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THE DETECTION OF NMR BY NUCLEAR RADIATION

D. A. Shirley

July 1968
I. INTRODUCTION

Recent progress in the detection of NMR in radioactive nuclei through the angular distributions of decay products has stimulated considerable interest in this area of physics. In this summary we describe some of the more important features of the various experiments known collectively as NMR/RD ("Radiative Detection of NMR"). In Section II, NMR/RD is contrasted with conventional NMR, to emphasize their essential differences. Section III gives a sketch of a unified theoretical description of NMR/RD. Experimental results are discussed in Section IV.

II. CONTRASTS WITH CONVENTIONAL NMR

In a conventional NMR experiment an assembly of identical nuclei of spin I is subjected to a time-independent magnetic field \( \vec{H}_0 \), usually taken along the z axis. The interaction

\[
H = -\gamma \vec{H}_0 \cdot \vec{I}
\]

is diagonal in an \( |m\rangle \) representation along this z axis. For any continuous-wave experiment the observables have symmetry about z. Populations of the \( |m\rangle \)
states are made unequal by allowing the system to equilibrate with a heat bath. This population unbalance, which is essential to the detection of NMR, is manifest in the magnetization

\[
\vec{M} = \vec{I}_z \frac{N\mu}{I} \text{Tr} (\rho m) .
\]  

(2)

Here \( N \) is the number of nuclei in the sample, \( \mu \) is the nuclear moment, \( \vec{I}_z \) is the unit vector along \( z \), and \( \rho \) is the density matrix. To detect NMR we drive the system with a radiofrequency field

\[
\vec{H}_0 (t) = 2 \vec{I}_x H_0 \cos \omega t .
\]  

(3)

A change in \( \vec{M} \) is produced which is detected by a macroscopic measurement, showing a Lorentzian variation with \( \omega \). The smallness of \( \mu \) renders conventional NMR a rather insensitive technique: i.e., large numbers of nuclei are required for a successful measurement.

Now let us draw some contrasts between conventional NMR and NMR/RD, to emphasize the ways in which the newer method is really different. We shall examine the above description of conventional NMR and observe the ways in which it would require modification to be applicable to NMR/RD.

First, an assembly of nuclei is not necessary. We may study systems in which only one nucleus at a time is in the nuclear state under study. We should therefore in principle take ensemble averages in the time variable, as well as in other variables, when describing an NMR/RD experiment.

Second, \( \vec{H}_0 \) may not be the most useful axis along which to take an \( |m\rangle \) representation. In many NMR/RD studies a more convenient "natural"
symmetry axis is defined by an accelerator beam direction or by the propagation direction of a preceding radiation.

Third, a continuous-wave experiment need not impose cylindrical symmetry about z on the observables. In some NMR/RD experiments a natural time scale is defined by either a preceding radiation or a beam pulse, and synchronization of $\bar{N}_z(t)$ with this time scale removes the cylindrical symmetry about z: even without synchronization this symmetry only appears for very long-lived states.

Fourth, there are several ways in NMR/RD to create a "population" unbalance among the $|m\rangle$ states. If radioactive nuclei oriented at low temperatures are studied (NMR/ON), the unbalance arises through contact with a heat bath, as in conventional NMR. In nuclear reaction studies (NMR/NR), however, momentum transfer orients the nuclei. Finally, in perturbed angular correlations (NMR/PAC) only those nuclei with suitable orientation are chosen, by detection of the preceding radiation.

For all of these methods a nonzero value of $\bar{M}$ is unnecessary. The nuclei may be only aligned, and not polarized. A succinct description of this situation may be adapted from the field of nuclear orientation. If we expand the density matrix in spherical tensors $\rho^N_\nu$ of rank $\nu$, then $\bar{M}$ is a first-rank tensor: it is proportional to $\rho^0_1$. The generalization of Eq. (2) is

$$\rho^N_\nu = \sum_{nn'} (2\nu + 1)^{1/2} (-1)^{I-m} \binom{I}{m',-m} \binom{I}{\nu} \rho^mm', \tag{4}$$

Fifth, the existence and detection of these higher-rank statistical tensors, with $\nu > 1$ (which are also present in conventional NMR for $I > 1/2$; the triangle conditions require $\nu < 2I$) lead to "multipole structure" in the
lineshapes. For random-phase $H_1(t)$, this structure appears as $v$ peaks in the response function.

Finally, the NMR/RD methods involve detection by microscopic means. A quantum from a single decaying nucleus may be registered as a count. This "nuclear digitization" provides the ultimate sensitivity afforded by nature: it is a limit that macroscopic detection methods can only approach. The NMR/RD methods are at present many orders of magnitude more sensitive than conventional methods.

The three NMR/RD methods are compared with conventional NMR in Table I.

III. THEORETICAL DESCRIPTION OF NMR/RD

Figure 1 shows the vectors necessary to describe an NMR/RD experiment. The vectors are depicted in the rotating frame, and only the component of $H_1(t)$ that is polarized in the correct sense is shown, along the $x''$ axis.

The "effective" field, $H_{\text{eff}}$, is familiar from the NMR literature. The vector $\mathbf{k}_1$ denotes the "natural" symmetry direction set by the conditions of the experiment, and $\mathbf{k}_2$ is the propagation direction of the final radiation, the anisotropy of which is used to detect resonance. Let us first review the three methods of preparing a sample for an NMR/RD experiment.

A. NMR/ON

The first method, low-temperature nuclear orientation, is illustrated in Fig. 2. The NMR/ON method is most similar to conventional NMR. The $H_0$ field provides a quantization axis along which the radioactive nuclei are oriented. Thus $\mathbf{k}_1$ coincides with $H_0$. The angular distribution of radiation with propagation vector $\mathbf{k}_2$ is given by
Table I. Comparison of NMR Techniques.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Conventional NMR</th>
<th>NMR/ON</th>
<th>NMR/NR</th>
<th>NMR/PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of nuclei in sample (a)</td>
<td>(10^{20})</td>
<td>(10^{10})</td>
<td>(10^8)</td>
<td>(10^{10})</td>
</tr>
<tr>
<td>Number present at one time</td>
<td>(10^{20})</td>
<td>(10^{10})</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Symmetry axis</td>
<td>(H_0)</td>
<td>(H_0)</td>
<td>beam direction</td>
<td>(E_{1b})</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>variable</td>
<td>&lt; 1° K</td>
<td>variable</td>
<td>variable</td>
</tr>
<tr>
<td>Spin temperature?</td>
<td>sometimes</td>
<td>sometimes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Detection</td>
<td>macroscopic</td>
<td>microscopic</td>
<td>microscopic</td>
<td>microscopic</td>
</tr>
<tr>
<td>Rank of detected tensor</td>
<td>1</td>
<td>(&gt;1)</td>
<td>(&gt;1)</td>
<td>(&gt;1)</td>
</tr>
</tbody>
</table>

\(a\) These are typical numbers, not lower limits.

\(b\) Direction of preceding radiation.

\(c\) Usually \(>2\).
\[ W(\theta) = 1 + \sum \rho^0_v A_v P_v(\cos \theta') , \] where \( \theta' \) is the angle \((k'_2, H_0')\). The coefficients \( A_v \) are calculated from angular momentum theory. Note that NMR is done on the parent nucleus, and \( \gamma \) rays are observed from the daughter. Reorientation in intermediate states merely change the \( A_v \) values. Usually the parent lifetime \( \tau \) is too long for decay to compete effectively with RF absorption, and \( T_1 \) is the important competing process. There is no "natural" time scale for NMR/ON experiments.

The intensity requirement for resonance is that the nucleus should precess \( \sim 1 \) radian about \( H_1 \) before relaxing or decaying. It is met if

\[ \frac{\gamma H_1}{\hbar} T_1 \geq 1 , \] where \( H_1 \) is the field actually experienced by the nucleus within a frequency range \( \sim 1/T_2 \) of \( \omega_0 \). Often the inhomogeneously-broadened linewidth \( \Gamma \) is much larger than \( 1/T_2 \). Then a large effect can be obtained by frequency modulation over the inhomogeneous-broadening \( \Gamma \). If the applied field is \( H^{\text{app}}_1 \), then \( H_1 = H^{\text{app}}_1 / 2\pi T_2 \Gamma \). Combining with Eq. (6), we then have

\[ \gamma H^{\text{app}}_1 \geq H_1 \Gamma T_2 / T_1 \] as a condition for resonance.
B. NMR/PAC

In perturbed angular correlations (Fig. 3), the nuclear state under study is "prepared" by observing a preceding radiation quantum. The propagation direction of this quantum is $\vec{k}_l$, and the moment of its emission defines $t = 0$ on the natural time scale in which the $\rho^N_v$ evolve. At $t = 0$, $\rho_v$ is symmetrical about $\vec{k}_l$.

The angular dependence of coincidence between two successive radiations is given by

$$W(\theta) = 1 + \sum \frac{F^{(1)}_v F^{(2)}_v}{F^v} P_v(\cos \theta),$$

where $F^{(1)}_v$ depends on the spins and multipolarities of the first transition and $F^{(2)}_v$ on those of the second. The resonance is done in the short-lived intermediate state. Equations (5) and (8) are essentially equivalent, but we have not yet introduced the perturbing effect of $\vec{H}^\text{eff}$ on the intermediate state. In NMR/ON $\vec{k}_l$ was constrained to be along $\vec{I}_z$, but in NMR/PAC many more possibilities exist: $\vec{k}_l$ may be anywhere. The time-evolution of $\vec{k}_l$ is obtained by solving a generalization of the torque equation:

$$\frac{d\vec{k}_l}{dt} = \gamma \vec{k}_l \times \vec{H}^\prime.$$  

We may write $\vec{k}_l$ in place of $\vec{M}$ in the torque equation in this way because $\vec{k}_l$ and $\vec{M}$ transform together. Of course by $\vec{k}_l$ we mean the direction about which $\rho_v$ has cylindrical symmetry, not just the direction of propagation of $\gamma_1$, for which we reserve the notation $\vec{k}_l$; (i.e., $\vec{k}_l(t = 0) = \vec{k}_l$).
Although NMR/PAC is distinguished from NMR/ON by its lack of symmetry about $H_0$ (unless $H_0$ and $K_\perp$ are parallel), there are two limits in every NMR/PAC experiment at which the symmetry of $W(\theta)$ is simple. At $t = 0$, $\rho$ has cylindrical symmetry about $K_\perp$. For $\omega_\perp \tau \to \infty$, $W(\theta)$ has cylindrical symmetry about $H_0$. The time development of $\rho$ for all other cases may be worked out using Eqs. (5) and (9), but with (5) rewritten

$$W(\alpha) = 1 + \sum \rho_v A_v P_v(\cos \alpha),$$  \hspace{1cm} (10)$$

with $\alpha = \angle K_2, K_\perp$. From $t = 0$ onward the PAC and ON methods have a common theory: in both cases we have simply an ensemble of oriented nuclei with $\rho$ symmetrical about a vector $K_\perp$. The vector moves according to (9) and the nuclei emit radiation according to (10). For the (most common) time-integral NMR/PAC situation, we must integrate $\rho_v(t)$ to obtain the time-average value

$$\overline{\rho_v} = \frac{1}{\tau} \int^\infty_0 e^{-t/\tau} \rho_v(t) \, dt ,$$  \hspace{1cm} (11)$$

If the average value was obtained in the laboratory frame, we may write

$$\overline{W(\theta)} = 1 + \sum \overline{\rho_v} F_v Y_v(\theta, \phi),$$  \hspace{1cm} (12)$$

We shall in fact take our averages differently in the next section.

For NMR/ON all experiments are time-integral. We may therefore treat this method as a special case in which the integral is taken from any point in time to $t = \infty$, since $\omega_\perp \tau \gg 1$. 
C. NMR/NN

This method has some similarities to both of those above. Here those partial waves of the incoming beam that have $\ell > 0$ can impart angular momentum to the compound nucleus and from it to an isomeric state of large spin on which a resonance experiment is to be carried out (Fig. 4). Here $\vec{T}$ is oriented perpendicular to the beam direction $\vec{k}_1$: thus the isomeric state is also oriented perpendicular to $\vec{k}_1$. This affects the numerical values of the $p_v$: for $p_2$, for example, the sign is negative rather than positive as in the NMR/NN case. The theory is, however, identical to that outlined above for the other two methods. Pulsed accelerators render the observation of coherent $H_1(t)$ effects relatively straightforward (i.e., $\vec{H}_1$ and $\vec{k}_1$ can be related by a given phase). Both time-differential and time-integral effects may be studied. The angular distribution of radiation is observed with a single detector which plays the role of the $\vec{k}_2$ detector in NMR/PAC.

To summarize, the theoretical description of all three methods may be discussed in two parts. First an ensemble of oriented nuclei is created. This ensemble is described by $\rho_v$. The three methods differ only in the way that $\rho_v$ is created. Next $\rho(t)$ evolves in time as required by the perturbing fields $\vec{H}_0$ and $\vec{H}_1(t)$. Resonance is detected in the frequency dependence of the angular distribution pattern of a subsequently-emitted nuclear quantum. In this part of the process all three methods share a common theory. Let us now turn to a description of that theory.
D. Time Development of $W(\theta)$: Two Approaches

These are two quite distinct ways to calculate resonance curves for NMR/RD experiments. The first way\(^2\) comes directly from angular correlation theory. One transforms $\rho$ from the $\vec{k}_1$ direction to the laboratory frame. Knowing $\rho(t)$ in the laboratory frame, one can then calculate $W(\theta, \phi, t)$

$$W(\theta, t) = 1 + \sum \rho_{\nu}^N(t) F_\nu^N Y_\nu^N(\theta, \phi).$$  \hfill (13)

A somewhat less general version of this calculation, applicable for $\vec{k}_1 \parallel \vec{n}$, may be written out using the "Majorana factors,"\(^3\) $P_{m' m}(t)$, which give the probability that a nucleus in state $m$ at $t = 0$ will be in state $m'$ at time $t$:

$$W(\theta, t) = (2I + 1)^{1/2} \sum F_\nu P_\nu(\cos \theta) (2\nu + 1)^{1/2}$$

$$\times \sum_{m'm} (-1)^{I-m'} \left[ I I k \atop m'-m'0 \right] \rho_{m m}(0) P_{m' m}(t).$$  \hfill (14)

A second way to calculate resonance curves is a generalization of the standard NMR approach. We shall use it here because it offers certain intuitive advantages, especially if one is familiar with NMR theory. We recognize that the $\rho_{\nu}(t)$ are time-independent (except for uniform exponential nuclear decay) if they are taken along $\vec{k}_1$. We have an ensemble of nuclei oriented about a vector that rotates according to Eq. (9). The observables all have symmetry around $\vec{k}_1$: they appear through the products $\rho_{\nu} A_\nu P_\nu(\cos \alpha)$, where

$$\cos \alpha = \vec{k}_1 \cdot \vec{k}_2 / (|\vec{k}_1| \cdot |\vec{k}_2|): \alpha$$ is the instantaneous angle between $\vec{k}_1$ and the $\vec{k}_2$ detector. The Legendre functions are polynomials in $\cos \alpha$. Evaluation of
the resonance curve then consists of working out integrals of the form

\[ \frac{1}{\tau} \int_0^\infty e^{-t/\tau} (\cos \alpha)^m \, dt. \]

The explicit expression for \( \cos \alpha \) is

\[ \cos \alpha = (|\mathbf{E}_1| \cdot |\mathbf{E}_2|)^{-1} \mathbf{E}_2^T \mathbf{R}_1^T \mathbf{R}_2^T \mathbf{R}_3^T \mathbf{R}_2 \mathbf{R}_1 \mathbf{R}_1^T, \] (15)

where \( \mathbf{R}_1, \mathbf{R}_2, \) and \( \mathbf{R}_3 \) are rotation matrices transforming at time zero from the laboratory frame into \( \mathbf{r} \) the rotating frame \( (\mathbf{R}_1) \), from the rotating frame into the "effective field" frame \( \mathbf{r}' \), with \( z'' \) along \( \mathbf{H}_{\text{eff}} \) \( (\mathbf{R}_2) \), and from the \( \mathbf{r}' \) frame into a frame rotating about \( z''(\mathbf{R}_2) \). Note that \( \mathbf{R}_2^T \) and \( \mathbf{R}_1^T \) in (15) are taken in the laboratory frame. This approach applies directly to cases for which the phase, \( \Delta \), between \( \mathbf{H}_1 \) and \( x' \) is fixed. For random-phase cases, one must integrate over \( \Delta \). For \( \Delta = 0, t = 0, \mathbf{R}_1 \) and \( \mathbf{R}_2 \) reduce to identity matrices. The transpose matrices are time-dependent.

E. Some Symmetry Aspects of NMR/RD

The second approach outlined above lends itself to physical arguments. With a knowledge of the functional forms of the Legendre polynomials and a little thought one can easily derive most of the symmetry properties, and even the qualitative frequency dependence of the resonance curves, for any experimental situation. These symmetry properties have been discussed at length elsewhere, and we shall give only a brief summary here. First, however, let us review briefly the symmetry properties of nuclear radiation.
Both electromagnetic and nuclear forces are parity-conserving. Thus only even-rank statistical tensors are normally important in describing the directional distributions of γ rays, α particles, fission fragments, conversion electrons, etc. The circular polarization of those particles that have nonzero spins will, of course, also depend on odd-rank $\rho_\nu$ and $P_\nu$, but we shall not discuss this property. Weak interactions, on the other hand, are parity-nonconserving, and angular distributions of electrons following beta decay will depend on odd $P_\nu$. We note $\vec{M}$ is transformed under rotation as $\rho_1$, and we therefore expect that the $P_1$ terms in NMR/RD theory could be handled by conventional theory (pulsed NMR corresponds to those cases for which $\vec{k}_1$ and $\vec{H}_0$ are not parallel). For $\nu > 1$ additional structure appears with no analog in conventional NMR.

We shall consider both fixed-phase (one value of $\Delta$) and random-phase experiments. The frequency variables are $\omega_0$, $\omega_1$, and $1/\tau$. The quality factor or "sharpness" of a resonance increases both with $\omega_0/\omega_1$ and with $\omega_0 \tau$. We shall choose $(\omega-\omega_0)/\omega_1$ as our frequency variable and we shall parameterize the curves in $\omega_1 \tau$. For $\omega_1 \tau = 1$ the average nucleus precesses one radian about $H_1$ before decay. For $\omega_1 \tau \to 0$ nuclear decay becomes the dominant line-broadening process, while $H_1$ plays this role for $\omega_1 \tau \to \infty$.

The simplest geometry consists of $\vec{k}_1$ and $\vec{k}_2$ along $z$. For this case $\Delta$ is meaningless: the fixed- and random-phase cases are identical. The second-rank tensor response function is given by
where $\theta$ is the angle $(H_{\text{eff}}, z)$ (Fig. 1), and $\omega_e$ is just $\gamma H_{\text{eff}}/h$. $G_2$ is illustrated in Fig. 5.

The curves have two striking features. First, the nuclear orientation cannot be destroyed at resonance, but must take a "hard-core" value. This is a general result for even-rank statistical tensors. The hard-core value is given by

$$ (G_v)_{hc} = \frac{1}{2\pi} \int_0^\pi P_v(\cos \alpha) \, d\alpha, $$

which has the value $P_v(0)^2$, or zero for $v$ odd and $(v!)^2(v!^2)^{1/4}$ for $v$ even. Olsen, Matthias, and Steffen\(^2\) have shown that this equation is more general. Their result may be written

$$ (G_v)_{hc} = [P_v(\cos \theta)]^2, $$

in our notation.

The second striking feature of the curves in Fig. 5 is the complexity of the NMR lines, particularly the multiplicity of minima. We term this property "multipole structure" as it has a purely geometrical origin. There are $v$ minima for a tensor of rank $v$. It is important to understand the purely geometrical origin of multipole structure, because the temptation
might otherwise exist to put forth other explanations. Let us examine the above case from a geometrical point of view. For a given frequency $\omega$, $G_2$ is obtained from the integral of $P_2 = \frac{3}{2} \cos^2 \alpha - \frac{1}{2}$, which has values 1 at $\alpha = 0$ and $-\frac{1}{2}$ at $\alpha = \pi/2$. The average is taken as $\mathbf{K}_1$ precesses about $\mathbf{H}_{\text{eff}}$ (Eq. (1)), starting at $+\mathbf{z}'$ (or $-\mathbf{z}'$). Since $\mathbf{k}_2$ is along $\mathbf{z}'$, the average would be the same in the $\mathbf{r}$ or $\mathbf{r}'$ frame. For $|\omega - \omega_0| >> |\omega_1|$, $\mathbf{H}_{\text{eff}}$ is nearly parallel to $\mathbf{H}_0$ and $P_2$ is averaged around a small circle on a sphere centered at the origin. The circle must of course pass through the axis $\mathbf{z}'$ on the sphere, and $\mathbf{H}_{\text{eff}}$ passes through its center. The angle $\alpha$ has the limits $0 \leq \alpha \leq 2\theta$, $P_2 (\cos \alpha)$ is always near unity, and $G_2 \approx 1$. As $\theta$ increases the circle of integration increases, and for $\theta = \pi/4$ much of its perimeter lies in the equatorial regions of the sphere. There $\alpha \sim \pi/2$, $P_2 < 0$, and $G_2$ decreases to zero. As $\theta$ increases to its "resonance" value $\pi/2$ the circle of integration increases to a great circle, on the sphere, which passes through both poles. Then the equatorial regions have relatively less weight in the integral and $G_2$ increases again to its hard-core value of 1/4 (Eq. (17)). Similar intuitive pictures can be visualized for other geometries. These arguments are illustrated in Fig. 6.

In fixed-phase experiments it is possible to determine the sign of $\gamma_N$ without using a circularly-polarized $\mathbf{H}_1(t)$, provided that the sign of $A_v$ is known. The effect of the sign of $\gamma_N$ on the resonance line is illustrated in Fig. 7. An interesting comparison can be made between this experiment and conventional time-integral PAC measurements. In fact for $\omega = \omega_0$ an NMR/PAC experiment in the geometry of Fig. 7 is entirely equivalent to a time-integral PAC experiment in the rotating frame, with the intermediate state precessing about $\mathbf{H}_1$. At resonance the asymmetry in $G_2$ arising from the sign of $\gamma_N$
is easily shown to be
\[ A_2 = 2 \frac{W(+) - W(-)}{W(+) + W(-)} = -\frac{3\omega_1 \tau A_2 \sin 2\theta_1}{[1 + \frac{1}{4} A_2][1 + (2\omega_1 \tau)^2] + \frac{3}{4} \cos 2\theta_1} \]

This result is obtained by integrating an expression of the form
\[ W(t) = \frac{1}{\tau} [1 + A_2 P_2 \cos (\theta_1 \pm \omega_1 t)] e^{-t/\tau} \]

over \(0 < t < \infty\). Equation (19) is well-known in the theory of perturbed angular correlations. For time-integral PAC experiments \(\theta_1\) is chosen as \(\pi/4\) and the applied field is chosen, where possible, such that \(\omega_1 \tau\) is near \(\pm 1/2\): these are the conditions which maximize \(A_2\). An important feature of Eq. (19) is that \(A_2 \to 0\) as \(\omega_1 \tau \to \infty\). This is a general result, well-known in PAC theory: asymmetries that are sensitive to the sign of \(\gamma_N\) vanish for \(\omega_1 \tau \gg 1\). The result is valid for all geometries and all \(v\). Again the "physical" reason for this is obvious: if the average nucleus precesses many radians before decay the sense of the rotation over which the \(G_2\) average is taken becomes irrelevant.

The curves in Fig. 7 all have even symmetrical about \(\frac{\omega_0}{\omega_1}\): i.e.,
\[ \bar{G}_2(\frac{\omega_0 - \omega}{\omega_1}) = \bar{G}_2(\frac{\omega_0 - \omega}{\omega_1}) \]
For some geometries, with \(\Delta\) fixed, this symmetry is broken and is replaced (for \(v\) even) by
\[ \bar{G}_v(\frac{\omega_0 - \omega}{\omega_1} , \gamma_N > 0) = \bar{G}_v(\frac{\omega_0 - \omega}{\omega_1} , \gamma_N < 0) \]
For \(v\) even this asymmetry is "transient" for all geometries: it disappears for \(\omega_1 \tau \to \pm \infty\), as did the asymmetry in Fig. 7, and \[ \bar{G}_v(\frac{\omega_0 - \omega}{\omega} , \gamma_N) \]
becomes independent of the signs of both of its arguments.
For odd-rank tensors $\overline{g}_v$ can display two types of asymmetry. A transient asymmetry is possible. Like the transient symmetries for $v$ it depends on the signs of $\gamma_N$ and/or $\frac{\omega - \omega_0}{\omega_1}$: like them it also disappears for $\omega_1 \tau \to \pm \infty$. Another, "persistent" asymmetry is found for $v$ odd. This asymmetry depends on the sign of $A_v$ and arises from parity nonconservation. It persists as $\omega_1 \tau \to \infty$, but in this limit contains no information about the sign of $\gamma_N$.

Figures 8 and 9 illustrate lineshapes for $1 \leq v \leq 2$, in some of the simplest geometries, for $\omega_1 \tau \to \infty$. In each case $\Delta$ is either zero or random. $k_1$ and $k_2$ are taken along the Cartesian axes.

F. Multipole Structure in Atomic Spectroscopy

Multipole structure in a resonance line is possible whenever resonance is detected through an observable that transforms as a tensor of rank $v \geq 2$. The angular distribution of (electric dipole) radiation from the $2537 \, \AA$, $6^3\text{P}_1 \to \text{(ground state)}$ transition in atomic mercury has tensor rank $v = 2$, and a $P_2(\cos \theta)$ term should appear in the angular distribution should appear if the $6^3\text{P}_1$ state is oriented. Guichon, Blamont, and Brossel reported multipole structure in magnetic resonance experiments on this state in 1956. Their experiment can be analyzed as a special case of the NMR/RD theory. The level structure is shown in Fig. 10. Similarities to Fig. 3 and 4 are striking. Plane-polarized $\pi$ components of the $2537 \, \AA$ resonance radiation are incident upon the sample. Both $H_0$ and $k_1$ are taken along $z$ and $H_1$ is random in the $x' y'$ plane. Only the $|10\rangle$ state is populated: thus $\rho_2$ is negative. Clearly $\rho_v = 0$ for $v \neq 2$. Magnetic
resonance populates the $|1 \pm 1\rangle$ states. This may be observed either through depolarization of the de-exciting radiation, or through a change in its angular distribution.

IV. RESULTS TO DATE

The NMR/RD field is still in its infancy, and is growing rapidly. Thus we shall emphasize its evolution in this section, by starting with a historical summary. A few qualitative results are mentioned next, and finally experiments to date are listed in tabular form.

A. Historical

Broadly speaking there have been three stages so far in the development of the NMR/RD field. In 1951 Deutsch and Brown used annihilation quanta to detect magnetic resonance in positronium. Two theoretical papers appeared in 1953, in which Bloembergen and Temmer suggested NMR/ON, while Abragam and Pound suggested NMR/PAC, both in a rather general way. These two papers did not lead directly to successful experiments or even, to our knowledge, to very widespread efforts aimed at NMR/RD experiments. The two papers were well-known, however, and only the widely-held (and largely correct) view that the experiments were not feasible in the lattices commonly used for nuclear orientation and PAC studies prevented more experimental efforts.

Between 1957 and 1966 a number of rather elegant experiments in NMR/RD were carried out by several groups. One of these involved NMR/ON, one the Mössbauer Effect and the rest were in the NMR/NR area. These studies seemed to be largely based on special properties of the nuclei studied, such as beta asymmetry in the decay of a ground state, and it was not clear that extension to many
other isotopes was feasible. Again the samples were either in the gas phase or in special lattices (such as LiF) that were compounds of the element under study. These experiments were individually very nice but they did not seem to bring realization of the two 1953 proposals any nearer.

In 1966 and 1967 this picture changed rapidly. After several conventional PAC studies on $^{100}$Rh the Berkeley group realized that this was an ideal case for an NMR/PAC experiment. Once the first resonance (on $^{100}$Rh in nickel) was observed, an NMR/ON resonance quickly followed, on $^{60}$Co in iron. Meanwhile K. Sugimoto and co-workers were extending their NMR/NR studies into metallic hosts. At the Asilomar Conference on Hyperfine Interactions and Nuclear Radiations in August, 1967, an entire session was devoted to NMR/RD studies. All three variants on the method have been carried out in solute atoms in metal lattices, thus ensuring a certain generality of future applications.

Several major questions must be answered before the full potential of NMR/RD can be realized. In fact we need these answers to know what the potentials of the field are. We would like to know in what sample environment NMR/RD is feasible, with special emphasis on cases for which NMR/RD is uniquely suitable. These questions can usually be formulated as "materials problems". A case in point is the matter of NMR in metal single crystals. Several interesting anisotropic effects might be observed in an oriented single crystal if the intrinsic linewidths are sufficiently small and NMR/RD provides the sensitivity to permit observation of a resonance in one crystal. Another possibility is the observation of chemical shifts of NMR in a nucleus that is produced in a nuclear reaction and allowed to find an active site on a macromolecule in solution. Again the high sensitivity of NMR/RD would qualify it uniquely for
this type of study. But first we must learn more about the spin-relaxation process in such samples following nuclear reactions.

B. Some Qualitative Results

The earliest measurements of magnetic resonance (not necessarily nuclear magnetic resonance) by radiative detection yielded fine- and hyperfine-structure intervals and gyromagnetic ratios, for important and rather isolated cases. Now that resonances are being observed in a variety of solids, including metals, solid-state applications are beginning to emerge.

The accuracy now available in NMR/RD can be assessed from the error limits quoted in Table II below. We may alternatively note that Sugimoto et al. have observed a Knight shift of \(-0.067\%\) for \(^{11\text{B}}\text{Pt}\) relative to \(^{11\text{B}}\text{Au}\), or that Matthias et al. reported evidence for a hyperfine anomaly in \(^{100}\text{Rh} - ^{103}\text{Rh} \Delta ^{100} = 3\%\), from comparison or NMR/PAC results on \(^{100}\text{Rh} \text{Fe}\) with the results of spin-echo studies by Kontani and Itoh. Here the accuracy of the comparison was limited by the conventional NMR result.

Considerable efforts have been directed toward NMR/ON studies in single-crystals of ferromagnetic metals in our laboratory. So far the results have been somewhat disappointing. We had hoped for considerably narrower lines in single crystals than in polycrystalline samples. While some improvement is observed it is not very dramatic: factors of 2-5 have been seen in various samples. J. A. Barclay has found qualitative improvement in the \(^{60}\text{Co Ni}\) resonance on going to a single crystal. He found no resonance in a polycrystalline sample and a good one in a single crystal.
Templeton and Shirley\textsuperscript{23} found that relaxation effects could be studied using NMR/ON. Niesen, Lubbers, and Huiskamp\textsuperscript{24} extended the NMR/ON method to dilute paramagnetic crystals and studied both homogeneous and inhomogeneous broadening. Recently Brewer, Shirley, and Templeton\textsuperscript{25} have observed in \textsuperscript{60}Co\textsubscript{Fe} the breakdown of the Korringa approximation \(T_1 = \text{constant}\), valid for metals at high temperatures, in the 10\(^{-2}\) °K region (Fig. 11). Both the Korringa Law and its low-temperature breakdown are direct consequences of the Fermi statistics of conduction electrons: both are expected to occur in all metals, with the low-temperature form \(T_1 = \text{constant}\) applying when the magnetic quantum exceeds the thermal energy: \(\hbar \nu > kT\). To understand this let us review the relaxation process for nuclei in metals. For simplicity we can consider two adjacent nuclear levels. The operator \(A S_+ I_+\) connects them: \(S\) is a (spin or orbital) angular momentum operator for a conduction electron. Nuclei may relax downward in energy via the \(S_+ I_+\) operator or upward via the \(S_- I_-\) operator, but in each case an electronic transition in the opposite direction is also present. Now the electronic part of the process is strongly affected by statistics. At high temperatures the relative probabilities \(W_+\) and \(W_-\) for the upward and downward transitions are nearly equal. If \(\hbar \nu \ll kT\) both \(W_+\) and \(W_-\) vary as the thermal width of the Fermi surface (or as \(kT\)): hence the Korringa relation (Fig. 12).

As \(T\) is lowered the Fermi surface becomes sharp. Both \(W_+\) and \(W_-\) decrease, but \(W_-\) becomes constant, while \(W_+\) goes to zero, as shown Fig. 11. Consequently all relaxation times must approach constancy for \(\hbar \nu \gg kT\). There is a nice analogy between this relaxation problem and the two-level radiation problem. Here the limiting value of \(W_-\) plays the role of
spontaneous emission and the temperature-dependent parts of $W_+$ and $W_-$ correspond respectively to absorption and induced emission. Thermal broadening of the Fermi distribution is the analogue of the radiation field.

C. Numerical Results

Table II contains a summary of the NMR/RD resonances known to the author as of July 1968.

ACKNOWLEDGEMENTS

This survey paper contains several ideas developed in conversation or correspondence with my colleagues in Berkeley and elsewhere. Some unpublished data are also mentioned. This work will be discussed in detail elsewhere. I wish to acknowledge especially the contributions of Mr. J. A. Barclay, Mr. W. D. Brewer, Dr. E. Matthias and Dr. J. E. Templeton.
### Table II. Numerical results of NMR/RD experiments.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Level energy (keV)</th>
<th>Radiation</th>
<th>Host</th>
<th>Type of experiment</th>
<th>Frequency or moment</th>
<th>Ref.</th>
<th>Year</th>
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<tr>
<td>positronium</td>
<td>-</td>
<td>γ</td>
<td>-</td>
<td>-</td>
<td>$E_0/h = 2.052(3)$</td>
<td>6</td>
<td>1952</td>
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<tr>
<td>76 As</td>
<td>-</td>
<td>γ</td>
<td>-</td>
<td>NMR/ON</td>
<td>$\mu = -0.903(5)$ nm</td>
<td>9</td>
<td>1957</td>
</tr>
<tr>
<td>8 Li</td>
<td>-</td>
<td>β</td>
<td>LiF</td>
<td>NMR/NR</td>
<td>$\mu = +1.653(8)$ nm</td>
<td>11</td>
<td>1959</td>
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<tr>
<td>57 Fe</td>
<td>14.4</td>
<td>γ</td>
<td>Fe</td>
<td>NMR/Mössbauer</td>
<td>$\nu = 26$MHz</td>
<td>10</td>
<td>1960</td>
</tr>
<tr>
<td>muonium</td>
<td>-</td>
<td>β</td>
<td>-</td>
<td>-</td>
<td>$E_0/h = 4461.3$ (22)MHz</td>
<td>13</td>
<td>1962</td>
</tr>
<tr>
<td>20 F</td>
<td>-</td>
<td>β</td>
<td>CaF$_2$</td>
<td>NMR/NR</td>
<td>$\mu = +2.094(2)$ nm</td>
<td>12</td>
<td>1963</td>
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<tr>
<td>19 Ne</td>
<td>-</td>
<td>β</td>
<td>gas</td>
<td>NMR/NR</td>
<td>$\mu = -1.886(1)$ nm</td>
<td>14</td>
<td>1963</td>
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<td>17 F</td>
<td>-</td>
<td>β</td>
<td>CaF$_2$</td>
<td>NMR/NR</td>
<td>$\mu = 4.722(12)$ nm</td>
<td>15</td>
<td>1965</td>
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<tr>
<td>100 Rh</td>
<td>74</td>
<td>γ</td>
<td>Ni</td>
<td>NMR/PAC</td>
<td>$\nu_0 = 330$MHz</td>
<td>15</td>
<td>1966</td>
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<td>60 Co</td>
<td>-</td>
<td>γ</td>
<td>Fe</td>
<td>NMR/ON</td>
<td>$\nu_0 = 166$MHz</td>
<td>250</td>
<td>18, 23</td>
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<tr>
<td>54 Mn</td>
<td>-</td>
<td>γ</td>
<td>Fe</td>
<td>NMR/ON</td>
<td>$\mu = 3.302(5)$ nm</td>
<td>200</td>
<td>23</td>
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<tr>
<td>100 Rh</td>
<td>74</td>
<td>γ</td>
<td>Fe</td>
<td>NMR/PAC</td>
<td>$\nu_0 = 882$MHz</td>
<td>200</td>
<td>20</td>
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<tr>
<td>125 Sb</td>
<td>-</td>
<td>γ</td>
<td>Fe</td>
<td>NMR/ON</td>
<td>$\mu = 2.62(6)$ nm</td>
<td>50</td>
<td>26</td>
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<tr>
<td>54 Mn</td>
<td>-</td>
<td>γ</td>
<td>La$_2$Mg$_3$(NO$<em>3$)$</em>{12}$ .24 H$_2$O</td>
<td>NMR/ON</td>
<td>$505.80$, $513.36$, $511.00$, $517.85$MHz</td>
<td>10,000</td>
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<td>Isotope</td>
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<td>Radiation</td>
<td>Host</td>
<td>Type of experiment</td>
<td>Frequency or moment</td>
<td>Q (FWHM)</td>
<td>Ref.</td>
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<td>---------------------</td>
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</tr>
<tr>
<td>$^{12}$B</td>
<td>-</td>
<td>$\beta^-$</td>
<td>Cu, Au, Pt</td>
<td>NMR/NR</td>
<td>$\mu=+1.003(1)$μm</td>
<td>3000</td>
<td>19</td>
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<tr>
<td>$^{12}$N</td>
<td>-</td>
<td>$\beta^+$</td>
<td>Pt</td>
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<td>$\mu=0.457$</td>
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<td>19</td>
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<td>-</td>
<td>$\beta^+$</td>
<td>Ne gas</td>
<td>NMR/ON</td>
<td>$\mu=2.46(8)$μm</td>
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<td>16</td>
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<tr>
<td>$^{8}$Li</td>
<td>-</td>
<td>$\beta^-$</td>
<td>LiF</td>
<td>NMR/NR</td>
<td>(T&lt;sub&gt;1&lt;/sub&gt; studies)</td>
<td>400</td>
<td>27</td>
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<tr>
<td>$^{20}$F</td>
<td>-</td>
<td>$\beta^-$</td>
<td>CaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NMR/NR</td>
<td>(T&lt;sub&gt;1&lt;/sub&gt; studies)</td>
<td>-</td>
<td>27</td>
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<tr>
<td>$^{56}$Co</td>
<td>-</td>
<td>$\gamma$</td>
<td>Fe</td>
<td>NMR/ON</td>
<td>(T&lt;sub&gt;1&lt;/sub&gt; studies)</td>
<td>250</td>
<td>28</td>
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<tr>
<td>$^{60}$Co</td>
<td>-</td>
<td>$\gamma$</td>
<td>Fe</td>
<td>NMR/ON</td>
<td>(T&lt;sub&gt;1&lt;/sub&gt; studies)</td>
<td>250</td>
<td>25</td>
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<tr>
<td>$^{60}$Co</td>
<td>-</td>
<td>$\gamma$</td>
<td>Ni, single crystal</td>
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<td>$\nu=68.58(5)$MHz</td>
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<td>-</td>
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<td>273.1(1)MHz</td>
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<td>$^{198}$Au</td>
<td>-</td>
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<td>Fe</td>
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<td>260.3(1)MHz</td>
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<td>29</td>
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<td>$^{199}$Au</td>
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<td>Fe</td>
<td>NMR/ON</td>
<td>168.0(5)MHz</td>
<td>100</td>
<td>29</td>
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</table>
REFERENCES


2. B. Olsen, E. Matthias, and R. M. Steffen, UUIP-583, Institute of Physics, University of Uppsala (April 1968).


4. Dr. J. E. Templeton worked out this approach. A full account will be published elsewhere.


22. J. A. Barclay, Lawrence Radiation Laboratory, Berkeley (unpublished).


FIGURE CAPTIONS

Fig. 1. Diagram showing the vectors that are basic to all NMR/RD experiments, in the rotating frame. The magnetic-field vectors are familiar from NMR theory. The vectors \( \vec{k}_1 \) and \( \vec{k}_2 \) represent respectively the initial symmetry axis and the propagation direction of radiation. These vectors are shown in their positions at \( t = 0 \). For \( t > 0 \), \( \vec{k}_2 \) is fixed in the laboratory frame, while \( \vec{k}_1 \) obeys the torque equation as discussed in text.

Fig. 2. Typical level scheme for an NMR/ON experiment. Parent cobalt isotope is oriented and resonance transitions occur in this state. Transitions are detected through changes in the angular distribution either of \( \beta^\prime \) or of \( \gamma_2 \). Spin-memory is retained through short-lived intermediate states, though some orientation may be lost because of angular momentum coupling, as indicated in population profiles. In this diagram populations are inverted as indicated if hyperfine-structure constant changes sign from Co to Ni. Only one component of transitions is shown, for clarity.

Fig. 3. Typical level scheme (left), and experimental coincidence arrangement (right) for NMR/PAC experiment. A 0 (dipole) 1 (dipole) 0 cascade is depicted. For the detector-source-detector angle \( \theta = \pi \), and \( \vec{H}_0 \parallel \vec{k}_1 \vec{r}_2 \), only \( \sigma - \sigma \) coincidences are observed and only \( M = \pm 1 \) components of the intermediate state are populated: symmetry of population is a consequence of parity conservation. Note that NMR is done on the intermediate state.
Fig. 4. Energy level scheme for an NMR/NR experiment. Beam particles impart orbital angular momentum, perpendicular to the beam direction, to the system: this appears as an oriented isomeric state. In the case depicted here the orientation is symmetrical, as in NMR/PAC, and NMR is detected in perturbation of the γ-ray anisotropy.

Fig. 5. Time-integral response function for a second-rank tensor with \( \vec{k}_1 \parallel \vec{k}_2 \parallel \vec{H}_0 \). Note multipole structure and hard-core value of \( 1/4 \).

Fig. 6. Left: paths of integration of \( \vec{k}_1(t) \) on a sphere: \( P_2 \) is negative in shaded regions. Right: portion of response function derived from each diagram, in bold line: (a) \( \omega_0 \omega \gg \omega_1 \); (b) \( \omega_0 \omega = \omega_1 \); (c) \( \omega_0 \omega \ll \omega_1 \). Only positive region of \( \frac{\omega_0}{\omega_1} \) is treated: for negative regions \( H_{\text{eff}} \) is below \( x y \) plane.

Fig. 7. Time-integral response function for a second-rank tensor with \( \vec{k}_1 \) along \( \vec{i}_z + \vec{i}_y \), \( \vec{k}_2 \parallel \vec{i}_z \), and \( \Delta = 0 \). Sensitivity to sign of \( \gamma_N \) is exhibited: this sensitivity is maximum for \( |\omega_1 \tau| = 1/2 \): it vanishes as \( (\omega_1 \tau) \) approaches zero or infinity.

Fig. 8. Time-integral response functions for first- and second-rank tensors, with \( \omega_1 \tau = \infty \), and with \( \vec{k}_1 \) and \( \vec{k}_2 \) directions as indicated. Two "random-phase" curves are indicated: for the rest \( \Delta = 0 \).

Fig. 9. Time-integral response functions for third- and fourth-rank tensors, with \( \omega_1 \tau = \infty \), and with \( \vec{k}_1 \) and \( \vec{k}_2 \) directions as indicated. Two "random-phase" curves are indicated: for the rest \( \Delta = 0 \).

Fig. 10. Level scheme for the optical pumping experiment on Hg. Similarities to NMR/PAC and NMR/NR are apparent. Here \( \vec{k}_1 \) is established by the incident beam direction.
Fig. 11. Temperature dependence of relaxation time for $^{60}$Co Fe, showing approach to constancy. Dashed line is Korringa curve: $1/W_+$ and $1/W_-$ are given by upper and middle solid curves.

Fig. 12. Origins of constancy in $T_1$ at low temperatures. Left: for $kT \ll hv$, Fermi statistics of conduction electrons allows only upward electron transitions (top), downward nuclear transitions (bottom).

Right: for $kT \gg hv$ transitions both ways are allowed.
Parent nucleus (e.g., Cobalt)

\[ \tau > T_1 \]

<table>
<thead>
<tr>
<th>I</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
</tr>
</tbody>
</table>

\[ \beta^- \]

\[ \tau < 10^{-9} \text{ sec} \]

\[ \gamma' \]

\[ \tau < 10^{-9} \text{ sec} \]

\[ \gamma_2 \]

Stable

Daughter nucleus (e.g., Nickel)

Population profiles

Fig. 2.
Fig. 3.
Fig. 4.
Fig. 5.
Fig. 6.
Fig. 7.
Fig. 8.
Fig. 9.
\[ W(\theta) \propto \sin^2 \theta \]

\[ W(\theta) \propto 1 + \cos^2 \theta \]

Magnetic resonance transition

\[ M = 1 \quad 0 \quad -1 \]

\[ \text{HgI, } ^1S_0 \quad \text{and} \quad ^3P_1 \]

Fig. 10.
Fig. 11.
Electronic States: $S_+ \text{ only}$

Nuclear Levels: "Spontaneous Emission" only

$kT \ll h\nu$

Fig. 12.

Electronic States: Both $S_+$ and $S_-$

Nuclear Levels: "Induced Emission and Absorption" from thermal broadening of $N(E)$

$kT \gg h\nu$
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