

Recursive Calculation of Dimensional Expansions for Two-Electron Atoms

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An efficient procedure is developed for calculation of perturbation expansions in $\delta=1/D$, the reciprocal of the Cartesian dimensionality of space, for the ground-state energy of two-electron atoms. The method uses recursion relations between moments of the coordinate operators. Results through tenth order are presented for the helium atom. The perturbation series is divergent but Padé summation gives accurate results.

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Perturbation theory parametrized by the Cartesian dimensionality D of space offers a promising new approach to electronic structure calculations. The limit $D \rightarrow \infty$ reduces to a classical electrostatic problem in which the electrons take fixed positions.¹ This configuration corresponds to the minimum of an effective potential which includes centrifugal terms arising from the D dependence as well as the Coulomb interactions.²⁻⁴ Excursions of the electrons about the limiting rigid configuration are described by a perturbation expansion in powers of $\delta=1/D$. For two-electron atoms, closed analytic formulas have been obtained for the zeroth-order energy, at the $\delta=0$ limit, and for the first-order perturbation, linear in δ , which corresponds to harmonic vibrations.^{1,2} Approximate values have been computed for the leading anharmonic term⁴ in δ^2 and several further terms.⁵ However, the number of significant figures dwindles rapidly (from six in second order to only one in fifth order) so that these results cannot be used with Padé summation or other techniques to construct accurate solutions. Here we present a recursive method which provides extremely accurate perturbation coefficients to high order. We report results for helium through tenth order that are accurate to ten or more significant figures.

The Schrödinger equation for the ground state of the two-electron atom can be written as

$$\left\{ -\frac{1}{2}(\partial^2/\partial r_1^2 + \partial^2/\partial r_2^2) - G(r_1, r_2) \partial^2/\partial \theta^2 + D^2[V_{\text{eff}}(r_1, r_2, \theta) - E] \right\} \Psi = 0, \quad (1)$$

where $G = \frac{1}{2}(r_1^{-2} + r_2^{-2})$ and V_{eff} is an effective potential given by

$$V_{\text{eff}} = \frac{1}{4} \left[\left[1 - \frac{6}{D} + \frac{8}{D^2} \right] \sin^{-2} \theta - \frac{1}{D^2} \right] G(r_1, r_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z} (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{-1/2}. \quad (2)$$

The units of energy are atomic units multiplied by $Z^2 \delta^2$ and the wave function has been scaled by the square root of the D -dimensional Jacobian.² For atoms with $Z > 1.228 \dots$, the minimum of V_{eff} as $\delta \rightarrow 0$ corresponds to a symmetric configuration (at $r_{1m} = r_{2m}, \theta_m$). The zeroth-order approximation to the energy is $E_0 = V_{\text{eff}}(r_m, r_m, \theta_m)$ and the first-order perturbation E_1 is obtained from second derivatives evaluated at the minimum. Analytic expressions for r_m , θ_m , E_0 , and E_1 in terms of Z are given elsewhere.²⁻⁴

We assume that the energy and wave function can be expanded as

$$E = \sum_{n=0}^{\infty} \epsilon_{2n} \delta^n = \sum_{n=0}^{\infty} E_n \delta^n$$

and

$$\Psi = \sum_{n=0}^{\infty} \Psi_n \delta^{n/2},$$

respectively, with the normalization of Ψ chosen such that $\langle \Psi_0 | \Psi_0 \rangle = 1$ and $\langle \Psi_0 | \Psi_{n \neq 0} \rangle = 0$. It is convenient to transform to the internal vibration coordinates $r_1 \pm r_2$ and to introduce dimensionality-scaled displacement

coordinates,

$$x = \delta^{-1/2} [\frac{1}{2}(r_1 + r_2) - r_m],$$

$$y = \delta^{-1/2}(\theta - \theta_m), \quad z = \delta^{-1/2} [\frac{1}{2}(r_1 - r_2) - r_m].$$

We then expand G and V_{eff} about $\delta=0$ in the form

$$G = \sum_{q=0}^{\infty} \delta^{q/2} G_q(x, z), \quad V_{\text{eff}} = \sum_{q=0}^{\infty} \delta^{q/2} V_q(x, y, z),$$

where G_q and V_q are polynomials in the displacement coordinates. Substituting these expansions into Eq. (1) and collecting terms according to powers of $\delta^{1/2}$ yields a set of differential equations,

$$\mathcal{H}_p = \sum_{q=0}^p (H_q - \epsilon_{q+2}) \Psi_{p-q} = 0, \quad (3)$$

where $\epsilon_{2n+1} = 0$, $p = 0, 1, 2, \dots$, and

$$H_0 = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - r_m^{-2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + V_2, \quad (4a)$$

$$H_{n>0} = G_n \frac{\partial^2}{\partial y^2} + V_{n+2}. \quad (4b)$$

To solve Eq. (3) we generalize a procedure developed by Ader⁶ for central-force problems in which recursion relations are derived for the moments of the coordinate operators, in our case the quantities $A_{jkl}^p = \langle \Psi_0 | x^j y^k z^{2l} | \Psi_p \rangle$. Equation (3) with $p=0$ is simply a harmonic oscillator, which we solve by making the substitution

$$\Psi_0 = N_0 \exp[-\frac{1}{2}(\omega_{ss}x^2 + 2\omega_{s\theta}xy + \omega_{\theta\theta}y^2 + \omega_{tt}z^2)],$$

and collecting terms of like powers in the coordinates. N_0 is a normalization constant. For $p > 0$ we take matrix elements of \mathcal{H}_p with $x^j y^k z^{2l} \Psi_0$ and thereby convert each of the differential equations into a set of algebraic

equations. The Hamiltonian is Hermitian so that

$$\langle x^j y^k z^{2l} \Psi_0 | H_q \Psi_q \rangle = \langle H_q (x^j y^k z^{2l} \Psi_0) | \Psi_p \rangle.$$

Thus, the differential operators need only act on Ψ_0 and not on any of the $\Psi_p > 0$, which are much more complicated. For this reason, the recursion relations for the moments have a much simpler form than obtained, for example, by generalization to two electrons of the recursive method of Mlodinow and Shatz.⁷ We find

$$\tau_{jkl} A_{jkl}^p + j\omega_{s\theta} A_{j-1,k+1,l}^p + 2kr_m^{-2} \omega_{s\theta} A_{j+1,k-1,l}^p = \mathcal{C}_{jkl}^p, \quad (5)$$

where $\tau_{jkl} = j\omega_{ss} + 2kr_m^{-2} \omega_{\theta\theta} + 2l\omega_{tt}$, and

$$\mathcal{C}_{jkl}^p = \mathcal{G}_{jkl}^p - \mathcal{V}_{jkl}^p - \mathcal{G}_{jkl}^p + \frac{1}{2}j(j-1)A_{j-2,k,l}^p + r_m^{-2}k(k-1)A_{j,k-2,l}^p + l(2l-1)A_{j,k,l-1}^p, \quad (6)$$

$$\mathcal{G}_{jkl}^p = \sum_{q=1}^p \langle G_q (\partial^2 / \partial y^2) (x^j y^k z^{2l} \Psi_0) | \Psi_{p-q} \rangle, \quad \mathcal{V}_{jkl}^p = \sum_{q=1}^p \langle x^j y^k z^{2l} \Psi_0 | V_{q+2} | \Psi_{p-q} \rangle, \quad \mathcal{G}_{jkl}^p = \sum_{q=1}^{p/2} E_{q+2} \langle x^j y^k z^{2l} \Psi_0 | \Psi_{p-2q} \rangle.$$

Here \mathcal{C}_{jkl}^p depends only on those moments $A_{j'k'l'}^{p'}$ for which $p' < p$ or $j'+k'+2l' < j+k+2l$, so that Eq. (5) provides a recursive solution for the A_{jkl}^p , starting with the moments A_{jkl}^0 which are Gaussian integrals that can be evaluated explicitly. If we set $j=k=l=0$ in Eq. (5) then we have

$$E_p = \mathcal{G}_{000}^{2p-2} + \mathcal{V}_{000}^{2p-2}. \quad (7)$$

This relation expresses the coefficients of the energy expansion in terms of the moments.

The $A_{\Sigma=n}^p$, where " $\Sigma=n$ " represents the set $\{(j,k,l): j+k+2l=n\}$, must be calculated in order of increasing p , and for a given p , in order of increasing n . If the sum $p+n$ is odd then the moment is equal to zero. The moments that are needed to calculate E_p , beyond those needed for E_{p-1} , are

$$A_{\Sigma=3,1}^{2p-3}, A_{\Sigma=6,4,2}^{2p-4}, A_{\Sigma=9,7,5}^{2p-5}, \dots,$$

$$A_{\Sigma=3i-6,3i-8,3i-10}^{2p-i}, \dots, A_{\Sigma=6p-6,6p-8,6p-10}^0.$$

We have calculated the first eleven coefficients E_n of the perturbation series for $Z=2$ and list the values in Table I. Our calculations were carried out on a Micro VAX-II minicomputer. For the first ten terms the computations were performed in quadruple precision (~ 33 decimal digits), and for the last term in double precision (~ 16 decimal digits). Roundoff error was estimated by comparison of the quadruple-precision and double-precision results for the first ten terms. The recursion relations seem to be only moderately unstable to roundoff error. The time required to calculate E_n was about twice that for E_{n-1} . With double precision the total time for the calculation through tenth order was about 2 h. Quadruple precision slowed the computation considerably. The calculation was stopped at E_{10} because beyond that some of the moments become larger than the maximum allowed value of a double-precision constant, about 10^{38} .

A major obstacle to use of dimensional perturbation theory with Coulomb potentials is the poor convergence of the δ series. For example, the ground-state energy of the one-electron atom is given by $E_H = -2(1-\delta)^{-2}$. The expansion in δ does converge at $\delta = \frac{1}{3}$, but only rather slowly due to the presence of the second-order pole at $\delta=1$. In Fig. 1 we compare partial sums for the hydrogenic case with those for helium, which exhibit behavior typical of a divergent asymptotic expansion. For helium the energy is again singular at $\delta=1$, where it has a second-order pole and a confluent first-order pole.⁸ The effect of these poles can be removed by our writing the series in the form⁹

$$E = \frac{a-2}{(1-\delta)^2} + \frac{a-1}{(1-\delta)} = \sum_{n=0}^{\infty} \hat{E}_n \delta^n, \quad (8)$$

where $\hat{E}_n = E_n - (n+1)a_{-2} - a_{-1}$, in units of a.u. times $Z^2 \delta^2$. This improves the asymptotic convergence of the

TABLE I. Coefficients of the δ series for helium. Units are atomic units times Z^2 . Number in parentheses gives power of 10 to be included in the coefficient.

n	E_n	
0	-0.273 776 914 112 772 414 745 516 871 119 506	(1)
1	-0.605 759 194 836 364 666 736 140 463 770 836	(1)
2	-0.886 218 378 983 331 935 295 531 457 592 580	(1)
3	-0.139 006 372 818 208 166 137 138 749 181 895	(2)
4	-0.543 672 043 287 805 001 297 034 059 420 4	(1)
5	-0.827 394 676 588 397 342 542 587 754 995	(2)
6	+0.131 269 893 398 517 115 348 441 012 84	(3)
7	+0.101 260 076 492 362 399 786 146 586 07	(5)
8	-0.433 338 867 474 867 247 981 893 617 39	(6)
9	+0.142 144 642 644 792 873 543 602 734 89	(8)
10	-0.443 814 218 45	(9)

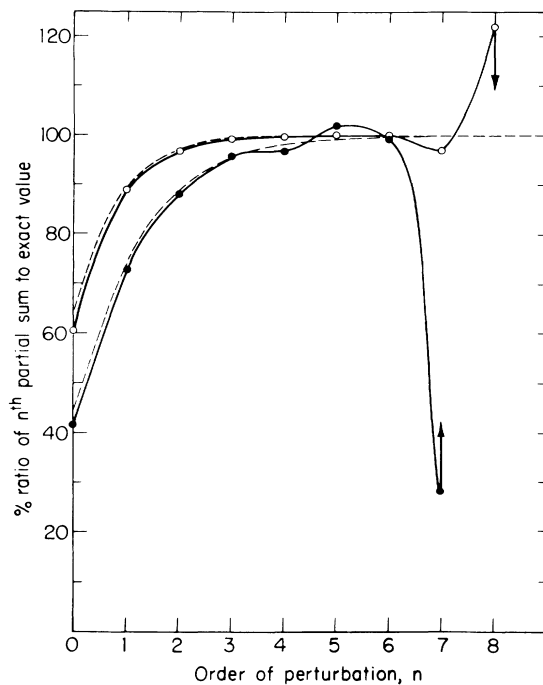


FIG. 1. Partial sums of dimensional expansions of order n , expressed as percentage of the exact energy. Points connected by solid curves show results for helium ground state (solid circles; $Z=2$, $D=3$) or the $(2p)^2\ ^3P$ doubly excited state (open circles; equivalent to $D=5$ ground state). Dashed curves show results for the hydrogenic limit ($Z \rightarrow \infty$).

first few terms but eventually the series still diverges.

We employ Padé summation¹⁰ to calculate the residues a_{-2} and a_{-1} and then to sum Eq. (8). The residues can be expressed in terms of the perturbation expansion according to

$$a_{-2} = \lim_{\delta \rightarrow 1} (1 - \delta)^2 E(\delta), \quad (9a)$$

$$a_{-1} = \lim_{\delta \rightarrow 1} (1 - \delta)[E(\delta) - a_{-2}(1 - \delta)^{-2}]. \quad (9b)$$

We expand Eqs. (9) in δ and then calculate the residues from Padé approximants evaluated at $\delta=1$. Our results for the residues and the energy at $\delta=\frac{1}{2}$ from the $[N/N]$, $[N/N+1]$ Padé sequence are shown in Table II and compared with exact values.^{12,13} The Padé approximants are apparently convergent although the rate of convergence is somewhat uneven.¹¹ The result from $[5/5]$ agrees with the essentially exact energy of Pekeris¹³ to 0.005%. The locations of the poles and zeros of the approximants confirm a conjecture⁸ that the energy as a function of δ has an infinite sequence of poles on the negative real axis. These poles approach an essential singularity at $\delta=0$ and so the radius of convergence is zero. We will discuss elsewhere¹¹ further aspects of the singularity analysis.

The accuracy of our result for the helium ground state

TABLE II. Residues and energy for $Z=2$ from Padé approximants of δ series of order n . $[N/N]$, $[N/N+1]$ sequence. Approximants in parentheses do not accurately reflect the singularity structure (see Ref. 11). Units are a.u. times Z^2 .

n	a_{-2}	a_{-1}	E
1	-3.47698	0.93880	-0.736646
2	-3.04652	0.16378	-0.721896
3	-3.27788	0.60821	-0.727789
4	-3.14702	0.30793	-0.725665
5	-3.17019	0.37090	-0.725868
6	-3.14674	0.30745	(-0.725658)
7	-3.20468	0.45742	-0.726242
8	-3.16606	0.34711	-0.725981
9	(-2.97364)	(-0.73797)	-0.725758
10	-3.16497	0.34457	-0.725969
Exact	-3.15539 ^a	0.31645 ^a	-0.725931 ^b

^aFrom variational calculation of Ref. 12.

^bFrom variational calculation of Ref. 13.

is about the same as that obtained from configuration-interaction calculations.^{14,15} Of course, for smaller δ the divergence is less strong (as illustrated in Fig. 1) and more accurate results are obtained. The five-dimensional ground state is degenerate with the doubly excited $(2p)^2\ ^3P$ state in three dimensions.¹⁶ Evaluating the $[5/5]$ Padé approximant at $\delta=\frac{1}{2}$ gives $E=0.71050049$ a.u., which differs from the exact value¹⁷ by only 0.00004%. This is the only such interdimensional degeneracy known for the two-electron atom.¹⁸

The recursive method presented here can be applied with only slight modification to the Hartree-Fock approximation and may thereby provide invaluable information about the dimension dependence of electron correlation. It is also straightforward to treat excited states with total angular momentum; these correspond to higher eigenvalues for electron oscillations in the same effective potential used for the ground state. Applications to states with nonzero angular momentum or to many-electron systems appear feasible, but require development of a reduced equation analogous to Eq. (1) or some equivalent. Although extremely accurate results for two-electron atoms have already been obtained from variational calculations¹³ and from the $1/Z$ perturbation expansion,^{18,19} both those methods become prohibitively difficult for many-electron systems. Dimensional perturbation theory has the virtue that the zeroth-order effective potential includes all the interactions, electron repulsion as well as nuclear attraction. The method thus is not handicapped by the number or magnitude of the interactions but rather is governed by the dimension dependence. This may enable dimensional perturbation theory to reduce the prevalent reliance on arduous configuration-interaction calculations of the correlation error.

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