Energy levels for the stable isotopes of atomic helium (^{4}He I and ^{3}He I)

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Abstract: We calculate very accurate ab initio ionization energies for both ^{4}He I and ^{3}He I as well as the isotope shifts for $n = 1$ to 10, $L = 0$ to 7 and combined these with precise laboratory data to produce a new table of levels for ^{4}He I and the first table for ^{3}He I. We adopted an experimental ionization potential of 5945 204 290 ± 33 MHz for ^{4}He I and derived 5944 890 770 ± 33 MHz for ^{3}He I. Additional calculations of the magnetic perturbations of ^{3}He I provide the hyperfine levels, which compare favourably with the available measurements.

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Résumé : Nous avons fait un calcul ab initio de haute précision des énergies d'ionisation pour ^{4}He I et ^{3}He I, ainsi que des déplacements isotopiques pour $n = 1$ à 10 et $L = 0$ à 7 et avons combiné le tout avec des mesures précises en laboratoire , afin de produire une nouvelle table des niveaux de ^{4}He I et la toute première table pour ^{3}He I. Nous avons accepté la valeur expérimentale de 5945 204 290 ± 33 MHz pour le potentiel d'ionisation de ^{4}He I et fixé celui de ^{3}He I à 5944 890 770 ± 33 MHz. Des calculs additionnels sur les perturbations magnétiques dans ^{3}He I nous donnent des niveaux hyperfins qui se comparent favorablement avec les mesures publiées.

[Traduit par la Rédaction]

1. Introduction

The goal of the present paper is to publish a critical tabulation of the energy levels for both ^{4}He I and ^{3}He I by combining the best available theoretical results and laboratory experiments. A subsequent paper will present a multiplet table for ^{4}He I with oscillator strengths. The isotopes of helium provide sensitive tests of quantum electrodynamics because very accurate calculations are now possible for this two-electron neutral atom for comparison with precise frequency measurements [1–6]. Helium is also important in astrophysics because it is the second most abundant element in the Universe. Its spectrum is prominent wherever the temperature is hot enough to excite the transitions.

The rare ^{3}He I isotope is interesting because its spectral lines can be comparable in strength with ^{4}He I in certain peculiar stars [7], presumably a consequence of mass-dependent diffusion. However, the lower mass isotope, has lacked the usual critical listing of energy levels. The nuclear spin I is 1/2

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for ^{3}He [8] so that all levels except $^1S_0$ have hyperfine structure (hfs) with $F = J \pm I$. This structure is exceptionally strong in ^{3}He I, often comparable with the fine structure, so that in many cases J is not a good quantum number.

2. Theoretical ionization energies of ^{4}He I and ^{3}He I

Table 1 lists the latest ab initio calculations of ionization energies (IE) for the two isotopes of helium and the isotope shifts IE(^{3}He)–IE(^{4}He) for each level up to $n = 10$. These results include the mixing of the singlet and triplet angular momentum states with $J = L$ for $L \geq 3$ to form levels often designated as ^+L_L and ^-L_L but here labeled ^1L_L and ^3L_L, respectively. The details of the calculations for ^{4}He are described in full by Drake and Martin [1]. Those results are here updated to include the high-precision Bethe logarithms from Drake and Goldman [9] for the electron self-energy part of the quantum electrodynamic (QED) shift. This makes the QED part of the calculation essentially exact up to terms of order α^3 Ry. In addition, terms of order α^4 Ry are included in the lowest lying levels $1\ ^1S_0$ from Korobov and Yelkhovsky [5, 10], and $2\ ^3S_1$ from Pachucki [2]. The QED terms of order α^4 Ry are also estimated in an extended Kabir–Salpeter approximation [1] with an uncertainty of about $\pm 10\%$. Because of the improved Bethe logarithms, the present values for the low-lying S- and P-states are more accurate than the previous Drake and Martin tabulation, and should be taken in preference.

For the separate IE values, the main source of uncertainty comes from relativistic and QED corrections of order α^4 that are not included. The uncertainty due to these terms is taken to be the entire magnitude of the hydrogenic Dirac energies of this order for the Rydberg electron, using a screened nuclear charge of $Z - 1$ for $L \geq 1$, and the full nuclear charge Z for $L = 0$. The uncertainties, therefore, represent the expected magnitude of higher order terms not included in the calculation. No error is quoted if all the figures are expected to be correct. The values for the Rydberg and fine structure constant are $R_\infty = 10\,973\,731.568\,525(73)\ \mathrm{m}^{-1}$ and 1/137.035 999 11(46), respectively, according to the CODATA 2002 adjustment of the fundamental constants. The assumed values for the nuclear charge radii are $R_c(^4\mathrm{He}) = 1.673(1)$ fm and $R_c(^3\mathrm{He}) = 1.9659(14)$ fm. The latter value is derived from the isotope shift measured by Shiner et al. [11], as discussed by Drake et al. [12]. The former is deduced from the Lamb shift in muonic helium [13]. Although attempts to reproduce the measurement have not been successful [14], the result is still consistent with, but less accurate than, the value 1.676(8) fm obtained from electron scattering [15]. The uncertainties in R_c do not contribute significantly to the tabulated energies for ^{3}He, but they do affect the isotope shifts at the $0.1/n^3$ MHz level of accuracy, where n is the principal quantum number. A re-analysis of some of the older data on isotope shifts for ^{3}He will be published separately [16].

It is clear from Table 1 that the the uncertainties in the isotope shifts are considerably smaller than for the individual IE values. This is because, to a first approximation, the uncertainties due to higher order relativistic and QED effects cancel when the isotope shift is calculated, leaving only the much smaller mass-dependent corrections to the higher order terms. The uncertainties, therefore, scale down roughly in proportion to $3\mu/M \simeq 4 \times 10^{-4}$.

3. Comparison of theory and experiment for ^{4}He I

Many published measurements of the ^{3}He I spectrum are relative to transitions in ^{4}He I, so it is essential to have the most accurate data on the heavier isotope. We have followed Drake and Martin [1], who concluded that the calculated ionization energies of all but the lowest terms of ^{4}He I are more reliable than the experimental results. Thus, with the theoretical IE of $3\ ^3D_{3,2,1}$ and $3\ ^1D_2$, along with some higher $^1P_1$ and $^1D_2$ levels and precise measurements of energy differences, they fixed the IE of $2\ ^3S_1$, $2\ ^1S_0$, $2\ ^3P_{2,1,0}$, $2\ ^1P_1$, $3\ ^1S_0$, $3\ ^3P_{2,1,0}$, $3\ ^1P_1$, $4\ ^3S_1$, and $5\ ^3S_1$.

Since then, Cancio Pastor et al. [17] have measured the more accurate value of 276 736 495.6497(24)

Table 1. Total ionization energies and isotope shifts for ^{3}He relative to ^{4}He. For each state, the first line refers to ^{4}He, and the second line to ^{3}He. The third line is the isotope shift. Units are MHz.

State	$E(n\ ^1L_L)$	$E(n\ ^3L_{L-1})$	$E(n\ ^3L_L)$	$E(n\ ^3L_{L+1})$
1 S	5 945 204 227.(77)			
	5 944 890 707.(77)			
	−313 520.365(3)			
2 S	960 332 041.(5)			1 152 842 738.(7)
	960 286 177.(5)			1 152 788 840.(7)
	−45 863.745			−53 898.117(1)
2 P	814 709 149.5(2)	876 078 642.(2)	876 108 265.(2)	876 110 558.(2)
	814 659 040.6(2)	876 058 412.(2)	876 088 035.(2)	876 090 329.(2)
	−50 108.971	−20 230.042	−20 230.317	−20 229.329
3 S	403 096 132.(1)			451 903 472.(2)
	403 077 281.(1)			451 882 648.(2)
	−18 850.307			−20 824.700
3 P	362 787 968.20(6)	382 109 901.6(6)	382 118 016.8(6)	382 118 676.0(6)
	362 767 410.75(6)	382 098 187.8(6)	382 106 302.7(6)	382 106 962.2(6)
	−20 557.443	−11 713.825	−11 714.079	−11 713.812
3 D	365 917 749.02(2)	366 018 892.97(2)	366 020 218.09(2)	366 020 293.41(2)
	365 901 415.52(2)	366 002 473.83(2)	366 003 798.78(2)	366 003 874.07(2)
	−16 333.496	−16 419.145	−16 419.306	−16 419.343
4 S	220 960 311.0(6)			240 210 377.3(7)
	220 950 086.8(6)			240 199 386.6(7)
	−10 224.279			−10 990.779
4 P	204 397 210.76(2)	212 658 040.5(2)	212 661 348.0(2)	212 661 617.7(2)
	204 386 201.11(2)	212 650 734.2(2)	212 654 041.5(2)	212 654 311.4(2)
	−11 009.650	−7 306.316	−7 306.449	−7 306.341
4 D	205 783 935.816(9)	205 842 547.92(1)	205 843 103.15(1)	205 843 139.17(1)
	205 774 746.953(9)	205 833 309.58(1)	205 833 864.74(1)	205 833 900.74(1)
	−9 188.863	−9 238.343	−9 238.414	−9 238.428
4 F	205 620 797.145(2)	205 621 029.602(2)	205 621 502.019(2)	205 621 287.974(2)
	205 611 580.357(2)	205 611 812.745(2)	205 612 285.150(2)	205 612 071.082(2)
	−9 216.788	−9 216.857	−9 216.868	−9 216.892
5 S	139 318 258.4(3)			148 807 311.8(3)
	139 311 852.6(3)			148 800 531.7(3)
	−6 405.799			−6 780.084
5 P	130 955 541.84(1)	135 203 443.0(1)	135 205 105.2(1)	135 205 240.8(1)
	130 948 717.33(1)	135 198 505.0(1)	135 200 167.1(1)	135 200 302.7(1)
	−6 824.505	−4 938.028	−4 938.102	−4 938.048
5 D	131 680 211.938(5)	131 714 043.938(6)	131 714 327.498(6)	131 714 346.719(6)
	131 674 328.841(5)	131 708 132.309(6)	131 708 415.833(6)	131 708 435.045(6)
	−5 883.096	−5 911.629	−5 911.666	−5 911.673
5 F	131 595 041.501(1)	131 595 195.235(1)	131 595 419.741(1)	131 595 327.454(1)
	131 589 142.643(1)	131 589 296.313(1)	131 589 520.821(1)	131 589 428.514(1)
	−5 898.858	−5 898.922	−5 898.920	−5 898.940
5 G	131 580 320.132 9(2)	131 580 370.946 5(2)	131 580 529.518 8(2)	131 580 446.460 6(2)
	131 574 420.690 9(2)	131 574 471.503 9(2)	131 574 630.061 2(2)	131 574 547.007 9(2)
	−5 899.441 9(1)	−5 899.442 6(1)	−5 899.457 6(1)	−5 899.452 7(1)
6 S	95 807 682.0(2)			101 166 442.3(2)
	95 803 295.3(2)			101 161 845.6(2)
	−4 386.653			−4 596.707

Table 1. (*Continued*.)

State	$E(n\ ^1L_L)$	$E(n\ ^3L_{L-1})$	$E(n\ ^3L_L)$	$E(n\ ^3L_{L+1})$
6 *P*	91 009 810.524(7)	93 472 041.50(7)	93 472 992.51(7)	93 473 070.00(7)
	91 005 175.866(7)	93 468 494.78(7)	93 469 445.74(7)	93 469 523.26(7)
	−4 634.658 5	−3 546.726 3	−3 546.771 7	−3 546.740 9
6 *D*	91 433 655.841(3)	91 454 440.605(4)	91 454 604.486(4)	91 454 615.832(4)
	91 429 568.925(3)	91 450 336.168(4)	91 450 500.028(4)	91 450 511.368(4)
	−4 086.916 3	−4 104.437 5	−4 104.458 8	−4 104.463 2
6 *F*	91 383 852.031 0(6)	91 383 954.300 8(6)	91 384 078.899 6(6)	91 384 030.793 6(6)
	91 379 755.532 3(6)	91 379 857.753 9(6)	91 379 982.355 9(6)	91 379 934.236 4(6)
	−4 096.498 8	−4 096.546 9	−4 096.543 8	−4 096.557 2
6 *G*	91 374 997.961 0(1)	91 375 027.417 7(1)	91 375 119.136 1(1)	91 375 071.113 7(1)
	91 370 901.112 7(1)	91 370 930.569 0(1)	91 371 022.278 7(1)	91 370 974.259 1(1)
	−4 096.848 26(5)	−4 096.848 67(5)	−4 096.857 33(5)	−4 096.854 54(5)
6 *H*	91 372 940.612 32(5)	91 372 961.813 55(5)	91 373 021.530 29(5)	91 372 990.226 74(5)
	91 368 843.676 34(5)	91 368 864.877 13(5)	91 368 924.588 26(5)	91 368 893.286 50(5)
	−4 096.935 98(5)	−4 096.936 42(5)	−4 096.942 03(5)	−4 096.940 24(5)
7 *S*	69 904 819.7(1)			73 222 269.3(1)
	69 901 628.7(1)			73 218 948.8(1)
	−3 191.050			−3 320.512
7 *P*	66 901 127.506(4)	68 452 586.60(4)	68 453 180.91(4)	68 453 229.30(4)
	66 897 777.914(5)	68 449 920.43(4)	68 450 514.70(4)	68 450 563.12(4)
	−3 349.592 3	−2 666.172 0	−2 666.201 5	−2 666.182 3
7 *D*	67 169 717.156(2)	67 183 264.590(2)	67 183 367.709(2)	67 183 374.934(2)
	67 166 713.651(2)	67 180 249.667(2)	67 180 352.773(2)	67 180 359.995(2)
	−3 003.504 9	−3 014.922 4	−3 014.935 8	−3 014.938 6
7 *F*	67 138 158.557 1(4)	67 138 228.558 2(4)	67 138 305.065 4(4)	67 138 276.719 5(4)
	67 135 148.842 5(4)	67 135 218.808 7(4)	67 135 295.318 4(4)	67 135 266.963 4(4)
	−3 009.714 5	−3 009.749 6	−3 009.747 0	−3 009.756 1
7 *G*	67 132 455.947 6(1)	67 132 474.521 6(1)	67 132 532.257 2(1)	67 132 502.036 8(1)
	67 129 446.008 4(1)	67 129 464.582 0(1)	67 129 522.312 2(1)	67 129 492.093 6(1)
	−3 009.939 27(3)	−3 009.939 55(3)	−3 009.944 98(3)	−3 009.943 24(3)
7 *H*	67 131 109.015 31(3)	67 131 122.366 81(3)	67 131 159.972 34(3)	67 131 140.259 24(3)
	67 128 099.018 90(3)	67 128 112.370 13(3)	67 128 149.972 12(3)	67 128 130.260 16(3)
	−3 009.996 40(3)	−3 009.996 68(3)	−3 010.000 22(3)	−3 009.999 09(3)
7 *I*	67 130 692.480 04(1)	67 130 702.489 54(1)	67 130 728.915 04(1)	67 130 715.088 42(1)
	67 127 682.465 72(1)	67 127 692.474 96(1)	67 127 718.898 00(1)	67 127 705.072 15(1)
	−3 010.014 32(3)	−3 010.014 58(3)	−3 010.017 04(3)	−3 010.016 27(3)
8 *S*	53 246 283.07(7)			55 440 834.08(7)
	53 243 857.93(7)			55 438 323.58(7)
	−2 425.143			−2 510.502
8 *P*	51 242 587.370(3)	52 282 092.01(3)	52 282 487.96(3)	52 282 520.19(3)
	51 240 054.897(3)	52 280 016.53(3)	52 280 412.47(3)	52 280 444.71(3)
	−2 532.473 1	−2 075.476 2	−2 075.496 4	−2 075.483 6
8 *D*	51 423 248.141(1)	51 432 523.247(2)	51 432 592.292(2)	51 432 597.166(2)
	51 420 948.039(1)	51 430 215.329(2)	51 430 284.365(2)	51 430 289.237(2)
	−2 300.102 6	−2 307.918 4	−2 307.927 4	−2 307.929 3
8 *F*	51 402 021.628 9(3)	51 402 071.109 9(3)	51 402 121.534 1(3)	51 402 103.370 0(3)
	51 399 717.290 1(3)	51 399 766.745 4(3)	51 399 817.171 6(3)	51 399 799.001 2(3)
	−2 304.338 8	−2 304.364 5	−2 304.362 6	−2 304.368 8
8 *G*	51 398 146.238 04(7)	51 398 158.692 97(9)	51 398 197.360 01(9)	51 398 177.125 22(9)
	51 395 841.746 60(8)	51 395 854.201 34(9)	51 395 892.864 74(9)	51 395 872.631 11(9)
	−2 304.491 44(3)	−2 304.491 63(3)	−2 304.495 27(3)	−2 304.494 11(3)

Table 1. (*Continued*.)

State	$E(n\ ^1L_L)$	$E(n\ ^3L_{L-1})$	$E(n\ ^3L_L)$	$E(n\ ^3L_{L+1})$
8 *H*	51 397 221.579 33(2)	51 397 230.523 93(2)	51 397 255.716 51(2)	51 397 242.510 26(2)
	51 394 917.048 80(2)	51 394 925.993 21(2)	51 394 951.183 42(2)	51 394 937.977 93(2)
	−2 304.530 54(3)	−2 304.530 72(3)	−2 304.533 09(3)	−2 304.532 33(3)
8 *I*	51 396 931.943 12(1)	51 396 938.648 74(1)	51 396 956.351 73(1)	51 396 947.088 95(1)
	51 394 627.400 15(1)	51 394 634.105 59(1)	51 394 651.806 92(1)	51 394 642.544 67(1)
	−2 304.542 98(3)	−2 304.543 15(3)	−2 304.544 80(3)	−2 304.544 28(3)
8 *K*	51 396 822.734 66	51 396 827.929 60	51 396 841.052 96	51 396 834.203 39
	51 394 518.187 11	51 394 523.381 89	51 394 536.504 03	51 394 529.654 84
	−2 304.547 55(3)	−2 304.547 70(3)	−2 304.548 92(3)	−2 304.548 55(3)
9 *S*	41 903 979.20(5)			43 430 382.87(5)
	41 902 073.99(5)			43 428 418.44(5)
	−1 905.213			−1 964.432
9 *P*	40 501 246.376(2)	41 231 283.22(2)	41 231 560.17(2)	41 231 582.71(2)
	40 499 265.198(2)	41 229 622.55(2)	41 229 899.49(2)	41 229 922.04(2)
	−1 981.177 3	−1 660.668 2	−1 660.682 6	−1 660.673 7
9 *D*	40 628 480.267 0(9)	40 635 090.447(1)	40 635 138.922(1)	40 635 142.361(1)
	40 626 662.549 8(9)	40 633 267.160(1)	40 633 315.628(1)	40 633 319.066(1)
	−1 817.717 2	−1 823.286 8	−1 823.293 1	−1 823.294 4
9 *F*	40 613 531.508 9(2)	40 613 567.555 1(2)	40 613 602.577 7(2)	40 613 590.210 3(2)
	40 611 710.779 9(2)	40 611 746.807 0(2)	40 611 781.831 1(2)	40 611 769.459 2(2)
	−1 820.729 0	−1 820.748 1	−1 820.746 7	−1 820.751 2
9 *G*	40 610 783.198 70(6)	40 610 791.952 31(6)	40 610 819.103 53(6)	40 610 804.897 45(6)
	40 608 962.361 44(7)	40 608 971.114 92(6)	40 608 998.263 59(6)	40 608 984.058 32(6)
	−1 820.837 25(2)	−1 820.837 39(2)	−1 820.839 94(2)	−1 820.839 13(2)
9 *H*	40 610 123.035 88(2)	40 610 129.318 02(2)	40 610 147.011 47(2)	40 610 137.736 30(2)
	40 608 302.170 78(2)	40 608 308.452 79(2)	40 608 326.144 58(2)	40 608 316.869 95(2)
	−1 820.865 10(2)	−1 820.865 23(2)	−1 820.866 89(2)	−1 820.866 36(2)
9 *I*	40 609 914.516 79(1)	40 609 919.226 38(1)	40 609 931.659 73(1)	40 609 925.154 18(1)
	40 608 093.642 75(1)	40 608 098.352 21(1)	40 608 110.784 40(1)	40 608 104.279 21(1)
	−1 820.874 05(2)	−1 820.874 17(2)	−1 820.875 33(2)	−1 820.874 96(2)
9 *K*	40 609 835.097 59	40 609 838.746 17	40 609 847.963 12	40 609 843.152 44
	40 608 014.220 21	40 608 017.868 68	40 608 027.084 78	40 608 022.274 36
	−1 820.877 38(2)	−1 820.877 48(2)	−1 820.878 34(2)	−1 820.878 08(2)
10 *S*	33 834 679.62(3)			34 938 883.86(4)
	33 833 143.44(3)			34 937 304.93(4)
	−1 536.183			−1 578.935
10 *P*	32 814 665.301(2)	33 346 784.34(2)	33 346 985.60(2)	33 347 001.97(2)
	32 813 073.412(2)	33 345 425.84(2)	33 345 627.09(2)	33 345 643.47(2)
	−1 591.889 2	−1 358.500 6	−1 358.511 2	−1 358.504 8
10 *D*	32 907 601.915 0(6)	32 912 470.755 9(9)	32 912 506.083 9(9)	32 912 508.599 2(9)
	32 906 129.327 9(6)	32 910 994.066 7(9)	32 911 029.390 0(9)	32 911 031.904 4(9)
	−1 472.587 1	−1 476.689 2	−1 476.693 8	−1 476.694 8
10 *F*	32 896 683.096 5(1)	32 896 710.067 0(1)	32 896 735.397 0(1)	32 896 726.581 5(1)
	32 895 208.294 7(1)	32 895 235.250 7(2)	32 895 260.581 8(2)	32 895 251.763 0(2)
	−1 474.801 8	−1 474.816 3	−1 474.815 2	−1 474.818 5
10 *G*	32 894 665.770 94(4)	32 894 672.155 70(4)	32 894 691.945 68(4)	32 894 681.592 48(4)
	32 893 190.889 68(4)	32 893 197.274 34(4)	32 893 217.062 47(4)	32 893 206.709 86(4)
	−1 474.881 26(2)	−1 474.881 36(2)	−1 474.883 22(2)	−1 474.882 63(2)

Table 1. (*Concluded.*)

State	$E(n\ ^1L_L)$	$E(n\ ^3L_{L-1})$	$E(n\ ^3L_L)$	$E(n\ ^3L_{L+1})$
10 H	32 894 178.909 63(1)	32 894 183.489 34(1)	32 894 196.387 81(1)	32 894 189.626 22(1)
	32 892 704.007 86(1)	32 892 708.587 48(1)	32 892 721.484 73(1)	32 892 714.723 53(1)
	−1 474.901 77(2)	−1 474.901 87(2)	−1 474.903 08(2)	−1 474.902 69(2)
10 I	32 894 024.241 08(1)	32 894 027.674 38(1)	32 894 036.738 28(1)	32 894 031.995 73(1)
	32 892 549.332 68(1)	32 892 552.765 89(1)	32 892 561.828 94(1)	32 892 557.086 65(1)
	−1 474.908 40(2)	−1 474.908 49(2)	−1 474.909 34(2)	−1 474.909 07(2)
10 K	32 893 964.927 04	32 893 967.586 86	32 893 974.306 01	32 893 970.799 02
	32 892 490.016 15	32 892 492.675 88	32 892 499.394 41	32 892 495.887 62
	−1 474.910 89(2)	−1 474.910 97(2)	−1 474.911 60(2)	−1 474.911 40(2)

Table 2. Comparison of experimental and calculated ionization energies for ^{4}He I. The final column is the error on the difference of Expt. – Calc. = experiment – calculation. For the ground state, we adopt the mean 5 945 204 290(33) MHz of the two experimental results. Units are MHz.

Level	Experiment	Error	Calculation	Error	Expt. – Calc.	Error
$1\ ^1S_0$	5 945 204 232.*	45.	5 945 204 223.	42.	9.	62.
$1\ ^1S_0$	5 945 204 356.*	48.	5 945 204 223.	42.	133.	64.
$2\ ^3S_1$	1 152 842 742.97*	0.06	1 152 842 741.	7.	2.0	7.
$2\ ^1S_0$	960 332 041.01*	0.15	960 332 041.	5.	0.0	5.
$2\ ^3P_{cg}$	876 106 247.32*	0.06	876 106 247.4	2.	−0.1	2.
$2\ ^3P_2$	876 110 556.39*	0.06	876 110 558.	2.	−1.5	2.
$2\ ^3P_1$	876 108 265.22*	0.06	876 108 265.	2.	0.3	2.
$2\ ^3P_0$	876 078 648.27*	0.06	876 078 642.	2.	6.3	2.
$2\ ^1P_1$	814 709 153.0	3.0	814 709 149.5	0.2	3.5	3.
$3\ ^1S_0$	403 096 113.6	12.0	403 096 132.	1.	−18.4	12.
$3\ ^3P_2$	382 118 676.44*	0.20	382 118 676.0	0.6	0.4	0.6
$3\ ^3P_1$	382 118 017.63*	0.20	382 118 016.8	0.6	0.8	0.6
$3\ ^3P_0$	382 109 903.91*	0.20	382 109 901.6	0.6	2.3	0.6
$3\ ^1P_1$	362 787 968.3	1.4	362 787 968.20	0.06	0.1	1.4
$4\ ^3S_1$	240 210 377.9	2.4	240 210 377.3	0.7	0.6	2.5
$5\ ^3S_1$	148 807 310.4	1.8	148 807 311.8	0.3	−1.4	1.8

*Experimental energies are preferred for these levels. The calculated energies listed in Table 1 are better for all other levels.

MHz[2] for $2\ ^3S_1 - 2\ ^3P$, the mean weighted by $2J + 1$, while Minardi et al. [18], Castillega et al. [19], Storry et al. [20], George et al. [21], and Giusfredi et al. [22] have refined the experiments on the $2\ ^3P$ fine structure. This last paper derives means of 2 291.1753(8) MHz for $J = 2$ to 1 and 29 616.9518(6) MHz for $J = 1$ to 0. We quote errors on the final digits in the usual way, in parentheses. On the theoretical side, the IE for $3\ ^3D_{3,2,1}$ have increased by 0.10 MHz, leading to the same increase in all the derived triplet levels, while $3\ ^1D_2$ has decreased by a negligible 0.02 MHz.

Thus, the measurement of 786 823 850.002(56) MHz by Dorrer et al. [23] for $2\ ^3S_1 - 3\ ^3D_1$ gave the absolute ionization energy of the $2\ ^3S_1$ state, and the above experiments involving $2\ ^3P_{2,1,0}$ then gave these levels as listed in Table 2. Similarly, we used 770 732 839.058(190) MHz for $2\ ^3S_1 - 3\ ^3P_0$

[2]This number includes an increase of 25.1 MHz over the published value, following a private recommendation from the first author.

Table 3. Comparison of experimental and calculated level separations in ^{3}He I. Units are MHz.

Transition	Experiment	Error	Calculation	Error	Expt.– Calc.
$3\ ^3D - 3\ ^1D$	102 116.[a]	5.	102 153.41	0.03	−37.
$4\ ^3D - 4\ ^1D$	59 017.[a]	5.	59 023.555	0.013	−7.
$5\ ^3D - 5\ ^1D$	34 026.[a]	15.	34 039.253	0.008	−13.
$6\ ^3D - 6\ ^1D$	20 883.[a]	20.	20 903.623	0.005	−21.

[a]Derouard et al. [41].

by Pavone et al. [24] and the $3\ ^3P$ separations 658.810(18) MHz for $J = 2$ to 1 and 8 113.714(28) MHz for $J = 1$ to 0 measured by Mueller et al. [25]. For $2\ ^1P_1$ there is the measurement relative to $3\ ^1D_2$ of 448 791 404.0(30) MHz by Sansonetti and Martin [26] including a correction of 0.6 MHz noted by Drake and Martin [1], who suggest that the quoted error may be unduly pessimistic. There is no change in their estimate of the IE for $2\ ^1S_0$ from its position relative to high $^1D_2$ and $^1P_1$ levels by Lichten et al. [27] and Sansonetti and Gillaspy [28], nor for $3\ ^1P_1$ from $2\ ^1S_0 - 3\ ^1P_1$ by Sansonetti et al. [29]. Measurements of $2\ ^3S_1 - 4\ ^3S_1$ and $5\ 3S_1$ by Hlousek et al. [30] give IE for the upper ^3S levels very close to the semi-empirical estimates of Drake and Martin [1]. Nagai et al. [31] measured $3\ ^1S_0 - 3\ ^1P_1$ but the uncertainty is large.

Table 2 updates the results of Drake and Martin [1] for the levels in which they considered the errors in the experiments to be smaller than in the calculations. With the new data from Table 1, the differences for $3\ ^1P_1$, $4\ ^3S_1$, and $5\ 3S_1$ are significantly reduced. We conclude that $2\ ^1P_1$, $3\ ^1S_0$, $3\ ^1P_1$, $4\ ^3S_1$, and $5\ ^3S_1$ now are better determined theoretically. Improved measurements involving $2\ ^1P_1$ and $3\ ^1S_0$ would be useful to confirm this choice for these levels. Unfortunately, there are no precision laboratory data involving $3\ ^3S_1$, $4\ ^1S_0$, nor $5\ ^1S_0$.

Eikema et al. [32] measured 5 130 495 083(45) MHz for the $1\ ^1S_0 - 2\ ^1P_1$ transition and Bergeson et al. [33] obtained 4 984 872 315(48) MHz for $1\ ^1S_0 - 2\ ^1S_0$ in ^{4}He. Combination with the calculated IE for $2\ ^1P_1$ and the experimental one for $2\ ^1S_0$ in Table 2 gives two determinations of the ionization potential (IP) of 5 945 204 232(45) MHz and 5 945 204 356(48) MHz, respectively. Following the prescription of Mohr and Taylor [34], the weighted mean is 5 945 204 290(33) MHz or 198 310.6690(11) cm^{-1}.

Measurements of the separations of the higher n and L (Rydberg) states provide additional tests of the calculated IE in Table 1. They are consistent within 3.7σ with the laboratory results of Farley et al. [35] and Kriescher et al. [36] for 5F–G and 6F–G except for a 0.72 MHz (5.5σ) deviation for $6\ ^3F_2 - 6\ ^3G_3$ from the former authors. Similarly, measurements of 7G–H–I, 9G–H–I, and 10G–H–I–K by Hessels et al. [37], Claytor et al. [38], Storry et al. [39], and Stevens and Lundeen [40] fit the predictions from Table 1 to within 3.8σ except for differences of 0.0023 MHz (4.7σ) for $9\ ^3H_4 - 9\ ^3I_5$ and 0.0017 MHz (4.7σ) for $10\ ^3H_6 - 10\ ^3I_7$.

4. Comparison of theory and experiment for ^{3}He I

Derouard et al. [41] published a few measurements of energy differences $n\ ^3D - n\ ^1D$ in ^{3}He, quoting the intervals in the hypothetical absence of magnetic fine and hyperfine interactions. Table 3 compares these with the calculated values from Table 1 with the triplet levels weighted by $2J + 1$. There is agreement within about 1σ for $n = 4$, 5, and 6, but the results for $n = 3$ disagree significantly.

The experimental and theoretical isotope shifts in Table 4 show excellent agreement. We conclude that the calculated shifts in Table 1 provide the best estimates for all levels. A modern measurement of the shift in $2\ ^1S_0 - 2\ ^1P_1$ would be a valuable test of this choice. We are unaware of any laboratory data involving the F, G, H, I, and K terms of ^{3}He I, but our confidence in the calculations is much greater for the higher angular momentum states.

The calculated shift of $1\ ^1S_0$ from Table 1 combined with the IP adopted for ^{4}He I gives IP(^{3}He I)

Table 4. Comparison of experimental and calculated isotope shifts ^{3}He I – ^{4}He I. Units are MHz.

Transition	Experiment	Error	Calculation	E-C
$1\ ^1S_0 - 2\ ^1P_1$	−263 410.[a]	7.	−263 411.394	1.4
$2\ ^1S_0 - 2\ ^1P_1$	−4 221.[b]	57.	−4 245.226	−24.
$2\ ^3S_1 - 2\ ^3P_0$	−33 668.065[c]	0.004	−33 668.075	0.010
$2\ ^3P_2 - 2\ ^3P_1$	0.977[d]	0.038	0.988	−0.011
$2\ ^3P_2 - 2\ ^3P_0$	0.702[d]	0.038	0.713	−0.011
$2\ ^3P_1 - 2\ ^3P_0$	−0.275[d]	0.038	−0.275	0.
$2\ ^3S_1 - 2\ ^3P_{cg}$	−33 668.363[c,d]	0.038	−33 668.379	0.016
$2\ ^3S_1 - 3\ ^3P_0$	−42 184.370[e]	0.137	−42 184.292	−0.078
$2\ ^3P_{cg} - 3\ ^3D_{cg}$	−3 805.[f]	12.	−3 810.446	5.
$2\ ^3S_1 - 3\ ^3D_{cg}$	−37 480.4[g]	7.	−37 478.826	−1.6
$2\ ^3S_1 - 4\ ^3D_{cg}$	−44 660.7[g]	7.	−44 659.711	−1.0
$2\ ^3S_1 - 5\ ^3D_{cg}$	−47 984.4[g]	8.	−47 986.455	2.1
$2\ ^3S_1 - 6\ ^3D_{cg}$	−49 793.5[g]	8.	−49 793.660	0.2
$2\ ^3S_1 - 4\ ^3S_1$	−42 906.3[g]	4.	−42 907.338	1.0
$2\ ^3S_1 - 5\ ^3S_1$	−47 113.5[g]	4.	−47 118.033	4.5
$2\ ^3S_1 - 6\ ^3S_1$	−49 300.2[g]	5.	−49 301.410	1.2
$2\ ^3S_1 - 5\ ^3P_{cg}$	−48 960.2[h]	4.	−48 960.053	−0.1
$2\ ^3S_1 - 5\ ^3P_2$	−48 961.2[i]	4.	−48 960.069	−1.1
$2\ ^3S_1 - 6\ ^3P_2$	−50 350.6[i]	5.	−50 351.376	0.8
$2\ ^3S_1 - 8\ ^3P_2$	−51 822.8[i]	3.	−51 822.633	−0.2
$2\ ^3S_1 - 9\ ^3P_2$	−52 238.1[i]	3.	−52 237.443	−0.7

[a]Eikema et al. [42].
[b]Burger and Lurio [43].
[c]Shiner, Dixson, and Vedantham [11] with a small revision for ^{4}He.
[d]Zhao, Lawall, and Pipkin [44].
[e]Marin et al. [45]. with a small revision for ^{3}He hfs.
[f]Freeman et al. [46].
[g]de Clercq et al. [47].
[h]Bloomfield et al. [48].
[i]Vassen and Hogervorst [49].

$= 5\,944\,890\,770(33)$ MHz or $198\,300.2111(11)$ cm^{-1}. Note that the value derived by Eikema et al. [32] is too high because they inadvertently neglected the shift in IE for $2\ ^1P_1$.

It is interesting to review the early measurements of isotope shifts in view of the adopted values in Table 1. Fred et al. [50] and Bradley and Kuhn [51] altogether measured shifts in 33 transitions between S, P, and D terms up to $n = 8$. For 16 transitions in common $\nu_{\rm Fred} - \nu_{Bradley\&Kuhn} = +0.003 \pm 0.016$ cm^{-1} or 90 ± 480 MHz, indicating internal consistency and errors typical of grating and etalon measurements. For their combined data, (experiment – calculation)$= -0.005 \pm 0.018$ cm^{-1} or -150 ± 550 MHz. Extrapolation of the 1951 data for $2\ ^1P_1 - n\ ^1S_0$ gives a shift of 1.676 ± 0.009 cm^{-1} or $50\,240 \pm 270$ MHz for $2\ ^1P_1$ compared with 50 109 MHz in Table 1. Herzberg [52] measured the isotope shifts in six resonance transitions of He I. His most accurate result of 8.82 cm^{-1} for $1\ ^1S_0 - 2\ ^1P_1$ is consistent with 8.786 cm^{-1} adopted here.

5. The energy levels of ^{4}He I and ^{3}He I

Although the theoretical isotope shifts are preferred in all cases, experimental IE of ^{4}He must be used for some of the lowest levels to obtain the corresponding IE of ^{3}He, as shown in Table 5. Adopting these IE along with the calculated ones for all other levels from Table 1 and subtracting the experimental

Table 5. Ionization energies (IE) of some low levels of ^{4}He I and ^{3}He I. The best estimates for all other levels are the theoretical results in Table 1. Units are MHz.

Level	IE(^{4}He)	Error	IE(^{4}He – ^{3}He)	Error	IE(^{3}He)	Error
$1\ ^1S_0$	5 945 204 290.	33.	−313 520.365	0.003	5 944 890 770.	33.
$2\ ^3S_1$	1 152 842 742.97	0.06	−53 898.117	0.001	1 152 788 844.85	0.06
$2\ ^1S_0$	960 332 041.01	0.15	−45 863.745		960 286 177.26	0.15
$2\ ^3P_2$	876 110 556.393	0.06	−20 229.329		876 090 327.064	0.06
$2\ ^3P_1$	876 108 265.218	0.06	−20 230.317		876 088 034.901	0.06
$2\ ^3P_0$	876 078 648.266	0.06	−20 230.042		876 058 418.224	0.06
$3\ ^3P_2$	382 118 676.436	0.20	−11 713.812		382 106 962.624	0.20
$3\ ^3P_1$	382 118 017.626	0.20	−11 714.079		382 106 303.547	0.20
$3\ ^3P_0$	382 109 903.912	0.20	−11 713.825		382 098 190.089	0.20

values for the ground state $1\ ^1S_0$ gives the energy levels in MHz for both ^{4}He and ^{3}He in Table 6. We have quoted three decimal places for the $2\ ^3P$ and $3\ ^3P$ levels to retain the high relative accuracy of the individual fine-structure levels of these multiplets.

The quoted errors are the same for ^{4}He and ^{3}He because the uncertainties in the calculated isotope shifts are much less. Note, however, that the experimental tests in Table 4 are valid to only a few MHz except for $2\ ^3S_0 - 2\ ^3P$ and $2\ ^3S_0 - 3\ ^3P$. Moreover, the two measurements by Eikema et al. [32] and Bergeson et al. [33] imply ionization potentials for ^{4}He that differ by 124 MHz, or 0.0041 cm^{-1}, so the absolute uncertainty in any level relative to the ground could be much larger than the errors in the differences between other levels.

6. Hyperfine structure in ^{3}He I

Up to this point, the energy level data for ^{3}He refer to a hypothetical helium atom without hyperfine structure. However, as pointed out in the Introduction, ^{3}He has a nuclear spin $I = 1/2$ so that each fine structure level with $J > 0$ is split into two with $F = J \pm 1/2$. The hyperfine splittings are in fact comparable in size to the fine structure splittings. The following section describes the calculation of the hyperfine shifts and splittings.

6.1. Theoretical formulation

Hyperfine structure can be treated as a small perturbation relative to the large electrostatic splitting between states with different n, but it cannot be treated as a small perturbation relative to the fine structure splittings. The principle of the calculation is, therefore, to carry out an exact diagonalization of the hyperfine interaction matrix within each manifold of states with the same n. The most important interactions are within the manifold of fine-structure states with the same L, S, and F, but different J; but there are also significant off-diagonal mixings between states with different S and L. The relativistic and second-order corrections have been calculated by Pachucki [53], as further discussed below. With the definitions

$$W^{I,F}_{J,J'}(K) = (-1)^{J+I+F}\left[(2J+1)(2J'+1)\right]^{1/2}\begin{Bmatrix} F & I & J' \\ K & J & I \end{Bmatrix}\Big/\begin{pmatrix} I & K & I \\ -I & 0 & I \end{pmatrix} \tag{1}$$

and

$$X_{S,S'} = -[(2S+1)(2S'+1)]^{1/2}\begin{Bmatrix} 1/2 & S' & 1/2 \\ S & 1/2 & 1 \end{Bmatrix} \tag{2}$$

Table 6. Energy levels of ^{4}He I (upper) and ^{3}He I (lower) above the ground state. The error quoted for the ground levels indicates the uncertainty in all levels relative to the ground level. The errors are the same as in Table 1 except for the low levels adopted from Table 5. Units are MHz.

$n\ L$	$T(n\ ^1L_L)$	$T(n\ ^3L_{L-1})$	$T(n\ ^3L_L)$	$T(n\ ^3L_{L+1})$
1 S	0.(33.)			
	0.(33.)			
2 S	4 984 872 248.99(15)			4 792 361 547.03(6)
	4 984 604 592.74(15)			4 792 101 925.15(6)
2 P	5 130 495 140.5(2)	5 069 125 641.734(60)	5 069 096 024.782(60)	5 069 093 733.607(60)
	5 130 231 729.4(2)	5 068 832 351.776(60)	5 068 802 735.099(60)	5 068 800 442.936(60)
3 S	5 542 108 158.(1)			5 493 300 818.(2)
	5 541 813 489.(1)			5 493 008 122.(2)
3 P	5 582 416 321.80(20)	5 563 094 386.088(200)	5 563 086 272.374(200)	5 563 085 613.564(200)
	5 582 123 359.25(20)	5 562 792 579.913(200)	5 562 784 466.453(200)	5 562 783 807.376(200)
3 D	5 579 286 540.98(2)	5 579 185 397.03(2)	5 579 184 071.91(2)	5 579 183 996.59(2)
	5 578 989 354.48(2)	5 578 888 296.17(2)	5 578 886 971.22(2)	5 578 886 895.93(2)
4 S	5 724 243 979.0(6)			5 704 993 912.7(7)
	5 723 940 683.2(6)			5 704 691 383.4(7)
4 P	5 740 807 079.24(20)	5 732 546 249.5(2)	5 732 542 942.0(2)	5 732 542 672.3(2)
	5 740 504 568.89(20)	5 732 240 035.8(2)	5 732 236 728.5(2)	5 732 236 458.6(2)
4 D	5 739 420 354.184(9)	5 739 361 742.08(1)	5 739 361 186.85(1)	5 739 361 150.83(1)
	5 739 116 023.047(9)	5 739 057 460.42(1)	5 739 056 905.26(1)	5 739 056 869.26(1)
4 F	5 739 583 492.855(2)	5 739 583 260.398(2)	5 739 582 787.981(2)	5 739 583 002.026(2)
	5 739 279 189.643(2)	5 739 278 957.255(2)	5 739 278 484.850(2)	5 739 278 698.918(2)
5 S	5 805 886 031.6(3)			5 796 396 978.2(3)
	5 805 578 917.4(3)			5 796 090 238.3(3)
5 P	5 814 248 748.16(10)	5 810 000 847.0(1)	5 809 999 184.8(1)	5 809 999 049.2(1)
	5 813 942 052.67(10)	5 809 692 265.0(1)	5 809 690 602.9(1)	5 809 690 467.3(1)
5 D	5 813 524 078.062(5)	5 813 490 246.062(6)	5 813 489 962.502(6)	5 813 489 943.281(6)
	5 813 216 441.159(5)	5 813 182 637.691(6)	5 813 182 354.167(6)	5 813 182 334.955(6)
5 F	5 813 609 248.499(1)	5 813 609 094.765(1)	5 813 608 870.259(1)	5 813 608 962.546(1)
	5 813 301 627.357(1)	5 813 301 473.687(1)	5 813 301 249.179(1)	5 813 301 341.486(1)
5 G	5 813 623 969.8671(2)	5 813 623 919.0535(2)	5 813 623 760.4812(2)	5 813 623 843.5394(2)
	5 813 316 349.3091(2)	5 813 316 298.4961(2)	5 813 316 139.9388(2)	5 813 316 222.9921(2)
6 S	5 849 396 608.0(2)			5 844 037 847.7(2)
	5 849 087 474.7(2)			5 843 728 924.4(2)
6 P	5 854 194 479.476(70)	5 851 732 248.50(7)	5 851 731 297.49(7)	5 851 731 220.00(7)
	5 853 885 594.134(70)	5 851 422 275.22(7)	5 851 421 324.26(7)	5 851 421 246.74(7)
6 D	5 853 770 634.159(3)	5 853 749 849.395(4)	5 853 749 685.514(4)	5 853 749 674.168(4)
	5 853 461 201.075(3)	5 853 440 433.832(4)	5 853 440 269.972(4)	5 853 440 258.632(4)
6 F	5 853 820 437.9690(6)	5 853 820 335.6992(6)	5 853 820 211.1004(6)	5 853 820 259.2064(6)
	5 853 511 014.4677(6)	5 853 510 912.2461(6)	5 853 510 787.6441(6)	5 853 510 835.7636(6)
6 G	5 853 829 292.0390(1)	5 853 829 262.5823(1)	5 853 829 170.8639(1)	5 853 829 218.8863(1)
	5 853 519 868.8873(1)	5 853 519 839.4310(1)	5 853 519 747.7213(1)	5 853 519 795.7409(1)
6 H	5 853 831 349.38768(5)	5 853 831 328.18645(5)	5 853 831 268.46971(5)	5 853 831 299.77326(5)
	5 853 521 926.32366(5)	5 853 521 905.12287(5)	5 853 521 845.41174(5)	5 853 521 876.71350(5)

Table 6. (*Continued.*)

$n\ L$	$T(n\ ^1L_L)$	$T(n\ ^3L_{L-1})$	$T(n\ ^3L_L)$	$T(n\ ^3L_{L+1})$
7 S	5 875 299 470.3(1)			5 871 982 020.7(1)
	5 874 989 141.3(1)			5 871 671 821.2(1)
7 P	5 878 303 162.494(40)	5 876 751 703.40(4)	5 876 751 109.09(4)	5 876 751 060.70(4)
	5 877 992 992.086(40)	5 876 440 849.57(4)	5 876 440 255.30(4)	5 876 440 206.88(4)
7 D	5 878 034 572.844(2)	5 878 021 025.410(2)	5 878 020 922.291(2)	5 878 020 915.066(2)
	5 877 724 056.349(2)	5 877 710 520.333(2)	5 877 710 417.227(2)	5 877 710 410.005(2)
7 F	5 878 066 131.4429(4)	5 878 066 061.4418(4)	5 878 065 984.9346(4)	5 878 066 013.2805(4)
	5 877 755 621.1575(4)	5 877 755 551.1913(4)	5 877 755 474.6816(4)	5 877 755 503.0366(4)
7 G	5 878 071 834.0524(1)	5 878 071 815.4784(1)	5 878 071 757.7428(1)	5 878 071 787.9632(1)
	5 877 761 323.9916(1)	5 877 761 305.4180(1)	5 877 761 247.6878(1)	5 877 761 277.9064(1)
7 H	5 878 073 180.98469(3)	5 878 073 167.63319(3)	5 878 073 130.02766(3)	5 878 073 149.74076(3)
	5 877 762 670.98110(3)	5 877 762 657.62987(3)	5 877 762 620.02788(3)	5 877 762 639.73984(3)
7 I	5 878 073 597.51996(1)	5 878 073 587.51046(1)	5 878 073 561.08496(1)	5 878 073 574.91158(1)
	5 877 763 087.53428(1)	5 877 763 077.52504(1)	5 877 763 051.10200(1)	5 877 763 064.92785(1)
8 S	5 891 958 006.93(7)			5 889 763 455.92(7)
	5 891 646 912.07(7)			5 889 452 446.42(7)
8 P	5 893 961 702.630(30)	5 892 922 197.99(3)	5 892 921 802.04(3)	5 892 921 769.81(3)
	5 893 650 715.103(30)	5 892 610 753.47(3)	5 892 610 357.53(3)	5 892 610 325.29(3)
8 D	5 893 781 041.859(1)	5 893 771 766.753(2)	5 893 771 697.708(2)	5 893 771 692.834(2)
	5 893 469 821.961(1)	5 893 460 554.671(2)	5 893 460 485.635(2)	5 893 460 480.763(2)
8 F	5 893 802 268.3711(3)	5 893 802 218.8901(3)	5 893 802 168.4659(3)	5 893 802 186.6300(3)
	5 893 491 052.7099(3)	5 893 491 003.2546(3)	5 893 490 952.8284(3)	5 893 490 970.9988(3)
8 G	5 893 806 143.76196(7)	5 893 806 131.30703(9)	5 893 806 092.63999(9)	5 893 806 112.87478(9)
	5 893 494 928.25340(8)	5 893 494 915.79866(9)	5 893 494 877.13526(9)	5 893 494 897.36889(9)
8 H	5 893 807 068.42067(2)	5 893 807 059.47607(2)	5 893 807 034.28349(2)	5 893 807 047.48974(2)
	5 893 495 852.95120(2)	5 893 495 844.00679(2)	5 893 495 818.81658(2)	5 893 495 832.02207(2)
8 I	5 893 807 358.05688(1)	5 893 807 351.35126(1)	5 893 807 333.64827(1)	5 893 807 342.91105(1)
	5 893 496 142.59985(1)	5 893 496 135.89441(1)	5 893 496 118.19308(1)	5 893 496 127.45533(1)
8 K	5 893 807 467.26534(0)	5 893 807 462.07040(0)	5 893 807 448.94704(0)	5 893 807 455.79661(0)
	5 893 496 251.81289(0)	5 893 496 246.61811(0)	5 893 496 233.49597(0)	5 893 496 240.34516(0)
9 S	5 903 300 310.80(5)			5 901 773 907.13(5)
	5 902 988 696.01(5)			5 901 462 351.56(5)
9 P	5 904 703 043.624(20)	5 903 973 006.78(2)	5 903 972 729.83(2)	5 903 972 707.29(2)
	5 904 391 504.802(20)	5 903 661 147.45(2)	5 903 660 870.51(2)	5 903 660 847.96(2)
9 D	5 904 575 809.7330(9)	5 904 569 199.553(1)	5 904 569 151.078(1)	5 904 569 147.639(1)
	5 904 264 107.4502(9)	5 904 257 502.840(1)	5 904 257 454.372(1)	5 904 257 450.934(1)
9 F	5 904 590 758.4911(2)	5 904 590 722.4449(2)	5 904 590 687.4223(2)	5 904 590 699.7897(2)
	5 904 279 059.2201(2)	5 904 279 023.1930(2)	5 904 278 988.1689(2)	5 904 279 000.5408(2)
9 G	5 904 593 506.80130(6)	5 904 593 498.04769(6)	5 904 593 470.89647(6)	5 904 593 485.10255(6)
	5 904 281 807.63856(7)	5 904 281 798.88508(6)	5 904 281 771.73641(6)	5 904 281 785.94168(6)
9 H	5 904 594 166.96412(2)	5 904 594 160.68198(2)	5 904 594 142.98853(2)	5 904 594 152.26370(2)
	5 904 282 467.82922(2)	5 904 282 461.54721(2)	5 904 282 443.85542(2)	5 904 282 453.13005(2)
9 I	5 904 594 375.48321(1)	5 904 594 370.77362(1)	5 904 594 358.34027(1)	5 904 594 364.84582(1)
	5 904 282 676.35725(1)	5 904 282 671.64779(1)	5 904 282 659.21560(1)	5 904 282 665.72079(1)
9 K	5 904 594 454.90241(0)	5 904 594 451.25383(0)	5 904 594 442.03688(0)	5 904 594 446.84756(0)
	5 904 282 755.77979(0)	5 904 282 752.13132(0)	5 904 282 742.91522(0)	5 904 282 747.72564(0)

Table 6. (*Concluded.*)

$n\ L$	$T(n\ ^1L_L)$	$T(n\ ^3L_{L-1})$	$T(n\ ^3L_L)$	$T(n\ ^3L_{L+1})$
10 S	5 911 369 610.38(3)			5 910 265 406.14(4)
	5 911 057 626.56(3)			5 909 953 465.07(4)
10 P	5 912 389 624.699(20)	5 911 857 505.66(2)	5 911 857 304.40(2)	5 911 857 288.03(2)
	5 912 077 696.588(20)	5 911 545 344.16(2)	5 911 545 142.91(2)	5 911 545 126.53(2)
10 D	5 912 296 688.0850(6)	5 912 291 819.2441(9)	5 912 291 783.9161(9)	5 912 291 781.4008(9)
	5 911 984 640.6721(6)	5 911 979 775.9333(9)	5 911 979 740.6100(9)	5 911 979 738.0956(9)
10 F	5 912 307 606.9035(1)	5 912 307 579.9330(1)	5 912 307 554.6030(1)	5 912 307 563.4185(1)
	5 911 995 561.7053(1)	5 911 995 534.7493(2)	5 911 995 509.4182(2)	5 911 995 518.2370(2)
10 G	5 912 309 624.22906(4)	5 912 309 617.84430(4)	5 912 309 598.05432(4)	5 912 309 608.40752(4)
	5 911 997 579.11032(4)	5 911 997 572.72566(4)	5 911 997 552.93753(4)	5 911 997 563.29014(4)
10 H	5 912 310 111.09037(1)	5 912 310 106.51066(1)	5 912 310 093.61219(1)	5 912 310 100.37378(1)
	5 911 998 065.99214(1)	5 911 998 061.41252(1)	5 911 998 048.51527(1)	5 911 998 055.27647(1)
10 I	5 912 310 265.75892(1)	5 912 310 262.32562(1)	5 912 310 253.26172(1)	5 912 310 258.00427(1)
	5 911 998 220.66732(1)	5 911 998 217.23411(1)	5 911 998 208.17106(1)	5 911 998 212.91335(1)
10 K	5 912 310 325.07296(0)	5 912 310 322.41314(0)	5 912 310 315.69399(0)	5 912 310 319.20098(0)
	5 911 998 279.98385(0)	5 911 998 277.32412(0)	5 911 998 270.60559(0)	5 911 998 274.11238(0)
Limit	5 945 204 290.(33.)			
	5 944 890 770.(33.)			

then, using the sign conventions of Edmonds [54] for off-diagonal terms, the magnetic dipole and electric quadrupole hyperfine structure matrix elements in the $[(L, S)J, I]F$ coupled representation are [55]

$$\begin{aligned}\langle (L'S')J'IF|H_{\rm hyp}|(LS)JIF\rangle = W^{I,F}_{J,J'}(1)I\Bigg[& C_{S',S}\delta_{L',L}\sqrt{6}(-1)^{L+J'}X_{S,S'}\begin{Bmatrix} S' & J' & L \\ J & S & 1\end{Bmatrix} \\ & - D_S\delta_{S,S'}(-1)^{J+S+M}\begin{Bmatrix} L' & J' & S \\ J & L & 1\end{Bmatrix}\Big/\begin{pmatrix} L' & 1 & L \\ -M & 0 & M\end{pmatrix} \\ & + E_{S',S}\frac{12}{\sqrt{5}}(-1)^{S'-L'+M}X_{S,S'}\begin{Bmatrix} L' & L & 2 \\ S' & S & 1 \\ J' & J & 1\end{Bmatrix}\Big/\begin{pmatrix} L' & 2 & L \\ -M & 0 & M\end{pmatrix}\Bigg] \\ & + \frac{1}{4}W^{I,F}_{J,J'}(2)Q_S\delta_{S',S}(-1)^{J+S+M}\begin{Bmatrix} L' & J' & S \\ J & L & 2\end{Bmatrix}\Big/\begin{pmatrix} L' & 2 & L \\ -M & 0 & M\end{pmatrix} \end{aligned} \quad (3)$$

expressed in terms of $3-j$, $6-j$, and $9-j$ symbols. The last term is the electric quadrupole matrix element. The definitions for the structure-dependent constants [56, 57], extended to include off-diagonal matrix elements, are

$$C_{S',S} = -\frac{8\pi}{3}g_I\mu_0^2\langle\gamma',\ ^{2S'+1}LM \mid \delta(\mathbf{r}_1) + (-1)^{S'-S}\delta(\mathbf{r}_2) \mid \gamma,\ ^{2S+1}LM\rangle \quad (4)$$

$$D_S = -2g_I\mu_0^2\langle\gamma',\ ^{2S+1}L'M \mid l_{1,z}r_1^{-3} + l_{2,z}r_2^{-3} \mid \gamma,\ ^{2S+1}LM\rangle \quad (5)$$

$$E_{S',S} = -\frac{5}{2}g_I\mu_0^2\langle\gamma',\ ^{2S'+1}L'M \mid (-1)^{S'-S}C^0_2(\hat{\mathbf{r}}_1)r_1^{-3} + C^0_2(\hat{\mathbf{r}}_2)r_2^{-3} \mid \gamma,\ ^{2S+1}LM\rangle \quad (6)$$

evaluated with $M = L$ throughout (3)–(6). Here, $C^0_2(\hat{\mathbf{r}}) = \sqrt{4\pi/5}\,Y^0_2(\hat{\mathbf{r}})$, $\boldsymbol{l}_i = \mathbf{r}_i \times \mathbf{p}_i$, and μ_0 is the Bohr magneton. Using $\boldsymbol{\mu} = -g_I\mu_0\mathbf{I}$, and $g_I = 2.317\,4824(7) \times 10^{-3}$ [57, 58], the conversion factor from atomic units to MHz is $g_I\mu_0^2 = 202.998\,180(61)$ MHz.

Finally, for completeness, the electric quadrupole coupling constant Q_S is related to $E_{S,S}$ by

$$Q_S = -E_{S,S}\left(\frac{16IQ}{5g_I\alpha^2 a_0^2}\right) \tag{7}$$

where Q is the electric quadrupole moment, and $a_0 \simeq 0.529\,177 \times 10^{-8}$ cm is the Bohr radius. The quadrupole term does not contribute for the case of ^{3}He because $I = 1/2$.

We have calculated high-precision values for all the matrix elements in (4)–(6), using the double basis set wave functions in Hylleraas co-ordinates described previously [59–62]. In brief, the wave function is expanded in the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{l_1=0}^{[L/2]} \sum_{i,j,k}^{i+j+k \le \Omega} c_{ijk}^{(l_1)} r_1^i r_2^j r_{12}^k \exp(-\alpha^{(l_1)} r_1 - \beta^{(l_1)} r_2) \mathcal{Y}^M_{l_1,l_2,L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm \text{exchange term} \tag{8}$$

where l_1 and $l_2 = L - l_1$ are the individual electronic orbital angular momenta, r_1, r_2, and $r_{12} = |\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|$ are the radial electronic coordinates, the symbol [ ] denotes "greatest integer in," and $\mathcal{Y}^M_{l_1,l_2,L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ denotes the vector-coupled product of solid spherical harmonics

$$\mathcal{Y}^M_{l_1,l_2,L}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = r_1^{l_1} r_2^{l_2} \sum_{m_1,m_2} \langle l_1\, l_2\, m_1\, m_2 \mid LM\rangle Y_{l_1}^{m_1}(\hat{\mathbf{r}}_1) Y_{l_2}^{m_2}(\hat{\mathbf{r}}_2) \tag{9}$$

to form a state of total orbital angular momentum L. The $c_{ijk}^{(l_1)}$ are linear variational parameters obtained by diagonalizing the Hamiltonian in the basis set defined by (8), and the quantities $\alpha^{(l_1)}$, $\beta^{(l_1)}$ are nonlinear scale factors that are adjusted by an iterative procedure to obtain the lowest energy for a given state and basis set size. The quantity Ω defines a "Pekeris shell" of basis set members such that the powers of r_1, r_2, and r_{12} satisfy $i + j + k \le \Omega$. The usual procedure is to increase Ω progressively until a given degree of convergence is obtained. The largest basis sets contain about 2000 terms. The strategy of doubling the basis set helps to increase the numerical stability so that standard quadruple precision (32 decimal digit) arithmetic in FORTRAN is sufficient. For the $1s2s\ ^3$S state, Frolov [63] has recently extended some of our results to the heliumlike ions using stochastic basis sets.

Mass polarization corrections to the wave functions are also included, and the term linear in μ/M extracted. The final results are then expressed in the forms

$$C_{S',S} = C^{(0)}_{S',S}\left[1 + (\delta^C_{\rm MP} - 3)\frac{\mu}{M} + \frac{\alpha}{2\pi} + \delta^C_{\rm ho}\right] \tag{10}$$

$$D_S = D^{(0)}_S\left[1 + (\delta^D_{\rm MP} - 3)\frac{\mu}{M} + \delta^D_{\rm ho}\right] \tag{11}$$

$$E_{S',S} = E^{(0)}_{S',S}\left[1 + (\delta^E_{\rm MP} - 3)\frac{\mu}{M} + \frac{\alpha}{2\pi} + \delta^E_{\rm ho}\right] \tag{12}$$

where $\delta_{\rm MP}$ is the mass polarization correction coefficient for each term, $-3\mu/M$ is the reduced mass correction, and $\delta_{\rm ho}$ represents higher order relativistic, QED, and finite nuclear size corrections. Using the 2002 CODATA value for the helion (^{3}He) to electron mass ratio of 5495.885 269(11), the value of μ/M is $1.819\,212\,065(4) \times 10^{-4}$.

To achieve experimental accuracies for the hyperfine structure, it is necessary to estimate $\delta^C_{\rm ho}$ in (10) for the dominant Fermi contact term $C_{1,1}$. This is difficult to do directly because of nuclear structure and QED uncertainties. The argument suggested by Hambro [56] and used by Hinds et al. [57] is to assume that for the P states, $\delta^C_{\rm tot}(1s2p) \simeq \delta^C_{\rm tot}(1s)$ where $\delta^C_{\rm tot}(1s)$ is the total anomaly (i.e., the sum of the corrections in (10)) for the corresponding one-electron ion. The justification is that the anomaly comes predominantly from the $1s$ electron. We can now do somewhat better than this by assuming

Table 7. Calculated hyperfine shifts S in ^{3}He I relative to the theoretical fine structure levels in Table 6. Units are MHz.

$n\ L$	$S(n\ ^1L_L, F)$ $-S(n\ ^1L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L-1}, F)$ $-S(n\ ^3L_{L-1})$ $F = L - 1/2$ $F = L - 3/2$	$S(n\ ^3L_L, F)$ $-S(n\ ^3L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L+1}, F)$ $-S(n\ ^3L_{L+1})$ $F = L + 3/2$ $F = L + 1/2$
2 S	0.0606			−2246.5873[a] 4493.1139[a]
2 P	−6.7036 14.0805	323.954(2)	−2664.429(8) 1847.761(6)	−2153.147(8) 4807.956(16)
3 S	0.2585			−2186.533(3) 4372.807(5)
3 P	−0.8219 3.7829	1283.069[b]	3779.211[b] 885.569[b]	−2162.785[b] −1620.422[b]
3 D	199.5696(1) 59.7188(1)	3669.877(14) −2164.155(35)	4073.049(32) −1561.591(14)	−2167.014(1) −2107.370(28)
4 S	0.6665			−2174.263(1) 4347.859(2)
4 P	1.4474 2.1104	2538.17(14)	4101.83(28) −371.37(14)	−2164.864(1) −1940.43(28)
4 D	298.2202(2) 193.0624(2)	3871.886(8) −2165.441(17)	4005.902(16) −1897.818(8)	−2166.650(1) −2138.196(13)
4 F	−2387.2256(12) −2167.0641(12)	6231.7045(23) −2166.0402(9)	−2166.1018(8) −1897.8190(13)	−2166.6604(9) 6719.4605(22)
5 S	1.3601			−2170.252(1) 4339.145(2)
5 P	3.4937 2.7502	3320.647(95)	4213.58(15) −1155.699(95)	−2165.631(1) −2052.47(15)
5 D	505.0825(4) 408.6854(4)	3784.532(5) −2165.910(9)	3812.433(8) −2026.441(4)	−2166.531(1) −2151.356(7)
5 F	−2291.9615(10) −2168.6797(13)	6373.5243(22) −2166.2200(9)	−2165.5161(7) −2038.2562(10)	−2166.8174(9) 6623.7816(21)
5 G	−2223.5332(7) −2166.4017(10)	6410.8132(21) −2166.3082(9)	−2166.4198(9) −2077.8915(7)	−2166.4766(9) 6556.2986(21)
6 S	2.4153			−2168.569(1) 4334.722(2)
6 P	6.0592 4.6931	3724.913(60)	4260.477(83) −1562.449(60)	−2165.965(1) −2101.168(83)
6 D	846.9245(7) 754.4218(7)	3497.005(3) −2166.120(6)	3476.867(5) −2084.801(3)	−2166.481(1) −2157.525(5)
6 F	−2243.5737(9) −2168.8390(13)	6430.7642(21) −2166.3018(9)	−2165.5872(7) −2095.4112(9)	−2166.4671(9) 6575.5086(21)
6 G	−2199.4329(7) −2166.4040(10)	6447.9743(21) −2166.3526(9)	−2166.4194(9) −2115.0964(7)	−2166.4497(9) 6532.2302(21)
6 H	−2189.1984(7) −2166.3995(10)	6466.5377(21) −2166.3739(9)	−2166.4254(9) −2133.6851(7)	−2166.4389(9) 6522.0108(21)
7 S	3.9082			−2167.742(1) 4331.575(2)

Table 7. (*Continued*.)

$n\ L$	$S(n\ ^1L_L, F)$ $-S(n\ ^1L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L-1}, F)$ $-S(n\ ^3L_{L-1})$ $F = L - 1/2$ $F = L - 3/2$	$S(n\ ^3L_L, F)$ $-S(n\ ^3L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L+1}, F)$ $-S(n\ ^3L_{L+1})$ $F = L + 3/2$ $F = L + 1/2$
7 P	9.4635	3940.328(39)	4281.926(52)	−2166.132(1)
	7.7801		−1781.226(39)	−2125.632(52)
7 D	1360.735(2)	3007.053(3)	2966.337(3)	−2166.454(1)
	1274.323(2)	−2166.229(3)	−2114.833(2)	−2160.753(2)
7 F	−2216.8297(9)	6457.8921(21)	−2165.7700(7)	−2166.4581(9)
	−2168.5009(13)	−2166.3428(9)	−2122.9152(8)	6548.9730(21)
7 G	−2187.1815(7)	6466.9113(21)	−2166.4260(9)	−2166.4360(9)
	−2166.4065(10)	−2166.3744(9)	−2134.0534(7)	6519.9893(21)
7 H	−2180.7439(7)	6478.6217(21)	−2166.4288(9)	−2166.4379(9)
	−2166.4036(10)	−2166.3888(9)	−2145.7793(7)	6513.5623(21)
7 I	−2176.9143(7)	6484.9580(21)	−2166.4282(9)	−2166.4326(9)
	−2166.3954(10)	−2166.3874(9)	−2152.1229(7)	6509.7369(21)
8 S	5.9159			−2167.289(1)
				4328.662(2)
8 P	13.9250	4061.637(27)	4291.292(35)	−2166.226(1)
	12.0628		−1906.973(27)	−2139.243(35)
8 D	2040.017(2)	2332.121(2)	2288.923(3)	−2166.448(1)
	1966.178(2)	−2166.285(2)	−2131.786(2)	−2162.589(2)
8 F	−2201.0143(10)	6472.3518(21)	−2165.9333(7)	−2166.4431(9)
	−2168.0862(13)	−2166.3577(9)	−2137.7980(8)	6533.3298(21)
8 G	−2180.3179(7)	6477.5665(21)	−2166.4217(9)	−2166.4349(9)
	−2166.3996(10)	−2166.3797(9)	−2144.7196(7)	6513.1316(21)
8 H	−2176.0073(7)	6485.4179(21)	−2166.4234(9)	−2166.4296(9)
	−2166.3999(10)	−2166.3899(9)	−2152.5811(7)	6508.8279(21)
8 I	−2173.4447(7)	6489.6671(21)	−2166.4230(9)	−2166.4260(9)
	−2166.4011(10)	−2166.3957(9)	−2156.8353(7)	6506.2682(21)
8 K	−2171.7882(7)	6492.2179(21)	−2166.4219(9)	−2166.4235(9)
	−2166.4026(10)	−2166.3994(9)	−2159.3885(9)	6504.6129(21)
9 S	8.5165			−2167.020(1)
				4325.524(2)
9 P	19.6350	4132.755(19)	4293.879(25)	−2166.281(1)
	17.6630		−1983.785(19)	−2147.409(25)
9 D	2792.948(2)	1572.532(2)	1537.137(3)	−2166.438(1)
	2736.018(2)	−2166.323(2)	−2142.067(1)	−2163.715(2)
9 F	−2191.1238(10)	6480.7588(21)	−2166.0511(7)	−2166.4340(9)
	−2167.7385(13)	−2166.3740(9)	−2146.5691(8)	6523.5661(21)
9 G	−2176.1757(7)	6484.0116(21)	−2166.4191(9)	−2166.4283(9)
	−2166.4034(10)	−2166.3895(9)	−2151.1712(7)	6508.9929(21)
9 H	−2173.1486(7)	6489.5279(21)	−2166.4202(9)	−2166.4245(9)
	−2166.4037(10)	−2166.3967(9)	−2156.6946(7)	6505.9706(21)
9 I	−2171.3501(7)	6492.5142(21)	−2166.4199(9)	−2166.4220(9)
	−2166.4045(10)	−2166.4008(9)	−2159.6843(9)	6504.1741(21)
9 K	−2170.1873(7)	6494.3065(21)	−2166.4192(9)	−2166.4202(9)
	−2166.4056(10)	−2166.4033(9)	−2161.4783(9)	6503.0122(21)

Table 7. (*Concluded.*)

$n\ L$	$S(n\ ^1L_L, F)$ $-S(n\ ^1L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L-1}, F)$ $-S(n\ ^3L_{L-1})$ $F = L - 1/2$ $F = L - 3/2$	$S(n\ ^3L_L, F)$ $-S(n\ ^3L_L)$ $F = L + 1/2$ $F = L - 1/2$	$S(n\ ^3L_{L+1}, F)$ $-S(n\ ^3L_{L+1})$ $F = L + 3/2$ $F = L + 1/2$
10 S	11.7888			−2166.851(1)
				4321.914(2)
10 P	26.7744	4175.012(14)	4292.019(18)	−2166.318(1)
	24.7301		−2033.168(14)	−2152.605(18)
10 D	3498.644(2)	857.917(2)	832.177(2)	−2166.431(1)
	3457.199(2)	−2166.347(2)	−2148.653(1)	−2164.439(1)
10 F	−2184.6447(10)	6485.9820(21)	−2166.1364(7)	−2166.4281(9)
	−2167.4628(13)	−2166.3844(9)	−2152.0785(8)	6517.1781(21)
10 G	−2173.5287(7)	6488.1355(21)	−2166.4174(9)	−2166.4240(9)
	−2166.4058(10)	−2166.3957(9)	−2155.2992(7)	6506.3482(21)
10 H	−2171.3219(7)	6492.1576(21)	−2166.4181(9)	−2166.4213(9)
	−2166.4061(10)	−2166.4010(9)	−2159.3264(7)	6504.1449(21)
10 I	−2170.0114(7)	6494.3355(21)	−2166.4179(9)	−2166.4195(9)
	−2166.4067(10)	−2166.4040(9)	−2161.5068(9)	6502.8358(21)
10 K	−2169.1640(7)	6495.6425(21)	−2166.4174(9)	−2166.4182(9)
	−2166.4075(10)	−2166.4059(9)	−2162.8151(9)	6501.9890(21)

[a]Coefficient $C_{1,1}$ adjusted to fit the calculated splitting to the value 6 739.701 177(16) MHz observed by Rosner and Pipken [64].

[b]$C_{1,1}$ adjusted from −4318.803 to −4319.080 to fit the calculated levels to the measurements of Marin et al. [45].

instead that $\delta^C_{\rm ho}(1snl) \simeq \delta^C_{\rm ho}(1s)$, since the $\delta^C_{\rm MP}$ contribution in (10) is known and can be subtracted out. The result is $\delta^C_{\rm tot} = 0.000\,5072(3)$ for $^3{\rm He}^+(1s_{1/2})$ (see Table V of ref. 62). For ^{3}He($1snp\ ^3P$), the anomaly still comes primarily from the $1s$ electron, but the additional $\delta_{\rm MP}$ term not present in the one-electron case must be added. Using the values in Table 4 of ref. 45,[3] the final correction factors are 1.000 497 for $n = 2$ and 1.000 505 for $n = 3$. These semi-empirical factors give the $C_{1,1}$ coefficients in the last column of that table. Pachucki [53] has calculated the relativistic and second-order contributions to the hyperfine structure of the $1s2s\ ^3{\rm S}_1$ state. These terms are included in part by our semi-empirical estimate of $\delta^C_{\rm ho}$. However, it is difficult to make a direct comparison with the results of Pachucki because he does not include the nuclear structure contributions that are also included in $\delta^C_{\rm ho}$.

6.2. Calculated hyperfine shifts

Table 7 lists the hyperfine shifts of the unperturbed fine structure levels in the S, P, D, F, G, H, I, and K terms for $n = 2$ to 10. The perturbation was applied in adiabatic steps to each ab initio J level in Table 1 so that the parent J is known, even though J may not be a good quantum number for the hyperfine levels.

[3]Note that for the 2 P state, the value of $C_{1,0}$ in Table 4 of this reference should be −4285.831 MHz in place of 2797.113 MHz.

Table 8. Hyperfine term values T for ^{3}He I. The error quoted for the ground level indicates the uncertainty in all levels relative to the ground. Units are MHz.

$n\ L$	$T(n\ ^1L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L-1}, F)$ $F = L - 1/2$ $F = L - 3/2$	$T(n\ ^3L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L+1}, F)$ $F = L + 3/2$ $F = L + 1/2$
1 S	0.(33.)			
2 S	4 984 604 592.80(15)			4792 099 678.56(6)
				4792 106 418.26(6)
2 P	5 130 231 722.7(2)	5 068 832 675.730(60)	5 068 800 070.670(60)	5068 798 289.789(60)
	5 130 231 743.5(2)		5 068 804 582.860(60)	5068 805 250.892(60)
3 S	5 541 813 489.(1)			5493 005 935.(2)
				5493 012 495.(2)
3 P	5 582 123 358.43(20)	5 562 793 862.982(200)	5 562 788 245.664(200)	5562 781 644.591(200)
	5 582 123 363.03(20)		5 562 785 352.022(200)	5562 782 186.954(200)
3 D	5 578 989 554.05(2)	5 578 891 966.05(2)	5 578 891 044.27(4)	5578 884 728.92(2)
	5 578 989 414.20(2)	5 578 886 132.02(4)	5 578 885 409.63(2)	5578 884 788.56(3)
4 S	5 723 940 683.9(6)			5704 689 209.1(7)
				5704 695 731.3(7)
4 P	5 740 504 570.34(20)	5 732 242 574.0(2)	5 732 240 830.3(3)	5732 234 293.7(2)
	5 740 504 571.00(20)		5 732 236 357.1(2)	5732 234 518.2(3)
4 D	5 739 116 321.267(9)	5 739 061 332.31(1)	5 739 060 911.16(2)	5739 054 702.61(1)
	5 739 116 216.109(9)	5 739 055 294.98(2)	5 739 055 007.44(1)	5739 054 731.06(2)
4 F	5 739 276 802.417(2)	5 739 285 188.960(3)	5 739 276 318.748(2)	5739 276 532.258(2)
	5 739 277 022.579(2)	5 739 276 791.215(2)	5 739 276 587.031(2)	5739 285 418.379(3)
5 S	5 805 578 918.8(3)			5796 088 068.0(3)
				5796 094 577.4(3)
5 P	5 813 942 056.16(10)	5 809 695 585.6(1)	5 809 694 816.5(2)	5809 688 301.7(1)
	5 813 942 055.42(10)		5 809 689 447.2(1)	5809 688 414.8(2)
5 D	5 813 216 946.242(5)	5 813 186 422.223(8)	5 813 186 166.60(1)	5813 180 168.424(6)
	5 813 216 849.844(5)	5 813 180 471.78(1)	5 813 180 327.726(7)	5813 180 183.599(9)
5 F	5 813 299 335.396(1)	5 813 307 847.211(2)	5 813 299 083.663(1)	5813 299 174.669(1)
	5 813 299 458.677(2)	5 813 299 307.467(1)	5 813 299 210.923(1)	5813 307 965.268(2)
5 G	5 813 314 125.7759(7)	5 813 322 709.309(2)	5 813 313 973.5190(9)	5813 314 056.5155(9)
	5 813 314 182.907(1)	5 813 314 132.1879(9)	5 813 314 062.0473(7)	5813 322 779.291(2)
6 S	5 849 087 477.1(2)			5843 726 755.8(2)
				5843 733 259.1(2)
6 P	5 853 885 600.193(70)	5 851 426 000.13(9)	5 851 425 584.7(1)	5851 419 080.78(7)
	5 853 885 598.827(70)		5 851 419 761.81(9)	5851 419 145.6(1)
6 D	5 853 462 048.000(3)	5 853 443 930.837(5)	5 853 443 746.839(6)	5853 438 092.151(4)
	5 853 461 955.497(3)	5 853 438 267.712(7)	5 853 438 185.171(5)	5853 438 101.107(6)
6 F	5 853 508 770.894(1)	5 853 517 343.010(2)	5 853 508 622.0569(9)	5853 508 669.297(1)
	5 853 508 845.629(1)	5 853 508 745.944(1)	5 853 508 692.233(1)	5853 517 411.272(2)
6 G	5 853 517 669.4544(7)	5 853 526 287.405(2)	5 853 517 581.3019(9)	5853 517 629.2912(9)
	5 853 517 702.483(1)	5 853 517 673.0784(9)	5 853 517 632.6249(7)	5853 526 327.971(2)

Table 8. (*Continued*.)

$n\ L$	$T(n\ ^1L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L-1}, F)$ $F = L - 1/2$ $F = L - 3/2$	$T(n\ ^3L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L+1}, F)$ $F = L + 3/2$ $F = L + 1/2$
6 H	5 853 519 737.1273(7)	5 853 528 371.661(2)	5 853 519 678.9863(9)	5853 519 710.2746(9)
	5 853 519 759.924(1)	5 853 519 738.7490(9)	5 853 519 711.7266(7)	5853 528 398.724(2)
7 S	5 874 989 145.2(1)			5871 669 653.5(1)
				5871 676 152.8(1)
7 P	5 877 993 001.550(40)	5 876 444 789.90(6)	5 876 444 537.23(7)	5876 438 040.75(4)
	5 877 992 999.866(40)		5 876 438 474.07(6)	5876 438 081.25(7)
7 D	5 877 725 417.084(3)	5 877 713 527.386(4)	5 877 713 383.564(4)	5877 708 243.551(2)
	5 877 725 330.672(3)	5 877 708 354.104(4)	5 877 708 302.394(3)	5877 708 249.252(3)
7 F	5 877 753 404.328(1)	5 877 762 009.083(2)	5 877 753 308.9116(8)	5877 753 336.579(1)
	5 877 753 452.657(1)	5 877 753 384.849(1)	5 877 753 351.7664(9)	5877 762 052.010(2)
7 G	5 877 759 136.8101(7)	5 877 767 772.329(2)	5 877 759 081.2618(9)	5877 759 111.4704(9)
	5 877 759 157.585(1)	5 877 759 139.0436(9)	5 877 759 113.6344(7)	5877 767 797.896(2)
7 H	5 877 760 490.2372(7)	5 877 769 136.252(2)	5 877 760 453.5991(9)	5877 760 473.3019(9)
	5 877 760 504.578(1)	5 877 760 491.2411(9)	5 877 760 474.2486(7)	5877 769 153.302(2)
7 I	5 877 760 910.6200(7)	5 877 769 562.483(2)	5 877 760 884.6738(9)	5877 760 898.4953(9)
	5 877 760 921.139(1)	5 877 760 911.1376(9)	5 877 760 898.9791(7)	5877 769 574.665(2)
8 S	5 891 646 917.99(7)			5889 450 279.13(7)
				5889 456 775.08(7)
8 P	5 893 650 729.028(30)	5 892 614 815.11(4)	5 892 614 648.82(5)	5892 608 159.06(3)
	5 893 650 727.166(30)		5 892 608 450.56(4)	5892 608 186.05(5)
8 D	5 893 471 861.978(2)	5 893 462 886.792(3)	5 893 462 774.558(4)	5893 458 314.315(2)
	5 893 471 788.139(2)	5 893 458 388.386(3)	5 893 458 353.849(3)	5893 458 318.174(3)
8 F	5 893 488 851.696(1)	5 893 497 475.606(2)	5 893 488 786.8951(8)	5893 488 804.556(1)
	5 893 488 884.624(1)	5 893 488 836.897(1)	5 893 488 815.0304(9)	5893 497 504.329(2)
8 G	5 893 492 747.9355(7)	5 893 501 393.365(2)	5 893 492 710.7136(9)	5893 492 730.9340(9)
	5 893 492 761.8538(1)	5 893 492 749.4190(9)	5 893 492 732.4157(7)	5893 501 410.500(2)
8 H	5 893 493 676.9439(7)	5 893 502 329.425(2)	5 893 493 652.3932(9)	5893 493 665.5925(9)
	5 893 493 686.551(1)	5 893 493 677.6169(9)	5 893 493 666.2355(7)	5893 502 340.850(2)
8 I	5 893 493 969.1552(7)	5 893 502 625.562(2)	5 893 493 951.7701(9)	5893 493 961.0293(9)
	5 893 493 976.199(1)	5 893 493 969.4987(9)	5 893 493 961.3578(7)	5893 502 633.724(2)
8 K	5 893 494 080.0247(7)	5 893 502 738.836(2)	5 893 494 067.0741(9)	5893 494 073.9217(9)
	5 893 494 085.410(1)	5 893 494 080.2187(9)	5 893 494 074.1075(9)	5893 502 744.958(2)
9 S	5 902 988 704.53(5)			5901 460 184.54(5)
				5901 466 677.08(5)
9 P	5 904 391 524.437(20)	5 903 665 280.21(3)	5 903 665 164.39(3)	5903 658 681.68(2)
	5 904 391 522.465(20)		5 903 658 886.73(3)	5903 658 700.55(3)
9 D	5 904 266 900.398(2)	5 904 259 075.372(2)	5 904 258 991.509(3)	5904 255 284.496(1)
	5 904 266 843.468(2)	5 904 255 336.517(2)	5 904 255 312.305(1)	5904 255 287.219(2)
9 F	5 904 276 868.096(1)	5 904 285 503.952(2)	5 904 276 822.1178(7)	5904 276 834.1068(9)
	5 904 276 891.482(1)	5 904 276 856.8190(9)	5 904 276 841.5998(8)	5904 285 524.107(2)
9 G	5 904 279 631.4629(7)	5 904 288 282.897(2)	5 904 279 605.3173(9)	5904 279 619.5134(9)
	5 904 279 641.235(1)	5 904 279 632.4956(9)	5 904 279 620.5652(7)	5904 288 294.935(2)
9 H	5 904 280 294.6806(7)	5 904 288 951.075(2)	5 904 280 277.4352(9)	5904 280 286.7056(9)
	5 904 280 301.426(1)	5 904 280 295.1505(9)	5 904 280 287.1608(7)	5904 288 959.101(2)

Table 8. (*Concluded.*)

$n\ L$	$T(n\ ^1L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L-1}, F)$ $F = L - 1/2$ $F = L - 3/2$	$T(n\ ^3L_L, F)$ $F = L + 1/2$ $F = L - 1/2$	$T(n\ ^3L_{L+1}, F)$ $F = L + 3/2$ $F = L + 1/2$
9 I	5 904 280 505.0072(7)	5 904 289 164.162(2)	5 904 280 492.7957(9)	5904 280 499.2988(9)
	5 904 280 509.953(1)	5 904 280 505.2470(9)	5 904 280 499.5313(9)	5904 289 169.895(2)
9 K	5 904 280 585.5925(7)	5 904 289 246.438(2)	5 904 280 576.4960(9)	5904 280 581.3054(9)
	5 904 280 589.374(1)	5 904 280 585.7280(9)	5 904 280 581.4369(9)	5904 289 250.738(2)
10 S	5 911 057 638.35(3)			5909 951 298.22(4)
				5909 957 786.98(4)
10 P	5 912 077 723.362(20)	5 911 549 519.17(2)	5 911 549 434.93(3)	5911 542 960.21(2)
	5 912 077 721.318(20)		5 911 543 109.74(2)	5911 542 973.93(3)
10 D	5 911 988 139.316(2)	5 911 980 633.850(2)	5 911 980 572.787(2)	5911 977 571.665(1)
	5 911 988 097.871(2)	5 911 977 609.586(2)	5 911 977 591.957(1)	5911 977 573.657(1)
10 F	5 911 993 377.061(1)	5 912 002 020.731(2)	5 911 993 343.2818(7)	5911 993 351.8089(9)
	5 911 993 394.243(1)	5 911 993 368.3649(9)	5 911 993 357.3397(8)	5912 002 035.415(2)
10 G	5 911 995 405.5816(7)	5 912 004 060.861(2)	5 911 995 386.5201(9)	5911 995 396.8661(9)
	5 911 995 412.705(1)	5 911 995 406.3300(9)	5 911 995 397.6383(7)	5912 004 069.638(2)
10 H	5 911 995 894.6702(7)	5 912 004 553.570(2)	5 911 995 882.0972(9)	5911 995 888.8552(9)
	5 911 995 899.586(1)	5 911 995 895.0115(9)	5 911 995 889.1889(7)	5912 004 559.421(2)
10 I	5 911 996 050.6559(7)	5 912 004 711.570(2)	5 911 996 041.7532(9)	5911 996 046.4939(9)
	5 911 996 054.261(1)	5 911 996 050.8301(9)	5 911 996 046.6643(9)	5912 004 715.749(2)
10 K	5 911 996 110.8199(7)	5 912 004 772.967(2)	5 911 996 104.1882(9)	5911 996 107.6942(9)
	5 911 996 113.576(1)	5 911 996 110.9182(9)	5 911 996 107.7905(9)	5912 004 776.101(2)

We have added these shifts to the ^{3}He I energies in Table 6 to obtain the hyperfine levels in Table 8. The listed errors are the uncertainties in the fine-structure levels from Table 6 while the number of decimal places reflects the relative error in the hyperfine levels. Only for the cases of the low-lying ($n = 1, 2, 3$) S- and P-levels are the experimental results for the energy levels of ^{4}He taken in preference to the theoretical ones. For these cases, the final uncertainty for ^{3}He just reflects the experimental uncertainty for ^{4}He. The theoretical uncertainties due to higher order QED contributions decrease in proportion to $1/n^3$, and are negligible for $L \geq 2$. Our estimates of the additional off-diagonal mixings with states of different principal quantum number $n' = n \pm 1$ induced by the main Fermi contact term indicate that they are less than the uncertainties for the hyperfine term values listed in Table 8.

Table 9 compares these results with various experimental energy differences available in the literature. In practice, the calculated differences were obtained from Tables 1, 5, and 7, rather than Table 8, to avoid including errors arising from large terms that cancel. In almost all cases, the agreement is remarkably good, with deviations of 3σ or less, except for $3\ ^3D_3\ 7/2 - 3\ ^3D_3\ 5/2$, where the predicted separation is 5σ different from an early experiment by Descoubes [67].

7. Opportunities for future investigations

Many of the He I measurements used here have exceptionally high accuracy, but there remain some where modern laboratory techniques could enhance our knowledge of this atom, as follows:

(1) Improved determinations of the $2\ ^1P_1$ and $2\ ^1S_0$ levels relative to others in ^{4}He would be useful tests of the calculations.

(2) An accurate measurement of the isotope shift of $2\ ^1S_0 - 2\ ^1P_1$ would check the reliability of the calculated value.

Table 9. Comparison of experiments (with references) and theory (without references) for hyperfine separations in ^{3}He I. Units are MHz.

Transition	ΔT	Transition	ΔT
$2\ ^3S_1\ 3/2 - 2\ ^3P_0\ 1/2$	810.608(30)[a]	$3\ ^3P_1\ 3/2 - 3\ ^3P_0\ 1/2$	5 617.109(200)[b]
Rel. to ^{4}He $2\ ^3S_1 - 2\ ^3P_2$	810.599(3)[c]		5 617.326(28)
	810.593(2)		
$2\ ^3S_1\ 3/2 - 2\ ^3P_0\ 1/2$	1480.573(30)[a]	$2\ ^3P_1\ 1/2 - 3\ ^3D_1\ 3/2$	667.(5)[d]
Rel. to ^{4}He $2\ ^3S_1 - 2\ ^3P_1$	1480.582(2)	Rel. to ^{4}He $2\ ^3P_1 - 3\ ^3D_2$	663.94(3)
$2\ ^3S_1\ 3/2 - 2\ ^3P_0\ 1/2$	323.9503(12)[c]	$2\ ^3P_0\ 1/2 - 3\ ^3D_1\ 3/2$	468.(8)[d]
Rel. to ^{4}He $2\ ^3S_1 - 2\ ^3P_0$	323.954(1)	Rel. to ^{4}He $2\ ^3P_0 - 3\ ^3D_1$	464.974(14)
$2\ ^3S_1\ 3/2 - 5\ ^3P_2\ 5/2$	48 878.8(30)[e]	$3\ ^3D_1\ 1/2 - 3\ ^3D_1\ 3/2$	5 830.(6)[f]
Rel. to ^{4}He $2\ ^3S_1 - 5\ ^3P_2$	48 878.9(30)[g]		5 834.03(4)
	48 879.113(1)		
$3\ ^3P_2\ 5/2 - 3\ ^3P_1\ 1/2$	3 706.90(24)[h]	$3\ ^3D_3\ 7/2 - 3\ ^3D_3\ 5/2$	55.8(8)[i]
	3 707.431(6)		59.64(3)
$3\ ^3P_1\ 1/2 - 3\ ^3P_1\ 3/2$	2 893.76(19)[h]	$3\ ^3D_2\ 5/2 - 3\ ^1D_2\ 5/2$	98 513.(6)[j]
	2 893.642		98 509.78(4)

	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$n\ ^3S_1\ 3/2 - n\ ^3S_1\ 1/2$	6 548.(16)[k]	6 522.4(15)[j]	6 511.4(15)[j]	6 504.6(30)[j]		
	6 559.340(2)	6 522.122(2)	6 509.397(2)	6 503.291(2)		
$n\ ^3D_3\ 5/2 - n\ ^3D_2\ 3/2$	623.(5)[j]	274.(3)[j]	144.(3)[j]	83.(5)[j]		
	621.07(4)	276.38(2)	144.127(12)	84.064(8)		
$n\ ^3D_2\ 3/2 - n\ ^3D_1\ 1/2$	725.(4)[f]					
	725.(4)[j]	289.(5)[j]	145.(5)[j]	84.(3)[i]		
	722.39(5)	287.54(2)	144.055(13)	82.541(9)		
$n\ ^3D_1\ 1/2 - n\ ^3D_2\ 5/2$	4 912.(4)[j]	5 619.(5)[i]	5 693.(5)[j]	5 477.(4)[j]		
	4 912.25(6)	5 616.18(3)	5 694.819(15)	5 479.127(10)		
$n\ ^3D_2\ 5/2 - n\ ^3D_1\ 3/2$	920.(7)[j]	422.(3)[j]	258.(4)[j]	181.(5)[j]		
	921.78(4)	421.14(2)	255.623(13)	183.998(8)		
$n\ ^1D_2\ 3/2 - n\ ^1D_2\ 5/2$	140.9(32)[k]	105.2(20)[k]	96.5(25)[k]	88.9(20)[k]	84.2(23)[k]	77.5(28)[k]
	139.8508(1)	105.1578(3)	96.3971(6)	92.5027(10)	86.412(3)	73.839(3)

	Relative to mean of $n\ ^3P_2\ 5/2$ and $n\ ^3P_2\ 3/2$				
	$n=5$	$n=6$	$n=8$	$n=9$	$n=10$
$n\ ^3P_2\ 5/2 - n\ ^3P_2\ 3/2$	113.5(5)[j]	64.0(2)[j]			
	113.5(10)[l]				
	115.7(30)[g]	57.3(40)[g]			
	113.16(14)	64.80(8)			
$n\ ^3P_2\ 5/2 - n\ ^3P_1\ 1/2$	1 144.4(25)[l]				
	1 145.7(30)[g]	682.4(40)[g]	282.1(30)[g]	196.8(30)[g]	143.5(30)[g]
	1 145.5(2)	681.04(12)	280.70(6)	197.50(4)	144.04(4)

Table 9. (*Concluded.*)

			Relative to mean of $n\ ^3P_2\ 5/2$ and $n\ ^3P_2\ 3/2$		
	$n = 5$	$n = 6$	$n = 8$	$n = 9$	$n = 10$
$n\ ^3P_2\ 5/2 - n\ ^3P_1\ 3/2$	6 513.7(25)[l]				
	6 513.7(30)[g]	6 508.2(40)[g]	6 479.3(30)[g]	6 477.4(30)[g]	6 470.1(30)[g]
	6 514.8(2)	6 503.96(13)	6 478.96(7)	6 475.16(5)	6 469.23(4)
$n\ ^3P_2\ 5/2 - n\ ^3P_0\ 1/2$	7 282.7(25)[l]				
	7 284.3(30)[g]	6 920.7(40)[g]	6 643.7(30)[g]	6 589.6(30)[g]	6 556.7(30)[g]
	7 284.0(2)	6 919.36(12)	6 645.25(6)	6 590.98(4)	6 553.47(4)

[a]Zhao et al. [44].
[b]Shiner, Dixson, and Vedantham [11].
[c]Bloomfield et al. [65].
[d]Vassen and Hogervorst [49].
[e]Marin et al. [45].
[f]Freeman et al. [46].
[g]Lawler et al. [66].
[h]Descoubes [67] quoted by Lawler et al. [66], Bloomfield et al. [48], Vassen and Hogervorst [49].
[i]Biraben et al. [68].
[j]Andersson and Pendrill [69].
[k]Brooks et al. [70].
[l]Bloomfield et al. [48].

(3) The ionization potential of both isotopes is uncertain by possibly 60 MHz. Additional measurements are needed for the separation of the ground state from other low-lying levels with known IE.

(4) Since the only serious disagreements with experiments involve the separations between the 3 ^{3}D and 3 ^{1}D levels in ^{3}He, further laboratory checks involving these would be helpful.

(5) Measurements involving some of the F and higher angular momentum states of ^{3}He I would provide additional tests of the calculated isotope shifts.

On the theoretical side, the next important step is a complete calculation of the relativistic corrections to hyperfine structure. In the present work, these are approximately taken into account, along with finite nuclear size effects, through the hyperfine anomaly coefficient $\delta^C_{\rm tot}$ discussed at the end of Sect. 6.1. Important progress in this direction has been achieved by Pachucki for the $1s2s\ ^3S_1$ state of helium [53] and the ground state of lithium [71]. It would be valuable to extend these calculations to the other states of helium, and to separate relativistic effects from the effects due to nuclear structure.

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