Variational calculations for excited states in He I: Improved estimation of the ionization energy from accurate energies for the $n\,^3S$, $n\,^1D$, $n\,^3D$ series

Akihiro Kono and Shuzo Hattori

Department of Electronics, Nagoya University, Nagoya 464, Japan

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Variational calculations with correlated basis sets have been carried out to obtain the nonrelativistic energies for the $n\,^3S$ ($n = 2$–6), $n\,^1D$ ($n = 3$–8), and $n\,^3D$ ($n = 3$–8) series in He I with estimated accuracies of 10^{-3}–10^{-5} cm^{-1}. A comparison of the results with recently reevaluated experimental energy values, with the aid of available relativistic and mass-polarization corrections, suggests a value of 198 310.773(1) cm^{-1} for the ionization energy for He I on an energy scale fixed by the $2\,^1P$ value of 171 135.0000 cm^{-1}.

Recent precision wave-number measurements for He I optical transitions[1-4] have improved the energy values of a number of $1snl$ states ($n = 2$–6) to accuracies of better than 10^{-3} cm^{-1}.[5] To compare these results with theory to full experimental accuracies, improvement of theoretical calculations is required except for a few low-lying states. Through variational calculations using wave functions with hundreds or more than a thousand expansion terms,[6-8] or using wave functions with logarithmic expansion terms,[9] the nonrelativistic energies for the states with $n = 2$ have been determined to within an accuracy of 10^{-4} cm^{-1} or better. However, numerical convergence of the results in these calculations was poorer for higher excited states, and it has been generally believed that variational calculations are unsuitable for high-lying excited states. As we have shown recently,[10] however, a careful choice of the basis functions greatly improves the convergence, and enables one to carry out precision calculations up to high-lying excited states by using reasonably compact wave functions. We have actually extended the previous calculations, to obtain the nonrelativistic energies for the $n\,^3S$ ($n = 2$–6), $n\,^1D$ ($n = 3$–8), and $n\,^3D$ ($n = 3$–8) states with estimated accuracies of 10^{-3}–10^{-5} cm^{-1}. In this Rapid Communication, we report these results and make comparison with accurate experiments.

The method of calculation was basically the same as that described previously.[10] The key to the acceleration of the convergence is to use a trial wave function consisting of two sets of correlated basis functions differing in the values of nonlinear parameters. Specifically, we employed wave functions consisting of symmetrized linear combinations of the bases of the forms $r_1^i r_2^j r_{12}^k e^{-\xi r_1 - \eta r_2}$ and $r_1^i r_2^j r_{12}^k e^{-\zeta(r_1 + r_2)}$ multiplied (except for S states) by angular factors (we refer to the former terms as "ξ terms" and the latter terms as "ζ terms"). Here, r_1 and r_2 are the radial coordinates of the two electrons, r_{12} the interelectronic separation, and i, j, and k non-negative integers. The values of the nonlinear parameters ξ and η were fixed, respectively, at $(-2E - Z^2)^{1/2}$ and Z, with E being the energy of the state in question and Z the nuclear charge, and the value of ζ was optimized for every wave function.[11] (The optimum value of ζ is much larger than ξ, and thus ζ terms mainly describe the electron correlation effect in the range of small and middle values of electron radial coordinates.) In the case of D states, ξ terms were given sd angular symmetry, while ζ terms were given both sd and pp angular symmetry in order that they form a complete set. In the present cal-

culations, we included in the expansion those ξ terms with

$$i \leqq n + 1, \quad j \leqq 1, \quad k \leqq 1 \ , \tag{1}$$

and those ζ terms with

$$i + j + k + |i - j|\delta_{k0} \leqq \nu \ , \tag{2}$$

where n is the principal quantum number, δ_{k0} the Kronecker δ, and ν a given integer. The maximum value of ν employed was 14 for S states and 12 for D states.

Convergence of the results as ν was increased is shown in Table I for selected states. The extrapolated energy values given in the table were calculated using the formula[7]

$$E_{\text{ext}} = E_1 + \frac{(E_1 - E_0)(E_2 - E_1)}{2E_1 - E_0 - E_2} \ , \tag{3}$$

where E_0, E_1, and E_2 are the energy eigenvalues obtained, respectively, for $\nu = 10$, 12, and 14 (S states) or $\nu = 8$, 10, and 12 (D states). It is seen that the convergence for high-lying states is comparable to or even better than that for low-lying states. Table I also lists the results of Pekeris[6] ($2\,^3S$ state) and Sims, Parmer, and Reese[12] ($3\,^1D$ state), which we think are the only cases where an accuracy comparable to or better than that of our results was attained. Agreement between these results and ours is satisfactory. Comparison of the number of expansion terms employed indicates the rapidity of the convergence of the present method.

The extrapolation formula (3) employed here is of course not an exact one, and it is possible that the improvement of the accuracy gained by extrapolation is not very significant. However, a number of cases,[6,8,9,13,14] where extrapolated values can be tested by more accurate calculations, indicate that the difference between the extrapolated value and the directly calculated value can at least be used as a good estimate of the uncertainty of the results (we hereafter refer to this difference as ϵ). In the present calculation, the number of ξ terms for a given state was fixed. For the states listed in Table I, the effect of including additional ξ terms was examined by adding those ξ terms with ($i \leqq n + 1$, $j = 2$, $k = 0$), ($i \leqq n + 1$, $j = 0$, $k = 2$), and ($i = n + 2$, $j = 0$, $k = 0$). The resulting extrapolated values differed from those given in Table I by 0.0ϵ, -0.9ϵ, 0.2ϵ, 0.2ϵ, and 0.9ϵ, respectively, for the $2\,^3S$, $6\,^3S$, $3\,^1D$, $3\,^3D$, and $8\,^3D$ states (the minus sign indicates that the new extrapolated value is smaller than, i.e., below, the old).[15] Calculations employing additional ξ terms with pp angular symmetry were also tried,

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TABLE I. Values of nonrelativistic energies in He I for wave functions of different expansion lengths. N_ξ denotes the number of ξ terms, N_ζ the number of ζ terms, and ζ_{opt} the optimum value of ζ. The results of Pekeris (Ref. 6) and Sims et al. (Ref. 12) are given by comparison. All values in a.u.

State	N_ξ	N_ζ	ζ_{opt}	Energy
$2\,^3S$	16	$70(\nu=10)$	1.7	$-2.175\,229\,377\,59$
	16	$112(\nu=12)$	1.7	$-2.175\,229\,378\,15$
	16	$168(\nu=14)$	1.7	$-2.175\,229\,378\,23$
	Extrapolated			$-2.175\,229\,378\,24$
	Perkeris	(715 terms)		$-2.175\,229\,378\,22$
		(1078 terms)		$-2.175\,229\,378\,237$
$6\,^3S$	32	70	1.6	$-2.015\,377\,452\,47$
	32	112	1.3	$-2.015\,377\,452\,87$
	32	168	1.3	$-2.015\,377\,452\,95$
	Extrapolated			$-2.015\,377\,452\,97$
$3\,^1D$	12	$86(\nu=8)$	0.9	$-2.055\,620\,701$
	12	$162(\nu=10)$	1.0	$-2.055\,620\,726$
	12	$273(\nu=12)$	1.1	$-2.055\,620\,732$
	Extrapolated			$-2.055\,620\,734$
	Sims	(247 terms)		$-2.055\,620\,718$
		(347 terms)		$-2.055\,620\,732$
		("exact")		$-2.055\,620\,74$
$8\,^1D$	32	86	0.9	$-2.007\,816\,508\,5$
	32	162	1.1	$-2.007\,816\,511\,7$
	32	273	1.2	$-2.007\,816\,512\,4$
	Extrapolated			$-2.007\,816\,512\,6$
$3\,^3D$	12	$70(\nu=8)$	0.9	$-2.055\,636\,275$
	12	$137(\nu=10)$	1.0	$-2.055\,636\,302$
	12	$236(\nu=12)$	1.1	$-2.055\,636\,308$
	Extrapolated			$-2.055\,636\,310$
$8\,^3D$	32	70	0.9	$-2.007\,817\,930\,4$
	32	137	1.1	$-2.007\,817\,933\,9$
	32	236	1.2	$-2.007\,817\,934\,6$
	Extrapolated			$-2.007\,817\,934\,8$

but the effect was negligible. From these observations we believe that a few times ϵ gives a safe estimate of the accuracy we have attained.

Our final results are summarized in the first column of Table II, the obtained extrapolated energies being converted to term values (ionization energies) by using a value of $109\,722.273\,09$ cm^{-1} for the ^{4}He Rydberg constant.[5] Except for the $n\,^{1,3}D$ states with $n=3-6$, the value of ϵ (defined above) for each state is less than one in the last digit quoted, and we believe that the results are accurate to ± 1 in the last digit. For the $n\,^{1,3}D$ states with $n=3-6$, we give the values of ϵ (units in the last decimal place) in the parentheses as a rough estimate of the uncertainty, since we do not wish to quote the results to one less significant figure.

Next we compare our results with accurate experimental energy values recently reevaluated by Martin.[5] Following Martin, we evaluate the (ground-state) ionization energy (E_I) by combining the theoretical and experimental results, and examine the consistency of E_I's resulting from different states. The values of E_I given in the last column of Table II are calculated as a sum $T_{NR}+\Delta_{R,M}+\Delta_L+E_{expt}$, where T_{NR} is the nonrelativistic term value, $\Delta_{R,M}$ the sum of relativistic and mass-polarization corrections to T_{NR} (for $^{1,3}D$ states this includes singlet-triplet mixing contribution), Δ_L the (mostly

assumed values of) Lamb shift correction, and E_{expt} the experimental energy values. The values of $\Delta_{R,M}$ for ^3S states are taken from variational calculations by Accad, Pekeris, and Schiff;[8] these are estimated to be correct to within ± 2 in the last digit quoted. Those for $^{1,3}D$ states are from Cok and Lundeen;[13] these are partly based on hydrogenic approximations and partly on perturbation theory, their uncertainties being not specified (for the mass-polarization corrections for the $3\,^1D$ and $3\,^3D$ states, we employ our preliminary values of $0.007\,51$ cm^{-1} and $-0.000\,77$ cm^{-1} resulting from our previous 132- and 112-term wave functions, respectively).

Lamb-shift corrections for most of the states treated here have not been calculated. For the $n\,^3S$ states with $n=3-6$, we assume the values of Δ_L so that they meet two requirements: (1) Δ_L of each state is derived from n^{-3} scaling of other Δ_L; (2) E_I becomes as nearly constant as possible, i.e., the dispersion of E_I becomes minimal. As seen from Table II, this choice of Δ_L gives fairly consistent values of E_I, and suggests that the exact value of E_I is near $198\,310.773$ cm^{-1}.[17] The assumed $3\,^3S$ Lamb shift of -0.0288 cm^{-1} seems not unreasonable, in rough agreement with -0.040 cm^{-1} obtained by n^{-3} scaling of Ermolaev's calculation for the $2\,^3S$ shift.[18]

For $^{1,3}D$ states, we assume $\Delta_L=0$. The resulting E_I's are

TABLE II. Theoretical and experimental energies for HeI. T_{NR} denotes the nonrelativistic term value (ionization energy), $\Delta_{R,M}$ the sum of the relativistic and mass-polarization corrections to T_{NR}, Δ_L the Lamb-shift correction, E_{expt} the experimental energy value, and E_I the sum $T_{NR} + \Delta_{R,M} + \Delta_L + E_{expt}$, giving the ionization energy from the ground state. Entries associated with ^3D states are the center-of-gravity values. All values in cm^{-1}.

State	T_{NR}[a]	$\Delta_{R,M}$	Δ_L	E_{expt}[b]	E_I
$2\,^3S$	38 453.131 39	1.6981[c]	-0.135[d]	159 856.0776(5)	198 310.772
$3\,^3S$	15 073.4412	0.4698[c]	(-0.0288)[e]	183 236.8906(10)	198 310.7728
$4\,^3S$	8 012.3775	0.1913[c]	(-0.0122)[e]	190 298.2165(5)	198 310.7731
$5\,^3S$	4 963.588 16	0.0958[c]	(-0.0062)[e]	193 347.0947(5)	198 310.7725
$6\,^3S$	3 374.498 19	0.055[c]	(-0.0036)[e]	194 936.2234(10)	198 310.7730
$3\,^1D$	12 205.6667(4)	0.0389[f]	(0)[g]	186 105.069 84(9)	198 310.7754
$4\,^1D$	6 864.1918(3)	0.0236[f]	(0)[g]	191 446.559(2)	198 310.7744
$5\,^1D$	4 392.3661(1)	0.0140[f]	(0)[g]	193 918.3931(5)	198 310.7732
$6\,^1D$	3 049.8903(1)	0.0089[f]	(0)[g]	195 260.8744(9)	198 310.7736
$7\,^1D$	2 240.5351	0.0059[f]			
$8\,^1D$	1 715.2911	0.0041[f]			
$3\,^3D_{cg}$	12 209.0849(5)	0.0323[f]	(0)[g]	186 101.659 69(3)	198 310.7769
$4\,^3D_{cg}$	6 866.1671(3)	0.0188[f]	(0)[g]	191 444.588 64(50)	198 310.7745
$5\,^3D_{cg}$	4 393.5054(2)	0.0112[f]	(0)[g]	193 917.256 82(50)	198 310.7734
$6\,^3D_{cg}$	3 050.5899(1)	0.0071[f]	(0)[g]	195 260.176 61(90)	198 310.7736
$7\,^3D_{cg}$	2 240.9910	0.0048[f]			
$8\,^3D_{cg}$	1 715.6032	0.0034[f]			

[a]Present work; for a discussion of estimated errors, see text.
[b] Martin, Ref. 5.
[c]Accad et al., Ref. 8.
[d]Ermolaev, Ref. 18.
[e]Assumed value, see text.
[f]Cok and Lundeen, Ref. 16; the effect of singlet-triplet repulsion, calculated from their fine-structure matrix elements, is also included. Mass-polarization contributions for the $3\,^1D$ and $3\,^3D$ states are taken from our preliminary results (see text).
[g]Assumed value.

around 198 310.7735 cm^{-1} for $n = 5, 6$, but are somewhat larger for $n = 3, 4$. Since the errors in $\Delta_{R,M}$ and Δ_L are expected to decrease with increasing n, the values of E_I for higher excited states should be more reliable. It is likely that the departure of the values of E_I for $n = 3, 4$ from the values for $n = 5, 6$ is caused by the inaccuracy in $\Delta_{R,M}$ and/or Δ_L.

For $n\,^{1,3}D$ states with $n \geq 7$, precise singlet-triplet intervals based on microwave-optical resonance measurements are available.[19] Table III compares our results with these data, together with the perturbation calculations of Chang and Poe.[20] Agreement between our results with the microwave-optical resonance data is quite satisfactory. Improvement of the accuracy over the results of Chang and Poe is also quite significant.

The above comparison supports the reliability of the values of $T_{NR} + \Delta_{R,M}$ for high-lying $1snd$ states. We can also use these term values to estimate E_I by fitting an appropriate series formula to E_{expt} (for $n = 3$–6) and to $T_{NR} + \Delta_{R,M}$ (for $n = 7, 8$). Following Martin,[5] we employed an extended Ritz formula:

$$E = E_I - R_{He}/(n^*)^2 , \tag{4}$$

$$T = R_{He}/(n^*)^2 , \tag{5}$$

$$n - n^* = a + b\,(n - \delta_0)^{-2} + c\,(n - \delta_0)^{-4} , \tag{6}$$

where E is the energy value of a state relative to the ground state, T the term value, R_{He} the ^4He Rydberg constant, E_I the ionization energy, and a, b, c, and δ_0 series constants [Eq. (4) is applied to $n = 3$–6, and Eq. (5) to $n = 7, 8$]. Least-squares adjustment of a, b, c, and E_I (δ_0 was fixed at 0) in an unweighted global fit for the $n\,^1D$ and $n\,^3D$ series gave a value of 198 310.7735(2) cm^{-1} for E_I, where the number in the parenthesis is the standard deviation. In this fit the root-mean-square deviation of E_{expt} and $T_{NR} + \Delta_{R,M}$ from the fitted values was 0.000 17 cm^{-1}.

All of the above results indicate that the present T_{NR} are consistent with E_{expt} provided the exact E_I is near 198 310.773 cm^{-1}, and we feel it safe to adopt this value with an uncertainty of 0.001 cm^{-1} for the ionization energy for helium in the energy scale adopted for E_{expt} (which is fixed by the $2\,^1P$ value of 171 135.0000 cm^{-1}). This result should be more accurate than the recent estimate of E_I given by Martin [198 310.7745(40) cm^{-1}].[5]

In conclusion, we have carried out precision variational

TABLE III. Values of $n\,^1D - n\,^3D_{cg}$ intervals in He (in MHz).

n	Present work[a]	Experiment[b]	Other theory[c]
7	13 635	13 633.3(2)	13 574
8	9336	9332.67(8)	9274

[a]Differences of the values of $T_{NR} + \Delta_{R,M}$ in Table II.
[b]Farley et al., Ref. 19.
[c]Chang and Poe, Ref. 20.

calculations for the $n\,^3S$, $n\,^1D$, and $n\,^3D$ series in He I up to high-lying excited states. From comparison of the results with accurate experiments, with the aid of relativistic and mass-polarization correction energies ($\Delta_{R,M}$) available in the literature, an improved value of the ionization energy (E_I) is suggested. To establish the present estimate of E_I more firmly, imporved values of $\Delta_{R,M}$ for $1snd$ states are required. Evaluation of $\Delta_{R,M}$ by use of the present wave functions is in progress and an extension of calculations to the $n\,^1S$, $n\,^1P$, and $n\,^3P$ series is intended.

Numerical computations in the present work were carried out at the Computation Center of Nagoya University.

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