



## The determination of accurate nuclear magnetic dipole moments and direct measurement of NMR shielding constants

Michał Jaszcuński<sup>a,\*</sup>, Andrej Antušek<sup>b</sup>, Piotr Garbacz<sup>c</sup>, Karol Jackowski<sup>c</sup>, Włodzimierz Makulski<sup>c</sup>, Marcin Wilczek<sup>c</sup>

<sup>a</sup>Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

<sup>b</sup>Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Paulínska 16, 917 24 Trnava, Slovak Republic

<sup>c</sup>Laboratory of NMR Spectroscopy, Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

### ARTICLE INFO

#### Article history:

Received 9 January 2012

Accepted 8 March 2012

Available online 22 March 2012

#### Keywords:

Nuclear magnetic resonance

Ab initio calculations

Nuclear magnetic dipole moments

Gas phase NMR

Absolute shielding constants

### Contents

1. Introduction	50
2. The determination of accurate nuclear magnetic dipole moments	50
2.1. Ab initio studies of NMR shielding constants	50
2.1.1. Shielding constants at molecular equilibrium geometry	51
2.1.2. Vibrational and temperature corrections	51
2.1.3. Relativistic effects	52
2.1.4. Solvent effects	53
2.2. Gas-phase measurement of NMR frequencies	53
3. Nuclear magnetic dipole moments	54
3.1. <sup>13</sup> C magnetic moment	56
3.2. <sup>15</sup> N magnetic moment	56
3.3. Recommended new values of magnetic moments	56
4. Direct NMR measurements of shielding constants	56
4.1. Magnetic shielding in gas-phase NMR experiments	57
4.2. <sup>1</sup> H and <sup>2</sup> H shielding constants	57
4.3. <sup>13</sup> C shielding measurements	58
4.4. <sup>15</sup> N shielding measurements	60
4.5. Shielding measurements – other nuclei	60

*Abbreviations:* aug-cc-pCVnZ, augmented correlation-consistent core-valence *n*-tuple-zeta [basis set]; BPPT, Breit–Pauli perturbation theory; BSC, bulk susceptibility correction; B3LYP, Becke–3-parameter–Lee–Yang–Parr [exchange–correlation functional]; cc-pCVnZ, correlation-consistent core-valence *n*-tuple-zeta [basis set]; cc-pVnZ, correlation-consistent valence *n*-tuple-zeta [basis set]; CCSD, coupled-cluster singles-and-doubles [model]; CCSDT, coupled-cluster singles-doubles-triples [model]; CCSDTQ, coupled-cluster singles-doubles-triples-quadruples [model]; CCSD(T), CCSD [model] with a noniterative perturbative triples correction; DFT, density-functional theory; FCI, full configuration-interaction [theory]; GIAO, gauge-including atomic orbital; HF, Hartree–Fock [model]; KT2, Keal–Tozer [exchange–correlation functional]; MAS, magic angle spinning; MCSCF, multiconfigurational self-consistent field [model]; SCF, self-consistent field [theory]; TMS, tetramethylsilane; ZPV, zero-point vibrations.

\* Corresponding author. Tel.: +48 22 3432333; fax: +48 22 6326681.

E-mail address: [michal.jaszunski@icho.edu.pl](mailto:michal.jaszunski@icho.edu.pl) (M. Jaszcuński).

5. Conclusions .....	60
Acknowledgments .....	61
Appendix A. Reference data for nuclear magnetic dipole moments .....	61
A.1. Source data for Table 7 .....	61
References .....	62

## 1. Introduction

Nuclei of isotopic atoms contain different number of neutrons and consequently have different spins and magnetic dipole moments. Only the nuclei with even numbers of protons and even numbers of neutrons are not magnetically active, all the other nuclides have nonzero magnetic moments which interact with external magnetic fields and can be used as probes in NMR spectroscopy. An important parameter, which characterizes a given atomic nucleus, is the magnitude of the magnetic dipole moment. It is manifest in molecular spectroscopies, whenever the existence of a magnetically active nucleus modifies the energetic transitions under observation. The case of NMR spectroscopy is of primary interest for us, but the nuclear magnetic moments also give contributions to the microwave spectra of gases, because the nuclear magnetic moments interact with the magnetic field induced by the molecular rotation, and to ESR spectra—via the hyperfine structure, due to the coupling between electron and nuclear magnetic moments (observed in the presence of unpaired electrons). In NMR spectroscopy, each nucleus can be unambiguously identified from the resonance frequency when its magnetic dipole moment is known. In addition, the interaction of two or more nuclear magnetic moments in a molecule leads to the dipolar and indirect spin–spin couplings, observed in NMR as the splitting of appropriate signals—a feature of the spectrum which we do not discuss in this work.

We describe first a method to determine accurate nuclear magnetic dipole moments, analyzing step by step the theoretical and experimental problems which had to be solved. For this purpose we discuss *ab initio* quantum chemical calculations of shielding constants in selected molecules and NMR experiments in the gas phase for the same molecules. We illustrate the accuracy of *ab initio* and spectroscopic results which can now be obtained, describing some examples in detail. Next, we present an original method of experimental measurement of absolute shielding constants. Accurate values of magnetic moments are needed in this approach; when they are available direct measurement of shielding can be used for the standardization of NMR spectra. We outline the perspectives for the application of this approach to a variety of magnetic nuclides. In practice, this step required gas phase experiments, including  $^3\text{He}$  NMR spectroscopy, and formulation of equations for direct reading of shielding for different nuclei, that permits the application of shielding measurements for routine analysis. After completing the above steps direct reading of shielding constants becomes available for many nuclei and the most popular applications in NMR spectroscopy.

## 2. The determination of accurate nuclear magnetic dipole moments

The nuclear magnetic moment  $\mu_X$  is related to the nuclear spin  $I_X$  of nuclear isotope X as

$$\mu_X = h\gamma_X I_X = \mu_N g_X I_X, \quad (1)$$

where  $\gamma_X$  is the nuclear gyromagnetic ratio,  $\mu_N$  is the nuclear magneton and  $g_X$  is the  $g$  factor of nucleus X, unique for each isotope. The resonance frequencies in NMR spectra correspond to the energy changes, related to  $\Delta\mu_X^z$ , the possible increments of the projection

of the magnetic moment on the axis of the external field. We assume here that the nuclear spin and the sign of the magnetic moment are known, thus a measurement of the resonance frequencies is sufficient to determine the magnetic moment. To simplify the notation, we shall discuss the numerical values of  $\mu_X$ , instead of  $\Delta\mu_X^z = \mu_X \Delta I_X^z / I_X$ , implying that all the necessary projection, sign and spin-related coefficients were properly taken care of. Moreover, we shall omit all the vector and tensor indexes; we discuss below only the shielding constants, not the tensors.

Let us consider the equations that determine the resonance frequencies of two different nuclei,  $\nu_X$  and  $\nu_Y$

$$h\nu_X = \Delta\mu_X^z (1 - \sigma_X) B_0, \quad (2)$$

$$h\nu_Y = \Delta\mu_Y^z (1 - \sigma_Y) B_0, \quad (3)$$

where  $\sigma_X$  and  $\sigma_Y$  are the absolute shielding constants. Using both equations and eliminating the external magnetic field induction  $B_0$  we obtain

$$\Delta\mu_X^z = \frac{\nu_X (1 - \sigma_Y)}{\nu_Y (1 - \sigma_X)} \Delta\mu_Y^z. \quad (4)$$

The formalism based on Eq. (4) has been applied to obtain the magnetic dipole moments of a large number of nuclei from NMR data. Most of these results have been obtained in the early years of NMR (more or less 50 years ago), and their accuracy has rarely been reconsidered. In particular, an essential assumption underlying the use of Eq. (4) is that the resonance frequency of nucleus X and its shielding constant  $\sigma_X$  should refer to precisely the same species; the same molecule in the same conditions (and similarly for  $\nu_Y$  and  $\sigma_Y$ , but—at least in theory—the nuclei X and Y do not have to be in the same molecule). This requirement was not met in the early NMR experiments, approximate absolute shielding constants were often used (for instance, atomic values have been used to estimate the shielding in a molecule). These approximations, acceptable long ago, are very crude by today's standards and sometimes the accuracy of nuclear magnetic dipole moments can be easily improved by applying accurate values of the shielding constants in Eq. (4).

### 2.1. *Ab initio* studies of NMR shielding constants

In quantum chemistry, the description of a molecule interacting with an external or internal electromagnetic field is based on the assumption that this weak interaction leads to only a small perturbation of molecular structure. This approximation is consistent with the definition of spectroscopic parameters; in spectroscopy it is also assumed that the molecule–field interaction can be described in terms of parameters defined for an isolated molecule in the absence of the fields. Thus, in *ab initio* calculations of molecular properties, such as NMR shielding constants, the starting point is a description of the molecule—for instance, an approximate solution of the Schrödinger equation in the absence of the magnetic field—obtained treating the nuclei as point charges, that is by neglecting their magnetic dipole moments. There are numerous advanced methods of quantum chemistry suitable for the calculation of linear and nonlinear response of the molecule to a small perturbation [1]; therefore we have in practice a hierarchy of methods of increasing reliability and we can examine the dependence of the computed property on the level of approximation [2].

Download English Version:

<https://daneshyari.com/en/article/5419597>

Download Persian Version:

<https://daneshyari.com/article/5419597>

[Daneshyari.com](https://daneshyari.com)