

Advances in laser spectroscopy of lithium

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Abstract. A number of recent experiments have employed novel spectroscopic techniques to precisely measure the fine and hyperfine structure splittings as well as the isotope shifts for several transitions at optical frequencies for the stable ${}^{6,7}\text{Li}$ and radioactive isotopes ${}^{8,9,11}\text{Li}$. These data offer an important test of theoretical techniques that have been developed over the last decade by two groups to accurately calculate effects due to Quantum Electrodynamics and the finite nuclear size in 2 and 3 electron atoms. Theory and experiment have studied several transitions in both singly ionized and neutral lithium. The work by multiple groups permits a critical examination of the consistency of separately, the experimental work as well as the theoretical calculations. Combining the measured isotope shifts with the calculated energy shifts passing these consistency tests, permits the determination of the relative nuclear charge radius with an uncertainty approaching 1×10^{-18} meter. These results are more than an order of magnitude more accurate than those obtained by electron scattering experiments and give insight into the mass and charge distributions of the nuclear constituents. Prospects for a precision measurement of the fine structure constant are also discussed.

1 Introduction

Neutral and singly ionized lithium are two of the simplest atomic systems to model theoretically. This has enabled precise calculations of QED shifts, isotope shifts, fine and hyperfine splittings [1–3]. Lithium has a relatively low melting point which is convenient for experimentalists when generating atomic or ion beams. It also has a number of transitions at visible wavelengths that can be studied using precision laser spectroscopy. Lithium is particularly of interest for studying QED effects such as the Lamb Shift that scales as Z^4 , where Z is the nuclear charge. Moreover, lithium has two stable isotopes ${}^{6,7}\text{Li}$ with natural abundances of 7.5% and 92.5%, respectively, as well as 3 radioactive isotopes ${}^{8,9,11}\text{Li}$ that facilitate nuclear studies and have led to the discovery of halo neutrons [4].

A number of review articles describing progress in lithium spectroscopy have been written [5, 6]. This review discusses the most recent theoretical and experimental advances made in studying the hyperfine and fine structure of the lower and upper

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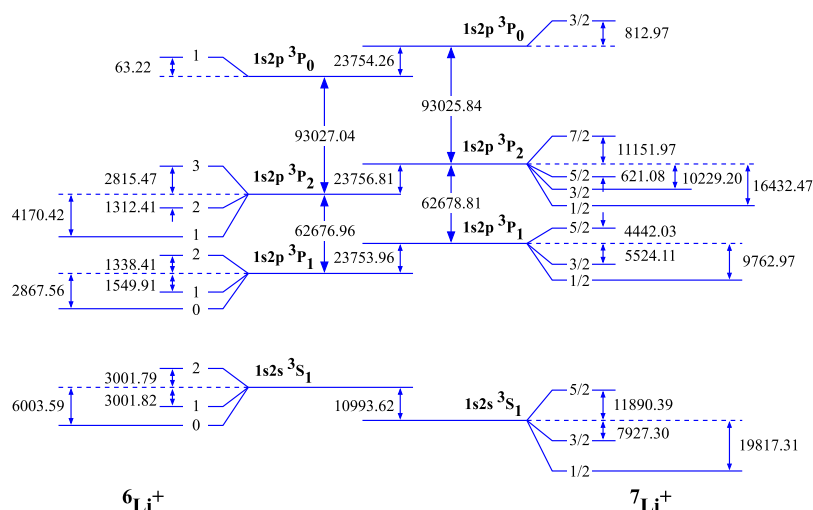


Fig. 1. Hyperfine Levels of $^{6,7}\text{Li}^+$ $1s2s\ ^3\text{S}$ and $1s2p\ ^3\text{P}$ States. All units are in MHz. The vertical energy axis is not drawn to scale.

states of the Li^+ $1s2s\ ^3\text{S}_1 \rightarrow 1s2p\ ^3\text{P}_1$ transition at 548 nm and the Li D1 and D2 lines at 670 nm. The measurements of fine and hyperfine structure splittings obtained by the latest experiments using newly developed spectroscopic techniques are compared to theoretical calculations of two independent groups that have generated results at times in sharp disagreement. The next section discusses the determination of the relative nuclear charge radii from measured isotope shifts of the aforementioned transitions as well as the two photon $\text{Li}\ 2\ ^2\text{S}_{1/2} \rightarrow 3\ ^2\text{S}_{1/2}$ transition at 735 nm. Finally, the future prospect to very precisely determine the fine structure constant α , is discussed.

2 Determination of fine and hyperfine splittings

Lithium is a multielectron system for which analytical solutions to the Schrödinger equation have not been found. However, numerical approximations to the wavefunctions have been obtained first for two electron and more recently for three electron systems by G.W.F. Drake and coworkers using the Hylleraas variational method [1, 7, 8]. These wavefunctions are then used to perturbatively evaluate fine and hyperfine interactions, QED and nuclear effects. More recently, the group of K. Pachucki and M. Puchalski has refined this technique [9]. A comparison of measured fine and hyperfine splittings with theoretical calculations tests our understanding of the two electron system Li^+ and its three electron neutral counterpart.

2.1 Li^+ $1s2s\ ^3\text{S} \rightarrow 1s2p\ ^3\text{P}$ transition

The Li^+ ion has a long lived metastable $1s2s\ ^3\text{S}$ state having a lifetime of about 1 minute lying 59 eV above its ground state. This state is populated by colliding a neutral atomic lithium beam with an electron beam. The $1s2s\ ^3\text{S} \rightarrow 1s2p\ ^3\text{P}$ transition at 548 nm has been studied by several groups [10–12]. Figure 1 shows the hyperfine levels of the lower and upper states of this transition for both $^{6,7}\text{Li}^+$. The hyperfine intervals are shown relative to the positions of the fine structure levels denoted by

Table 1. ${}^7\text{Li}^+$ $1s2p\ {}^3\text{P}$ fine structure splittings.

Interval $F \rightarrow F'$	Experiment (MHz)	Technique	Theory (MHz)	Reference
$1s2p\ {}^3\text{P}_{2 \rightarrow 1}$	62667.4(20)	LH [10]	62679.4(5)	[7]
	62678.41(65)	LIB [11]	62679.318(34)	[13]
	62679.46(98)	LIBEO [12]		
$1s2p\ {}^3\text{P}_{0 \rightarrow 1}$	155709.0(20)	LH [10]	155703.4(15)	[7]
	155704.27(66)	LIB [11]	155704.584(48)	[13]

Table 2. Li^+ hyperfine splittings of the $1s2s\ {}^3\text{S}$ and $1s2p\ {}^3\text{P}$ states.

Isotope	State	Hyperfine Interval $F \rightarrow F'$	Experiment (MHz)	Technique	Theory [11] (MHz)
${}^6\text{Li}^+$	$1s2s\ {}^3\text{S}_1$	$2 \rightarrow 1$	6003.600(50) 6003.66(51)	ODR [14] LIBEO [12]	6003.614(24)
		$1 \rightarrow 0$	3001.780(50) 3001.83(47)	ODR [14] LIBEO [12]	3001.765(38)
	$1s2p\ {}^3\text{P}_1$	$2 \rightarrow 1$	2888.98(63)	LIBEO [12]	2888.327(29)
		$1 \rightarrow 0$	1316.06(59)	LIBEO [12]	1317.649(46)
	$1s2p\ {}^3\text{P}_2$	$3 \rightarrow 2$	4127.16(76)	LIBEO [12]	4127.882(43)
		$2 \rightarrow 1$	2857.00(72)	LIBEO [12]	2858.002(60)
${}^7\text{Li}^+$	$1s2s\ {}^3\text{S}_1$	$5/2 \rightarrow 3/2$	19817.673(40) 19817.1(26) 19817.90(73)	ODR [14] LH [10] LIBEO [12]	19817.680(25)
		$3/2 \rightarrow 1/2$	11890.018(40) 11891.22(60)	ODR [14] LIBEO [12]	11890.013(38)
		$5/2 \rightarrow 3/2$	9965.2(6) 9966.30(69)	ODR [14] LIBEO [12]	9966.14(13)
	$1s2p\ {}^3\text{P}_1$	$3/2 \rightarrow 1/2$	4237.8(10) 4239.11(54)	ODR [14] LIBEO [12]	4238.86(20)
		$7/2 \rightarrow 5/2$	11775.8(5) 11774.04(94)	ODR [14] LIBEO [12]	11773.05(18)
		$5/2 \rightarrow 3/2$	9608.7(20) 9608.90(49)	ODR [14] LIBEO [12]	9608.12(15)
	$1s2p\ {}^3\text{P}_2$	$3/2 \rightarrow 1/2$	6203.6(5) 6204.52(80)	ODR [14] LIBEO [12]	6203.27(30)

dashed lines. The hyperfine splittings are the results of a theoretical computation while the isotope shifts and fine structure intervals are measured values [11].

Several different experiments have measured the fine and hyperfine structure intervals as shown in Tables 1 and 2. An optical double resonance (ODR) experiment obtained results having the smallest uncertainty [14]. This experiment used a laser to excite the $1s2s\ {}^3\text{S} \rightarrow 1s2p\ {}^3\text{P}$ transition. The ions were additionally excited as they passed through a waveguide resonant with the hyperfine interval under consideration. After the ions left the waveguide, they were excited by the laser and fluorescence was detected. A change in the fluorescent intensity was evident if the ions had undergone a microwave transition.

The group of Rong et al. used a laser heterodyne (LH) technique to determine frequency intervals [10]. Two dye lasers were used. One laser beam excited the lithium ion beam and its frequency was locked by maximizing the fluorescence. A second dye laser was locked to the saturation absorption signal observed in an iodine cell. Parts of the two dye laser beams were then focussed onto a fast photodiode which measured the beat signal.

The group of Riis et al. also used two dye lasers whose frequencies were each locked to an iodine transition to excite an ion beam (LIB) [11]. A saturated absorption signal was obtained as follows. The first laser beam copropagated with the ion beam and was Doppler tuned into resonance. The second laser beam counterpropagated relative to the ions and was tuned into resonance using an acousto-optic modulator. The observed fluorescence signal had a 25 MHz full width half maximum (FWHM) Lamb dip superimposed on a Doppler broadened lineshape. The absolute transition frequencies were then used to find the desired frequency intervals.

Our group developed a technique to determine frequency intervals using a laser beam modulated by an electro-optic modulator to excite an ion beam (LIBEO) [12]. The modulation frequency was specified to an accuracy of 1 part in 10^7 by a frequency synthesizer. The laser frequency was scanned across the resonance while fluorescence generated by the radiative decay of the $1s2p\ ^3P$ state was detected by a photomultiplier. Each transition generated multiple peaks separated by the modulation frequency in the spectrum allowing the change of laser frequency to be calibrated. The advantage of this technique is that it does not require constructing a resonant cavity to lock the laser frequency and only a single laser is required.

Tables 1 and 2 show all of the experimentally determined fine and hyperfine intervals agree very well except for the results obtained by the laser heterodyne experiment for the fine structure. The results of two other experiments are in agreement with each other and also are consistent with theoretical calculations. The most recent theoretical results have uncertainties more than an order of magnitude smaller than those found by Zhang et al. [7]. One may conclude that experimental and theoretical results for the hyperfine and fine structure intervals in the two electron system Li^+ agree to within several hundred kHz.

2.2 Li D lines

Figure 2 shows the fine and hyperfine splittings of the states giving rise to the D lines. The hyperfine splittings are the theoretically computed values [2]. These intervals have been studied using a number of different techniques as shown in Table 3. One of the earliest methods was level crossing (LC) spectroscopy where the effect of a magnetic field on the fluorescence intensity was monitored. This yielded a result of comparable accuracy to later results [15]. The group at Graz University has made several measurements using a laser to excite an atomic beam (LAB) [17,23]. Fluorescence was detected as the laser frequency was scanned across the resonance. The change of laser frequency was monitored by passing part of the laser through a Fabry Perot etalon. The difficulty with this technique is measuring the interferometer length which is subject to vibrations and pressure/temperature fluctuations. These problems are eliminated using a frequency modulated laser beam to excite an atomic beam (LABEO) [18,24]. The result of this experiment is comparable to that obtained using an optical double resonance experiment [22]. A recent experiment used a femtosecond frequency comb (FC) to precisely measure the laser frequency that excited atoms in an atomic beam [19–21].

The experiments are done using low laser power, considerably below the saturation intensity, to minimize ac Stark shifts. Similarly, the Earth's magnetic field is

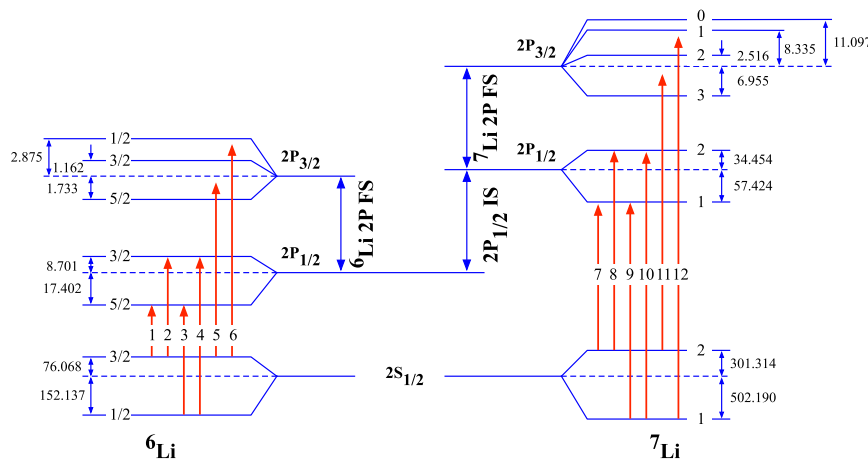


Fig. 2. Hyperfine Levels labelled by the quantum number F involved in transitions comprising the ${}^6,{}^7\text{Li}$ D lines. All numerical values are in units of MHz. FS and IS denote fine structure and isotope shift, respectively. The vertical energy axis is not drawn to scale.

Table 3. 2P fine structure splitting.

Isotope	Experiment (MHz)	Technique	Theory (MHz)	Reference
${}^6\text{Li}$	10052.76(22)	LC [15]	10050.846(12)	[16]
	10051.62(20)	LAB [17]	10051.477(8)	[2]
	10052.964(50)	LABEO [18]		
	10052.799(22)	FC [19,20]		
	10052.779(17)	FC [21]		
${}^7\text{Li}$	10053.24(22)	LC [15]	10051.214(12)	[16]
	10053.184(58)	ODR [22]	10050.932(8)	[2]
	10053.4(2)	LAB [17]		
	10053.119(58)	LABEO [18]		
	10053.393(21)	FC [19,20]		
	10053.310(17)	FC [21]		

cancelled using Helmholtz coils and mu-metal shielding to minimize Zeeman shifts. An important test done by the LABEO and FC experiments is to measure the ${}^6,{}^7\text{Li}$ ground state hyperfine splitting and check that it agrees with the result obtained by the magnetic resonance technique used by an atomic clock [25]. The accuracy of the 2P fine structure determination is limited by the small hyperfine splittings of the $2P_{3/2}$ state which are less than or comparable to the 6 MHz natural linewidth of the lithium D lines. Figure 3 shows the fluorescence produced when the laser is scanned across peak 11, which is generated as shown in Fig. 2 by exciting the ${}^7\text{Li}$ $2S_{1/2}$ $F=2$ level to the $F=1, 2, 3$ hyperfine levels of the $2P_{3/2}$ state. In both the LABEO and FC experiments, the fluorescence from peak 11 was fitted using three Lorentzian lineshapes whose center frequencies were fixed to equal the theoretically computed hyperfine intervals. In the FC experiment, after an initial fitting, the parameters giving the locations of the 3 peaks were allowed to vary. The final results for the hyperfine splittings were very close to the theoretical values. In the LABEO experiment, the fluorescence contributions of the $F=1, 2, 3$ levels of the $2P_{3/2}$ state

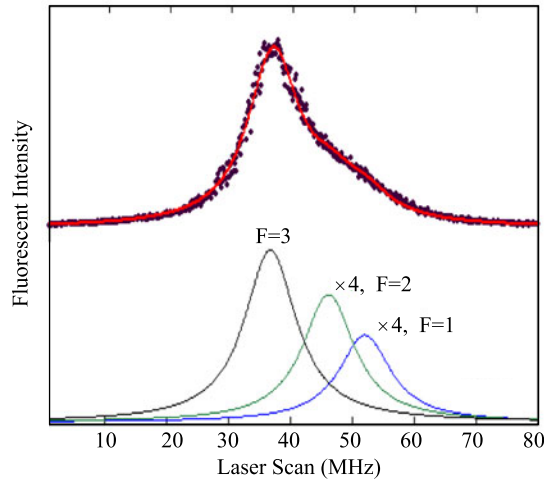


Fig. 3. Fluorescence produced by the excitation of peak 11 shown in Fig. 2. The fitted curve is comprised of three Lorentzian functions due to the radioactive decay of the $F = 1, 2, 3$ hyperfine levels of the $2P_{3/2}$ state. The fluorescence contributions from the $2P_{3/2}$ $F = 1, 2$ hyperfine levels are magnified by a factor of 4.

was modelled to take into account optical pumping effects arising from repeated excitation of the atoms as they passed through the laser beam. The modelled amplitudes of the 3 Lorentzian functions agreed very closely with the observed results. The FC experiment has been repeated. An error in the ${}^6\text{Li}$ and ${}^7\text{Li}$ $2P_{3/2}$ center of gravities of approximately twice the reported uncertainties in the $2P$ fine structure was found [19,20]. Additional refinements occurred in the most recent version of this experiment [21]. The frequencies of the fine structure intervals have been found directly by applying a strong magnetic field so that the Zeeman shift greatly exceeds the hyperfine splittings [26]. The frequencies of the fluorescent peaks were measured at various fields. An extrapolation to zero field then gave the center of gravity position of the hyperfine levels. The accuracy of the final result was limited by the uncertainty of the magnetic fields and did not give a result more accurate than those shown in Table 3.

The two theoretical calculations claim comparable accuracy but disagree by about 30 standard deviations. This difference is believed to arise principally because of hyperfine mixing of the $2P_{1/2,3/2}$ states taken into account by Puchalski [2]. Both theoretical values are several MHz below the experimental values. It is believed this discrepancy arises because the calculations do not consider QED correction terms proportional to α^4 times the Rydberg energy which for helium contribute several MHz to the fine structure splitting [27].

3 Determination of the relative nuclear charge radius

The relative nuclear charge radius squared Δr_c^2 is found using

$$\begin{aligned} \Delta r_c^2 &= r_c^2({}^6\text{Li}) - r_c^2({}^7\text{Li}) \\ &= \frac{\Delta\nu_{\text{ISO}} - \delta E}{C} \end{aligned} \quad (1)$$

where $\Delta\nu_{\text{ISO}}$ is the measured isotope shift, δE is the theoretically computed mass shift and C is the shift dependence on nuclear size. Table 4 shows the computed

Table 4. Theoretical parameters determining relative nuclear charge radius.

Transition	δE (MHz)	C (MHz/fm ²)	Reference
Li ⁺ 2 ³ S ₁ → 2 ³ P ₀	34740.17(3)	9.705	[11]
Li ⁺ 2 ³ S ₁ → 2 ³ P ₁	34739.87(3)	9.705	[11]
Li ⁺ 2 ³ S ₁ → 2 ³ P ₂	34742.71(3)	9.705	[11]
Li 2 ² S _{1/2} → 3 ² S _{1/2}	11453.010(56)	1.5661	[28]
	11452.822(2)	1.5732	[29]
	11452.821(2)	1.5732	[1]
	11452.821(2)	1.5719(16)	[3]
Li D1 line	10532.17(7)	2.457	[30]
	10532.111(6)	2.457	[1]
	10532.0237(28)	2.4658	[9]
Li D2 line	10532.57(7)	2.457	[30]
	10532.506(6)	2.457	[1]
	10532.5682(28)	2.4658	[9]

Table 5. ^{6,7}Li relative nuclear charge radius.

Group	Year & Reference	Transition	Isotope Shift (MHz)	Average Δr_c^2 (fm ²)
Electron scattering	1972 [31]			0.79(25)
Strathclyde	1994 [11]	Li ⁺ 2 ³ S ₁ → 2 ³ P ₀	34747.73(55)	0.733(36)
		Li ⁺ 2 ³ S ₁ → 2 ³ P ₁	34747.46(67)	
		Li ⁺ 2 ³ S ₁ → 2 ³ P ₂	34748.91(62)	
TRIUMF	2011 [3]	Li 2 ² S _{1/2} → 3 ² S _{1/2}	11453.970(34)	0.731(22)
York	2006 [18]	Li D1 line	10534.039(70)	0.736(24)
		Li D2 line	10534.194(104)	
NIST	2011/2012 [19, 20]	Li D1 line	10533.763(9)	0.713(3)
		Li D2 line	10534.357(29)	
	2012 [21]	Li D1 line	10533.763(9)	0.700(3)
		Li D2 line	10534.293(22)	
Nuclear theory	2001 [32]			0.74(15)

values. The most recent results for δE computed for the Li D1 and D2 transitions by the two theoretical groups disagree by over 10 times the quoted uncertainty.

An important test is that an experiment that measures isotope shifts of different transitions, obtains consistent values for the relative nuclear charge radius [3, 6, 33]. Table 5 lists the results for such experiments. The results for Δr_c^2 obtained for the Li D lines do depend on which theoretical values of δE are used. However, the change in Δr_c^2 obtained by averaging the results for the Li D1 and D2 lines found using the values of δE by the two theoretical groups, is less than the listed uncertainty of the average value of Δr_c^2 . The isotope shift of the 2²S_{1/2} → 3²S_{1/2} transition has been studied in three experiments by the same group [3, 34–36]. Systematic effects are believed to be best understood in the most recent experiment whose result is listed in Table 5. The

Table 6. Splitting isotope shift.

Year & Reference	Result (MHz)	Technique
2006 [18]	0.155(60)	LABEO
2008 [1]	0.396(9)	Theory
2009 [2]	0.5447(1)	Theory
2011, 2012 [19,20]	0.594(30)	FC
2012 [21]	0.531(24)	FC

values obtained for the relative nuclear charge radius by the different experimental groups are in good agreement although the results obtained by the NIST group are somewhat lower. Taking the unweighted average of the Strathclyde, TRIUMF, York and the most recent NIST experiments, one obtains $\Delta r_c^2 = 0.725 \pm 0.017 \text{ fm}^2$ where the uncertainty equals one standard deviation of the 4 experimental results about the average value. Using the value of $r_c(^7\text{Li}) = 2.39(3) \text{ fm}$ obtained from electron scattering [31], one finds $r_c(^6\text{Li}) - r_c(^7\text{Li}) = 0.147 \pm 0.003 \text{ fm}$. This is more than an order of magnitude more accurate than obtained by electron scattering [31] and can test nuclear theory [32].

Theorists believe the most reliable computation is the so called splitting isotope shift (SIS) which equals the difference of the D1 and D2 isotope shifts, because this quantity is largely independent of QED and nuclear size corrections [1]. Table 6 shows strong disagreement between the two theoretical results. This is believed to arise primarily because of mixing of the fine structure states due to off diagonal elements of the hyperfine interaction not taken into account in the earlier calculation as well as the use of a larger basis of Hylleraas functions in the later work [2]. The successive experimental results of the NIST group appear to be converging to the latest theoretical result.

4 Future work: Measurement of the fine structure constant

The possibility of determining the fine structure constant α by measuring the 2P fine structure of Helium was first suggested by [37]. The advantage of studying Li^+ is that the 2P fine structure intervals are up to 5 times larger facilitating a more accurate determination [38,39]. A further advantage is that nuclear size effects can be tested by measuring intervals separately in the two stable lithium isotopes. The motivation for determining the fine structure constant is to test QED and eventually check for a possible time evolution of α as predicted by cosmology and field theory [40]. The most accurate determination of the α arises from the $g - 2$ experiment for the electron in the Penning trap [41,42]. The electron Landé g factor is measured to an accuracy of 0.28 ppt. QED computations of $g - 2$ then enable one to find $\alpha^{-1} = 137.035999084(51)$ with a relative uncertainty of 0.35 ppb. This disagreed sharply with that found by various other experiments including the Quantum Hall, Josephson experiments etc. [43].

Recently, however, an atom interferometric experiment resolved this discrepancy in favor of the $g - 2$ based result. The fine structure constant was found from 3 separate measurements using

$$\alpha^2 = 2 \frac{R}{h} \frac{M}{m} \frac{v_{\text{Rec}}}{\lambda}. \quad (2)$$

Here, R/h is the Rydberg constant measured in units of frequency which is known with a relative uncertainty of 14 ppt [44]. The ratio of the Rb or Cs mass M to the

electron mass m is known with a relative uncertainty of 0.5 ppb [45]. Finally, the recoil velocity v_{Rec} divided by the transition wavelength λ was measured using atom interferometry. This has been done for both cesium [43] and rubidium [46]. The final result of $\alpha^{-1} = 137.035999037(91)$ agrees with the $g-2$ result although it has a larger relative uncertainty of 0.66 ppb.

A measurement of the $\text{Li}^+ 2\text{P}$ fine structure would be limited by the 3.6 MHz natural linewidth of the $1s2s\ ^3\text{S} \rightarrow 1s2p\ ^3\text{P}$ transition. An experiment that carefully determines the line centers to better than one part in 10^3 as has been claimed by several groups studying other transitions [19, 47], would determine the fine structure to 1 ppb. This represents an accuracy improvement of more than two orders of magnitude, and would stringently test our understanding of Li^+ . The fine structure which is proportional to α^2 would then be found with a relative uncertainty of about 0.5 ppb. Such a determination would require improved measurement and calculations of the hyperfine splittings of the $\text{Li}^+ 1s2s\ ^3\text{S}$ and $1s2p\ ^3\text{P}$ states. This challenge is likely to motivate continuing theoretical and experimental advances in precision spectroscopy of lithium.

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