 1, it was used in 1674 by Seki Kowa, the probably most famous Japanese mathematician of that period [56, pp. 90 - 91], and according to Todd [84, p. 5] it was in principle already known to Kummer [85].

The power and practical usefulness of Aitken's Δ^2 formula is of course limited since it is designed to eliminate only a single exponential term from the elements of the model sequence (3.1). However, the quantities $\mathcal{A}_1^{(n)}$ can again be used as input data in (3.2). Hence, the Δ^2 process can be iterated, yielding the following nonlinear recursive scheme [74, Eq. (5.1-15)]:

$$\mathcal{A}_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (3.4a)$$

$$\mathcal{A}_{k+1}^{(n)} = \mathcal{A}_k^{(n)} - \frac{[\Delta \mathcal{A}_k^{(n)}]^2}{\Delta^2 \mathcal{A}_k^{(n)}}, \quad k, n \in \mathbb{N}_0. \quad (3.4b)$$

In the case of doubly indexed quantities like $\mathcal{A}_k^{(n)}$, it will always be assumed that the difference operator Δ only acts on the superscript n but not on the subscript k :

$$\Delta \mathcal{A}_k^{(n)} = \mathcal{A}_k^{(n+1)} - \mathcal{A}_k^{(n)}. \quad (3.5)$$

The numerical performance of Aitken's iterated Δ^2 process was studied in [74, 86]. Concerning the theoretical properties of Aitken's iterated Δ^2 process, very little seems to be known. Hillion [87] was able to find a model sequence for which the iterated Δ^2 process is exact. He also derived a determinantal representation for $\mathcal{A}_k^{(n)}$. However, Hillion's expressions for $\mathcal{A}_k^{(n)}$ contain explicitly the lower order transforms $\mathcal{A}_0^{(n)}, \dots, \mathcal{A}_{k-1}^{(n)}, \dots, \mathcal{A}_0^{(n+k)}, \dots, \mathcal{A}_{k-1}^{(n+k)}$. Consequently, it seems that Hillion's result [87] – although interesting from a formal point of view – cannot help much to understand the theoretical properties of $\mathcal{A}_k^{(n)}$.

A more detailed discussion of Aitken's iterated Δ^2 process as well as additional references can for instance be found in Section 5 of [74] or in [78]. The iteration of other sequence transformations is discussed in [88].

An obvious generalization of the model sequence (3.1) would be the following model sequence which contains k exponential terms:

$$s_n = s + \sum_{j=0}^{k-1} c_j \lambda_j^n, \quad n \in \mathbb{N}_0. \quad (3.6)$$

Here, we assume that $|\lambda_0| > |\lambda_1| > \dots > |\lambda_{k-1}|$ holds. Although the Δ^2 process (3.2) is by construction exact for the model sequence (3.1), the iterated Δ^2 process (3.4) is not exact for the model sequence (3.6). Instead, this is true for Wynn's epsilon algorithm [61], which is another generalization of the Δ^2 process (3.2) and which corresponds to the following nonlinear recursive scheme:

$$\epsilon_{-1}^{(n)} = 0, \quad \epsilon_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (3.7a)$$

$$\epsilon_{k+1}^{(n)} = \epsilon_{k-1}^{(n+1)} + 1/[\epsilon_k^{(n+1)} - \epsilon_k^{(n)}], \quad k, n \in \mathbb{N}_0. \quad (3.7b)$$

Only the elements $\epsilon_{2k}^{(n)}$ with *even* subscripts provide approximations to the limit s of the sequence $\{s_n\}_{n=0}^{\infty}$ to be transformed. The elements $\epsilon_{2k+1}^{(n)}$ with *odd* subscripts are only auxiliary quantities which diverge if the whole process converges.

A straightforward calculation shows that $\mathcal{A}_1^{(n)} = \epsilon_2^{(n)}$. Accordingly, Aitken's iterated Δ^2 process may also be viewed as an iteration of $\epsilon_2^{(n)}$. However, for $k > 1$, $\mathcal{A}_k^{(n)}$ and $\epsilon_{2k}^{(n)}$ are in general different, although they of course have similar properties in convergence acceleration and summation processes.

If the input data s_n are the partial sums $f_n(z) = \sum_{\nu=0}^n \gamma_{\nu} z^{\nu}$ of the (formal) power series for some function $f(z)$, $s_n = f_n(z)$, then Wynn [61] could show that his epsilon algorithm produces Padé approximants according to

$$\epsilon_{2k}^{(n)} = [n + k/k]_f(z). \quad (3.8)$$

For Padé approximants, we use the notation of Baker and Graves-Morris [62], i.e., the Padé approximant $[l/m]_f(z)$ to some function $f(z)$ is the ratio of two polynomials $P_l(z) = p_0 + p_1 z + \dots + p_l z^l$ and $Q_m(z) = 1 + q_1 z + \dots + q_m z^m$ of degrees l and m in z according to

$$[l/m]_f(z) = P_l(z)/Q_m(z). \quad (3.9)$$

Since the epsilon algorithm can be used for the computation of Padé approximants according to (3.8), it is discussed in books on Padé approximants such as [62]. However, there is also an extensive literature which deals directly with the epsilon algorithm. On p. 120 of Wimp's book [67] it is mentioned that over 50 articles on the epsilon algorithm were published by Wynn alone, and at least 30 articles by Brezinski. As a fairly complete source of references Wimp recommends Brezinski's first book [63]. However, this book was published in 1977, and since then many more articles on the epsilon algorithm have been published. Moreover, the epsilon algorithm is not restricted to scalar sequences but can be generalized to cover for example vector sequences. A very recent review of these developments can be found in [89].

Aitken's iterated Δ^2 process (3.4) as well as Wynn's epsilon algorithm (3.7) are powerful accelerators for sequences which according to (2.18) converge linearly. However, contrary to a widespread misconception, the epsilon algorithm is not necessarily the most efficient convergence accelerator for linear convergence. In 1973 Levin [90] introduced a sequence transformation which uses as input data not only a finite substring $s_n, s_{n+1}, \dots, s_{n+k}$ of the sequence to be transformed, but also explicit estimates $\omega_n, \omega_{n+1}, \dots, \omega_{n+k}$ for the corresponding remainders $r_n, r_{n+1}, \dots, r_{n+k}$. The explicit incorporation of the information contained in the remainder estimates into the convergence acceleration or summation process makes Levin's sequence transformation [90] as well as closely related generalizations [74, 91] potentially very powerful. Some recent applications of Levin-type transformations plus additional references can for example be found in [75, 92–96].

However, the use of explicit remainder estimates is not only the major advantage but also the major weakness of Levin-type transformations. If it is possible to find remainder estimates that are good approximations to the actual remainders of the sequence to be transformed, then experience indicates that Levin-type transformations can be extremely powerful. In contrast, Levin-type transformations will perform quite poorly if good remainder estimates cannot be found.

If we want to extrapolate oligomer calculations, then we have to struggle not only with potentially large numerical inaccuracies in the input data but also with the fact that oligomers with a small number of repeat units may behave very irregularly. As a result large *prediction* errors can occur leading to poor performance of Levin-type transformations.

Wynn's epsilon algorithm (3.7) only uses the elements of the sequence to be transformed as input data and it is not possible to feed in any additional information into the transformation process. Consequently, the epsilon algorithm is not as powerful as Levin-type transformation can be under optimal conditions. On the other hand, there is no prediction error. Moreover, as for example discussed in [74, Section 15.2], the epsilon algorithm is also remarkably insensitive to rounding errors and it can tolerate input data which either have a low relative accuracy or which behave in a comparatively irregular way. Thus, the real strength of the epsilon algorithm is its robustness. Due to its remarkable robustness, the epsilon algorithm is often able to produce meaningful and reliable results in situations in which other sequence transformations, which are in principle more powerful, fail. Experience indicates that Aitken's iterated Δ^2 process (3.4) is also less robust and more susceptible to rounding errors than Wynn's epsilon algorithm.

4 Richardson Extrapolation, Wynn's Rho Algorithm, and Related matters

In Section 3, we discussed sequence transformations which work in the case of sequences that converge *linearly* according to (2.18). Typical examples of linearly convergent sequences are the partial sums of power series with a nonzero but finite radius of convergence. The computational problems, which occur in that case, can be studied via the Gaussian hypergeometric series

$${}_2F_1(a, b; c; z) = \sum_{m=0}^{\infty} \frac{(a)_m (b)_m}{(c)_m m!} z^m. \quad (4.1)$$

This series terminates if either a or b is a negative integer. Otherwise it converges linearly in the interior of the unit circle, i.e., for $|z| < 1$, and it diverges for $|z| > 1$. Moreover, the convergence of this series can for most values of the parameters $a, b, c \in \mathbb{C}$ be accelerated quite efficiently by sequence transformations [97].

Generally speaking, the acceleration of linear convergence is comparatively simple, both theoretically and practically, as long as ρ in (2.18) is not too close to 1 (this would be a borderline case to logarithmic convergence). With the help of Germain-Bonne's formal theory of convergence acceleration [98] and its extension [74, Section 12], it can be decided rigorously whether a sequence transformation is capable of accelerating linear convergence or not. Moreover, many sequence transformations are capable of accelerating linear convergence effectively.

The situation is much more difficult in the case of logarithmic convergence. It follows from the expansion (2.5) for the truncation error that the partial sums $\sum_{\nu=0}^n (\nu+1)^{-z}$ of the Dirichlet series (2.1) converge logarithmically to $\zeta(z)$. As already discussed in Section 2, the convergence of the Dirichlet series can become so slow that the evaluation of $\zeta(z)$ by successively adding up the terms $(\nu+1)^{-z}$ is practically impossible. Of course, analogous problems can also occur in the case of other logarithmically convergent sequences and series,

Moreover, there are also some principal theoretical problems. Delahaye and Germain-Bonne [79, 80] showed that no sequence transformation can exist which is able to accelerate the convergence of *all* logarithmically convergent sequences. Consequently, in the case of logarithmic convergence the success of a convergence acceleration process cannot be guaranteed unless additional information is available. Also, an analogue of Germain-Bonne's beautiful formal theory of the acceleration of linear convergence [98] and its extension [74, Section 12] cannot exist.

In spite of these complications, many sequence transformations are known which work reasonably well at least for suitably restricted subsets of the class of logarithmically convergent sequences. Examples, which will be discussed later, are Richardson extrapolation [57], Wynn's

rho algorithm [99] and its iteration [74, Section 6], as well as Osada's modification of the rho algorithm [100], and the modification of the Δ^2 process by Bjørstad, Dahlquist, and Grosse [101]. Nevertheless, there is a considerable amount of theoretical and empirical evidence that sequence transformations speed up logarithmic convergence in general less efficiently than linear convergence.

Another problem with logarithmic convergence is that numerical instabilities are more likely than in the case of linear convergence. A sequence transformation can only accelerate convergence if it succeeds in extracting some information about the index-dependence of the truncation errors from a finite set $s_n, s_{n+1}, \dots, s_{n+k}$ of input data. Normally, this is done by forming arithmetic expressions involving higher weighted differences. However, forming higher weighted differences is a potentially unstable process which can easily lead to a serious loss of significant digits or even to completely nonsensical results. If the input data are the partial sums of a *strictly alternating* series, the formation of higher weighted differences is normally a remarkably stable process. If, however, the input data all have the *same sign*, numerical instabilities due to cancellation are quite likely, in particular if convergence is very slow. Thus, if the sequence to be transformed converges logarithmically, numerical instabilities are a serious problem and at least some loss of significant digits is to be expected.

In [95], a combined nonlinear-condensation transformation was described which first converts a slowly convergent monotone series into a strictly alternating series. Since the subsequent transformation of a strictly alternating series is a remarkable stable process, it is in this way possible to evaluate special functions, that are defined by extremely slowly convergent series, not only relatively efficiently but also very close to machine accuracy. Unfortunately, an analogous approach is not possible if oligomer calculations produce logarithmically convergent sequences: The conversion of the monotone series to the alternating series requires that series terms with large indices can be computed. This is of course not possible in the case of oligomer calculations.

For the construction of sequence transformations, the standard interpolation and extrapolation methods of numerical mathematics are quite helpful. Let us assume that the values of a function $f(x)$ are only known at some discrete points $x_0 < x_1 < \dots < x_m$, and that we want to estimate the value of f at some point $\xi \notin \{x_0, x_1, \dots, x_m\}$. If $x_0 < \xi < x_m$, this problem is called *interpolation*, and if either $\xi < x_0$ or $x_m < \xi$, this problem is called *extrapolation*. These topics are discussed in any book on numerical analysis. More specialized treatments can for instance be found in [102, 103].

For the construction of extrapolation processes, we postulate the existence of a function \mathcal{S} of a continuous variable which coincides on a set of discrete arguments $\{x_n\}_{n=0}^{\infty}$ with the elements of the sequence $\{s_n\}_{n=0}^{\infty}$ to be transformed:

$$\mathcal{S}(x_n) = s_n, \quad n \in \mathbb{N}_0. \quad (4.2)$$

This ansatz reduces the problem of accelerating the convergence of a sequence to an extrapolation problem. If a finite string $s_m, s_{m+1}, \dots, s_{m+k}$ of $k+1$ sequence elements is known one can construct an approximation $\mathcal{S}_k(x)$ to $\mathcal{S}(x)$ which satisfies the $k+1$ interpolation conditions

$$\mathcal{S}_k(x_{m+j}) = s_{m+j}, \quad 0 \leq j \leq k. \quad (4.3)$$

In the next step, the value of $\mathcal{S}_k(x)$ has to be determined for $x \rightarrow x_{\infty}$. If this can be done and if there exists a function $\mathcal{S}(x)$ which can be approximated at least locally by a suitable set of interpolating functions, one can expect that $\mathcal{S}_k(x_{\infty})$ will provide a better approximation to the limit $s = s_{\infty}$ of the sequence $\{s_n\}_{n=0}^{\infty}$ than the last sequence element s_{m+k} which was used for the construction of $\mathcal{S}_k(x)$.

The most common interpolating functions are either polynomials or rational functions. These two sets will also lead to different convergence acceleration methods. If a sequence transformation is constructed on the basis of polynomial interpolation, it is implicitly assumed that the k -th order approximant $\mathcal{S}_k(x)$ is a polynomial of degree k in x :

$$\mathcal{S}_k(x) = c_0 + c_1x + \cdots + c_kx^k. \quad (4.4)$$

For polynomials, the most natural extrapolation point is $x = 0$. Consequently, the interpolation points x_n have to satisfy the conditions

$$x_0 > x_1 > \cdots > x_m > x_{m+1} > \cdots > 0, \quad (4.5a)$$

$$\lim_{n \rightarrow \infty} x_n = 0. \quad (4.5b)$$

The choice $x_\infty = 0$ as the extrapolation point implies that the approximation to the limit is to be identified with the constant term c_0 of the polynomial (4.4).

Several different methods for the construction of interpolating polynomials $\mathcal{S}_k(x)$ are known in the mathematical literature. Since only the constant term of a polynomial $\mathcal{S}_k(x)$ has to be computed and since in most applications it is desirable to compute simultaneously a whole string of approximants $\mathcal{S}_0(0), \mathcal{S}_1(0), \mathcal{S}_2(0), \dots$, the most economical choice is Neville's scheme [104] for the recursive computation of interpolating polynomials. If we set $x = 0$, Neville's algorithm reduces to the following 2-dimensional linear recursive scheme [64, p. 6]:

$$\mathcal{N}_0^{(n)}(s_n, x_n) = s_n, \quad n \in \mathbb{N}_0, \quad (4.6a)$$

$$\mathcal{N}_{k+1}^{(n)}(s_n, x_n) = \frac{x_n \mathcal{N}_k^{(n+1)}(s_{n+1}, x_{n+1}) - x_{n+k+1} \mathcal{N}_k^{(n)}(s_n, x_n)}{x_n - x_{n+k+1}}, \quad k, n \in \mathbb{N}_0. \quad (4.6b)$$

In the literature on convergence acceleration this variant of Neville's recursive scheme is usually called Richardson extrapolation [57]. Obviously, $\mathcal{N}_k^{(n)}(s_n, x_n)$ is exact if elements s_n of the sequence to be transformed are polynomials of degree k in the interpolation points x_n :

$$s_n = s + \sum_{j=0}^{k-1} c_j x_n^{j+1}, \quad k, n \in \mathbb{N}_0. \quad (4.7)$$

As is well known, some functions can be approximated by polynomials only quite poorly, but by rational functions they can be approximated very well. Consequently, it is to be expected that at least for some sequences $\{s_n\}_{n=0}^\infty$ rational extrapolation will give better results than polynomial extrapolation. Let us therefore assume that the approximant $\mathcal{S}_k(x)$ can be written as the ratio of two polynomials of degrees l and m , respectively:

$$\mathcal{S}_k(x) = \frac{a_0 + a_1x + a_2x^2 + \cdots + a_lx^l}{b_0 + b_1x + b_2x^2 + \cdots + b_mx^m}, \quad k, l, m \in \mathbb{N}_0. \quad (4.8)$$

This rational function contains $l + m + 2$ coefficients a_0, \dots, a_l and b_0, \dots, b_m . However, only $l + m + 1$ coefficients are independent since they are determined only up to a common nonvanishing factor. Usually, one requires either $b_0 = 1$ or $b_m = 1$. Consequently, the $k + 1$ interpolation conditions (4.3) will determine the coefficients a_0, \dots, a_l and b_0, \dots, b_m provided that $k = l + m$ holds.

The extrapolation point $x_\infty = 0$ is also the most obvious choice in the case of rational extrapolation. Extrapolation to $x_\infty = 0$ implies that the interpolation points $\{x_n\}_{n=0}^\infty$ in (4.8) have to satisfy (4.5) and that the approximation to the limit is to be identified with the ratio a_0/b_0 of the constant terms of the polynomials in (4.8).

If $l = m$ holds in (4.8), extrapolation to infinity is also possible. In that case the interpolation points $\{x_n\}_{n=0}^\infty$ have to satisfy

$$0 < x_0 < x_1 < \cdots < x_m < x_{m+1} < \cdots, \quad (4.9a)$$

$$\lim_{n \rightarrow \infty} x_n = \infty. \quad (4.9b)$$

In the case of extrapolation to infinity, only the coefficients a_l and b_l of the polynomials in (4.8), that are proportional to highest power x^l , contribute. Consequently, the approximation to the limit has to be identified with the ratio a_l/b_l .

As in the case of polynomial interpolation, several different algorithms for the computation of rational interpolants are known. A discussion of the relative merits of these algorithms as well as a survey of the relevant literature can be found in [105, Chapter III].

The most frequently used rational extrapolation technique is probably Wynn's rho algorithm [61]:

$$\rho_{-1}^{(n)} = 0, \quad \rho_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.10a)$$

$$\rho_{k+1}^{(n)} = \rho_{k-1}^{(n+1)} + \frac{x_{n+k+1} - x_n}{\rho_k^{(n+1)} - \rho_k^{(n)}}, \quad k, n \in \mathbb{N}_0. \quad (4.10b)$$

Formally, the only difference between Wynn's epsilon algorithm (3.7) and Wynn's rho algorithm is that the rho algorithm involves a sequence of interpolation points $\{x_n\}_{n=0}^\infty$ which have to satisfy (4.9). As in the case of the epsilon algorithm, only the elements $\rho_{2k}^{(n)}$ with even subscripts serve as approximations to the limit. The elements $\rho_{2k+1}^{(n)}$ with odd subscripts are only auxiliary quantities which diverge if the whole process converges.

Wynn's rho algorithm is designed to compute even-order convergents of Thiele's interpolating continued fraction [106] and to extrapolate them to infinity. The even-order convergents are rational functions of the following type:

$$S_{2k}(x) = \frac{a_k x^k + a_{k-1} x^{k-1} + \cdots + a_1 x + a_0}{b_k x^k + b_{k-1} x^{k-1} + \cdots + b_1 x + b_0}, \quad k \in \mathbb{N}_0. \quad (4.11)$$

Thus, the ratio a_k/b_k is to be identified with the approximation to the limit.

The epsilon and the rho algorithm have complementary features. The epsilon algorithm is a powerful accelerator for linear convergence and is also able to sum many divergent alternating series, whereas the rho algorithm fails to accelerate linear convergence and is not able to sum divergent series. However, it is a very powerful accelerator for some logarithmically convergent sequences.

The properties of Wynn's rho algorithm are for example discussed in books by Brezinski (see [63, pp. 102 - 106] and [64, pp. 96 - 102] and Wimp [67, pp. 168 - 169]. In these books the connection of the ρ algorithm with interpolating continued fractions is emphasized and it is also shown that the transforms $\rho_{2k}^{(n)}$ can be represented as the ratio of two determinants. Moreover, there is an article by Osada [107], discussing its convergence properties. But otherwise, relatively little seems to be known about this sequence transformation.

In the case of the rho algorithm, we can proceed as in the case of the Aitken formula (3.2) and construct an iterated transformation. For $k = 1$, we obtain from (4.10):

$$\rho_2^{(n)} = s_{n+1} + \frac{(x_{n+2} - x_n)[\Delta s_{n+1}][\Delta s_n]}{[\Delta x_{n+1}][\Delta s_n] - [\Delta x_n][\Delta s_{n+1}]}, \quad n \in \mathbb{N}_0. \quad (4.12)$$

This expression, which can be viewed to be a kind of weighted Δ^2 formula, can be iterated

yielding [88, Section 6.3]

$$\mathcal{W}_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.13a)$$

$$\mathcal{W}_{k+1}^{(n)} = \mathcal{W}_k^{(n+1)} + \frac{(x_{n+2k+2} - x_n)[\Delta\mathcal{W}_k^{(n+1)}][\Delta\mathcal{W}_k^{(n)}]}{(x_{n+2k+2} - x_{n+1})[\Delta\mathcal{W}_k^{(n)}] - (x_{n+2k+1} - x_n)[\Delta\mathcal{W}_k^{(n+1)}]}, \quad (4.13b)$$

$$k, n \in \mathbb{N}_0.$$

This is not the only possibility of iterating $\rho_2^{(n)}$. However, in [88] it was shown that other iterations of $\rho_2^{(n)}$ – for instance the one derived by Bhowmick, Bhattacharya, and Roy [108] – are significantly less efficient than $\mathcal{W}_k^{(n)}$, which has similar properties as Wynn’s rho algorithm (4.10), from which it was derived.

The main problem with the practical application of those sequence transformations, that are based upon interpolation theory, is that one has to find a sequence $\{x_n\}_{n=0}^\infty$ of interpolation points which produces good extrapolation results for a given sequence $\{s_n\}_{n=0}^\infty$ of input data. For example, in most practical applications the Richardson extrapolation scheme (4.6) is used in combination with the interpolation points $x_n = 1/(n + \beta)$, where β is a positive shift parameter. Then, $\mathcal{N}_k^{(n)}(s_n, 1/(n + \beta))$ possesses a closed form expression (see for example [68, Lemma 2.1 on p. 313] or [74, Eq. (7.3-20)])

$$\begin{aligned} \Lambda_k^{(n)}(\beta, s_n) &= \mathcal{N}_k^{(n)}(s_n, 1/(n + \beta)) \\ &= (-1)^k \sum_{j=0}^k (-1)^j \frac{(\beta + n + j)^k}{j!(k-j)!} s_{n+j}, \quad k, n \in \mathbb{N}_0, \end{aligned} \quad (4.14)$$

and the recursive scheme (4.6) assumes the following form [74, Eq. (7.3-21)]

$$\Lambda_0^{(n)}(\beta, s_n) = s_n, \quad n \in \mathbb{N}_0, \quad (4.15a)$$

$$\Lambda_{k+1}^{(n)}(\beta, s_n) = \Lambda_k^{(n+1)}(\beta, s_{n+1}) + \frac{\beta + n}{k+1} \Delta \Lambda_k^{(n)}(\beta, s_n), \quad k, n \in \mathbb{N}_0. \quad (4.15b)$$

Similarly, Wynn’s rho algorithm (4.10) and its iteration (4.13) are normally used in combination with the interpolation points $x_n = n + 1$, yielding the standard forms (see for example [74, Eq. (6.2-4)])

$$\rho_{-1}^{(n)} = 0, \quad \rho_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.16a)$$

$$\rho_{k+1}^{(n)} = \rho_{k-1}^{(n+1)} + \frac{k+1}{\rho_k^{(n+1)} - \rho_k^{(n)}}, \quad k, n \in \mathbb{N}_0, \quad (4.16b)$$

and [88, Section 6.3]

$$\mathcal{W}_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.17a)$$

$$\mathcal{W}_{k+1}^{(n)} = \mathcal{W}_k^{(n+1)} - \frac{(2k+2)[\Delta\mathcal{W}_k^{(n+1)}][\Delta\mathcal{W}_k^{(n)}]}{(2k+1)\Delta^2\mathcal{W}_k^{(n)}}, \quad k, n \in \mathbb{N}_0. \quad (4.17b)$$

In the literature on convergence acceleration and extrapolation, Richardson extrapolation as well as Wynn’s rho algorithm and its iteration are normally used in their standard forms (4.15), (4.16), and (4.17). However, it is important to recognize that their general forms (4.6), (4.10), and (4.13), respectively, which all involve unspecified interpolation points, may be required for oligomer calculations. Let us assume that the elements s_n of a logarithmically convergent sequence can be expressed by series expansions of the following kind,

$$s_n = s + (n + \beta)^{-\alpha} \sum_{j=0}^{\infty} c_j / (n + \beta)^j, \quad n \in \mathbb{N}_0, \quad (4.18)$$

where α is a positive decay parameter, β is a positive shift parameter, and the c_j are unspecified coefficients. In general, we have no *a priori* reason to assume that oligomer calculations would only produce sequences of that kind with an integral decay parameter, and we want to accelerate the convergence of sequences of that kind even if α is nonintegral.

In Theorem 14-4 of [74], it was shown rigorously that the standard form (4.15) of Richardson extrapolation is able to accelerate the convergence of the model sequence (4.18) if $\alpha = 1, 2, \dots$, but fails if α is nonintegral. In the case of Wynn's rho algorithm and its iteration, we are not aware of any explicit proof, but there is considerable experimental evidence that the standard forms (4.16) and (4.17) of these transformations also fail to accelerate the convergence of the model sequence (4.18) if the decay parameter α is nonintegral (see Section 14.4 of [74]).

If the decay parameter α of a sequence of the type of (4.18) is known, then Osada's variant of Wynn's rho algorithm can be used [100, Eq. (3.1)]:

$$\bar{\rho}_{-1}^{(n)} = 0, \quad \bar{\rho}_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.19a)$$

$$\bar{\rho}_{k+1}^{(n)} = \bar{\rho}_{k-1}^{(n+1)} + \frac{k + \alpha}{\bar{\rho}_k^{(n+1)} - \bar{\rho}_k^{(n)}}, \quad k, n \in \mathbb{N}_0. \quad (4.19b)$$

For $\alpha = 1$, Osada's variant becomes identical with the standard form (4.16). Osada also demonstrated that his variant accelerates the convergence of the model sequence (4.18), and that the transformation error satisfies the following asymptotic estimate [100, Theorem 4]:

$$\bar{\rho}_{2k}^{(n)} - s = O(n^{-\alpha-2k}), \quad n \rightarrow \infty. \quad (4.20)$$

Osada's variant of the rho algorithm can also be iterated. From (4.19) we obtain the following expression for $\bar{\rho}_2^{(n)}$ in terms of s_n , s_{n+1} , and s_{n+2} :

$$\bar{\rho}_2^{(n)} = s_{n+1} - \frac{(\alpha + 1)}{\alpha} \frac{[\Delta s_n][\Delta s_{n+1}]}{[\Delta^2 s_n]}, \quad n \in \mathbb{N}_0. \quad (4.21)$$

If this iteration is done in such a way that α is increased by 2 with every recursive step, we obtain the following recursive scheme [88, Eq. (2.29)] which was derived originally by Bjørstad, Dahlquist, and Grosse [101, Eq. (2.4)]:

$$\overline{\mathcal{W}}_0^{(n)} = s_n, \quad n \in \mathbb{N}_0, \quad (4.22a)$$

$$\overline{\mathcal{W}}_{k+1}^{(n)} = \overline{\mathcal{W}}_k^{(n+1)} - \frac{(2k + \alpha + 1)}{(2k + \alpha)} \frac{[\Delta \overline{\mathcal{W}}_k^{(n+1)}][\Delta \overline{\mathcal{W}}_k^{(n)}]}{\Delta^2 \overline{\mathcal{W}}_k^{(n)}}, \quad k, n \in \mathbb{N}_0. \quad (4.22b)$$

For $\alpha = 1$, this weighted iterated Δ^2 algorithm becomes identical with the standard form (4.17) of the iteration of Wynn's rho algorithm.

Bjørstad, Dahlquist, and Grosse showed that $\overline{\mathcal{W}}_k^{(n)}$ accelerates the convergence of the model sequence (4.18), and that the transformation error satisfies the following asymptotic estimate [101, Eq. (3.1)]

$$\overline{\mathcal{W}}_k^{(n)} - s = O(n^{-\alpha-2k}), \quad n \rightarrow \infty. \quad (4.23)$$

The two sequence transformations $\bar{\rho}_{2k}^{(n)}$ and $\overline{\mathcal{W}}_k^{(n)}$ require the same set $s_n, s_{n+1}, \dots, s_{n+2k}$ of elements of the model sequence (4.18) as input data. Since the asymptotic error estimates (4.20) and (4.23) are equivalent, the two transformations are also *asymptotically* equivalent, i.e., in the limit of large indices n , although they of course may produce different results for small indices n . Moreover, these two transformations are also *optimal*, since the elimination of two terms of the infinite series on the right-hand side of (4.18) requires the input of the numerical values of

two sequence elements. Thus, no sequence transformation, which only uses the numerical values of the elements of the model sequence (4.18) as input data, could improve on the asymptotic ($n \rightarrow \infty$) error estimates (4.20) and (4.23).

The knowledge of the decay parameter α is crucial for an application of the transformations (4.19) and (4.22) to a sequence of the type of (4.18). An approximation to α can be obtained with the help of the following nonlinear transformation:

$$T_n = \frac{[\Delta^2 s_n][\Delta^2 s_{n+1}]}{[\Delta s_{n+1}][\Delta^2 s_{n+1}] - [\Delta s_{n+2}][\Delta^2 s_n]} - 1, \quad n \in \mathbb{N}_0. \quad (4.24)$$

The transformation T_n , which was first derived in a somewhat disguised form by Drummond [109] and later rederived by Bjørstad, Dahlquist, and Grosse [101], is essentially a weighted Δ^3 method. Consequently, it is potentially a very unstable method if the relative accuracy of the input data is low, and stability problems can never be excluded. Bjørstad, Dahlquist, and Grosse [101, Eq. (4.1)] also showed that

$$\alpha = T_n + O(1/n^2), \quad n \rightarrow \infty, \quad (4.25)$$

if the elements of the model sequence (4.18) are used as input data.

5 An Example: Extrapolation of Oligomer Calculations for Unit Cell Energy of Polyacetylene

All-trans polyacetylene with the repeat unit $-(\text{CH}=\text{CH})-$, which contains 14 electrons, is the simplest *quasi*-onedimensional polymer containing conjugated double bonds. As a result of the conjugation and the pronounced anisotropy, polyacetylene exhibits a variety of interesting properties. Included amongst these properties is an enormous increase in conductivity induced by doping (see for example [1, 110]) and a very large electric field induced polarization [2, 47] compared to the corresponding non-conjugated polymer polyethylene with the repeat unit $-(\text{CH}_2-\text{CH}_2)-$. Accordingly, there is an enormous number of articles dealing with polyacetylene. A reasonably complete bibliography would clearly be beyond the scope of this article.

In this article, we want to demonstrate that sequence transformations are useful numerical tools for the extrapolation of oligomer calculations. Consequently, we are not so much interested in obtaining highly accurate results. Instead, we want to study the typical behavior of quantum chemical calculations on a sequence of oligomers with increasing size. For this purpose, it is sufficient to use relatively small basis sets which allowed us to carry out calculations on fairly large oligomers expeditiously.

Here we some consider calculations for the ground state energy of the oligomers $\text{H}-(\text{CH}=\text{CH})_N-\text{H}$. These will illustrate how new and improved results can be obtained but, by no means exhaust the range of possibilities. Other *quasi*-onedimensional polymers, as well as the application to other properties such as hyperpolarizabilities and electronic transition energies, will be discussed elsewhere [111]. The calculated total ground state energy E_N of an oligomer consisting of N repeat units is an *extensive* quantity. This means that we first have to convert E_N to an *intensive* quantity before we can do extrapolations to the infinite chain limit. The most obvious approach consists in defining average energies or energies per repeat unit according to

$$E_N^{(\text{av})} = E_N/N. \quad (5.1)$$

If we compare the total energy of an oligomer $\text{H}-(\text{CH}=\text{CH})_N-\text{H}$ with the total energy of a hypothetical ring molecule consisting of N repeat units $-(\text{CH}=\text{CH})-$, and if we also assume

that N is so large that angular strain can be neglected, then we see that the saturation of the terminal free valences by hydrogen atoms should lead to an energy contribution which is nearly constant, i.e., which depends on N only quite weakly. Consequently, we may reasonably assume that the average energy $E_N^{(\text{av})}$ will contain a contribution which is proportional to $1/N$ arising from the chain ends and, therefore, can be expressed as

$$E_N^{(\text{av})} = E_\infty^{(\text{av})} + C/N + \Phi_N^{(\text{av})}, \quad (5.2)$$

where C is an N -independent constant and $\Phi_N^{(\text{av})}$ is an unknown function of N which should decay faster than $1/N$ as N becomes large.

If we want to extrapolate the average energies successfully to the infinite chain limit, then we must have an idea of how the unknown function $\Phi_N^{(\text{av})}$ depends upon N . It is a relatively obvious idea to express $\Phi_N^{(\text{av})}$ or equivalently $E_N^{(\text{av})}$ by a power series in $1/N$ according to

$$E_N^{(\text{av})} = E_\infty^{(\text{av})} + \sum_{j=1}^{\infty} C_j/N^j. \quad (5.3)$$

If this is case, then the sequence of the average energies converges logarithmically to the infinite chain limit according to (2.18). As discussed in Section 4, the acceleration of logarithmic convergence is normally more difficult than the acceleration of linear convergence. Nevertheless, the standard forms (4.15), (4.16), and (4.17) of Richardson extrapolation, Wynn's rho algorithm and its iteration should be effective accelerators for sequences of the kind of (5.3).

However, there are still some unresolved theoretical questions. According to Cioslowski and Lepetit [112, p. 3544], who performed a perturbation theoretic analysis of the N -dependence of Hartree-Fock oligomer energies, the power series expansion (5.3) for the average energy $E_N^{(\text{av})}$ can not only contain powers of $1/N$ but also nonanalytic terms of the type $\exp(-\gamma N)$ with $\gamma > 0$. For sufficiently large values of N , these nonanalytic contributions will be negligible. However, they could well have a negative effect on the performance of convergence acceleration processes. Sequence transformations designed for the acceleration of logarithmic convergence are usually not good at eliminating nonanalytic contributions typical of linear convergence, and vice versa.

Alternatively, Cui, Kertesz, and Jiang [41] proposed to compute the energy per repeat unit not via the average energies (5.1) but via the energy differences

$$E_N^{(\text{dif})} = E_{N+1} - E_N = (N+1)E_{N+1}^{(\text{av})} - N E_N^{(\text{av})}. \quad (5.4)$$

The argument of Cui, Kertesz, and Jiang was that the energies of two oligomers containing $N+1$ or N monomer units, respectively, should essentially differ by the energy of an *inner* monomer unit [113]. Equivalently, this means that the effects due to the finite size of the oligomers as well as the $1/N$ errors due to the saturation of free terminal valences should depend on N only quite weakly and are largely canceled by forming differences.

If we now combine (5.2) with (5.4), we obtain

$$E_N^{(\text{dif})} = E_\infty^{(\text{av})} + \Delta[N\Phi_N^{(\text{av})}], \quad (5.5)$$

where $\Phi_N^{(\text{av})}$ is the function defined in (5.2) that describes the higher order effects of the N -dependence of the average energies. Comparing (5.2) and (5.5) and taking into account that $\Phi_N^{(\text{av})}$ has been assumed to decay faster than $1/N$, we see that $E_N^{(\text{dif})}$ does not contain a $1/N$ contribution and converges more rapidly than $E_N^{(\text{av})}$ to the infinite chain limit. If, for example, it is assumed that $\Phi_N^{(\text{av})} \sim 1/N^2$ as $N \rightarrow \infty$, we obtain $\Delta[N\Phi_N^{(\text{av})}] \sim 1/N^2$ which shows that the energy differences converge faster than the average energies.

In order to illustrate some of the above procedures we carried out Hartree-Fock ground state energy calculations for the oligomers $\text{H}-(\text{CH}=\text{CH})_N-\text{H}$ with $N \leq 16$ using an ST0-3G basis set. A fixed geometry was used for all oligomers with $R_{\text{C}=\text{C}} = 1.366 \text{ \AA}$, $R_{\text{C}-\text{C}} = 1.450 \text{ \AA}$, $R_{\text{C}-\text{H}} = 1.085 \text{ \AA}$, $\angle_{\text{C}=\text{C}-\text{C}} = 123.90 \text{ deg}$, $\angle_{\text{H}-\text{C}-\text{H}} = 117.13 \text{ deg}$, and $\angle_{\text{H}-\text{C}-\text{H}} = 117.13 \text{ deg}$. This geometry implies $\angle_{\text{H}-\text{C}=\text{C}} = 118.97 \text{ deg}$, except for the terminal hydrogen on either end, for which $\angle_{\text{H}-\text{C}=\text{C}} = 123.90 \text{ deg}$. In Table I, we list the total energies E_N , the average energies $E_N^{(\text{av})}$ defined in (5.1), and the energy differences $E_N^{(\text{dif})}$ defined in (5.4). The data displayed in Table I show that the energy differences converge indeed much more rapidly than the average energies.

Table I: Total Hartree-Fock energies E_N , average energies $E_N^{(\text{av})}$, and energy differences $E_N^{(\text{dif})}$ using an ST0-3G basis set.
For geometry see the text.

N	E_N	$E_N^{(\text{av})}$	$E_N^{(\text{dif})}$
1	-77.0672438490	-77.0672438490	-75.943944441
2	-153.011188290	-76.5055941450	-75.945112888
3	-228.956301178	-76.3187670593	-75.945528271
4	-304.901829449	-76.2254573623	-75.945641947
5	-380.847471396	-76.1694942792	-75.945676982
6	-456.793148378	-76.1321913963	-75.945688518
7	-532.738836896	-76.1055481280	-75.945692475
8	-608.684529371	-76.0855661714	-75.945693869
9	-684.630223240	-76.0700248044	-75.945694368
10	-760.575917608	-76.0575917608	-75.945694549
11	-836.521612157	-76.0474192870	-75.945694615
12	-912.467306772	-76.0389422310	-75.945694639
13	-988.413001411	-76.0317693393	-75.945694649
14	-1064.35869606	-76.0256211471	-75.945694650
15	-1140.30439071	-76.0202927140	-75.945694650
16	-1216.25008536	-76.0156303350	

In the next step, we want to analyze whether the average energies and the energy differences behave like the elements of the model sequence (4.18), i.e., whether we can identify a well-defined decay parameter α . For that purpose, we use the transformation T_n defined in (4.24). All sequence transformations discussed in this article are gauged in such a way that the indices of the elements of the sequence to be transformed start with zero. Thus, we use the average energies and the energy differences as input data for T_n according to either $s_n = E_{n+1}^{(\text{av})}$ with $0 \leq n \leq 16$ or $s_n = E_{n+1}^{(\text{dif})}$ with $0 \leq n \leq 14$.

The results in the third column of Table II show quite clearly that the average energies possess a contribution which is proportional to $1/N$. On the basis of these results alone, one might be tempted to generalize this observation and conclude that the average energies can be expressed by expansions in powers of $1/N$ according to (5.3). However, the approximations to the decay parameter of the energy differences in the fifth column show an erratic behavior and there is no indication that they might converge. Thus, we have no reason to assume that energy

Table II: Approximations to the decay parameter α of the average energies $E_{n+1}^{(\text{av})}$ and the energy differences $E_{n+1}^{(\text{dif})}$ according to (4.24).

n	$E_{n+1}^{(\text{av})}$	T_n	$E_{n+1}^{(\text{dif})}$	T_n
0	-77.0672438490	1.0026524	-75.943944441	-6.7203517
1	-76.5055941450	0.9972079	-75.945112888	13.549818
2	-76.3187670593	0.9976702	-75.945528271	21.022075
3	-76.2254573623	0.9984106	-75.945641947	31.065636
4	-76.1694942792	0.9990241	-75.945676982	44.885592
5	-76.1321913963	0.9994399	-75.945688518	72.270674
6	-76.1055481280	0.9996933	-75.945692475	84.907033
7	-76.0855661714	0.9998391	-75.945693869	210.38728
8	-76.0700248044	0.9999177	-75.945694368	-403.50000
9	-76.0575917608	0.9999589	-75.945694549	6.0000000
10	-76.0474192870	0.9999827	-75.945694615	-2.6578947
11	-76.0389422310	0.9999829	-75.945694639	-10.000000
12	-76.0317693393	0.9999976	-75.945694649	
13	-76.0256211471		-75.945694650	
14	-76.0202927140		-75.945694650	
15	-76.0156303350			

differences decay like a fixed power of $1/N$. In view of 5.4) and (5.5) this observation implies that the unknown function $\Phi_N^{(\text{av})}$ defined in (5.2), which describes the higher order effects of the truncation errors in the average energies, also does not decay like a fixed power of $1/N$. Consequently, our observation contradicts the perturbation theoretic analysis of Cioslowski and Lepetit [112] who concluded that the average energies can be expressed by a power series in $1/N$ according to (5.3) plus possibly some nonanalytic contributions.

If we want to apply sequence transformations to speed up the convergence of oligomer calculations to the infinite chain limit, we have to assume that the N -dependence of the truncation errors in the energy differences possesses a structure which is sufficiently regular to be detected and utilized in convergence acceleration processes. The energy differences in the last column of Table I showed a remarkably rapid convergence, indicating that the truncation errors might converge exponentially. A rigorous theoretical proof of this assumption is of course not in sight. So, we have to provide numerical evidence for our conjecture.

There is a simple ratio test related to the ratio test for infinite series, which can provide evidence for exponential decay. If we form the ratio

$$\mathcal{R}_n = \frac{s_{n+2} - s_{n+1}}{s_{n+1} - s_n} = \frac{\Delta s_{n+1}}{\Delta s_n} \quad (5.6)$$

of the elements of the model sequence (3.1), then we obtain $\mathcal{R}_n = \lambda$. If the input data do not have the simple form of the elements of this model sequence, but nevertheless decay exponentially, then we only get a constant as $n \rightarrow \infty$. In Table III, we apply the ratio test (5.6) to the input data $s_n = E_{n+1}^{(\text{dif})}$ with $0 \leq n \leq 11$. The results in the last column of Table III seem to converge, albeit slowly. Therefore, they provide evidence that the energy differences indeed converge exponentially to the infinite chain limit.

Table III: Ratio test (5.6) of the energy differences

n	$E_{n+1}^{(\text{dif})}$	\mathcal{R}_n
0	-75.943944441	0.3555
1	-75.945112888	0.2737
2	-75.945528271	0.3082
3	-75.945641947	0.3293
4	-75.945676982	0.3430
5	-75.945688518	0.3523
6	-75.945692475	0.3580
7	-75.945693869	0.3627
8	-75.945694368	0.3646
9	-75.945694549	0.3636
10	-75.945694615	
11	-75.945694639	

There is another approach which can provide evidence that the truncation errors of the energy differences indeed decay exponentially. If we apply sequence transformations, that are known to accelerate linear convergence but fail in the case of logarithmic convergence like Aitken's iterated Δ^2 process (3.4) or Wynn's epsilon algorithm (3.7), and observe an acceleration of convergence, then we have very strong evidence for our conjecture.

There is a problem with the acceleration of the convergence of the energy differences. The last column of Table I shows that the energy differences $E_N^{(\text{dif})}$ have for $N = 14$ already converged to all digits given. Thus, there are no additional digits left which could provide information to the extrapolation methods. All sequence transformations form higher weighted differences of the input data, and so does Aitken's iterated Δ^2 process or Wynn's epsilon algorithm. If, however, the input data have almost reached convergence and there are no additional digits left, numerical instabilities or even completely nonsensical results can never be excluded.

If the input data s_0, s_1, \dots, s_{2k} are known, then the transform with the highest possible subscript, that can be computed with the help Wynn's epsilon algorithm (3.7), is $\epsilon_{2k}^{(0)}$. In general, this is the most efficient approach and one can normally expect the best results. If, however, the input data behave like the energy differences and differ at most with respect to a few digits, it is recommended that one apply the epsilon algorithm differently. Instead, we start from the initial string $\epsilon_n^{(2)} = E_{n+1}^{(\text{dif})}$ with $0 \leq n \leq n_{\max}$ and compute the string $\epsilon_n^{(2)}$ with $0 \leq n \leq n_{\max} - 2$. Then we analyze the convergence and reliability of this string and compute, if necessary and possible, the next string $\epsilon_n^{(4)}$ with $0 \leq n \leq n_{\max} - 4$. This process can be repeated until either convergence has been achieved or the accumulation of rounding errors makes it impossible to proceed.

In Table IV, we show the effect of Wynn's epsilon algorithm (3.7) on the energy differences. The extrapolation results provide strong evidence that the truncation errors of the energy differences converge exponentially. For example, $\epsilon_6^{(1)} = -75.945694655$, which requires the initial values $\epsilon_0^{(1)} = E_2^{(\text{dif})}$, $\epsilon_0^{(2)} = E_3^{(\text{dif})}$, \dots , $\epsilon_0^{(7)} = E_8^{(\text{dif})}$ for its computation, reproduces all but the last digit of $\epsilon_0^{(13)} = E_{14}^{(\text{dif})} = -75.945694650$. Thus, the epsilon algorithm makes it unnecessary to compute the oligomer energies E_N with $9 \leq N \leq 14$, which is indeed a remarkable achievement.

We also used Aitken's iterated Δ^2 process (3.4) for the extrapolation of the energy differ-

Table IV: Epsilon extrapolation of the energy differences.

n	$\epsilon_0^{(n)} = E_{n+1}^{(\text{dif})}$	$\epsilon_2^{(n)}$	$\epsilon_4^{(n)}$	$\epsilon_6^{(n)}$
0	-75.943944441	-75.945757392	-75.945691527	-75.945694631
1	-75.945112888	-75.945684777	-75.945694512	-75.945694655
2	-75.945528271	-75.945692590	-75.945694634	-75.945694651
3	-75.945641947	-75.945694181	-75.945694652	-75.945694652
4	-75.945676982	-75.945694541	-75.945694651	-75.945694653
5	-75.945688518	-75.945694627	-75.945694654	-75.945694652
6	-75.945692475	-75.945694646	-75.945694653	-75.945694653
7	-75.945693869	-75.945694652	-75.945694653	-75.945694763
8	-75.945694368	-75.945694653	-75.945694653	
9	-75.945694549	-75.945694653	-75.945694654	
10	-75.945694615	-75.945694656		
11	-75.945694639	-75.945694650		
12	-75.945694649			
13	-75.945694650			

ences. These extrapolation results were virtually identical with the epsilon extrapolation results presented in Table IV.

When we performed oligomer calculations for polyacetylene using more extensive basis sets and other geometries, or for other *quasi*-onedimensional polymers, we again observed an exponential decay of the energy differences [111]. Thus, this exponential decay seems to be a general feature which is not restricted to polyacetylene.

6 Summary and Conclusions

Quasi-onedimensional stereoregular polymers like polyacetylene are currently of considerable interest, not only scientifically but also because of numerous possible technological applications. There are basically two different approaches for doing *ab initio* electronic structure calculations on such systems which have largely complementary advantages and disadvantages. One method, the so-called crystal orbital method, is based on the concepts of solid state theory. It uses periodic boundary conditions and leads to a band structure treatment. Accordingly, this approach is well suited to describe those features that depend crucially on the in principle infinite extension of the polymer. However, there are still some open computational problems with the crystal orbital method. For example, it is very difficult to properly take into account the effect of nonperiodic perturbations such as the interaction with an electric field or to incorporate high level electron correlation effects.

The other method is essentially a quantum chemical approach. It approximates the polymer by oligomers consisting of a finite number of monomer units, i.e., by molecules of finite size. In this way, the highly developed technology of quantum chemical molecular *ab initio* programs can be used. Thus, electron correlation can be treated using any of the techniques available in these programs. In addition, nonlinear optical properties may be calculated via this approach. At the present time, this cannot be done reliably within the framework of crystal orbital theory even at

the Hartree-Fock level.

Unfortunately, oligomers of finite size are not necessarily able to model those features of a polymer which crucially depend on its in principle infinite extension since finite oligomer calculations can suffer badly from slow convergence to the infinite chain limit. However, one can perform electronic structure calculations for a sequence of oligomers with an increasing number of monomer units and try to determine the limit of this sequence with the help of suitable extrapolation methods.

Many different approaches for doing the extrapolations are possible. In this article, we use sequence transformations. The mechanism, whereby sequence transformations accomplish an acceleration of convergence, can be understood via the Euler-Maclaurin formula which is able to produce rapidly convergent approximations to the truncation errors of some slowly convergent infinite series like the Dirichlet series for the Riemann zeta function. Although the Euler-MacLaurin formula is extremely powerful in some cases, it is an analytic convergence acceleration method and cannot be used if only the numerical values of some elements of a slowly convergent sequence are known. Sequence transformations also try to accomplish an acceleration by constructing approximations to the truncation errors of the elements of a slowly convergent sequence which are subsequently eliminated from the input data. However, they do this by purely numerical means.

Two practically very important classes of sequences are linearly and logarithmically convergent sequences. The partial sums of a power series with a nonzero, but finite radius of convergence constitute a typical example of a linearly convergent sequence, whereas the partial sums of the Dirichlet series for the Riemann zeta function, which is notorious for slow convergence, is a typical example of a logarithmically convergent sequence. Thus, the properties of these two classes of slowly convergent sequences differ considerably, and so do the sequence transformations which are able to accelerate effectively either linear or logarithmic convergence. In general, the acceleration of logarithmic convergence is more difficult than the acceleration of linear convergence, both theoretically and practically.

Two powerful accelerators for linear convergence are Aitken's iterated Δ^2 process and Wynn's epsilon algorithm which, in the case of the partial sums of a power series, produces Padé approximants. However, these two transformations fail to accelerate logarithmic convergence, whereas the powerful accelerators for logarithmic convergence – for example Richardson extrapolation or Wynn's rho algorithm and its iteration – fail to accelerate linear convergence.

There are also some other problems with the acceleration of logarithmic convergence. In the literature on convergence acceleration, the transformations mentioned above are usually treated in their so-called standard forms. However, the standard forms are not able to accelerate the convergence of those logarithmically convergent sequences whose elements decay like a negative nonintegral power of the index. There is no *a priori* reason why sequences with a nonintegral decay parameter cannot occur in the context of oligomer calculations. Therefore, we also discuss transformations like Osada's variant of Wynn's rho algorithm or the weighted Δ^2 algorithm introduced by Bjørstad, Dahlquist, and Grosse, which are both able to accelerate the convergence of sequences of that kind.

We carried out calculations of the Hartree-Fock ground state energy for oligomers $\text{H} - (\text{CH}=\text{CH})_N - \text{H}$ using a **ST0-3G** basis set with a fixed geometry, and extrapolated these energies to the infinite chain limit corresponding to all-trans polyacetylene. The extrapolations were greatly facilitated by the fact that no accelerators were needed for the more troublesome logarithmic convergence. Contrary to previous belief we showed that the truncation error for the average energy per monomer unit contains linear term in $1/N$, where N is the number of monomer units, but no higher powers. This leading contribution can be eliminated easily by

forming differences. and the higher order contributions converge exponentially. Thus, accelerators for linear convergence sufficed for our purposes and Wynn's epsilon algorithm proved very effective in this regard. The ground state energy is just one property of interest. Future applications will deal with nonlinear optical properties and electronic transition energies which have a different dependence upon N and are more problematic from the practical point of view since they converge more slowly.

Acknowledgments

EJW thanks the Fonds der Chemischen Industrie for financial support.

References

- [1] M.D. McGehee, E.K. Miller, D. Moses and A. J. Heeger, Twenty years of conducting polymers: From fundamental science to applications, *Advances in Synthetic Metals Twenty Years of Progress in Science and Technology* (Edited by P. Bernier, S. Lefrant and G. Bidan), pp. 98 - 205, Elsevier, Amsterdam, 1999.
- [2] B. Kirtman and B. Champagne, Nonlinear optical properties of quasilinear conjugated oligomers, polymers and organic molecules, *Int. Rev. Phys. Chem.* **16**, 389 - 420, (1997).
- [3] J.C.W. Chien, *Polyacetylene*, Academic Press, Orlando, (1984).
- [4] D.R. Hartree, The wave mechanics of an atom with a non-Coulomb central field, *Proc. Cambridge Phil. Soc.* **24**, 89 - 132, (1928).
- [5] V. Fock, *Näherungsmethoden zur Lösung des quantenmechanischen Mehrkörperproblems*, Z. Physik **61**, 126 - 148, (1930).
- [6] W. Kohn and L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 - A1139, (1965).
- [7] C.C.J. Roothaan, New developments in molecular orbital theory, *Rev. Mod. Phys.* **23**, 69 - 89, (1951).
- [8] J.-M. André, D.H. Mosley, M.-C. André, B. Champagne, E. Clementi, J.G. Fripiat, L. Leherter, L. Pisani, D.R. Vercauten, and M. Vracko, *Exploring Aspects of Computational Chemistry - Concepts*, Presses Univ. de Namur, Namur (1997).
- [9] A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd edition, Gaussian, Inc., Pittsburgh (1996).
- [10] C. Pisani, R. Dovesi, and C. Roetti, *Hartree-Fock Ab Initio Treatment of Crystalline System*, Springer-Verlag, Berlin, (1988).
- [11] J.J. Ladik, *Quantum Theory of Polymers as Solids*, Plenum Press, New York, (1988).
- [12] J.-M. André, J. Delhalle, and J.-L. Brédas, *Quantum Chemistry Aided Design of Organic Polymers*, World Scientific, Singapore, (1991).
- [13] J.-M. André, Quantum mechanical methods for regular polymers, *Adv. Quantum Chem.* **12**, 65 - 102, (1980).
- [14] M. Kertész, Electronic structure of polymers, *Adv. Quantum Chem.* **15**, 161 - 214, (1982).
- [15] J.J. Ladik, Polymers as solids: A quantum mechanical treatment, *Phys. Rep.* **313**, 171 - 235, (1999).
- [16] C. Kittel, *Introduction to Solid State Physics*, Wiley, New York (1971).
- [17] C. Kittel, *Quantum Theory of Solids*, Wiley, New York (1963).
- [18] D. Jacquemin, J.-M. André, and B. Champagne, Long-range effects in optimizing the geometry of stereoregular polymers. I. Formalism, *J. Chem. Phys.* **111**, 5306 - 5323, (1999).
- [19] P.N. Prasad and D. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York (1991).

- [20] B. Champagne, D.H. Mosley, and J.-M. André, Ab initio coupled and uncoupled ab initio Hartree-Fock calculations of the polarizabilities of finite and infinite polyacetylene chains, *Int. J. Quantum Chem. S* **27**, 667 - 685, (1993).
- [21] B. Champagne and Y. Öhrn, *Chem. Phys. Lett.* **217**, 551, (1994).
- [22] B. Champagne, D.H. Mosley, J.G. Fripiat, and J.-M. André, Towards the calculations of polarizabilities of stereoregular polymers, *Adv. Quantum Chem.* **35**, 95 - 110, (1999).
- [23] P. Otto, Calculation of the polarizability and hyperpolarizabilities of periodic quasi-one-dimensional systems, *Phys. Rev. B* **45**, 10876 - 10885, (1992).
- [24] J. Ladik, Theory of nonlinear optical properties of quasi-1D periodic polymers, in *Non-linear Optical Materials: Theory and Modeling*, *ACS* **628**, American Chemical Society, Washington, DC, 1996, Chap. 10, 174 - 188.
- [25] P. Otto, F.L. Gu, and J. Ladik, Calculation of *ab initio* dynamic hyperpolarizabilities of polymers, *J. Chem. Phys.* **110**, 2717 - 2726, (1999).
- [26] D. Jacquemin and B. Champagne, Comment on "Calculation of *ab initio* dynamic hyperpolarizabilities of polymers" [J. Chem. Phys. 110, 2717 (1999)], *J. Chem. Phys.* **112**, 1616 - 1617, (2000).
- [27] P. Otto, F.L. Gu, and J. Ladik, Response to "Calculation of *ab initio* dynamic hyperpolarizabilities of polymers" [J. Chem. Phys. 112, 1616 (2000)], *J. Chem. Phys.* **112**, 1618, (2000).
- [28] S. Wilson, *Electron Correlation in Molecules*, Clarendon Press, Oxford, (1984).
- [29] P. Fulde, *Electron Correlation in Atoms and Molecules*, Springer-Verlag, Berlin, (1991).
- [30] F.E. Harris, H.J. Monkhorst, and D.L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory*, Oxford U.P., Oxford, (1992).
- [31] J.L. Toto, T.T. Toto, and C.P. de Melo, A comparative study of the effect of electron correlation in the hyperpolarizability of polyynes, polyacetylene and polypyrrole, *Chem. Phys. Lett.* **245**, 660, (1995).
- [32] S.J.A. van Gisbergen, P.R.T. Schipper, O.V. Gritsenko, E.J. Baerends, J.G. Snijders, B. Champagne, and B. Kirtman, Electric field dependence of the exchange-correlation potential in molecular chains, *Phys. Rev. Lett.* **83**, 694 - , (1999).
- [33] B. Champagne, E.A. Perpete, S.J.A. van Gisbergen, E.J. Baerends, J.G. Snijders, C. Soubra-Ghaoui, K.A. Robins, and B. Kirtman, Assessment of conventional density functional schemes for computing the polarizabilities and hyperpolarizabilities of conjugated oligomers: An ab initio investigation of polyacetylene chains, *J. Chem. Phys.* **109**, 10489 - 10498, (1998).
- [34] B. Champagne, E.A. Perpete, D. Jacquemin, S.J.A. van Gisbergen, E.J. Baerends, C. Soubra-Ghaoui, and K.A. Robins, Assessment of conventional density functional schemes for computing the dipole moment and (hyper)polarizabilities of push-pull π -conjugated systems, *J. Phys. Chem.*, in press.
- [35] B. Kirtman, W.B. Nilsson, and W.E. Palke, Small chain approximation for the electronic structure of polyacetylene, *Solid State Commun.* **46**, 791 - 794, (1983).
- [36] G.J.B. Hurst, M. Dupuis, and E. Clementi, *Ab initio* analytic polarizability, first and second hyperpolarizabilities of large conjugated organic molecules: Application to polyenes C_4H_6 to $C_{22}H_{24}$, *J. Chem. Phys.* **89**, 385 - 395, (1988).
- [37] B. Kirtman, Convergence of finite chain approximation for linear and non-linear polarizabilities of polyacetylene, *Chem. Phys. Lett.* **143**, 81 - 83, (1988).
- [38] J. Cioslowski, On extracting the bulk properties from results on small cluster calculations, *Chem. Phys. Lett.* **153**, 446 - 450, (1988).
- [39] H.O. Villar, M. Dupuis, J.D. Watts, G.J.B. Hurst, and E. Clementi, Structure, vibrational spectra, and IR intensities of polyenes from *ab initio* SCF calculations, *J. Chem. Phys.* **88**, 1003 - 1009, (1988).
- [40] E.J. Weniger and C.-M. Liegener, Extrapolation of finite cluster and crystal-orbital calculations on trans-polyacetylene, *Int. J. Quantum Chem.* **38**, 55 - 74, (1990).
- [41] C.X. Cui, M. Kertesz, and Y. Jiang, Extraction of polymer properties from oligomer calculations, *J. Phys. Chem.* **94**, 5172 - 5179, (1990).

- [42] J. Cioslowski and E.J. Weniger, Bulk properties from finite cluster calculations. VIII. Benchmark calculations on the efficiency of extrapolation methods for the HF and MP2 energies of polyacenes, *J. Comp. Chem.* **14**, 1468 - 1481, (1993).
- [43] J.L. Toto, T.T. Toto, C.P. de Melo, M. Hasan, and B. Kirtman, Ab initio finite oligomer method for nonlinear optical properties of conjugated polymers. Effect of electron correlation on the static longitudinal hyperpolarizability of polyacetylene, *Chem. Phys. Lett.* **244**, 59 - 64, (1995).
- [44] J.L. Toto, T.T. Toto, C.P. de Melo, and K.A. Robins, Ab initio polarizability study of polypyrrole, *J. Chem. Phys.* **102**, 8048 - 8052, (1995).
- [45] D. Jacquemin, B. Champagne, and J.-M. André, Møller-Plesset evaluation of the static first hyperpolarizability of polymethineimine, *Chem. Phys. Lett.* **284**, 24 - 30, (1998).
- [46] B. Champagne, J.M. Luis, M. Duran, J.L. Andrés, and B. Kirtman, Anharmonicity contributions to the vibrational second hyperpolarizability of conjugated oligomers, *J. Chem. Phys.* **112**, 1011 - 1019, (2000), and references cited therein.
- [47] For an up-to-date review see B. Champagne and B. Kirtman, Theoretical approach to the design of organic molecular and polymeric nonlinear optical materials, in *Handbook of Advanced Electronic and Photonic Materials and Devices*, (Edited by H.S. Nalwa), Academic Press, San Diego (2000).
- [48] B. Kirtman, C.E. Dykstra, and B. Champagne, Major intermolecular effects on nonlinear electrical response in a hexatriene model of solid state polyacetylene, *Chem. Phys. Lett.* **305**, 132 - 138, (1999). A second paper in this series is in preparation.
- [49] P.C.M. McWilliams and Z.G. Soos, Interchain dispersion and second hyperpolarizability of conjugated polymers, *J. Chem. Phys.* **95**, 2127 - 2134, (1991).
- [50] J. Tanaka and C. Tanaka, Structure models of metallic polyacetylene, *Synth. Met.* **69**, 647 - 650, (1995).
- [51] L.L. Rodriguez-Monge, *Theoretical Studies on Electronic Structure, Spectra and Conductivity of Pristine and Alkali Doped Polyacetylene*, Ph.D.Thesis, Department of Physical Chemistry, Chalmers University of Technology (1996).
- [52] B. Kirtman, M. Spassova, and B. Champagne, work in progress.
- [53] K. Knopp, *Theorie und Anwendung der unendlichen Reihen*, Springer-Verlag, Berlin, (1964).
- [54] J. Stirling, *Methodus Differentialis sive Tractatus de Summatione et Interpolatione Serium Infinitarum*, London, (1730). English translation by F. Holliday, *The differential method, or, a treatise concerning the summation and interpolation of infinite series*, London, (1749).
- [55] L. Euler, *Institutiones Calculi Differentialis cum Eius Usu in Analysi Finitorum ac Doctrina Serium. Part II.1. De Transformatione Serium*, Academia Imperialis Scientiarum Petropolitana, St. Petersburg, (1755). This book was reprinted as Vol. X of *Leonardi Euleri Opera Omnia, Series Prima*, Teubner, Leipzig und Berlin, (1913).
- [56] C. Brezinski, *History of Continued Fractions and Padé Approximants*, Springer-Verlag, Berlin, (1991).
- [57] L.F. Richardson, The deferred approach to the limit. I. Single lattice, *Phil. Trans. Roy. Soc. London A* **226**, 229 - 349, (1927).
- [58] A.C. Aitken, On Bernoulli's numerical solution of algebraic equations, *Proc. Roy. Soc. Edinburgh* **46**, 289 - 305, (1926).
- [59] C. Brezinski, Extrapolation algorithms and Padé approximations: a historical survey, *Appl. Numer. Math.* **20**, 299 - 318, (1996).
- [60] D. Shanks, Non-linear transformations of divergent and slowly convergent sequences, *J. Math. and Phys.* (Cambridge, Mass.) **34**, 1 - 42, (1955).
- [61] P. Wynn, On a device for computing the $e_m(S_n)$ transformation, *Math. Tables Aids Comput.* **10**, 91 - 96 (1956).
- [62] G.A. Baker, Jr., and P. Graves-Morris, *Padé Approximants*, 2nd edition, Cambridge U.P., Cambridge, (1996).
- [63] C. Brezinski, *Accélération de la Convergence en Analyse Numérique*, Springer-Verlag, Berlin, (1977).
- [64] C. Brezinski, *Algorithmes d'Accélération de la Convergence - Étude Numérique*, Editions Technip, Paris, (1978).

- [65] C. Brezinski, *Padé-Type Approximation and General Orthogonal Polynomials*, Birkhäuser, Basel, (1980).
- [66] C. Brezinski and M. Redivo Zaglia, *Extrapolation Methods*, North-Holland, Amsterdam, (1991).
- [67] J. Wimp, *Sequence Transformations and Their Applications*, Academic Press, New York, (1981).
- [68] G.I. Marchuk and V.V. Shaidurov, *Difference Methods and Their Extrapolations*, Springer-Verlag, New York, (1983).
- [69] J.-P. Delahaye, *Sequence Transformations* Springer-Verlag, Berlin, (1988).
- [70] C.B. Liem, T. Lü, and T.M. Shih, *The Splitting Extrapolation Method*, World Scientific, Singapore, (1995).
- [71] G. Walz, *Asymptotics and Extrapolation*, Akademie Verlag, Berlin, (1996).
- [72] C. Brezinski, *Projection Methods for Systems of Equations* Elsevier, Amsterdam, (1997).
- [73] A.J. Guttman, Asymptotic analysis of power series expansions, in *Phase Transitions and Critical Phenomena* **13**, (Edited by C. Doms and J.L. Lebowitz), pp. 3 - 234, Academic Press, London, (1989).
- [74] E.J. Weniger, Nonlinear sequence transformations for the acceleration of convergence and the summation of divergent series, *Comput. Phys. Rep.* **10**, 189 - 371, (1989).
- [75] E.J. Weniger, Nonlinear sequence transformations: A computational tool for quantum mechanical and quantum chemical calculations, *Int. J. Quantum Chem.* **57**, 265 - 280, (1996); Erratum: Nonlinear sequence transformations: A computational tool for quantum mechanical and quantum chemical calculations, *Int. J. Quantum Chem.* **58**, 319 - 321, (1996).
- [76] E.K. Dalskov, J. Oddershede, and D.M. Bishop, Static and dynamic polarizability calculations for the polyne series ($C_{2n}H_2$) with extrapolation to the infinite chain, *J. Chem. Phys.* **108**, 2152 - 2161, (1998).
- [77] F.W.J. Olver, *Asymptotics and Special Functions*, Academic Press, New York, (1974).
- [78] E.J. Weniger, Prediction properties of Aitken's iterated Δ^2 process, of Wynn's epsilon algorithm, and of Brezinski's iterated theta algorithm, to appear in the special millenium edition "Extrapolation and Convergence Acceleration Methods" of *J. Comput. Appl. Math.* (edited by C. Brezinski). Los Alamos preprint math/0002111 (<http://xxx.lanl.gov>).
- [79] J.P. Delahaye and B. Germain-Bonne, Résultats négatifs en accélération de la convergence, *Numer. Math.* **35**, 443 - 457, (1980).
- [80] J.P. Delahaye and B. Germain-Bonne, The set of logarithmically convergent sequences cannot be accelerated, *SIAM J. Numer. Anal.* **19**, 840 - 844, (1982).
- [81] C. Schneider, Vereinfachte Rekursionen zur Richardson-Extrapolation in Spezialfällen, *Numer. Math.* **24**, 177 - 184, (1975).
- [82] C. Brezinski, A general extrapolation algorithm, *Numer. Math.* **35**, 175 - 180, (1980).
- [83] T. Håvie, Generalized Neville type extrapolation schemes, *BIT* **19**, 204 - 213, (1979).
- [84] J. Todd, Motivation for working in numerical analysis. In *Survey of Numerical Analysis*, (Edited by J. Todd), pp. 1 - 26, McGraw-Hill, New York, (1962).
- [85] E.E. Kummer, Eine neue Methode, die numerischen Summen langsam convergirender Reihen zu berechnen, *J. Reine Angew. Math.* **16**, 206 - 214, (1837).
- [86] D.A. Smith and W.F. Ford, Numerical comparisons of nonlinear convergence accelerators, *Math. Comput.* **38**, 481 - 499, (1982).
- [87] P. Hillion, Méthode d'Aitken itérée pour les suites oscillantes d'approximations, *C. R. Acad. Sc. Paris A* **280**, 1701 - 1704, (1975).
- [88] E.J. Weniger, On the derivation of iterated sequence transformations for the acceleration of convergence and the summation of divergent series, *Comput. Phys. Commun.* **64**, 19 - 45, (1991).
- [89] P.R. Graves-Morris, D.E. Roberts, and A. Salam, The epsilon algorithm and related topics, to appear in the special millenium edition "Extrapolation and Convergence Acceleration Methods" of *J. Comput. Appl. Math.* (edited by C. Brezinski).
- [90] D. Levin, Development of non-linear transformations for improving convergence of sequences, *Int. J. Comput. Math. B* **3**, 371 - 388, (1973).

- [91] H.H.H. Homeier, *Scalar Levin-type sequence transformations*, to appear in the special millenium edition "Extrapolation and Convergence Acceleration Methods" of J. Comput. Appl. Math. (edited by C. Brezinski).
- [92] E.J. Weniger, A convergent renormalized strong coupling perturbation expansion for the ground state energy of the quartic, sextic, and octic anharmonic oscillator, *Ann. Phys. (NY)* **246**, 133 - 165, (1996).
- [93] E.J. Weniger, Computation of the Whittaker function of the second kind by summing its divergent asymptotic series with the help of nonlinear sequence transformations, *Comput. Phys.* **10**, 496 - 503, (1996).
- [94] E.J. Weniger, Construction of the strong coupling expansion for the ground state energy of the quartic, sextic and octic anharmonic oscillator via a renormalized strong coupling expansion, *Phys. Rev. Lett.* **77**, 2859 - 2862, (1996).
- [95] U.D. Jentschura, P.J. Mohr, G. Soff, and E.J. Weniger, Convergence acceleration via combined nonlinear-condensation transformations, *Comput. Phys. Commun.* **116**, 28 - 54, (1999).
- [96] U.D. Jentschura, J. Becher, E.J. Weniger, and G. Soff, Resummation of QED perturbation series by sequence transformations and prediction of perturbative coefficients. Los Alamos preprint hep-ph/9911265 (<http://xxx.lanl.gov>).
- [97] E.J. Weniger, Irregular input data in convergence acceleration and summation processes: General considerations and some special Gaussian hypergeometric series as model problems, *Comput. Phys. Commun.*, submitted. Los Alamos preprint math.NA/0003227 (<http://xxx.lanl.gov>).
- [98] B. Germain-Bonne, Transformations de suites, *Rev. Française Automat. Informat. Rech. Operat.* **7** (R-1), 84 - 90, (1973).
- [99] P. Wynn, On a Procrustean technique for the numerical transformation of slowly convergent sequences and series, *Proc. Camb. Phil. Soc.* **52**, 663 - 671, (1956).
- [100] N. Osada, A convergence acceleration method for some logarithmically convergent sequences, *SIAM J. Numer. Anal.* **27**, 178 - 189, (1990).
- [101] P. Bjørstad, G. Dahlquist, and E. Grosse, Extrapolations of asymptotic expansions by a modified Aitken δ^2 -formula, *BIT* **21**, 56 - 65, (1981).
- [102] P.J. Davis, *Interpolation and Approximation*, Dover, New York, (1975).
- [103] D.C. Joyce, Survey of extrapolation processes in numerical analysis, *SIAM Rev.* **13**, 435 - 490, (1971).
- [104] E.H. Neville, Iterative interpolation, *J. Indian Math. Soc.* **20**, 87 - 120, (1934).
- [105] A. Cuyt and L. Wuytack, *Nonlinear Methods in Numerical Analysis*, North-Holland, Amsterdam, (1987).
- [106] T.N. Thiele, *Interpolationsrechnung*, Teubner, Leipzig, (1909).
- [107] N. Osada, An acceleration theorem for the ρ algorithm, *Numer. Math.* **73**, 521 - 531, (1996).
- [108] S. Bhowmick, R. Bhattacharya, and D. Roy, Iterations of convergence accelerating nonlinear transforms, *Comput. Phys. Commun.* **54**, 31 - 36 (1989).
- [109] J.E. Drummond, Summing a common type of slowly convergent series of positive terms, *J. Austral. Math. Soc. B* **19**, 416 - 421, (1976).
- [110] A.J. Heeger and A.G. MacDiarmid, (1980), Conducting organic polymers: Doped polyacetylene, *The physics and chemistry of low dimensional solids* (Edited by L. Alcácer), pp. 353 - 392, Reidel, Dordrecht, (1980).
- [111] B. Kirtman and E.J. Weniger, work in progress.
- [112] J. Cioslowski and M.B. Lepetit, Bulk properties from finite cluster calculations. VI. A finite-size perturbation theory for the Hartree-Fock energy of linear oligomers, *J. Chem. Phys.* **95**, 3536 - 3548, (1991).
- [113] See also B. Kirtman, Nonlinear optical properties of conjugated polymers from ab initio finite oligomer calculations, *Int. J. Quantum Chem.* **43**, 147-158, (1992).