Two-electron atoms: o(4,2) operator replacements and large-order perturbation theory with respect to the replaced kinetic-energy operator

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The Schrödinger equation for two-electron atoms is transformed into an alternative equation depending on a free dimensionless parameter β, according to the method of o(4,2) operator replacements. These operator replacements are well defined except for the case where both the orbital and spin momenta are zero, i.e., except for singlet S states. When β goes to positive infinity, the solutions of this present equation should correspond to the solutions of the Schrödinger equation. When β goes to negative infinity, the present equation becomes exactly solvable. These exact solutions are the zero-order solutions for a Rayleigh-Schrödinger perturbative expansion where the perturbation is the nondiagonal part of the replaced kinetic-energy operator. An essential property of this method is that the perturbative operator is bounded, and therefore the convergence radius of the series is nonzero. The method is purely nonvariational. A numerical application for the triplet S even-parity ground-state helium atom is performed.

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I. INTRODUCTION

The recently introduced method of o(4,2) operator replacements [1] has been used to study the properties of two-electron atoms [1,4]. This method transforms the Schrödinger equation into a new equation depending on a free dimensionless parameter β. This alternative equation will be referred to as the replaced equation below. When β goes to positive infinity, the solutions of the replaced equation should correspond to the solutions of the Schrödinger equation.

Some eigenvalues of the replaced equation have been studied with the use of numerical diagonalization in a truncated basis [1]. This method is well suited to the determination of eigenvalues corresponding to finite β values. A disadvantage of this procedure is that a calculation has to be carried out for each different finite β value, and the extrapolation to the limit where β goes to positive infinity has to be done from the results corresponding to finite β values.

The present paper describes a way to obtain the β-dependent solutions and in particular the physical solutions corresponding to the limit where β goes to positive infinity. The starting point is the fact that, at the limit where β goes to negative infinity, the replaced equation becomes exactly solvable. These solutions are the zero-order solutions for a Rayleigh-Schrödinger large-order perturbative expansion. The perturbative operator is proportional to the nondiagonal part of the replaced kinetic-energy operator. The parameter that measures the strength of the perturbation is $\exp(\beta)$. An essential result is that the perturbative operator is bounded. As a result, it follows [5,6] that the radius of convergence of the perturbation series is nonzero if the zero-order solution is an isolated eigenvalue. The fundamental problem thus is reduced to an analytic continuation along the positive real axis of a function of $\exp(\beta)$, a power series for which is known a Taylor expansion in the vicinity of the point $\exp(\beta)=0$.

In the present paper the possibility to carry out effectively this analytic continuation from the numerical computation of a finite set of the coefficients of the perturbation series is considered. The numerical application performed in this paper is mainly exploratory. It concerns the triplet S even-parity ground state of the helium atom. The zero-order solution for this state is nondegenerate and thus the Rayleigh-Schrödinger perturbative method for the nondegenerate case has been used. (See, e.g., Ref. [7].) Up to 50 nonzero terms of the series for the energy expanded in powers of $\exp(\beta)$ have been calculated. The coefficients of the series are easily obtained due to the three following facts. First, the zero-order basis is discrete, and thus the problems connected with the handling of continuum, which are present when the zero-order Hamiltonian is a hydrogenic one, are completely avoided. Second, the action of the perturbative operator on an arbitrary zero-order basis vector yields a linear combination involving only a finite number of zero-order basis vectors. The problem of infinite summation for the computation of the perturbative series is thus also avoided. Third, the matrix elements of the perturbative operator in the zero-order basis are explicitly known and extremely simple. The three above properties trace back to the fact that all the replaced operators are expressed in terms of o(4,2) generators and to the fact that the zero-order basis is directly related to discrete unitary irreducible representations of o(4,2).

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II. GENERAL FORMULATION

The method of o(4,2) operator replacements is only very briefly recalled here since it has been described in much details elsewhere [1]. The emphasis is on the perturbative approach. The Schrödinger equation for a two-electron atom in the limit of infinite nucleus mass and for nuclear charge Z, is

$$\left[\frac{p^2}{2}-\frac{Z}{r}+\frac{p'^2}{2}-\frac{Z}{r'}+\frac{1}{|\mathbf{r}-\mathbf{r}'|}-E\right]|\Psi\rangle=0 . \quad (1)$$

Atomic units are used. The symbols $\mathbf{r},\mathbf{p}$ denote the position and momentum operators associated with an electron. The prime refers to the second electron. The above equation can be considered within the o(4,2) algebra framework because a realization of this algebra in terms of position and momentum operators has been obtained (see, e.g., Refs. [1,8–12]):

$$\mathbf{a}(\beta)\equiv\exp(-\beta)[\tfrac{1}{2}\mathbf{r}p^2-\mathbf{p}(\mathbf{r}\cdot\mathbf{p})]-\tfrac{1}{2}\exp(\beta)\mathbf{r} ,$$

$$\mathbf{l}\equiv\mathbf{r}\times\mathbf{p} ,$$

$$\mathbf{g}\equiv r\mathbf{p} ,$$

$$t_2\equiv rp_r ,$$

$$\mathbf{b}(\beta)\equiv\mathbf{a}(\beta)+\exp(\beta)\mathbf{r} ,$$

$$t_1(\beta)\equiv r[\exp(-\beta)p^2-\exp(\beta)]/2 ,$$

$$t_3(\beta)\equiv r[\exp(-\beta)p^2+\exp(\beta)]/2 .$$

The above operators indeed satisfy the commutation relations characterizing an o(4,2) algebra. The o(4,2) generators are Hermitian. It is emphasized that the terms Hermitian, unitary, and normalized imply in this paper $1/r$ scalar product [or $1/(rr')$ scalar product when both electrons are considered]. The so-called o(4,2) operator replacements [1,13] are the following:

$$r\rightarrow 2\exp(-\beta)t_3(\beta) ,$$

$$\mathbf{r}\rightarrow -2\exp(-\beta)\mathbf{a}(\beta) ,$$

$$\mathbf{p}\rightarrow\exp(\beta)t_3^{-1}(\beta)\mathbf{g}/2 ,$$

$$\mathbf{p}^2\rightarrow\exp(2\beta)[t_3^{-1}(\beta)t_1(\beta)+1]/2 .$$

If one goes back to the expression in terms of r and p, the above r replacement, for example, gives $r\rightarrow r[1+\exp(-2\beta)p^2]$. It is thus apparent that the solution of the replaced problem is expected to converge to the solution of the initial problem if the limit β going to positive infinity is taken at the end of the calculations. According to the operator replacements described above, the Schrödinger equation (1) is transformed into Eq. (2):

$$\{\exp(\beta)T(\beta)+2[-Z(1/t_3(\beta)+1/t_3'(\beta))+1/A(\beta)] -\mathcal{E}(\beta)\}[t_3(\beta)t_3'(\beta)]^{1/2}|\Psi(\beta)\rangle=0 , \quad (2)$$

$$T(\beta)\equiv[t_3(\beta)]^{-1/2}t_1(\beta)[t_3(\beta)]^{-1/2} +[t_3'(\beta)]^{-1/2}t_1'(\beta)[t_3'(\beta)]^{-1/2} , \quad (3)$$

$$A(\beta)\equiv|\mathbf{a}(\beta)-\mathbf{a}'(\beta)| , \quad (4)$$

$$\mathcal{E}(\beta)\equiv[4\exp(-\beta)E(\beta)-2\exp(\beta)] , \quad (5)$$

where $T(\beta)$ is Hermitian. In Eq. (2), we consider $\mathcal{E}(\beta)$ as the eigenvalue and $[t_3(\beta)t_3'(\beta)]^{1/2}|\Psi(\beta)\rangle$ as the eigenvector. The physical energy is obtained by considering the limit of $E(\beta)$ [see Eq. (5)] when β goes to positive infinity.

The replaced equation (2) is well defined except for the case where both the total orbital angular momentum and the total spin are zero. The difficulty for this singlet S case originates [1] from the fact that the operator defined by Eq. (4), corresponding to the operator of an interelectronic distance, has zero among its eigenvalues in the subspace of states with orbital and spin momenta equal to zero, and therefore is not invertible.

An orthonormal basis for two-electron states of definite parity π, total orbital angular momentum L with projection M on an arbitrary axis, and total spin S has been described in Ref. [1]. The vectors of this basis are denoted $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$. The projection of the spin S is not explicitly displayed in this notation. The ket notation does not include spin space. Specifically, if P denotes the two-electron permutation operator, one has

$$P|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle =(-1)^S|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle .$$

The symbols n,n' are nonzero positive integers. The symbols J_1,J_2 are the numbers associated with the coupling of two angular momenta with quantum numbers $(n-1)/2,(n'-1)/2$. Depending on the n,n' values, J_1,J_2 are therefore integers or half integers. The coupling of J_1,J_2 yields the total orbital angular momentum L. With the further following restrictions

$$n\geq n',\ J_1\geq J_2,\ J_1\neq J_2 \ \text{ if } \pi\neq(-1)^L , \quad n\neq n' \ \text{ if } \pi\neq(-1)^{J_1+J_2+S} , \quad (6)$$

the infinite set of vectors $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$ provides an orthogonal basis for two-electron atomic states. Useful relations are the following:

$$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle =\pi(-1)^{J_1-J_2+S}|(n',n,J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle , \quad (7)$$

$$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle =\pi(-1)^{J_1-J_2+L}|(n,n',J_2,J_1,{}^{2S+1}L^{\pi},M)\beta\rangle . \quad (8)$$

For more details, we refer to Ref. [1].

The important fact is that all operators appearing in Eq. (2), except $T(\beta)$, are diagonal in this basis. Specifically, $1/t_3(\beta)+1/t_3'(\beta)$ has eigenvalues equal to $1/n+1/n'$; $1/A(\beta)$ has eigenvalues equal to $\{2[J_1(J_1+1)+J_2(J_2+1)]-L(L+1)\}^{-1/2}$. The only nondiagonal operator is $T(\beta)$, whose explicit action on the vectors $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$ is given by Eqs. (20, 21) of Ref. [1]. It can be seen from these equations that T changes n,n' by unity and J_1,J_2 by one-half. It is important to note that all matrix elements of the β-dependent operators in the β-dependent basis

$|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$ are β *independent.* If we consider Eq. (2) expressed in the basis $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$, we can suppress the β dependence in the operator *and* in the basis vectors. Thus Eq. (2) can be written as

$$\{\exp(\beta)T+2[-Z(1/t_3+1/t_3')+1/A] - \mathcal{E}(\beta)\}[t_3t_3']^{1/2}|\Psi\rangle=0 . \quad (9)$$

In Eq. (9), the abstract β-independent operators T, t_3, t_3', and A are defined as the operators having the same matrix elements in the separable Hilbert space spanned by the abstract orthonormal basis $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\rangle$ as the β-dependent operators $T(\beta)$, $t_3(\beta)$, and $t_3'(\beta)$ have in the separable Hilbert space spanned by the basis $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\beta\rangle$. It is now clear that in the limit where β goes to negative infinity, the eigenvalue problem becomes exactly solvable. The unperturbed operator has only a point spectrum corresponding to the eigenvalues

$$\mathcal{E}(-\infty)=2(-Z(1/n+1/n')+\{2[J_1(J_1+1)+J_2(J_2+1)]-L(L+1)\}^{-1/2}) . \quad (10)$$

For $\exp(\beta)$ different from zero, T is the perturbing operator with $\exp(\beta)$ as the parameter that measures the strength of the perturbation. As all matrix elements of all operators are known, the Rayleigh-Schrödinger series can be calculated for a given initial unperturbed state. We consider from now on the case where the zero-order eigenvalue $\mathcal{E}(-\beta)$ is nondegenerated. It can be seen from the explicit action of the operator T on the basis vectors $|(n,n',J_1,J_2,{}^{2S+1}L^{\pi},M)\rangle$ that in the expansion of $\mathcal{E}(\beta)$ in powers of $\exp(\beta)$, all odd powers are zero. This can be seen immediately if, for example, one notes that as a result of the action of the operator T [explicit formulas for it are given by formula (21) of Ref. [1]] the sum $n+n'$ changes its parity. Therefore, the projection of a given state on the state obtained after m-fold application of operator T to this state is certainly zero if m is an odd number. It follows then from Eq. (5) that the expansion for $E(\beta)$ can be written as

$$E(\beta)=c_1z+\tfrac{1}{2}z^2+\sum_{j=1}^{\infty}c_{2j+1}z^{2j+1} , \quad (11)$$

$$z\equiv\exp(\beta) , \quad (12)$$

$$c_1=\mathcal{E}(-\infty)/4 . \quad (13)$$

The notation z for $\exp(\beta)$ will be retained in the rest of this paper. The calculation of the Rayleigh-Schrödinger series has been made for the triplet S even-symmetry ground state of helium: $Z=2$, $n=2$, $n'=1$, $J_1=J_2=\frac{1}{2}$. The coefficients c_{2j+1} for j between 0 and 50 are reported in Table I.

III. ANALYTIC CONTINUATION

A fundamental property of the Hermitian perturbing operator T is that it is bounded (and therefore self-adjoint). This essential property is common to all operators acting in a separable Hilbert space and that can be described in a given orthonormal basis by a matrix, all elements of which are zero except a finite set of nonzero-bounded elements on each column and on each row. (See, e.g., Ref. [14].) As a result, the Rayleigh-Schrödinger series has a nonzero radius of convergence if the unperturbed eigenvalue is isolated and has finite multiplicity [5,6].

The Rayleigh-Schrödinger perturbation theory produces the Taylor expansion of the energy E as a function of the complex variable z near the point $z=0$. This defines a germ for an analytic function, and the basic problem reduces to the determination of an analytic continuation along the real axis, outside the circle of convergence. Of course only a finite number of coefficients of the Taylor series can be computed. The coefficients of the series are reported in Table I. The only nonzero even-order coefficient is $c_2=\frac{1}{2}$. This section is devoted to extraction of the information contained in Table I. These coefficients were obtained by using double precision on a Cray computer. Double precision is necessary for performing the subsequent Euler transformation discussed below. The double-precision results of Table I modify at most the last three digits of the results that are obtained with single precision. Thus one can reasonably expect that the coefficients of Table I are accurate up to 25 digits.

The first interesting point in Table I is that the series is alternating for odd powers of z (except for the coefficient c_1). If the series continues to be alternating up to infinite order, this means (see, i.e., Ref. [15]) that there exists a singularity at $z^2=-\rho$ where ρ denotes the radius of convergence of the function S of the variable z^2:

$$S(z^2)\equiv E/z-z/2=\sum_{j=0}^{\infty}C_j(z^2)^j , \quad (14)$$

with $C_j\equiv c_{2j+1}$ and E defined by Eq. (11). In order to determine the radius of convergence of the function S, we have performed a so-called Neville-Richardson analysis of the Cauchy ratios C_j/C_{j-1}. This means that we are looking for an expansion in inverse powers of j for the Cauchy ratios:

$$C_j/C_{j-1}=a_0+a_1/j+a_2/j^2+\cdots . \quad (15)$$

Specifically, a_0 is determined by recursive computation with respect to the index k of

$$r_j^{(k)}\equiv\{jr_j^{(k-1)}-(j-k)r_{(j-1)}^{(k-1)}\}/k , \quad (16)$$

with

$$r_j^{(0)}=C_j/C_{j-1} . \quad (17)$$

When a limit for a_0 has been obtained, the procedure is repeated with the starting value $r_j^{(0)}=[C_j/C_{j-1}-a_0]j$.

When applied to the coefficients C_j of Table I, this procedure appears to be surprisingly stable. Thus the radius of convergence ρ in terms of the variable z^2 is found to be approximately

TABLE I. Coefficients of the expansion of the energy $E=c_1z+\frac{1}{2}z^2+\sum_{j=1}^{\infty}c_{2j+1}z^{2j+1}$ in powers of $\exp\beta$, where $c_2=\frac{1}{2}$, $c_{2j}=0$ if $j\geq 2$. The numbers in brackets denote multiplicative powers of ten.

$2j+1$	$c_{2j+1}\equiv C_j$
1	−0.121 132 486 540 518 711 774 542 560 97[E+01]
3	−0.285 293 148 066 891 740 036 261 497 21[E+00]
5	0.438 305 035 184 204 386 220 701 928 80[E+00]
7	−0.176 920 713 916 245 686 125 518 609 99[E+01]
9	0.932 083 228 945 964 420 906 344 933 71[E+01]
11	−0.559 294 916 901 944 288 894 007 786 25[E+02]
13	0.362 544 729 012 304 365 050 018 249 92[E+03]
15	−0.247 331 529 647 765 159 852 114 492 90[E+04]
17	0.174 974 421 462 754 801 496 447 698 49[E+05]
19	−0.127 192 312 063 452 219 203 982 807 31[E+06]
21	0.944 265 790 071 862 360 087 433 975 35[E+06]
23	−0.712 903 821 582 965 564 844 170 359 67[E+07]
25	0.545 674 911 309 983 803 676 256 039 79[E+08]
27	−0.422 477 000 466 163 450 936 754 387 25[E+09]
29	0.330 270 815 066 127 114 605 479 410 00[E+10]
31	−0.260 335 195 040 916 108 810 454 258 40[E+11]
33	0.206 685 384 064 432 605 691 859 474 66[E+12]
35	−0.165 123 982 019 372 342 693 443 268 40[E+13]
37	0.132 651 630 452 687 017 904 154 386 29[E+14]
39	−0.107 090 121 235 737 436 140 123 755 70[E+15]
41	0.868 351 071 444 561 870 862 407 576 43[E+15]
43	−0.706 901 705 266 633 674 838 349 519 40[E+16]
45	0.577 532 616 276 005 566 328 168 996 54[E+17]
47	−0.473 376 040 215 149 933 801 599 787 94[E+18]
49	0.389 157 380 839 208 539 046 733 332 43[E+19]
51	−0.320 793 751 596 056 475 864 110 652 58[E+20]
53	0.265 102 293 923 121 426 611 400 411 01[E+21]
55	−0.219 585 823 783 451 574 786 964 711 39[E+22]
57	0.182 273 667 667 019 437 734 157 016 22[E+23]
59	−0.151 602 360 289 412 845 505 056 889 69[E+24]
61	0.126 325 448 714 772 501 602 800 261 75[E+25]
63	−0.105 444 762 839 966 542 001 450 341 33[E+26]
65	0.881 576 634 696 275 144 576 887 752 16[E+26]
67	−0.738 162 835 024 677 703 971 276 569 07[E+27]
69	0.618 958 418 302 552 504 955 714 392 33[E+28]
71	−0.519 698 703 326 621 665 518 877 539 11[E+29]
73	0.436 907 437 102 090 819 637 788 147 00[E+30]
75	−0.367 743 022 684 962 439 022 759 969 77[E+31]
77	0.309 876 520 777 438 310 281 449 896 89[E+32]
79	−0.261 394 450 231 280 329 310 993 846 36[E+33]
81	0.220 721 040 907 891 010 142 839 592 29[E+34]
83	−0.186 555 816 623 609 518 394 482 358 23[E+35]
85	0.157 823 312 506 751 711 061 891 728 33[E+36]
87	−0.133 632 436 742 868 938 576 927 611 63[E+37]
89	0.113 243 527 205 719 985 464 717 360 36[E+38]
91	−0.960 415 697 765 081 030 775 683 895 18[E+38]
93	0.815 143 674 450 240 841 418 035 191 44[E+39]
95	−0.692 347 000 093 849 356 554 200 638 13[E+40]
97	0.588 457 101 344 603 442 629 795 416 82[E+41]
99	−0.500 489 053 257 527 195 117 421 928 59[E+42]
101	0.425 942 865 860 196 052 285 713 073 09[E+43]

$$\rho\approx 0.113\,959\,189\,957\,3\ . \tag{18}$$

If the series S is dominated by a singularity of the type $(\rho+z^2)^{\alpha}$, the exponent α will be given by $\alpha=-a_1/a_0-1$. The Neville-Richardson analysis of the coefficients of Table I gives $\alpha\approx 0.500\,000\,000$.

To summarize, we conclude that the series S has a square-root branch-point singularity on the circle of convergence at $z^2\approx -0.113\,959\,189\,957\,3$. This result is also supported by Padé analysis of the series S. For the numerical computations of Padé approximants to the series S, it is convenient to introduce a scaled variable

$$u=sz^2 \tag{19}$$

so that the coefficients of the expansion of the function S in the variable u be approximately of the same order of magnitude. This is obtained by choosing $s=8$, for example. There is a succession of poles and zeros of the Padé approximants on the negative real axis of the z^2 plane. This succession of alternating poles and zeros corresponds to a cut, as usual in Padé analysis of functions with branch points [16]. The pole closest to the origin moves toward the point $z^2=-\rho$ as the order of the diagonal Padé approximants increases. In order to get more information on the series S, in particular concerning the location and nature of other possible singularities, we also have performed a Padé analysis on the second-order logarithmic derivative [17], on the series obtained from the series S by dividing each coefficient by the coefficient of the series associated with $(1+z^2)^{1/2}$ [18] and finally used the so-called GJ3 analysis [16]. No definitive conclusions have been presently obtained.

The analytic continuation has been done by means of a Euler transformation (see, e.g., Ref. [19]) as follows. The Euler transformation is produced by the change of variables

$$u\equiv sz^2=y/(1-ey)\ . \tag{20}$$

The parameters s and e of this change of variables will be qualified as scaling parameter and Euler parameter, respectively. When z^2 increases from zero to infinity on the real axis, y increases from zero up to $1/e$. If all the singularities on the z^2 plane are on the negative real axis at a distance from the origin larger or equal to the radius of convergence given by Eq. (18), it is seen that with the choices $e=1$ and $s=8$, for example, that there are no singularities in the y plane inside the circle $|y|=1/e$. These values of the parameters will be retained in all subsequent calculations. These choices are not critical. Other values can be chosen; the essential point is that the final series for the energy as a series in powers of y converges inside the circle $|y|=1/e$. The energy can be expressed as a function of y as

$$E=c_1(s)\sqrt{y/(1-ey)}+c_2(s)y/(1-ey)+[y/(s(1-ey))]^{3/2}F(y)\ , \tag{21}$$

$$F(y)\equiv s^{3/2}\sum_{j=0}^{\infty}C_{j+1}(s)u^j \tag{22}$$

$$=\sum_{j=0}^{\infty}f_jy^j\ , \tag{23}$$

$$c_j(s)\equiv c_j/s^{j/2},\quad C_j(s)\equiv c_{2j+1}(s)\ . \tag{24}$$

The function $F(y)$ is analytic inside the circle $|y|=1/e$. Numerical calculation of energy with the use of expansion for $F(y)$ in the vicinity of point $y=1/e$ is difficult, since at the vicinity of this point a mutual compensation of different terms becoming large when y tending to $1/e$ takes place. One can explicitly take into account this compensation, having introduced a new function $G(y)$ according to

$$F(y)=(1-ey)^{3/2}G(y)-(s^{3/2})\times\{c_2(s)[e(1-ey)]^{1/2}+c_1(s)e(1-ey)\}\ , \tag{25}$$

through which energy is expressed as

$$E=c_1(s)\sqrt{y}\sqrt{1-ey}+c_2(s)y/(1+\sqrt{ey})+(y/s)^{3/2}G(y)\ . \tag{26}$$

According to Eq. (25) $G(y)$ is related to $F(y)$ according to

$$G(y)=F(y)[1-cy]^{-3/2}+s^{3/2}\times[c_2(s)\sqrt{e}/(1-ey)+c_1(s)e(1-ey)^{-1/2}] \tag{27}$$

$$=\sum_{j=0}^{\infty}g_jy^j\ . \tag{28}$$

Relation (27) shows that $G(y)$ is analytic inside the circle $|y|\le 1/e$. Expression (27) is much more convenient for calculation since all the terms remain bounded, y tending to $1/e$. All further numerical analysis is accomplished, assuming that $y=1/e$.

From an operational point of view, one first computes the coefficients f_j of the Taylor-series expansion of $F(y)$ near the point $y=0$ from Eqs. (21)–(23) and Table I. Afterwards one can calculate the coefficients g_j of the Taylor-series expansion of $G(y)$ near the point $y=0$ from Eqs. (27) and (28).

At this stage it is of interest to look at the function $G(y)$ corresponding to the exactly solvable case of a model atom with two noninteracting electrons. The function $G(y)$ for two independent electrons will be denoted $G_i(y)$ in order to avoid confusion with the case of two interacting electrons. The two-electron hydrogenic case is exactly solvable [1], and the energy is

$$E=\varepsilon(n)+\varepsilon(n')\ , \tag{29}$$

$$\varepsilon(k)=(z/4)\{z-\sqrt{z^2+(2Z/k)^2}\}\ . \tag{30}$$

The expansion of the squared roots in power series coincide with the Rayleigh-Schrödinger perturbative series. The function $G_i(y)$ for two noninteracting electrons can be obtained from Eqs. (21), (27), (29), and (30):

$$G_i(y)=\sqrt{1-ey}\,[s/(4y)][(1/\nu)+(1/\nu')]+[2(1-ey)]^{-1}\times\{\sqrt{se}-[s/(2y)][(1/\nu)\sqrt{1+((\nu^2/s)-e)y}+(1/\nu')\sqrt{1+((\nu'^2/s)-e)y}\,]\}\ , \tag{31}$$

where $\nu\equiv n/(2Z)$, $\nu'\equiv n'/(2Z)$. This function contains a squared-root singularity at $y=1/e$. The convergence near $y=1/e$ of the power series for this function $G_i(y)$ will be improved if one removes this singularity without changing the value $G_i(1/e)$. This is achieved by introducing the function $G_i^m(y)$:

$$G_i^m\equiv G_i(y)+(s/4)[(1/\nu)+(1/\nu')]\times\{-e+[1-\sqrt{1-ey}\,]/y\}\ . \tag{32}$$

The superscript m distinguishes this modified function from the original function G_i. In complete analogy, one expects that the convergence of the series $G(y)$ for the two interacting electrons can be improved if one introduces the function

$$G^m\equiv G(y)+(s/4)[-4c_1]\{-e+[1-\sqrt{1-ey}\,]/y\} \tag{33}$$

$$=\sum_{i=0}^{\infty}g_i^my^i\ , \tag{34}$$

with c_1 given by Eq. (13). One can verify that $G^m(1/e)=G(1/e)$. The convergence of the sequence

$$E_j(y)=c_1(s)\sqrt{y}\sqrt{1-ey}+c_2(s)y/(1+\sqrt{ey})+(y/s)^{3/2}\sum_{i=0}^{j}g_iy^i \tag{35}$$

has been found much more difficult to accelerate than the one of the sequence

$$E_j^m(y)=c_1(s)\sqrt{y}\sqrt{1-ey}+c_2(s)y/(1+\sqrt{ey})+(y/s)^{3/2}\sum_{i=0}^{j}g_i^my^i\ . \tag{36}$$

This indicates that a squared-root singularity at $y=1/e$ has been effectively removed for $E_\infty^m(y)$.

There are several methods for the acceleration of the convergence of sequences (see, e.g., Refs. [20,21]). Among the most effective nonlinear methods for the sequence $E_j^m(1/e)$, we found the so-called Levin's transformations and the so-called iterated Aitken transformation. The Levin's transformations can be expressed as [20]

$$L_k^{(j)}=\frac{\{\Delta^k[(j+b)^{k-1}S_j/g(j)]\}}{\{\Delta^k[(j+b)^{k-1}/g(j)]\}}\ , \tag{37}$$

where $S_{-1}=0$, S_j denotes the initial sequence, and Δ is the forward difference operator which acts on the index j only:

$$\Delta f_j\equiv f_{j+1}-f_j\ . \tag{38}$$

Among the three Levin transformations, usually called u,t,v transformations, we found that the v transformation accelerates the convergence slightly better than the other.

This Levin v transformation corresponds to the choice

$$g(j)=-\Delta S_{j-1}\Delta S_j/\Delta^2 S_{j-1}\ . \tag{39}$$

For practical computation of Levin's v transformation, we use the computer program entitled MLEVINT contained in the flexible disk of Ref. [20] with the constant b equal to unity.

The first column of Table II contains the numbers of terms of the sequence. The second column is the nonaccelerated sequence of the partial sum for the energy, E_j^m. See Eq. (36). Only two digits are printed in order to save space, but all digits of Cray double precision were used to produce the accelerated sequences of columns 3–6 from

TABLE II. Sequence of partial sums for the energy $E_j^m(1/e)$ and accelerated sequence by Levin's v transformation and Aitken's iterated transformation.

$j+1$	E_j^m	Levin $k=5$	Levin $k=15$	Aitken $k=5$	Aitken $k=10$
1	−0.56[E+00]	−0.561 26[E+00]	−0.561 26[E+00]	−0.561 26[E+00]	−0.561 26[E+00]
2	−0.68[E+00]	−0.561 26[E+00]	−0.561 26[E+00]	−0.675 85[E+00]	−0.675 85[E+00]
3	−0.77[E+00]	−0.502 02[E+00]	−0.502 02[E+00]	−0.109 83[E+01]	−0.109 83[E+01]
4	−0.84[E+00]	−0.629 45[E+00]	−0.629 45[E+00]	−0.121 47[E+01]	−0.121 47[E+01]
5	−0.91[E+00]	−0.432 67[E+00]	−0.432 67[E+00]	−0.164 64[E+01]	−0.164 64[E+01]
6	−0.96[E+00]	−0.935 33[E+00]	−0.935 33[E+00]	−0.172 29[E+01]	−0.172 29[E+01]
7	−0.10[E+01]	0.801 97[E+01]	0.801 97[E+01]	−0.197 67[E+01]	−0.197 67[E+01]
8	−0.11[E+01]	−0.260 98[E+01]	−0.224 80[E+01]	−0.200 71[E+01]	−0.200 71[E+01]
9	−0.11[E+01]	−0.246 09[E+01]	−0.244 24[E+01]	−0.220 30[E+01]	−0.220 30[E+01]
10	−0.11[E+01]	−0.237 63[E+01]	−0.230 21[E+01]	−0.211 38[E+01]	−0.211 38[E+01]
11	−0.12[E+01]	−0.232 44[E+01]	−0.226 05[E+01]	−0.213 11[E+01]	−0.213 11[E+01]
12	−0.12[E+01]	−0.228 96[E+01]	−0.222 90[E+01]	−0.213 97[E+01]	−0.213 97[E+01]
13	−0.12[E+01]	−0.226 52[E+01]	−0.221 14[E+01]	−0.212 90[E+01]	−0.213 49[E+01]
14	−0.13[E+01]	−0.224 74[E+01]	−0.219 89[E+01]	−0.215 92[E+01]	−0.213 69[E+01]
15	−0.13[E+01]	−0.223 40[E+01]	−0.219 15[E+01]	−0.217 06[E+01]	−0.213 48[E+01]
16	−0.13[E+01]	−0.222 37[E+01]	−0.218 60[E+01]	−0.216 86[E+01]	−0.217 04[E+01]
17	−0.13[E+01]	−0.221 57[E+01]	−0.218 27[E+01]	−0.217 00[E+01]	−0.216 94[E+01]
18	−0.14[E+01]	−0.220 93[E+01]	−0.218 03[E+01]	−0.217 07[E+01]	−0.216 67[E+01]
19	−0.14[E+01]	−0.220 41[E+01]	−0.217 89[E+01]	−0.217 13[E+01]	−0.216 79[E+01]
20	−0.14[E+01]	−0.219 99[E+01]	−0.217 79[E+01]	−0.217 18[E+01]	−0.216 87[E+01]
21	−0.14[E+01]	−0.219 64[E+01]	−0.217 72[E+01]	−0.217 23[E+01]	−0.216 90[E+01]
22	−0.15[E+01]	−0.219 35[E+01]	−0.217 67[E+01]	−0.217 26[E+01]	−0.216 87[E+01]
23	−0.15[E+01]	−0.219 11[E+01]	−0.217 63[E+01]	−0.217 29[E+01]	−0.217 46[E+01]
24	−0.15[E+01]	−0.218 91[E+01]	−0.217 61[E+01]	−0.217 32[E+01]	−0.217 46[E+01]
25	−0.15[E+01]	−0.218 74[E+01]	−0.217 59[E+01]	−0.217 34[E+01]	−0.217 46[E+01]
26	−0.15[E+01]	−0.218 59[E+01]	−0.217 57[E+01]	−0.217 36[E+01]	−0.217 46[E+01]
27	−0.15[E+01]	−0.218 46[E+01]	−0.217 56[E+01]	−0.217 38[E+01]	−0.217 53[E+01]
28	−0.16[E+01]	−0.218 35[E+01]	−0.217 56[E+01]	−0.217 40[E+01]	−0.217 52[E+01]
29	−0.16[E+01]	−0.218 26[E+01]	−0.217 55[E+01]	−0.217 41[E+01]	−0.217 52[E+01]
30	−0.16[E+01]	−0.218 18[E+01]	−0.217 54[E+01]	−0.217 42[E+01]	−0.217 52[E+01]
31	−0.16[E+01]	−0.218 11[E+01]	−0.217 54[E+01]	−0.217 43[E+01]	−0.217 52[E+01]
32	−0.16[E+01]	−0.218 05[E+01]	−0.217 54[E+01]	−0.217 44[E+01]	−0.217 52[E+01]
33	−0.16[E+01]	−0.217 99[E+01]	−0.217 54[E+01]	−0.217 45[E+01]	−0.217 52[E+01]
34	−0.16[E+01]	−0.217 94[E+01]	−0.217 53[E+01]	−0.217 45[E+01]	−0.217 52[E+01]
35	−0.16[E+01]	−0.217 90[E+01]	−0.217 53[E+01]	−0.217 46[E+01]	−0.217 52[E+01]
36	−0.17[E+01]	−0.217 86[E+01]	−0.217 53[E+01]	−0.217 47[E+01]	−0.217 52[E+01]
37	−0.17[E+01]	−0.217 83[E+01]	−0.217 53[E+01]	−0.217 47[E+01]	−0.217 52[E+01]
38	−0.17[E+01]	−0.217 80[E+01]	−0.217 53[E+01]	−0.217 48[E+01]	−0.217 52[E+01]
39	−0.17[E+01]	−0.217 78[E+01]	−0.217 53[E+01]	−0.217 48[E+01]	−0.217 52[E+01]
40	−0.17[E+01]	−0.217 75[E+01]	−0.217 53[E+01]	−0.217 48[E+01]	−0.217 52[E+01]
41	−0.17[E+01]	−0.217 73[E+01]	−0.217 53[E+01]	−0.217 49[E+01]	−0.217 52[E+01]
42	−0.17[E+01]	−0.217 71[E+01]	−0.217 53[E+01]	−0.217 49[E+01]	−0.217 52[E+01]
43	−0.17[E+01]	−0.217 70[E+01]	−0.217 53[E+01]	−0.217 49[E+01]	−0.217 52[E+01]
44	−0.17[E+01]	−0.217 68[E+01]	−0.217 52[E+01]	−0.217 49[E+01]	−0.217 52[E+01]
45	−0.17[E+01]	−0.217 67[E+01]	−0.217 54[E+01]	−0.217 50[E+01]	−0.217 52[E+01]
46	−0.18[E+01]	−0.217 66[E+01]	−0.217 52[E+01]	−0.217 50[E+01]	−0.217 52[E+01]
47	−0.18[E+01]	−0.217 64[E+01]	−0.217 53[E+01]	−0.217 50[E+01]	−0.217 52[E+01]
48	−0.18[E+01]	−0.217 63[E+01]	−0.217 52[E+01]	−0.217 50[E+01]	−0.217 52[E+01]
49	−0.18[E+01]	−0.217 63[E+01]	−0.217 36[E+01]	−0.217 50[E+01]	−0.217 52[E+01]

the input sequence of partial sums E_j^m. These double-precision inputs can easily be obtained from Table I by performing the Euler transformation. It is stressed, however, that these input double-precision data are affected by numerical rounding errors in the process of Euler transformation. Specifically, the loss of accuracy occurs when going from Eq. (22) to Eq. (23). Therefore about 25 digits should be reliable for the computation of only the first few terms of the sequence in the second column of Table II. The loss of accuracy for the coefficients f_j [see Eq. (23)] has been estimated. It increases with the order j of the coefficient f_j. We found, for example, that the f_{15} should be accurate to about 20 digits, f_{30} to about 15 digits, and f_{48} to about 7 digits.

If calculations were performed with an infinite number of digits, the natural choice would be to choose a number k in Eq. (37) as large as possible. Rounding errors, however, increase with k in practical computations due to the insufficient accuracy of the input data. The third column of Table II reports the values $L_0^{(0)}, L_0^{(0)}, L_1^{(0)}, L_2^{(0)}, \ldots, L_k^{(0)}, L_k^{(1)}, L_k^{(2)}, \ldots$, for $k=5$. The fourth column is for $k=15$. It is seen that the behavior of the last terms of the sequence in column 4 begins to be irregular, and we interpret this as the manifestation of numerical instabilities. For larger k values, the irregular behavior is amplified.

The iterated Aitken transformation can be described as [20]

$$X_{k+1}^{(j)} = X_k^{(j)} - \{[\Delta X_k^{(j)}]^2\} / \{\Delta^2 X_k^{(j)}\} , \tag{40}$$

with $X_0^{(j)} = S_j$. Again the forward difference operator acts only on the index j. For practical computation of the iterated Aitken transformation, we use the program entitled MIDELTA contained in the flexible disk of Ref. [20]. Column 5 of Table II reports the values $X_0^{(0)}, X_0^{(1)}, X_1^{(0)}, X_1^{(1)}, X_2^{(0)}, \ldots, X_k^{(0)}, X_k^{(1)}, X_k^{(2)}, \ldots$, for $k=5$. In the sixth column results for $k=10$ are presented. The result obtained by variational calculations [22] is $-2.175\,299\ldots$ a.u. We do not claim that we have selected the best methods for accelerating our series. Our purpose was to illustrate that a relative accuracy of the order of 10^{-5} can presently be obtained. In our opinion, however, significant improvement with final precision comparable with the most accurate variational calculation could be achieved by calculating coefficients of Table I with many more digits. The present limiting factor is the number of digits available for the coefficients c_j rather than the number of these coefficients.

IV. REMARKS AND PROSPECTS

If the o(4,2) operator replacements are carried out on the hydrogenic Hamiltonian, the replaced problem is exactly solvable for any β values [see Eq. (30)], and the limiting value of energies corresponds indeed to the hydrogenic one, $-Z^2/(2n^2)$. If the starting Hamiltonian is the Schrödinger Hamiltonian for two-electron atoms, the method of o(4,2) operator replacements can be carried out, except for the case of singlet S symmetry [1]. The results obtained in Ref. [1] and in the present work show that the limiting values of energies when β goes to positive infinity correspond within numerical accuracy to the correct results, as expected. It would be interesting to find the necessary and sufficient conditions that the initial Hamiltonian should satisfy in the general case in order for the o(4,2) operator replacements to give the correct answer in the limit where β goes to positive infinity.

The perturbative method described in this paper requires the usual modifications [7] when the zero-order eigenvalue [see Eq. (10)] is degenerated. A more subtle case occurs when the zero-order eigenvalue is not isolated. This occurs, for example, for the case of the singlet P odd state with $Z=2$, $n=2$, $n'=1$, $J_1=J_2=\frac{1}{2}$. The zero-order eigenvalue [Eq. (10)] is then equal to -4. This value is an accumulation point for the set of zero-order eigenvalues [Eq. (10)] corresponding to the cases $Z=2$, $n'=1$, $J_1=J_2=(n-1)/2$ in the limit where n goes to infinity.

The difficulties in accelerating the convergence of sequences, or, more generally, the difficulty in performing the analytic continuation up to infinity, could be resolved if the nature and location of other possible singularities of the functions could be detected from the numerical coefficients or from general arguments. The determination of the analytical continuation of perturbative series is of considerable interest not only for a precise determination of bound state or resonance energies, but also for a classification scheme. The evolution of the energies when $\exp(\beta)$ moving along the real axis in the complex plane from negative infinity to positive infinity provides a classification scheme, since the limit of negative infinity is exactly solvable. The usefulness of this classification depends of course on the complexity of the connection between the two limits [numbers and distributions of crossing or avoided crossing in the complex plane of $\exp(\beta)$]. Information about singularities in the plane $\exp(\beta)$ can be imported also when considering the problems connected with the chaotic behavior of a system. For a discussion of a connection of distribution of singularities and chaos see, e.g., Ref. [23].

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