

Nonrelativistic-energy Z -expansion coefficients for singly excited S and P states of two-electron ions

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Coefficients E_k in the Z -expansion series for $E(Z)$, where $E(Z)$ is the nonrelativistic total energy and Z the nuclear charge, are tabulated for singly excited $n(1^3S)$ and $n(1^3P)$ states of two-electron ions, $n = 2-5$. These results were obtained largely from an analysis of variational $E(Z)$ values given by Accad, Pekeris, and Schiff but were taken in some cases from variational-perturbation calculations of other authors. The Z -expansion estimates of nonrelativistic term values for ions with $Z \geq 11$ have been compared with the corresponding results of Ermolaev and Jones, and agreement within 1 or 2 parts in 10^7 was found for most states.

INTRODUCTION

The landmark 1971 paper¹ of Accad, Pekeris, and Schiff (hereafter APS I) on helium-sequence S and P states has become a standard reference for calculated properties of two-electron ions through nuclear charge $Z=10$. Recently, with the aim of facilitating extrapolations to still higher sequence members, these authors published an alternative tabulation² (hereafter APS II) of their computed energy levels in which values are listed to greater numbers of significant figures, reflect a more consistent choice of basis, and are given in the original atomic units. The APS II data permit in particular a more reliable determination of the E_k coefficients in the Z -expansion series³

$$E(Z) = E_0 Z^2 + E_1 Z + E_2 + E_3 Z^{-1} + \dots, \quad (1)$$

where $E(Z)$ is the nonrelativistic (NR) total energy. For $1s n l (1^3 L)$ states of two-electron systems, E_0 is given (in atomic units) by

$$E_0 = -\frac{1}{2}(1 + 1/n^2) \quad (2)$$

and the E_1 coefficients (which may be calculated exactly) have been tabulated to great precision.⁴ Values of the higher-order E_k are required in Z -expansion estimates of NR term values for high- Z ions and as input data for Z -expansion quantum-defect theory.⁵ The correlated, two-electron E_2 coefficients find further application in NR calculations of three-electron energies⁶ through second order in Z^{-1} .

The present study was undertaken to determine higher-order E_k coefficients for helium-sequence $n(1^3S)$ and $n(1^3P)$ states, $n=2-5$. All of these coefficients were obtained initially from an analysis of the Accad-Pekeris-Schiff energies; however, the results of variational-perturbation E_k calculations carried out by other authors proved to be of equal or greater accuracy in some cases, and the final tabulation lists preferred values for each

state. The NR ionization energies furnished for $Z \geq 11$ by the Z -expansion series are in acceptable agreement with (but probably more accurate than) the corresponding results of Ermolaev and Jones,⁷ who extrapolated the APS I data by a Padé-approximant technique.⁸

Atomic units are used throughout.

PROCEDURE

Estimates of the E_k coefficients for all states were first determined by fitting the Accad-Pekeris-Schiff $E(Z)$ values to a series of the form (1) through the differencing technique of Scherr, Silverman, and Matsen⁹; the details of this procedure are described by Blanchard and Drake.¹⁰ The APS II data were employed here except in the 4-5(1S) cases, for which the extrapolated APS I energies (of greater absolute accuracy) were used. The series-fit E_k were then compared where possible with E_k calculated directly from variational-perturbation theory^{11, 12} by other authors.¹²⁻¹⁸ As approximate E_2 coefficients furnished by either of these variationally-based approaches must be upper bounds to the exact NR values,¹² the most accurate calculation is that which yields the lowest E_2 value.

Variational-perturbation E_k have been computed to high order for the $2(1^3S)$, $3(1^3S)$, $2(1^3P)$, and $3(1^3P)$ states.¹²⁻¹⁷ Of these, only the 2-3(3S) values of Aashamar *et al.*^{15, 16} and the 2(3S) results of Sanders and Scherr¹⁷ were found to be distinctly more accurate than the corresponding series-fit E_k . The $2(1^3P)$ calculations of Sanders and Scherr¹⁷ proved to yield E_k coefficients nearly equivalent to those of the series-fit procedure, but here a "hybrid" method (described below) allowed refined E_2 estimates to be obtained from the APS II data. The E_k furnished by the remaining high-order variational-perturbation calculations were found to be considerably less accurate and have not been adopted.

Additional variational-perturbation results, extending only through E_3 , are available for nS and nP states^{17, 18} with $n=2-10$. Although restricted to low order, such values have the advantage of being given to greater numbers of significant figures than could be obtained by a differencing of the Accad-Pekeris-Schiff energies. In those cases for which consistency with the series-fit E_k was found, the variational-perturbation results were adopted and incorporated into the differencing procedure to increase the precision and extent of the series fit.

THE S STATES

The preferred E_k values appear in Table I. The sets of coefficients for the 2-3(³S) states are abbreviations of the more extensive tabulations given by Aashamar *et al.*,^{15, 16} whose 2(³S) values supersede those of Sanders and Scherr.¹⁷ Variational-perturbation E_2, E_3 coefficients for the $n(1,^3S)$ states through $n=10$ have also been calculated in preliminary, unpublished work by Sanders,¹⁸ and these proved sufficiently accurate to warrant adoption in several other instances. The remaining E_k were determined by fits to the APS II data except for the $n=4-5$ singlet states, for which the extrapolated APS I energies were employed. In the latter cases, the smaller number of significant figures given in the APS I tabulation precluded an extensive application of the differencing procedure; an average of the first-order differences¹⁰ for $Z=4-10$ was therefore used to determine the E_2 coefficients, the values E_3 through E_5 being adjusted for best fit to the data for $Z \geq 4$.

THE P STATES

The preferred E_k values are given in Table II. The most accurate P -state variational-perturbation calculations are those of Sanders and Scherr¹⁷ (hereafter SS), who employed a 100-term basis set to compute the E_k coefficients to high order for the 2(^{1,3}P) cases and through E_3 for the $n(1,^3P)$ states, $n=3-10$. In the 2(^{1,3}P) cases, a differencing of the APS II energies yielded systematic agreement (within the numerical uncertainty of the procedure) with the SS results through fifth order,¹⁹ even though the APS II total energies are slightly lower than those obtained by summing the SS Z -expansion. As SS list the E_k to much higher order, however, a more sensitive "hybrid" method may be used to obtain refined E_2 estimates from the APS II data. Several studies^{10, 12-14} have shown that the collective accuracy of the E_k when used in Z -expansion series is greater than that of any individual value. If the contributions of E_0, E_1 , and the E_k

given by SS for $k \geq 3$ are subtracted from the APS II total energies for $Z=2-10$, the residuals are observed to converge rapidly with increasing Z to the E_2 values of Table II. The revised E_2 are slightly lower than the original SS estimates¹⁷ and bring the 2(^{1,3}P) perturbation energy sums into almost exact agreement with the APS II values for $Z \geq 6$. The E_2 refinements should in principle be accompanied by corrections to the remaining E_k , but these were beyond the accuracy of the APS II data to determine and are presumably very slight.²⁰ For the $n(1,^3P)$ states with $n \geq 3$, the APS II energies yielded consistently lower E_2 values than those of SS, although the two sets of E_3 coefficients are in close agreement for the triplet states.

APPLICATION TO HIGH-Z IONS

The E_k furnish estimates of the NR contribution I_{NR} to the ionization energy for $Z \geq 11$ through the series

$$I_{NR}(Z) = Z^2/2n^2 - E_1Z - E_2 - E_3Z^{-1} - \dots \quad (3)$$

The Z -expansion approach has the advantage of yielding I_{NR} values numerically reliable to a fixed number of decimal places beyond $Z=10$, a precision determined by the number of significant figures to which the E_k are known; see Table III. As the contribution $Z^2/2n^2$ dominates for large Z , the relative numerical accuracy of the Z -expansion (3) is certain to increase with increasing Z . The Z -expansion I_{NR} have been compared in the range $11 \leq Z \leq 26$ with the corresponding NR results of Ermolaev and Jones⁷ (hereafter EJ), who suggest a numerical accuracy of roughly one part in 10^7 for their procedure. The Padé-approximant technique employed by these authors is more sophisticated than the Z -expansion method, but their use of the less smoothly Z -dependent APS I data is open to the objections listed in APS II.

The extrapolated I_{NR} values of Ermolaev and Jones were found to be systematically higher than the Z -expansion results for all but the 3(¹P) states. The sense of this persistent discrepancy is particularly surprising in the cases of the 2-3(³S) states, for which the APS I ionization energies (upon which the EJ extrapolation is based) are systematically lower than the more accurate values of Aashamar *et al.*^{15, 16} (adopted here) in the range $Z=2-10$. By contrast, preliminary Z -expansion I_{NR} values for these states obtained from an analysis of the APS II data proved to be slightly lower than, and in much better agreement with, the results of Aashamar *et al.* for $Z \geq 11$. These comparisons suggest the possibility that the EJ ioniza-

TABLE I. Values of energy Z -expansion coefficients E_k (in atomic units) for $n(1^3S)$ states in the helium sequence.

State k	$2(1^1S)$	$3(1^1S)$	$4(1^1S)^b$	$5(1^1S)^b$	$2(3^1S)^c$	$3(3^1S)^d$	$4(3^1S)$	$5(3^1S)$
1	0.231 824 417	0.105 255 127	0.059 972 92	0.038 693 69	0.187 928 669 41	0.093 719 482 4	0.055 293 644 8	0.036 340 030 3
2	-0.114 510 15	-0.049 104 7 ^a	-0.028 156	-0.018 334	-0.047 409 304	-0.032 317 54	-0.021 301 54	-0.014 846 86
3	0.009 328 0	-0.001 274 ^a	-0.000 84	-0.000 47	-0.004 872 28	-0.002 136 9	-0.001 107 2 ^a	-0.000 639 4 ^a
4	-0.001 286	-0.001 5	-0.000 8	-0.000 5	-0.003 457 8	-0.001 519	-0.000 721	-0.000 394
5	0.006 2	0.005	0.002	0.001	-0.002 030	-0.000 79	-0.000 37	-0.000 20
6	-0.001 5	-0.001 29	-0.000 5	-0.000 2	-0.000 1
7	-0.005	-0.000 9	-0.000 3	-0.000 1	...
8	-0.000 6	-0.000 2

^a F. C. Sanders, Ref. 18.^b Values found from APS I energies of Ref. 1.^c Abbreviation of values in Ref. 15.^d Abbreviation of values in Ref. 16.TABLE II. Values of energy Z -expansion coefficients E_k (in atomic units) for $n(1^3P)$ states in the helium sequence.

State k	$2(1^1P)^a$	$3(1^1P)$	$4(1^1P)$	$5(1^1P)$	$2(3^1P)^a$	$3(3^1P)$	$4(3^1P)$	$5(3^1P)$
1	0.259 868 922 4	0.113 357 544	0.063 360 47	0.040 420 88	0.225 727 785 40	0.104 293 823	0.059 672 105	0.038 562 985
2	-0.157 028 59 ^b	-0.060 752 9	-0.032 977	-0.020 787	-0.072 998 976 ^b	-0.041 856 3	-0.025 644 4	-0.017 163 1
3	0.026 105 0	-0.000 257	-0.000 73	-0.000 48	-0.016 585 44	-0.003 352 ^c	-0.001 323 ^c	-0.000 670
4	0.005 789	0.003 77	0.001 5	0.000 7	-0.010 353 1	-0.002 72	-0.001 05	-0.000 51
5	-0.005 04	0.006 9	0.003	0.002	-0.005 425	-0.001 5	-0.000 6	-0.000 3
6	-0.007 1	-0.010	-0.002 02	-0.000 8	-0.000 4	-0.000 2
7	-0.001	0.002	0.000 2
8	0.003	0.002

^a Except for E_2 , abbreviation of values in Ref. 17.^b Value from "hybrid" method (see discussion of P states).^c In agreement with rounded value of Ref. 17.

TABLE III. Estimated numerical accuracy, in decimal places, of the Z -expansion I_{NR} (when expressed in atomic units) for $Z \geq 11$.

State n	$n(^1S)$	$n(^3S)$	$n(^1P)$	$n(^3P)$
2	7	9 ^a	8	9
3	6	8 ^b	7	7
4	5	7-8	5-6	6-7
5	5	7	5-6	6-7

^a 12-decimal accuracy if the E_k of Ref. 15 are used.

^b 10-decimal accuracy if the E_k of Ref. 16 are used.

tion energies suffer from a positive bias, perhaps an artifact of the EJ extrapolation procedure. The magnitude of the discrepancy (relative to the Z -expansion values) in the range $11 \leq Z \leq 26$ is nevertheless only one or two parts in 10^7 for the $2(^1S)$, $2-3(^1P)$, and all triplet states. The disagreement rises to one part in 10^6 for the $3(^1S)$, $4-5(^1P)$ states and to several times this for the $4-5(^1S)$

states. These differences would seem unlikely to be of observational importance except possibly in predictions of $n \rightarrow n$ transition energies, for which severe cancellation occurs; here one may wish to consider the slight revisions to the Ermolaev-Jones I_{NR} values for $Z \geq 11$ implied by the present work. The most important effect of such revisions upon transition energies would occur in the $5^1S_0 \rightarrow 5^1P_1$ cases and result in a lowering of the EJ predicted transition-energy values (incorporating relativistic and other corrections) by about four parts in 10^4 .

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²⁰Values of E_2 and E_3 for the $2(^1,^3P)$ states even more accurate than those of Table II were found by Sanders and Scherr with a 200-term basis set (footnote 11 of Ref. 17), suggesting that variational-perturbation calculations as elaborate as those of Refs. 15 and 16 might produce significant revisions of many E_k coefficients listed in the present work.