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Bulk magnetic susceptibility corrections for precise resonance frequency ratios

CERN Summer Student Programme 2023 report

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Abstract

The main aim of this CERN Summer Student Programme project was to calculate the influence of the magnetic susceptibility of liquids and quartz on the magnetic field at the site of NMR tubes used at the VITO setup at ISOLDE. Simulations for NMR tubes with two different samples were performed: water and ionic liquid EMIM-DCA (1-ethyl-3-methyl-imidazolium dicyanamide). The calculated magnetic field values in samples parallel and perpendicular to the magnetic field were used to obtain the magnetic field shift, σ_χ. Using these values, the measured resonance frequency ratios of $^{23}Na^+$ and $^{26}Na^+$ in EMIM-DCA and deuterons in D_2O at CERN ($^{23}Na^+$ and $^{26}Na^+$) and UNIGE (University of Geneva) (only $^{23}Na^+$) will be corrected, with the aim to determine accurate magnetic moment of ^{23}Na and unstable ^{26}Na.

Keywords

Bulk magnetic susceptibility (BMS), shape factor, ionic liquid, EMIM-DCA, CST Studio, NMR, β-NMR, nuclear magnetic dipole moment

Introduction

In comparison to the conventional NMR spectroscopy, β-NMR spectroscopy is 10^{10} times more sensitive [1]. In addition, performing β-NMR studies in liquids has allowed to largely increase the precision in determining Larmor frequencies of short-lived radioactive nuclei [1].

However, when trying to profit from the improvement to measure magnetic moments of short-lived radioactive nuclei with higher accuracy, accurate Larmor frequency ratios are essential. Among others, because of the magnetic susceptibility of the sample and probe material, the resonance frequency depends on the geometry and direction in which the sample is put in NMR spectrometer.

The main aim of this work is to model NMR tubes used for water and EMIM-DCA to simulate and calculate the magnetic field inside of the sample. By obtaining the magnetic field shift, from the value of external applied magnetic field, we can correct the already measured resonance frequency ratio of stable $^{23}Na^{+}$ and unstable $^{26}Na^{+}$ in EMIM-DCA to deuterons in D_2O.

Theory

When a solvated nucleus is exposed to an applied magnetic field, the local magnetic field the nucleus "feels" is shifted due to the bulk magnetic properties of the materials and its chemical environment. We can describe this phenomenon using formula (1) [1]

$$B_{nucl} = [1 + (1/3 - \alpha)\kappa](1 - \sigma)B_0 \quad (1)$$

where κ is bulk magnetic susceptibility (BMS), α is the shape factor that modifies BMS due to samples shape, and σ is the NMR shielding. The NMR shielding can be nowadays determined theoretically by accurate *ab initio* quantum chemical calculations [2,3]. In this summer student project, we do not consider the NMR shielding effect and are interested only in the magnetic susceptibility for the samples used in experiments of the ISOLDE team.

The shape factor kappa, which is interesting for us, depends on the geometry and direction in which the sample is put inside a magnetic field. Table 1 shows calculated shape factors of selected idealised sample shapes [4]. However, real samples have finite dimensions, thus for accurate studies, the effect of susceptibility should be determined more accurately.

Table 1. Shape factors of selected samples

Shape of a sample	α
Sphere	1/3
Infinite cylinder parallel to magnetic field	0
Infinite cylinder perpendicular to magnetic field	1/2

We therefore introduce a more general factor:

$$\sigma_\chi = (1/3 - \alpha)\kappa \quad (2)$$

Where σ_χ is the magnetic field shift due to magnetic susceptibility of the sample calculated as $B_{nucl} - B_0$. Given this formula, we can rewrite the formula (1) using formula (2) into

$$B_{nucl}/B_0 = 1 + \sigma_\chi \quad (3)$$

and a magnetic field ratio is obtained. Due to the direct proportionality between the magnetic field strength and resonance frequency $\nu_L = \mu \times B_0$ the magnetic field ratio is equalled to the resonance frequency ratio, such that:

$$B_{nucl}/B_0 = \nu_{meas}/\nu_0 \quad (4)$$

where ν_{meas} is the measured resonance frequency of a nucleus of interest. Considering formula (3) and formula (4), we can write formula (5) that shows the relation between the desired ν_0 and calculated σ_χ:

$$\nu_0 = \nu_{meas}/(1 + \sigma_\chi) \quad (5)$$

When given a measured resonance frequency, we can modify it using formula (6), where X is a studied nucleus and Y is the reference, A and B are two different environments.

$$\frac{\nu_{0XA}}{\nu_{0YB}} = \frac{\nu_{XA}}{\nu_{YB}}\frac{1+\sigma_{\chi B}}{1+\sigma_{\chi A}} \quad (6)$$

Modelling in CST Studio

The CST Studio package was used to simulate the influence of BMS on the field inside samples of our geometries. While working in CST Studio, one must model a proper NMR tube with all its parameters and dimensions. This step leads to precise simulations, which should correspond to the experimental conditions. The most important parameters needed for precise simulations are bulk magnetic susceptibility values for NMR tube (quartz) and sample material: water and EMIM-DCA. In Table 2 magnetic susceptibility values are summarized.

Table 2. Magnetic susceptibility values of selected materials

material	κ (ppm)
NMR tube (glass)	-11
water	-9.04
EMIM-DCA	-6.33

NMR tube for water

Parameters for the NMR tube used for water are listed here: 15 mm length, 1.65 mm radius, 0.8 mm thickness. Figure 1 shows how the water NMR tube looks in CST studio, with a cutting plane view also shown.

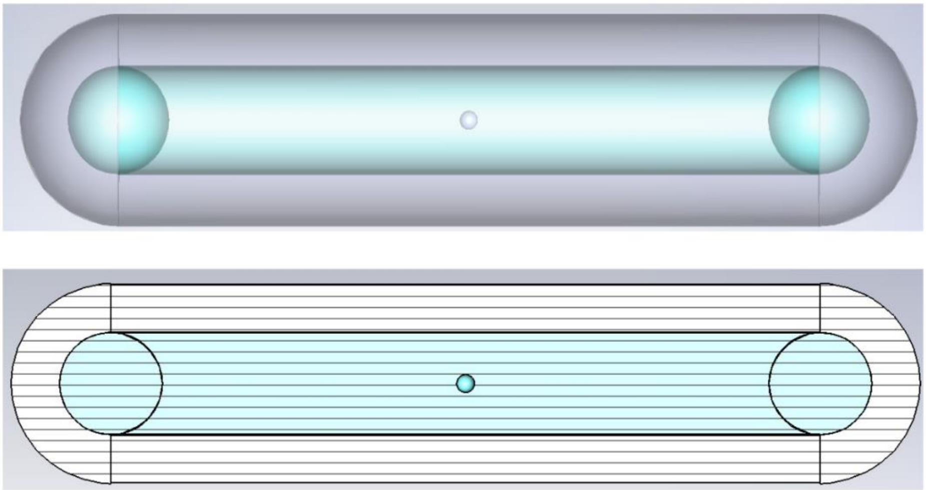


Figure 1. The NMR tube used for water

NMR tube for EMIM-DCA

The NMR tubes used at VITO-ISOLDE containing ionic liquids have different parameters and dimensions, which are following: 25 mm length, 2.5 mm radius, 0.4 mm wall thickness. Figure 2 shows how the ionic liquid NMR tube looks in CST studio, with a cutting plane view also shown.

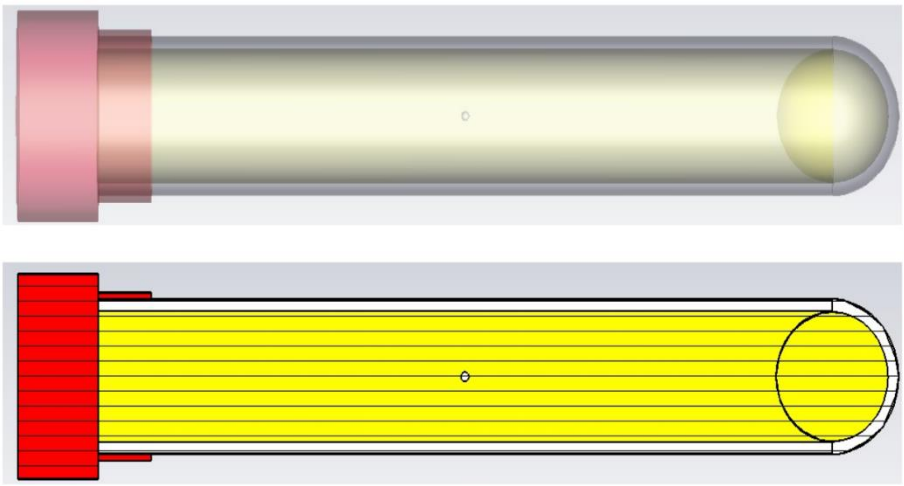


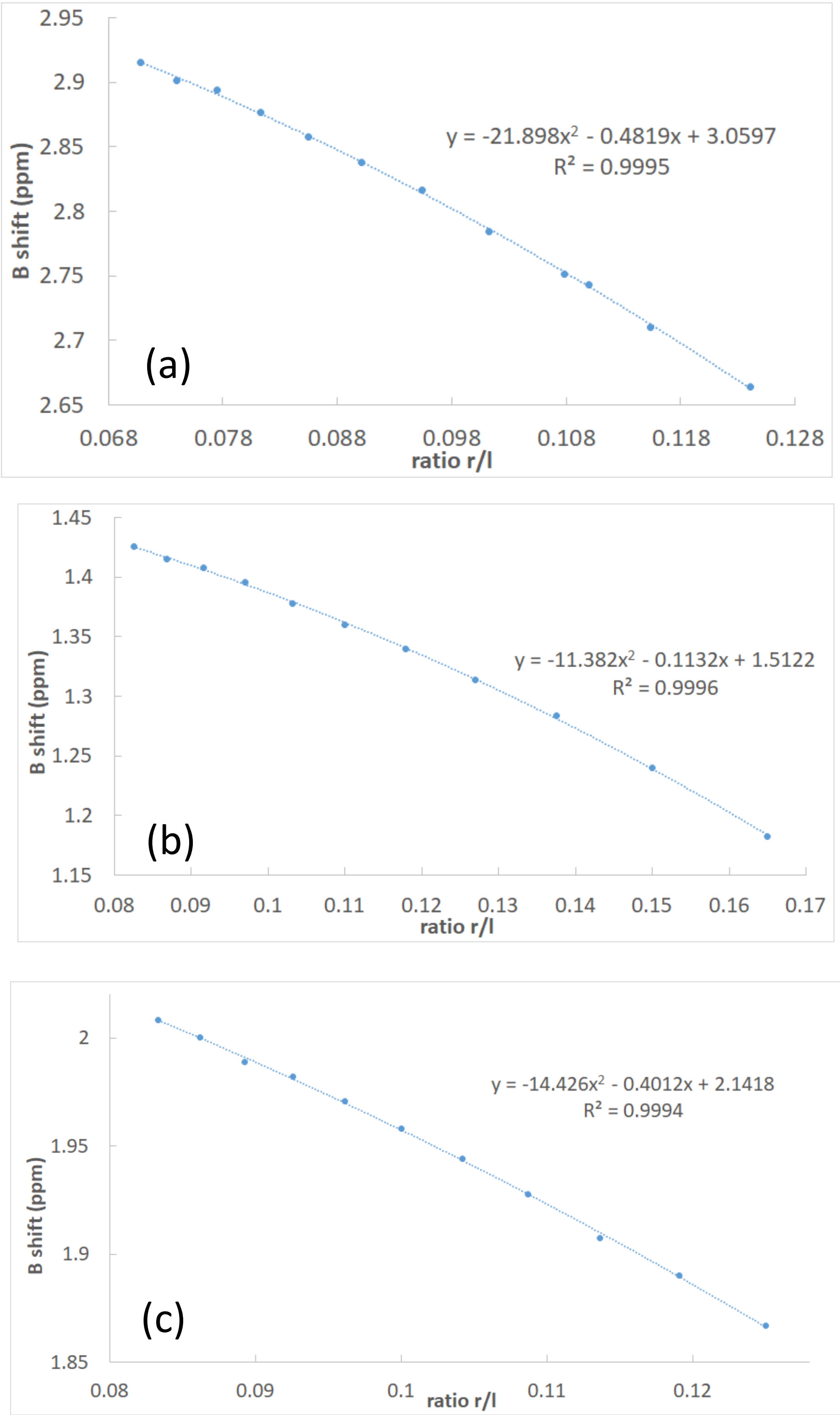
Figure 2. The NMR tube used for ionic liquids

It is necessary to point out a small bubble in the middle of the sample is modelled, which simulates a cavity around the nuclei of our interest.

Results

Plots showing σ_χ vs. radius to length (r/l) ratio

Figure 3 shows the plot σ_χ vs. r/l ratio for both water and EMIM-DCA samples and in both parallel and perpendicular directions with respect to the magnetic field direction.



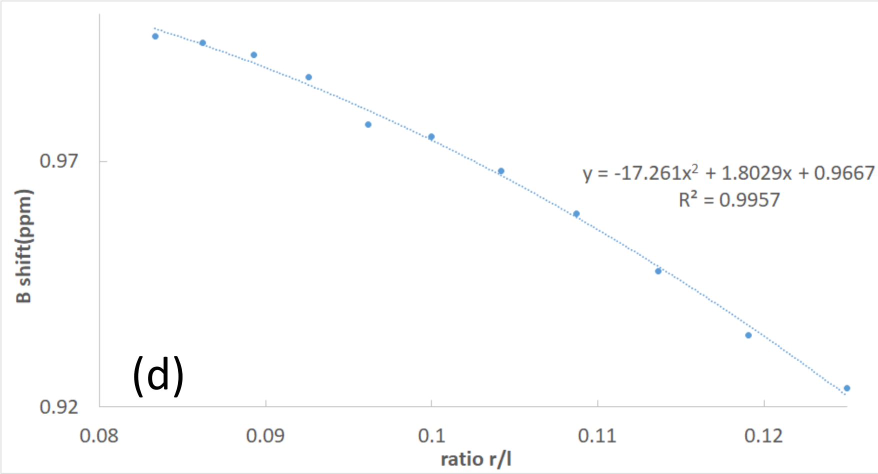


Figure 3. Plots showing σ_χ vs. r/l ratio (a) water parallel (b) water perpendicular (c) EMIM-DCA parallel (d) EMIM-DCA perpendicular

Using these plots and the polynomial fits shown, we are able check if the calculations and fits give correct values when extrapolating σ_χ with r/l=0 (i.e., infinitely long tube). If correct, this step should lead to the values using shape factors in Table 1. Table 3 shows exact and extrapolated σ_χ values, as well as the absolute and relative error of extrapolation.

Table 3. Exact and extrapolated σ_χ values from plots in Figures 3, as well as absolute and relative error

Sample	Direction	Exact value (ppm)	Extrapolated value (ppm)	Absolute error (ppm)	Relative error
water	parallel	-3.01	-3.06	0.05	1.54 %
water	perpendicular	1.507	1.512	0.005	0.37 %
EMIM-DCA	parallel	-2.11	-2.14	0.03	1.51 %
EMIM-DCA	perpendicular	1.06	0.97	-0.09	8.37 %

Calculating σ_χ values for given r/l ratio

However, the parameters and dimensions mentioned for modelling NMR tubes for water and ionic liquids in CST Studio are only indicative. Once we know the relation between σ_χ value and r/l ratio, it is possible to calculate/extrapolate for any ratio given. In UNIGE and CERN, different NMR tubes are used for measurements. Fortunately, only the r/l ratios are needed. Table 4 (below) shows the given r/l ratios needed for correcting the resonance frequency ratios measured in UNIGE and CERN, as well as the calculated σ_χ values for each ratio, sample and direction.

Table 4. The calculated σ_χ values for given r/l ratios for different samples and its directions with respect to the magnetic field

Sample	Direction	r/l	σ_χ (ppm)
D2O	parallel	0.15	-2.5
D2O	perpendicular	0.25	0.8
EMIM-DCA	parallel	0.25	-1.1
EMIM-DCA	perpendicular	0.25	0.3

Frequency ratio correction

Once we know the correct and exact σ_χ value, we can use formula (5) to correct the resonance frequency or use formula (6) to directly correct the frequency ratio. The frequency ratio correction was done for the measured frequency ratio at ISOLDE. Table 5 shows the measured and corrected frequency ratio using exact σ_χ values shown in Table 3.

Table 5. The measured and corrected frequency ratio of ^{23}Na in EMIM-DCA and ^{2}H in D2O

$\nu_{Na,EMIM\text{-}DCA}/\nu_{D,D2O}$	Sample	Facility	$\nu_{Na,EMIM\text{-}DCA}/\nu_{D,D2O}$
1.72318099 measured	perpendicular	CERN	1.72318174 corrected

Outlook

While correction for measured frequency ratio at CERN is already done, our aim is to correct the frequency ratio measured at UNIGE, using the given σ_χ value (at UNIGE the measurement was done parallel to the magnetic field).

There are more things and effects that should be considered while simulating and calculating the magnetic field inside the NMR tube in CST Studio. Implanting sodium ions directly to EMIM-DCA is not possible, due to insolubility of NaCl (sodium chloride), the source of sodium ions, in this ionic liquid. Thus, we need to dissolve NaCl in water, implant this solution to EMIM-DCA and degas the sample to get rid of remaining water.

Considering a mixture of EMIM-DCA and water is a great step in more precise σ_χ values, due to precise simulation of the sample material and the change of the bulk magnetic susceptibility value. What's more, chloride ions can make effects on the magnetic susceptibility and NMR shielding value as well. Considering all factors mentioned, more precise σ_χ values should be obtained.

Conclusion

Simulations and calculations of the magnetic field inside of an NMR tube were made using different samples and directions with respect to the magnetic field in CST Studio. Small theoretical overview was given for a better understanding of the topic that connects electromagnetism and accurate NMR spectroscopy.

Exact σ_χ values were obtained for samples used for ^{23}Na and ^{2}H, which allowed correcting the resonance frequency ratio measured at CERN.

These calculations should be extended to mixtures of ionic liquid and water, using to-be-measured susceptibility values, to enable a more precise determination of material effects in simulations and thus more precise σ_χ and magnetic moment values.

Acknowledgement

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Sources

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