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Principles of High Resolution NMR in Solids

Second, Revised and Enlarged Edition

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Preface

The field of Nuclear Magnetic Resonance (NMR) has developed at a fascinating pace during the last decade. It always has been an extremely valuable tool to the organic chemist by supplying molecular "finger print" spectra at the atomic level. Unfortunately the high resolution achievable in liquid solutions could not be obtained in solids and physicists and physical chemists had to live with unresolved lines open to a wealth of curve fitting procedures and a vast amount of speculations.

High resolution NMR in solids seemed to be a paradoxon. Broad structureless lines are usually encountered when dealing with NMR in solids. Only with the recent advent of multiple pulse, magic angle, cross-polarization, two-dimensional and multiple-quantum spectroscopy and other techniques during the last decade it became possible to resolve finer details of nuclear spin interactions in solids.

I have felt that graduate students, researchers and others beginning to get involved with these techniques needed a book which treats the principles, theoretical foundations and applications of these rather sophisticated experimental techniques. Therefore I wrote a monograph on the subject in 1976. Very soon new ideas led to the developement of "two-dimensional spectroscopy" and "multiple-quantum spectroscopy", topics which were not covered in the first edition of my book. Moreover an exponential growth of literature appeared in this area of research leaving the beginner in an awkward situation of tracing back from a current article to the roots of the experiment. I therefore felt a second enlarged edition was necessary. Springer-Verlag demanded to publish it in the same series and to keep the chapters of the first edition. Only some chapters covering new aspects were supposed to be added. Some revisions of the old chapters, however, were also necessary. Then Springer-Verlag decided to publish it as a separate book. It therefore contains most parts of the first edition and some new chapters. Parts of these were written in Dortmund, parts on the train when commuting between Münster, Dortmund and Stuttgart. The final version was finished in Stuttgart where I moved in spring 1982. Like in the first edition this book contains some material which has never been published separately.

Prerequisite to reading this monograph is some familiarity with the principles of magnetic resonance as can be found in the fundamental books by A. Abragam, M. Goldmann and C.P. Slichter. Additional reading of the monograph written by U. Haeberlen is highly recommended. I have tried very hard to cover the whole current literature in this rapidly expanding field; however, I am aware that I have certainly missed important contributions. Among these are multiple-pulse experiments applied to liquids. Of those who suffer from this, I herewith beg pardon.

Among my friends and colleagues I am particularly indebted to O. Kanert, A. Pines and J.S. Waugh for their criticisms, discussions and comments. Among these my friend A. Pines has encouraged and stimulated me continously. I gratefully acknowledge the kind hospitality of John S. Waugh during my stay at the Massachusetts Institute of Technology in 1969–1971, where I was introduced to these fascinating experiments. My friend O. Kanert has continously encouraged me during the time of writing. I am very much obliged to my co-workers who supplied some of the material covered in this book. There are numerous scientists from whose discussion I have benefited greatly in the past. Among these I am particularly indebted to R.G. Griffin, the late R.W. Vaughan and U. Haeberlen.

I also gratefully acknowledge the patience and endurance of Mrs. R. Beck and Mrs. E. Winkler who typed and edited the additional chapters.

Finally I want to apologize to my wife Sabine and the children for spoiling many evenings and sunny weekends by working on this monograph. Their patience and endurance is gratefully acknowledged here.

This book would never have been completed without the patience, support and constant urge by Dr. F.L. Boschke and Mrs. A. Heinrich from Springer-Verlag.

Stuttgart, September 1, 1982 Michael Mehring

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1 Introduction

Manipulation and Dilution
Tools for Ruling Abundant Species

Spin engineering has brought about a wealth of techniques to overcome the natural line broadening mechanisms in solids, such as dipole-dipole and quadrupole interactions. We are going to review in this monograph the different techniques involved and we shall discuss the results obtained. For the convenience of the unbiased reader let us first take a look at some representative results.

As is well known to the chemist, the NMR spectrum of a liquid consists of numerous sharp lines typically with less than 1 Hz linewidth, due to magnetic field inhomogeneities or spin relaxation [1]. In order to supply a reference to this concept of "High Resolution NMR", Fig. 1.1 displays as a representative example the spectrum of ethyl alcohol [2]. Neither *manipulation* nor *dilution* is indicated in order to obtain the NMR spectrum of this compound in the

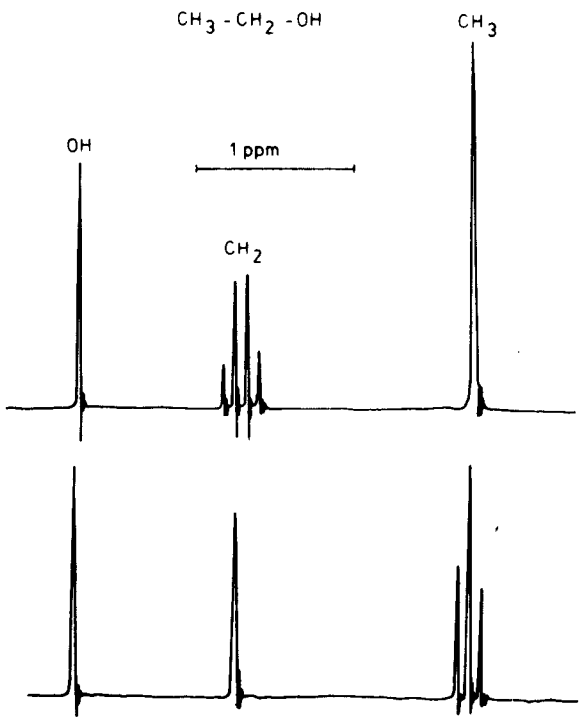

Fig. 1.1. Highly resolved proton spectrum of ethanol using spin decoupling. Top: While recording the methyl group line, irradiation was performed on the methylene resonance. Bottom: While recording the methylene group line, irradiation was performed on the methyl group resonance [2]

liquid state. It may be obtained in a rather standard fashion by taking simply the NMR spectrum of the liquid sample. However, also high resolution NMR spectroscopists like to manipulate on their spectra as is demonstrated in Fig. 1.1. We note in advance that in general "High Resolution NMR in Solids" has not lived up to this state of the art. The interaction Hamiltonian in a liquid sample is represented by isotropic chemical shift and scalar spin-spin interactions. All possible anisotropic interactions, namely chemical shift anisotropy, dipole-dipole interaction, quadrupole interaction etc. are averaged to zero due to the rapid isotropic molecular motion i.e., nature performs some manipulations in this case.

In the solid state, however, all these anisotropic interactions are retained and may be used to monitor the symmetry properties and the electronic state of the solid [1]. Unfortunately in many cases (like ^{19}F and ^{1}H) the dipole-dipole interaction is overwhelming at ordinary magnetic field strength (1–6 Tesla). This results in a more or less bell shaped, structureless line shape, from which very little information can be extracted about the local symmetry and electronic configuration, In this sense the goal of high resolution NMR in solids can be formulated as designing methods to repress the "unwanted" dipolar interaction considerably, leaving chemical shift anisotropies, scalar interaction etc. more or less unaffected.

The natural way of achieving this goal would be by *dilution* of the spins, since the dipolar interaction is proportional to r^{-3}, where r is the distance between the spins. This, however, leads to "High Resolution" only in that case, where no other heteronuclear spins are present. In favourable cases such as in a dilute spin system with small gyromagnetic ratio and large chemical shift anisotropy, already the ordinary NMR spectrum yields a "High Resolution Spectrum" in the sense that anisotropic shift interactions are observable. If in addition considerable molecular motion is present, highly resolved spectral lines can be observed in a solid, as was demonstrated by Andrew and co-workers [3] in the case of solid P_4S_3 whose spectrum is shown in Fig. 1.2.

In this monograph, however, we are dealing with the case where the natural line broadening due to dipolar and quadrupolar interactions masks other weak interactions, such as shift interactions and scalar couplings. The first attempt to overcome this obstacle was made independently by E.R. Andrew et al. [4]

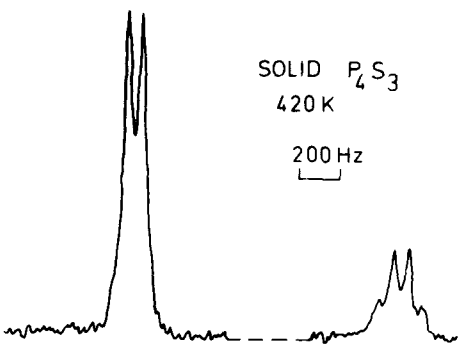

Fig. 1.2. ^{31}P NMR spectrum in solid P_4S_3 at 420 K (melting point 446 K) by Andrew, Hinshaw and Jasinski [3]. The spectrum is strongly narrowed by molecular motion in the solid. The AB_3 type fine structure is represented by a chemical shift separation between the doublet (basal nuclei) and the quartet (apical nuclei) of 185 ± 2 ppm. The coupling constant is $J = 70 \pm 3$ Hz

and by I. Lowe [5] by using a specimen rotation method. The whole sample is rapidly rotated, in this method, about an axis tilted by the "magic angle" $\vartheta_m = 54°44'8''12'''$ ($\tan\vartheta_m = \sqrt{2}$) with respect to the static magnetic field B_0. It can be shown that the average dipolar interaction vanishes in this case. A representative example is shown in Fig. 1.3. The reader will realize that shielding

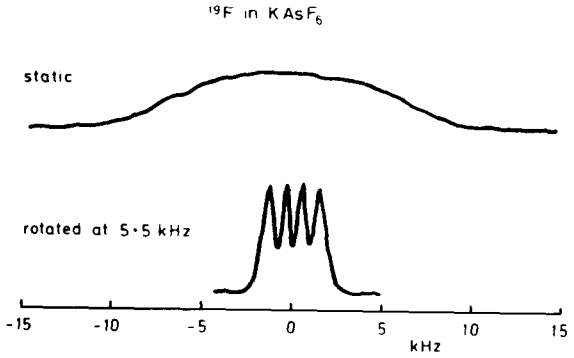

Fig. 1.3. Application of the magic angle specimen rotation method of ^{19}F in polycrystalline $KAsF_6$ by Andrew, Farnell and Gledhill [6b]. The upper spectrum shows the ordinary NMR line without sample rotation. Dipolar coupling among the spins governs the line width. The lower spectrum corresponds to a magic angle rotation of the sample with 5.5 KHz, displaying a quartet structure due to electron-coupled interaction between ^{19}F and ^{75}As nuclei ($I = 3/2$). The coupling constant is $J = 905$ Hz

anisotropies are also averaged to zero and only the isotropic shift is retained. On the other hand, homonuclear and heteronuclear dipolar interactions vanish, since this technique is not spin specific. Excellent review articles have been written on this subject by E.R. Andrew [6]. Therefore we are not treating this subject in detail; however, we shall touch upon it occasionally. One of our main purposes is to review the recently developed techniques of *manipulation*, which operate in spin space and which are capable of reducing dipolar as well as quadrupolar interactions considerably. The first useful multiple pulse cycle which has successfully been applied in this sense, was the four-pulse cycle of J.W. Waugh, L.M. Huber and U. Haeberlen [7], often referred to as WAHUHA experiment. Patent holders: J.S. Waugh and U. Haeberlen, U.S. patent No. 3,530,374. Figure 1.4 represents the "High Resolution" spectrum of ^{19}F in C_6F_{12} obtained with such a four-pulse experiment in comparison with the ordinary NMR spectrum [8]. The great potential of these techniques for the resolution of weak spin interactions is demonstrated clearly. The reason why no such anisotropy is observed in Fig. 1.4 is because nature supplies enough motion at the applied temperature, to average anisotropic shielding, leaving only the scalar interactions. Since this method operates in spin space, all anisotropic spin interactions which are linear in the spin variable are retained and have been extensively studied in powder samples as well as in single crystals [9–12]. Modifications of this basic multiple-pulse line narrowing

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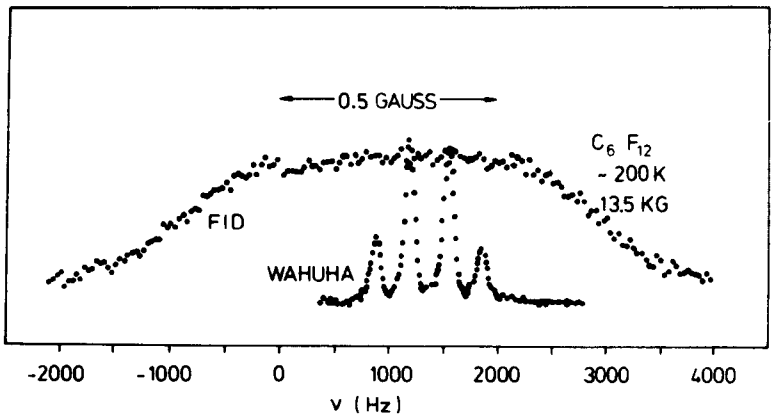

Fig. 1.4. Application of the multiple pulse method to ^{19}F in polycrystalline C_6F_{12} at 200 K by Ellett, Haeberlen and Waugh [8]. Upper curve: Normal NMR spectrum governed by dipolar coupling among the ^{19}F nuclei. Lower curve AB type spectrum ($J = 310$ Hz, $\delta = 17.5$ ppm) after removal of the dipolar interaction by applying a multiple-pulse sequence (WAHUHA). Chemical shift anisotropy is removed by isotropic molecular motion in the solid, but is observed at a lower temperature

experiment have been developed which in some cases are capable of extremely high resolution [13].

Dilution of spin systems is often done on purpose, however, nature supplies a wealth of diluted spin systems with very low natural abundance, such as ^{13}C, ^{15}N, ^{43}Ca etc. in a surrounding of abundant spins like ^{1}H and ^{19}F. In order to obtain a high signal to noise, high resolution spectrum, the rare spins are first polarized by the virtue of spin order transfer from the abundant spins. During the subsequent observation of the rare spins, the abundant spins are decoupled, in order to repress the broadening due to heteronuclear dipolar interaction. This technique was first applied by A. Pines, M. Gibby, and J.S. Waugh and is

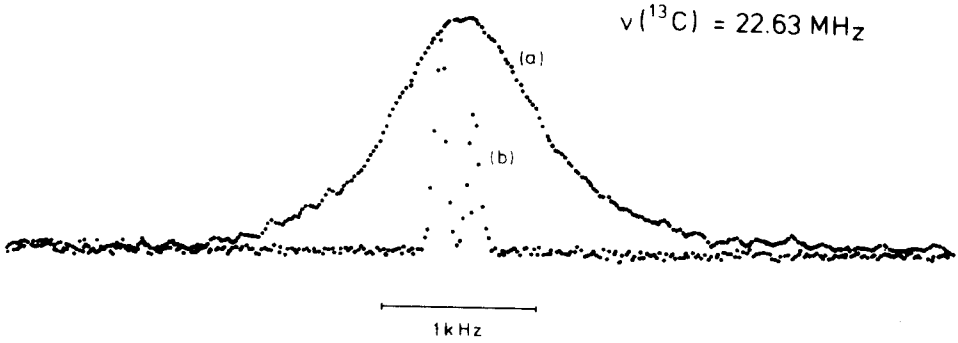

Fig. 1.5a, b. Application of the cross-polarization method of Pines, Gibby and Waugh [14] to ^{13}C in polycrystalline adamantane at room temperature. **a** Undecoupled ^{13}C spectrum governed by ^{13}C-^{1}H dipolar coupling. **b** Decoupled ^{13}C spectrum displaying two chemically inequivalent ^{13}C nuclei. Chemical shift anisotropy is not observed due to the rapid isotropic motion of the molecules. (Courtesy of G. Sinning)

referred to as "Proton Enhanced Nuclear Induction Spectroscopy" [14]. Patentholders: A. Pines, M. Gibby and J.S. Waugh, U.S. Pat. No. 3792,346 (1974). Figure 1.5 shows the ^{13}C spectrum of natural abundant (1.1 %) ^{13}C in adamantane, obtained by this technique. There is considerable motion present in adamantane at room temperature to average out chemical shift anisotropies, leaving only the isotropic shift [15].

Very often, however, molecular motion is very slow in solids, leading to broad spectral features, known as powder pattern. If several nonequivalent ^{13}C nuclei are present in the sample, overlapping powder pattern may cause severe difficulties in spectrum analysis. Therefore magic angle spinning (MAS) of the sample is a useful technique to average all anisotropies, leaving only the trace, i.e. the isotropic part of the tensor interaction. An example of this technique is shown in Fig. 1.6.

There is, however, a different way of disentangling complicated spectra, called two-dimensional (2D) spectroscopy, originally proposed by Jeener [17] and extended and applied by Ernst and co-workers [18], Freeman and Morris [19] and others. Figure 1.7 shows an example due to Waugh and co-workers [20]. In these experiments the heteronuclear dipole-dipole interaction between ^{13}C and ^{1}H is used as a second frequency axis.

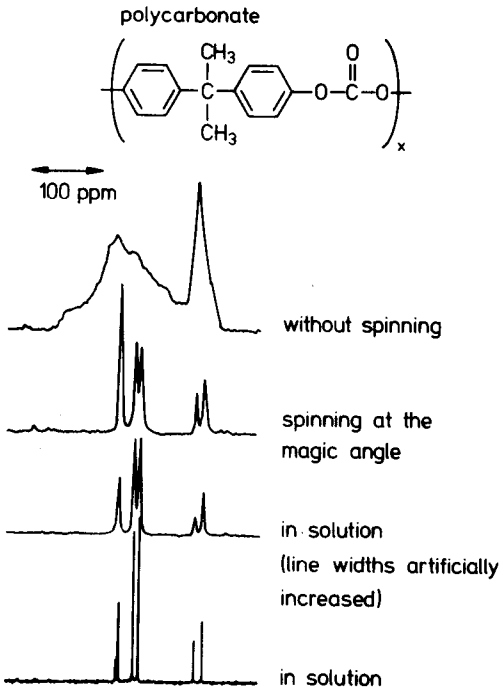

Fig. 1.6. Cross-polarization (CP) ^{13}C NMR spectra (22.6 MHz) of polycarbonate, with and without magic-angle spinning (MAS) (3 kHz) according to Schaefer, Stejskal and Buchdahl [16]

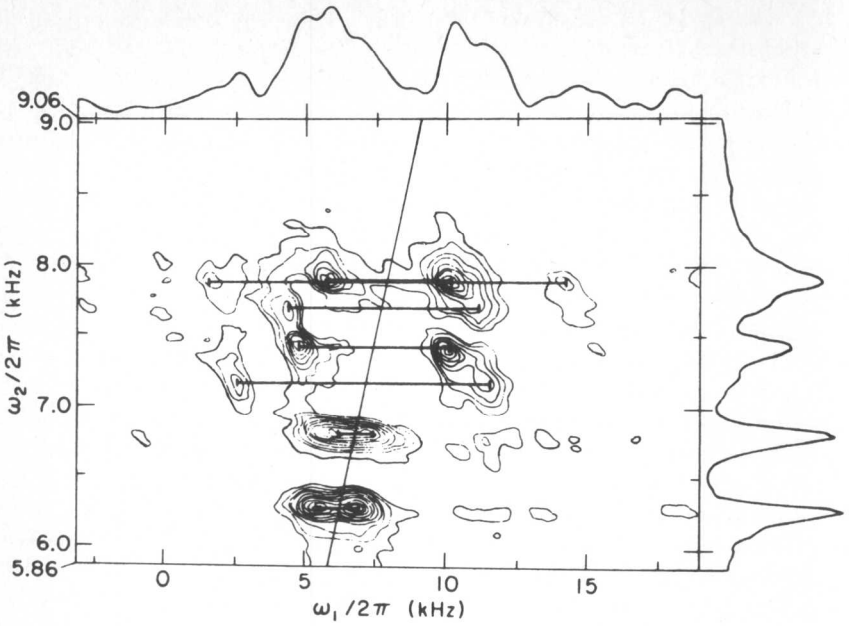

Fig. 1.7. Two-dimensional ^{13}C spectrum of calcium formate $Ca(HCO_2)_2$ according to Hester et al. [20b]. Dipolar splittings for each of the observed seven lines are indicated by the heavy lines. The ordinary one-dimensional spectrum is obtained by a projection onto the ω_2-axis as shown on the right hand side

Another new technique, recently initiated by Pines and co-workers [21] leads to multiple quantum coherence spectroscopy. Multiple quantum transitions are excited in order to resolve n-quantum spectra. An example is given in Fig. 1.8. This technique, so far mainly applied to liquids or liquid crystals may find interesting applications in solids too.

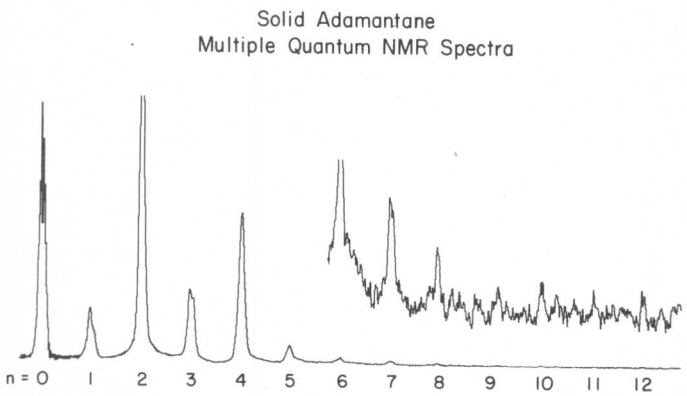

Fig. 1.8. Multiple-quantum NMR spectra of protons in adamantane ($C_{10}H_{16}$) according to A. Pines and Yu Sze Yen. Up to $n=12$ quanta are seen to be coherently absorbed. (Courtesy of A. Pines)

In Chap. 2 we remind the reader of the tensorial character of all spin interactions which manifest itself by second rank tensors in ordinary solids. There may be interactions of higher rank in principle, but no valid experimental verification has been given of this to my knowledge. There has been a discussion on the transformation properties of these interactions. We restrict ourselves, however, in this chapter to rotations in real space. In this context also magic angle spinning (MAS) is discussed as well as molecular reorientation.

Chapter 3 deals with multiple-pulse experiments, discussing the application of pulse cycles to the spin system, mainly serving the goal of *repressing* the dipolar interaction. Coherent averaging, second averaging and the influence of pulse imperfections are treated in detail.

Double resonance experiments on rare spins with the purpose of obtaining high resolution spectra in solids are analyzed in Chap. 4. After reviewing the principles of double resonance we turn to cross-polarization experiments, which recently have supplied a wealth of ^{13}C spectra in solids. Cross-polarization dynamics and spin decoupling dynamics are discussed also.

Two-dimensional (2D) spectroscopy in solids and the underlying principle is treated in Chap. 5. Although multiple-quantum spectroscopy has not yet been applied to solids extensively, we will nevertheless discuss its principles and potential usefulness in Chap. 6.

The main application of the techniques of *manipulation* and *dilution* has been the determination of magnetic shielding tensors, which we deal with in Chap. 7. After a brief introduction to the concepts we summarize the shielding tensors, thus far determined by these techniques.

Spin lattice relaxation has not played a dominant role in high resolution NMR in solids so far. However, as we see in Chap. 8 there are some useful applications of the techniques which have been described in the preceding chapters about the investigation of spin lattice relaxation processes. The *appendices* summarize for the convenience of the reader some useful aspects to which we refer in the text. Reviews on the subject have been written by P. Mansfield [22], R.W. Vaughan [23], R.G. Griffin [24] and E.R. Andrew [6]. The monograph by U. Haeberlen [25] covers part of this subject taking a slightly different approach and is highly recommended to the reader. This applies also to the review written more recently by H.W. Spiess [26], who deals with line shapes and relaxation of diluted spins.

2 Nuclear Spin Interactions in Solids

For the convenience of the reader we summarize in this section the basic nuclear spin interactions which occur in solids. The notation will be in tensorial form throughout to emphasize the anisotropy of these interactions. In order to keep the presentation as compact as possible we shall avoid detailed derivations and refer the reader to the outstanding book by A. Abragam [1]. Also Pool and Farach [2a] have given a detailed description of spin interactions in tensorial form. As a further reference the book by C.P. Slichter [2b] is recommended.

2.1 Basic Nuclear Spin Interactions in Solids

Figure 2.1 can serve as a guide to the different basic interactions occurring in solids. It represents the sevenfold way a nuclear spin can communicate with its surrounding. We shall refer to this figure later in the text. We first distinguish nuclear spin interactions between external fields (B_0, B_1) and internal fields:

$$\mathcal{H} = \mathcal{H}_{ext} + \mathcal{H}_{int} \tag{2.1}$$

where

$$\mathcal{H}_{ext} = \mathcal{H}_0 + \mathcal{H}_1 .$$

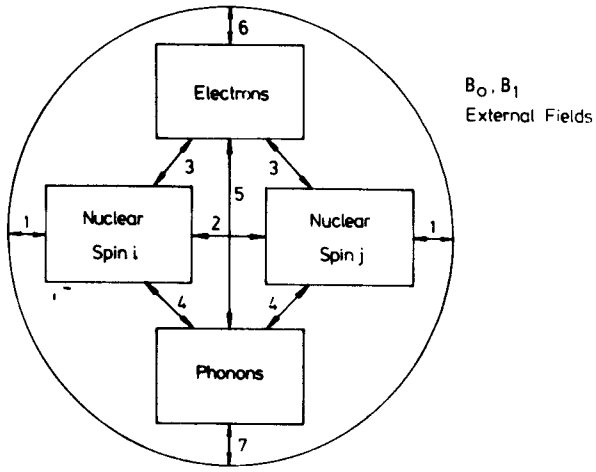

Fig. 2.1. The seven-fold way a nuclear spin system can interact with its surrounding. *1* Zeeman interaction of spins. *2* Direct spin interaction. *3* Nuclear spin-electron interaction and indirect spin interaction. *4* Direct spin-lattice interaction. *3–5* Indirect spin lattice interaction via electrons. *3–6* Shielding and polarization of nuclear spins by electrons. *4–7* Coupling of nuclear spins to sound fields etc.

$\mathcal{H}_0$ and $\mathcal{H}_1$ are the Zeeman interactions with the external fields B_0 and B_1, respectively. This distinction is appropriate in fact, because we are going to work in a regime where the "size" of $\mathcal{H}_0$ and $\mathcal{H}_1$ is much larger than the "size" of $\mathcal{H}_{\text{int}}$. By the "size" of an Hamiltonian we mean unless otherwise stated:

$$\|\mathcal{H}\| = [\mathrm{Tr}\{\mathcal{H}^2\}]^{1/2}. \tag{2.2}$$

The spin interactions of two different types of spins (I, S) (gyromagnetic ratios γ_I and γ_S) with internal fields may be written as

$$\mathcal{H}_{\text{int}} = \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS} + \mathcal{H}_Q + \mathcal{H}_S + \mathcal{H}_L \tag{2.3}$$

where $\mathcal{H}_{II}$ and $\mathcal{H}_{SS}$ represent the direct (dipolar) as well as the indirect interactions among I spins and S spins respectively (path 2 and 3 in Fig. 2.1). The same paths are involved in the I-S interaction as expressed by $\mathcal{H}_{IS}$, which covers the direct as well as the indirect interactions between I spins and S spins. $\mathcal{H}_Q$ is the quadrupole Hamiltonian of the I and S spins respectively. $\mathcal{H}_S$ contains all shielding Hamiltonians (chemical shift and Knight shift) of the I and S spins (path 3, 6 in Fig. 2.1).

$\mathcal{H}_L$ describes the spin lattice interaction (path 4 and 3, 5 in Fig. 2.1). We find it convenient to express all Hamiltonian in frequency units (ω-units) throughout this monograph. In the following we assume that the symmetry of the solid is such that all the spin interactions can be represented by second rank Cartesian tensors in the following way (1, 2] (see Table 2.1):

$$\mathcal{H} = \mathbf{I}\cdot\tilde{\mathbf{A}}\cdot\mathbf{S} = (I_x, I_y, I_z)\begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{zz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix}\begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix} \tag{2.4}$$

Table 2.1. Interaction Hamiltonians

Interaction	Form of the Hamiltonian
Chemical shift	$\mathcal{H}_S = \gamma\mathbf{I}\cdot\tilde{\sigma}\cdot\mathbf{B}_0$
Dipole-dipole	$\mathcal{H}_D = \sum_{i<j} \hbar\gamma_i\gamma_j r_{ij}^{-3}\left(\mathbf{I}_i\cdot\mathbf{I}_j - \frac{3(\mathbf{I}_i\cdot\mathbf{r}_{ij})(\mathbf{I}_j\mathbf{r}_{ij})}{r_{ij}^2}\right)$
	$\mathcal{H}_D = \sum_{i=j} \mathbf{I}_i\cdot\tilde{\mathbf{D}}\cdot\mathbf{I}_j$
	$D_{\alpha\beta} = \hbar\gamma_i\gamma_j r_{ij}^{-3}(\delta_{\alpha\beta} - 3e_\alpha e_\beta)$
	$\alpha, \beta = x, y, z$; e_α: α-component of the unit vector along r_{ij}
J-coupling	$\mathcal{H}_J = \sum_{i\neq j} \mathbf{I}_i\cdot\tilde{\mathbf{J}}\cdot\mathbf{I}_j$
Spin-rotation	$\mathcal{H}_{CR} = \sum_i \mathbf{I}_i\cdot\tilde{\mathbf{C}}_i\cdot\mathbf{J}$
Quadrupole	$\mathcal{H}_Q = \frac{eQ}{2I(2I-1)\hbar}\mathbf{I}\cdot\tilde{\mathbf{V}}\cdot\mathbf{I}$
	$\tilde{V} = \{V_{\alpha\beta}\}$; $\alpha, \beta = x, y, z$

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