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Review

Nuclear Dipole Moments and Shielding Constants of Light Nuclei Measured in Magnetic Fields

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Abstract: Nuclear magnetic resonance (NMR) is a branch of spectroscopy commonly used for identifying the chemical structure of various materials. One of the areas in which NMR provides accurate data is the determination of nuclear magnetic moments. This work reviews NMR experiments with the nuclei of light elements in simple molecules. Since nuclear shielding constants from up-to-date quantum calculations are now available, very accurate dipole moments of many nuclei can be determined. Recent experimental measurements of ^{1}H, ^{2}H, ^{3}H, ^{3}He, ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, and ^{11}B nuclear magnetic moments and the appropriate theoretical predictions are presented and commented upon. Several achievements in this field using different methodologies, such as NMR spectroscopy, molecular beam experiments, and the Penning trap method are reported.

Keywords: nuclear dipole moments; nuclear shielding constants; light nuclei; NMR spectroscopy

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1. Introduction

The magnetic moment is a fundamental property of many physicochemical objects, e.g., intrinsic moments belong to many subatomic particles such as electrons, muons, protons, neutrons, and nuclei in their ground and excited states. Magnetic interactions are generally weak, but despite this, magnetic moments of particles can be measured with great accuracy. One of many reasons for trying to conduct very accurate measurements of magnetic moments is their importance in the standard model of particle physics and in the search for interactions beyond that model.

Only a non-zero spin particle has a magnetic dipole moment. The property of an elementary particle measured most precisely is the magnetic moment of the electron $-9.2847647043(28) \times 10^{-24}$ J T^{-1} [1]. The magnetic moment of the electron has a much larger magnitude than the moments of other particles and is 658.21068789(20) [2] times larger in magnitude than that of the proton. The presence of the magnetic dipole moments in particles leads to the development of two related branches of spectroscopy: nuclear magnetic resonance spectroscopy (NMR) and electron paramagnetic resonance spectroscopy (EPR). The former is observed in the span of frequencies of up to 1.2 GHz, while the latter is observed in the span from 9 to 100 GHz in the magnetic fields of currently used strengths. EPR spectroscopy requires a sample with unpaired electrons (e.g., radicals), while NMR spectroscopy mainly focuses on diamagnetic molecules and requires the presence of non-zero spin nuclei (so-called active nuclei).

One can express magnetic moments of particles using g-factors, also known as dimensionless magnetic moments. In particular, the magnetic moment of nucleus X can be expressed using the g-factor as $\mu_X = g_X I_X \mu_N$, where I_X is the spin operator, g_X is the g-factor of nucleus X, and $\mu_N = e{\cdot}\hbar/2m_p$ (where m_p is the mass of the proton) is the nuclear magneton; $\mu_N = 5.050783699(31) \times 10^{-27}$ JT^{-1}. Several examples of the magnetic properties of fundamental particles are included in Table 1.

Table 1. Magnetic properties of selected particles [2,3].

Particle	Spin Number	Magnetic Dipole Moment, 10^{-27} JT^{-1}	Lifetime	*g*-Factor	Electric Quadrupole Moment, Barn
electron (e^-)	1/2	−9284.7647043(28)	>6.6 × 10^{28} y	−2.00231930436146(056)	
positron (e^+)	1/2	9284.764704(430)	stable (as for e^-)	2.00231930437580(860)	
proton (p, $^1H^+$)	1/2	14.1060679736(66)	>1.67 × 10^{34} y	5.5856946893(16)	
neutron (n)	1/2	−9.6623651(23)	14.6 min	−3.82608545(90)	
deuteron ($^2H^+$)	1	4.330735094(11)	stable	0.8574382338(22)	0.00286(2)
muon (μ^-)	1/2	−44.9044830(10)	2.19703(4) μs	−2.00233184121(82)	

In an external magnetic field $\boldsymbol{B_0}$ that is oriented along the *z*-axis, a nucleus with the spin number I may have $2I + 1$ orientations, the projections of which are $m_I\hbar$ on the *z*-axis where $-I \leq m_I \leq I$. The spin number I of given nuclei can be either an integer or a half-integer. Nuclei with an even number of neutrons and an even number of protons (so-called even-even nuclei) have $I = 0$ and they are not active in NMR spectroscopy. The + or − symbol following nuclear spin numbers means even and odd parity, respectively, i.e., wave functions unchanged or with a reversed sign upon spatial inversion. Furthermore, the nuclei with $I \geq 1$ have an electric quadrupole moment, given in barns (1 b = 10^{-28} m^2). In a static magnetic field NMR/EPR experiment, only the maximum projection of the magnetic moment on the axis of the external magnetic field can be directly observed; therefore, $\mu_X = \hbar\,\gamma_X\,I_X = g_X\,I_X\,\mu_N$, where γ_X is the magnetogyric ratio of the nucleus X.

The simplest possible nucleus is just a single proton. Recently, the magnetic moment of a single proton was measured directly as 14.106067842(97) × 10^{-27} J·T^{-1} [2,4]. On the other hand, the best magnetic moment available for the neutron is μ_n = −9.6623651(23) × 10^{-27} JT^{-1} [2].

Apart from ^{1}H, each nucleus comprises nucleons, neutrons, and protons, which can also possess a magnetic moment. The simple case represents a deuteron nucleus with one neutron and one proton, both of a spin number 1/2. Two spin-1/2 particles can form states with a total spin of 0 or 1. However, only the latest wave function is symmetric, leading to $I = 1$ for the deuteron (spin triplet state). If we add the magnetic moments of the proton and neutron, the result, 4.443703173 × 10^{-27} J·T^{-1} will be in reasonable agreement with the experimentally measured deuteron magnetic moment 4.330735094(11) × 10^{-27} J·T^{-1}.

In the standard model of particle physics, the neutron, the proton, and the deuteron are not considered to be elementary particles but are composed of quarks of spin 1/2 and gluons, which contribute to the nuclear magnetic moment [5]. It is not only the stable particles that have a magnetic moment, but also short-living particles such as the muon. This elemental particle is notable for having an electric charge of −e, a much greater mass (about 207 times that of the electron), and a mean lifetime of 2.1969811(22) × 10^{-6} s. Muons can form muonic atoms when they replace electrons. Physicists have found the anomalous magnetic dipole moment for the muon as the difference between the experimentally observed value of the magnetic dipole moment and the theoretical value predicted by the Dirac equation. This difference is crucial for the precision testing of the QED theory [6,7]. Interestingly, theoretical studies show that even neutrino particles, due to induced spin oscillations, can possess a magnetic moment, probably less than 10^{-19} of an electron [8]. The magnetic moment depends explicitly on mass, which leads us beyond the standard model, where neutrinos are massless particles. The uncertainties and controversies mentioned above place magnetic moments at the forefront of the main problems in contemporary physics [9].

Since their discovery, nuclear magnetic moments have been perceived more as experimentally measurable than theoretical. This is caused by the long-standing problems of quantum physical theories for calculating these values. The first theoretical description of nuclear magnetic moments was based on the single-particle model. In this model, nuclear dipole moments of odd nuclei can be estimated by the supposition that they are entirely dependent on one surplus nucleon. Several different, sophisticated methods for predicting nuclear magnetic moments exist today: the shell model (spherical/deformed),

the liquid drop model, and the collective, or unified, models (both shell and collective) [10] Simultaneously, the standard model is developed where the intrinsic quark structure of nucleons is taken into account. This approach can be used in the predictions of specific nuclear properties such as nuclear charge radii, the binding energy of nucleons, the size and shape of a given nucleus, stability, and, finally, the spin numbers and nuclear magnetic moments. Since the total nuclear magnetic moment results from the spins of quarks and gluons in a particular nucleon mediated by complicated interactions, coming up with precise calculations of the magnetic moments is exceptionally challenging [11]. Generally, the non-relativistic approaches of quantum mechanics do not provide accurate results compared to the relativistic ones. We do not intend to discuss problems and difficulties in theoretical computations for the light nuclei mentioned in this work. However, several recently calculated results are cited and commented upon for comparison with elaborated experimental values.

Magnetic moments of excited states of nuclei can be accurately measured by the so-called β-NMR experiment carried out in condensed matter if only the beta decay of the unstable nucleus takes place [12]. This unique method of spectroscopy utilizes spin precession of beta emission nuclei. Highly polarized beams of radioactive nuclei are used. A high degree of accuracy and the possibility of using even ten orders of magnitude smaller number of nuclei required for measurements compared with standard NMR spectroscopy makes it possible to effectively determine the nuclear moment. Several examples of nuclear magnetic moments for short-lived lithium and boron isotopes are presented in Section 4, the Conclusions of this article [13].

This work aims to review and complete methods for establishing nuclear magnetic moments of light nuclei. The NMR method, which is efficient and popular, is elaborately detailed. Originally, nuclear magnetic moments were observed in the studies of I. I. Rabbi in what are known as atomic and molecular beam experiments performed in the 1930s [14]. The basis of the experiment is the splitting of resonance lines in an external static magnetic field, known as the Zeeman effect. Next, nuclear magnetic moments were derived using different experimental methods: optical spectroscopy, optical double resonance and pumping techniques, microwave spectroscopy, atomic-molecular beam spectroscopy, and classical NMR spectroscopy. These methods differ with respect to sample preparation and precision of determined nuclear magnetic moments. Since the earliest work of Purcell and Bloch [15,16] several attempts to determine nuclear magnetic moments have been made using several modified methods (see, for example, Ref. [17]) for measuring radiofrequencies in a strong magnetic field. Over the last few decades, the increase in the power of NMR spectroscopy was achieved mainly by using very stable superconducting magnets, sensitive probe design, and specific pulse sequences which offer high precision and well-resolved spectra.

In chemistry and physics, the term "light nuclei" may be ambiguous; therefore, for the purpose of this work, we limit the nuclei to ^{1}H, ^{2}H, ^{3}H, ^{3}He, ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, and ^{11}B with mass numbers from 1 to 11. The predominant part of the experimental results was performed using NMR spectroscopy. Additional data regarding valuable results that have appeared in the literature are also provided.

2. Methodology for Determination of Nuclear Magnetic Moments

2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

Measurements are conducted for specific chemical species [18,19] where nuclear magnetic shielding (screening by moving electrons) for a specific nucleus in a particular molecule should be known. One way to include these effects is to use theoretical calculations. Quantum chemical methods of nuclear magnetic shielding calculations are less damaging for light nuclei than for heavy nuclei since relativistic effects are small and, in some cases, can be omitted. Those circumstances have led to the establishment of very precise values of nuclear magnetic moments for light nuclei.

The resonance frequency ν_X of nucleus X in an isotropic sample is: $\Delta\mu_X^Z(1-\sigma_X)B_0$, where σ_X is the isotropic part of the nuclear magnetic shielding tensor (also referred to as "(absolute) shielding constant"), and $\Delta\mu_X^Z$ means the possible increments of the projection of the magnetic moment of the axis of the external field B_0. In the NMR experiment, transitions are observed at a frequency that is proportional to $\Delta\mu_X^Z = \mu_X \Delta I_X^Z / I_X$.

Let us suppose that two nuclei (X and Y) are placed in the magnetic field of the same strength. The ratio of their resonance frequencies ν_X and ν_Y is proportional to the ratio of their magnetic moments according to equation [20]:

$$\frac{\Delta\mu_X^Z}{\Delta\mu_Y^Z} = \frac{\nu_X}{\nu_Y} \cdot \frac{(1-\sigma_Y)}{(1-\sigma_X)} \cdot \frac{I_X}{I_Y} \approx \frac{\nu_X}{\nu_Y} \cdot \frac{(1+\sigma_X)}{(1+\sigma_Y)} \cdot \frac{I_X}{I_Y}, \quad (1)$$

where the factor that takes into account the fact that electrons may shield the externally applied magnetic field B_0 is called in the further text the correction factor: $(1 + \sigma_X)/(1 + \sigma_Y)$. The new magnetic moment values of the nuclei under inspection in this work using correction factors are provided in the tables included in the next stages of this work. Using Equation (1), one can determined a magnetic dipole moment based on the magnetic shielding known from quantum chemistry computations, the measured ratio of resonance frequencies, and obtained from other measurements of the magnetic moment of the reference nuclei.

2.2. Atomic Beam Magnetic Resonance (ABMR)

The subject of molecular or atomic beams is the study of neutral atomic or molecular species at very low densities where intermolecular interactions can be practically eliminated [14]. Precision measurements of nuclear magnetic moments with the introduction of the molecular/atomic resonance method were first reported by I. I. Rabi [21]. The appropriate molecules were heated or cooled in the chamber (known as the oven) depending on the vapor-pressure properties and afterward introduced through a small slit in the vacuum line, where they were subjected to three magnetic fields. They passed through two inhomogeneous magnetic fields produced by two deflecting and refocusing magnets. Between these two magnets, an oscillatory field was introduced to cause the molecular transition connected to nuclear spin space quantization, which leads to radiofrequency resonance signals. Several magnetic moments (e.g., ^{1}H and ^{2}H) were measured in this way for the first time.

2.3. Penning Trap Experiments

A new and more prospective physical method for research into mass, fission product yield, isomeric yield ratios, and magnetic moments of charged particles is the Penning trap method [22,23]. In a Penning trap device, a charged particle is confined by the application of the homogenous magnetic field and the spatial quadrupole electric field. It can be used to store the ions and stable subatomic particles. In this experiment, the magnetic moment can be determined by measurements of a frequency ratio ν_L/ν_C, where ν_C is a cyclotron frequency, and ν_L is a spin precession frequency. Both values are measured in the same magnetic field $\boldsymbol{B_0}$. The cyclotron frequency can be considered using a combination of characteristic oscillation fragments of the trapped particle, the modified cyclotron, and the axial frequencies and magnetron frequency

$$\nu_c = \frac{q}{2\pi\, \mathrm{m}} B_0. \quad (2)$$

In Equation (2), q and m are the charge and mass of the particle, respectively.

If we use the cyclotron frequency, the B_0 field can be eliminated from Equation (2), and if the spin precession frequency is known, the magnetic moment of the single particle can be determined. The Larmor frequency is measured using the continuous Stern-Gerlach effect [24]. The magnetic moments of the electron, proton, and antiproton were determined

with unprecedented precision using a slightly upgraded method is known as the double Penning trap experiment.

2.4. Theoretical Approach

The methods mentioned above can provide very precise and accurate measurements of nuclear magnetic moments. Nevertheless, many attempts have been made by physicists to predict these results theoretically. Different models were used to describe particular nuclear properties: the liquid drop model, the shell model, collective model, and the standard model. The shell model was successful in describing spin numbers of nuclei, but it failed to predict nuclear moment. Several realistic, unified models try to include shell and collective behaviors. Today, the standard model is the most significant in modern physics, based on the observation that protons and neutrons are not fundamental particles but have the internal quark structures—composite hadron particles. The quarks in a proton or neutron structure are bound by gluons—particles which also participate in the final magnetic moment value. The theory of quarks and gluons is known as Quantum Chromodynamics (lattice QCD theory) e.g., [25]. An excellent review of theoretical studies of nuclear magnetic moments was published by E.G. Zhao [26]. His final remark is this: " ... a quantitative and universal description of nuclear magnetic moments would definitely require further theoretical investigations". In general, the theoretical results are far from our expectations here ($\pm$10%). The arbitrarily selected theoretical results of nuclear magnetic moments of light nuclei can be found in the Summary.

3. Magnetic Moments of Selected Nuclei

3.1. Magnetic Moments of Hydrogen Isotopes

Elemental hydrogen consists of three isotopes: ^{1}H(A1, protium), ^{2}H(A2, deuterium) and ^{3}H(A3, tritium). The first two isotopes are stable; triton has a half-life of 12.3 years. Tritium nucleus is an β-emitter of low energy electrons (5.7 keV) that can be fully absorbed in glass test tubes, so with care, it can be handled in an NMR laboratory.

3.2. Proton (^1_1H Nucleus)

The proton is a stable particle often connected to one electron, forming a hydrogen atom that is a constituent of many chemical compounds. In the standard model, protons are hadrons and are composed of three quarks. The nuclear magnetic moment of the proton is known from an experiment that used a hydrogen atom maser; it was performed in a static magnetic field by Winkler et al. [20]. The frequencies of the proton transitions and those of the electron transition were measured. The electron/proton resonance frequency ratio in the hydrogen atom gives a result of μ_p = 2.792 847 344 63(82)μ_N. These data were recommended by CODATA 2021 fundamentals [2] as primary physical constants. The value was measured recently when Schneider et al. [4] used a single proton in the double Penning trap technique directly. It is worth noting that excellent experiments on the antiproton magnetic moment have been carried out recently. Direct measurements of antiproton were conducted in the single Penning trap with a superimposed strong magnetic bottle with a final result of $\mu_{\text{antip}} = -2.7928465(23)\mu_N$ [27]. These kinds of measurements can undoubtedly improve the nuclear physics knowledge of the symmetry between matter and antimatter.

Moreover, the proton nucleus is a favorable reference for many applications, e.g., NMR measurements of dipole moments of other nuclei present in hydrogen-containing compounds, and ^{1}H NMR has high sensitivity. Several simple gaseous hydrides can be handled for this purpose (HD, HCl, PH_3, CH_4, SiH_4, B_2H_6, etc.).

3.3. Deuteron (^2_1H Nucleus)

The deuteron (nucleus of deuterium) is an isospin singlet boson (I = 1) composed of one neutron and one proton (a system of six quarks) with a total spin of 1 and even parity. The deuteron has a non-zero quadrupole moment known from an experiment

($Q = 0.2859(3)$ fm^2) [28]. Interestingly, the deuteron consisting of one proton and one neutron is only a weakly bound nucleus with the binding energy of ~2.22MeV.

The three most abundant isotopomers of molecular hydrogen are H_2, HD, and D_2. Hydrogen gas (H_2) contains two spin isomers: ~75% *ortho*-H_2 and ~25% *para*-H_2 at room temperature. Similar spin isomeric molecules are present in fully deuterated hydrogen D_2.

Hydrogen deuteride (HD) is an ideal research subject for establishing a deuterium magnetic moment against that of a proton. HD is a minor component—to the extent of 0.015%—of naturally occurring hydrogen, but intriguingly is a trace component of some planet atmospheres (e.g., Jupiter). HD can be used in the pure state, in the gas phase, where intermolecular interactions are eliminated when extrapolation to the zero-density limit takes place. In this case, the correction factor is almost 1. Because of the small quadrupole moment of the deuteron, quadrupole relaxation of this nucleus does not broaden its NMR lines significantly. The gas phase results of the measurements for HD at different gaseous densities of mixtures are shown in Table 2 (for experimental details, see the Supplementary Materials). The linear dependences were analyzed using the linear regression method. The frequency ratio $\nu_D/\nu_H = 0.153506100$ leads to the nuclear magnetic ratio 0.3070122013 without diamagnetic corrections and 0.3070122028 corrected for shielding effects taken from Ref. [29]. It should be noted that the correction factors in the HD molecule are very small, less than 10^{-5}%, due to a small difference in the shielding factors between the proton and deuteron nuclei in hydrogen deuteride $\Delta\sigma = 0.012$ ppm. Other correction factors can be used [30,31] along with the results of the H_2/D_2 mixture investigations [29]. Correction factors can be presented as a ratio for two nuclei according to Equation (1). The findings are in good agreement with the previous investigations of the Neronov study [32] where pressure dependences were analyzed.

Table 2. NMR parameters of hydrogen isotopes in gaseous mixtures.

Gaseous Mixtures	ν_0(HD) MHz	ν_0(HD) MHz	Correction Factor ^{1}H/^{2}H	References	μ(D)/μ_N
pure HD	500.60906811(37)	76.84654599(52)	1.000026339(3)/ 1.000026327(5)	[19]	0.8574382214(133)
			1.00002634242/ 1.00002633323	[30]	0.8574382190(64)
			1.0000263436(48)/ 1.0000263329(12)	[31]	0.8574382203(64)
	$\nu_0(H_2)$MHz	$\nu_0(D_2)$MHz			
$H_2/D_2/CO_2$	500.609339	76.846713	1.000026388(3)/ 1.000026293(5)	[29]	0.857439692
				[33]	0.8574382346(53)
				[34]	0.8574382338(26)
				[2]	0.8574382308(72)
				[35]	0.857438228(91)

3.4. Triton (^3_1H Nucleus)

Triton (T) with a 12.32-year half-life consists of a proton and two neutrons and decays by beta emission to ^{3}He according to equation

$$^3_1\mathbf{H}^{1+} \rightarrow {}^3_2\mathbf{He}^{+} + \mathbf{e}^{-} + \bar{\nu}_\mathbf{e}\ (+18.6\ \text{keV}). \quad (3)$$

Tritium beta radiation has low energy (average energy 5.7 keV) and can penetrate only about 6 mm of air. Analyses of emitted electrons can provide an idea of the mass of the electron antineutrino [9]. Tritium can be produced in nuclear reactors by capturing neutrons in deuterium or in the neutron and 6-lithium nucleus fusion reaction through the reaction ^{6}Li(n,α)^{3}H. Naturally occurring tritium is very rare on Earth (traces). In practice, the substances are gaseous tritium gas (HT) and tritiated water (diluted HTO in excess of

H_2O). The first investigations of the tritium magnetic moment were carried out by Duffy in 1959 [36] along with his original new measurements performed on a sample of 20% of tritiated water. The experimental problems in tritium investigations are mainly due to the radioactivity of the sample and the skills required for high radiofrequency transmission. In general, when compounds are labeled, the sensitivity of analyses is high enough to observe the resonance signal.

The spin of the triton is $\frac{1}{2}$, and its dipole moment, recently tabulated by CODATA (2021) is 2.9789624656(59)μ_N [2]. The HT molecule is an ideal research subject for establishing the triton magnetic moment against that of a proton. The first advanced investigations in this field were performed by Neronov et al. in 1977 [37] His result was improved shortly thereafter [38,39], and further studied by Garbacz et al. [29]. Experimental results were used to calculate tritium-3 magnetic moments with shielding corrections made at different theoretical levels. Shielding constants in isotopic forms of the hydrogen molecule differ only slightly, and the final magnetic moment depends mostly on the measured frequencies. The experimental results of the ratio $\nu(^3He)/\nu(^1H)$ in the HT molecule, are shown in Table 3.

Table 3. NMR parameters for establishing the ^3T nuclear magnetic moment.

Experimental Details	$\nu(^3T)/\nu(^1H)$ *	Correction Factor	References	$\mu(^3T)/\mu_N$
H_2O/**H**OT/$\mathbf{T}_2$O liquid	1.06663975(2)	1.000000	[36]	2.978961993
HT gaseous	1.066693887(33)	1.000000221877	[37]	2.979113851(1)
HT gaseous	1.066639908(10)	1.000000221877	[38]	2.978963095(28)
HT gaseous	1.066693898(2)	1.000000221877	[39]	2.979113881(1)
HT extrapolated	1.066639898(2)	1.000000221877	[29]	2.978963044(10)
T_2/H_2	1.066639768	1.0000001900	[29]	2.978962609
T_2/D_2	6.948505774	1.000000086	[29]	2.978962582

* $\mu(^3T)$ referenced against proton 2.79284734462(82)μ_N [4] and deuteron 0.857438228(91)μ_N [35].

3.5. Magnetic Moment of Helium-3

Helium is the second most abundant element in the universe. It has two isotopes: ^3He and ^4He. The atmosphere of Earth contains a ~5.2 ppm volume of helium with a $^3He/^4He$ ratio of 1.4×10^{-6}. ^4He is made up of two protons and two neutrons; it is a very stable isotope where the nucleons are paired, resulting in the total spin of 0. This isotope is not magnetically active, in contrast to the ^3He isotope with a spin of $I = 1/2$, and it is suitable for NMR spectroscopy. ^3He atoms can be obtained from the decay of tritium in nuclear fission reactors [40] see Equation (3).

The final value of the ^3He nuclear magnetic moment cannot be verified by NMR measurements of any chemical compounds because helium does not form stable chemicals. In this case, it is useful to examine a gaseous mixture that includes the helium-3 gas, a mixture of helium-3 with gaseous hydrogen. The chemical shielding of isolated hydrogen molecules is well established by theory [30,31] and experiment [37] with high precision. The ^1H NMR spectra are of great sensibility, so we prepared three different mixtures, namely $^3He/H_2$ in CO_2, N_2O, and CF_4. None of the buffers used have protons, so they do not obscure the molecular hydrogen ^1H NMR signal. The ^1H and ^3He frequencies extrapolated to the zero density limit are shown in Table 4 (for experimental details, see Supplementary Materials). The ^3He magnetic moment was calculated according to Equation (2), considering shielding factors. Correction for isolated helium atom (σ_0 (^3He) = 1.00005996743(10)) reused in all cases in Table 4. [41].

Table 4. NMR parameters of gaseous mixtures of $H_2/^3He$ in buffer gases.

Gaseous Mixtures	$\nu_0(H_2)$ MHz	$\nu_0(^3He)$ MHz	Correction Factor	References	$\mu(^3He)/\mu_N$
$H_2/^3He/CO_2$	500.6089846(8)	381.3572152(2)	1.000026293(5)	[19]	2.127625319(16)
			1.000026298	[30]	2.127625304(16)
			1.0000262886(15)	[31]	2.127625328(16)
$H_2/^3He/N_2O$	500.6089867(7)	381.3572161(2)	1.000026293(5)	[19]	2.127625315(16)
			1.000026298	[30]	2.127625304(16)
			1.0000262886(15)	[31]	2.127625324(16)
$H_2/^3He/CF_4$	500.6089905(7)	381.3572162(2)	1.000026293(5)	[19]	2.127625300(16)
			1.000026298	[30]	2.127625289(16)
			1.0000262886(15)	[31]	2.127625309(16)

From these results, one can see that the values established here are essentially in good agreement with those in operation today $-2.127625308(25)\mu_N$. This last result was established by comparing the ^1H NMR frequency in a water sample and the ^3He NMR frequency in another sample filled with optically pumped low pressure (3 Torr 400 Pa), helium-3. Both samples had spherical shape and, consequently, the measured frequencies were not affected by the bulk magnetic susceptibility. Moreover, the accuracy of such measurements is limited by the line width of gaseous hydrogen.

The use of helium atoms as a reference has three main advantages: $\sigma_0(^3He)$ is known from QED computations, good miscibility and long T_2 relaxation time (good digitalization of FID). Results from gas phase experiments are shown in Table 4. They can be compared with the best results established in the last few years [42–45]: $-2.1276253298\mu_N$, $-2.127625227\mu_N$, $-2.127625222\mu_N$ and $-2.127625311(22)\mu_N$.

3.6. Magnetic Moments of 6,7-Lithium Isotopes

Lithium has several isotopes with mass numbers between 4 and 12. Most of them are unstable and have half-lives of between 10 nanoseconds and 840 milliseconds. Only two isotopes are stable and can be studied in bulk using spectroscopic methods: ^6Li (abundance—7.59%, I = 1^+) and ^7Li (abundance—92.41%, I = $3/2^-$). Both nuclei are quadrupolar $Q(^6Li) = 0.808$ mb and $Q(^7Li) = -40.1$ mb (1 mbarn = $1 \times 10^{-31} m^2$). The ^7Li nucleus has a charge radius smaller than ^6Li and has about a 40% larger Zemach radius [46].

The magnetic moment of lithium was derived from two kinds of experiments: ABMR [47,48] and NMR carried out in lithium-water solutions. The first approach leads to $\mu(^7Li) = 3.256427(2)\mu_N$ and $\mu(^6Li) = 0.8220473(6)\mu_N$ [48]. These moments were improved by the new m_p/m_e and g_J factors and are included in Table 5. The NMR experiments were performed by Lutz [49] in a LiCl and LiBr water solution and in a solid state. Much more accurate measurements have only recently been performed and published [50]. The series of LiCl and $LiNO_3$ in the water solutions with helium-3 components were measured as concentration functions in the $^{6/7}Li$ and $^{14}N/^{35}Cl$ NMR frequency mode. Lithium magnetic moments were calculated against those of helium-3 nuclei with high precision. New shielding corrections of lithium cations in water clusters were involved due to theoretical calculations [51]. Small deviations of the order of ~1ppm were observed when the hexa and tetracoordinated (Li^+)aq. water clusters were present in the solution. The NMR results [50] correspond well to the ABMR values [47,48] and demonstrate the consistency of both methods. It is important to remember that Equation (1) connects the appropriate nuclear moments with the shielding constants in a specific chemical species. Therefore, it is possible to check the consistency of these two parameters in different situations. Previous measurements of chemical shifts in Cl^- and NO_3^- anions accompanying lithium cations in solutions confirm the proper lithium magnetic moments [50]. Recently, we decided to carry out some experiments with CH_3COOLi and $LiBF_4$ solutions to make use of the well-known ^{13}C and ^{11}B magnetic moments established previously in our laboratory [52,53]. The exper-

imental results, which were extrapolated to the zero-point concentration, are contained in Table 5. They consist of several radiofrequencies and chemical shifts/shielding measured for the H_2O, CH_3COO^-, $^{6/7}Li^+$, and $^{11}BF_4$ species. The results of NMR radiofrequencies and absolute shielding of ^1H, ^{13}C, ^{19}F and ^{11}B will be used to recalculate the shielding constants of $^{6/7}Li$ using Equation (1).

Table 5. NMR parameters measured in CH_3COOLi and $LiBF_4$ water solutions. σ_0(relative) were established against tetramethylsilane (^1H and ^{31}C), $CFCl_3$ (^{19}F) and $BF_3(OEt)_2$ ($^{10/11}B$).

Solution	Nuclide	ν_0 (Radiofrequency) (MHz)	δ_0/ppm	σ_0/ppm (Relative)	σ_0/ppm (Absolute)
CH_3COOLi	$^1H(H_2O)$	500.6081739(2)	4.096(2)	−7.101	25.714
	$^1H(CH_3)$	500.6067408(37)	1.23 1(1)	−4.236	28.579
	$^{13}C(CH_3)$	125.8803604(2)	23.383(1)	−26.388	159.982
	$^{13}C(COOLi)$	125.9002810(10)	181.642(2)	−184.64	1.723
	^6Li	73.6695828(4)	0.110(2)	−3.116	
	^7Li	194.5544566(1)	0.111(2)	−3.117	
$LiBF_4$	^{11}B	160.6140109(1)	−1.711(1)	−1.294	109.60
	$^{19}F(^{10}BF_4)$	470.9694439(38)	−150.125(1)	147.119	339.82
	$^{19}F(^{11}BF_4)$	470.9694194(39)	−150.177(1)	147.171	339.87
	^7Li	194.5544570(11)	0.110(1)		

Consequently, according to Equation (1), we check the absolute shielding values of lithium cations in water solutions at infinite dilution. These values are included in the last column in Table 6. New nuclear magnetic moments of ^7Li and ^6Li calculated from tetracoordinated and hexacoordinated water complexes, were used: 3.2564169(98) and 3.2564195(95) for $\mu(^7Li)$ and 0.8220453(25) and 0.8220459(25) for $\mu(^6Li)$. We can see that the related results are very consistent when the new magnetic moments are confronted with the shielding factors of lithium cations. In most cases, the recalculated shielding of lithium cations differs by less than 1 ppm. For the $LiBF_4$ solution, the ^6Li NMR spectra were not obtained. Valuable discrepancies are observed when old nuclear magnetic moments of reference nuclei ^1H, ^{13}C, ^{11}B, and ^{19}F are considered Very recently, Neronov carried out similar experiments in $LiOH{\cdot}H_2O$ salt in liquid distilled water solutions by simultaneously recording two NMR signals. The most precise results were achieved: $\mu(^6Li) = 0.8220454(25)\mu_N$ and $\mu(^7Li) = 3.2564171(98)\mu_N$ [54]. In any case, all the results mentioned above are in very good agreement. The appropriate shielding correction factors of lithium cations are listed in Table 6.

Table 6. $^{6/7}Li^+$ NMR shielding values calculated from Equation (1). Nuclear magnetic moments of $^{6/7}Li$, ^{13}C, ^1H, ^{19}F, and ^{11}B from data in the literature.

Solution	$\mu(^7Li)$ [a]	$\mu(^{13}C)$	Correction Factor [g]	σ (^7Li) (ppm)	$\mu(^6Li)$ [a]	σ (^6Li) (ppm)
CH_3COOLi	3.2564169(98)	0.70236944(68) [b]	1.000159982	90.76	0.8220453(25)	90.71
			1.000001723	90.72		90.68
	3.2564195(98)		1.000159982	91.55	0.8220459(25)	91.44
			1.000001723	91.52		91.41
	3.2564169(98)	0.7024118(14) [c,d]	1.000159982	30.45	0.8220453(25)	30.41
			1.000001723	30.42		30.38
	3.2564195(98)		1.000159982	31.25	0.8220459(25)	30.41
			1.000001723	31.22		30.38

Table 6. *Cont.*

Solution	μ(^{7}Li) [a]	μ(^{13}C)	Correction Factor [g]	σ (^{7}Li) (ppm)	μ(^{6}Li) [a]	σ (^{6}Li) (ppm)
		μ(^{1}H)				
	3.2564169(98)	2.7928477350(9) [e]	1.000028579	90.74	0.8220453(25)	90.66
				91.53		91.43
	3.2564195(98)		1.000025714	90.73	0.8220459(25)	90.69
				91.53		91.42
	μ(^{7}Li)	μ(^{11}B)				
	3.2564169(98)	2.6883781(11) [f]	1.0001096	90.93		
	3.2564195(98)			91.73		
	3.2564169(98)	2.6886489(10) [c,d]	1.0001096	−9.79		
	3.2564195(98)			−8.98		
		μ(^{19}F)				
$LiBF_4$	3.2564169(98)	2.6283214(132) [c,d]	1.00033987	90.78		
			1.00033982	90.79		
	3.2564195(98)		1.00033987	91.16		
			1.00033982	91.16		
	3.2564169(98)	2.628868(8) [c,d]	1.00033987	−117.2		
			1.00033982	−117.2		
	3.2564195(98)	2.628868(8) [d]	1.00033987	−117.1		
			1.00033982	−117.1		

([a]) [50]; ([b]) [53]; ([c]) [19]; ([d]) [55]; ([e]) [4]; ([f]) [52]; ([g]) two values correspond to carbon atoms in the CH_3^- group and COO^-, respectively.

3.7. Magnetic Moment of the Beryllium-9 Isotope

Beryllium has 12 known isotopes, but only one is stable, composed of an even number of protons (four) and an odd number of neutrons (five). Radioactive ^{10}Be has a half-life of 1.39 million years (indicating unusual stability with a high neutron/proton ratio 2/3) and ^{7}Be has a half-life of 53.22 days. Other isotopes have half-lives of less than 13.85 s. Most of the stable beryllium atoms in the cosmos are assumed to have been initially created in interstellar space during the induced fission of heavier elements under cosmic ray interactions. ^{9}Be has a spin number of 3/2; it is a quadrupole nucleus with moderate electric quadrupole moment Q = +0.0529(4) barn [28] and can be used in the NMR method.

In principle, it is possible to carry out tentative experiments in the gas phase with beryllium borohydride $Be(BH_4)_2$. Unfortunately, this compound is very unstable and tends to explode when in contact with traces of water or air.

The first measurements of the ^{9}Be nuclear magnetic moment were conducted using the ABMR method by Rabi et al. in 1939 [56]. Then, the NMR method was used in a water solution of $Be(NO_3)_2$ [57], and the subsequent measurements were performed using the NMR/OP method [58]. Spectacular experiments took place and theoretical accounts were recorded only recently [59] (see Table 7), taking into account the Zeeman's hyperfine splitting when the ratio of the nuclear to the electron g-factors in $^{9}Be^{+}$ ion [60] was estimated as g_I'/g_J = 2.134779853(2) × 10^{-4} or 2.13478083(28). Additionally, the shielding constant was calculated with all significant contributions, including the relativistic correction, σ($^{9}Be^{+}$) = 141.85(3) ppm, where the uncertainty arises from errors in relativistic corrections. The final value depending on the experimental factors [59] is $\mu(^{9}Be) = -1.17743159(3)\mu_N$. This result is one of the most accurate of all magnetic moments of isotopes in the periodic table.

We have tried to check the consistency of this last result and the shielding effect in the aquatic ion Be^{2+} that is always present in water solutions of beryllium salts. Relatively easy measurements can be performed for the beryllium nucleus in a high-degree geometry position. Several Hz of the half-line can be seen in a water complex of the beryllium cation $Be[(H_2O)_4^{+}]$. It is worth remembering that the beryllium cation exists in bulk water in a

well-defined tetrahedral solvation shell. It can be easily recorded in water solutions due to its narrow line widths [61].

To summarize the presented results, the experimental details for the beryllium experiment are presented in Supplementary Materials. The results extrapolated to the zero-concentration point are collected in Table 7. These frequencies and, consequently shielding are not corrected for susceptibility.

The frequency position is primarily a function of the electronic structure of the central ion Be^{+2} and the water molecules in the first solvation sphere. Additionally, in aqueous solutions, chemical processes may affect the sample composition since the Be^{+2} cations can easily hydrolyze and oligomerize even in very diluted solutions [61–65]. Fortunately, complexes such as $Be_3(OH)_3(H_2O)_6{}^{+3}$ and $Be(H_2O)_3OH^+$, show only minor differences compared to $Be(H_2O)_4{}^{+2}$, 0.61 ppm and 1.97 ppm, respectively [63]. The calculation of several beryllium aquo and hydroxo complexes provides results in the shielding region of ±15 ppm. Moreover, the extrapolation of shielding to the zero-concentration limit eliminates the impact of anion inclusion into beryllium water complexes [66].

Table 7. NMR parameters used to calculate the ^{9}Be nuclear magnetic moment.

Solution	Atom	ν_0/MHz	δ/ppm	σ(rel.)/ppm	σ(abs.)/ppm	$\mu(^nX)/\mu_N$
$BeSO_4$	^{3}He	381.3564692	2.858	−0.267	59.700	−2.127625309
	^{1}H	500.6081735	4.104	−7.11	25.705	2.792847345
	^{9}Be	70.344232	0.104		112.18	−1.177432(5) [a]
						−1.175 [b]
						−1.1778(9) [c]
						−1.177432(3) [d]
						−1.17747(27) [e]
						−1.17743159(3) [f]
						−1.177430(5) [g]

([a]) this work, ([b]) [56], ([c]) [58], ([d]) [35], ([e]) [62], ([f]) [59], ([g]) [65].

3.8. Magnetic Moments of 10,11-Boron Isotopes

The naturally occurring ^{10}B (18.83%, I = 3) and ^{11}B (81.17%, I = 3/2) boron isotopes are both magnetically active and can be relatively easily measured by NMR spectroscopy due to their high abundance and high resonance frequencies. Both isotopes possess electric quadrupole moments: +0.0847(6) for ^{10}B and +0.0407(3) barn (1barn = 10^{-28} m^2) for ^{11}B, so quadrupole broadening of resonance signals often occurs and, consequently, in many cases multiplets become unresolved. Usually, the heavier isotope is preferred because of its higher sensitivity. Isotopically enriched boron compounds are now commercially available. Additionally, several unstable isotopes of boron are known with mass numbers and half-lives: 6, 7 (3.255×10^{-22} s), 8 (770 ms), 9 (8.439×10^{-19} s), 12 (20.20 ms), 13 (17.33 ms), 14 (12.5 ms), 15 (9.93 ms), 16 (<190 ps), 17 (5.08 ms), 18 (26 ns), 19(2.92 ms), 20, and 21.

At first, boron magnetic moments were established by Rabi et al. [21] in 1939 by the molecular beam magnetic resonance method with a mistake covering the spin number of the boron-10 isotope which was used as 1: $\mu(^{11}B) = 2.682(8)\mu_N$ and $\mu(^{10}B) = 0.597(3)\mu_N$ (corrected for the correct spin number $1.791(9)\mu_N$. Trifluoroborane (BF_3), a stable and simple gaseous compound, was chosen for determining of the magnetic moments of boron by applying NMR spectroscopy [52]. BF_3 has a planar trigonal structure and is a nonpolar molecule notable for its low melting and boiling points which are favorable properties for gas-phase NMR studies. The ^{11}B, ^{10}B and ^{19}F resonance frequencies of BF_3 in gaseous samples with different densities and a very small amount of helium-3 added were examined at a temperature of 300K. The $\mu(^{10}B)$ and $\mu(^{11}B)$ magnetic moments in nuclear magnetons were calculated against that of ^{3}He and ^{19}F nuclei according to Equation (1). At the same time, highly accurate shielding constants were obtained with vibrational, temperature, and relativistic corrections: $\sigma_0(^{10}B) = 97.879$, $\sigma_0(^{19}F) = 331.949$ ppm for $^{10}BF_3$

and $\sigma_0(^{11}B)$ = 97.882, and $\sigma_0(^{19}F)$ = 332.009 ppm for $^{11}BF_3$ used as correction factors. The reference standard for boron isotopes for chemical shielding scales was then established in neat $BF_3{\cdot}OEt_2$ as equal to 110.9 ppm for ^{11}B and 110.8 ppm for ^{10}B, respectively. This first value was used in experiments in $LiBF_4$ water solutions to calculate the shielding constant at infinite dilution of the $^{11}BF_4^-$ anion (see results in Tables 6 and 8). These results and frequencies measured in water solutions can be used to recalculate the ^{11}B nuclear magnetic moment against that of ^{19}F according to Equation (1):

$$\Delta\mu^z\left(^{11}B\right) = \frac{160.6140107}{470.9694205} \cdot \left(\frac{1.00010959}{1.00033987}\right) \cdot \frac{\frac{3}{2}}{\frac{1}{2}} \cdot 2.628321 = 2.6883781(5)\mu_N. \quad (4)$$

Excellent agreement was achieved with the original value $\Delta\mu(^{11}B)$ obtained in the gas phase experiments [52] which confirms the correctness of the previously calculated shielding corrections to the magnetic moments. Methods performed in gas and liquid states can be equally effective.

4. Conclusions

In Table 8, we list the most recent values of light nuclei magnetic moments. Along with experimental nuclear magnetic moments discussed widely in previous sections, selected theoretical results are included.

The more precise and accurate nuclear magnetic moments provide valuable data for comparison with theoretical results achieved using present-day quantum methods. We chose the results of the nuclear quark-like model performed by Ghahramany et al. [67–69]. For ^{3}He, $^{6/7}$Li, ^{9}Be, $^{10/11}$B, the ab initio calculations were made by Beane et. al. [25]. Comparison of theoretical results with experimental values shows discrepancies that strongly increase with atomic number: 0.03% (proton), 0.5% (deuterium), 5% (helium-3), 11% (beryllium), and 25% (11-boron) (see Table 8 and Figure 1); see also Ref. [70] for a list of magnetic moments determined from gas-phase NMR. In general, it is believed that the best method of calculating nuclear magnetic moments is lattice QCD (Quantum Chromodynamics) [67,69,71], but as a non-perturbative theory, quarks and gluons have their own limitations. The description of nucleon mutual interactions on the short distances in the strong electric field in real-time dynamics makes this method insufficient. In conclusion, currently available data indicate that nuclear magnetic moments are rather experimental quantities, because even recently treated theoretical models are quite approximate.

Table 8. Magnetic properties of light nuclei.

Nuclide	I^π	Q (Barn)	Abundance %	$\mu_{exp.}$	Ref.	$\mu_{theor.}$	Ref.
^{1}H	$1/2^+$		99.9885	2.79284734462(82)	[2,4]	2.792(37)	[25]
^{2}H(D)	1^+	0.00286(2)	0.0115	0.857438228(9)	[35]	0.8615978	[71]
						0.8748046	[71]
^{3}H(T)	$1/2^+$		10^{-18}	2.978962471(10)	[29,33,39]	2.79284734(3)	[67]
						2.91(20)	[67]
						3.56(18)	[25]
^{3}He	$1/2^+$		0.000134	−2.127625308(25)	[68]	−2.004914	[69]
						−1.913042	[69]
						−2.2905	[25]
^{6}Li	1^+	0.000806(6)	7.59(4)	0.8220454(25)	[54]	0.8339	[72]
						0.843	[73]
^{7}Li	3/2	0.0400(3)	92.41(4)	3.2564171(98)	[54]	3.168(13)	[74]
						2.954(5)	[72]
						3.01(2)	[73]
^{9}Be	3/2	−0.0529(4)	100	−1.177743185(15)	[59]	−1.06(6)	[75]
						1.22(9)	[75]
^{10}B	3^+	0.0845(2)	19.9	1.86004636(8)	[52]	1.83	[76]
^{11}B	$3/2^-$	0.04059(10)	80.1	2.6883781(11)	[52]	2.09	[76]

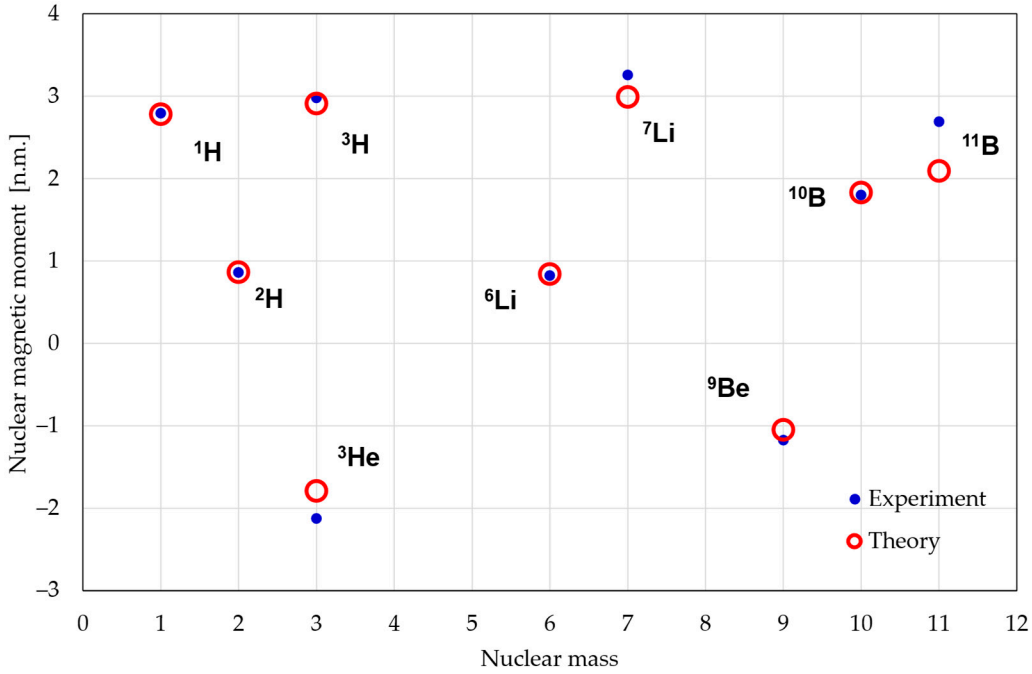

Figure 1. Nuclear magnetic moments in nuclear magnetons found experimentally (●) and computed based on theory (○). For numerical values, see Table 8.

This work is focused on stable isotopes, but magnetic properties can be also determined for short-lived isotopes and their magnetic moments can be measured with great accuracy. A good example can be served by the unstable lithium, beryllium and boron isotopes whose magnetic moments are $\mu(^{8}\mathrm{Li}) = 1.65350(2)\mu_N$ (840 ms), $\mu(^{9}\mathrm{Li}) = 3.43678(6)\mu_N$ (178 ms) [77], $\mu(^{11}\mathrm{Li}) = 3.6711(2)\mu_N$ (8.75ms), $\mu(^{7}\mathrm{Be}) = -1.3995(5)\mu_N$ (53.2 d) [73], $\mu(^{11}\mathrm{Be}) = -1.6816(8)\mu_N$ (13.8 s) [78], and $\mu(^{13}\mathrm{B}) = 3.1778(5)\mu_N$ (17.3 ms); the lifetime of each nucleus is given in the brackets. In the past, a few compilations of these values were consecutively published by Mack J. E. [79], Walchli H. E. [80], Kuntz W. [81], Fuller G. H. [82], Raghavan P. [55], Stone J. [28,35], Mertzimekis T.J. [83], and MacDonald A. [84].

The results of nuclear magnetic moments measured or corrected recently by shielding factors provide an order of magnitude improvement in accuracy over the previously reported results. This work includes a review of the first five elements of the periodic table. The most recent values of nuclear magnetic moments of stable isotopes ^{1}H, ^{2}H, ^{3}H, ^{3}He, ^{6}Li, ^{7}Li, ^{9}Be, ^{10}B, and ^{11}B can be found in Table 8.

The magnetic moments expressed in nuclear magnetons can be converted to the g_I factors ($g_I = \mu_X/I$) and the gyromagnetic ratios $\gamma_I = gI\mu_X/\hbar$ (see Table S1 in Supplementary Materials). We checked the consistency of NMM for several heavier elements in our laboratory: ^{13}C, $^{14/15}$N, ^{17}O, ^{29}Si, ^{31}P, ^{33}S, $^{35/37}$Cl. Because of the recent rise in quantum calculations for heavy atoms, in relativistic treatment, we measured NMM in ^{83}Kr, $^{117/119}$Sn, $^{129/131}$Xe, ^{183}W, ^{207}Pb, and ^{209}Bi isotopes. We hope that new, radically more precise, and accurate nuclear magnetic moments values will be good reference points for upcoming theoretical studies [85]. The subject of nuclear magnetic moments should be seen from a broader perspective in the range of problems related to the magnetic properties of physical elementary particles. These moments sometimes show anomalous and unexpected effects and are therefore of prime importance for modern nuclear physics and the standard model of particle physics.

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