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Summation methods for dimensional perturbation theory

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We examine strategies for approximating the sum of a perturbation expansion for Coulombic systems in inverse powers of the spatial dimension D using only the few lowest-order terms. Several summation methods are tested on energy expansions of the following systems: the ground state of He, the ground state of Li^+, the first two excited S states and the lowest $^3P^e$ state of He, and the ground state of $\mathrm{H_2}^+$. The origin of the expansions, the limit $D \to \infty$, corresponds to a *pseudoclassical* limit, but lower-order terms are strongly affected by poles at $D \to 1$, a *hyperquantum* limit. Two alternative methods are recommended, *weighted truncation* and *hybrid Padé summation,* which exploit these poles to reduce the summation error. In effect, these methods modify a semiclassical $1/D$ expansion by incorporating corrections that are often large. Weighted truncation appears to be slightly more dependable at very low orders, while hybrid Padé summation is preferable when more than the three lowest-order terms are available or when the residue of the second-order pole at $D=1$ is known. We demonstrate that the present methods are superior to the shifted-expansion method, which does not correctly model the singularity structure.

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I. INTRODUCTION

The large-dimension limit of the Schrödinger equation [1–4] is a simple, yet in some ways remarkably accurate, model for the physical three-dimensional solution. It offers a clear and straightforward explanation for two very subtle and widely studied effects of electron correlation in the two-electron atom: the apparent moleculelike behavior of the system, which was discovered by Kellman and Herrick [5], from an analysis of the electronic energy spectrum and demonstrated by Berry and co-workers [6] using configuration-interaction calculations, and the approximate separability of the two-electron wave function in terms of hyperspherical coordinates, first noted by Macek [7]. The molecular behavior of the atom becomes quite obvious at large dimension. In the limit of infinite dimension, with suitable dimensional scalings, the electrons become fixed in a rigid symmetric configuration with the radial vectors separated by an angle of 95.3°. We call this the *Lewis structure.* At large but finite dimension the electrons undergo small oscillations about the Lewis structure, which we call the *Langmuir vibrations.* Although the analysis of Kellman and Herrick [5] was based on the assumption of a linear but very floppy structure, the spectrum can be explained just as well in terms of the bent Lewis structure [8]. Within first-order perturbation theory in $1/D$, where D is the dimension treated as a continuous variable, the Langmuir vibrations are harmonic and therefore separable in terms of normal coordinates. To a good approximation, the normal coordinates can be considered to be a symmetric stretch, a bend, and an antisymmetric stretch, with only a small coupling between the symmetric stretch and the bend. In the large-dimension limit the hyperspherical radius becomes equivalent to the symmetric stretch [9] and is therefore approximately separable. This argument also offers an explanation of the approximate separability of the wave function in terms of the molecular coordinates of Briggs and co-workers [10].

Despite these qualitative successes of the large-dimension limit, the attempt to calculate energy eigenvalues by simply adding subsequent terms in the $1/D$ expansion leads to remarkably *poor* results [1]. The key problem with dimensional-continuation techniques is to find a way to rigorously and systematically connect the large-dimension limit with the physical solution at $D=3$. The source of the difficulty is the presence of singularities in the energy when considered as a function of $1/D$. In particular, a second-order pole at $D=1$ is a characteristic feature of Coulombic systems [11,12] due to the divergence of the Coulombic potentials at particle coalescences. A coincident first-order pole is often present as well. These *Coulombic* poles greatly slow the convergence of the $1/D$ expansion.

In this paper we present two alternative summation methods for the $1/D$ expansion that explicitly incorporate information about the dimensional-singularity structure at $D=1$. We demonstrate the effectiveness of these methods using energy expansions through fifth order for the ground states of He and Li^+, for three excited states of He, and for the ground state of $\mathrm{H_2}^+$. The expansion coefficients for most of these systems [13–17] have become available only recently. They are the most complex systems for which dimensional expansions have yet been calculated beyond first order.

One of our methods, Padé summation of the hybrid expansion, was briefly described by us in a preliminary account of this work [13]. Here we discuss the procedure in greater detail and compare its effectiveness with that of earlier summation techniques. We show that it is the method of choice in most of the cases considered here. Our other method, weighted truncation, appears to be the best method to use at very low orders if the residue of the second-order Coulombic pole is not known.

We find in general that summation methods that have been designed to model the effects of the poles are much more effective than the more conventional techniques of partial sums or Padé approximants, which do not explicitly include the known singularity structure. One other method lies between these two groups. This is the shifted-expansion procedure of Sukhatme and Imbo [18], which does place a singularity at $D=1$, but a singularity of the wrong form. Not surprisingly, we find that the shifted expansion is more effective than the methods that do not include any singularity at $D=1$, but is less effective than those that include a singularity of the proper form. The shifted expansion has been rather widely used in recent years [19]. We suggest that it now be replaced by methods based on dimensional-singularity analysis.

II. SUMMATION METHODS

A. Previous approaches

For Coulombic systems, asymptotic expansions of the energy eigenvalues about the point $\delta=0$, with $\delta\equiv 1/D$, have the form [1]

$$E(\delta)=\delta^2\sum_{k=0}^{\infty}E_k\delta^k\ . \tag{1a}$$

It is convenient to remove the prefactor δ^2 by absorbing it into the energy units. This leads to a dimension-scaled energy $\tilde{E}$,

$$\tilde{E}(\delta)\equiv D^2E=\sum_{k=0}^{\infty}E_k\delta^k\ . \tag{1b}$$

The partial sums

$$S_n^{(\mathrm{PS})}(\delta)=\sum_{k=0}^{n}E_k\delta^k \tag{2}$$

form a sequence of approximants to $\tilde{E}$ in terms of the index n. This is not a suitable summation method for dimensional expansions of systems with Coulomb potentials, due to the approximants' inability to model the dimensional-singularity structure of the function $\tilde{E}(\delta)$. The functions $S_n^{(\mathrm{PS})}(\delta)$ are polynomials in δ, and therefore have no singularities at any finite value of δ, whereas $\tilde{E}(\delta)$ is known to have a rather rich singularity structure [20]. In particular, the Coulombic poles [11,12] at $\delta=1$, which have the form

$$\tilde{E}(\delta\sim 1)\sim a_{-2}(1-\delta)^{-2}+a_{-1}(1-\delta)^{-1}\ , \tag{3}$$

greatly slow the rate of convergence of the partial sums. The exact solution for $\tilde{E}(\delta)$ for the one-electron atom is [21]

$$\tilde{E}_{\mathrm{H}}(\delta)=-2Z^2(1-\delta)^{-2}\ . \tag{4}$$

The physical solution $\delta=\frac{1}{3}$ is within the radius of convergence so the partial sums of the δ expansion are convergent at that point. However, the rate of convergence is quite slow. At orders 0, 1, 2, 3, and 4 the accuracy is, respectively, 44%, 74%, 89%, 95%, and 98%. The rate of convergence of the first few terms for the He ground state is almost identical until large-order divergence begins to set in at fourth order.

The fact that the low-order convergence is similar in both cases suggested [2] rescaling the δ expansion by factoring out the hydrogenic energy; thus one obtains a rescaled approximant

$$\begin{aligned}S_n^{(\mathrm{re})}&=|2\tilde{E}_{\mathrm{H}}|[|2\tilde{E}_{\mathrm{H}}|^{-1}(E_0+E_1\delta+E_2\delta^2+\cdots+E_n\delta^n)]\\&\sim(1-\delta)^{-2}[E_0+(E_1-2E_0)\delta+(E_2-2E_1+E_0)\delta^2\\&\qquad+\cdots+(E_n-2E_{n-1}+E_{n-2})\delta^n]\ ,\end{aligned} \tag{5}$$

where $\tilde{E}_{\mathrm{H}}$ is the energy of the one-electron atom given by Eq. (4). On account of the scale factor $|2\tilde{E}_{\mathrm{H}}|^{-1}$, which is proportional to $(1-\delta)^2$, the power series within the brackets in Eq. (5) represents a function that is regular at $\delta=1$ and that can therefore be more accurately modeled by a power series. The improvement in the rate of convergence due to this rescaling is dramatic. The first-order result from the rescaled expansion is in error by less than 1%, as compared to the 26% error from the unscaled partial sums.

Another type of rescaled approximant is the *shifted expansion*, which was discovered empirically by Sukhatme and Imbo [18] before the dimensional-singularity structure had been elucidated. This method consists of recasting the expansion parameter $\delta\equiv 1/D$ in terms of $(D-\sigma)^{-1}$, where σ is an arbitrary shift parameter. For the ground state of He the optimal shift parameter was found to be $\sigma=1$, which leads to approximants of the form

$$S_n^{(\mathrm{sh})}=(1-\delta)^{-2}\sum_{i=0}^{n}E_i^{(\mathrm{sh})}(D-1)^{-i}\ , \tag{6}$$

where

$$E_i^{(\mathrm{sh})}=\sum_{i=0}^{n}(-1)^i\begin{Bmatrix}n+1\\ i\end{Bmatrix}E_{n-i}\ . \tag{7}$$

For $n=0$, Eqs. (5) and (6) are identical, with a second-order pole at $\delta=1$, but they differ at higher order since the shifted expansion adds additional higher-order poles at $\delta=1$. Singularity analysis [11] of the Schrödinger equation shows that there are no poles at $\delta=1$ of order higher than 2. Therefore, we can expect that the shifted expansion will be less and less accurate than the approximants of Eq. (5) as n increases. We will show below that this is indeed what happens.

An alternative approach to the summation problem is to identify a functional form for the singularity and then subtract its δ expansion from the expansion of the energy. According to Eq. (3), the Coulombic singularities have the form of a second-order pole and a confluent first-order pole. Suppose the residues of these poles were known. Then one could use an approximant of the form

$$S_n^{(\mathrm{hy})}=\frac{a_{-2}}{(1-\delta)^2}+\frac{a_{-1}}{1-\delta}+\sum_{i=0}^{n}E_i'\delta^i\ , \tag{8}$$

where

$$E_i' = E_i - (i+1)a_{-2} - a_{-1} \ . \tag{9}$$

This technique has been called the *hybrid expansion* [12], since it can be thought of as the sum of a truncated Laurent expansion about $\delta=1$ and a truncated Taylor expansion about $\delta=0$. The summation in Eq. (8) is equivalent to the nth partial sum of the function

$$\tilde{E}'(\delta) \equiv \tilde{E}(\delta) - a_{-2}(1-\delta)^{-2} - a_{-1}(1-\delta)^{-1} \ . \tag{10}$$

This function is regular at $\delta=1$, so we can expect that it will be more accurately modeled by partial sums than will the original function $\tilde{E}$.

B. Weighted truncation

The residue a_{-2} can often be calculated by solving the Schrödinger equation at $D=1$. This has been done for the one- and two-electron systems treated in this paper [11,15,21,22], but the calculation may be more difficult for more complicated systems. In principle, the residue of the first-order pole a_{-1}, can be calculated from perturbation theory about the $D=1$ solution, although in practice this is rather complicated. It would be useful to have a method that could yield an accurate summation from the expansion coefficients alone. Therefore, we require a technique for estimating the residues using only the expansion coefficients.

The partial sums for the He ground state at first steadily approach the correct value but then, after a certain point, become steadily worse. This behavior is typical for divergent asymptotic series [23]. An estimate of the error in the nth partial sum is given by the term in the expansion of order $n+1$, that is, $E_{n+1}\delta^{n+1}$. The partial sum for which this error estimate is smallest is called the *optimal asymptotic approximation* (OAA) [23]. If δ is sufficiently small, then the OAA will be the point of closest approach to the correct value. We can use the asymptotic error estimate as a criterion for fitting the residues. Consider an approximant of the form

$$S_n = \frac{\mu}{(1-\delta)^2} + \sum_{i=0}^{n} [E_i - (i+1)\mu]\delta^i \ , \tag{11}$$

with μ treated as a variable parameter. The error estimate for S_{n-1} is

$$\Delta S_{n-1} = [E_n - (n+1)\mu]\delta^n \ , \tag{12}$$

which suggests that we choose $\mu = E_n/(n+1)$ so as to set $\Delta S_{n-1}=0$. In this way we can construct a new sequence of approximants,

$$S_n^{(\mathrm{WT})} = \frac{E_n/(n+1)}{(1-\delta)^2} + \sum_{i=0}^{n-1} \left[E_i - \frac{i+1}{n+1}E_n \right] \delta^i \ . \tag{13}$$

We call this technique *weighted truncation*. Each of these approximants is the OAA of a series that has been weighted by subtracting out the expansion of a pole with the residue chosen so as to minimize the asymptotic error of the truncation. If the exact value of a_{-2} is known, then weighted truncation can be used to determine a_{-1}. This leads to the approximant

$$S_n^{(\mathrm{WT1})} = \frac{a_{-2}}{(1-\delta)^2} + \frac{E_n-(n+1)a_{-2}}{1-\delta} + \sum_{i=0}^{n-1} [E_i + (n-i)a_{-2} - E_n]\delta^i \ . \tag{14}$$

C. Hybrid Padé summation

The techniques we have described thus far only attempt to model singularities at $\delta=1$; however, analysis [15–17,20] of the large-order behavior of dimensional expansions for Coulombic systems has indicated in addition the presence of a singularity at or near $\delta=0$, which ultimately causes the partial sums for He and H_2^+ to diverge. The form of the singularity at the origin is rather complicated, and to characterize it from the expansion requires the knowledge of the expansion coefficients through rather high order. Fortunately, since the effect of this additional singularity on the low-order coefficients is often not very large, one can expect that for the purposes of summation at low order a very accurate characterization is not necessary.

Padé summation [24] is a simple and often very successful technique for modeling functions whose singularity structure is not known. Padé approximants are ratios of polynomials,

$$S_{[L/M]}(\delta) = \frac{p_0 + p_1\delta + p_2\delta^2 + \cdots + p_L\delta^L}{1 + q_1\delta + q_2\delta^2 + \cdots + q_M\delta^M} \ . \tag{15}$$

L and M are non-negative integers chosen such that $L+M=n$, where n is the order through which the expansion coefficients are available. The p_i and q_i are assigned by expanding Eq. (15) in powers of δ and then equating it order by order with the energy expansion. The function $S_{[L/M]}(\delta)$ has poles at the zeros of the denominator polynomial, which gives it some flexibility for describing functions with singularities.

We find that in the case of dimensional expansions the convergence of Padé approximants with increasing n tends to be rather slow and uneven. However, their rate of convergence can be improved considerably if they are used in conjunction with the hybrid expansion of Eq. (8). The Padé approximants of the E_i' converge quite well even at low order. At low order the Padé approximants of the full energy expansion Eq. (1b) use much of the limited amount of information at their disposal to model the poles at $\delta=1$, so they are not able at first to accurately model the complicated singularity at $\delta=0$. The Padé approximants of the hybrid expansion, which we call *hybrid Padé approximants,* can immediately devote their full attention to modeling the singularity at the origin.

If the residues are not known, then they too can be estimated using Padé approximants. The residues can be expressed in terms of the δ expansion according to

$$a_{-2} = \lim_{\delta\to 1}(1-\delta)^2\tilde{E}(\delta) \ , \tag{16a}$$

$$a_{-1} = \lim_{\delta\to 1}(1-\delta)[\tilde{E}(\delta) - a_{-2}(1-\delta)^{-2}] \ . \tag{16b}$$

We can expand Eqs. (16) in powers of δ and then calculate the residues from Padé approximants evaluated at $\delta=1$. The values for the residues obtained in this way are not extremely accurate, but they are usually accurate enough to remove the poles at $\delta=1$ from the Padé approximants for $\tilde{E}'$. We find that the rate of convergence for the energy approximants using these approximate residues is almost as good as the rate of convergence obtained using the exact values for the residues.

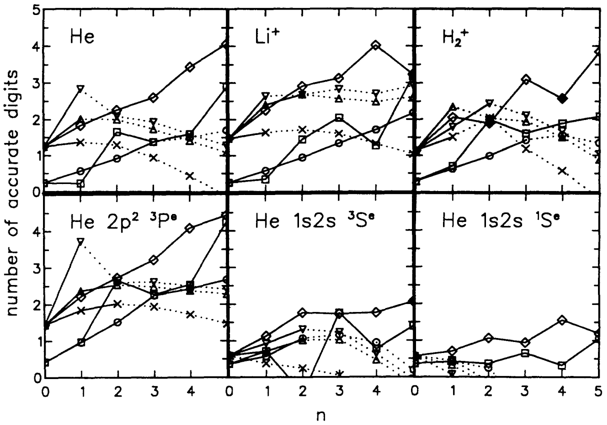

FIG. 1. Accuracy of summation methods that do not require exact values for the residues of the Coulombic poles, labeled as follows: ○, partial sums, Eq. (2): ×, shifted expansion, Eq. (6); □, Padé approximants; △, rescaled approximants, Eq. (5); ▽, weighted truncation, Eq. (13); ◇, hybrid Padé approximants with residues from Eqs. (16). Solid diamonds indicate hybrid Padé approximants that can be predicted to be inaccurate on account of an inaccurate value for a_{-2}, as described in the text. The number of accurate digits is defined as $-\log_{10}|(S_n-E)/E|$, where E is the exact energy. For those summation methods that have an optimal asymptotic approximation (OAA), the values before the OAA are connected by solid lines, while the values past the OAA are connected by dotted lines.

III. RESULTS

We now compare the convergence of the various summation methods discussed above by applying them to some prototypical systems. The energy expansions that we will use were calculated using the moment method [25], a recursive procedure that yields an exact solution for the expansion coefficients subject only to the numerical precision of the computer. We will only consider here expansions through order 5, at which point roundoff error is not yet a problem. Analysis of the large-order behavior of these expansions is presented elsewhere [15–17,20].

The expansion coefficients are shown in Table I. The results for the ground state of H_2^+ [14,15] and for the ground states of the two-electron atom isoelectronic sequence [13,16] come from perturbation theory about the ground state of the vibrating Lewis structure. The He $1s2s$ triplet and singlet states correspond to one quantum of excitation in the antisymmetric-stretch and symmetric-stretch normal modes, respectively [17]. The He $2p^2\,{}^3P^e$ state at $D=3$ is a doubly excited bound state embedded in the continuum. However, it is exactly degenerate with the $D=5$ He ground state [26,27]. The results we present for the doubly excited state were obtained by evaluating the ground state δ expansion at $\delta=\frac{1}{5}$. The H_2^+ expansion was calculated [15] within the Born-Oppenheimer approximation with the internuclear distance scaled by the factor $D(D-1)/6$.

Figure 1 shows a comparison of the accuracy obtained using the six summation methods that do not require the exact values of the residues of the Coulombic poles. The level of accuracy is expressed in terms of the number of accurate decimal digits, defined as $-\log_{10}|(S_n-E)/E|$, where E is the exact energy eigenvalue and S_n is the estimate for the energy given by any of the various types of approximants using the expansion coefficients through order n. For the methods that do not involve Padé summation, the most accurate value obtainable from the approximants is given, in principle, by the OAA. All points in Fig. 1 that are beyond the OAA are connected by dotted lines, while those before it are connected by solid lines. In the case of the Padé methods, we show only the diagonal sequences: [0/0], [0/1], [1/1], ...

The three methods that incorporate by assumption a second-order pole at $D=1$, weighted truncation, hybrid Padé approximants, and the rescaled expansion, are seen to be generally more accurate than the two methods that

TABLE I. Coefficients of the $1/D$ expansions of energy eigenvalues. The atomic results are in units of Z^2 hartree, while the results for H_2^+ are in units of hartree. The number in square brackets that follows each entry indicates the power of ten multiplying the entry.

n	He $1s^2$ [a]	Li^+ $1s^2$ [b]	He $1s2s\,{}^3S^e$ [c]	He $1s2s\,{}^1S^e$ [c]	H_2^+ $1s$, $R=1$ [d]
0	−0.273 776 91 [1]	−0.312 538 34 [1]	−0.273 776 91 [1]	−0.273 776 91 [1]	−0.623 916 75 [1]
1	−0.605 759 19 [1]	−0.662 015 08 [1]	−0.250 856 41 [1]	−0.631 212 36 [0]	−0.112 603 51 [2]
2	−0.886 218 38 [1]	−0.993 704 79 [1]	−0.803 530 93 [1]	−0.415 806 50 [2]	−0.155 617 77 [2]
3	−0.139 006 37 [2]	−0.136 745 86 [2]	−0.217 406 30 [1]	+0.924 638 52 [3]	−0.231 006 81 [2]
4	−0.543 672 04 [1]	−0.158 349 34 [2]	−0.733 985 74 [2]	−0.396 416 19 [5]	−0.105 755 25 [2]
5	−0.827 394 68 [2]	−0.225 074 70 [2]	+0.918 913 73 [3]	+0.213 025 95 [7]	−0.230 152 88 [3]

[a] Reference [13].
[b] Reference [16].
[c] Reference [17].
[d] Reference [15].

do not—partial sums and ordinary Padé approximants. The shifted expansion includes a singularity at $D=1$, but for $n>0$ the form of the singularity is not correct. This method tends to be more accurate than the methods that do not include any singularity at $D=1$, but less accurate than those that have a singularity of the proper form. The OAA does prove to be a good indicator of the highest accuracy that can be obtained from the given method in those cases where it is applicable. (The only exception is the shifted expansion for H_2^+, in which case the OAA comes one order too soon.) For the shifted expansion, the rescaled expansion, and weighted truncation, the OAA comes quite early, at the latest by second order.

The two types of Padé summation should be considered separately from the other methods. They do not have an OAA; they can be expected to continue to increase in accuracy with increasing order. It is clear from Fig. 1 that hybrid Padé summation is at least as accurate as direct Padé summation and usually significantly more accurate. Furthermore, the convergence of the hybrid method is considerably steadier.

Only a few of the hybrid Padé approximants are less accurate at a given order n than at order $n-1$, and in those cases the cause appears to be relatively low accuracy in the estimate for the residue a_{-2}. Table II compares the exact value for a_{-2} with the estimates used by the hybrid approximants, obtained from Padé summation of Eq. (16a). The estimates are given by Padé approximants evaluated at the point $\delta=1$. This point is considerably farther from the origin than is $\delta=\frac{1}{3}$, so the accuracy obtained for the residues is somewhat less than the accuracy obtained for the energy. For the ground states, there is a close correspondence between the relative accuracy of the residue and the relative accuracy of the energy approximant. For Li^+ and H_2^+ we could identify the inaccurate results for a_{-2}, even if we did not know the exact results, from the fact that $|S_n - S_{n-1}|$, where S_n is the nth-order approximant for a_{-2}, increases from its value at the previous order. (Applying this analysis to the approximants for the *energy* would not identify the inaccurate ones.) Another way to predict the quality of an approximant for a_{-2} is to examine the roots of the denominator polynomial of the hybrid approximant for the energy. The hybrid Padé approximant is designed so that the series that is summed by the Padé summation is regular at the point $\delta=1$. If the denominator polynomial is found to have a zero in the neighborhood of that point, then we can expect that the value at that order for the residue is not very good. Thus, we could eliminate the [2/3] approximant for Li^+, which has a pole at 0.89, and perhaps the [1/1] approximant for H_2^+, which has a pole at 1.69. Approximants that can be ruled out by either of these two criteria are indicated in Fig. 1 by solid diamonds. For the two singly excited states of He, the correlation between the accuracy of a_{-2} and the accuracy of the corresponding energy approximant is weaker. This is probably due to the fact that another dimensional singularity, at $\delta=0$, is relatively more important for these states [17]. Even so, hybrid Padé summation is still significantly more effective than direct Padé summation.

Analysis [15–17,20] of the higher-order terms in the energy expansions suggests, in all five cases, the presence of a complicated singularity at $\delta=0$. This singularity appears to have the form of a product of a square-root branch point and an essential singularity. The Padé approximants model this by tracing out a branch cut with a series of nearly coincident poles and zeros. This behavior is well illustrated by the [2/3] hybrid Padé approximant for H_2^+. The poles and zeros of this approximant are shown in Fig. 2. The branch cut is placed along the negative real axis. All of the Padé approximants of Fig. 1 generally conform to this pattern although some of them have stray poles along the positive real axis. If such a pole is close to 1 then it probably represents a remnant of the Coulombic poles, as discussed above. Several of the approximants have a pole farther out along the positive axis, which is probably spurious. As long as any spurious pole is well removed from the point $\delta=\frac{1}{3}$, at which the approximant is evaluated, it should not have a direct effect on the accuracy. However, it could have an indirect effect since the extra pole is not being used productively to model the singularity at the origin. Such approximants should be regarded as suspect. The [0/1], [1/2], and [2/3] approximants for the He ground state (and $^3P^e$ state), the [0/1] and [1/2] approximants for Li^+, and the [2/2] approximant for H_2^+ have spurious poles at large positive δ; the accuracies of most of these appear to be at least slightly degraded.

TABLE II. Residues of the second-order pole in the energy at $D=1$, in units of Z^2 hartree. The first entry in each column is the exact solution, while subsequent entries are from Padé summation of Eq. (16a).

	He $1s^2$	Li^+ $1s^2$	He $1s2s\ ^3S^e$	He $1s2s\ ^1S^e$	H_2^+ $1s$, $R=1$
Exact	−3.155 39[a]	−3.403 53[a]	−2	−2	−5.048 79[b]
[0/0]	−2.7378	−3.1254	−2.7378	−2.7378	−6.2392
[0/1]	−3.4770	−3.5443	−1.3139	−0.9886	−5.2201
[1/1]	−3.0465	−3.3747	−1.7286	−2.2478	−3.2616
[1/2]	−3.2779	−3.4550	−1.7045	−1.1959	−5.0593
[2/2]	−3.1470	−3.4128	−1.7285	−2.0434	−4.7266
[2/3]	−3.1467	−3.9978	−6.0260	−1.3754	−5.0252

[a] Reference [22].

[b] Reference [15].

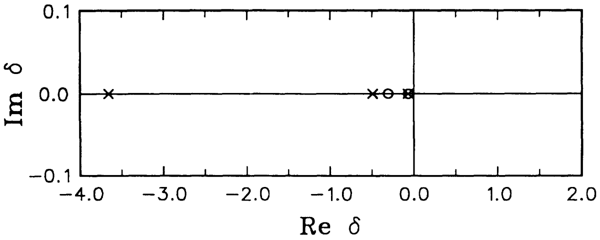

FIG. 2. Singularity structure of the [2/3] hybrid Padé approximant for H_2^+. × represents a zero in the denominator polynomial and ○ represents a zero in the numerator polynomial.

It is clear from Fig. 1 that the hybrid Padé summation is generally the method of choice at order higher than that corresponding to the OAA of the rescaled expansion or of weighted truncation, which is the point at which the large-order behavior due to the singularity at $\delta=0$ begins to become important. At lower orders it is not quite as clear which of these three methods is best. Figure 3 compares the accuracy of these methods for the ground state of the two-electron atom over a range of $\lambda \equiv 1/Z$. The dashed curves represent approximants of order 1 and the solid curves represent approximants of order 2. Weighted truncation at order 1 appears to be the most robust of the methods, working well over the entire range. At order 2 it works rather poorly for large λ, where it lies beyond its OAA. Figure 4 shows the accuracy for H_2^+ over a range of internuclear distance. Here the most robust approximant is weighted truncation at order 2, which in this case is the OAA over most of the range.

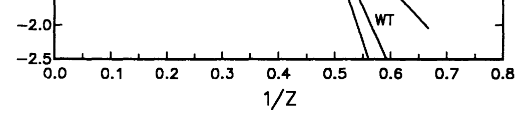

FIG. 3. Accuracy of summation methods for the ground state of the two-electron atom as a function of the inverse of the nuclear charge. The dashed curves are approximants of order 1 while the solid curves are approximants of order 2. The curves are labeled as follows: Re, rescaled approximants, Eq. (5); WT, weighted truncation, Eq. (13); HPA, hybrid Padé approximants with both residues calculated according to Eqs. (16).

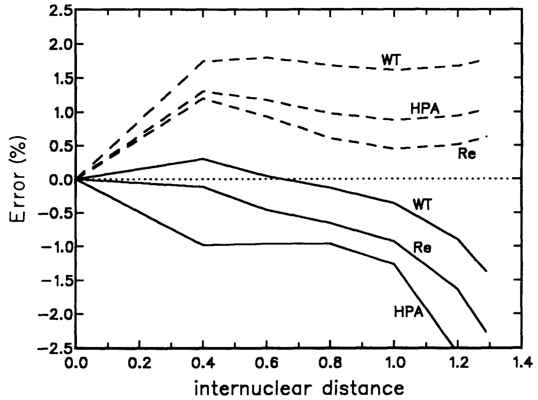

FIG. 4. Accuracy of summation methods for the ground state of H_2^+, as a function of the internuclear distance in atomic units. The dashed curves are approximants of order 1, while the solid curves are approximants of order 2. The curves are labeled as follows: Re, rescaled approximants, Eq. (5); WT, weighted truncation, Eq. (13); HPA, hybrid Padé approximants with both residues calculated according to Eqs. (16).

The residues of the second-order poles for each of our systems are known exactly. They are the energy eigenvalues of appropriately dimension-scaled Schrödinger equations at $D=1$ [11,15]. For the singly excited states of He the calculation of the residue is particularly simple. For $D=1$ it has been shown [11] that the dimension-scaled Schrödinger equation in the limit $\lambda \rightarrow 0$ has only one eigenstate in which both electrons are bound. This result continues to hold for nonzero λ, since the addition of interelectron repulsion can only further destabilize the system. Therefore, any excited state of the two-electron atom ionizes in the limit $D \rightarrow 1$ leaving a one-electron atom, whose energy eigenvalue (at any D) is given by Eq. (4). Thus the residue of the second-order pole is $a_{-2}=-2Z^2$. For H_2^+, a_{-2} can be determined by solving a simple transcendental equation [15]. In the case of the two-electron ground state the calculation is more complicated, but the solution can be expressed in terms of an integral equation that can be solved numerically to arbitrary precision [22]. For the doubly excited He $2p^2\,{}^3P^e$ state, we use the residue corresponding to the ground state, since we evaluate the eigenvalue of the excited state as a ground-state energy at $D=5$ [26].

Figure 5 shows the accuracy of the three summation methods that can incorporate a known value for a_{-2}: the hybrid expansion, Eq. (8); the biased weighted truncation, Eq. (14); and hybrid Padé summation with the residue of the first-order pole fit from Padé summation of Eq. (16b). Hybrid Padé summation here generally appears to be the method of choice at all orders. The one exception is the He ground state at order 2, in which case the hybrid expansion is better, but this result appears to be anomalous. In all the other cases the Padé summation is at least about as good but usually significantly better. The [2/2] approximant for H_2^+ and the [1/2] for the triplet singly excited state are about equal in accuracy to the hybrid expansion, but both have poles near $\delta=1$. The [2/2] approximant for Li^+ has a spurious pole near 22 but this does not seem to affect its accuracy. The estimates for a_{-1} from Padé summation are shown in Table III. There is an excellent correspondence between the relative accuracy of the residue and the relative accuracy of the corresponding energy approximant, although it is

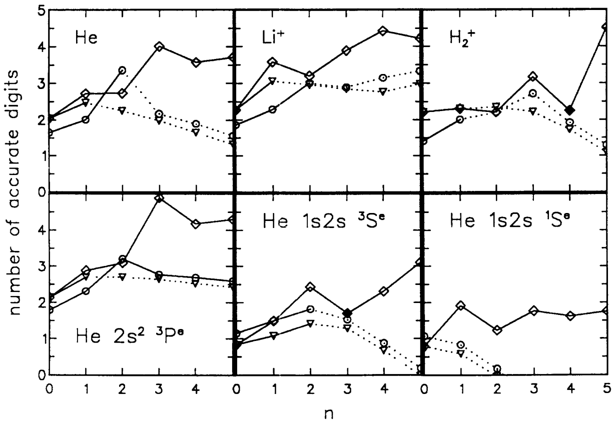

FIG. 5. Accuracy of summation methods that require the exact value for the residue of the second-order pole a_{-2}, but not for the residue of the first-order pole a_{-1}, labeled as follows: ○, hybrid expansion, Eq. (8), with $a_{-1}=0$; ▽, weighted truncation, Eq. (14); ◇, hybrid Padé approximants with a_{-1} from Eq. (16b). Solid diamonds indicate hybrid Padé approximants that can be predicted to be inaccurate on account of a pole in the vicinity of $\delta=1$. The number of accurate digits is defined as $-\log_{10}|(S_n-E)/E|$, where E is the exact energy. For those summation methods that have an optimal asymptotic approximation (OAA), the values before the OAA are connected by solid lines, while the values past the OAA are connected by dotted lines.

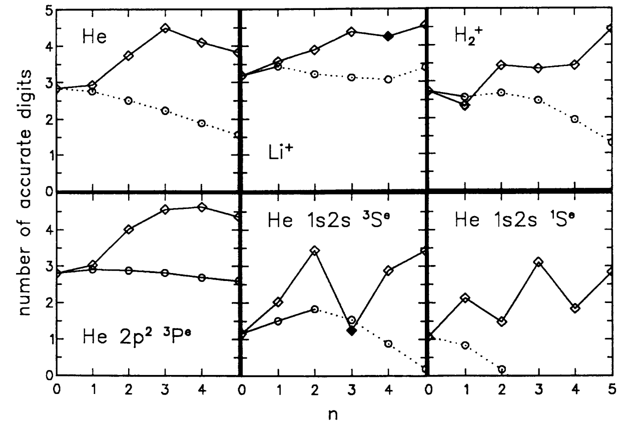

FIG. 6. Accuracy of summation methods that require exact values for both a_{-2} and a_{-1}, labeled as follows: ○, hybrid expansion, Eq. (8); ◇, hybrid Padé approximants. Solid diamonds indicate hybrid Padé approximants that have a nearly coincident pole and zero on the positive real axis. The number of accurate digits is defined as $-\log_{10}|(S_n-E)/E|$, where E is the exact energy. For those summation methods that have an optimal asymptotic approximation (OAA), the values before the OAA are connected by solid lines, while the values past the OAA are connected by dotted lines.

not always possible to identify the less accurate residue estimates from the behavior of $|S_n-S_{n-1}|$. All of these summation methods have been improved by using the exact value for a_{-2}.

Knowledge of both a_{-2} and a_{-1} would allow the complete removal of the poles at $\delta=1$ using the hybrid expansion, Eq. (8). The energy could then be determined either from partial sums or from Padé summation. For the singly excited states of He we have $a_{-1}=0$ as discussed above. For our other systems this residue is much more difficult to calculate. In principle, it should be possible to calculate it exactly using perturbation theory in powers of $(D-1)$ about the one-dimension limit. This has been carried out for central-potential problems [11], but not for the more complicated systems that we are considering here. In order to determine how helpful it would be to know the exact a_{-1}, we will use estimates for this residue obtained through other means. For the ground states of He and Li^+, values for a_{-1} have been extracted from numerical fits [28] to direct calculations of E, from the Hylleraas-Pekeris method [29], over a range of D. For $\mathrm{H_2}^+$, we estimate a_{-1} from Padé summation of Eq. (16b) using expansion coefficients through 35th order [15]. Our estimates for the exact values for a_{-1} are listed in table III.

Figure 6 compares the accuracy of the two hybrid-expansion methods using accurate values for both residues. Both methods are improved by using the exact a_{-1}. It is clearly better in general to use the Padé summation. Spurious poles are present in [2/3] for the He

TABLE III. Residues of the first-order pole in the energy at $D=1$, in units of Z^2 hartree. The first entry in each column is the exact solution (or an estimate of the exact solution, as described in the text), while subsequent entries are from Padé summation of Eq. (16b) using the exact value of a_{-2}.

	He $1s^2$	Li^+ $1s^2$	He $1s2s$ $^3S^e$	He $1s2s$ $^1S^e$	$\mathrm{H_2}^+$ $1s$, $R=1$
Exact	0.316 45[a]	0.209 30[a]	0	0	−0.9830[b]
[0/0]	0.417 6	0.278 2	−0.7378	−0.7378	−1.1904
[0/1]	0.299 6	0.209 5	−0.1835	−0.1124	−1.1634
[1/1]	0.365 1	0.231 4	0.1256	−0.3461	−1.1914
[1/2]	0.323 3	0.214 9	−3.0591	−0.1220	−1.0175
[2/2]	0.330 8	0.202 7	0.1399	−0.1646	−1.3295
[2/3]	0.325 8	0.213 0	0.0268	−0.1226	−0.9819

[a] From numerical fit to Hylleraas-Pekeris calculations, Ref. [28].

[b] From 35th-order Padé summation, Ref. [15].

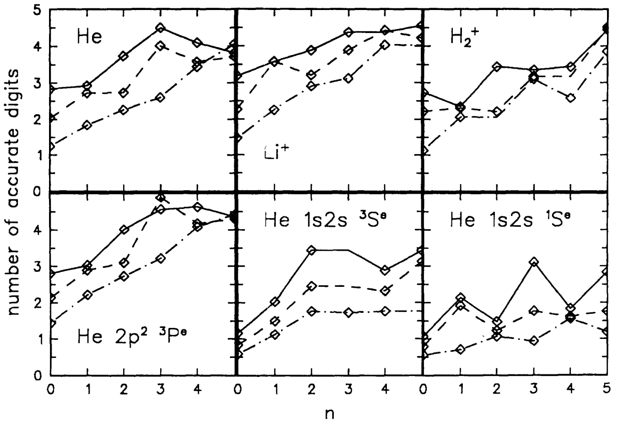

FIG. 7. Effect of the manner of obtaining residues on the accuracy of hybrid Padé summation. The solid lines connect points obtained using the exact values of both residues, the dashed lines connect points obtained with a_{-1} estimated from Padé summation, and the dash-dot lines connect points obtained with both residues estimated from Padé summation. The diamonds indicate approximants with acceptable singularity structure: approximants with poles near $\delta=1$ or with defects have been omitted and the value of the next lower-order approximant has been used instead.

ground state (and the $^3P^e$ state), [2/2] for Li$^+$, [0/1] and [1/2] for H$_2$$^+$, and [1/2] for the triplet He state; each of these approximants is relatively poor. The [2/2] approximant for Li$^+$ and the [1/2] for triplet He have spurious poles that are nearly coincident with zeros. These are *defects* [24], an occasional problem with Padé approximants. In the latter case the defect occurs at approximately 0.3 and has a profound effect on the accuracy due to its promixity to the physical solution $\delta=\frac{1}{3}$. The former occurs near 0.7 and has less of an effect. The accuracy of the hybrid Padé approximants for the singly excited states is significantly improved at most orders by the exact a_{-1}, although the convergence is rather uneven, probably on account of the importance of the singularity at $\delta=0$.

In Fig. 7 we show the improvement in the accuracy of the hybrid Padé approximants that comes from using exact values for the residues. For the two singly excited states of He the improvement from using exact residues is quite significant. The residues in these cases are trivial to derive, so there is no excuse not to use the exact values. For the other systems the improvement is substantial at lower orders, but appears to be less significant at orders 4 and 5.

IV. DISCUSSION

We have introduced in this paper two summation procedures, weighted truncation and Padé summation of the hybrid expansion. They are significantly more accurate than the shifted expansion [18,19] and appear to be the best techniques yet available for summing dimensional expansions of Coulombic systems given expansion coefficients through order $n\leq5$. If the residue of the second-order Coulombic pole is known or if the expansion coefficients are known at least through third order, then we recommend Padé summation of the hybrid expansion. If the exact values of the residues are not available and the expansion coefficients are not known beyond second order, then two other methods, the rescaled expansion and weighted truncation, are also competitive. Weighted truncation seems to be the most robust of the three. The convergence of the hybrid Padé approximants can be improved by discarding approximants whose singularity structure is inconsistent with the known dimensional singularities. It is sometimes possible to replace discarded diagonal approximants with off-diagonal approximants that have the proper singularity structure.

An advantage of weighted truncation and hybrid approximants over the rescaled expansion is that singularities more complicated than poles can also be treated. A pertinent example is the case of a relativistic particle in a Coulomb potential. Dimensional singularity analysis of the energy revealed [30] a complicated structure involving four branch points, instead of the second-order pole found in the nonrelativistic version. It would be difficult to accommodate a singularity of such complexity with a simple rescaling, but it is straightforward to incorporate it into the methods that subtract out the singularity. Using weighted truncation, with only the zeroth-order term in the energy expansion, was found [30] to immediately yield the exact solution for the relativistic energy.

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