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## INTRODUCTION TO THE MEASURABLE QUANTITIES OF NMR

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A summary introduction is given to most of the terms in the general nuclear spin Hamiltonian and to how their measurable effects on NMR spectrum and relaxation contain information on the microscopic properties, both static and dynamic, of the nuclear surroundings.

### 1. Introduction

This paper attempts to summarize how the wealth of phenomena that can be studied by nuclear magnetic resonance techniques arises from the differences in symmetry of only a few terms in a nuclear spin Hamiltonian. It does not deal with experimental considerations. To give here a full derivation of all relevant equations is of course both impossible and unnecessary : several excellent books on the subject exist. Instead, the key results are presented and their relationships discussed in a rather general and formal framework. The actual applications of these theories to problems in solid state physics and materials science will be shown in other contributions to this series : in this paper very few specific results will be dealt with. Its main purpose is to provide a quick reference for concepts used in the following papers. Readers who want to obtain a deeper understanding should consult one of the monographs (cited in the references) that have been used in preparing this text.

## 2. The Nuclear Operators and the Nuclear Spin Hamiltonian [1,2]

Most elements of the periodic table have at least one isotope that in its ground state has a nonzero total nuclear angular momentum  $\vec{I}$  (usually named "the" spin of the nucleus, although it is composed of spin and angular momentum operators of the constituent nucleons). Since parity is well-defined, the multipole expansion of the nuclear charge distribution contains only odd electric multipoles and only even magnetic multipoles. According to the Wigner-Eckart theorem, the only multipoles that can have nonzero matrix elements are of order  $\ell \leq 2 I$ . Therefore, in addition to the  $\ell = 0$  point charge, nuclei of spin one-half (e.g.  $^1H$ ,  $^{13}C$ ,  $^{31}P$ ,  $^{195}Pt$ ) can only have a magnetic dipole moment  $\vec{\mu}$ ; those of spin  $\geq 1$  can have an electric quadrupole moment  $\vec{eQ}$ ; for  $I \geq 3/2$  the magnetic octupole is possible, and so on. It turns out that the only moments of importance in NMR are those with  $\ell = 1$  and  $\ell = 2$ : the higher ones can always be neglected (and the  $\ell = 0$  part does not give different couplings for different spin substates). To establish the relation between  $\vec{I}$ ,  $\vec{\mu}$  and  $\vec{eQ}$  we need the spherical tensors  $I_{\ell m}$  with  $\ell = 1$  and  $\ell = 2$  and where  $m$  runs from  $-\ell$  to  $+\ell$ . As an example we have for  $I_{1m}$ :

$$I_{1\pm 1} = \mp \frac{1}{2} \sqrt{2} (I_x \pm i I_y) \quad (1)$$

$$I_{10} = I_z$$

The Wigner-Eckart theorem now says that  $\vec{\mu}$  is proportional to  $I_{1m}$ . By convention, the proportionality constant is denoted  $\gamma\hbar$  and  $\gamma$  is called the gyromagnetic ratio. Similarly,  $\vec{eQ}$  is proportional to  $I_{2m}$ , and the conventional notation for the proportionality constant is  $eQ/I(2I-1)$  where now  $eQ$  is called "the" quadrupole moment of the nucleus.

Basically, a magnetic resonance experiment observes  $\langle \vec{\mu} \rangle$  (or more precisely: its component perpendicular to the Zeeman field), but since  $\vec{I}$ ,  $\vec{\mu}$  and  $\vec{eQ}$  are tied together,  $\langle \vec{\mu} \rangle$  is influenced not only by purely magnetic couplings with a field  $\vec{B}$  of the form  $\vec{\mu} \cdot \vec{B}$ , but also by couplings  $\vec{I} \cdot \vec{J}$  to another angular momentum  $\vec{J}$  and by couplings to an electric field gradient  $\vec{V}$  of form  $\vec{eQ} \cdot \vec{V}$ . It is therefore useful to write all interactions as "spin" interactions, using the representations of the nuclear operators given above. Neglecting for the moment the "external" part of the nuclear spin Hamiltonian,

due to the externally applied static and rf magnetic fields, the following terms can be important in an NMR experiment :

1) The shielding ("chemical shift" or "Knight shift") Hamiltonian  $\mathcal{H}_s$ . The physical origins for chemical and Knight shifts are slightly different, but both modify the magnetic field at the site of the nucleus and can be written

$$\hbar \mathcal{H}_s = \hbar \gamma \vec{I} \cdot \overline{\overline{S}} \cdot \vec{B} \quad (2)$$

where  $\overline{\overline{S}}$  is a tensor of rank two, characteristic for the nuclear site.

2) The quadrupolar Hamiltonian  $\mathcal{H}_Q$ . Just as a magnetic dipole is aligned by a magnetic field, an electrical quadrupole is aligned by an electric field gradient. But while a magnetic field  $\vec{B}$  can be represented as a vector, the electric field gradient  $\overline{\overline{V}}$  is a second-rank tensor : its Cartesian elements  $V_{xy}$  are the second partial derivatives of the electric potential :

$$\hbar \mathcal{H}_Q = \frac{eQ}{6 I (2 I - 1)} \vec{I} \cdot \overline{\overline{V}} \cdot \vec{I} \quad (3)$$

3) The spin-rotation Hamiltonian  $\mathcal{H}_R$ . This describes the coupling of the nuclear spins  $\vec{I}$  in a molecule with the angular momentum  $\vec{J}$  of the molecule :

$$\hbar \mathcal{H}_R = \hbar \vec{I} \cdot \overline{\overline{C}} \cdot \vec{J} \quad (4)$$

The mechanism is seldom important in NMR of solids, and will be neglected in the following.

4) The dipolar Hamiltonian  $\mathcal{H}_D$ . Nuclear spins are well-localized and well separated, and therefore their magnetic dipole coupling can be described classically (unlike the case of electrons). Contrary to the first three mechanisms, that are described by single-spin Hamiltonians, the dipolar interaction couples every spin  $i$  in a sample with all other spins  $k$  :

$$\hbar \mathcal{H}_D^i = \sum_k (-2 \gamma^i \gamma^k h^2) \vec{I}^i \cdot \overline{\overline{D}}^{ik} \cdot \vec{I}^k \quad (5)$$

where the cartesian representation of  $\overline{\overline{D}}$  has elements

$$\overline{\overline{D}}_{\alpha\beta} = \frac{3}{2} r^{-5} (r_\alpha r_\beta - \frac{1}{3} r^2 \delta_{\alpha\beta})$$

and  $\vec{r}$  is the vector from nucleus  $i$  to nucleus  $k$ .

5) The indirect spin-spin coupling Hamiltonian  $\mathcal{H}_J$ . In addition to the direct dipolar coupling, there exists coupling between nuclei mediated by the electrons. The physics is slightly different for insulators and metals (where it is also called Rudermann-Kittel coupling) but its general form is similar for both cases :

$$\hbar \mathcal{H}_J^i = \hbar \sum_k \vec{I}^i \cdot \vec{J}^{ik} \cdot \vec{I}^k \quad (6)$$

The general structure of all these Hamiltonians is

$$\mathcal{H} = C \vec{R} : \vec{T} \quad (7)$$

where the  $C$  is some proportionality constant (like  $\gamma\hbar$  for  $\mathcal{H}_S$ ),  $\vec{R}$  a tensor reflecting microscopic properties of the surroundings of the nucleus under study (like  $\vec{V}$  for  $\mathcal{H}_Q$ ), and  $\vec{T}$  a dyadic constructed from two vectors, one of which is always the nuclear spin vector and the other is one of the following : a magnetic field, for  $\mathcal{H}_S$ ; the same spin, for  $\mathcal{H}_Q$ ; the molecular angular momentum, for  $\mathcal{H}_R$ ; a different spin, for  $\mathcal{H}_D$  and  $\mathcal{H}_J$ .

All the properties of a solid, liquid or gaseous system that can be studied by NMR are contained in the static and dynamic properties of the tensors  $\vec{R}$  : their time-averaged values show up in shifts and splittings of the resonance lines, and their time-variation in the nuclear spin relaxation times. Typical examples are : the study of the conformation of proteins in solution by probing  $\mathcal{H}_D$  and  $\mathcal{H}_J$  [3]; of structural phase transitions in ionic crystals by  $\mathcal{H}_Q$  [4]; of molecular geometry by  $\mathcal{H}_S$  [1]; of properties of the electronic structure in metals by  $\mathcal{H}_S$  and  $\mathcal{H}_J$  [5].

To discuss the general properties of the tensors  $\vec{R}$  it is convenient to use their irreducible representation  $R_{lm}$ . From a general second-order Cartesian tensor (with nine elements) one can form a zero-rank tensor ( $l = 0, m = 0$ ; an invariant, containing one element), a first-rank tensor ( $l = 1, m = 0, \pm 1$ ; the antisymmetric part, containing three elements) plus a second-rank tensor ( $l = 2, m = 0, \pm 1, \pm 2$ ; the traceless symmetric part, containing five elements). It can be shown that the effects of the antisymmetric part (if it is not already zero by the nature of  $\vec{R}$ ) can be neglected in magnetic resonance, so that we are left with six independent components. These are conveniently described by three values (denoted  $\sigma, \delta, \eta$ ) in the principal axes system

(PAS) of  $\vec{R}$ , plus the three Euler angles ( $\alpha, \beta, \gamma$ ) that describe the orientation of the principal axes system with respect to some reference system (e.g. the crystal axes). The definition of  $\sigma, \delta, \eta$  is chosen such that  $\sigma$  measures the isotropic part of the interaction (invariant under rotations),  $\delta$  measures the biggest principal value (axial deviation from isotropy), and  $\eta$  the deviation from cylindrical symmetry around the "biggest principal axis". According to the nature of the different internal Hamiltonians, one or two of these parameters may be zero : the dipole-dipole coupling has no isotropic part (its average over a sphere vanishes) and is symmetric around the dipole-dipole vector; therefore its  $\sigma$  and  $\eta$  are both zero. From Laplace's law it follows that the isotropic part of the quadrupole coupling vanishes ( $\sigma = 0$ ). In cubic point symmetry its  $\delta$  and  $\eta$  vanish also; in tetragonal symmetry  $\delta$  is non-zero (and called "the" field gradient by convention), and in lower symmetry both  $\delta$  and  $\eta$  (called the asymmetry parameter) are nonzero. For reference, the constants in the conventional representation of the components of  $\vec{R}$  in the Hamiltonians are given in Table I, and the corresponding irreducible representations of the tensors  $\vec{T}$  (cf. Eq. (7)) in Table II.

The NMR experiment (the observation of  $\langle \vec{\mu} \rangle$ ) is done in the laboratory axes system (LAB) rather than in the principal axes system. The components of irreducible tensors in different axes systems are related by Wigner rotation matrices  $D_{mm}^{\ell}$ , ( $\alpha, \beta, \gamma$ ), where  $\alpha, \beta, \gamma$  are the Euler angles to rotate one

Table I. Constants in the conventional representation of internal Hamiltonians. (See Eqs. (7) and (9)).

Hamiltonian	C	$\sigma$	$\delta$	$\eta$
S	$\gamma \hbar$	$\kappa^1, \sigma^2$	$\delta_S$	$\eta_S$
Q	$eQ/6I(2I-1)$	0	eq	$\eta$
D	$-2\gamma^i \gamma^k \hbar^2$	0	$r_{ik}^{-3}$	0
J	$\hbar$	J	$\delta_J$	$\eta_J$

1) Knight shift, in metals

2) chemical shift, in molecules

Table II. Irreducible spin operators  $T_{\ell m}$  (see Eq. (7)).

Hamiltonian	$T_{00}$	$T_{20}$	$T_{2\pm 1}$	$T_{2\pm 2}$
S	$I_0^i B_0$	$\sqrt{\frac{2}{3}} I_0^i B_0$	$\frac{1}{\sqrt{2}} I_{\pm 1}^i B_0$	0
Q	$(I^i)^2$	$\frac{1}{\sqrt{6}} [3(I_0^i)^2 - (I^i)^2]$	$\frac{1}{\sqrt{2}} [I_{\pm 1}^i I_0^i + I_0^i I_{\pm 1}^i]$	$(I_{\pm 1}^i)^2$
$\begin{matrix} D \\ J \end{matrix}$	$I^i \cdot I^k$	$\frac{1}{\sqrt{6}} [3 I_0^i I_0^k - I^i \cdot I^k]$	$\frac{1}{\sqrt{2}} [I_{\pm 1}^i I_0^k + I_0^i I_{\pm 1}^k]$	$I_{\pm 1}^i I_{\pm 1}^k$

axis system into the other :

$$R_{\ell m} (\text{LAB}) = \sum_{m'=-\ell}^{\ell} R_{\ell m'} (\text{PAS}) D_{m'm}^{\ell} (\alpha, \beta, \gamma) \quad (8)$$

### 3. Spectral Structure [1]

We will consider only the case where all "internal" Hamiltonians are much smaller than the Zeeman Hamiltonian  $\mathcal{H}_z$ , so that the spectra can be calculated from first order perturbation theory, starting from the eigenfunctions of  $\mathcal{H}_z$ . We only retain those parts of the  $T_{\ell m}$  that have nonvanishing diagonal elements  $\langle I, m_z | T_{\ell m} | I, m_z \rangle$ . (The approximation is often excellent in NMR, but rarely so in EPR, where exact diagonalization has to be used in many cases). In the case of  $\mathcal{H}_D$  and  $\mathcal{H}_J$  we need to distinguish the coupling between "like" spins  $\vec{I}^i$  and  $\vec{I}^j$  (that have the same Hamiltonians) and "unlike" spins  $\vec{I}$  and  $\vec{S}$ . This restriction on the number of  $T_{\ell m}$  considered is known as "restriction to secular terms" or "truncation of internal Hamiltonians". The only elements that survive are  $T_{00}$  and  $T_{20}$ , as given in Table II.

Using the irreducible representations, the Hamiltonian (7) reduces to

$$\mathcal{H} = C \sigma T_{00} + C \delta \left(\frac{3}{8}\right)^{\frac{1}{2}} [(3 \cos^2 \theta - 1) - \eta \sin^2 \theta \cos 2\phi] T_{20} \quad (9)$$

where  $\theta$  and  $\phi$  are the polar angles of the magnetic field in the principal axes system of the interaction considered. Note that  $\mathcal{H}$ , and therefore the energy values, depends on five variables (of the six generally available)

only : in the laboratory frame there is invariance under rotations around the magnetic field and the Euler angle  $\alpha$  disappears. Note also that the  $\theta, \phi$ -angular dependence of the spectrum (when the Zeeman field is rotated with respect to the crystal axes) is the same for all internal Hamiltonians. This does not mean, of course, that the spectrum is the same for all  $\mathcal{H}_{\text{int}}$ . In the basis  $|I, m_z\rangle$ , with the frequency shifts of the NMR lines (w.r.t.  $\gamma B_0$ ) given by

$$\hbar\nu_m = \langle I, m_z | \mathcal{H}_{\text{int}} | I, m_z \rangle - \langle I, m_z - 1 | \mathcal{H}_{\text{int}} | I, m_z - 1 \rangle \quad (10)$$

we see that  $\mathcal{H}_S$  gives one single line;  $\mathcal{H}_Q$  gives  $2I$  lines; and  $\mathcal{H}_D$  and  $\mathcal{H}_J$  give  $(2I+1)$  or  $(2S+1)$  lines. Furthermore, the spectra are symmetric around the frequency determined by  $C\sigma T_{00}$ .

This implies that for half-integer spin under influence of  $\mathcal{H}_Q$  the central transition  $(+\frac{1}{2}, -\frac{1}{2})$  is not shifted, at least in first order. In a number of cases however,  $\mathcal{H}_Q$  is not very small compared to  $\mathcal{H}_z$ , and a second-order treatment is necessary. Then the central transition is shifted as well, with an angular variation different from that in Eq. (9); for  $\eta=0$  it is

$$\Delta\nu \propto \sin^2\theta \cdot (9\cos^2\theta - 1) \quad (11)$$

If the sample is in the form of a powder, rather than a single crystal, each constituent crystallite has its own  $\theta$  and  $\phi$ , and the distribution of crystallite axes is a random distribution on a sphere. The spectrum becomes an average over  $\theta$  and  $\phi$ , weighed by the distribution. The mathematics can be worked out exactly, but is rather long. As an example consider the case of axial symmetry ( $\eta=0$ ). Then we need only consider the variation of  $(3\cos^2\theta - 1)$ . The extrema of this function are 2 (for  $\theta=0$ ) and -1 (for  $\theta=\pi/2$ ), and the probability to find a certain  $\theta$  is maximum for  $\theta=\pi/2$  and minimum for  $\theta=0$ .

#### 4. Nuclear Spin Relaxation [6,7]

In simple cases, nuclear spin relaxation is described by the famous Bloch equations :

$$\frac{d\langle M_z^{(t)} \rangle}{dt} = \frac{\langle M_z(t) \rangle - \langle M_z(\infty) \rangle}{T_1}$$

$$\frac{d \langle M_{xy}^{(t)} \rangle}{dt} = - \frac{\langle M_{xy}^{(t)} \rangle}{T_2} \quad (12)$$

where  $T_1$  is called the longitudinal or spin-lattice relaxation,  $T_2$  the transversal or spin-spin relaxation, the angular brackets denote expectation values, and  $M$  the nuclear magnetization. In NMR of solids there are only few cases where these equations can be derived from fundamental considerations.

To obtain spin-lattice relaxation we have to consider the coupling between the pure spin-system ( $\mathcal{H}_z + \mathcal{H}_{rf}$ ) and the purely non-spin variables ( $\mathcal{H}_{lattice}$ ). All Hamiltonians  $\mathcal{H}_{int}$  presented before are examples of such couplings : in the form of Eq. (6) the tensors  $\vec{R}$  depend on lattice variables only and the tensors  $\vec{T}$  on spin variables only. The components of  $\mathcal{H}_{int}$  that are active in relaxation are those that are time-dependent and have zero time average (the static parts give line shifts and spectral structure).

As a simplification, let the internal Hamiltonian, Eq. (6), be given by a product of classical "lattice" functions  $R_{2m}$  and quantum mechanical spin operators  $T_{2m}$  (the classical approximation for the lattice is often sufficient : the two typical exceptions being the electron-nucleus interaction in metals, and the spin-phonon interaction in ionic solids). In that case, second-order perturbation theory leads to the following equation for the relaxation of the irreducible components  $I_m$ , (see Eq. (1)) of the nuclear spin :

$$\begin{aligned} \frac{d}{dt} \langle I_m \rangle &= - C^2 \sum_{m=-2}^2 \langle [T_{2m}, [T_{2-m}, I_m]] \rangle \times \\ &\times \int_0^\infty \langle R_{2-m}(t) R_{2m}(t-\tau) \rangle \exp i m \omega_0 \tau \, d\tau \end{aligned} \quad (13)$$

Here the  $\langle R_{2-m}(t) R_{2m}(t-\tau) \rangle$  is the autocorrelation function of the "lattice motion", caused e.g. by diffusion of the atom bearing the nucleus under consideration. It is customary (but not always justified) to assume that all autocorrelations are simple exponential decays, with characteristic time  $\tau_c$  (the correlation time). The spectral density  $J_{lm}(\omega)$  is the Fourier transform of the autocorrelation function :

$$J_{\ell m}(\omega) = \langle R_{\ell-m}(0) R_{\ell m}(0) \rangle \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (14)$$

In most cases where this kind of spectral density is found, it is due to thermal motion, e.g. translational or rotational diffusion, where  $\tau_c$  is the average time between thermally activated jumps. Then  $\tau_c$  can be well described by an Arrhenius equation :  $\tau_c = \tau_0 \exp(E_a/kT)$ , where  $E_a$  is called the activation energy.

If the motion is very rapid,  $(m\omega_0\tau_c)^2 \ll 1$ , (a condition known as "extreme narrowing", because it diminishes the line width), the relaxation equations become independent of the Larmor frequency, and (for most mechanisms) the Bloch equations are obeyed.

Another condition under which simple spin-lattice relaxation curves occur is the existence of a "spin-temperature" during the relaxation (its existence in equilibrium is assured by the coupling with the lattice). This is a very useful general concept in NMR of solids, although it is hard to justify on a priori grounds : it has rather the status of a postulate. It states that after a disturbance such as a  $\pi/2$  pulse, the off-diagonal elements of the density matrix vanish very rapidly (loosely speaking :  $T_2$  is very short) while the relative values of the diagonal elements can be described by a time-dependent temperature  $T_s$ , higher than that of the lattice  $T_L$ . This forces a certain structure on the part of the density matrix that describes the lattice  $\rho_L$ , at all times, and it is found that  $(T_s - T_L)^{-1}$  relaxes exponentially : its time constant is  $T_1$ .

The spin-lattice relaxation rates essentially probe the spectral densities of the motion at the Larmor frequency, as illustrated by Eqs. (13) and (14). For most nuclei, and for typical values of the field  $B_0$ , this frequency is between 10 and 100 MHz. Very low ( $< 1$  MHz) frequency motion has little effect on  $T_1^{-1}$ , except in very low Zeeman fields, that lead to low sensitivities and sometimes complex second-order spectra, and therefore are impractical to use. To measure low-frequency motion it is preferable to use an rf pulse sequence that aligns the magnetization along an rf field  $B_1$  in the rotating frame (where  $B_1$  is a static field) and watch its time evolution described by  $T_{1\rho}$ , the spin-lattice relaxation time in the rotating frame, that in

analogy to  $T_1$  is sensitive to the rotating frame Larmor frequency  $\gamma B_1$ . Since  $B_1$  is typically 10 G, these frequencies are in the kHz range. This method of measuring low-frequency motion is rather generally applicable. If the internal Hamiltonian that is being modulated leads to a structured spectrum (in absence of motion), then the washing out of the spectral structure when the motion becomes faster than the spectral splittings is another way of probing motion at lower than Larmor frequencies. This latter method is often used to study chemical exchange [2].

### 5. Metals [5,8]

Most characteristic magnetic resonance properties of metals are due to the hyperfine coupling between conduction electron and nuclear magnetic moments. The hyperfine coupling may originate in several ways : coupling to the electron's orbital momentum, similar to Eq. (4), dipole-dipole interaction as in Eq. (5) or the non-classical Fermi contact interaction :

$$\mathcal{H}_F = - \frac{8\pi}{3} \gamma_S \gamma_I \hbar \vec{I} \cdot \vec{S} \delta(\vec{r}_I - \vec{r}_S) \quad (15)$$

which is similar to the  $C\sigma T_{00}$  part of Eq. (6) in the case of "unlike" spins I and S. But the effect of the Hamiltonian (15) on the nuclear magnetic resonance of  $\vec{I}$  is easier to see by considering  $8\pi\gamma_S\gamma_I\hbar/3$  as the constant C in Eq. (7),  $\vec{S} \delta(\vec{r}_I - \vec{r}_S)$  as a quantum mechanical "lattice operator", analogous to  $\vec{R}$ , and  $\vec{I}$  as the operator in nuclear spin space, corresponding to T. The expectation value of the "lattice operator"  $S_0 \delta(\vec{r}_I - \vec{r}_S)$  (that involves a trace over electron spin and space variables for a N-electron system) can be related to the density of states at the Fermi level, and the probability to find the electron at the site of the nucleus. The density of states in turn can be represented by the Pauli susceptibility, and the final result for the Knight shift K is :

$$\frac{\Delta\nu}{\nu} = K = \frac{8\pi}{3} \chi_p |U_{kF}(0)|^2 \quad (16)$$

where Bloch wave functions  $U_k(\vec{r}) \exp(i\vec{k} \cdot \vec{r})$  have been used. Eq. (16) says that this contribution to the Knight shift K is isotropic, nonzero only for

s-electrons, temperature independent, and always positive (in a given field  $B_0$  the metal resonance frequency is higher). It is the prevailing term in simple metals, like the alkalis. In more complicated cases, like the transition metals, the other terms mentioned above play a role, but a more important effect is "core polarization" : an electron belonging to the innermost s-shells (like 1s or 2s) causes a very large hyperfine field, and if the probabilities of spin-up and spin-down are slightly different, a considerable net effect can result. The slight difference is due to the Pauli exclusion principle : the s-shells are very extended in space, and the inner s-electrons have an "exchange" interaction with the outermost, polarized, d-electrons. In NMR of transition metals the exclusion principle makes that the Knight shift due to core polarization is negative : the metal resonance is at lower frequency in constant field. The effect is important e.g. for Pt.

The fluctuating part of the Fermi contact interaction causes a characteristic spin-lattice relaxation, according to Eq. (13). The "lattice correlation function"  $\langle R_{\ell-m}(t) R_{\ell m}(t-\tau) \rangle_L$  now has to be evaluated by quantum mechanics. It describes a spin-flip of the electron, accompanied by a scattering from a wave vector  $\vec{k}$  to a wave vector  $\vec{k}'$  : the difference in Zeeman energy (nuclear plus electronic) is carried away by the difference in kinetic energy of states  $k$  and  $k'$ . The correlation function is resonant ( $\exp i\omega\tau$ ) rather than dissipative ( $\exp -t/\tau_c$ ), but otherwise the standard procedure of  $T_1$ -calculations gives, for the Hamiltonian (15) and a free electron gas :

$$K^2 T_1 T/S = 1 \quad (17)$$

with  $S = \gamma_e^2 \hbar / 4\pi k_B \gamma_n^2$ ,  $K$  is the Knight shift, and  $T$  the temperature. The relation (17) is known as Korringa relation, and its left-hand side as Korringa ratio. The latter turns out to be different from 1 for electronic systems more complicated than the free electron gas. The  $T_1 T = \text{constant}$  is a fairly generally valid result however, and the order of magnitude of  $T_1$  at low temperatures is much smaller in metals than in diamagnetic ionic solids. These two results can be considered typical for the metallic state.

## 6. Ionic Solids [9]

For most nuclei in ionic solids, the quadrupole Hamiltonian, Eq. (2), describes the important properties of the nuclear magnetic resonance. The static part of the field gradient tensor, whose elements are the second partial derivatives of the electric potential at the site of a nucleus, can often be calculated to an excellent approximation by a classical point-charge model. The dynamic part (that may lead to relaxation) is often due to the vibrations of the crystal lattice that modulate the electric field gradient at the site of the nucleus. This coupling between phonons and spins enables a relaxation process whereby a phonon is scattered, and takes the nuclear Zeeman energy with it : the process is often called Raman relaxation. There is a similarity with the relaxation in metals, but since electrons are fermions and phonons are bosons, their occupation number statistics are different, and so are the temperature dependences of the spin-lattice relaxation processes. In the case of Raman relaxation, a high-temperature approximation to a Debye phonon spectrum predicts a spin-lattice relaxation rate proportional to the square of the temperature, but the proportionality constant is hard to evaluate.

## 7. Molecular Solids and Polymers [10]

The most important static effects are chemical shielding and spin-spin coupling, both direct dipolar and indirect. The typical dynamic effect is molecular rotation. A very simple  $^{13}\text{C}$  spectrum of a molecular solid is the powder spectrum of solid benzene, showing axial symmetry (the value of  $\eta$  in Eq. (7) seems to be zero). Since the point symmetry of the carbon site in benzene is known to be lower, one concludes that this is a dynamic effect : the molecules rotate around their hexad axes at a speed larger than the splitting, and the expected fully asymmetric powder pattern is washed out : we observe the component of the shielding perpendicular to the molecule's plane, and the average of the two components in the plane.

An interesting experimental method to collapse such a broad line into a single narrow line at a position determined by the trace of the tensor (the isotropic shift  $\sigma$ ) is to apply a rapid rotation  $\omega_r$  in real space (a mechanical rotation) around a well-defined axis.

Consider an axes system fixed in the rotating powder sample (RP) : in this axes system, the  $R_{\ell m}$  in the Hamiltonian are given by the equivalent of Eq. (8) where the arguments of the  $D_{m',-m}^{\ell}$  are different for each crystallite, but constant in time. Next apply a transformation from the RP axes system to the LAB system :

$$R_{\ell m} (\text{LAB}) = \sum_{m'=-\ell}^{\ell} R_{\ell m'} (\text{RP}) D_{m',m}^{\ell} (\text{rotation}) =$$

$$= \sum_{m'',m'=-\ell}^{\ell} R_{\ell m'} (\text{PAS}) D_{m''m'}^{\ell} (\text{fixed}) D_{m',m}^{\ell} (\text{rotation}) \quad (18)$$

Restriction to secular terms as in Eq. (9) in the LAB system leaves only the  $m = 0$  term. Then the  $m'$  dependence of  $D_{m',m}^{\ell} (\text{rotation})$  introduces the time dependence due to rotation at a speed  $\omega_r$  as factors  $\exp(i m' \omega_r t)$ . If  $\omega_r$  is "sufficiently" high, we observe only time averages : the only term that survives is  $m' = 0$ , so the spectrum is determined by

$$R_{\ell 0} (\text{LAB}) = D_{00}^{\ell} (0, \beta, 0) \sum_{m''=-\ell}^{\ell} R_{\ell 0} (\text{PAS}) D_{m''0}^{\ell} (\text{fixed}) \quad (19)$$

where  $\beta$  is the angle between the axis of rotation and the magnetic field. From the explicit form of  $D_{00}^2$  one finds that the "magic angle" for which  $R_{20} (\text{LAB})$  vanishes for all crystallites in the powder is  $\beta = \arccos(1/\sqrt{3}) \approx 54^\circ$ . This technique has been applied e.g. to the study of  $^{13}\text{C}$  in solid glassy polymers in ref. 11. These authors find that a short  $T_{10}$  for carbons in the main chain of the polymer indicates motions fast enough to lead to plastic flow, thereby dissipating impact energy as heat, without stress concentration, crack formation or brittle failure. As an example of this correlation between microscopic ( $T_{10}$ ) and macroscopic (impact strength) properties, they discuss the effect of annealing on quenched films of poly (ethylene terephthalate). Annealing increases the  $T_{10}$  for the ethylene carbons, and decreases the tensile strength.

8. References

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