Magnetic moments of short-lived nuclei with part-per-million accuracy
Paving the way for applications of β-detected NMR in chemistry and biology

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We determine the magnetic dipole moment of a short-lived nucleus with part-per-million (ppm) accuracy for the first time. To achieve this two orders of magnitude improvement over previous studies, we implement a number of innovations into our β-detected Nuclear Magnetic Resonance (β-NMR) setup at ISOLDE/CERN. Using liquid samples as hosts leads to narrow, sub kHz linewidth, resonances. A simultaneous in-situ stable-isotope NMR measurement allows to calibrate and stabilize the magnetic field to ppm precision. To eliminate a large systematic error, we improve the accuracy of the reference magnetic moment using ab initio calculations of NMR shielding constants. We demonstrate the potential of this combined approach for the 1.1 s half-life radioactive nucleus 26Na. Our technique can be extended to other isotopic chains, providing accurate magnetic moments for many short-lived nuclei. This will open the path towards interdisciplinary applications of β-NMR in biochemistry, where ppm shifts in signals need to be detected.

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INTRODUCTION

The magnetic dipole moment is a fundamental property of elementary particles and atomic nuclei. Recently, the magnetic moment of the proton has been measured with part-per-billion precision [1]. However, the experimental uncertainty for other atomic nuclei is typically three orders of magnitude lower. More importantly, as the measurements are typically not performed on bare nuclei, shielding of the applied external magnetic field by electrons (NMR shielding) has to be taken into account. Until recently, this effect has been poorly characterized and sometimes neglected, introducing a systematic error to the original magnetic moment data [2]. However, modern ab initio methods are capable of providing reliable NMR shielding constants [3]. Among nuclear magnetic dipole moments of stable nuclei corrected in this way [4], extreme cases exhibited systematic errors at the per-mill level [5, 7]. In comparison, the precision for magnetic moments of unstable short-lived nuclei is still limited by the uncertainty in the frequency measurement [2], which is at a per-mill to per-cent level.

Accurate magnetic moments of atomic nuclei are important for a number of research fields. One such example is the extensive experimental program devoted to the tests of QED in the strong electromagnetic fields of highly-charged ions [8, 9]. Here, a significant difference was found in highly-charged 209Bi ions between the measured and predicted hyperfine splitting (an effect of the interaction between the nuclear magnetic moment and magnetic field produced by the atomic electrons) [10]. This discrepancy was resolved by introducing a more accurate value of the magnetic moment of 209Bi [6, 7] based on ab initio NMR shielding calculations.

Furthermore, NMR spectroscopy applied to materials science, chemistry, and biology is currently based on the
Relative scale of chemical shifts and separate NMR standards for every NMR-active nucleus \[\text{[14]}\]. However, a single NMR standard can be defined and a direct measurement of the NMR shielding can be performed once the nuclear magnetic dipole moments are known with sufficient precision \[\text{[12]}\].

Recently, efforts have been made to perform NMR studies using not only stable but also short-lived nuclei by applying $^\beta$-NMR, which is based on the directional asymmetry of $^\beta$-particle emission from $^\beta$-decaying nuclei \[\text{[13–14]}\]. This technique, originally developed to measure the magnetic moments of short-lived nuclei \[\text{[15–18]}\], has found applications in materials science \[\text{[13–19–21]}\], and very recently also in chemistry and biochemistry \[\text{[23–25]}\]. The most attractive feature of $^\beta$-NMR, in comparison with conventional NMR, is its high sensitivity. This is achieved by a high degree of nuclear spin-polarization in the beam using various external methods \[\text{[29]}\], and resonance detection by counting emitted $^\beta$-particles instead of detecting faint radiofrequency signals using induction coils. $^\beta$-NMR thus allows recording NMR signals from as few as $10^7$ to $10^8$ resonating nuclei \[\text{[18]}\] implanted in the host material of interest, which makes it up to $10^{10}$ times more sensitive than the conventional NMR. However, in chemistry and biology, $^\beta$-NMR is far from being a routinely applicable spectroscopic method. There are numerous experimental challenges and the absence of practical NMR standards is one of them. Due to low-pressure conditions of $^\beta$-NMR experiments, solid-state samples are often used for chemical shift referencing \[\text{[27–28]}\], which brings the pitfall of wide resonance signals. This status can be used as an opportunity to introduce a novel $^\beta$-NMR standardization scheme reflecting advances of quantum chemistry methods for NMR shielding calculations. Following the procedure of ref. \[\text{[12]}\], a single $^\beta$-NMR standard can be defined and a direct measurement of NMR shielding instead of chemical shifts becomes possible. As a necessary prerequisite for such a standardization, the magnetic dipole moments of relevant $^\beta$-NMR nuclei have to be determined with high enough accuracy.

Here, we present a high-accuracy determination of a magnetic dipole moment of a short-lived nucleus $^{26}$Na, using stable $^{23}$Na as a reference. We describe our improvements of the $^\beta$-NMR technique in order to measure the resonance frequencies of short-lived nuclei with sub-ppm precision. We also report on the corresponding conventional NMR experiment on the stable isotope, and how the systematic error in the reference $^{23}$Na magnetic moment is corrected using \textit{ab initio} NMR shielding calculations.

**TECHNIQUES**

$\beta$-NMR on short-lived $^{26}$Na

$^\beta$-NMR studies were performed on laser-polarized short-lived $^{26}$Na ($t_{1/2} = 1.1$ s). The nuclei were produced at the ISOLDE facility at CERN \[\text{[30]}\], in reactions induced by a 1.4-GeV proton beam of up to 2 $\mu$A, impinging every 3.6 s on a UC$_6$ (uranium carbide) target. After fast diffusion out of the heated target, sodium atoms were surface-ionized, accelerated to 50 keV and mass separated using the High Resolution Separator (HRS). The pure isotopic beam of $^{26}$Na, with an intensity of $2 - 5 \times 10^7$ ions/second, was transported to the laser polarization beamline \[\text{[31–32]}\] shown in Fig. 1.

There, the $^{26}$Na$^+$ beam is overlapped with circularly-polarised laser light. Next, it passes through a neutralization cell, where it picks up an electron as it flies through a vapour of stable $^{23}$Na. Over the next 1.5 m the neutral atomic $^{26}$Na beam is polarized via optical pumping in the D2 line at 589 nm \[\text{[31]}\]. This takes place in a weak guiding magnetic field of 2 mT (applied along the beam path), which defines the quantization axis and prevents the coupling of the electron spins to possible stray fields in the surrounding environment. Next, the atoms pass through a region of a transitional field of $\approx 10 - 20$ mT, where the atomic spins undergo an adiabatic rotation towards the perpendicular magnetic field of the NMR magnet. The spin-polarized atoms pass through a collimator and reach a liquid sample located in a vacuum chamber that is placed between the poles of a Bruker BE25 electromagnet set to a field of 1.2 T (Fig. 2). At this point, the nuclear and electronic spins are decoupled and the nuclear spin couples to the large static field.

The liquid sample is deposited on a sample holder made of mica. The collimated atom beam and the holder have a diameter of 8 mm. Four such sample holders are attached to a sample ladder that can be moved in and out of the beam path. The emitted $^\beta$ particles are registered in two pairs of thin organic scintillators, coupled to compact silicon photo-detectors. The sample at the center of the electromagnet is surrounded by a 30 mm diameter coil to which an rf signal can be applied. See Fig. 2 for details.

To record an NMR spectrum, such as the one shown in Fig. 3, 200 equally spaced rf frequencies are sequentially set. For each frequency, the $^{26}$Na beam is implanted over 200 ms following the proton-bunch impact. After the start of implantation the $^\beta$ particles are counted for 1 s in the detectors at 0° and 180° to the direction of the magnetic field. From these counts the $^\beta$-decay asymmetry is determined, as a normalized difference in the counts. At the same time the sample is irradiated with a continuous wave rf field of 0.3 mT and a frequency corresponding to the point in the scan. This procedure
is repeated for consecutive proton bunches (arriving every 3.6 s seconds), to allow the nuclei from the previous bunch to decay. If required by the signal-to-noise ratio, several spectra of the same sample can be recorded and summed.

To increase the precision of the NMR measurements to the ppm level, the magnetic field across the sample had to be homogeneous with a temporal stability at the ppm level during a measurement. To ensure the former, a weak magnetic field on the order of 0.02 mT was produced by two shimming coils placed in contact with the magnet poles \[33\]. In this way the field homogeneity across the sample volume was improved by more than an order of magnitude in all three axes: 1 ppm along the symmetry axis of the magnet, 3 ppm in the vertical axis, and 5 ppm in the horizontal axis (ion-beam propagation). Since the magnetic field is symmetric with respect to the center of the sample, the remaining inhomogeneity contributes to a broadening of the resonance peak, without a significant shift in the resonance frequency, compared to a point-like sample. The temporal drift in the magnetic field was addressed using an active stabilization system based on the \(^1\)H resonance frequency measured in a tailor-made vacuum-compatible H\(_2\)O NMR probe. The probe was located just outside the main excitation rf coil, as shown in Fig. 2 with its middle only 25 mm away from the center of the sample. The resulting temporal stability was better than 1 ppm between sub-second and 24-h timescales, compared to drifts as big as 1 ppm/minute without it.

Previous \(^\beta\)-NMR studies of the magnetic moments of short-lived nuclei have relied on solid-state hosts. For sodium, the studies were performed using a cubic NaF crystal which retained polarization for several dozen seconds, leading to NMR resonances with a full width at half maximum (FWHM) in the order of \(10^{-4}\) of the resonance frequency \[17\]. In comparison, with liquid-state hosts it is possible to obtain resonances with a FWHM up to two orders of magnitude smaller, whilst retaining the nuclear polarization long enough to employ \(^\beta\)-NMR. This resonance narrowing is due to molecular tumbling within the liquid sample, effectively averaging out the anisotropic contributions found in solid state NMR spectra \[34\]. Unfortunately, most liquid-state hosts used for NMR studies have a high vapour pressure. Thus, when placed inside vacuum they either freeze or evaporate. However, room-temperature ionic liquids, which are salts in a liquid state at room temperature, have an extremely low vapour pressure \[35\]. This makes them suitable hosts for high-precision NMR studies in vacuum environments, as encountered in most \(^\beta\)-NMR setups. For measuring the Larmor frequency of \(^{26}\)Na two different ionic liquids were selected: 1-ethyl-3-methylimidazolium dicyanamide (EMIM-DCA) and 1-butyl-3-methylimidazolium formate (BMIM-HCOO). The EMIM-DCA sample contained \(\approx 1 \mu\)M of \(^{23}\)Na\(^+\) while the BMIM-HCOO sample contained 0.5 M. Both samples were degassed slowly at \(10^{-5}\) mbar pressure for several hours in a separate vacuum chamber. 20 \(\mu\)L of each solution was then deposited onto one of the sample holders attached to the sample ladder. The ladder was then placed in the \(^\beta\)-NMR chamber, as shown in Fig. 2 and the pressure inside was lowered slowly from atmospheric pressure to \(10^{-5}\) mbar. The sample was oriented at 45 degrees to the atom beam. Due to the high viscosity of both liquids, the thin film remained on each substrate at this high vacuum for up to 24 h.

**Conventional NMR on stable \(^{23}\)Na**

At the time of investigation, it was not possible to obtain a conventional NMR signal from \(^{23}\)Na at the \(^\beta\)-NMR beamline. Therefore, \(^{23}\)Na and \(^1\)H NMR spectra were recorded on a conventional NMR spectrometer. Our earlier systematic NMR studies showed that changing \(^{23}\)Na concentration from micro-molar to molar ranges and degassing for an extended period shifts the \(^{23}\)Na resonance by less than 0.5 ppm. This was taken as our experimental uncertainty for \(^{23}\)Na and degassing was not carried out during the measurements presented here. The field of
7.05 T was provided by a Bruker Avance DMX 300 MHz spectrometer and a basic pulsed-NMR scheme was applied (single $\pi/2$ rf pulse) on samples kept at room temperature. The sample preparation and Na$^+$ concentration were as close as possible to those in the $\beta$-NMR experiment: $\approx 1 \mu$M in the EMIM-DCA sample and 0.5 M in the BMIM-HCOO sample.

For the measurements, 200 $\mu$L of each solution were sealed inside a 3-mm diameter NMR tube. The tube was placed inside a 5-mm diameter tube filled with D$_2$O, whose $^2$H NMR signal was used to stabilise the magnetic field automatically during the measurements (field locking). $^1$H NMR resonances were also recorded within several minutes from $^{23}$Na spectra, using the same setup with two concentric tubes. Here, the 3-mm tube was filled with H$_2$O. Due to the way the field locking was performed, the magnetic field was the same for all measurements.

**Ab initio NMR shielding calculations**

*Ab initio* calculations of NMR shielding constants in the sodium atom and in the model aqueous Na$^+$ complexes were carried out. These NMR shielding constants were then used to correct the reference $^{23}$Na magnetic moment from the original Atomic Beam Magnetic Resonance (ABMR) [39] and NMR experiments [11].

NMR shielding in the sodium atom with the doublet electronic ground state was calculated using the Dirac-Hartree-Fock (DHF) method applying the paramagnetic NMR theory for open-shell systems [37–39]. Dyall-VXZ [40] basis set series were used (X = D, T, Q represents double-$\zeta$, triple-$\zeta$ and quadruple-$\zeta$ basis sets).

According to a recent experiment [41], the coordination number of the aqueous Na$^+$ ion depends on the NaCl solution concentration and varies between 5 and 6. Therefore, NMR shielding of the Na$^+$ ion in the aqueous solution was calculated for model Na$^+$($\text{H}_2\text{O})_5$ and Na$^+$($\text{H}_2\text{O})_6$ complexes. Their structures were optimized using Density Functional Theory (DFT) with the B3LYP density functional [42–44] and Def2-TZVP basis set [45]. The D3 dispersion correction [46] was applied. A distorted octahedral structure ($D_{2h}$ symmetry) was obtained for the Na$^+$($\text{H}_2\text{O})_6$ complex, with an average Na-O distance of 2.386 Å. For Na$^+$($\text{H}_2\text{O})_5$ the corresponding structure was found to be a trigonal bipyramid ($C_{2v}$ symmetry) with an average Na-O distance of 2.368 Å. The average Na-O distances for both structures are in good agreement with the experimental Na-O distances obtained with two different experimental methods giving $2.384 \pm 0.003$ Å and $2.37 \pm 0.024$ Å [41].

NMR shielding constants for aqueous sodium complexes were calculated using the non-relativistic coupled cluster (CC) method with single and double excitations (CCSD) and with non-iterative triple excitations CCSD(T) [47, 48]. All electrons were correlated. Dunning core-valence basis set series cc-pCVXZ [49] were used for sodium and valence series cc-pVXZ [50] for hydrogen and oxygen, combining basis sets with the same cardinal number X (X = D, T, Q). In order to estimate the error due to incompleteness of the basis set, the pcS-n basis set series by Jensen [51] was also used. In all NMR shielding calculations Gauge-Including Atomic Orbitals (GIAO) [52] were used.

The effect of the water solvent (outside the first solvation shell) on the NMR shielding in the sodium complex was incorporated by the polarized continuum model (PCM) COSMO [53]. This effect was evaluated using DFT with the PBE0 functional [54, 55]. The water dielectric constant of 78 was used in this implicit solvent model.
Relativistic corrections were calculated as the difference between the relativistic NMR shielding and the corresponding non-relativistic limit using two different methods: the DKS method with the PBE0 functional and the DHF method. The non-relativistic limit was obtained by re-scaling the speed of light in the Hamiltonian by a factor of 20. In the relativistic calculations, the Dunning basis sets were fully uncontracted and a restricted magnetic balance scheme was employed to generate the small component basis set. The nucleus was modeled by a Gaussian charge distribution.

For the structure optimization and for non-relativistic DFT calculations of NMR shielding constants the NWChem package was used. Non-relativistic coupled cluster NMR shielding calculations were carried out in the CFOUR package. For relativistic NMR shielding calculations, the ReSpect program was used.

RESULTS

First the ratio $R$ of the magnetic moment of $^{26}$Na to that of $^{23}$Na in the same ionic liquid host was determined, as this value is independent of the NMR shielding:

$$R = \frac{\mu(26\text{Na})}{\mu(23\text{Na})} = \frac{\nu_L(26\text{Na}) I(26\text{Na}) B(23\text{Na})}{\nu_L(23\text{Na}) I(23\text{Na}) B(26\text{Na})}.$$  \(1\)

Here $I$ is the nuclear spins, $B$ the external magnetic field, $\nu_L$ the Larmor frequency and $\mu$ the nuclear magnetic moment. The ratio of the magnetic fields $B$ can be represented by the ratio of $^1$H Larmor frequencies during the $^{26}$Na and $^{23}$Na measurements.

The $^{20}$Na $\beta$-NMR spectra in EMIM-DCA and BMIM-HCOO recorded at 1.2 T are shown in Fig. 3 while Table 1 shows the corresponding Larmor frequencies, together with reference frequencies for $^{23}$Na at 7.05 T.

During the $^{26}$Na measurements, the $^1$H stabilising NMR probe had a resonance frequency of 52008500(30) Hz. This was 1050(300) Hz lower than when the probe was placed at the position of the sample in the middle of the magnet, which lead to a corrected frequency of 52009550(300) Hz. During the $^{23}$Na measurements, the $^1$H NMR Larmor frequency was 300131415(100) Hz.

The derived value of $R$ for each measurement is shown in Table 1. The error in round brackets results from the statistical uncertainty on the $^{26}$Na resonance position. The systematic error present in all measurements is shown in square brackets, and includes systematic uncertainties in the resonance frequencies of $^1$H and $^{23}$Na. Here, the biggest contribution by far is the error in the frequency of $^1$H during the $\beta$-NMR measurements, caused by the uncertainty in the position of the probe, which can be improved in the future. The final value of the ratio of $\mu(26\text{Na})$ to $\mu(23\text{Na})$ is $R = 1.284951(1)[8]$ or $R = 1.284951(8)$ with the uncertainties combined. Figure 4 shows the individual results in comparison to the literature value based on the hyperfine-structure measurement, which is two orders of magnitude less precise than our result. Our weighted average is indicated by the purple line. The purple shaded region represents the statistical uncertainty while the orange region represents the systematic uncertainties.

In order to determine $\mu(26\text{Na})$, a reliable reference $\mu(23\text{Na})$ value is needed. In Nuclear Data Tables, the values of $\mu(26\text{Na})$ based on ABMR and NMR experiments differ by $1.34\times10^{-4}$ $\mu_N$, which is much larger than the individual error bars. This introduces a larger uncertainty than the uncertainty of the frequency-ratio measurement in our $\beta$-NMR experiment. The above discrepancy stems from applying an obsolete diamagnetic correction for the derivation of $\mu(23\text{Na})$ from the experiments. This inconsistency can be corrected using ab initio NMR shielding constants calculated for the species used in both experiments: a sodium atom in ABMR and...
correlation effects for the NMR shielding in the sodium atom are small. Therefore the NMR shielding in the sodium atom can be approximated with a very good accuracy by the DHF value. The electron correlation contributions can be used as an error estimate. Our final NMR shielding in the sodium atom, 637.1(2) ppm, is consistent with the shielding in ref. [64].

The NMR shielding for the solvated sodium ion was approximated by the NMR shielding in a six-coordinated Na+(H2O)6 complex (the prevalent coordination number according the experiment [41]). The five coordinated Na+(H2O)5 complex was used to estimate the error of the NMR shielding due to the structural uncertainty. The NMR shielding constants calculated using non-relativistic and relativistic approximations for the Na+(H2O)6 complex are shown in Tab. [II]. The Hartree-Fock and DHF NMR shielding, electron correlation contributions (Δcorr, Δcorr(T)) and relativistic contributions (Δrel, Δrel(KS)) reach good convergence with the basis size. The final NMR shielding for the Na+(H2O)6 complex, 582.0 ppm, is a composite value of (i) the non-relativistic shielding calculated using the CCSD(T) method, (ii) relativistic correction (Δrel), and (iii) the PCM solvent contribution (ΔPCM). All contributions entering the final NMR shielding were calculated using the quadruple-ζ (QZ) basis set.

The systematic error of the NMR shielding in the Na+(H2O)6 complex was evaluated as the square root of the sum of squares of the following errors. The structural uncertainty (2 ppm) was evaluated as the difference between the CCSD NMR shielding for aqueous sodium complexes with the coordination number of five and six. The basis set incompleteness error (1 ppm) was estimated from the variations of the NMR shielding constants calculated using non-relativistic HF method with Dunning and Jensen basis set series. The coupled cluster expansion truncation error was approximated by Δcorr(T) ≈ 1 ppm. Considering the convergence of the PCM solvent contribution (ΔPCM), the error was estimated to be 1 ppm. The systematic error introduced by assuming an additivity of the electron correlation and the relativistic effects is negligible as indicated by the small difference between the Δrel and Δrel(KS) relativistic corrections.

The final approximation of the NMR shielding of the aqueous sodium ion is (582.0 ± 2.6) ppm. This result is consistent with the NMR shielding in ref. [65], but in the present study, the error bar was reduced by a factor of four. This was achieved by calculations with much larger basis sets, which led to a better convergence of all contributions.

Table [III] presents the new values of the 23Na reference magnetic moment re-derived using our new NMR shielding constants. The ABMR-based magnetic moment was obtained using our ab initio NMR shielding of the sodium atom and the original ABMR experiment [39].
The NMR-based magnetic moment was re-derived using (i) our ab initio NMR shielding of the aqueous sodium ion, (ii) the experimental frequency ratio 0.26451900 \[11\] of \(^{23}\text{Na}\) in 0.1 M NaCl water solution to the proton in tetramethylsilane (TMS), (iii) the reference proton magnetic moment \(\mu(\text{H}) = 2.792847348(7)\) \[1\], and (iv) the reference NMR shielding of the proton in TMS \(\sigma(\text{H}) = 33.480 \pm 0.5\) ppm \[66\].

The newly extracted ABMR- and NMR-based values of \(^{23}\text{Na}\) nuclear magnetic dipole moment are now consistent within the error bars and the discrepancy between them was decreased by a factor of \(\approx 30\).

For the derivation of the \(^{26}\text{Na}\) nuclear magnetic dipole moment, the NMR-based \(^{23}\text{Na}\) nuclear magnetic dipole moment was used, because the corresponding NMR shielding calculations for aqueous sodium complexes are based on a better approximation and the error bar was estimated more rigorously. The resulting \(^{26}\text{Na}\) nuclear magnetic dipole moment (Tab. IV) is consistent with the previous experimental value \[17\] within the error bar, but the present experiment and ab initio calculations improved its accuracy by two orders of magnitude.

Magnetic moments which have been linked to \(^{26}\text{Na}\) can also benefit from the improved accuracy of \(\mu(\text{Na})\). This is the case for \(^{27-31}\text{Na}\), which were investigated using \(\beta\)-NMR in solid-state hosts at the collinear laser spectroscopy beamline at ISOLDE \[17\], and whose \(g\)-factors \(g_I = \mu(I\mu_N)\) were referenced to that of \(^{26}\text{Na}\).

Table IV presents our new values of the \(^{23}\text{Na}\) and \(^{26}\text{Na}\) magnetic moments, as well as the \(^{27-31}\text{Na}\) magnetic moments obtained using our improved \(\mu(\text{Na})\) and the aforementioned \(g\)-factors. Literature magnetic moments \[17\] are also shown for comparison. The new values of the \(^{27-31}\text{Na}\) magnetic moments have a relative uncertainty of \(\approx 100\) ppm. This is a ten-fold improvement compared to the values deduced in \[17\] and up to 50 times more accurate than the values tabulated in the latest compilation of nuclear magnetic dipole and electric quadrupole moments \[2\]. Previously, the uncertainty was dominated by the uncertainty in the magnetic moment of the reference \(^{26}\text{Na}\). At present, it is determined by the uncertainty in \(^{27-31}\text{Na}\) \(\beta\)-NMR resonance frequency in solid-state hosts. If new measurements in liquid-state hosts are performed, this uncertainty could be decreased even further to the ppm level.

The precise magnetic moments of \(^{26-31}\text{Na}\) presented above, together with that of \(^{23}\text{Na}\), provide a self-consistent set of isotopes. These can be used to probe via \(\beta\)-NMR the chemical and biological processes on different timescales and via different types of interactions, as each isotope has a different nuclear spin, half-life and electric quadrupole moment (see Tab. IV). For example, the quadrupole moments of \(^{26}\text{Na}\) and \(^{23}\text{Na}\) are respectively 20 and 15 times smaller compared to the stable \(^{23}\text{Na}\). This means a weaker interaction with the gradient of the electric field \[34\], leading to longer relaxation times and narrower resonances. This should permit the observation of NMR signals in hosts which display broad \(^{23}\text{Na}\) resonances due to a fast quadrupolar relaxation. The same approach can be applied to other isotopic chains, thus increasing the palette of nuclei available for NMR studies.

**CONCLUSIONS AND OUTLOOK**

In summary, using \(^{26}\text{Na}\) as an example, we have presented the first determination of a magnetic moment of a short-lived nucleus with ppm accuracy. This represents an improvement by two orders of magnitude in comparison with a previous experiment and other \(\beta\)-NMR based magnetic moments. The achievement was made possible by replacing the solid host material by liquid hosts.

| Table III. \(\mu(26\text{Na})/\mu_N\) reference nuclear magnetic dipole moment from ABMR and NMR experiments |
|-------------------------------------|------------------|
| old reference \[2\] | This work |
| ABMR | +2.217522(2) | 2.217495(2) |
| NMR | +2.2176556(6) | 2.217500(7) |

\(a\) using the original ABMR experiment \[36\] and NMR shielding of the sodium atom (637.1 \pm 0.2) ppm

\(b\) using the standard NMR frequency ratio of \(^{23}\text{Na}\) in NaCl water solution to proton in TMS \[11\] and NMR shielding of Na\(^+\)(\(\text{H}_2\text{O}\))\(_6\) (582.0 \pm 2.6) ppm. See the text for details on NMR shielding calculations.
TABLE IV. Magnetic moments of $^{23,26-31}$Na determined in this work, compared to literature values \[17\], and other nuclear properties relevant for NMR.

| Isotope | $I$ | $T_{1/2}$ (ms) | $Q$ (mb) | old $\mu$ ($\mu_N$) | new $\mu$ ($\mu_N$) |
|---------|----|---------------|---------|----------------------|---------------------|
| $^{23}$Na | 3/2 | stable | +105.6(12) | 2.217500(7)$^a$ |
| $^{26}$Na | 3 | 1071 | -5.3(2) | 2.851(2) | 2.849378(20)$^b$ |
| $^{27}$Na | 5/2 | 301 | -7.2(3) | 3.894(3) | 3.89211(11) |
| $^{28}$Na | 1 | 31 | +39.5(12) | 2.457(2) | 2.45534(8) |
| $^{29}$Na | 3/2 | 44 | +86(3) | 2.069(2) | 2.0681(5) |
| $^{30}$Na | 2 | 48 | | 2.298(2) | 2.29668(8) |
| $^{31}$Na | 3/2 | 17 | | | |

$^a$ Corrected $\mu(^{23}$Na) based on NMR experiment, see Table [III]

$^b$ Based on our improved ratio of the magnetic moments of $^{26}$Na to $^{23}$Na

by improving substantially the magnetic-field homogeneity and stability to the ppm level, and by correcting the reference $^{23}$Na magnetic moment employing \textit{ab initio} calculations of NMR shielding.

The procedure described in this article represents a universal protocol for measurements of magnetic dipole moments of $\beta$-decaying nuclei with ppm accuracy. It can be directly applied to studies with other nuclei used in $\beta$-NMR.

The results presented here are of direct relevance to our $\beta$-NMR investigations of the role of Na in the folding (and dynamics) of G-quadruplex DNA structures \[67, 68\].

Precise magnetic moments could also be combined with precision measurements of the hyperfine structure, to address the distribution of the magnetization of the nucleus. One application would be the study of the neutron ‘halo’ in very neutron-rich nuclei. For example, in $^{11}$Be the magnetisation is mostly due to the ‘halo’ neutron \[69, 70\], whose distribution is difficult determine with other techniques.

Finally, the results could set foundations for a standardization of $\beta$-NMR spectroscopy. By applying the presented procedure to correct the magnetic moments of other $\beta$-decaying nuclei, it would be possible to provide a diverse set of nuclear probes, capable of direct measurements of NMR shielding. Within the set of $\beta$-decaying nuclei with corrected magnetic moments, a single $\beta$-NMR standard could be defined. This would remove the dependence of the emerging $\beta$-NMR spectroscopy from ambiguous and often \textit{ad hoc} standards defined for every element separately. An improvement of the reference magnetic moment for the stable counterpart nucleus is an essential part of the described protocol. Therefore the present work also establishes a bridge between the emerging $\beta$-NMR spectroscopy and conventional NMR spectroscopy, paving the way for $\beta$-NMR applications in chemistry and biochemistry.

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