- 1 Article
- 2 The radiofrequency NMR spectra of lithium salts in
- 3 water; Reevaluation of Nuclear Magnetic Moments
- 4 for ⁶Li and ⁷Li nuclei

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Abstract: The LiCl and LiNO₃ water solutions in the presence of small amounts of 3-helium have been investigated by means of multinuclear resonance spectroscopy. The resulting concentration dependences of the 3 He, 6,7 Li⁺, 14 NO₃ and 35 Cl resonance radiofrequencies are reported in the infinite limit. This data along with new theoretical corrections of shielding lithium ions was analyzed by a known NMR relationship method. Consequently, the nuclear magnetic moments of 6 Li and 7 Li were established against that of the helium-3 dipole moment: $\mu(^6$ Li)=+0.822046(5) μ N and $\mu(^7$ Li)=+3.256418(20) μ N. The new results were shown to be very close to the previously obtained values of the (ABMR) atomic beam magnetic resonance method. This experiment proves that our helium method is well suited for establishing dipole moments from NMR measurements performed in water solutions. This technique is especially valuable when gaseous substances of the needed element are not available. All shielding constants of species present in water solutions are consistent with new nuclear magnetic moments and these taken as a reference. Both techniques – NMR and ABMR – give practically the same results providing that all shielding corrections are properly made.

Keywords: ⁶Li and ⁷Li nuclear magnetic moments; NMR liquid-phase studies; nuclear magnetic shielding constants

1. Introduction

The electromagnetic moments of nuclei, dipole and quadrupole, have great significance for theory of nuclear structure. The magnetic moments are of prime importance for all nuclei with spin number $I \ge 1/2$. They were established for the first time in the famous molecular beam experiments carried out by I.I. Rabi (1939) [1] and, afterwards, improved values were experimentally determined by means of NMR bulk experiments e.g. by Walchli (1954), for the sequence of nuclear moments from lithium up to thallium [2]. The method relies on the accurate measurements of two frequencies for different nuclei placed in one sample at the same magnetic field. One of these frequencies should belong to the nucleus with the

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well-known magnetic moment and can be taken as a reference. The main problem with this procedure lies in ensuring that the shielding effects of nuclei in the particular experimental conditions are known with enough accuracy. The spectacular growth of quantum theoretical methods in this field provided new impetus for improving existing data. Several such works were performed in the Laboratory of NMR Spectroscopy at the University of Warsaw. We utilise the gas phase conditions as a rule, because of the importance of the shielding results for the isolated molecules when extrapolation to the zero-pressure limit is possible [3,4]. Unfortunately, we don't have any stable gaseous substances at normal conditions available for several elements (e.g.: Li, Be, Na, K, Sc). Instead of gaseous species, the liquid solutions should be used in these cases. In this work, water solutions of common salts of lithium were applied – LiCl and LiNO₃ in the presence of dissolved ³He atoms. This procedure has several advantages: very narrow NMR signals, good sensitivity and well known shielding parameters of different ions in liquid samples. Without a doubt, the lithium nuclei are of great account from the point of view of nuclear physics. Accurate and precise experimental values of nuclear properties are of prime importance in this case. There are eight lithium isotopes ranging from ⁴Li up to ¹¹Li; only two of them are stable: ⁶Li (7.59(4)%) and ⁷Li (92.41(4)%) [5]. Both these nuclei possess different moments, electric quadrupole and dipole magnetic, connected with magnetic numbers $I^{\pi}=1^+$ (with three neutrons) and $I^{\pi}=3/2^-$ (with four neutrons), respectively. Since the two isotopes vary by a single spin-1/2 neutron, they exhibit different quantum statistics: ⁶Li is a composite fermion while a ⁷Li nucleus is a composite boson particle. In these circumstances, they represent one of the smallest objects, whose nuclear parameters could be precisely calculated in the near future. Interestingly, in spite of different mass numbers, the charge radius in ⁷Li is smaller, which indicates the valuable differences in the magnetic distribution inside both nuclei [6]. The first hints about the ⁷Li nuclear magnetic moment were made by Goudsmit and Young [7] and soon after deduced by Granath [8] as the nuclear spin 3/2 and magnetic moment possess 3.29 times the theoretical magnetic moment of the proton ($\mu_N = e\hbar/2m_p$, where e is the elementary charge and m_p is the proton's mass). A further investigation into the

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magnetic properties of lithium isotopes was carried out by Rabi's molecular/atomic beam MR experiments in the resonance absorption method. The determination of the nuclear spin and magnetic moment of lithium isotopes was obtained for LiCl, LiF and Li₂ molecules [9,10]. Next, more precise results were received by NMR measurements performed in water solutions of lithium salts and calculated against the deuterium NMR reference [11,12]. Soon after, precise lithium nuclei dipole moments were measured by the atomic beam magnetic resonance method [13]. These last results were cited later in the most pronounced tabulated compilations of magnetic moments for stable nuclei [14-16]. All of the remaining lithium nuclei are radioactive and have very short half-lives (4Li-4.9-8.9×10⁻²³ s, 5Li-5.4×10⁻²² s, 8Li-0.84 s, ${}^{9}\text{Li}$ - 0.178 s, ${}^{10}\text{Li}$ - 5.5×10^{-22} - $5.5 \times 10^{-21} \text{ s}$ and ${}^{11}\text{Li}$ - 0.0087 s) [5]. The aim of this work is twofold. Firstly, precise NMR measurements of frequencies for LiCl and LiNO₃ in water solutions were performed and analysis of new ⁶Li/⁷Li NMR data collected for water solutions at low concentrations was performed and compared to the results for ³He dissolved in the same samples. Up to now, the addition of helium ingredients has only been carried out in our lab only in the gas phase. We are now trying to extend our method to the liquid samples. As a second step, the nuclear magnetic moments of ⁶Li and ⁷Li nuclei were recalculated using new shielding constants of lithium cations solvated in water solutions [17]. New magnetic moments measured in our work were compared with these established before by the atomic beam method. It is obvious that accurate values of the nuclear ground-state properties of isotopes, such as the magnetic dipole and electric

2. Materials and Methods

LiNO₃ (Sigma-Aldrich, 99,99%) and LiCl (Sigma-Aldrich,99.998%, anhydrous) were used for preparing water solutions at total densities in the range 0.25-1.2 mol/L. Samples of 0.3 mL in Pyrex tubes (4 mm o.d. and 56 mm long) were frozen in liquid nitrogen and pumped to a pressure of ~ 10^{-3} mmHg. Small amounts of 3 He (Chemgas, 99.9%) $\leq 3.0 \times 10^{-3}$ mol/L were then added before sealing the ampoules by torch. Only a small amount of helium

quadrupole moments, are ideal tools for testing the validity of nuclear structure models.

Subsequently a comparison of different experimental and purely theoretical results was

94 can be dissolved in water solutions (~0.0015g/kg in pure H₂O at room temperature). These 95 ampoules were fitted into standard 5 mm o.d. NMR test tubes (Wilmad-Glass Co., 548-PP) 96 or 10 mm tubes with liquid D₂O in the annular space. The reference samples were 1M NaCl in D₂O for 35,37 Cl NMR spectra ($\Delta_{1/2}$ = 0.38 Hz) and 0.1M LiCl for 6,7 Li NMR spectra. The 97 lock system, operated at 76.8464 MHz, allows the same magnetic field B₀=11.7570 T to be 98 99 preserved. All measurements were performed at a constant temperature of 300K. The small 100 isotope effect when H₂O was changed by D₂O was equal to 0.02 ppm in 1M lithium chloride 101 solution. The rise of temperature causes deshielding effect of the lithium-7 signal by 0.0076 102 ppm/deg in the range 288.8 - 328.8K. 103 High resolution ^{6,7}Li, ³⁵Cl and ¹⁴N NMR spectra were recorded on a Varian-INOVA 500 104 spectrometer equipped with sw5 (switchable) and BB10 (broad band) probes operating at 105 194.5544 MHz, 73.6695 MHz, 49.0491 MHz and 36.1752 MHz, respectively. For the 106 enhancement of ⁶Li signals, the ²H(D) filter was omitted in the detection circuit. The primary reference solutions – ^{6,7}LiCl (9.7M in D₂O), Na³⁵Cl (1.0 M in D₂O), CH₃¹⁴NO₂ (liquid) were 107 108 used for standardisation of lithium, chlorine and nitrogen spectra. The ³He NMR spectra in 109 liquid water solutions were measured by a special, homemade (Helium) probe, relative to the 110 gas phase result, received from the extrapolation of helium shielding in gaseous mixtures 111 CF₄-³He and C₂F₆-³He to the zero-point density. 112 The shielding susceptibility effect for water (3.006 ppm) was calculated treating the formula $\sigma_{1b} = -4\pi/3\chi_y$ and $\chi_y = \chi_M \cdot M_p/\rho$ where $\chi_M = -12.97$, $M_p = 18.0002$ and $\rho = 0.999865$ 113 $g/cm^{3}[18]$. 114

3. Results and Discussion

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3.1. NMR experiments in water solutions

Lithium has NMR spectroscopy based on two different nuclei. Both are quadrupolar, then the interaction with the electric field gradient at the nucleus is important by definition. It is worth noting anomalous, very small quadrupolar moment of ^6Li (0.00082(2) barn, 1 barn= m^2) [15] (contrary to that of $^7\text{Li} - 0.0406(8)$ barn) which as a consequence yields rather sharp resonance signals. The chemical shift range of both nuclides is small and reaches only ~ 30 ppm. Fortunately, lithium cation shows a high symmetric structure characterised by a small

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electric field gradient and its linewidth for reference solution (9.7 M LiCl in D_2O) not even achieving \sim 0.1 Hz. For this reason water solutions of lithium salts seem to be ideal for precise measurements.

For the derivation of the lithium nuclear magnetic moments we have used the usual form of equation which connects two observed frequencies at the zero concentration of lithium salts and nuclear dipole moments. They should be corrected for shielding values of Li⁺ and ³He measured in aqueous solutions:

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$$\Delta \mu_{Li}^{z} = \frac{\nu_{Li}}{\nu_{He}} \cdot \frac{(1 - \sigma_{He})}{(1 - \sigma_{Li})} \cdot \frac{I_{Li}}{I_{He}} \Delta \mu_{He}^{z}, \qquad (1)$$

where v_{Li} and v_{He} mean appropriate radiofrequencies extrapolated to the infinite diluted solutions. I_x are magnetic quantum numbers of measured nuclei, and $\sigma_{He,Li}$ are also shielding corrections for nuclei in the experimental conditions. The above equation makes it possible to calculate the magnetic moment μ_{Li} when all other quantities are known. The experimental results of NMR measurements are shown in Table 1. The suitable concentration dependencies of specific extrapolations are illustrated in Figs.1 and 2. In general, the concentration dependences of chemical shifts/shielding for cations or anions should not be linear, particularly at higher concentrations. For uniformity, all analyses were done by single-variable quadratic functions. It is known that virial expansions can be used for models of aqueous ionic solutions [19]. All coefficients are shown in Table 1 as δ [ppm], δ_1 [ppm×ml×mol⁻¹] and δ_2 [ppm×ml× mol⁻²].

A crucial role in the estimations of lithium nuclear magnetic moments has been played by knowledge of the diamagnetic corrections for helium atoms and lithium cations. At the beginning, we measured the 3 He NMR signal against that of gaseous systems; the difference is 2.7675(25) ppm in the chemical shift category, independently on the concentration of helium in water. It corresponds to the 0.2384(5) ppm deshielding effect when going from isolated molecule in gaseous state to the liquid water solution. This value was used to correct the helium frequency by electron screening. For comparison, the chemical shift corrected for the susceptibility of 3 He in water solution against that of gaseous sample (1-atm gas sample used for the gas reference) was measured previously by Jokisaari [20] - $\Delta \delta$ = 0.297(39) ppm.

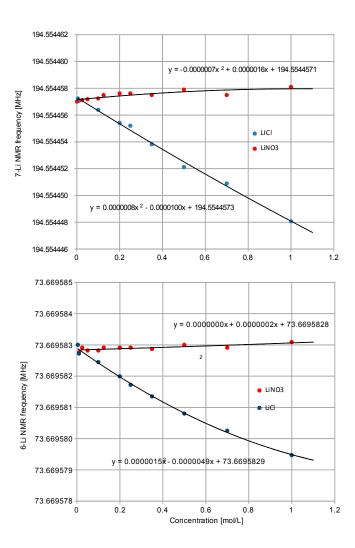
Table 1.
NMR parameters measured in LiCl and LiNO₃ water solutions.

Water	Nuclide	ν ₀ (radiofrq.)	δ/ppm	δ ₁ /ppm ml mol ⁻¹	σ/ppm	Reference
solution		MHz		$\delta_2/ppm\ ml\ mol^{-2}$		
LiCl						
	$(^6Li^+)_{aq}$.	73.6695828(1)	-0.1472	-0.0632	90.89(300)	[15]
				0.0148		
	$(^{7}Li^{+})_{aq}$.	194.5544573(1)	-0.1469	-0.0632	90.89(300)	
				0.0148		
	³⁵ Cl ⁻	49.0491386(1)	4.7125	0.9358	998.28(500)	[21]
				-0.0461		
	³ He	381.3564690(1)	-2.7675	-0.0478	59.729(1)	[This work]
				0.0102		
LiNO ₃						
	$(^6Li^+)_{aq.}$	73.6695829(1)	-0.147	-0.003	90.89(300)	[15]
				-0.0059		
	$(^{7}Li^{+})_{aq.}$	194.5544571(1)	-0.147	-0.003	90.89(300)	
				0.0059		
	$^{14}NO_3^-$	36.1752096(1)	-5.595	-0.107	-132.14	[4]
				0.0165		
	³ He	381.3564691(1)	-2.7676	-0.0045	59.729(1)	[This work]
		,		-0.004	` ,	

^{*} $\nu(D_2O)=76.8464 \text{ MHz}$

Figure 1. ⁶Li and ⁷Li NMR frequencies versus concentration of LiCl and LiNO₃ in water solutions.

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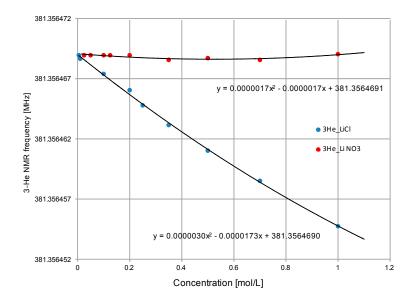


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Figure 2. The ³He NMR frequencies in LiCl and LiNO₃ water solutions against concentrations.

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More significant correction is needed in the case of lithium nuclei. The ^{6,7}Li⁺ cation's solvation properties in water solutions were actively studied in many theoretical simulations [22,23] and experimental research used different spectroscopy techniques [24-26]. The structure of the water complex is the subject of many controversies. The Li⁺ cation in water solution has the smallest ionic radius of 90 pm (as 4-coordinated) and 76 pm (as-6-coordinated), and the highest positive charge density compared to other alkali metals. The stability of four, five or six water molecules in the inner shell of Li⁺ ion is still under consideration. Most of this data refers to strong solutions in which there are very few water molecules that are not in the primary hydration spheres of the lithium cation, which may account for some of the solvation number variations with solute concentration. In the lithium aqueous ions have been found to have the solvation numbers of 3-6 and solvation numbers less than 4 can be suitable when the formation of contact ion pairs is possible. In the infinite dilution, we can exclude the possibility of interaction between a solvated cation and an anion and forming an ion pair. It is clear that the measured solvation number is a time-averaged value in the water solutions. The primary solvation number seen is fractional; there are two or more species with integral solvation numbers present in equilibrium with each other: $[Li(H_2O)_6]^+ \rightleftharpoons [Li(H_2O)_5]^+ + H_2O \rightleftharpoons [Li(H_2O)_4]^+ + 2H_2O$ (2) The higher solvation numbers may be interpreted in terms of water molecules in a tetrahedron coordination [Li(H₂O)₄]⁺ or even higher coordinated complexes e.g. an octahedral agua ions which are revealed by molecular dynamic simulations. The final suggestion of Mason et al. [25] shows that an infinitely diluted water solution at room temperature is mainly composed of 4 coordinated lithium complexes of great stability. Without pre-empting composition at the infinite dilution we decided to calculate lithium moments when tetrahedral or/and octahedral coordination take place. If the coordination number of central lithium cation varies, it's shielding values change, starting from 95.30 – 95.41 ppm for an isolated ion up to 90.18 ppm in the hexacoordinated complex [17]. In the last case the small correction of 0.8 ppm for 2 water molecules, which distorts the first tetrahedral solvation shell of lithium ion, was applied [27]. The final shielding effect, with the small relativistic term 0.08 ppm calculated by the CCSD/utA,tz (Coupled Cluster)

quantum method, was then 90.89 ppm. If four coordinating lithium cations are present then shielding constant 91.69 ppm should be valid [17]. Taking into account of the v_{Li}/v_{He} frequency ratio (see Table 1) and both shielding corrections for 3 He and 6,7 Li nuclei we can deduce the nuclear magnetic dipole moments of 6 Li and 7 Li nuclei (see Table 2). Two values in the table were quoted for different shielding corrections for the lithium nucleus (90.89 and 91.69 ppm) as the lower and upper limit for the magnetic moment. It is worth noting that both results are in good agreement with previously results used in establishing the absolute lithium shielding scale by Mason [28, see also[13]]: 90.0(8) ppm (6 Li) and 90.4(7) ppm (7 Li). In any case, the effect is small and will be used as reference against ABMR results (see Table 3).

3.2. ABMR experiments for atoms

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An extensive ABMR (atomic beam magnetic resonance) experiment was carried out to examine ^{6,7}Li nuclear magnetic moments [13]. Several improvements to the original technique were made to avoid all systematic errors involved in this approach. The method of separated oscillatory fields with triple resonance technique and special calibration of the magnetic field offered very precise final results. For a proper comparison of our results with ABMR values, several new corrections were applied to the original quantities, i.e.: proton-to-electron mass ratio $m_p/m_e = 1836.15267389(17)$ [29] and diamagnetic correction factor in Li atom $(1-\sigma_{Li})^{-1} = 1.0000101472$ [30]. This last value is very consistent with previous received theoretical results -101.4 and 101.45 ppm [31,32]. The g_J factor for the 2²S_{1/2} state was taken from the original work - 2.002301100(64) which agrees very closely with the purely theoretical data, 2.00230101 [33]. The final, corrected magnetic moments established by Beckmann et al. [13] are shown in Table 2 as ABMR* results. The differences between nuclear magnetic moments measured in our NMR investigation and the ABMR method are then of the order 0.8-1.5×10⁻⁴ %. Remarkably, our refine results are much closer to the ABMR results than those cited in several current specifications [14-16] received from previous NMR measurements performed in aqueous solutions. It is certainly not without significance that the final results are more closely related to the ABMR results when shielding lithium cations were used for the strictly hexacoordinated water complex.

3.3.Shielding factors

The new nuclear magnetic moments from NMR and ABMR experiments (Table 2) can certainly be tested, because a few shielding constants of different additional nuclei present in the solution are known with great precision. The concentration dependencies for $^{35}Cl^{-}$ and $^{14}NO_3^{-}$ anions are shown in Fig.3.

224 Table 2.

^{6/7}Li nuclear magnetic shielding from nuclear magnetic moments.

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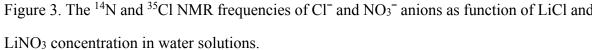
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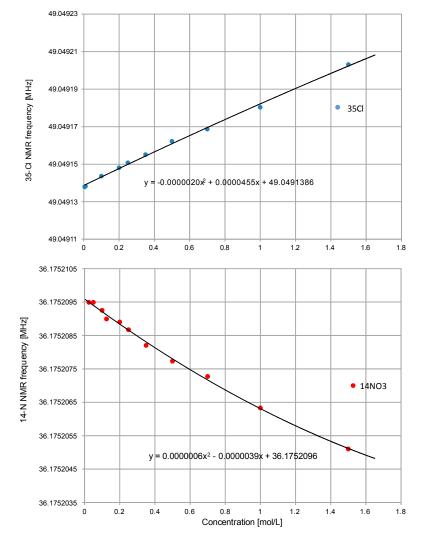
$\mu(^7\text{Li})/\mu_N$	Method/Reference	Reference nucleus	$\sigma(^7Li^+)_{aq}/ppm$
	Theory/[21]		90.89(300)
3.2564170(98)	NMR/[This work]	³⁵ Cl ⁻	91.16
		¹⁴ NO ₃ ⁻	90.36
3.2564182(98)	NMR/[This work]	³⁵ C1 ⁻	91.53
		¹⁴ NO ₃ ⁻	90.73
3.2564157(30)	ABMR/[12]	³⁵ Cl ⁻	90.76
		¹⁴ NO ₃ ⁻	89.96
3.2564625(4)	NMR/[12]	³⁵ Cl ⁻	105.13
		¹⁴ NO ₃	104.33
$\mu(^6\text{Li})/\mu_N$			$\sigma(^6Li^+)_{aq}./ppm$
	Theory/[21]		90.89(300)
0.8220453(25)	NMR/[This work]	³⁵ Cl ⁻	91.09
		$^{14}NO_3^-$	90.30
0.8220459(25)	NMR/[This work]	³⁵ Cl ⁻	91.82
		¹⁴ NO ₃ ⁻	91.03
0.8220445(10)	ABMR/[12]	³⁵ Cl ⁻	90.12
		¹⁴ NO ₃ ⁻	89.32
0.822567(3)	NMR/[12]	³⁵ Cl ⁻	725.27
. ,		¹⁴ NO ₃ ⁻	724.47

In order to verify the conformity of the nuclear shielding values of lithium nuclei in 227 water solution a different form of Eq.(1) was used: 228

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$$\sigma_{X} = 1 - \frac{v_{X}}{v_{Y}} \cdot \frac{\Delta \mu_{X}}{\Delta \mu_{Y}} \cdot \frac{I_{X}}{I_{Y}} (1 - \sigma_{Y}), \tag{3}$$

Formula (3) was carried out for each pair of nuclei: ^{6,7}Li/¹⁴N and ^{6,7}Li/³⁵Cl present in our samples of H₂O solutions. ¹⁴N nuclear shielding in the NO₃⁻ anion at infinite dilution was calculated from nuclear magnetic shielding of liquid CH₃NO₂ which is equal to -132.14 ppm [4]. ³⁵Cl nuclear shielding in the Cl⁻ anion was calculated against shielding value in 1.0 M NaCl/D₂O solution which is equal to 1006(5) ppm [33]. From the results collected in Table 2, it is clear that only our new ^{6,7}Li nuclear magnetic moments are consistent with shielding calculations against D₂O, ³⁵Cl⁻ and ¹⁴NO₃⁻ species accordingly to the Eq.(3). Figure 3. The ¹⁴N and ³⁵Cl NMR frequencies of Cl⁻ and NO₃⁻ anions as function of LiCl and





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Subsequently, the uncertainty error of lithium shielding is much less then suggested by theoretical predictions (± 3 ppm) [17] and possibly remains ± 1.5 ppm an order of magnitude.

It is worth noting that measurements of lithium dipole moments, contrary to many heavier isotopes, depend on diamagnetic corrections of NMR frequencies only in limited degree. This is a consequence of the relatively narrow spectral ranges of all nuclei in magnetic resonance studies (6,7Li,2H,3He) and the small screening factors. It means that 6,7Li magnetic moments belong to the class of most precise and accurately known dipole moments for all elements in the whole periodic table.

Table 3. Electromagnetic properties of lithium, chlorine, nitrogen, helium and deuterium nuclei.

Nuclide	I^{π}	Q barn	Abundance	μ/μν	Diamagnetic correction	gı factor	γι ×10 ⁷	Reference
⁶ Li 1	1+	0.00082(2)	7.59(4)	0.8220453(25)	1.00009089	0.822045(3)	3.93712(1)	[This work]
				0.8220459(25) 0.8220445(10)	1.00009169 1.000101472			[13]
				0.8220445(10) 0.839(2); 0.800(1)	1.000101472			[34]
				0.843(5); 0.843(2)				[35]
Li	3/2-	0.0406(8)	92.41(4)	3.2564170(98)	1.00009089	2.170945(7)	10.39756(3)	[This work]
				3.2564195(98) 3.2564157(2)	1.00009169 1.000101472			[13]
				2.954(5); 3.168(13)	1.000101472			[34]
				3.01(2); 3,02(2)				[35]
Cl	3/2+	0.0850(11)	75.78(4)	0.821721(5)		0.547814(3)	2.62371(1)	[21]
N	1+	0.02001(10)	99.632(7)	0.4035729(45)		0.403573(5)	1.93288(2)	[4]
Не	1/2+		0.000137	2.127625308(25)	1.00005973	4.25525061(5)	20.3801680(2)	[29]
H(D)	1+	0.00286(2)	0.0156	0.8574382311(48)		0.857438231(5	4.1066289(1)	[29]

The lithium nuclei are very promising objects in the theoretical quantum calculation field. It is known that pure theoretical methods are still a long way from the precision of

252 resonance experiments. Recently performed calculations are valid to the three or four digit 253 numbers, i.e. $\mu(^{6}\text{Li})=0.843(5)\mu\text{N}$ and $\mu(^{7}\text{Li})=3.01(2)\mu\text{N}$ [34] or $\mu(^{6}\text{Li})=0.839(2)\mu\text{N}$ and 254 $\mu(^{7}\text{Li})=3.168(13)\mu_{\text{N}}$ [35]. On the other hand the lithium magnetic moments of another 255 isotopes are still a subject of great interest. New developments have also involved short living isotopes: 8,9,11Li nuclei. The investigation into magnetic moments for stable isotopes 256 257 forms only a part of the studies which include the short living isotopes at different excitation levels. The nuclear moments of ${}^{8}\text{Li}(1.653560(18))\mu\text{N}$, ${}^{9}\text{Li}(3.43682(5))\mu\text{N}$ and 258 259 ¹¹Li(3.6712(5)) μ N were measured by β-NMR experiments with major precision [36]. 260 5. Conclusions 261 The nuclear magnetic moment is a very important basic parameter of each nuclide which 262 is a fundamental measure of nucleus magnetic structure. The lithium isotopes belong to the 263 most investigated nuclei of the past eight decades. NMR measurements offer the highest precision in relative measurements. In this work the dipole moments of ⁶Li and ⁷Li were 264 found to be $\mu(^6\text{Li}) = +0.8220448(25) \div +0.8220453(25)$ and $\mu(^7\text{Li}) = +3.2564148(98) \div$ 265 266 +3.2564170(98) in nuclear magnetons (μ_N). Our new results are more valuable than those 267 previously established by NMR spectroscopy of lithium salts in water solvents. The results 268 are very close to the earlier given numbers measured by the ABMR method: 269 $\mu(^{6}\text{Li})=+0.8220445(10)\mu\text{N}$ and $\mu(^{7}\text{Li})=+3.2564157(30)\mu\text{N}$. Because both lithium nuclei differ 270 by one only neutron this indicates significant differences in the magnetic distribution in ⁶Li 271 and ⁷Li nuclei, which is confirmed by the nuclear theory. 272 The shielding constants received from theoretical calculations were verified by our 273 experimental investigations against other shielding constants measured simultaneously in 274 solutions. Both kinds of procedures lead to general agreement what means that nuclear 275 shielding and magnetic moments built the orderly set of compatible data. This provided a 276 very important check of the consistency and reliability of the magnetic properties of lithium 277 nuclei. The limiting factor of the nuclear magnetic moments values is therefore diamagnetic 278 corrections. 279 The applicability of the dissolved helium as a shielding reference in salt water solutions 280 is then proved. Our new measurements did not solve the problem of the different kinds of

- 281 lithium water complex ions present in solutions. Further investigations into these questions
- are strongly recommended. Nevertheless, our experimental findings can give new input
- 283 towards the understanding of subnucleonic effects in magnetic moments when compared to
- 284 new theoretical calculations involving higher-order corrections.
- 285 Conflicts of Interest: The author declare no conflict of interest.
- The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the
- writing of the manuscript, and in the decision to publish the results.
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