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Finite-element computation of perturbation energies for the two-electron atom

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Perturbation energies E_2, E_3, and E_4 in the $1/Z$ expansion for the ground-state two-electron atom are calculated using accurate representations of the partial waves $L=0,1,2,\ldots$ of the first- and second-order eigenfunctions. These are obtained by combining L-Hylleraas basis functions with a one-dimensional finite-element procedure. The contribution to E_2, E_3, and E_4, made by partial waves $L \gg 1$, can, with a surprising accuracy, be covered by numerical extrapolation with the help of a Schwartz-type expression in powers of $1/(L+\frac{1}{2})$.

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I. INTRODUCTION

This paper is concerned with the first- and second-order functions of the $1/Z$ expansion for the two-electron atom [1,2]. First-order pair functions (for different electronic states) are known to build up the entire first-order wave function of an atom with N electrons [3] and thus determine the second- and third-order energy of the atom. We study a finite-element method that is to furnish the individual partial waves $L=0,1,2,\ldots$ of the pair function. The two-electron ground state will be treated. Finite-element (FE) methods [4,5] are known for their versatility and numerical stability. They have already been applied to numerous quantum-mechanical problems including the electronic structure of atoms [6–8] and of diatomic molecules [8,9], and to reactive scattering [10]. Recently, an accurate FE calculation of the second-order energy (within Møller-Plesset perturbation theory) for the ten-electron atom has been reported [11]. Our method makes use of the decoupling [12] of a pair function in partial waves that holds in perturbation theory. L-projected Hylleraas functions [13,14] will be applied as local basis functions that represent a partial wave within a particular finite element. A one-dimensional discretization (for the coordinate $s=r_1+r_2$) is used. This appears to be more suitable for the problem than a full two-dimensional discretization. The method is outlined in Sec. II, results are given in Sec. III. Our calculations provide values for the (previously not known) L increments of the third- and fourth-order energies so that the numerical behavior of these at large L can be studied (Sec. IV).

There are two principal reasons for the present investigation. (i) The partial-wave method developed here can likewise be applied within the Møller-Plesset expansion. (ii) Recent numerical results on the behavior of the (generalized) correlation energy along atomic isoelectronic sequences [15,16] indicate the function $E_{\rm corr}(1/Z)$ to be well approximated by the first two terms of its $1/Z$ expansion,

$$E_{\rm corr}(1/Z)=[E_2-E_2({\rm HF}')]+[E_3-E_3({\rm HF}')]/Z+O(1/Z^2)\ . \tag{1}$$

HF′ refers to the single- or few-configurational Hartree-Fock approximation (depending on the electronic state; Refs. [17,18]. Estimates of correlation energies from Eq. (1) require reliable values of the occurring perturbation energies. While E_2, $E_2({\rm HF}')$ as well as $E_3({\rm HF}')$ can be readily calculated for atoms with 2–10 electrons [3,19,20], the evaluation of E_3 is more demanding for any atom with three or more electrons.

II. METHOD

Perturbation theory, which offers the $1/Z$ expansion, gives for the ground state of the two-electron atom [1,2] the wave function

$$\psi(\zeta)=\psi_0+\zeta\psi_1+\cdots\ ,\quad \zeta=1/Z \tag{2}$$

and the total energy

$$E(\zeta)=E_0+\zeta E_1+\zeta^2E_2+\zeta^3E_3+\cdots\ . \tag{3}$$

Atomic units are used and it is found that $E_0=-1$, $E_1=\frac{5}{8}$. The unperturbed Hamiltonian H_0 is the sum of two hydrogenic Hamiltonians, the perturbation is the electron-electron repulsion $H_1=1/r_{12}$. The equation for the first-order wave function ψ_1 reduces [12] to independent equations for its "partial waves" $\psi_1(L)$ $(L=0,1,2,\ldots)$,

$$\psi_1=\sum_{L=0}^{\infty}\psi_1(L)\ , \tag{4}$$

$$\psi_1(L)=R_L(r_1,r_2)P_l(\cos\nu)\ , \tag{5}$$

where ν is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, and P_L in the Lth Legendre polynomial. The second- and third-order perturbation energies take the form

$$E_2=\sum_{L=0}^{\infty}\Delta E_2(L)\ , \tag{6}$$

where $\Delta E_2(L)=\langle\psi_0|1/r_{12}-E_1|\psi_1(L)\rangle$,

$$E_3=\langle\psi_1|1/r_{12}-E_1|\psi_1\rangle\ . \tag{7}$$

For each partial wave (5), $R_L(r_1,r_2)$ will be approximated in terms of a basis set using the variation-perturbation principle [2]. The exact solution R_L exhibits a finite discontinuity of the third derivative at $r_1=r_2$. Orbital products, $f(r_1)g(r_2)$, do not represent this efficiently. A more useful basis is obtained [13,14] by projecting Hylleraas's functions (expressed in terms of $u=r_{12}$, $s=r_1+r_2$, and $t=r_2-r_1$) onto $P_L(\cos v)$. We refer to these projections as "L-Hylleraas functions." A satisfactory set is obtained from projections of the set

$$F_{ab}=u^a s^b \psi_0 \ , \quad a,b\in\{0,1,2,\cdots\} \ . \tag{8}$$

Here $\psi_0 \sim \exp(-s)$ is the zeroth-order function of the $1s^2$ pair. The L projection of (8) is to be denoted (F_{ab},L).

Any (F_{ab},L) is a global basis function in the sense that it is defined in the full domain $0\leq r_1$, $r_2\leq\infty$. We partition this domain in "elements" of the shape shown in Fig. 1. The restrictions of the (F_{ab},L) to a particular element now form local basis functions. The procedure amounts to a one-dimensional discretization with respect to the coordinate $s=r_1+r_2$. Along the second coordinate (that can be chosen as $q=r\langle /r\rangle$) the (F_{ab},L) functions continue to be used as global basis functions. There are two reasons for using an s-only discretization: (i) The expansion of R_L in the form

$$R_L=f_0+(u,L)f_1+(u^2,L)f_2+(u^3,L)f_3+\cdots \ , \tag{9}$$

wherein $(\ ,L)$ denotes L projection and $f_0,f_1,f_2,\ldots$ depend only on the variable s turns out to converge rapidly, in particular when $L\gg 1$. So, a few powers of u suffice to obtain an adequate basis set provided that there is enough flexibility to represent the $f_i(s)$. (ii) For large L, $R_L(r_1,r_2)$ becomes more and more concentrated [12] along the diagonal $r_1=r_2$ and a two-dimensional grid method might have some difficulty in treating high L partial waves. Even with a suitable grid for each L (thus providing an accurate second-order energy), the evaluation of the third-order energy (where all partial waves enter simultaneously) would still remain complicated.

It is noted that the local functions (8) include the $\exp(-s)$ factor. Thus, within a give FE, some $f_i=f_i(s)$ in Eq. (9) is expressed by the product of a (fourth-order) polynomial in s times $\exp(-s)$. For one and the same grid, this form should do better than the customary pure polynomial ansatz. Our basis functions lead to elementary integrations: All matrix elements can be expressed in terms of the integrals

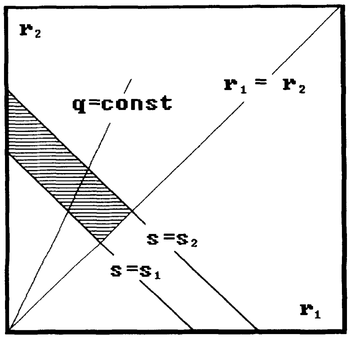

FIG. 1. Finite elements (in the range $r_1\leq r_2$ of the radial coordinates) arise by subdivision along the axis $s=r_1+r_2$. Hatched area corresponds to the particular element $s_1\leq s\leq s_2$. No discretization is used for the $q=r_1/r_2$ coordinate.

$$U_{mn}(s_1,s_2)=a_n(s_1,s_2)U_{mn}(0,\infty) \ , \tag{10}$$

wherein $U_{mn}(0,\infty)$ are the integrals of James and Coolidge [21]. Descending recursion (Sec. III of Ref. [14]) furnishes accurate values for the integrals. The factor $a_n(s_1,s_2)$ reads

$$a_n(s_1,s_2)=\frac{2^{n+2}}{(n+1)!}\int_{s_1}^{s_2} s^{n+1}\exp(-2s)ds \tag{11}$$

$$=\exp(-2s_1)e_{n+1}(2s_1) - \exp(-2s_2)e_{n+1}(2s_2) \ , \tag{12}$$

where $e_n(x)=1+x+\cdots+x^n/n!$. The direct evaluation of (12) is hindered for large n by cancellation of digits. It is then helpful to rewrite (12) so that a continued-fraction expression (formula 4.2.41 of Ref. [22]) for the difference $\exp(x)-e_{n+1}(x)$ can be employed.

The main steps in the calculation of a partial wave are the following. (i) Set up James-Coolidge integrals $U_{mn}(0,\infty)$. (ii) For each FE, evaluate the factors a_n and calculate matrix elements $\langle h|H_0-E_0|h'\rangle$ for any pair of (local) L-Hylleraas functions h and h'; also calculate right-hand sides $\langle\psi_0|1/r_{12}-E_1|h\rangle$. (iii) transform to shape functions [4]. (iv) On the resulting block matrix (one block corresponding to one FE) impose the conditions that the wave function be continuous between adjacent elements and vanish at the boundary of the outermost element. (v) Solve the resulting (sparse-matrix) linear system.

A dominant contribution to $\psi_1(L)$ at large L is $(\frac{1}{2})(u,L)\psi_0$ [12]. Therefore, for sufficiently large L_0 the sum over partial waves $L_0<L\leq\infty$ can be covered in closed form [23] by

$$\psi_1(L>L_0)=(\tfrac{1}{2})(u,L>L_0)\psi_0 \ , \tag{13}$$

where $(u,L>L_0)$ is the projection of $r_{12}=u$ onto the space of all $L>L_0$,

$$(u,L>L_0)=u-(u,0)-(u,1)-\cdots-(u,L_0) \ . \tag{14}$$

Unless L_0 is very large, accuracy can be gained by using, rather than (13), the two-parameter variational expression,

$$\psi_1(L>L_0)=(a_0+a_1 s)(u,L>L_0)\psi_0 \ , \tag{15}$$

where the parameters a_0 and a_1 are found by minimizing Hylleraas's variational principle for $E_2(L>L_0)$. The values of $a_0=0.499\,981\,533$, $a_1=-7.212\,555\times10^{-4}$ and $E_2(L>15)=-14.235\,820\times10^{-6}$ follow for $L_0=15$.

Partial-wave separation holds also in higher perturbation orders. The $(H_0$-$E_0)$ matrix remains unchanged unless a new basis is introduced. The vector of right-hand sides is new. We have computed second-order partial waves $\psi_2(L)$ together with their fourth-order energies $\Delta E_4(L)$.

III. RESULTS

Each of the partial waves $\psi_1(L)$ $(L=0,1,\ldots,20)$ and $\psi_2(L)$ $(L=0,1,\ldots,12)$ has been treated by applying one and the same grid of four finite elements along the $s=r_1+r_2$ coordinate (cf. Fig. 1) covering the range $0\leq s\leq 30$ bohrs. Mesh points have been chosen as a geometric progression,

$$s=2,\ 4.93,\ 12.1,\ 30 \text{ bohrs} .$$

Changing the grid with L could improve the accuracy for some of the partial waves; it would, however, complicate the E_3 and E_4 evaluations. Fourth-degree shape functions have been used throughout. For any L, the basis set used arises by L projection from the same set $\{F_{ab}, a\leq 8, b\leq 4\}$ of Hylleraas functions (8). The number of powers of u having a nonzero projection diminishes with increasing L, as given in Table I. Dimensions of final FE matrices vary between 144 (at $L=0$) and 64 (at any $L\geq 5$). The resulting second-order partial-wave energies (Table I) are more accurate than previous values [14,23,25]. Our overall E_2 perturbation energy compares well with some accurate results of the previous literature (see Table I). Our result does not reach the accuracy of the very large (not L separated) calculation of Baker, Freund, Hill, and Morgan [26].

For evaluating the third-order energy (7) the partial-wave vectors (first emerging as sums over L-Hylleraas functions) have been rewritten as sums over simple powers of $r<$ and $r>$. One uses the L expansion of $1/r_{12}$ and the $3j$ symbols [27] to obtain the partial waves of the product $(1/r_{12})\psi_1$ and, finally, the value of E_3. The first set of results (Table II, column I) refers to the "L-truncated case" where the expansion of ψ_1 [Eq. (4)] is cut off after angular momentum L_0. When the large L are added through Eq. (15) the numbers in column II of Table II are obtained. As expected, approximation (15) improves rapidly with L_0. At the level of $L_0=5$, 10, and 15, the errors of the overall E_3 amount to 380, 7, and 0.7 $(\times 10^{-9}$ a.u.), respectively. Some, presumably small, por-

TABLE I. Second-order partial-wave energies $\Delta E_2(L)$ (in 10^{-6} charge-scaled atomic units). Parameters of FE calculation are n (number of projections of u powers contained in basis set) and the overall matrix dimension. The same grid of four FE's is used for all L.

L	n	Dimension	$\Delta E_2(L)$
0	9	144	−125 333.831 218
1	8	128	−26 495.162 363
2	7	112	−3906.133 970
3	6	96	−1077.728 858
4	5	80	−406.098 264
5	4	64	−184.995 357
6	4	64	−95.789 185
7	4	64	−54.396 022
8	4	64	−33.119 686
9	4	64	−21.294 131 4
10	4	64	−14.302 920 6
11	4	64	−9.957 945 2
12	4	64	−7.143 737 2
13	4	64	−5.256 643 2
14	4	64	−3.953 266 0
15	4	64	−3.029 807 1
16	4	64	−2.360 833 03
17	4	64	−1.866 661 41
18	4	64	−1.495 249 83
19	4	64	−1.211 764 00
20	4	64	−0.992 372 78
Sum $(0\leq L\leq 20)$	−157 660.120 259		
Closed sum $(20<L\leq\infty)$[a]	−6.309 085		
Total	−157 666.429 34		
Scherr and Knight[b]	−157 666.405		
Midtdal[c]	−157 666.428		
"Exact," Baker *et al.*[d]	−157 666.429 469 14		

[a] Variational upper bound resulting from Eq. (15).

[b] Reference [2]. Basis set of 100 Kinoshita functions.

[c] Reference [24]. Extrapolated value, based on calculations in terms of 203 Hylleraas functions.

[d] Reference [26]. Basis set of dimension 476 consists of generalized Hylleraas functions with inclusion of logarithmic terms. Implementation in terms of quadruple-precision arithmetics.

TABLE II. Third-order energy E_3 evaluated in terms of partial waves. Column I: Wave function truncated after partial wave L_0. Column II: Asymptotic partial waves represented by closed sum (15). Energies in 10^{-6} charge scaled atomic units.

L_0	E_3 I	II
0	−5214.847 877[a]	5144.30
1	2893.454 630	8493.80
2	6394.190 373	8673.92
3	7598.400 017	8694.25
4	8097.620 850	8697.81
5	8337.215 532	8698.64
6	8465.354 587	8698.890
7	8539.723 499	8698.973
8	8585.713 425	8699.004
9	8615.627 245	8699.018
10	8635.900 418	8699.024
11	8650.115 428	8699.027 55
12	8660.371 948	8699.029 15
13	8667.955 020	8699.030 01
14	8673.680 637	8699.030 52
15	8678.083 665	8699.030 81
Scherr and Knight[b]	8698.991	
Midtdal[c]	8699.029	
"Exact," Baker *et al.*[d]	8699.031 528	

[a] Third-order perturbation energy of the "radial approximation"; an older estimate [28] is −5215.41.

[b] Reference [2].

[c] Reference [24], extrapolated vlaue.

[d] Reference [26].

tion of these errors is due to the residual inaccuracy in the low-L partial waves. An E_3 evaluation similar to that of the scheme II has been done for a one-parameter $\psi_1(L>L_0)$, where the a_1 term is dropped from Eq. (15). The resulting E_3 values (at $L_0=5$, 10, and 15) are 8697.2, 8698.95, and 8699.020 (10^{-6} a.u.), respectively. They stay noticeably behind the values from Eq. (15). Conversely, one may conclude that a better approximation for $\psi_1(L>L_0)$ than (15) would be useful since, in effect, it would lower the number of partial waves that need explicit calculation.

Second-order partial waves have been computed for the "L-truncated case" only, that is, on the basis of a ψ_1 that contains angular momenta up to L_0, but no asymptotic term like (15). Denote these partial waves by $\psi_2(L_0,L)$. For given L_0, $\psi_2(L_0,L)$ and its energy $\Delta E_4(L_0,L)$ are of interest for $L=0,\ldots,L_0$. The sum

$$E_4(L_0)=\sum_{L=0}^{L_0}\Delta E_4(L_0,L) \tag{16}$$

represents the fourth-order energy coefficient of a configuration-interaction (CI) -like variational calculation comprising angular momenta up to L_0. As $L_0\to\infty$, (16) reaches the full $1/Z$ perturbation energy E_4. (Numerical results for $L_0=0,1,\ldots,12$ are collected in Table V.)

On the occasion of the present publication, a small error is to be noted that occurs in the paper by Schmidt [14]. A summation of the asymptotic formula for the second-order partial-wave energies furnishes (rather than −14.2481 as given in Table V [14]), the value of −14.2358 (10^{-6} a.u.). This means that the best E_2 result obtained in the paper (Table VI [14]) deteriorates slightly to

$$E_2(\text{Ref. [14]})=-157\,666.413\times10^{-6}\ . \tag{17}$$

IV. EXTRAPOLATING "L-TRUNCATED ENERGIES"

The cleanest way of calculating the third-order energy E_3 is to use a complete wave function ψ_1 that encompasses the asymptotic partial waves $L\gg1$. These are covered in closed form by an expression like (13) or (15) in which the first power of the interelectronic coordinate r_{12} appears. The resulting integrations over r_{12} are easy as long as the two-electron atom is treated. In processing pair functions into the E_3 of a larger atom, however, the problem of difficult integrals emerges that generally limits the usefulness of basis functions with explicit r_{ij} dependence. On the other hand, "L-truncated" pair functions (containing low-L partial waves only) do not introduce difficult integrals of this type.

Angular extrapolation ($L\to\infty$) on the basis of L-truncated calculations has been applied already with some success. Third-order calculations for the ten-electron atom by Jankowski, Rutkowska, and Rutkowski [29] and, very recently, second-order calculations by Flores [11] indicate angular extrapolation can do well, provided that L-truncated results are available that are "radially" well converged. For the two-electron atom, extrapolation in powers of $\lambda=1/(L+1/2)$ with a leading fourth power for singlet states has its origin in Schwartz's analytical result [12] on the L asymptotics of the E_2 perturbation energy. Kutzelnigg and Morgan [30] have recently generalized Schwartz's finding to pair functions of many electronic states. Total energies of $1s^2$ helium (obtained from CI wave functions reaching to $L=11$) have been analyzed by Carroll, Silverstone, and Metzger [31] to obtain the following fit for the L increments of the CI energy.

$$\Delta E(L)=A_0\lambda^4+A_1\lambda^5+O(\lambda^6)\ , \tag{18}$$

with $A_0=-0.074$ and $A_1=-0.031$. Hill [32] has demonstrated the coefficients in (18) to be connected to integrals over the restriction of the helium eigenfunction $\psi(r_1,r_2,r_{12})$ to the line $(r_1=r_2=r,r_{12}=0)$. Accurate numerical evaluation yielded $A_0=-0.074\,225\,7$ and $A_1=-0.030\,989$.

We refer to

$$\Delta E_k(L)=E_k(L)-E_k(L-1)\ ,\quad k=2,3,4,\ldots, \tag{19}$$

as the L increment [29,31] of the "truncated perturbation energy" $E_k(L)$ that results when wave functions $\psi_1,\psi_2,\ldots$ are cut off after angular momentum L. [For $L=0$, let $\Delta E_k(0)=E_k(0)$.] Clearly, the L increment of E_2 is identical to the partial-wave energy $\Delta E_2(L)$ Eq. (6). We use the following five-parameter Schwartz-type ex-

TABLE III. Extrapolation of E_2 perturbation energy by fitting partial-wave energies $\Delta E_2(L)$ to Schwartz-type expression (20). Energies in 10^{-6} charge scaled atomic units.

L_0	$E_2(L_0)$[a]	Support points (L values)	E_2 (extrap)[b]
5	−157 403.950 033	1,2,3,4,5	−157 666.423[c]
10	−157 622.851 979	2,4,6,8,10	−157 666.4274[c]
15	−157 652.193 378	7,9,11,13,15	−157 666.429 34[c]
20	−157 660.120 259	12,14,16,18,20	−157 666.429 36[c]
"Exact," Ref. [26]	−157 666.429 469 14		

[a] Sum ($0 \leq L \leq L_0$) of calculated $\Delta E_2(L)$ from Table I.

[b] Partial-wave energies for $L_0+1 \leq L \leq \infty$ taken from fit.

[c] Coefficients to Eq. (20) read: $L_0=5$: $a_0=-0.175\,530$, $a_1=-0.007$, $a_2=-0.296$, $a_3=-0.41$; $L_0=10$: $a_0=-0.175\,658$, $a_1=-0.0041$, $a_2=0.274$, $a_3=-0.34$; $L_0=15$: $a_0=-0.175\,773$, $a_1=-0.0004$, $a_2=0.229$, $a_3=-0.10$; $L_0=20$: $a_0=-0.175\,780$, $a_1=-0.00008$, $a_2=0.222$, $a_3=-0.038$. Exact expansion coefficients, known from theory [12,30] read $a_0=-45/256=-0.175\,781\,25$, $a_1=0$, $a_2=-(5/4)a_0=0.219\,72\ldots$, $a_3=0$.

pression for fitting energy increments of both E_2, E_3, and E_4:

$$\Delta E_k(L)=\lambda^4[a_0+a_1\lambda+a_2\lambda^2+a_3\lambda^3+a_4\lambda^4] \ . \tag{20}$$

Results for the second-order energy (based on the data of Table I) are given in Table III. We note that the full expansion of $\Delta E_2(L)$ in powers of λ is expected to be an asymptotic (semiconvergent) series [23]. The leading four coefficients of ΔE_2 (belonging to λ^4 through λ^7) are known exactly [12,23,30]. The fit is seen to furnish a good value for a_0 and to show a steady behavior for the higher coefficients as the support for the fit moves to higher L. Summing (20) over the range $L_0+1<L\leq\infty$ and adding the sum to the "truncated energy" [sum of $E_2(L)$ over $L=0,\ldots,L_0$] furnishes extrapolated values of good quality (last column of Table III). These estimates are, in fact, not inferior to E_2 values from the explicit calculation using the wave function (15) for $\psi_1(L>L_0)$.

TABLE IV. Extrapolation of E_3 perturbation energy by fitting energy increments $\Delta E_3(L)$ to Schwartz-type expression (20). Energies in 10^{-6} charge scaled atomic units.

L_0	$E_3(L_0)$[a]	Support points (L values)	E_3 (extrap)[b]
5	8337.215 532	1,2,3,4,5	8699.145[c]
9	8615.627 245	1,3,5,7,9	8699.018[c]
10	8635.900 418	2,4,6,8,10	8699.023
11	8650.115 428	3,5,7,9,11	8699.0280
12	8660.371 948	4,6,8,10,12	8699.0300[c]
13	8667.955 020	5,7,9,11,13	8699.0307[c]
14	8673.680 637	6,8,10,12,14	8699.030 95[c]
15	8678.083 665	7,9,11,13,15	8699.031 14[c]
"Exact," Ref. [26]	8699.031 528		

[a] Explicitly calculated values from Table II.

[b] Increments for $L_0+1 \leq L \leq \infty$ obtained through fit.

[c] Coefficients to Eq. (20) read: $L_0=5$: $a_0=0.266\,18$, $a_1=-0.125$, $a_2=-0.98$, $a_3=1.5$; $L_0=9$: $a_0=0.265\,36$, $a_1=-0.1138$, $a_2=-1.04$, $a_3=1.6$; $L_0=12$: $a_0=0.265\,83$, $a_1=-0.1270$, $a_2=-0.912$, $a_3=1.1$; $L_0=15$: $a_0=0.265\,95$, $a_1=-0.1315$, $a_2=-0.845$, $a_3=0.68$. Exact expansion coefficient a_1, known from theory [30] is $a_1=-0.134\,287$.

Corresponding results (Tables IV and V) for E_3 and E_4 exhibit a sufficiently steady behavior of the fit. Inspection reveals somewhat poorer stability than in the E_2 case. The cause may lie in the numerical $E_3(L_0)$ and $E_4(L_0)$ increments, the errors of which arise by superposition of the residual errors of all partial waves of ψ_1 and (for the E_4) of ψ_2. The E_3 (extrap) are found to be of similar quality as the "explicitly calculated" values of Table II. Altogether, extrapolation using (20) is able to reduce the errors of the truncated E_2, E_3, and E_4 (at the level of $L_0=10$) by factors between 0.4×10^{-4} and 3×10^{-4}, that is by three or four orders of magnitude.

The coefficients of the leading terms of the asymptotic expansion can be estimated as follows:

$$\Delta E_3(L)=0.2660\lambda^4-0.133\lambda^5-0.81\lambda^6+O(\lambda^7) \ , \tag{21}$$

$$\Delta E_4(L)-0.1397\lambda^4-0.18\lambda^5+1.0\lambda^6+O(\lambda^7) \ . \tag{22}$$

The exact value of the λ^5 coefficient of ΔE_3 has recently been deduced from theory [30] to be $-0.134\,287$.

Extending Eq. (20) by two more powers of λ is found to slightly improve the extrapolated energies. Yet, as to be expected, the fit become more sensitive to inaccuracies of the input data. We have, in addition, tested the seven-parameter Padé-type quotient

$$P(\lambda)=a_0\lambda^4\frac{1+p_1\lambda+p_2\lambda^2+p_3\lambda^3}{1+q_1\lambda+q_2\lambda^2+q_3\lambda^3} \tag{23}$$

on the same data as above. The overall Padé results differ little from those of the seven-parameter polynomial fit. Taylor coefficients $a_0,a_1,a_2,\ldots$ extracted from (23) turn out to be more stable than those resulting from the poly-

TABLE V. Fourth-order energy calculated in terms of partial waves. $E_4(L_0)$ results when both ψ_1 and ψ_2 are truncated after $L=L_0$. Extrapolation by fitting $E_4(L_0)$ increments to Schwartz-type expression (20) furnishes the values of the last column. Energies in 10^{-6} charge scaled atomic units.

L_0	$E_4(L_0)$	Support points (L values)	E_4 (extrap)
0	-3009.8307[a]		
1	66.4394		
2	-185.1562		
3	-477.2226		
4	-640.5218		
5	-730.6115	1,2,3,4,5	-889.287[e]
6	-782.7864		
7	-814.6491		
8	-835.0554		
9	-848.6698	1,3,5,7,9	-888.703[e]
10	-858.0749	2,4,6,8,10	-888.698[e]
11	-864.7684	3,5,7,9,11	-888.702[e]
12	-869.6556	4,6,8,10,12	-888.705[e]
Scherr and Knight[b]	-888.587		
Midtdal[c]	-888.7045		
"Exact," Baker *et al.*[d]	$-888.707\,284\,2$		

[a] Fourth-order perturbation energy of the "radial approximation"; an older estimate [28] is -3010.07.

[b] Reference [2].

[c] Reference [24], extrapolated value.

[d] Reference [26].

[e] Coefficients to Eq. (20) read: $L_0=5$: $a_0=-0.1436$, $a_1=0.230$, $a_2=0.93$, $a_3=-2.1$; $L_0=9$: $a_0=-0.1392$, $a_1=0.163$, $a_2=1.30$, $a_3=-2.9$; $L_0=10$: $a_0=-0.1390$, $a_1=0.158$, $a_2=1.35$, $a_3=-3.2$; $L_0=11$: $a_0=-0.1392$, $a_1=0.163$, $a_2=1.30$, $a_3=-2.9$; $L_0=12$; $a_0=-0.1394$, $a_1=0.168$, $a_2=1.24$, $a_3=-2.6$.

nomial fit (20). The values of the coefficients given in (21), (22) have been obtained in this way.

Finally, for the L increment of the total energy of helium ($Z=2$), using coefficients from Table III, Eqs. (21) and (22), and disregarding perturbation orders $k>4$, one obtains the following large L behavior that is not too different from the known result (18):

$$\Delta E_2(L)+\tfrac{1}{2}\Delta E_3(L)+\tfrac{1}{4}\Delta E_4(L)$$
$$=-0.0777\lambda^4-0.021\lambda^5+0.06\lambda^6\ . \qquad (24)$$

V. CONCLUSION

Individual partial waves of the first- and second-order $1s^2$ wave function have been calculated with high accuracy. We have applied a finite-element procedure that uses L-projected Hylleraas functions as local basis functions for a one-dimensional sequence of finite elements. Asymptotic partial waves $L \gg 1$ have been covered by a closed expression as in Kutzelnigg's method [23], now using the two-parameter variational form (15).

The calculations have furnished L increments for the third- and fourth-order energies E_3 and E_4 that were not available previously. Fitting the increments to the Schwartz-type expression (20) leads to extrapolated E_3 and E_4 values that are by three to four orders of magnitude more accurate than the underlying "L-truncated" values. L extrapolation works well also for the second-order energy. The steadiness of the extrapolation is found to depend crucially on the accuracy of the explicitly calculated partial waves $L \le L_0$. Extrapolation in L [11,12,29] is of interest for applications to larger atoms since L-truncated energies are accessible without difficult integrations.

According to Carroll, Silverstone, and Metzger (Ref. [31]), *total* energies of the helium atom can be L extrapolated with fair success, provided that L-truncated energies of good quality are available. The CI wave functions of Ref. [31] are composed of products $f(r_1)g(r_2)$. By employing basis functions written in terms of $r<$ and $r>$ (also the present finite-element form of such functions) one could try to enhance the accuracy of L-truncated variational energies of atoms and, thus, further explore L extrapolation.

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