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Variational calculations for ^{4}He I: Improved energies for singlet and triplet $n\,D$ and $n\,F$ levels ($n = 3-8$)

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Hylleraas method variational calculations with up to 458 expansion terms are reported for the $n\,^1D$, $n\,^3D$ terms and for the $n\,^1F$, $n\,^3F$ terms ($n = 4-8$) of neutral helium. Convergence arguments are presented to obtain new estimates of the exact nonrelativistic energies of these terms. The reliability of the estimates ranges from 3×10^{-10} a.u. in the worst case to 10^{-11} a.u. in the best case. The nonrelativistic singlet and triplet energies are combined with previously calculated values for relativistic and other small energy contributions to evaluate the total ionization energies for the $n\,D$ and $n\,F$ levels. Comparisons of the $n\,^1D$ and $n\,^3D$ energies with other calculations and available data yield improved values for relativistic contributions. The calculated relativistic $n\,F$ ionization energies agree with values based on core-polarization theoretical $n\,G$ and $n\,H$ energies within deviations of 3 MHz (5×10^{-11} a.u.) for $n=5$ to 1 MHz (1.5×10^{-11} a.u.) for $n=7,8$. The calculated $n\,F$ fine-structure separations generally agree with experiment for $n = 5-8$ within uncertainties of the order of 1 to 0.1 MHz. Predicted values given for the 4 F fine-structure separations and the $4\,^1F$ ionization energy are probably accurate within a few MHz.

I. INTRODUCTION

Recent improvements in experimental wavelength measurements of He optical transitions[1-4] have led to improved values for a number of $1snl$ energy levels ($n = 2-6$). The accuracies of these experimental results have sparked renewed interest in the theoretical determination of these energy values. Comparisons of experimental and theoretical results provide important tests of the theory for this basic two-electron atom, and certain combinations of experimental and theoretical results have yielded increasingly more accurate ionization energies for $1snl$ levels ($n \geq 2$).[5-9]

To obtain energy values theoretically at least as accurate as the experimental results requires accurate systematic variational calculations employing hundreds of terms produced from a correlated basis set, such as the pioneering work of Pekeris and co-workers.[10-12] Pekeris and co-workers treated only low-lying S and P levels of He, presumably because in their method a new procedure is required for each different angular momentum. In a previous paper,[13] we have performed calculations on low-lying ^1D and ^1F levels in the spirit of the definitive calculations by Pekeris and co-workers on low-lying ^1P levels. However our previous approach suffered the same problem as the previous S and P calculations in that the numerical convergence of the calculations gets progressively poorer for higher and higher levels.

In recent papers, Kono and Hattori[14,15,6,7] have shown that a careful choice of basis functions greatly improves the convergence and permits very accurate energy level calculations to be performed for essentially any level. In this work we have used Kono and Hattori's method of basis set selection to obtain new estimates of the nonrelativistic energies of the $n\,^1D$, $n\,^3D$ terms ($n = 3-8$) and of the $n\,^1F$, $n\,^3F$ terms ($n = 4-8$). The D results extend Kono and Hattori's results to greater precision. The ^1F results extend the results of Sims, Parmer, and Reese to greater precision, and the ^3F results are on a level of accuracy never before achieved. We have combined these new results with available calculated values for the relativistic and other small contributions to obtain new predictions for $n\,D$ and $n\,F$ ionization energies. These ionization energies are tested for consistency with $n\,G$ and $n\,H$ ionization energies calculated from core-polarization theory and are used to test the accuracy of the Breit-Pauli fine-structure theory as applied to $1snf$ configurations.

II. WAVE FUNCTIONS

The method used in the calculations is the combined configuration interaction (CI)-Hylleraas (Hy) method, originally proposed by Sims and Hagstrom.[16] This method has been shown to be capable of giving very accurate values for the energies, oscillator strengths, and polarizabilities of two-, three-, and four-electron systems (Ref. 13 and references therein), and its utility for N-electron systems up to and including $N=10$ has been demonstrated by Clary and Handy.[17] The CI-Hy method wave functions can be written in a form which is conventional for the two-electron Hy method calculations[10-12,18]

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_K C_K \Phi_K(\mathbf{r}_1,\mathbf{r}_2) , \tag{1}$$

where the terms Φ_K are specifically of the form

$$\Phi_K(\mathbf{r}_1,\mathbf{r}_2)=(1\pm P_{12}) r_1^i r_2^j r_{12}^k \times Y_0^0(1) Y_l^l(2) \exp(-\xi r_1 - \eta r_2) . \tag{2}$$

P_{12} is the operator which permutes electrons 1 and 2, Y_l^l is the ($m=l$) spherical harmonic chosen to give $S\,(l=0)$, $P\,(l=1)$, $D\,(l=2)$, or $F\,(l=3)$ symmetry, and the plus sign is for singlet levels, the minus sign for triplet levels. In addition to terms of the form of Eq. (2), for D and F levels terms of the form

$$\Phi_K(\mathbf{r}_1,\mathbf{r}_2)=(1\pm P_{12}) r_1^i r_2^j r_{12}^k Y_1^1(1) Y_{l-1}^{l-1}(2) \times \exp(-\xi r_1 - \eta r_2) \tag{3}$$

are required to form a complete set of D and F angular momentum functions.[14,19]

Following Kono and Hattori we employ two sets of basis functions, differing in the nonlinear parameters ξ and η, to accelerate convergence. The first set is chosen to have the correct asymptotic form as $r_1, r_2 \rightarrow \infty$. Hence, for the first set (which we refer to as the ξ set), ξ and η are fixed at the values Z and $(-2E-Z^2)^{1/2}$, respectively, where E is an estimate of the energy eigenvalue of the level in question and Z is the nuclear charge. Terms are chosen for this set by taking all terms for which $i=0,1$; $k=0,1$; and $L \leq j \leq N+4$, where N and L are quantum numbers for the state in question. This choice of terms gives a rough approximation to the true wave function using a relatively small number of terms but is slowly convergent. To guard against errors due to using a fixed number of ξ terms, we have included more ξ terms in our wave functions than Kono and Hattori.[20] For the second set[20] (referred to as the ζ set), $\xi=\eta=\zeta$, where ζ is the (single) nonlinear parameter to be optimized. Terms are chosen for this set by taking all terms for which

$$i+j+k+|i-j|(1-\delta_{k0}) \leq \nu , \tag{4}$$

where δ_{k0} is the Kronecker δ. The nonlinear parameter was optimized for each wave function essentially by determining whether a change in sign of the derivative of $E(\zeta)$ has occurred over the interval ζ to $\zeta+2\epsilon$ (ϵ is an arbitrary small interval). This requires solving the eigenvalue equation for a series of ζ points taken at intervals of 0.1 (when $\zeta \geq 1$) or 0.05 (when $\zeta < 1$) in atomic units (a.u.). In order to carry out convergence studies, calculations were performed for $\nu=8$, 10, 12, and 14. Following Pekeris and co-workers, the eigenvalues have been extrapolated, using the formula[11]

$$E_{\text{extrapolated}}=E_1+\frac{(E_1-E_0)(E_2-E_1)}{2E_1-E_0-E_2} , \tag{5}$$

where E_0, E_1, and E_2 are the values at $\nu=10$, 12, and 14, respectively.

III. NONRELATIVISTIC ENERGIES—RESULTS AND DISCUSSION

The calculations reported here were carried out at the National Bureau of Standards on a Cyber 205 in double precision ($\sim$29 digits).

A. ^1D, ^3D terms

The results of our ^1D and ^3D calculations are reported in Tables I and II. These calculated values are rigorous upper bounds to the exact nonrelativistic energies. In these tables, we have also included our *estimates* of the exact nonrelativistic energies of these terms, obtained using Eq. (5). Our estimates are the values labeled "Extrapolated." These results show a definite convergence of the eigenvalues as the number of expansion terms is increased. Note that the convergence is not degraded for higher principal quantum numbers. In Table III we compare these results with the best previous calculations of these energy eigenvalues, the calculations of Kono and Hattori,[6,7] and the calculations of Sims, Parmer, and Reese.[13]

Our calculations essentially take the calculations of Kono and Hattori one step further to $\nu=14$. We increased the value of ν (a) to obtain better eigenvalues and (b) to test the extrapolation formula used by both Kono and Hattori and us. Our calculated results are consistent with Kono and Hattori's results for all ν, but our estimates of the exact nonrelativistic energies of these terms are in all cases higher than those of Kono and Hattori. Thus it appears that the extrapolation formula overshoots the exact nonrelativistic energies (our wave functions are more complete than those of Kono and Hattori). This suggests that using the difference between calculated and estimated energies as a measure of the uncertainty in the estimated energies should be a conservative procedure. Comparing our present calculations with our earlier results makes it evident that the previously calculated energies got progressively worse as the principal quantum number increased. In contrast, the accuracy of the present results increases with increasing n. The worsening of the energy eigenvalues as n increased in the previous work (which we took note of in the uncertainty in our energy estimates) was due primarily to two factors: (1) the lack of optimization of the nonlinear parameters employed in the calculation and (2) the choice of terms employed in the wave functions. The comparison suggests that the addition of the term $|i-j|(1-\delta_{k0})$ in Eq. (4) significantly improves the energy convergence of the wave functions, especially for higher n (we previously employed $i+j+k \leq \nu$ as the selection criterion). This term eliminates some expansion terms with nonzero k and large $|i-j|$, a desirable elimination since where large

$|i-j|$ terms are important (electrons far apart), the r_{ij} dependency is small. Using the difference between calculated and estimated energies as a measure of the uncertainty of the estimated exact energies, we estimate the uncertainties for the D terms reported in Tables I and II to vary from 3×10^{-10} a.u. in the worst case to 10^{-11} a.u. in the best case.

B. ^1F, ^3F terms

The results of our ^1F and ^3F calculations (rigorous upper bounds to the exact nonrelativistic energies) are reported in Tables IV and V. In these tables we have again also included our *estimates* (the values labeled "Extrapolated") of the exact nonrelativistic energies of these terms, obtained using Eq. (5). A definite convergence of the eigenvalues is again evident as the number of expansion terms is increased. The convergence is not degraded for higher principal quantum numbers, but appears to be about the same for all principal quantum numbers.

In Table VI we compare these results with the best previous calculations, the calculations of Godefroid and Verhaegen,[21] the calculations of Brown,[22] and those of Sims, Parmer, and Reese.[13] Comparing our present ^1F results with those of Ref. 13, we note again that in the previous work the calculated energies got worse as the principal quantum number increased, a defect the present calculations correct. Our present results are consistent with the previous results. Using the difference between calculated and estimated energies as a measure of the uncertainty in the estimated energies, we estimate the uncertainties for the F terms reported in Tables IV and V to vary from 6×10^{-11} a.u. in the worst case to 3×10^{-11} a.u. in the best case.

IV. ENERGIES FOR n D AND n F LEVELS INCLUDING RELATIVISTIC AND OTHER CONTRIBUTIONS

A. Exchange energies, theoretical 1*snl* level structures

The nonrelativistic singlet-triplet separations $n\,^3D$-$n\,^1D$ and $n\,^3F$-$n\,^1F$ from our results yield very accurate values of the corresponding exchange energies K. For example, the difference between our final calculated value for the nonrelativistic $3\,^3D$-$3\,^1D$ separation and the extrapolated value, $1.557\,638\times10^{-5}$ a.u., is only 2.4×10^{-10} a.u. We take this separation as $2K=1.557\,638(30)\times10^{-5}$ a.u. and include the corresponding value in MHz units under "Present calculation" in Table VII. (In the remainder of this paper ionization energies, or term

TABLE I. Values of nonrelativistic energies for ^1D terms of He I. N_ξ denotes the number of ξ expansion terms, N_ζ the number of ζ expansion terms, N_{tot} the total number of terms in the wave function, and ζ_{opt} the optimum value of ζ. Energies are in atomic units.

Term	ν	N_ξ	N_ζ	N_{tot}	ζ_{opt}	Energy
$3\,^1D$	8	24	86	110	1.05	−2.055 620 721 71
	10	24	162	186	1.20	−2.055 620 732 14
	12	24	271	295	1.20	−2.055 620 732 56
	14	24	414	438	1.20	−2.055 620 732 79
				Extrapolated		−2.055 620 733 07
$4\,^1D$	8	28	86	114	1.05	−2.031 279 836 97
	10	28	162	190	1.20	−2.031 279 844 54
	12	28	271	299	1.20	−2.031 279 845 68
	14	28	414	442	1.10	−2.031 279 846 03
				Extrapolated		−2.031 279 846 19
$5\,^1D$	8	32	86	118	1.05	−2.020 015 829 18
	10	32	162	194	1.10	−2.020 015 834 88
	12	32	271	303	1.20	−2.020 015 835 91
	14	32	414	446	1.20	−2.020 015 836 09
				Extrapolated		−2.020 015 836 13
$6\,^1D$	8	36	86	122	1.05	−2.013 898 222 02
	10	36	162	198	1.10	−2.013 898 226 46
	12	36	271	307	1.20	−2.013 898 227 26
	14	36	414	450	1.20	−2.013 898 227 39
				Extrapolated		−2.013 898 227 42
$7\,^1D$	8	40	86	126	0.95	−2.010 210 024 26
	10	40	162	202	1.10	−2.010 210 027 71
	12	40	271	311	1.20	−2.010 210 028 34
	14	40	414	454	1.20	−2.010 210 028 43
				Extrapolated		−2.010 210 028 45
$8\,^1D$	8	44	86	130	0.95	−2.007 816 509 44
	10	44	162	206	1.10	−2.007 816 511 98
	12	44	271	315	1.20	−2.007 816 512 48
	14	44	414	458	1.20	−2.007 816 512 55
				Extrapolated		−2.007 816 512 56

values, are taken as positive quantities; the sign of any energy contribution is positive or negative according to whether it increases or decreases the ionization energy.)

The values of the $n\,^3F$-$n\,^1F$ separations from the energies in Tables IV and V converge more rapidly than the individual $n\,^1F$ and $n\,^3F$ energies; we estimate uncertainties less than 2×10^{-11} a.u. for these separations as obtained from the final estimated individual energies. The corresponding values of these separations in MHz units are given in Table VII for $n=4-8$.

Correlation contributions to the $1snd$ exchange energies are, of course, effectively included to a very high order in our variational singlet-triplet separations. Chang and Poe[23] calculated exchange energies for $1snd$ and $1snf$ configurations using Brueckner-Goldstone perturbation theory through second-order contributions. Their values, included under "Other calculations" in Table VII, have errors smaller than 1% for the $1snd$ configurations, but their $1snf$ exchange energies are too small by 10 to 15 %. The nonrelativistic *$n\,^3D$-$n\,^1D$ separations* obtained from Kono and Hattori's extrapolated energies[7] agree with our values within $< 10^{-4}$ cm^{-1} (3 MHz) for all $n=3-8$.

We can now use our results to obtain improved theoretical descriptions of the $1snd$ and $1snf$ level structures. The Hamiltonian of the Breit equation in the Pauli approximation leads to three "magnetic" interactions and a relativistic contribution, denoted here by Δ_r, in addition to the exchange energy.[24,25] We also include the mass-polarization energy ϵ_M and, for $1snd$ terms, the Lamb shift Δ_L. Cok and Lundeen[25] have given a convenient tabulation of the 4×4 $1snl$ energy matrix using LS-coupling basis states. Since the relativistic, mass-polarization, and Lamb-shift interactions are diagonal in the approximation of interest, the separations of the four $1snl$ levels are affected only by the differences of these interactions for the triplet and singlet states. We denote these differences by $\Delta_{r,st}$, $\epsilon_{M,st}$, and $\Delta_{L,st}$; thus, for example, $\Delta_{r,st}(1snd)\equiv\Delta_r(n\,^3D)-\Delta_r(n\,^1D)$.

B. $n\,^3D$-$n\,^1D$ separations and semiempirical values for the relativistic contributions

In their treatment of the $1s3d$ configuration for ^{4}He I and ^{3}He I, Sansonetti and Martin[4] used the experimental data to evaluate several energy contributions, including the separation E_{st}. The latter quantity is defined as the triplet-singlet separation given by the energy matrix with all three magnetic interactions set equal to zero:

$$E_{st}=2K+\Delta_{r,st}+\epsilon_{M,st}+\Delta_{L,st}\ . \qquad (6)$$

TABLE II. Values of nonrelativistic energies for ^3D terms of He I. N_ξ denotes the number of ξ expansion terms, N_ζ the number of ζ expansion terms, $N_{\rm tot}$ the total number of terms in the wave function, and $\zeta_{\rm opt}$ the optimum value of ζ. Energies are in atomic units.

Term	ν	N_ξ	N_ζ	N_{tot}	$\zeta_{\rm opt}$	Energy
$3\,^3D$	8	24	70	94	0.90	−2.055 636 298 53
	10	24	137	161	1.10	−2.055 636 307 57
	12	24	236	260	1.20	−2.055 636 309 17
	14	24	369	393	1.20	−2.055 636 309 41
				Extrapolated		−2.055 636 309 45
$4\,^3D$	8	28	70	98	0.95	−2.031 288 838 32
	10	28	137	165	1.10	−2.031 288 845 75
	12	28	236	264	1.20	−2.031 288 847 06
	14	28	369	397	1.20	−2.031 288 847 32
				Extrapolated		−2.031 288 847 38
$5\,^3D$	8	32	70	102	0.95	−2.020 021 020 62
	10	32	137	169	1.10	−2.020 021 026 25
	12	32	236	268	1.20	−2.020 021 027 23
	14	32	369	401	1.20	−2.020 021 027 37
				Extrapolated		−2.020 021 027 39
$6\,^3D$	8	36	70	106	1.00	−2.013 901 410 05
	10	36	137	173	1.10	−2.013 901 414 55
	12	36	236	272	1.20	−2.013 901 415 31
	14	36	369	405	1.20	−2.013 901 415 41
				Extrapolated		−2.013 901 415 43
$7\,^3D$	8	40	70	110	0.95	−2.010 212 102 04
	10	40	137	177	1.10	−2.010 212 105 25
	12	40	236	276	1.20	−2.010 212 105 85
	14	40	369	409	1.20	−2.010 212 105 93
				Extrapolated		−2.010 212 105 94
$8\,^3D$	8	44	70	114	0.95	−2.007 817 931 66
	10	44	137	181	1.10	−2.007 817 934 16
	12	44	236	280	1.20	−2.007 817 934 63
	14	44	369	413	1.20	−2.007 817 934 69
				Extrapolated		−2.007 817 934 70

TABLE III. Selected nonrelativistic energy estimates for ^1D and ^3D terms of He I. Energies are in atomic units.

Term	Authors	Calculated	Exact (estimated)
$3\,^1D$	Sims *et al.*	−2.055 620 731 7	−2.055 620 74
	Kono and Hattori	−2.055 620 732	−2.055 620 734
	Present work	−2.055 620 732 79	−2.055 620 733 07
$4\,^1D$	Sims *et al.*	−2.031 279 837 1	−2.031 279 86
	Present work	−2.031 279 846 03	−2.031 279 846 19
$5\,^1D$	Sims *et al.*	−2.020 015 708 1	−2.020 017
	Kono and Hattori	−2.020 015 836	−2.020 015 837
	Present work	−2.020 015 836 09	−2.020 015 836 13
$8\,^1D$	Kono and Hattori	−2.007 816 512 5	−2.007 816 512 7
	Present work	−2.007 816 512 55	−2.007 816 512 56
$3\,^3D$	Kono and Hattori	−2.055 636 308	−2.055 636 310
	Present work	−2.055 636 309 41	−2.055 636 309 45
$5\,^3D$	Kono and Hattori	−2.020 021 027	−2.020 021 028
	Present work	−2.020 021 027 37	−2.020 021 027 39
$8\,^3D$	Kono and Hattori	−2.007 817 934 6	−2.007 817 934 8
	Present work	−2.007 817 934 69	−2.007 817 934 70

Sansonetti and Martin used an energy matrix including E_{st} and the three magnetic interactions but omitting the $\Delta_{r,st}$ and $\Delta_{L,st}$ contributions. They assumed an experimental value for the off-diagonal spin-orbit matrix element[26] and evaluated the other two magnetic interactions and E_{st} by parametrically adjusting their values to obtain optimal agreement of the resulting calculated level separations with the experimental separations. The neglect of the $\Delta_{r,st}$ and $\Delta_{L,st}$ contributions did not significantly affect the values obtained for E_{st} and for the two diagonal magnetic interactions; the effect of the omitted contributions was mainly absorbed by the exchange-energy parameter.

We have evaluated the $\Delta_{r,st}$ energies for ^{4}He $1s3d$ and

TABLE IV. Values of nonrelativistic energies for ^1F terms of He I. N_ξ denotes the number of ξ expansion terms, N_ζ the number of ζ expansion terms, N_{tot} the total number of terms in the wave function, and ζ_{opt} the optimum value of ζ. Energies are in atomic units.

Term	v	N_ξ	N_ζ	N_{tot}	ζ_{opt}	Energy
$4\,^1F$	8	24	66	90	0.75	−2.031 255 138 87
	10	24	140	164	0.80	−2.031 255 143 63
	12	24	254	278	0.85	−2.031 255 144 20
	14	24	414	438	0.95	−2.031 255 144 34
				Extrapolated		−2.031 255 144 39
$5\,^1F$	8	28	66	94	0.75	−2.020 002 930 56
	10	28	140	168	0.80	−2.020 002 936 23
	12	28	254	282	0.85	−2.020 002 936 93
	14	28	414	442	0.95	−2.020 002 937 14
				Extrapolated		−2.020 002 937 14
$6\,^1F$	8	32	66	98	0.75	−2.013 890 677 28
	10	32	140	172	0.80	−2.013 890 682 91
	12	32	254	286	0.85	−2.013 890 683 60
	14	32	414	446	0.95	−2.013 890 683 76
				Extrapolated		−2.013 890 683 81
$7\,^1F$	8	36	66	102	0.75	−2.010 205 242 04
	10	36	140	176	0.80	−2.010 205 247 27
	12	36	254	290	0.85	−2.010 205 247 88
	14	36	414	450	0.95	−2.010 205 248 03
				Extrapolated		−2.010 205 248 08
$8\,^1F$	8	40	66	106	0.75	−2.007 813 291 72
	10	40	140	180	0.80	−2.007 813 296 40
	12	40	254	294	0.85	−2.007 813 296 95
	14	40	414	454	0.95	−2.007 813 297 07
				Extrapolated		−2.007 813 297 10

TABLE V. Values of nonrelativistic energies for ^3F terms of He I. N_ξ denotes the number of ξ expansion terms, N_ζ the number of ζ expansion terms, N_{tot} the total number of terms in the wave function, and ζ_{opt} the optimum value of ζ. Energies are in atomic units.

Term	ν	N_ξ	N_ζ	N_{tot}	ζ_{opt}	Energy
$4\,^3F$	8	24	66	90	0.75	−2.031 255 163 27
	10	24	140	164	0.75	−2.031 255 167 83
	12	24	254	278	0.80	−2.031 255 168 24
	14	24	414	438	0.95	−2.031 255 168 36
				Extrapolated		−2.031 255 168 41
$5\,^3F$	8	28	66	94	0.75	−2.020 002 951 48
	10	28	140	168	0.80	−2.020 002 956 75
	12	28	254	282	0.90	−2.020 002 957 19
	14	28	414	442	0.95	−2.020 002 957 32
				Extrapolated		−2.020 002 957 37
$6\,^3F$	8	32	66	98	0.75	−2.013 890 691 88
	10	32	140	172	0.80	−2.013 890 697 69
	12	32	254	286	0.85	−2.013 890 698 16
	14	32	414	446	0.95	−2.013 890 698 30
				Extrapolated		−2.013 890 698 36
$7\,^3F$	8	36	66	102	0.75	−2.010 205 253 42
	10	36	140	176	0.80	−2.010 205 257 88
	12	36	254	290	0.85	−2.010 205 258 23
	14	36	414	450	0.95	−2.010 205 258 34
				Extrapolated		−2.010 205 258 39
$8\,^3F$	8	40	66	106	0.75	−2.007 813 300 35
	10	40	140	180	0.80	−2.007 813 304 12
	12	40	254	294	0.85	−2.007 813 304 42
	14	40	414	454	0.95	−2.007 813 304 51
				Extrapolated		−2.007 813 304 55

^{3}He $1s3d$ using Eq. (6) and the previously derived E_{st} values. The relevant data are given in Table VIII. In addition to our value for the exchange energy, we used calculated $\epsilon_{M,st}$ and $\Delta_{L,st}$ contributions from Kono and Hattori.[7] The estimated errors of the latter quantities are too small to contribute significantly to the uncertainties of the resulting $\Delta_{r,st}$ values. We have included the ^{3}He data in Table VIII mainly to show the consistency of the $\Delta_{r,st}$ values obtained for ^{4}He and ^{3}He. This consistency depends on the fact that the calculated $\epsilon_{M,st}(^4\text{He})$ value used in the table (-247.6 MHz) falls well within the range of values -243 ± 18 MHz required to fit the difference in the E_{st} values[4] for ^{4}He and ^{3}He.

Kono and Hattori[7] evaluated the relativistic contribu-

TABLE VI. Selected nonrelativistic energy estimates for ^1F and ^3F terms on He I. Energies are in atomic units.

Term	Authors	Calculated	Exact (estimated)
$4\,^1F$	Godefroid and Verhaegen	−2.031 255	
	Brown	−2.031 254 28	−2.031 255
	Sims *et al.*	−2.031 255 144 1	−2.031 255 145
	Present work	−2.031 255 144 34	−2.031 255 144 39
$5\,^1F$	Brown	−2.020 001 64	−2.020 004
	Sims *et al.*	−2.020 002 931 6	−2.020 002 95
	Present work	−2.020 002 937 09	−2.020 002 937 14
$6\,^1F$	Brown	−2.013 889 50	−2.013 889
	Sims *et al.*	−2.013 890 664 9	−2.013 890 7
	Present work	−2.013 890 683 76	−2.013 890 683 81
$4\,^3F$	Godefroid and Verhaegen	−2.031 255	
	Brown	−2.031 254 32	−2.031 255
	Present work	−2.031 255 168 36	−2.031 255 168 41
$5\,^3F$	Brown	−2.020 001 68	−2.020 004
	Present work	−2.020 002 957 32	−2.020 002 957 37
$6\,^3F$	Brown	−2.013 889 52	−2.013 889
	Present work	−2.013 890 698 30	−2.013 890 698 36

TABLE VII. Nonrelativistic singlet-triplet separations for the $1s3d$ and $1snf$ ($n=4$–8) configurations. These separations are equal to twice the exchange energies $2K(1snl)$. Units are MHz.

Separation	$2K$ Present calculation	$2K$ Other calculations
$3\,^3D$-$3\,^1D$	102 473.6(20)	102 475(15)[a] 102 000[b]
$4\,^3F$-$4\,^1F$	158.02(13)	137[b]
$5\,^3F$-$5\,^1F$	133.09(13)	119[b]
$6\,^3F$-$6\,^1F$	95.72(13)	86[b]
$7\,^3F$-$7\,^1F$	67.83(13)	61[b]
$8\,^3F$-$8\,^1F$	49.01(13)	44[b]

[a] Kono and Hattori, Ref. 7.

[b] Chang and Poe, Ref. 23.

TABLE VIII. Energy differences pertinent to semiempirical evaluation of the relativistic contribution to the $1s3d$ singlet-triplet separation. The E_{st} value represents the ^3D-^1D separation in the absence of the "magnetic" interactions. The E_{st} values for ^{4}He and ^{3}He $1s3d$ were obtained previously by fitting the experimental level structures (Refs. 4 and 26). Calculated values are given for the exchange ($2K$), mass-polarization ($\epsilon_{M,st}$), and Lamb-shift ($\Delta_{L,st}$) contributions to E_{st}. The relativistic contribution $\Delta_{r,st}$ was evaluated by subtracting the other contributions from the E_{st} value. Units are MHz.

	^{4}He	^{3}He
E_{st}	102 200(3)[a]	102 116(5)[b]
$2K$	102 473.6(20)[c]	102 469.0(20)[d]
$\epsilon_{M,st}$	-247.6[e]	-328.6[f]
$\Delta_{L,st}$	2.7[e]	2.7[e]
$\Delta_{r,st}$	$-29(4)$	$-27(6)$

[a] Reference 4.

[b] Reference 26.

[c] Present result.

[d] Value for ^{3}He is 4.6 MHz smaller than for ^{4}He due to the difference of the reduced electron mass for the two isotopes (normal mass effect).

[e] Reference 7.

[f] Value for ^{3}He is equal to $1.3272\epsilon_M(^4\text{He})$, the numerical factor being the ratio of the ^{4}He and ^{3}He nuclear masses.

tions using their variationally calculated wave functions and the formula:

$$\Delta_r=\alpha^2\left[-\frac{Z^4}{8}+\frac{1}{4}\langle p_1^4\rangle-\pi Z\langle\delta(\mathbf{r}_1)\rangle-\pi\langle\delta(\mathbf{r}_{12})\rangle\right]+\frac{\alpha^2}{2}\left\langle\frac{\mathbf{p}_1\cdot\mathbf{p}_2}{r_{12}}+\frac{\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2}{r_{12}^3}\right\rangle , \qquad (7)$$

where α is the fine-structure constant. Table IX includes their $\Delta_r(^3D)$, $\Delta_r(^1D)$, and $\Delta_{r,st}$ values for the $1s3d$ and $1s7d$ configurations. The total calculated ionization energies $T(^3D)$ and $T(^1D)$ are also listed for these configurations.

The apparently more accurate $\Delta_{r,st}(1s3d)$ value derived semiempirically in Table VIII and given under "Present results" in Table IX indicates an error of about 16 MHz in Kono and Hattori's $\Delta_{r,st}$ value. This error is also essentially equal to the difference between the experimental $3\,^3D$-$3\,^1D$ separation,[4] 102 233(3) MHz, and Kono and Hattori's calculated value including all contributions, 102 217(24) MHz, since Kono and Hattori's calculated *nonrelativistic* $3\,^3D$-$3\,^1D$ separation agrees with our value within about 1 MHz (Table VII). As shown previously,[9] Kono and Hattori's calculated $n\,^3D$-$n\,^1D$ separations including all contributions are systematically smaller than the experimental values by amounts varying approxi-

TABLE IX. Relativistic contributions and total ionization energies for the $1s3d$ and $1s7d$ terms. The differences of the $\Delta_r(^3D)$ and $\Delta_r(^1D)$ relativistic contributions are labeled $\Delta_{r,st}$. The total ionization energies $T(^3D)$ and $T(^1D)$ under Kono and Hattori are the sums of all contributions calculated in Ref. 7, including the Lamb shifts. The $T(^3D)$ and $T(^1D)$ energies under Present results were obtained by combining the adjusted Δ_r values in this column with the present nonrelativistic ionization energies (Tables I and II) and using the other contributions from Ref. 7. The energies in cm^{-1} units are based on a value of 109 722.273 50(7) cm^{-1} for the ^{4}He Rydberg constant (Ref. 27).

	Kono and Hattori	Present results
$1s3d$		
$\Delta_r(^3D)$	833(9) MHz	841(6) MHz[a]
$\Delta_r(^1D)$	878(9) MHz	870(6) MHz[a]
$\Delta_{r,st}$	$-45(13)$ MHz	$-29(4)$ MHz
$T(^3D)$	12 209.1126(6) cm^{-1}	12 209.112 67(28) cm^{-1}
$T(^1D)$	12 205.7030(5) cm^{-1}	12 205.702 56(25) cm^{-1}
$1s7d$		
$\Delta_r(^3D)$	135.8(3) MHz	137.2(9) MHz[a]
$\Delta_r(^1D)$	141.8(3) MHz	140.4(9) MHz[a]
$\Delta_{r,st}$	$-6.0(4)$ MHz	$-3.2(8)$ MHz
$T(^3D)$	2 240.995 33(10) cm^{-1}	2 240.995 33(4) cm^{-1}
$T(^1D)$	2 240.540 66(10) cm^{-1}	2 240.540 57(4) cm^{-1}

[a] Value obtained by semiempirical adjustment of Δ_r value from Ref. 7; see text.

mately as $140/n^2$ MHz for $n=3-8$. Applying the procedure outlined above to the data and calculated energies for the higher 1*snd* configurations, we obtain results similar to those for 1*s*3*d*: the systematic errors of Kono and Hattori's $n\,^3D$-$n\,^1D$ separations are apparently mainly due to errors in their calculated Δ_r contributions.

Although we have not calculated the relativistic and other small contributions using our wave functions, we have combined the available data to deduce improved values for the $n\ D$ relativistic contributions. The $\Delta_r(^3D)$ and $\Delta_r(^1D)$ values given under "Present results" in Table IX were obtained by increasing Kono and Hattori's $\Delta_r(^3D)$ values by $70/n^2$ MHz and decreasing their $\Delta_r(^1D)$ values by the same amounts. The $T(^3D)$ and $T(^1D)$ ionization energies were then evaluated by adding these "adjusted" Δ_r values and all other small contributions[7] to our nonrelativistic ionization energies.[27] The 1*s*7*d* results are given as an example of this procedure for the higher n values. The $\Delta_r(^3D)$ and $\Delta_r(^1D)$ values obtained for $n=3-8$ by adjustment of Kono and Hattori's values in this manner are supported by the agreement, within small deviations, of the resulting $T(^3D)$ and $T(^1D)$ energies with the ^3D and ^1D ionization energies adopted in Ref. 9; the latter values for $n=5-8$ are ultimately based on core-polarization theoretical $n\ G$ and $n\ H$ term values[28] with uncertainties significantly smaller than the uncertainties of Kono and Hattori's Δ_r values. The adjusted Δ_r values and total $n\ D$ ionization energies for $n=4$, 5, 6, 8 may be easily obtained as above. The resulting total ionization energies for $n=5-8$ agree with the values adopted in Ref. 9 within a maximum deviation of 7×10^{-5} cm^{-1} (2 MHz) for $T(5\,^1D)$.

As noted above, Kono and Hattori's[7] extrapolated values for the nonrelativistic ionization energies $T_{nr}(^3D)$ and $T_{nr}(^1D)$ are systematically too large. Our results indicate that their total ^3D ionization energies include approximate cancellations of the errors of their $T_{nr}(^3D)$ and $\Delta_r(^3D)$ values, whereas the errors of their $T_{nr}(^1D)$ and $\Delta_r(^1D)$ values are in the same direction. The $2\,^3S_1$ ionization energy derived previously[9] by combining experimental data with Kono and Hattori's $T(4\,^3D)$ and $T(5\,^3D)$ total ionization energies is not significantly changed by use of "adjusted" theoretical $T(n\,^3D)$ and $T(n\,^1D)$ energies obtained as above.

The difference between our $\Delta_{r,st}(1s3d)$ value in Table IX and Kono and Hattori's value[7] is fairly consistent with their uncertainty estimates of about 1% for the $\Delta_r(3\,^3D)$ and $\Delta_r(3\,^1D)$ contributions. The discrepancy of 2.8 MHz between our $\Delta_{r,st}(1s7d)$ value and their value again indicates errors of about 1% in their $\Delta_r(7\,^3D)$ and $\Delta_r(7\,^1D)$ values, significantly larger than their uncertainty estimates of 0.2% for these quantities. Evaluations of the Δ_r contributions with more accurate wave functions are clearly needed.

C. 1*snf* level structures and ionization energies

We have used our nonrelativistic ionization energies for $n\,^3F$ and $n\,^1F$ terms together with 1*snf* energy matrix elements calculated by Cok and Lundeen[25] to obtain predicted ionization energies for the levels including relativistic and other contributions. The three magnetic interactions h_{so} (spin-orbit), h_{off} (off-diagonal element), and h_{ss} (spin-spin), as well as the Δ_r and $-\epsilon_M$ energies in Table X, were calculated in an "extended adiabatic" approximation.[25] The numbers in parentheses following the three magnetic-interaction values are the extended-adiabatic corrections to the corresponding hydrogenic-approximation values; we take these corrections as roughly indicative of the uncertainties.

The results of diagonalizing the 1*snf* energy matrices with values of the exchange energies from Table VII and the matrix elements from Ref. 25 are given under "Calculation" in Table XI. The quantity $\Delta T(^1F)$ is the calculated increase in the ^1F ionization energy with respect to the nonrelativistic (variational) ^1F position. The uncertainties given for the $\Delta T(^1F)$ displacement and for our calculated values of the three 1*snf* fine-structure separations include only the exchange and magnetic-interactions uncertainties; we have not attempted to estimate the errors of the Δ_r and ϵ_M energies from Ref. 25. The Lamb shifts were assumed to be negligible compared to other approximations in these calculations.

The experimental 1*s*5*f* and 1*s*6*f* fine structures in Table XI are from measurements of $n\ F$-$n\ G$ transitions by Farley *et al.*[29] Our estimates of the errors, which are very rough, are in general larger than would be obtained from the standard deviations of the individual determinations, in accordance with the discussion in Ref. 29. A similar comment applies to the errors given with the experimental 1*s*7*f* fine structure separations, which are from 7 *D*-7 *F* measurements by Farley, MacAdam, and Wing.[30] We averaged data from Cok and Lundeen's 8 *F*-8 *G* determinations[31] and from the 8 *D*-8 *F* measure-

TABLE X. Values for the magnetic (h_{so}, h_{off}, h_{ss}), relativistic (Δ_r), and mass-polarization ($-\epsilon_M$) energies for 1*snf* configurations ($n=4-8$). All values from Ref. 25. Units are MHz.

1*snf*	h_{so}	h_{off}	h_{ss}	$\Delta_r(^1F)^a$	$\Delta_r(^3F)^a$	$-\epsilon_M(^1F)^a$	$-\epsilon_M(^3F)^a$
1*s*4*f*	−32.509(55)	−97.841(48)	32.598(50)	268.97	268.99	9.53	9.25
1*s*5*f*	−16.639(37)	−50.081(38)	16.679(36)	190.27	190.29	5.49	5.25
1*s*6*f*	−9.625(26)	−28.976(28)	9.649(24)	130.38	130.40	3.38	3.20
1*s*7*f*	−6.060(18)	−18.245(20)	6.074(17)	91.23	91.25	2.20	2.08
1*s*8*f*	−4.059(13)	−12.222(14)	4.070(11)	65.70	65.70	1.50	1.42

[a] The quantities Δ_r and $-\epsilon_M$ are tabulated here for consistency with other parts of this paper. The absolute values of these energies are from the values of the H_{rel} and H_{mp} matrix elements in Table V of Ref. 25.

TABLE XI. Relative energies for $1snf$ levels ($n=4-8$). The energies under Calculation were obtained by diagonalization of the $1snf$ energy matrix with the exchange energy K from Table VII and the other matrix elements from Ref. 25. The quantity $\Delta T(^1F)$ is the resulting increase in the ^1F ionization energy with respect to the nonrelativistic ^1F energy. The calculated values for the $1snf$ fine-structure separations are given along with experimental values and values from series formulas (Ref. 32) for comparison. Units are MHz.

	Calculation	Experiment	Series formula
$1s4f\ \Delta T(^1F)$	21.67(17)		
$^3F_3$-$^1F_3$	704.11(33)		678.3(16)
$^3F_3$-$^3F_2$	471.71(29)		472.0(25)
$^3F_3$-$^3F_4$	213.72(28)		209.4(19)
$1s5f\ \Delta T(^1F)$	81.63(13)		
$^3F_3$-$^1F_3$	377.84(25)	378.50(40)[a]	376.66(35)
$^3F_3$-$^3F_2$	224.09(21)	224.52(80)[a]	224.87(62)
$^3F_3$-$^3F_4$	92.05(20)	92.57(60)[a]	91.59(42)
$1s6f\ \Delta T(^1F)$	73.05(10)		
$^3F_3$-$^1F_3$	226.66(18)	226.68(20)[a]	227.22(11)
$^3F_3$-$^3F_2$	124.32(15)	125.16(30)[a]	124.85(20)
$^3F_3$-$^3F_4$	47.94(15)	48.01(25)[a]	48.10(14)
$1s7f\ \Delta T(^1F)$	57.15(7)		
$^3F_3$-$^1F_3$	146.38(14)	146.19(20)[b]	146.60(8)
$^3F_3$-$^3F_2$	76.23(11)	74.61(150)[b]	76.62(12)
$^3F_3$-$^3F_4$	28.14(11)	28.38(150)[b]	28.43(11)
$1s8f\ \Delta T(^1F)$	43.76(5)		
$^3F_3$-$^1F_3$	99.91(11)	99.93(15)[c]	99.73(7)
$^3F_3$-$^3F_2$	50.27(8)	50.32(15)[c]	50.46(10)
$^3F_3$-$^3F_4$	18.06(8)	18.37(15)[c]	18.23(9)

[a] Separations derived from measurements of $n\ F$-$n\ G$ transitions ($n=5,6$) given in Ref. 29.

[b] Separations derived from measurements of 7 D-7 F transitions given in Ref. 30.

[c] Separations derived from measurements of 8 D-8 F transitions given in Ref. 30 and 8 F-8 G transitions in Ref. 31.

ments of Ref. 30 to obtain the experimental $1s8f$ fine-structure separations, the two sets of measurements agreeing within about 0.2 MHz.

Most of our calculated $1snf$ fine-structure separations agree with the experimental values within the combined estimated errors. It is interesting to note in connection with these results that only for $l=3$ is the $1snl$ exchange energy roughly comparable in order of magnitude with the corresponding magnetic and relativistic energies. Cok and Lundeen[25] calculated the fine structures for several $1snf$ configurations using their values for all interaction energies except the exchange energy and evaluating the latter quantity parametrically by fitting the experimental structure. The effect of any possibly significant diagonal interaction omitted from the matrix would have been absorbed by the exchange-energy value. Our results show that any such omitted contribution is at most at the level of the uncertainties.

Farley[32] obtained the $1snf$ fine-structure separations given under "Series formula" in Table XI by fitting experimental measurements[29-31] to the formula

$$T(n\,^3F_J)-T(n\,^1F_3)=An^{-3}+Bn^{-5} \tag{8}$$

and evaluating the constants A and B for each of the three series of intervals [three different J values for $n\,^3F_J$ in (8)]. Our calculated separations agree with the series-formula values within the errors in only about half the cases in Table XI, but the standard deviations quoted for the series-formula values are known to be typically smaller than the actual errors.[29] The series-formula prediction[32] for the $4\,^3F_3$-$4\,^1F_3$ separation is apparently low by about 26 MHz, which is about 16 times the standard deviation obtained from the fit of the data for higher n values. A good fit of these separations down to $n=4$ would probably require at least a third term on the right-hand side of (8).

In Table XII we compare $1snf$ ^1F ionization energies based on two very different types of calculations: the "variational" $T_r(^1F)$ term values in the fourth column were obtained by addition of the $\Delta T(^1F)$ corrections from Table XI to our calculated $T_{nr}(^1F)$ values from Table IV, whereas the $T_r(^1F)$ values for $n=5-8$ under Ref. 9 were derived from Drachman's[28] core-polarization theoretical term values for $1sng$ or $1snh$ configurations combined with microwave-spectroscopic data. We note again that the errors for our $\Delta T(^1F)$ corrections include no allowances for errors of the Δ_r relativistic contributions, and thus the errors given for the variational $T_r(^1F)$ energies may be unrealistically small. The difference between the variational $T_r(^1F)$ energy for each $n=5-8$ and the corresponding $T_r(^1F)$ value based on the core polarization theoretical $n\ G$ or $n\ H$ term value is given in the last column. The variational $T_r(^1F)$ values are systematically larger than the core-polarization/microwave-data values by about 3 MHz ($n=5$) to 1 MHz ($n=7,8$). These differences are comparable to the estimated errors of the $T_r(^1F)$ values from Ref. 9; in addition, the actual errors of our $\Delta T(^1F)$ values could be of the order of a few MHz.

The $1s4f$ levels have not yet been determined experimentally with high accuracy. The trend of the systematic differences between our $T_r(^1F)$ values and those based on theoretical $n\ G$ and $n\ H$ energies for $n=5-8$ indicates a corresponding difference of about 0.0002 cm^{-1} (6 MHz) for $n=4$; this extrapolated difference can be taken as a minimum uncertainty estimate for our predicted $4\,^1F$ ionization energy. The most accurate previous prediction for the $4\,^1F$ position was obtained in Ref. 9 by use of the nonrelativistic energy from Ref. 13 and an "adjusted" theoretical value of 77.5 MHz for the exchange energy K. As noted in Ref. 9, the net calculated displacement $\Delta T(4\,^1F)$ is relatively small because the $4\,^1F$ term-value increase due to the relativistic Δ_r contribution is almost canceled by the decrease due to the triplet-singlet repulsion. The $T_r(^1F)$ energy from Ref. 9 agrees with our new value within 3 MHz (Table XII), and the separations of the $1s4f$ levels in Ref. 9 agree with our predictions in Table XI within a maximum deviation of about 2 MHz.

V. CONCLUSION

Combined CI-Hy techniques have proven effective in obtaining new values of the nonrelativistic energies of the

TABLE XII. Ionization energies (term values) for $1snf\ ^1F$ levels ($n=4-8$). The nonrelativistic term values $T_{\text{nr}}(^1F)$ in the second column are from the present calculations (Table IV). These values were corrected by addition of the calculated $\Delta T(^1F)$ values from Table IX to obtain the $T_r(^1F)$ values in the fourth column. The $T_r(^1F)$ values for $n=5-8$ from Ref. 9 (fifth column) were obtained by a combination of core-polarization theoretical $1sng$ or $1snh$ term values (Ref. 28) and microwave-spectroscopic data. The difference of the $T_r(^1F)$ values in the fourth and fifth columns is given in the final column. All term values are based on a value of 109 722.273 50(7) cm^{-1} for the ^{4}He Rydberg constant (Ref. 27). Units are cm^{-1}.

$1snf$	$T_{\text{nr}}(^1F)$ Variational	$\Delta T(^1F)$	$T_r(^1F)$ Variational	$T_r(^1F)$ Ref. 9	Difference
$1s4f$	6858.771 002(11)	0.000 723(6)	6858.771 725(13)	6858.771 8(6)[a]	−0.000 1(6)
$1s5f$	4389.535 479(11)	0.002 723(5)	4389.538 202(12)	4389.538 10(7)[b]	0.000 10(7)
$1s6f$	3048.234 816(11)	0.002 437(4)	3048.237 253(12)	3048.237 19(5)[c]	0.000 06(5)
$1s7f$	2239.486 042(11)	0.001 906(3)	2239.487 948(12)	2239.487 918(37)[d]	0.000 030(39)
				2239.487 922(18)[e]	0.000 026(22)
$1s8f$	1714.585 443(6)	0.001 460(2)	1714.586 903(6)	1714.586 879(30)[f]	0.000 024(31)
				1714.586 866(19)[g]	0.000 037(21)

[a] Based on a previous variational calculation (Ref. 13).

[b] Based on 5 G theoretical term value.

[c] Based on 6 G theoretical term value.

[d] Based on 7 G theoretical term value.

[e] Based on 7 H theoretical term value.

[f] Based on 8 G theoretical term value.

[g] Based on 8 H theoretical term value.

$n\ ^1D$ and $n\ ^3D$ terms ($n=3-8$) and the $n\ ^1F$ and $n\ ^3F$ terms ($n=4-8$) of neutral helium. These calculations are superior to all previous results reported in the literature. We suggest that the exact nonrelativistic energies differ from our extrapolated energies by no more than 3×10^{-10} a.u. in the worst case and 10^{-11} a.u. in the best case.

Combining these results with available calculated values for relativistic and other small contributions, we have obtained new predictions for the ionization energies of the $n\ D$ and $n\ F$ energy levels. The predicted $n\ D$ and $n\ F$ ionization energies for $n=5-8$ are consistent with core-polarization theoretical $n\ G$ and $n\ H$ ionization energies and connecting data within uncertainties of the order of 1 to several MHz. These results and comparisons with experimentally determined $n\ ^3D$-$n\ ^1D$ separations ($n=3-8$) lead to suggested semiempirical values for the $n\ ^3D$ and ^1D relativistic contributions that should be checked and improved by more accurate calculations. Our calculated $n\ F$ fine-structure separations agree with the experimental values for $n=5-8$ within deviations of the order of the experimental uncertainties (~1 to 0.1 MHz), but more accurate evaluations of the relativistic, magnetic, and mass-polarization contributions would also allow improved tests of the theory for these configurations.

After this paper was submitted for publication, a paper by Schilling *et al.*[33] appeared giving measurements of the $1s4f$ level separations with estimated uncertainties of 1 to 2 MHz. Their experimental values for the three separations agree with our predicted values in Table XI within a maximum deviation of 0.22 MHz.

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