Dimensional expansions for two-electron atoms

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Approximate expansions in inverse powers of the dimensionality of space D are obtained for the ground-state energies of two-electron atoms. The method involves fitting polynomials in $\delta = 1/D$ to accurate eigenvalues of the generalized D-dimensional Schrödinger equation. To the maximum order obtainable from the data, about δ^7, the power series for nuclear charges $Z = 2$, 3, and 6 all diverge at $D = 3$. Asymptotic summation yields an energy for the $Z = 2$ atom 1% in excess of the true value at $D = 3$. However, expansions with a shifted origin, i.e., expansions in $(\delta - \delta_0)$, show improved convergence. Of particular interest is the case $\delta_0 = 1$, because the expansion coefficients can in principle be calculated by perturbation theory applied to the one-dimensional atom. Series in powers of $(\delta - 1)$ appear to converge rapidly. Also the series in $(\delta - 1)$ can be evaluated even for the hydride ion, with $Z = 1$. For helium, this series is quite comparable to the more familiar expansion in powers of $\lambda = 1/Z$, with errors in the partial sums decreasing by roughly an order of magnitude per term. Thus, for $Z = 2$ the first four terms of the expansion in $(\delta - 1)$ yield an energy within 0.02% of the true value at $D = 3$. Similar results are found in an analogous treatment of accurate eigenvalues for the Hartree–Fock approximation. This provides a rapidly convergent dimensional expansion for the correlation energy.

I. INTRODUCTION

Perturbation theory in the inverse dimensionality of space $1/D$ has recently received much attention.[1] This method (also known as the "large dimension expansion" or "$1/D$ expansion") offers prospects for treating many problems which have not yielded to more conventional approaches, such as the equations of quantum chromodynamics.[2] In contrast to usual perturbation methods, the $1/D$ expansion does not rely on partitioning the potential into two parts, one solvable and the other relatively small. Instead, the full Hamiltonian corresponding to the $D \to \infty$ limit is solved by a procedure that can be performed for any Hamiltonian, and then corrections for the effects of finite D are calculated order by order in $1/D$. The case $D \to \infty$ is a kind of classical limit,[1] since in suitable dimension-scaled coordinates a factor of $1/(D-1)$ appears in the kinetic energy where Planck's constant $\hbar$ occurs for ordinary, unscaled coordinates, and thus $D \to \infty$ resembles $\hbar \to 0$. Systems for which at least the leading terms of the large dimension expansion have been evaluated thus far include: the anharmonic oscillator[3] and other central force problems,[4] quantum spin models,[5] critical phenomena in $\lambda\phi^4$ theories,[6] the hydrogen atom in a uniform magnetic field,[7] and the helium atom.[8–15] At this stage, questions regarding the convergence properties and optimal form of the $1/D$ expansion remain open, but some inferences may be drawn from the results for such prototype systems.

This paper takes an empirical approach to dimensional expansions for the ground-state energy of two-electron atoms. In previous work,[13] we have calculated accurate energies for a wide range of D and several values of the nuclear charge Z by generalizing the Hylleraas–Pekeris treatment. Here we use these data to obtain various forms of expansions by regression and interpolation. Among other things, this yields approximate values for the coefficients of several more terms in the $1/D$ expansion than are presently known by direct calculation. We have also performed parallel calculations using a generalized Hartree–Fock algorithm.[14] The corresponding dimensional expansions are of interest because they reveal, term by term, the effect of omitting the correlation energy contributions.

In Sec. II we survey the sources of data concerning the D dependence of energy eigenvalues and the several methods used to obtain dimensional expansions from these data. In Sec. III we present results at various Z for two versions of the $1/D$ power series. These series all appear to diverge for $D = 3$ due to singular behavior at or near the point of expansion, and the accuracy attainable by asymptotic summation is limited. Thus, in Sec. IV we examine shifted expansions. Expansions in powers of $1/D - 1/D_0$ for several values of D_0 are evaluated. The series with $D_0 = 1$ appears to be well-behaved and offers greatly improved accuracy for $D = 3$. We consider also a hybrid expansion in which low order terms involve powers of $(D-1)/D$ and high-order ones powers of $1/D$. This likewise gives good accuracy and the expansion coefficients are more readily evaluated. In Sec. V we compare dimensional expansions with the more familiar expansion[16,17] in powers of $1/Z$ and also note some consequences and conjectures.

II. NUMERICAL ANALYSIS

Table I indicates the sources of data pertaining to the dimension dependence of ground-state energies for two-electron atoms.[12–21] We employed almost solely our numerical calculations, but also used the analytic results available for the $D \to \infty$ limit and the first-order perturbation in $1/D$ as

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TABLE I. Energy eigenvalues for D-dimensional two-electron atoms.[a]

Case	Full atom	Hartree–Fock	Refs.
$D\to\infty$	Cl(λ)	Cl(λ)	12;15
$D\to 1$	$\mathrm{Ex}_{20}(\lambda)$	Cl(λ)	18;19
$D=3$	$\mathrm{Ex}_{400}(\lambda)$	$\mathrm{Ex}_{5}(\lambda)$	16;17
$D=5$	$\mathrm{Ex}_{21}(\lambda)$	$\mathrm{Ex}_{1}(\lambda)$	20;21
Vary D	Nm(λ)	Nm(λ)	13;14

[a] Entries indicate whether ground-state energy eigenvalue as a function of $\lambda = 1/Z$ is known in the form of: (Cl) a closed expression; (Ex) a power-series expansion in λ; or (Nm) only as numerical values for particular λ. Subscript indicates number of perturbation coefficients known in the λ expansion. References listed to left-hand side of semicolon pertain to full (nonrelativistic) energy; those listed to right-hand side pertain to Hartree–Fock approximation.

well as results for the $D\to 1$ limit. The range of D and Z in our energy calculations was specified by $X = 12/D$, $Y = 6/Z$, and covered $X = 1$–12, $Y = 1$–6 in integer steps; for certain cases such as $Z = 2$ up to 30 more values of D were treated. The energy eigenvalues obtained from the generalized Hylleraas–Pekeris algorithm[13] are usually accurate to at least 10 significant digits except for D close to unity, where the accuracy drops to about 7 digits. The corresponding Hartree–Fock results[14] have somewhat greater accuracy, at least 12 significant digits, and this persists in the $D\to 1$ region.

Given energies at several different dimensionalities (typically 20 or more), our aim is to obtain an approximation to the $1/D$ perturbation series (or one of its variants) by fitting polynomials in $\delta = 1/D$ or related variables to that data. Although straightforward in principle, this method requires careful attention to numerical problems imposed by truncation, round-off, and errors in the input data. We discuss these in turn and then describe the procedures that we adopted.

A. Sources of error in coefficients

The first numerical problem arises from the limitations of polynomial approximations to infinite series, especially asymptotic ones. Because the monomials δ^n are not orthogonal over the data set, the coefficients of any finite polynomial approximation differ from those of the full Taylor series, particularly for the higher-order terms. To some extent, the error at a given order can be reduced simply by increasing the number of data points and the degree of the polynomial used. However, this is soon thwarted by a second problem, namely computer round-off error. Straightforward least-squares polynomial regression leads to a set of simultaneous linear equations for the optimal Taylor coefficients which have a strong tendency to be ill conditioned.[22] The standard way to overcome this difficulty is the method of Forsythe,[23] which avoids matrix inversion by using polynomials orthogonal with respect to the data set. We found that a double precision FORTRAN program based on the Forsythe algorithm can generate polynomials of degree up to about 20 from data in the range $0\leqslant\delta\leqslant 1$ before round-off becomes excessive. Another strategy for minimizing round-off error is to use an interpolating polynomial instead of regression. We found that, when applied to accurate test function data, standard techniques[24] for fitting an $(N-1)$st degree interpolating polynomial to N data points gave significantly more accurate Taylor coefficients than those obtained with the Forsythe algorithm. In addition, the interpolating polynomial could be taken to somewhat higher order. However, this interpolation technique has no capacity for smoothing of data containing errors, a prime virtue of the regression procedure.

In practice, the limited accuracy of the data is the most serious problem in obtaining Taylor coefficients by either interpolation or regression. To illustrate how errors in the data become magnified in the higher-order coefficients, we note that the nth coefficient in the Taylor series $\Sigma_n c_n (x-x_0)^n$ for a function $f(x)$ expanded about point x_0 might be approximated as

$$c_n = \frac{1}{n!} f^{(n)}(x_0) \simeq \frac{1}{n! h^n} \sum_{m=0}^{n} (-1)^m \times \binom{n}{m} f\left[x_0 + \left(\frac{n}{2} - m\right)h\right], \tag{1}$$

for some small step size h between the data points. If we ignore errors of order h^2 introduced by the finite step size, and regard the uncertainties in the function values as uncorrelated and of uniform magnitude σ_f, then the uncertainty σ_n in the coefficient is

$$\sigma_n = \frac{1}{n! h^n}\left[\sum_{m=0}^{n}\binom{n}{m}^2 \sigma_f^2\right]^{1/2} = \frac{1}{n! h^n}\binom{2n}{n}^{1/2}\sigma_f . \tag{2}$$

In our application, we seek a Taylor series in $\delta = 1/D$ from data in the range $0\leqslant\delta\leqslant 1$, so the minimum uncertainty in the coefficient is obtained by setting $h = 1/n$. With Stirling's formula, this yields

$$\sigma_n \geqslant \frac{(2e)^n}{(4\pi^3 n^3)^{1/4}}\sigma_f . \tag{3}$$

Thus, if typically $\sigma_f \simeq 10^{-7}$, then we can trust c_{10} at most to the nearest integer. For a well-behaved series, such an uncertainty could be orders of magnitude greater than the value of the tenth Taylor coefficient.

B. Computational procedures

Because of the several ways in which errors can enter the calculations, three complementary procedures were used to obtain polynomial fits. The first two were mentioned above: Forsythe's orthogonal polynomials method for determining the least-squares polynomial,[23] and Newton's divided-difference method for obtaining the interpolating polynomial.[24] In addition to these standard procedures, we employed a third which gave series of comparable accuracy while also making explicit the effects of errors in the data. In this, the nth coefficient in the Taylor series for $f(x)$ about x_0 is computed from[25]

$$c_n = \frac{1}{h^n}\sum_{m=n}^{\infty}\frac{S_m^{(n)}}{m!}\sum_{k=0}^{m}(-1)^k\binom{m}{k} f[x_0 + (n-m)h] . \tag{4}$$

Here $S_m^{(n)}$ is a Stirling number of the first kind. In contrast to Eq. (1), this formula for c_n is exact for any finite step size h, if the series converges. When Eq. (4) is used to compute the

Taylor coefficients, any random errors in the function values eventually force the infinite series to diverge. However, an approximate sum for the series may be found by treating it as if it were asymptotic, i.e., by truncating the series just before the smallest term. Furthermore, the smallest term gives a rough estimate of the error in the sum introduced by errors in the data. All these properties were verified in trial calculations with synthetic data. We call the polynomial approximation computed in this way the asymptotic polynomial.

By using a combination of least squares, interpolating, and asymptotic polynomials, we found that the effects of the various sources of error could be estimated and reduced. Comparing polynomials of different degrees and different kinds revealed the errors introduced by truncation of the Taylor series and by computer roundoff. These errors were also assessed by varying the data set and examining the errors in fits to test data of known functional form. The uncertainties in the Taylor coefficients resulting from errors in the data were surmised by use of the asymptotic method and by modeling with test data containing errors, and by direct computation of regression coefficient standard deviations.

Since exact values of the coefficients for the first two terms of the $1/D$ expansion are known,[8,12] we subtracted these terms from the data. This improved significantly the accuracy of the fitted polynomials. (It was checked beforehand that the data reproduced those two terms to high accuracy.) In all cases the data were transformed so that the fitting procedure dealt with a standard Taylor series in δ, beginning with a nonzero constant term. All results given below are reported to one digit beyond the last one judged to be trustworthy.

III. LARGE DIMENSION EXPANSIONS

We consider two versions of the expansion for the ground-state energy in powers of $\delta = 1/D$. Except for the zero- and first-order terms of these perturbation expansions, which are known as exact functions of $\lambda = 1/Z$, previous work[8] had determined numerically only the second-order term and that only for $Z = 2$ and 8. We have obtained accurate values of the second- and third-order terms and increasingly approximate values for several higher-order terms, for $Z = 2$, 3, and 6. Although our data[13] also provide energy eigenvalues for $Z = 1$, 1.2, and 1.5, we did not attempt to fit optimal $1/D$ series in this low-Z range. For $D \to \infty$, a symmetry-breaking transition[12] occurs at a critical nuclear charge, $Z_0 = 1.228$; this makes the $1/D$ expansion more difficult to evaluate and less useful for $Z < Z_0$. As shown in Sec. IV, the low-Z region proves amenable to another form of dimensional expansion.

A. Customary $1/D$ perturbation series

Table II lists the coefficients E_n obtained for the usual form[8] of the large-D perturbation expansion,

$$E(\delta) = \delta^2 \sum_{n=0}^{\infty} E_n \delta^n . \tag{5}$$

If electron repulsion is neglected (as in the $Z \to \infty$ limit), the energy is given by

TABLE II. Coefficients for $1/D$ expansion.[a]

n	$Z=2$	$Z=3$	$Z=6$
	Total energy, two-electron atom		
0	− 10.951 076 56	− 28.128 450 67	− 127.648 8585
1	− 24.230 367 79	− 59.581 357 42	− 261.766 4921
2	− 35.448 73	− 89.433 4	− 394.008 3
3	− 55.605	− 123.067	− 527.98
4	− 21.4	− 142.8	− 656
5	− 350	− 200	− 800
	Hartree–Fock approximation		
0	− 10.843 145 74	− 28.014 718 50	− 127.529 4372
1	− 23.771 000 32	− 59.149 961 06	− 261.343 1236
2	− 35.329 74	− 88.947 4	− 393.369 8
3	− 51.135	− 121.227	− 526.68
4	− 44.4	− 143.1	− 654
5	− 190	− 200	− 800

[a] Hartree units. Entries are E_n coefficients for ground-state energy expanded as in Eq. (5).

$$E(\delta) = -[2Z/(D-1)]^2 = -(2Z\delta)^2 \sum_{n=0}^{\infty} (n+1)\delta^n , \tag{6}$$

which is twice the exact energy for the corresponding hydrogenic atom. The first three large-D perturbation coefficients ($n = 0, 1, 2$) for both the two-electron atom and its Hartree–Fock approximation are seen to increase roughly in the ratio of successive integers and thus resemble the 1, 2, 3... progression for the hydrogenic atom. This led to the conjecture[8] that these series might converge for $D = 3$ as does the series for the hydrogenic atom. However, as illustrated in Fig. 1, our values for the higher order coefficients ($n = 3, 4, 5$) deviate markedly from the hydrogenic pattern. For $Z = 2$, the behavior is typical of an asymptotic expansion: the first few terms decrease smoothly, reach a minimum (at $n = 4$), and then diverge strongly. Also striking in Table II is how closely the Hartree–Fock series mimics the total energy expansion, but as Z decreases this resemblance begins rapidly to deteriorate.

Figure 2 shows how the partial sums (PS) up to order n of the perturbation series compare with the exact energy. These sums,

$$\mathrm{PS}_n(Z,D) = \delta^2 \sum_{k=0}^{n} E_k \delta^k , \tag{7}$$

are also compared with the hydrogenic case. For the latter, the ratio of the partial sum to the exact energy (denoted by RPS_n) is readily obtained[12] in analytic form,

$$\mathrm{RPS}_n = 1 - (n+2)\delta^{n+1} + (n+1)\delta^{n+2} , \tag{8}$$

and it is independent of Z. This hydrogenic RPS_n converges rather slowly; the residual errors for $n = 2$, 4, and 7 are 11.1%, 1.8%, and 0.1%, respectively. Up to fifth order, the partial sums for the two-electron atom or the Hartee–Fock approximation at $D = 3$ show only modest deviations from the hydrogenic case and the RPS_n likewise vary only slightly with Z. Again, this behavior occurs because in Eq. (5), the customary form of the $1/D$ expansion, the perturbation coefficients contain a large hydrogenic contribution representing the solution in the absence of electron repulsion.

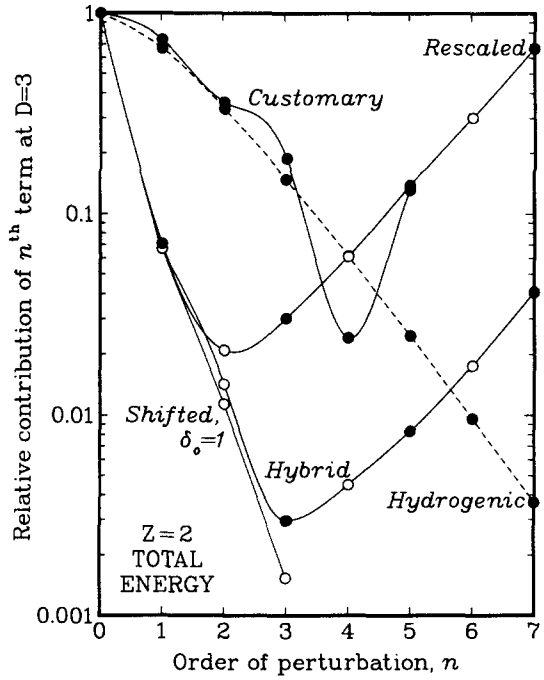

FIG. 1. Comparison of contributions at $D = 3$ from successive terms in various forms of dimensional expansions. Each series is normalized to make the first term ($n = 0$) unity. Solid curves pertain to a two-electron atom with $Z = 2$; terms are shown for the *customary* expansion of Eq. (5); *rescaled* expansion of Eq. (10); *shifted* expansion of Eq. (12) with $\delta_0 = 1$; and *hybrid* expansion of Eq. (15). Dashed curve shows the *hydrogenic* case of Eq. (6). Solid points indicate terms with same sign as the $n = 0$ term, open points terms with opposite sign.

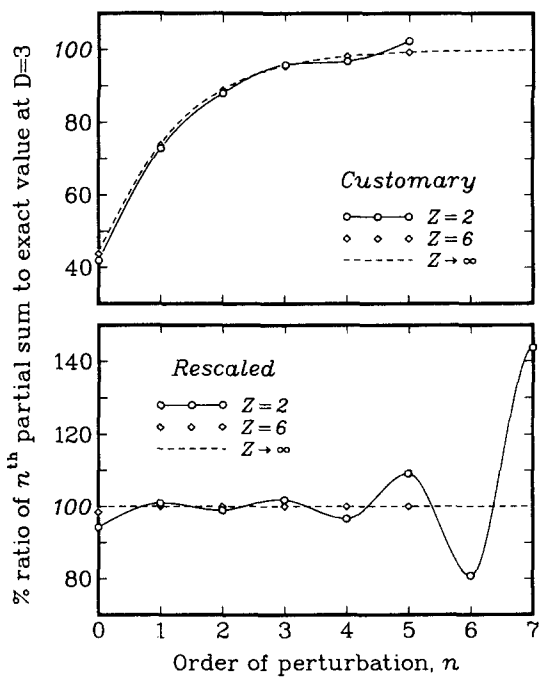

FIG. 2. Partial sums of customary and rescaled dimensional expansions, expressed as a percentage of the exact energy. Data points show the results for $Z = 2$ (○) and $Z = 6$ (◇), with those for $Z = 2$ connected by solid curves. Dashed curves show results for the hydrogenic limit $Z \to \infty$.

B. Rescaled $1/D$ series

The hydrogenic component of the energy can be factored out to obtain another expansion which contains only the contribution from electron repulsion.[12] Thus, we now use a reduced energy $\epsilon(\delta)$ defined by

$$E(\delta) = [2Z/(D-1)]^2 \epsilon(\delta) , \tag{9}$$

with the rescaled expansion

$$\epsilon(\delta) = \sum_{n=0}^{\infty} \epsilon_n \delta^n . \tag{10}$$

The coefficients are related to those in Eq. (5) by

$$\epsilon_0 = E_0/(2Z)^2 , \quad \epsilon_1 = (E_1 - 2E_0)/(2Z)^2 \tag{11a}$$

and

$$\epsilon_n = (E_n - 2E_{n-1} + E_{n-2})/(2Z)^2 \quad \text{for } n \geqslant 2 . \tag{11b}$$

Table III lists these coefficients. Except for the zero- and first-order terms, the ϵ_n were determined by fitting energy eigenvalues and Eq. (11) was used to check the results and assess accuracy. With this rescaling, the hydrogenic part of the energy is always equal to -1, for any Z or D. Reduced energies for bound states hence fall in the range $-1 \leqslant \epsilon < -1/2$, while the first ionization continuum is $-1/2 \leqslant \epsilon < 0$. In the $1/D$ expansion, all the coefficients ϵ_n with $n \geqslant 1$ arise from the electron repulsion and all vanish as $Z \to \infty$.

Figures 1 and 2 include curves for the rescaled expansion. Removal of the hydrogenic contribution greatly improves the initial convergence of the perturbation series at $D = 3$. Just the zero-order term of Eq. (10) is about as good as the third-order partial sum of Eq. (5). Also, increasing Z brings a marked improvement in Eq. (10) but only a slight improvement in Eq. (5). In both the progression of terms and the partial sums, the asymptotic character of the rescaled expansion is much more apparent than in the customary $1/D$ series (where it is hidden by the large, convergent hydrogenic contribution). For $D = 3$ and $Z = 2$, the terms in the rescaled series reach a minimum (in absolute value) already at $n = 2$ and then diverge strongly; together with the alternation in sign, this produces growing oscillations in the higher-order partial sums. For $Z = 6$, the minimum term occurs at $n = 3$ but it is so small and the subsequent terms diverge so weakly that the partial sums remain nearly constant; for $n = 2$ to 5 they deviate by less than $\pm 0.03\%$ from the exact value. Asymptotic summation by truncating the series at the term preceding the minimum term gives 100.97% of the true energy for $Z = 2$, 99.79% for $Z = 3$, and 99.98% for $Z = 6$. The Hartree–Fock results are quite similar.

IV. SHIFTED AND HYBRID EXPANSIONS

Our $1/D$ expansions do not extend far enough to permit the analysis necessary to establish whether or not convergence occurs for sufficiently large but finite values of D. As described elsewhere,[13] the behavior of our numerical calculations at negative values of δ gave indirect evidence that the radius of convergence for the $1/D$ expansions is very small or zero. If this is indeed the case, an expansion about some δ_0 sufficiently far removed from the origin would be preferable.

TABLE III. Coefficients for rescaled $1/D$ expansion.[a]

n	$Z=2$	$Z=3$	$Z=6$
		Total energy, two-electron atom	
0	−0.684 442 285 282	−0.781 345 851 974	−0.886 450 405 740
1	−0.145 513 416 527	−0.092 346 002 401	−0.044 922 050 747
2	0.128 808 1	0.044 467 7	0.013 026 6
3	−0.558 59	−0.105 23	−0.012 02
4	3.394	0.402	0.038
5	−23.0	−1.5	−0.1
6	150	5	
7	−1000		
		Hartree–Fock approximation	
0	−0.677 696 609 407	−0.778 186 628 493	−0.885 621 092 024
1	−0.130 294 305 049	−0.086 681 216 617	−0.043 640 618 774
2	0.085 569 4	0.037 160 4	0.012 409 3
3	−0.265 30	−0.068 90	−0.008 88
4	1.399	0.284	0.035
5	−8.8	−1.26	−0.11
6	64	6.1	0.3
7	−480	−30	−1
8	3300	150	
9	−20000		

[a] Units are $[2Z/(D-1)]^2$ hartree. Entries are ϵ_n coefficients for ground-state reduced energy expanded as in Eq. (10).

It should offer improved accuracy by accelerating convergence of at least the initial terms. We have examined several such series as well as two other variant expansions.

A. Shift of origin

Table IV gives for $Z=2$ the expansion coefficients $\epsilon_n(\delta_0)$ of Taylor series with the origin shifted to $\delta_0 = 1/D_0$. The expansions pertain to the reduced energy,

$$\epsilon(\delta) = \sum_{n=0}^{\infty} \epsilon_n (\delta - \delta_0)^n . \tag{12}$$

These series exhibit better convergence, at least to the order shown, as δ_0 is moved away from the origin. Again, the known coefficients are insufficient to determine a radius of convergence. However, as with Eq. (10), we can infer from the alternation of signs that all of these series are dominated by one or more singularities to the left, and all are consistent with the hypothesis[13] that the nearest nonanalytic point is at or near the origin in the complex δ plane.

The convergence properties of several shifted series are illustrated in Figs. 3 and 4. As shown in Fig. 3, the contributions from higher-order terms fall rapidly as δ_0 is moved away from the origin. This is due in part to the decreasing distance between $\delta = 1/3$ and the point of expansion δ_0, but primarily to the rapidly decreasing magnitudes of the coefficients. The steep decline in the coefficients is apparently due to the increasing distance between δ_0 and the nearest singularity. Figure 4 shows the accuracy attained by asymptotic summation of several shifted series for the full range of dimensionalities. As δ_0 is increased the accuracy of the optimal asymptotic approximation improves, and the range of dimensions over which truly accurate (apparently converged) results can be attained widens.

The most useful of the shifted expansions is that with $\delta_0 = 1$, particularly since the leading coefficients may be directly calculable from the $D \to 1$ "hyperquantum" limit. This expansion also behaves well for small Z, in contrast to the unshifted expansions. Table V gives coefficients for the $\delta_0 = 1$ series, at six values of Z. Because of the smaller numerical values of the coefficients and the diminished accuracy of the data in the vicinity of the point of expansion, this series is the most difficult to determine by the methods used

TABLE IV. Coefficients for shifted $1/D$ expansion, $Z=2$.[a]

n	$D_0=1$	2	3	6	12
0	−0.788 848 20	−0.743 738 89	−0.725 931 09	−0.706 449 40	−0.695 891 91
1	−0.079 113	−0.102 323 4	−0.111 548 0	−0.122 844 9	−0.131 072 3
2	0.020 19	0.026 254	0.029 542	0.041 104	0.060 868
3	−0.004 1	−0.004 61	−0.010 33	−0.047 02	−0.127 3
4		0.002 8	0.019 2	0.127 0	0.434
5		−0.005	−0.040	−0.320	−1.56
6			0.06	0.76	6.5
7				−2.1	−29

[a] Units are $[2Z/(D-1)]^2$ hartree. Entries are $\epsilon_n(\delta_0)$ coefficients in expansion of reduced energy, Eq. (12).

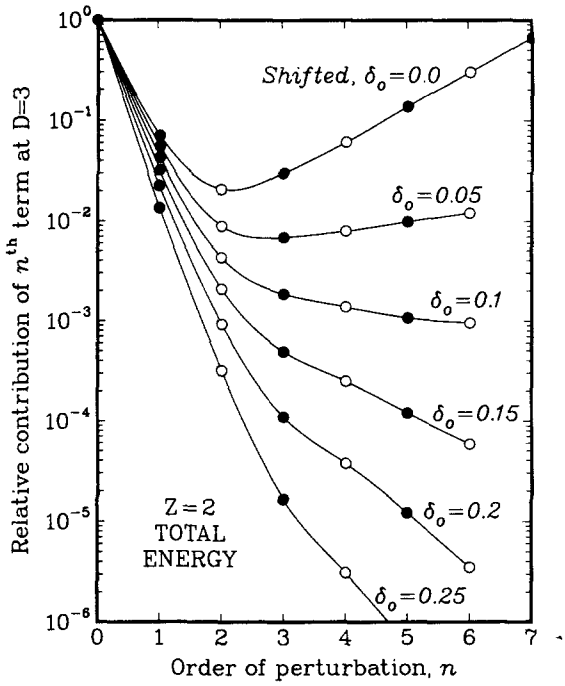

FIG. 3. Relative contributions at $D = 3$ from terms in shifted $1/D$ expansions, Eq. (12), at several values of δ_0. Each series is normalized by the value of its first term. Filled and open circles designate positive and negative normalized contributions, respectively.

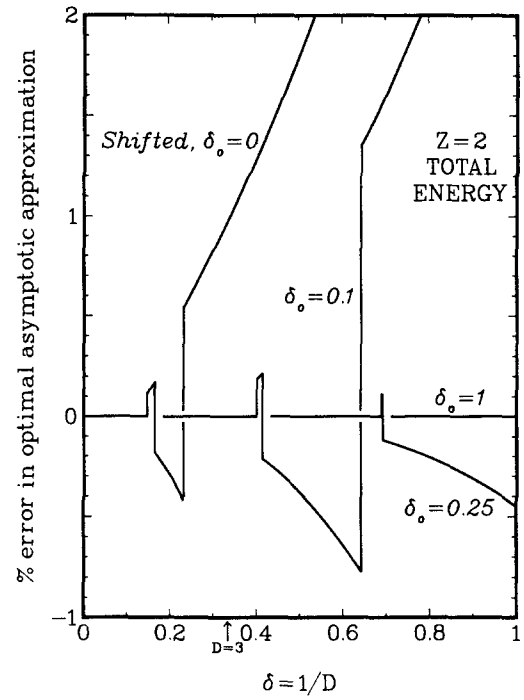

FIG. 4. Ability of *shifted* expansions in powers of $\delta - \delta_0$ to model the dimension dependence of the ground state energy of a two-electron atom with $Z = 2$. Ordinate shows the errors in values obtained by asymptotic summation (truncating the series at the term preceding the minimum term) of Eq. (12). Curves are labeled with values of $\delta_0 = 1/D_0$. The occasional "kinks" come from changes in the order of the asymptotic sum.

here. More extended series can be extracted from the Hartree–Fock data because of their greater accuracy. Figure 1 illustrates the very rapid decrease in the expansion coefficients. This cannot continue indefinitely, of course; if the $\delta_0 = 1$ series has a radius of convergence of at most slightly greater than unity, as the other shifted series in Table IV seem to require, then eventually $|a_n/a_{n-1}| \gtrsim 1$. Even if the $\delta_0 = 1$ series were ultimately to diverge, however, it is capable of yielding very accurate energies. For $D = 3$ and $Z = 2$, the series in Table V give both the total and Hartree–Fock energies to within 0.002% of their correct values.

B. Shift in argument

Another modified expansion, in which D rather than δ is shifted by a constant, has given good results for a sizable class of single-particle central force potentials.[26] For ground-state Coulombic systems, this prescribes an expansion in powers of $1/(D-1)$, equivalent to

TABLE V. Coefficients for $(\delta - 1)$ expansion.[a]

n	$Z=1$	$Z=1.2$	$Z=1.5$	$Z=2$	$Z=3$	$Z=6$
			Total energy, two-electron atom			
0	−0.647 210 2	−0.687 511	−0.734 553 0	−0.788 848 2	−0.850 883 6	−0.921 122 9
1	−0.158 527	−0.132 55	−0.105 975	−0.079 113	−0.052 325	−0.025 893
2	0.032 91	0.030 7	0.025 77	0.020 19	0.013 97	0.007 16
3	0.004 4	0.000	−0.003 7	−0.004 1	−0.003 1	−0.001 7
			Hartree–Fock approximation			
0	−0.583 333 333 3	−0.641 203 703 7	−0.703 703 703 7	−0.770 833 333 3	−0.842 592 592 6	−0.918 981 481 5
1	−0.118 268 92	−0.103 66	−0.086 962 13	−0.068 162 90	−0.047 368 61	−0.024 633 63
2	0.031 093 1	0.028 3	0.023 851 4	0.018 952 7	0.013 315 4	0.006 983 5
3	−0.007 496	−0.006	−0.005 844	−0.004 640	−0.003 233	−0.001 708
4	0.001 14		0.001 12	0.000 84	0.000 63	0.000 21
			Correlation energy			
0	−0.063 876 9	−0.046 307	−0.030 849 3	−0.018 014 9	−0.008 291 0	−0.002 141 4
1	−0.040 258 1	−0.028 89	−0.019 013	−0.010 950	−0.004 956	−0.001 259
2	0.001 82	0.002 4	0.001 92	0.001 24	0.000 65	0.000 18
3	0.011 9	0.006	0.002 1	0.000 5	0.000 1	

[a] Units are $[2Z/(D-1)]^2$ hartree. Entries are ϵ_n coefficients for ground-state reduced energy expanded in powers of $(\delta - 1)$, as in Eq. (12) with $\delta_0 = 1$.

$$\epsilon(\delta) = \sum_{n=0}^{\infty} \epsilon_n^* \delta^n (1-\delta)^{-n} . \quad (13)$$

The coefficients are related to those in Eq. (10) by

$$\epsilon_0^* = \epsilon_0 , \quad \epsilon_1^* = \epsilon_1 \quad (14a)$$

and

$$\epsilon_n^* = \sum_{m=1}^{n} (-1)^{n+m} \binom{n-1}{m-1} \epsilon_m , \quad \text{for } n \geqslant 2 . \quad (14b)$$

Since this $1/(D-1)$ expansion had not previously been evaluated for a two-electron atom, we computed the ϵ_n^* coefficients from our values of the ϵ_n given in Table III. The resulting series are much less good than the rescaled $1/D$ series, although better than the unscaled series. This poor performance occurs because the $(-1)^m$ factor in Eq. (14) offsets the alternation in sign of the ϵ_m coefficients. Transformation to a $1/(D-1)$ series will improve convergence if the coefficients in the corresponding $1/D$ series have the same sign, as in the unscaled series of Table II as well as previously treated examples. In the present case, the rescaled $1/D$ series and particularly the shifted $(\delta - 1)$ series are much superior.

C. Hybrid expansion

An analysis of the singularities of $E(\delta)$ for the two-electron atom[11] has shown that first- and second-order poles at $D = 1$ are the chief source of the poor convergence of the unscaled $1/D$ expansion of Eq. (5) and Table II. The big improvement found on factoring out the hydrogenic contribution, as in Eq. (10) and Table III, occurs because this removes a major part of the contribution from the second-order pole. Likewise, the further marked improvement brought by shifting the origin to $\delta_0 = 1$, as in Eq. (12) and Table V, occurs because in effect this takes out the remaining contributions from the first- and second-order poles. The $(\delta - 1)$ series has one drawback, however. The expansion coefficients are most readily determined from data near the $D \to 1$ limit, whereas in practice data near the $D \to \infty$ limit are more easily obtained. This can be remedied by constructing a hybrid series[27] in which the first two terms specify the $D \to 1$ poles while higher terms represent derivatives of the energy at the $D \to \infty$ limit. One such hybrid form is

$$\epsilon(\delta) = a_0 + a_1(\delta - 1) + (\delta - 1)^2 \sum_{n=2}^{\infty} a_n \delta^{n-2} . \quad (15)$$

The expansion coefficients are given by

$$a_0 = \epsilon(1) , \quad a_1 = \sigma(1) , \quad (16a)$$

$$a_2 = \epsilon_0 + a_1 - a_0 , \quad (16b)$$

$$a_n = \epsilon_{n-2} + 2a_{n-1} - a_{n-2} , \quad n > 2 . \quad (16c)$$

Here $\epsilon(1)$ denotes the reduced energy eigenvalue and $\sigma(1) = (\partial\epsilon/\partial\delta)_{\delta=1}$ its slope at $D \to 1$; the ϵ_n are the coefficients of Eq. (10), with $\epsilon_0 = \epsilon(0)$ and $\epsilon_1 = \sigma(0)$ the eigenvalue and slope at $D \to \infty$. The leading coefficients a_0 and a_1 are the same as in Eq. (12) for $\delta_0 = 1$.

Table VI gives the coefficients for the hybrid expansion. In Fig. 1 the initial convergence for $D = 3$ is seen to be substantially better than for the rescaled δ expansion of Eq. (10). Eventually the hybrid series exhibits divergence remarkably parallel to that for the rescaled expansion, but the result obtained from asymptotic summation is about an order of magnitude more accurate because the divergence sets in later. The hybrid expansion is comparable to but somewhat less accurate than the shifted expansion with $\delta_0 = 1$ in Eq. (12). However, in practice the choice between these expansions depends on the data available. To evaluate the shifted expansion through third order requires knowledge of the energy eigenvalue and its first three derivatives at $D = 1$. For the hybrid expansion, the third-order approximation is obtained by combining first-order calculations at $D = 1$ and at $D = \infty$. Higher-order hybrid expansions can be constructed by extending the perturbation treatment at either or both of the limits.

TABLE VI. Coefficients for hybrid expansion.[a]

n	$Z=2$	$Z=3$	$Z=6$
	Total energy, two-electron atom		
2	0.025 293	0.017 213	0.008 779
3	−0.015 815	−0.005 595	−0.001 470
4	0.071 886	0.016 064	0.001 307
5	−0.399 00	−0.067 51	−0.007 94
6	2.524	0.251	0.021
7	17.6	−0.9	−0.1
	Hartree–Fock approximation		
2	0.024 973 82	0.017 037 36	0.008 726 76
3	−0.012 183 76	−0.005 237 90	−0.001 553 47
4	0.036 228 1	0.009 647 3	0.000 575 6
5	−0.180 66	−0.044 37	−0.006 18
6	1.001	0.186	0.022
7	−6.6	−0.84	−0.06
	Correlation energy		
2	0.000 319	0.000 176	0.000 052
3	−0.003 633	−0.000 357	0.000 083
4	0.035 658	0.006 417	0.000 731
5	−0.218 34	−0.023 14	−0.001 76

[a] Units are $[2Z/(D-1)]^2$ hartree. Entries are a_n coefficients for Eq. (15). The $n = 0$ and $n = 1$ coefficients are identical to those given in Table V.

D. Correlation energy

Tables V and VI include expansion coefficients for the correlation energy, obtained from $\epsilon(\delta) - \epsilon^{HF}(\delta)$. As illustrated in Fig. 5, neither the customary nor the rescaled form of the $1/D$ expansion gives useful estimates of the correlation energy for $D = 3$. But both the shifted $(\delta - 1)$ expansion and the hybrid expansion provide good accuracy; indeed, for $Z = 2$, asymptotic summation retaining only the zero- and first-order terms gives the correlation energy within about 2%. This is a very satisfactory result, comparable to the accuracy attained in full-scale configuration interaction calculations.[10]

V. DISCUSSION

This study demonstrates the utility of rescaled, shifted, and hybrid expansions. By these means, dimensional expansions become practical for the calculation of accurate atomic energies. Rescaling takes out all but the interelectron repul-

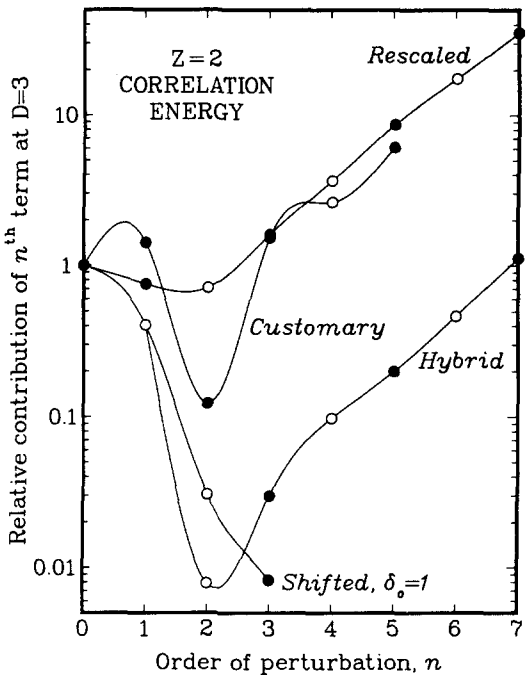

FIG. 5. Comparison of contributions to the correlation energy at $D = 3$ from successive terms in four versions of dimensional expansions, for $Z = 2$. Format as in Fig. 1.

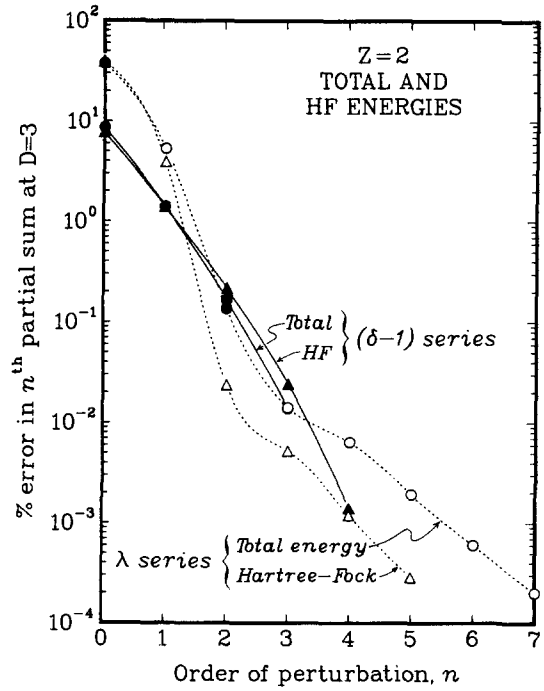

FIG. 6. Comparison of initial convergence properties of the perturbation expansion in powers of $(\delta - 1)$ with that in powers of λ, for $D = 3$ and $Z = 2$. Ordinate shows percentage error in partial sums to various orders. Full and open symbols represent positive and negative errors, respectively. The final values plotted for the two $(\delta - 1)$ series constitute upper bounds, and the true values could be lower.

sion, which proves to have a much weaker dependence on D than the attractive, hydrogenic terms. Shift of the origin to $D_0 = 1$ isolates in the zero- and first-order terms the major remaining contributions from the dimensional singularities characteristic of Coulombic interaction.[27] The residual dependence on D is so mild that the leading few terms of the expansion yield quite accurate results. These procedures work well even for the hydride ion ($Z = 1$), which is very difficult to treat by conventional methods. The shifted or hybrid expansions are particularly effective for the correlation energy, which we find is accurately given by just the zero- and first-order terms. These results exemplify the virtues of "small-D" expansions.[28]

Our expansions invite comparison with the familiar power series in $\lambda = 1/Z$ generated by applying perturbation theory to the interelectron repulsion. In the same reduced units, this is

$$\epsilon(\delta,\lambda) = \sum_{k=0}^{\infty} \epsilon^{(k)} \lambda^k . \tag{17}$$

As indicated in Table I, the perturbation coefficients $\epsilon^{(k)}$ for $D = 3$ are now known to very high order (up to 400!) for the total energy[16] and to fifth order for the Hartree–Fock approximation.[17] Figure 6 compares the convergence of the leading terms of the series in λ with the series in $(\delta - 1)$ for the helium atom. The initial convergence is quite similar, and the resemblance seems likely to persist to higher orders. Thus, beyond fourth order the series in Eq. (17) steadily approaches a geometric progression[16,20] with a radius of convergence near unity (about 1.1). As noted above, we expect that the $(\delta - 1)$ series of Eq. (12) will likewise have a radius of convergence equal to or close to unity.

The prospects for applying dimensional expansions to multielectron atoms and molecules appear much better than for the λ expansion. For an N-electron system, the Coulomb potential has N attractive terms $(1/r_i)$ for each nucleus but $N(N-1)/2$ interelectron repulsion terms $(1/r_{ij})$, so treating the entire repulsion as a perturbation soon becomes untenable. Dimensional expansions offer the great advantage that the complete Hamiltonian is solved for the limiting cases used to construct the expansion (here, $D \to 1$ and $D \to \infty$). Thus, the ability of the expansion to represent the $D = 3$ solution does not depend on the magnitude of the interaction but only on its dimension dependence. Our results for two-electron atoms[10–15] and other model problems[27] suggest that, aside from singularities calculable in the limiting cases, the dimension dependence is likely to remain gentle and smooth for multielectron systems.

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