PHYSICAL REVIEW VOLUME 92, NUMBER 4 NOVEMBER 15, 1953

Influence of Electric and Magnetic Fields on Angular Correlations

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(Received June 26, 1953)

The theory of the influence on angular correlations of perturbing interactions in the intermediate state is reformulated to allow the description of the effects of time-dependent as well as of static perturbations. For static interactions of the nuclear electric quadrupole moment with crystalline fields of axial symmetry in polycrystalline sources, attenuation factors are calculated for the coefficients of the various terms in the expansion of the correlation function in Legendre polynomials. No matter how strong the quadrupole interaction, some anisotropy must remain for polycrystalline sources but, for the same interaction in simple single crystals, the anisotropy can be either undisturbed or completely destroyed, depending on the orientation of the crystal. Fields of lower symmetry are shown also to leave, for polycrystalline sources, some anisotropy. Expressions for the influence of randomly fluctuating interactions, such as must exist in liquid sources, are calculated and these predict arbitrarily complete destruction of the correlation under certain conditions, but explain the more nearly unperturbed results usually found with such sources. For electronic shells having magnetic moments, the influences of electronic paramagnetic relaxation and of anisotropy of the hyperfine structure interaction are examined. An applied static magnetic field in the presence of static quadrupole interactions in polycrystalline sources is shown to have differing effects depending on the relative strengths of the two interactions. Application of a magnetic field directed toward a counter cannot reduce the disturbance of the intermediate state in liquid sources, except under special circumstances. The influences of an applied field in the presence of time dependent anisotropic hyperfine structure interactions are discussed. Finally, the feasibility of resonance experiments, for the precise determination of nuclear moments in the intermediate state, is explored.

I. INTRODUCTION

THE theory of the correlation of the directions of emission of a sequence of two particles by radioactive nuclei has been treated extensively in the literature. For references to the literature of that field the review articles by Deutsch[1] and by Frauenfelder[2] are recommended. The conclusions of those treatments are only applicable, as was clearly recognized from the beginning by D. R. Hamilton, if the intermediate state of the nucleus, between the first and second emissions, is completely unperturbed. Many angular correlations observed experimentally are found to depend on the physical and chemical nature of the source. In other examples of angular correlation the experimental results also do not agree with the theoretical predictions based on that simplifying assumption.

The effects of perturbation of the intermediate nucleus by interaction through its magnetic moment with its electronic shell, the interaction responsible for the well-known hyperfine structure in atomic spectra, and also with applied magnetic fields have been analyzed by Goertzel.[3] He showed, for a hyperfine-structure interaction, that only for an extremely short nuclear lifetime τ_N would the correlation be unaffected, and he gave formulas for the calculation of the resulting correlations for longer lifetimes. Alder[4] reformulated and extended that treatment in a way which very clearly displays the influence of the perturbation on the correlation.

The present paper treats the effect of several magnetic and electric perturbing interactions not previously discussed. Particular emphasis is given to the effect of the nuclear electric quadrupole moment of the nucleus in solid and liquid sources. This cause of disturbance has not been given much attention previously. In the course of this study a few brief reports of work along these lines by others have appeared,[2,5,6] including some most conclusive experiments at Zürich on the effect of the quadrupole interaction in a single crystal of indium.[7]

The basic theory of the effect of disturbances in the intermediate state is reformulated in the present paper in a manner that allows its application to both static and time-dependent perturbations. A particular application of the latter type is to the effect of electric quadrupole interactions in liquids. A short section is included describing the possibilities of observing resonant transitions, in the intermediate state, induced by suitable radio-frequency fields.

The possibility is discussed of applying the results of this work to the measuremnt of nuclear magnetic and electric moments. Some of these measurements would be analogs of the experiment of the Zürich group[8] on the magnetic moment of 8×10^{-8} -secCd^{111}.

II. GENERAL

The problem of the perturbation of angular correlations by atomic hyperfine structure, treated by Goertzel,[3] is complicated by the fact that the nuclear spin is coupled to the electron shell which must be considered quantum mechanically. In order to simplify the discussion, we shall first assume that the fields acting on the nuclear spin in the intermediate state

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(but not the nuclear spin itself) can be described classically. This is true, for instance, of applied magnetic fields or, to a very good approximation, of crystalline electric fields which will be our main concern. The coupling of the nuclear spin to the field can be described by a certain Hamiltonian **K**, represented by a $(2I+1)$ by $(2I+1)$ matrix, where I is the spin of the intermediate state. The field partially or completely lifts the $(2I+1)$-fold degeneracy of the intermediate state B.

Goertzel shows the angular correlation to be given by

$$W=S_1S_2\sum_{a,b,b',c}\frac{(a|H_1|b)(b|H_2|c)(c|H_2|b')(b'|H_1|a)}{1-i\tau_N(E_b-E_{b'})/\hbar}. \qquad (1)$$

In this formula, a and c are quantum numbers specifying the different substates of the initial state A and the final state C; $|b)$ and $|b')$ are the eigenstates of the Hamiltonian **K** in the intermediate nuclear state B and E_b and $E_{b'}$ are the corresponding eigenvalues of **K**. The eigenstates $|b)$ can be expressed as linear combinations of the states $|m)$ which are eigenstates of the projection I_z of the nuclear spin along a certain axis $0z$;

$$|b)=\textstyle\sum_m c_{bm}|m). \qquad (2)$$

In Eq. (1), H_1 and H_2 are the Hamiltonians for the emission of the first and second radiation. The symbols S_1 and S_2 indicate summations over the unobserved features of these radiations, such as their polarizations, and τ_N is the exponential lifetime of the intermediate nuclear state.

Goertzel's proof is based essentially on an extension of the Weisskopf-Wigner theory of natural line width. It is a self-consistent theory in the sense that the existence of a nuclear lifetime τ_N is a consequence of the Schrödinger equations describing the evolution of the nucleus as a radiating system. Although straightforward in principle, Goertzel's proof, even simplified by the introduction of the Laplace transform as suggested by Biedenharn and Rose,[9] remains somewhat involved. Also, the domain of applicability of Eq. (1) is somewhat restricted. First, it applies only if the perturbing fields are static. This requires that the nuclear spin in the external field, or, more generally, the quantum-mechanical system formed by the nuclear spin and its surroundings, such as the electronic shell, have stationary energy states. Goertzel's formula makes no provision for the perturbation of the correlation by time-dependent fields such as electric fields that fluctuate due to thermal vibrations or to Brownian motion, in crystals or liquids respectively, or applied rf fields. Second, Eq. (1) cannot be applied directly to the measurement of delayed coincidence rates with finite resolving time.

An expression applying in the above situations and reducing to Goertzel's formula, Eq. (1), in the same domain of validity can be derived simply in the following manner. Let us first assume that no perturbation acts on the nucleus in the intermediate state. The correlation can then be written:

$$W=S_1S_2\sum_{a,c,\beta,\beta'}(a|H_1|\beta)(\beta|H_2|c)(c|H_2|\beta')(\beta'|H_2|a). \qquad (3)$$

Apart from the absence of denominators, Eq. (3) differs from Eq. (1) by the fact that the state vectors $|\beta)$ form an arbitrary complete set in the intermediate state B, whereas in Eq. (1) the $|b)$ represented eigenstates of **K**. Suppose, now, that the second emission takes place at time t exactly (the first emission being taken as the time origin) and that the perturbing Hamiltonian **K**, which may be time-dependent, acts on the nuclear spin during this time t. This can be taken into account by replacing in Eq. (3), the quantities $(\beta|H_2|c)(c|H_2|\beta')$ by $(\beta|\mathbf{U}^+H_2|c)(c|H_2\mathbf{U}|\beta')$, where $\mathbf{U}(t)$ is a unitary operator describing the evolution of a state vector $|\beta')$ during the time t and $\mathbf{U}^+$ is its Hermitian conjugate. The corresponding hypothetical correlation $w(t)$ can be written

$$w(t)=S_1S_2\sum_{a,c,\beta,\beta'}(a|H_1|\beta)(\beta|\mathbf{U}^+H_2|c)\times(c|H_2\mathbf{U}|\beta')(\beta'|H_1|a). \qquad (3')$$

If the perturbing Hamiltonian **K** is time-independent, **U** is simply $\exp(-i\mathbf{K}t/\hbar)$. If **K** depends on t, we can still write symbolically $\mathbf{U}=\exp[-(i/\hbar)\int_0^t\mathbf{K}(t')dt']$, where the integral has to be evaluated according to Feynman's prescriptions on ordered operators.[10]

The second radiation, however, is not emitted t seconds after the first but rather has a probability $\exp(-t/\tau_N)(dt/\tau_N)$ to be emitted between times t and $t+dt$. If all coincidences taking place between t_1 and t_2 are registered, the correlation becomes

$$\begin{aligned}W&=(1/\tau_N)\int_{t_1}^{t_2}e^{-t/\tau_N}w(t)dt\\&=S_1S_2\sum_{a,\beta,\beta',c}(1/\tau_N)\int_{t_1}^{t_2}e^{-t/\tau_N}(a|H_1|\beta)\\&\qquad\times(\beta|\mathbf{U}^+(t)H_2|c)(c|H_2\mathbf{U}(t)|\beta')(\beta'|H_1|a)dt.\end{aligned} \qquad (4)$$

If the Hamiltonian **K** is static, the eigenstates $|b)$ of **K** may be chosen as the state vectors $|\beta)$. Equation (4) can then be written

$$\begin{aligned}W=S_1S_2\sum_{a,b,b',c}(1/\tau_N)\int_{t_1}^{t_2}&e^{-t/\tau_N}\exp[i(E_b-E_{b'})t/\hbar]\\&\times(a|H_1|b)(b|H_2|c)(c|H_2|b')(b'|H_1|a)dt.\end{aligned} \qquad (5)$$

For $t_1=0$ and $t_2=\infty$, Eq. (5) reduces to Eq. (1).

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[9] L. C. Biedenharn and M. E. Rose, Revs. Modern Phys. **25**, 729 (1953).

[10] R. P. Feynman, Phys. Rev. **84**, 108 (1951).

The generalization to a nuclear spin coupled to another quantum mechanical system S surrounding it, such as the electronic shell in an atom or molecule, is straightforward. There the Hamiltonian $\mathbf{K}$ contains variables characterizing the surroundings S as well as the nuclear spin. The hyperfine coupling $a\mathbf{I}\cdot\mathbf{J}$, between nuclear and electronic moments in free atoms provides an example of this situation. Each of the quantum numbers a, b, c, β, and β' in Eqs. (1), (3), (4), and (5) must now be thought of as a set of quantum numbers describing a state of the entire system, atom or molecule, rather than of the nuclear spin alone. An eigenstate $|b)$ of the Hamiltonian $\mathbf{K}$ can be represented by a formula of the type

$$|b)=\sum_{m,n} C_{mn}{}^{b}|m)|n), \tag{6}$$

where m and n are the magnetic quantum numbers specifying nuclear and electronic states, respectively. The coefficients $C_{mn}{}^{b}$ are elements of a unitary matrix that depends on the nature of the problem. In the hyperfine structure interaction of free atoms they are the Clebsch-Gordan coefficients.

From now on, to simplify notations, we shall usually omit summation and average signs and sum over repeated indices.

In order to apply Eq. (1), one must know the energies E_b and the eigenstates $|b)$ of the static Hamiltonian $\mathbf{K}$ defined by Eq. (2) or Eq. (6). This may require the solving of a secular equation in the more complicated cases. The solving of the secular equation can always be avoided if the perturbation introduced by the Hamiltonian $\mathbf{K}$ is small, which, according to Eq. (1), requires that $(E_b-E_{b'})\tau_N/\hbar$ be small compared to unity. If this is true, we can expand the operator $\mathbf{U}=\exp[-(i/\hbar)\mathbf{K}t]$ as

$$\begin{aligned}\mathbf{U}&=\mathcal{E}-(i\mathbf{K}t)/\hbar-\mathbf{K}^2t^2/2\hbar^2+\cdots,\\ \mathbf{U}^{+}&=\mathcal{E}+(i\mathbf{K}t)/\hbar-\mathbf{K}^2t^2/2\hbar^2+\cdots,\end{aligned} \tag{7}$$

where $\mathcal{E}$ is the unit operator. Using only the first-order terms from the expansion, Eq. (4) becomes

$$\begin{aligned}W=W_0-(1/\tau_N)\int_{t_1}^{t_2} te^{-t/\tau_N}dt[(i/\hbar)(a|H_1|\beta)\\ \times(\beta|H_2|c)(c|H_2|\beta'')(\beta''|\mathbf{K}|\beta')(\beta'|H_1|a)\\ +\text{complex conjugate}],\end{aligned}$$

and for $t_1=0$ and $t_2=\infty$,

$$\begin{aligned}W=W_0-(\tau_N/\hbar)[i(\beta''|\mathbf{K}|\beta')(a|H_1|\beta)\\ \times(\beta|\mathrm{H}_2|c)(c|H_2|\beta'')(\beta'|H_1|a)\\ +\text{complex conjugate}],\end{aligned} \tag{8'}$$

where W_0 is the unperturbed correlation. It often happens, and it will be shown to be true for perturbation of the correlation by an electric quadrupole interaction, that the first-order term in τ_N vanishes. Higher order terms in the expansion of Eq. (7) must then be used.

Equation (8′) shows that, when the perturbation is small, it is sufficient to know the matrix elements of the perturbing Hamiltonian in an arbitrary representation and, thus, it is not necessary to diagonalize $\mathbf{K}$.

Alder[4] has given an important reformulation of Eq. (1). He has shown that Eq. (1) can be rewritten as follows:

$$W=\sum_{k_1k_2\mu}\mathrm{I}(k_1)\mathrm{II}(k_2)\mathrm{III}(k_1k_2,\mu)Y_{k_1}{}^{\mu}(\mathbf{\Omega}_1)Y^*{}_{k_2}{}^{\mu}(\mathbf{\Omega}_2). \tag{9}$$

In this formula the $Y_k{}^{\mu}$ are ordinary spherical harmonics, and $\mathbf{\Omega}_1$ and $\mathbf{\Omega}_2$ specify the directions of emission of the first and second radiation. The indices k_1 and k_2 are even integers which obey the inequalities:

$$\begin{aligned}0\leqslant k_1\leqslant 2I,\quad 0\leqslant k_2\leqslant 2I,\\ 0\leqslant k_1\leqslant 2L_1,\quad 0\leqslant k_2\leqslant 2L_2,\end{aligned}$$

where L_1 and L_2 are the highest orders in the multipole expansions of the first and second radiation, respectively. We need not concern ourselves with the exact expressions for the coefficients $\mathrm{I}(k_1)$ and $\mathrm{II}(k_2)$. All we need to know is that they are independent of $\mathbf{K}$. The influence of $\mathbf{K}$ on the correlation is entirely contained in the third coefficient $\mathrm{III}(k_1k_2,\mu)$, for which Alder gives the formula:

$$\begin{aligned}\mathrm{III}(k_1k_2,\mu)=\sum_{m,m'}(Ik_1m'\mu|Ik_1Im)(Ik_2m'\mu|Ik_2Im)\\ \times[1-(i/\hbar)(E_m-E_{m'})\tau_N]^{-1},\end{aligned} \tag{10}$$

where the factors (|) are the Clebsch-Gordon coefficients. If in Eq. (10), $(i/\hbar)(E_m-E_{m'})\tau_N$ can be neglected in comparison with 1, it follows from the properties of the Clebsch-Gordan coefficients that

$$\mathrm{III}(k_1k_2,\mu)=\frac{2I+1}{2k+1}\delta(k_1,k_2).$$

(A slightly different normalization of the coefficients I, II, III which would lead to $\mathrm{III}(k_1k_2,\mu)=\delta(k_1,k_2)$ in the absence of perturbation would have been preferable. However, to avoid any confusion we shall retain Adler's definitions.)

Alder's formulas, Eq. (9) and Eq. (10), are only valid if there exists an axis 0z such that the projection I_z of the nuclear spin on this axis is a good quantum number; that is to say, if the operator I_z commutes with the perturbing Hamiltonian $\mathbf{K}$. These formulas are valid, in particular, if $\mathbf{K}$ represents the coupling of the nuclear magnetic moment to an applied magnetic field or of the nuclear quadrupole moment to an electric field gradient of axial symmetry. The well-known result, that the correlation is unperturbed by such a coupling if either one of the two radiations is emitted along 0z, follows immediately from Eq. (9) and Eq. (10).

We want to extend Alder's formulation to more general perturbations. We first consider the case in which the perturbing field can be described classically. The formula (3′) in which we replace β by m, the value of I_z along an arbitrary axis 0z, can be rewritten:

$$w(t)=(a|H_1|m)(m|\mathbf{U}^{+}|m'')(m''|H_2|c)\times(c|H_2|m''')(m'''|\mathbf{U}|m')(m'|H_1|a). \qquad (11)$$

From Eq. (11) it is easy to show, retracing the steps which led Alder from Eq. (1) to Eq. (9) and Eq. (10), that $w(t)$ can be expressed as:

$$w(t)=\mathrm{I}(k_1)\mathrm{II}(k_2)\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)Y_{k_1}{}^{\mu_1}(\boldsymbol{\Omega}_1)Y_{k_2}{}^{\mu_2*}(\boldsymbol{\Omega}_2), \qquad (12)$$

where $\mathrm{I}(k_1)$ and $\mathrm{II}(k_2)$ are the same as Alder's and $\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)$ is given by:

$$\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)=(Ik_1m'\mu_1|Ik_1Im)\times(Ik_2m'''\mu_2|Ik_2Im'')(m|\mathbf{U}^{+}|m'')(m'''|U|m'). \qquad (13)$$

If the Hamiltonian $\mathbf{K}$ is static and has eigenstates $|b)$ and eigenvalues E_b, the unitary evolution operator $\mathbf{U}$ can be written

$$\mathbf{U}=\textstyle\sum_b|b)(b|\ \exp(-iE_bt/\hbar),$$

and Eq. (12) becomes:

$$\begin{aligned}\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)&=(Ik_1m'\mu_1|Ik_1Im)(Ik_2m'''\mu_2|Ik_2Im'')\\&\quad\times(m|b)(b|m'')(m'''|b')(b'|m')\\&\quad\times\exp[i(E_b-E_{b'})t/\hbar]. \qquad (14)\end{aligned}$$

If all coincidences are registered, the observed correlation W is equal to $\int_0^\infty w(t)e^{-t/\tau_N}dt/\tau_N$ and can be written

$$W=\mathrm{I}(k_1)\mathrm{II}(k_2)\mathrm{III}(k_1k_2,\,\mu_1\mu_2)Y_{k_1}{}^{\mu_1}(\boldsymbol{\Omega}_1)Y_{k_2}{}^{\mu_2*}(\boldsymbol{\Omega}_2), \qquad (15)$$

where

$$\begin{aligned}\mathrm{III}(k_1k_2,\,\mu_1\mu_2)&=(Ik_1m'\mu_1|Ik_1Im)\\&\quad\times(Ik_2m'''\mu_2|Ik_2Im'')(m|b)(b|m'')(m'''|b')\\&\quad\times(b'|m')[1-i(\tau_N/\hbar)(E_b-E_{b'})]^{-1}. \qquad (16)\end{aligned}$$

Among other things, Alder's formula, Eq. (9), differs from the more general formula, Eq. (15), by the fact that in the latter the indices μ_1 and μ_2 of $Y_{k_1}{}^{\mu_1}(\boldsymbol{\Omega}_1)$ and $Y_{k_2}{}^{\mu_2*}(\boldsymbol{\Omega}_2)$ are independent. This is to be expected. If in Eq. (15) we choose the direction to the counter detecting, say, particle one as the 0z axis, only terms with $\mu_1=0$ remain. If μ_2 were equal to μ_1, and thus also zero, as in Eq. (9), only correlations independent of rotations about the z axis could be described by the formulation. This would represent a restriction on the generality of the Hamiltonian $\mathbf{K}$.

When the electronic shell must be described quantum mechanically, the problem is handled by the same methods. The formulas, Eq. (12) and Eq. (15), are still valid but Eq. (13) and Eq. (14) have to be modified as follows:

$$\begin{aligned}\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)&=(Ik_1m'\mu_1|Ik_1Im)(Ik_2m'''\mu_2|Ik_2Im'')\\&\quad\times(mn|\mathbf{U}^{+}|m''p)(m'''p|\mathbf{U}|m'n), \qquad (13')\end{aligned}$$

where n and p are electronic magnetic quantum numbers. In the derivation of Eq. (13′) the assumption has been made that the nuclear transitions leave the electronic shell unaffected, which is equivalent to say that the Hamiltonians H_1 and H_2 responsible for these transitions commute with the electronic variables. If the Hamiltonian $\mathbf{K}$ is static, Eq. (14) must be replaced by

$$\begin{aligned}\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)&=(Ik_1m'\mu_1|Ik_1Im)(Ik_2m'''\mu_2|Ik_2Im'')\\&\quad\times(mn|b)(b|m''p)(m'''p|b')(b'|m'n)\\&\quad\times\exp[(i/\hbar)(E_b-E_{b'})t], \qquad (14')\end{aligned}$$

where the state vectors $|b)$ are eigenstates of $\mathbf{K}$, and coefficients like $(mn|b)$ are the $C_{mn}{}^b$ in Eq. (6).

Equation (16) must be replaced by Eq. (16′):

$$\begin{aligned}\mathrm{III}(k_1k_2,\,\mu_1\mu_2)&=\frac{1}{\tau_N}\int_0^\infty e^{-t/\tau_N}\mathrm{III}(k_1k_2,\,\mu_1\mu_2,\,t)dt\\&=(Ik_1m'\mu_1|Ik_1Im)(Ik_2m'''\mu_2|Ik_2Im'')\\&\quad\times(mn|b)(b|m''p)(m'''p|b')(b'|m'n)\\&\quad\times[1-(i/\hbar)\tau_N(E_b-E_{b'})]^{-1}. \qquad (16')\end{aligned}$$

It has already been pointed out that when $\mathbf{K}$ is the magnetic hyperfine structure, $a\mathbf{I}\cdot\mathbf{J}$, the coefficients $(mn|b)$ are the Clebsch-Gordan coefficients. Racah's summation rules can then be used to bring Eq. (16′) to a closed form leading to Alder's formula, Eq. (33) of reference 4, for a correlation perturbed by isotropic magnetic hyperfine structure. In that case, it follows from the properties of Clebsch-Gordan coefficients that that $\mu_1=\mu_2$ in Eq. (16′). This is natural since there is no privileged direction in space.

III. CRYSTALLINE POWDERS

The description of angular correlations perturbed by a static Hamiltonian $\mathbf{K}$ is greatly simplified if the radioactive source has the behavior of a crystalline powder which is an ensemble of microcrystals oriented at random. Each microcrystal gives a certain correlation W described by Eq. (15) where the directions of emission $\boldsymbol{\Omega}_1$ and $\boldsymbol{\Omega}_2$ are referred to a frame of reference attached to the microcrystal. The observed correlation W is obtained by averaging Eq. (15) over all orientations of the frame of reference. This is obviously equivalent to keeping the frame of reference fixed and averaging over the directions of emissions $\boldsymbol{\Omega}_1$ and $\boldsymbol{\Omega}_2$, keeping constant the angle $\psi=(\boldsymbol{\Omega}_1,\,\boldsymbol{\Omega}_2)$ between the two counters registering the coincidences. From the orthogonality properties of spherical harmonics, it is easily seen that this procedure leads to the disappearance from Eq. (15) of all terms except those for which

$\mu_1=\mu_2=\mu$ and $k_1=k_2=k$. The correlation $\bar{W}$ can then be written:

$$\bar{W}=\sum_k G_k A_k P_k(\cos\psi), \tag{17}$$

where the A_k are the coefficients of the expansion in Legendre polynomials of the unperturbed correlation W_0 and the G_k are attenuation coefficients given by

$$G_k=\frac{1}{(2I+1)}\sum_\mu \mathrm{III}(kk,\,\mu\mu). \tag{18}$$

If instead of the integrated correlation $\bar{W}$ we consider the time dependent expression $w(t)$, defined in Eq. (3′), we can similarly write:

$$w(t)=\sum_k G_k(t) A_k P_k(\cos\psi),$$

where

$$G_k(t)=\frac{1}{2I+1}\sum_\mu \mathrm{III}(kk,\,\mu\mu,\,t). \tag{19}$$

The attenuation coefficients G_k, which contain all the information on the perturbation of the angular correlation, depend only on the intermediate nuclear state but not on the radiative transitions to and from it.

We rewrite below the explicit expressions for the attenuation coefficients G_k, both integrated and time dependent, in the following cases.

(a) The perturbing static field is described classically and has axial symmetry.

$$G_k=\left(\frac{1}{2I+1}\right)\sum_{m,m',\mu}(Ikm'\mu|IkIm)^2 \times\left[1-\frac{i\tau_N}{\hbar}(E_m-E_{m'})\right]^{-1}, \tag{20}$$

$$G_k(t)=\left(\frac{1}{2I+1}\right)\sum_{m,m',\mu}(Ikm'\mu|IkIm)^2 \times\exp[i(E_m-E_{m'})t/\hbar]. \tag{20′}$$

(b) The perturbing static field is described classically but with no restrictions on its symmetry.

$$G_k=\frac{1}{2I+1}(Ikm'\mu|ikIm)(Ikm'''\mu|IkIm'') \times(m|b)(b|m'')(m'''|b')(b'|m') \times\left[1-\frac{i\tau_N}{\hbar}(E_b-E_{b'})\right]^{-1}, \tag{21}$$

$$G_k(t)=\frac{1}{2I+1}(Ikm'\mu|IkIm)(Ikm'''\mu|IkIm'') \times(m|b)(bm'')(m'''|b')(b'|m') \times\exp[i(E_b-E_{b'})t/\hbar]. \tag{21′}$$

(c) There is a quantum-mechanical coupling between the nucleus and the electronic shell.

$$G_k=\frac{1}{(2I+1)r}(Ikm'\mu|IkIm)(Ikm'''\mu|IkIm'') \times(mn|b)(b|m''p)(m'''p|b')(b'|m'n) \times\left[1-\frac{i\tau_N}{\hbar}(E_b-E_{b'})\right]^{-1}, \tag{22}$$

$$G_k(t)=\frac{1}{(2I+1)r}(Ikm'\mu|IkIm)(Ikm'''\mu|IkIm'') \times(mn|b)(b|m''p)(m'''p|b')(b'|m'n) \times\exp[(i/\hbar)(E_b-E_{b'})t]. \tag{22′}$$

In Eqs. (22) and (22′) r is a normalizing factor equal to the number of degrees of freedom of the electronic shell. If the shell has a moment J, $r=2J+1$. From the expressions (20), (21), and (22) it is easy to see that $G_0=1$ and that $G_k\rightarrow 1$ when all the differences $E_m-E_{m'}$ or $E_b-E_{b'}$ tend toward zero.

One interesting feature of the formulas (20), (21), and (22) is that, even when the perturbing Hamiltonian becomes so large or the lifetime τ_N so long that $\tau_N(E_b-E_{b'})/\hbar$ is much larger than unity, the attenuation coefficients G_k with $k>1$ have finite limits or "hard cores" given by the contribution of the terms for which $m=m'$ in Eq. (20) or $b=b'$ in (21) and (22).

The anisotropy of the correlation is never completely wiped out. For instance, for axial symmetry we obtain from Eq. (20) with no degeneracies:

$$G_k(\lim)=\frac{1}{2I+1}\sum_m (Ikmo|IkIm)^2=\frac{1}{2k+1}. \tag{23}$$

This is obviously only a lower limit. If there are degeneracies such that, for some levels, one has $E_m=E_{m'}$ for $m\neq m'$, $G_k(\lim)$ can be larger than $1/(2k+1)$. The existence of such hard cores has already been pointed out by Alder[4] for the case of isotropic magnetic hfs.

It is important to emphasize that the existence of a hard core is subordinated to the following assumptions:

(a) The perturbing interactions are static;
(b) No privileged direction exists in the radioactive source considered as a whole.

If either one of these assumptions is violated, the correlation can be wiped out completely.

IV. STATIC ELECTRIC QUADRUPOLE INTERACTIONS

A. Crystalline Powders

An important example of the effect on the angular correlation of a perturbation describable by Eqs. (20) and (20′) is that of the interaction of the nuclear electric quadrupole moment[11] with an electric field

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[11] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (De Erven F. Bohn N.V., Haarlem, 1936).

having an axis of threefold or higher symmetry in a sample composed of a large number or randomly oriented microcrystals. Such interactions in solids are well known in nuclear magnetic resonance and in pure quadrupole resonance.[12–14] Separations of adjacent levels as high as about 900 Mc/sec have been observed. For example, the levels $m=\pm 5/2$ and $m=\pm 3/2$ of I^{127} in the solid ICN are separated by about 750 Mc/sec. Thus, such a perturbation could be significant even with intermediate nuclear lifetimes as short as 10^{-10} sec. Axially symmetric fields are not the most general kind nor is the method of treatment limited to them, but the calculations are simplest and results can most easily be displayed for such fields. Some features of the results with fields of lower symmetry are discussed in Sec. IV(C). The results discussed here should be directly applicable, for example, for a nucleus in its normal lattice site in a metal of hexagonal crystal structure.

The energy levels specified in terms of the component m of the spin along the axis of symmetry[12] are given by

$$E_m=[eQ(\partial^2V/\partial z^2)/4I(2I-1)][3m^2-I(I+1)]. \quad (24)$$

Using these values in Eq. (20′), the attenuation coefficients $G_k(t)$, for the detection of delayed coincidences, for $1\leqslant I\leqslant 3$ are:

$$I=1:\quad G_2(t)=\tfrac{1}{5}(3+2\cos\omega_0 t), \quad (25)$$

$$I=\tfrac{3}{2}:\quad G_2(t)=\tfrac{1}{5}(1+4\cos\omega_0 t), \quad (26)$$

$$I=2:\begin{cases} G_2(t)=\dfrac{1}{5}\left[\dfrac{13}{7}+\dfrac{2}{7}\cos\omega_0 t+\dfrac{12}{7}\cos3\omega_0 t+\dfrac{8}{7}\cos4\omega_0 t\right], & (27)\\[2ex] G_4(t)=\dfrac{1}{9}\left[\dfrac{29}{7}+\dfrac{12}{7}\cos\omega_0 t+\dfrac{16}{7}\cos3\omega_0 t+\dfrac{6}{7}\cos4\omega_0 t\right]. & (28)\end{cases}$$

$$I=\frac{5}{2}:\begin{cases} G_2(t)=\dfrac{1}{5}\left[1+\dfrac{13}{7}\cos\omega_0+\dfrac{10}{7}\cos2\omega_0 t+\dfrac{5}{7}\cos3\omega_0 t\right], & (29)\\[2ex] G_4(t)=\dfrac{1}{9}\left[1+\dfrac{15}{7}\cos\omega_0 t+\dfrac{18}{7}\cos2\omega_0 t+\dfrac{23}{7}\cos3\omega_0 t\right], & (30)\end{cases}$$

$$I=3:\begin{cases} G_2(t)=\dfrac{1}{5}\left[\dfrac{11}{7}+\dfrac{2}{21}\cos\omega_0 t+\dfrac{5}{7}\cos3\omega_0 t+\dfrac{20}{21}\cos4\omega_0 t+\dfrac{25}{21}\cos5\omega_0 t+\dfrac{10}{21}\cos8\omega_0 t\right], & (31)\\[2ex] G_4(t)=\dfrac{1}{9}\left[\dfrac{17}{7}+\dfrac{30}{77}\cos\omega_0 t+\dfrac{92}{77}\cos3\omega_0 t+\dfrac{6}{77}\cos4\omega_0 t+\dfrac{60}{77}\cos5\omega_0 t+\dfrac{192}{77}\cos8\omega_0 t+\dfrac{126}{77}\cos9\omega_0 t\right], & (32)\\[2ex] G_6(t)=\dfrac{1}{13}\left[5+\dfrac{50}{33}\cos\omega_0 t+\dfrac{23}{11}\cos3\omega_0 t+\dfrac{32}{33}\cos4\omega_0 t+\dfrac{67}{33}\cos5\omega_0 t+\dfrac{34}{33}\cos8\omega_0 t+\dfrac{4}{11}\cos9\omega_0 t\right]. & (33)\end{cases}$$

In these formulas, ω_0 is the angular frequency equivalent to the smallest nonvanishing energy difference or, thus, 2π times the lowest frequency of resonance that could be observed were pure quadrupole resonance practicable. For integer I, or for half-odd integer I, respectively,

$$\omega_0(\text{even})=[\tfrac{3}{4}I(2I-1)][eQ(\partial^2V/\partial z^2)/\hbar], \quad (34)$$

or

$$\omega_0(\text{odd})=[\tfrac{3}{2}I(2I-1)][eQ(\partial^2V/\partial z^2)/\hbar]. \quad (35)$$

The quantity $eQ(\partial^2V/\partial z^2)/\hbar$ is 2π times the frequency $\Delta\nu_Q$ frequently used to describe the electric quadrupole interaction.

As an application of these formulas, an example that would allow the determination of an electric quadrupole interaction may be considered. The $\gamma-\gamma$ cascade of Cd^{111}, following K capture in In^{111}, studied by the Zürich group and others[2] has an angular correlation described by $W(\theta)=1+A_2P_2(\cos\theta)+A_4P_4(\cos\theta)$ with $|A_4|\ll|A_2|$. The intermediate state has I equal to 5/2 and a half-life of 8×10^{-8} sec or $\tau_N=1.2\times10^{-7}$ sec. The ratio of delayed coincidences at 180° to those of same delay at 54°, where P_2 vanishes, should, as a function of the delay time t behave just as $1+A_2G_2(t)$, where $G_2(t)$ is given by Eq. (29), provided that a number of conditions are satisfied. First, all Cd^{111} nuclei must be in closely similar electric fields of axial symmetry. Because a nuclear recoil plus a chemical change accom-

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[12] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[13] R. V. Pound, Progr. Nuclear Phys. **2**, 21 (1952).

[14] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley & Sons, Inc., New York, 1953), Chap. 5.

panies the K capture, it is not safe simply to assume that the symmetry and uniformity pertaining to the indium of the source would apply for the Cd^{111} daughter. However, the beautiful experiment of Albers-Schönberg, Hänni, Heer, Novey, and Scherrer[7] with a single crystal of indium show that, for that lattice, the daughter element does remain in the indium lattice site and, thus, a polycrystalline metallic indium source would satisfy this condition.

The second condition is that ω_0 must not be much smaller than $1/\tau_N$ in order that coincidences be still observable with a delay time as large as $2\pi/\omega_0$. This condition is also satisfied by the indium metal source, as evidenced by the Zürich experiments and those of Steffen,[15] in that the time-integrated correlation is severely perturbed by the crystalline field.

Finally, the resolving time of the coincidence circuits must be much shorter than $2\pi/\omega_0$, or, thus, ω_0 cannot be determined if it is too large. With a resolving time not negligible compared to $2\pi/\omega_0$, some smearing out of the function $G_2(t)$ would result. The function $G_2(t)$, Eq. (29), is plotted in Fig. 1. The time of the first maximum is $2\pi/\omega_0$ or $40\pi/3\Delta\nu_Q$.

From such a measurement the magnitude of the electric quadrupole moment (but not the sign) could be determined if the difficult problem of determining the value of $(\partial^2 V/\partial z^2)$ could be solved. In this respect the problem is less easy for the In^{111} source than for some others because, in spite of remaining at an indium lattice site, the Cd^{111} is both an impurity and in an unknown electronic state. These additional complexities could be avoided by the use of 48-min Cd^{111} in metallic cadmium as a source instead, which has the same intermediate state. Even in the pure metal, however, reliable values for $\partial^2 V/\partial z^2$ are not available.

A more informative example would be an element that has a stable isotope of spin higher than $\frac{1}{2}$. For it, by rf resonance methods, the electric quadrupole interaction of the stable isotope in the same chemical form as used in the source could be determined and, thus, the magnitude of the ratio of the electric quadrupole moments established.

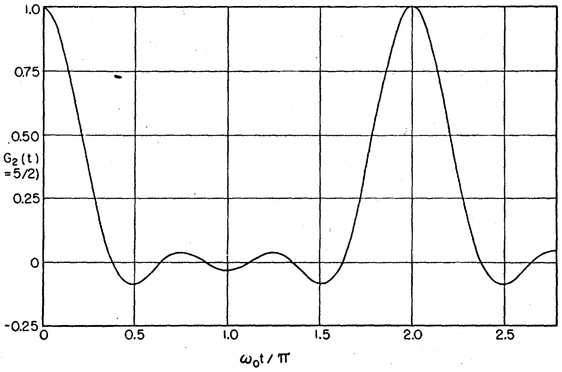

FIG. 1. The attenuation coefficient $G_2(t)$ for $I=5/2$ as a function of $\omega_0 t/\pi$.

TABLE I. Observed frequencies, $\Delta\nu_Q$, of electric quadrupole interactions of stable nuclei in representative compounds.

Nucleus	Compound	$\Delta\nu_Q$, Mc/sec	Reference
D^2	$Li_2SO_4\cdot D_2O$	0.30	a
Li^6	$LiAl(SiO_3)_2$	0.0015	b
Li^7	$LiAl(SiO_3)_2$	0.066	b
B^{11}	$B(CH_3)_3$	4.87	c
N^{14}	ICN	3.39	c
Na^{23}	Na_2NO_3	0.33	d
Al^{27}	Al_2O_3	2.39	d
Cu^{63}	Cu_2O	52	c
As^{75}	As_4O_6	232	c
Br^{79}	Br_2	765	c
Sb^{123}	$SbCl_3$	489	c
I^{127}	ICl	3037	c
Bi^{209}	$Bi(C_6H_5)_3$	669	c

[a] R. V. Pound (unpublished).
[b] N. A. Schuster and G. E. Pake, Phys. Rev. **81**, 157 (1951).
[c] See Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley & Sons, Inc., New York, 1953), Appendix, Table A.6.
[d] See reference 12.

The effect of the static quadrupole interaction, in powdered sources, on angular correlations of the usual type in which the resolving time is longer than τ_N and delays are not used, is given by attenuation factors G_k. These are found from the functions $G_k(t)$ of Eqs. (25)–(33) by replacing all quantities of the form $\cos n\omega_0 t$ by $[1+(n\omega_0\tau_N)^2]^{-1}$. In the limit $\omega_0\tau_N \ll 1$, the attenuation factors approach unity, or the correlation is undisturbed. For $\tau_N = 10^{-7}$ sec, $\Delta\nu_Q$ must, for this, be small compared to 1 Mc/sec. As examples of what might be expected, Table I lists electric quadrupole interactions in solids determined by rf resonance. It is reasonable to assume that the quadrupole moments, and, so, the quadrupole interactions of low-lying excited nuclear levels would be of similar magnitudes. Thus an effect from this interaction must be expected to be present in a large fraction of cases of observation of angular correlations from solid sources.

The situation obtaining in the source for many angular correlation measurements is complicated by recoil of the nucleus in emissions preceding the formation of the intermediate state. For example, in the $\alpha-\gamma$ correlation of radio thorium observed by Battey *et al.*[16] and by Beling *et al.*[17] one cannot ascribe any properties of the symmetry or the chemical bonding of the primary compound to the surroundings of the intermediate nucleus because the recoil energy of approximately 100 kev from the α decay is certainly sufficient to move the nucleus many atomic radii through the lattice. One would, then, expect some dispersion in the values of ω_0 from nucleus to nucleus and, thus, to be able only to observe some average effect. Nevertheless, as reported earlier,[18] application of the appropriate formulas, G_2 and G_4 for $I=2$, to the results

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[15] Rolf M. Steffen, Phys. Rev. **89**, 903 (1953); Phys. Rev. **90**, 1119 (1953).
[16] Battey, Madansky, and Rasetti, Phys. Rev. **89**, 182 (1953).
[17] Beling, Feld, and Halpern, Phys. Rev. **84**, 155 (1951).
[18] A. Abragam and R. V. Pound, Phys. Rev. **89**, 1306 (1953).

shows that a value of $\omega_0\tau_N$ a little larger than unity brings the results into agreement with the 0–2–0 scheme predicted on other grounds for that cascade. Indeed, convincing evidence of the validity of this explanation of the original discrepancy is the consistency of the experimentally determined values $G_2=0.42$ and $G_4=0.50$ with $G_2=0.40$ and $G_4=0.52$ obtained for $\omega_0\tau_N$ taken as 1.8. This test differentiates much more clearly from magnetic perturbations for $I=2$ than it does for half-odd integral spins because, for $I=2$, $G_4>G_2$ for all values of $\omega_0\tau_N$. For other spins the contrasts between the relative attenuations from the two effects are less marked. A value for $\Delta\nu_Q$ of 160 Mc/sec, by no means unreasonably large, is required if τ_N is taken as 1.5×10^{-8} sec.

Extensive studies of the dependence of the correlation on the nature of the source have been made by Aeppli *et al.*[19] and by Steffen[15] for the γ-γ cascade of the Cd^{111} daughter of In^{111}. It seems likely that the ability to obtain a correlation near to the unperturbed one (the anisotropy observed later by the Zürich group with one counter along the hexagonal axis of the single crystal of indium[7] must be considered more completely unperturbed) from a source of In^{111} embedded in metallic silver[19] is a result of the indium, and its cadmium daughter, being situated and remaining in a vacancy of the cubic silver lattice, even though some recoil energy is imparted in the K capture. Consistent with this is the observation that thin films did not give as large anisotropies as thick, which may be the result of the existence of considerable lattice strain in thin films, with consequent departures from cubic symmetry. The retention of the Cd^{111}, with a recoil energy probably smaller than 1.5 volts at a lattice site, or else its capture in a neighboring one, in both a silver and an indium lattice must be considered demonstrated by these experiments.

It is not entirely safe to assume that the quadrupole effect is absent even if the nucleus is known to lie in a cubic lattice at a good lattice site. Studies of nuclear paramagnetic resonance of iodine and bromine in crystals of KI and KBr have revealed that these ions are extremely sensitive to the symmetry of their surroundings.[20] Even in the most perfect single crystals obtainable, lattice strains probably resulting from a certain density of dislocations, cause a mean squared electric quadrupole interaction of many kilocycles. Much larger interactions, perhaps of the order of a megacycle/sec, are found in powders. Metallic ions seem less sensitive to this source of interaction.

The nuclei most likely to be observable in predictable environments would be reasonably long lived isomers from which a γ-γ correlation can be studied. With such nuclei, the chemistry of preparing a source can be performed with the isomer itself, and, unless it is very energetic, the recoil from the first γ emission would be insufficient to break a chemical bond or to displace the nucleus from its lattice site. Furthermore, the electronic shell should remain unexcited for such nuclei for which the γ ray is not internally converted. An n-γ reaction, in a metal, that produces such an isomer could be used directly, although the recoil energy in the (n-γ) reaction could certainly be sufficient to displace the nuclei. Annealing or melting and refreezing the metal should restore the normal metallic lattice. Such a simple remedy may not work for compounds, especially for molecular crystals.

It has already been noted that, even for $\omega_0\tau_N\gg1$, no term in the correlation is completely destroyed by the axially symmetric quadrupole interaction in the polycrystalline source. This means that the mechanism described, if the compounds are truly randomly oriented powders, cannot explain the results of the Zürich group and of Steffen for several solid compounds where the correlation was found to be much smaller than the hard core for G_2.

The attenuations measured for coincidences with resolving times longer than τ_N can, of course, be used to determine $(\omega_0\tau_N)^2$ and, thus, if τ_N is known, $\Delta\nu_Q$. For $\omega_0\tau_N>1$, the functions G_k are nearly reduced to the hard cores and the accuracy of determination of $(\omega_0\tau_N)^2$ is correspondingly poor. For large $\omega_0\tau_N$ the delayed coincidence technique would be much superior if sufficiently short resolving time can be obtained.

The failure of magnetic fields, directed toward a counter, to restore the correlations perturbed by quadrupole interactions can be understood in terms of the discussion in Sec. VI(B).

B. Single Crystals

In discussing the influence of the quadrupole interaction in single crystals, we restrict ourselves for simplicity to cases where all the radioactive nuclei experience fields of threefold or higher symmetry, identical in direction as well as in magnitude. It is evident from Eq. (10) and it has been demonstrated experimentally[7] that, if the axis of symmetry of such a crystal is parallel to the direction of emission of one of the radiations, the correlation is the same as if no quadrupole interaction were present. If the axis of the crystal is perpendicular to the plane of the counters, the correlation can be written

$$W=\textstyle\sum_\mu B_\mu e^{i\mu\psi}, \tag{36}$$

where

$$B_\mu=\mathrm{I}(k_1)\mathrm{II}(k_2)a(k_1,\mu)a^*(k_2,\mu)(Ik_1m'\mu|Ik_1Im)\times(Ik_2m'\mu|Ik_2Im)[1-i\omega_q\tau_N(m^2-m'^2)]^{-1}, \tag{37}$$

and, of course, no summation is made over the index μ. In Eq. (37), the quantities $a(k,\mu)$ are defined by

$$Y_k{}^\mu(0,\psi)=a(k,\mu)e^{i\mu\psi}.$$

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[19] Aeppli, Bishop, Frauenfelder, Walter, and Zünti, Phys. Rev. **82**, 550 (1951).

[20] G. D. Watkins, thesis, Harvard University, 1952 (unpublished); G. D. Watkins and R. V. Pound, Phys. Rev. **89**, 658 (1953).

The quantity ω_q is ω_0, defined by Eq. (34) for integral I and is $(\omega_0/2)$ of Eq. (35) for half-odd integral I.

Interference terms with $k_1 \neq k_2$ exist in Eq. (36). No simple relationship can be established between B_μ and the analogous coefficient b_μ of the unperturbed correlation, given by

$$b_\mu = \mathrm{I}(k)\mathrm{II}(k)|a(k,\mu)|^2(2I+1)/(2k+1). \qquad (38)$$

The situation is more complicated than when the perturbation is entirely caused by a magnetic field since then the terms with $k_1 \neq k_2$ vanish. To interpret the results of an experiment which intends to determine ω_q or $\Delta\nu_Q$ by comparing the experimental values of b_μ and B_μ, the coefficients $I k_1$ and $II k_2$ must be known separately, rather than only through their diagonal product $I_k II_k$ given by a measurement of the unperturbed correlation. In general, this requires an accurate knowledge of the multipole expansion of both the first and the second radiation. The requirement may prove difficult to meet when one of them or both are mixtures of different multipoles. The interference terms disappear, and

$$\frac{B_\mu}{b_\mu} = \frac{2k+1}{2I+1}(Ikm'\mu|IkIm)^2[1 - i\omega_q\tau_N(m^2 - m'^2)]^{-1}, \qquad (39)$$

only when $\mathrm{I}(k_1)$ and $\mathrm{II}(k_2)$ vanish for k_1 and k_2 larger than two. This condition is more restrictive than the requirement that the expansion of the unperturbed correlation contain no harmonics higher than the second. The present condition is satisfied only when the spin I is smaller than two or when both radiations are dipolar. The difficulty of interferences can, of course, always be met by taking averages of correlations measured with different crystalline orientations.

C. Rhombic Fields

We now briefly consider the effects of quadrupole interactions of lower than axial symmetry, limiting ourselves to sources in the form of crystalline powders. The attenuation coefficients G_k are given by Eq. (21). In order to apply that equation we must know the eigenstates and eigenvalues of the general quadrupole interaction, as it is given, for instance, by Eq. (15) of reference 12.

Symmetry considerations somewhat reduce the order of the secular equations to be solved. The maximum order of these equations is $I+\frac{1}{2}$, if I is a half-odd integer, $(I/2)+1$ if I is an even integer, and $(I/2)+(1/2)$ if I is an odd integer.[21] If I is an integer, the $\pm m$ degeneracy of the axial case is lifted but if I is half-odd, an essential so-called Kramers' degeneracy remains. The two degenerate states $|b)$ and $|\bar{b})$ are sometimes called Kramers' conjugate and satisfy the condition

$$(b|m) = (-m|\bar{b}). \qquad (40)$$

For any spin, the only nonvanishing matrix elements of the quadrupole interaction $\mathbf{K}$ are $(m|\mathbf{K}|m)$ and $(m|\mathbf{K}|m\pm 2)$ if one of the principal axes of the electric field is chosen as the z axis.[12,22] As a consequence, if an eigenstate $|b)$ has components along two states $|m)$ and $|m')$, $m-m'$ is even; if two Kramers' conjugate states have components along two states m and m', respectively, $m-m'$ is odd.

Our main interest in considering fields of lower than axial symmetry is to find out whether such interactions could lead to very small values of the hard cores and thereby explain the very small attenuation coefficients G_k observed in some crystalline compounds such as indium chloride.[15,19] The hard core, having been defined as the limit of G_k when the strength of the interaction tends toward infinity, is given, for integral spin where there is no remaining degeneracy, by Eq. (21) taking $b=b'$;

$$G_k(\mathrm{lim}) = \left(\frac{1}{2I+1}\right)(Ikm'\mu|IkIm)(Ikm'''\mu|IkIm'')$$
$$\times (m|b)(b|m'')(m'''|b)(b|m'). \qquad (41)$$

For half-odd integral spins, terms of the form

$$(Ikm'\mu|IkIm)(Ikm'''\mu|IkIm'')$$
$$\times (m|b)(b|m'')(m'''|\bar{b})(\bar{b}|m') \qquad (42)$$

would seem to contribute to $G_k(\mathrm{lim})$. However, to each term of the sum (42) corresponds another term obtained by replacing m by $-m'$, and m' by $-m$. This latter term is equal and opposite to the former because of the properties of the Clebsch-Gordan coefficients. Equation (41) is therefore valid for all I, integral or half-odd integral.

The values of $G_k(\mathrm{lim})$ for a few values of I are given below:

$I=1$; $G_2(\mathrm{lim})=\frac{2}{5}$. It will be remembered that the value of the hard core for an axially symmetric field was $\frac{3}{5}$. Although the degeneracy is completely lifted $G_k(\mathrm{lim})$ does not reach the value $1/(2k+1)$, equal to $\frac{1}{5}$.

$I=\frac{3}{2}$; $G_2(\mathrm{lim})=\frac{1}{5}$. This is the same as for a field of axial symmetry.

$I=2$; $G_2(\mathrm{lim})=G_4(\mathrm{lim})=2/7$. This can also be written 10/35 or 18/63. For axial symmetry $G_2(\mathrm{lim})$ and $G_4(\mathrm{lim})$ were, respectively, 13/35 and 29/63.

$I=5/2$. Here the hard core depends on the amount of the asymmetry which can be characterized by the coefficient η defined in reference 12 or 22. A cubic equation must be solved to find the eigenstates $|b)$ of the quadrupole interaction. For small η, perturbation formulas can be used to determine the states $|b)$ and G_2 is found to be

$$G_2(\mathrm{lim}) = \frac{1}{5} + \frac{1373}{210\times 27}\eta^2 + 0(\eta^4) \simeq \frac{1}{5} + 0.24\eta^2.$$

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[21] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943).

[22] R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

For maximum anisotropy $|\eta|=1$, the cubic secular equation reduces to a quadratic and a linear equation.[22] Thus, for $|\eta|=1$,

$$G_2(\lim)=443/1715\simeq 0.258.$$

It is seen that $G_2(\lim)$ is larger than the value $\frac{1}{5}$ of axial symmetry. An asymmetric field therefore cannot explain the very low values of anisotropy observed in the solid indium compounds.

The following sum rule can be deduced from Eq. (41):

$$\textstyle\sum_k(2k+1)G_k(\lim)=2I+1. \tag{43}$$

In this formula both odd and even k should be counted. However, if I is integral, it follows from the properties of the Clebsch-Gordan coefficients that the quantities $G_k(\lim)$ vanish for odd k. For that case the summation in Eq. (43) can be limited to even k.

D. Free Molecules and Atoms

We now briefly consider the problem when the system producing the inhomogeneous electric in the quadrupole interaction must itself be treated quantum mechanically. This is true for free atoms or molecules and would apply to gaseous radioactive sources. The reason why, in solids or liquids, the pure quadrupole interaction can be treated classically as far as the electronic shell is concerned, is that, there, the orbital degeneracy of the shell is lifted. The shell can still have degrees of freedom connected with spin degeneracy in a solid but the electric field does not depend on these. Classical treatment is not valid in the presence of magnetic hyperfine structure.

The interaction between the nuclear spin I and the gradient of the electric field can be represented by the usual operator,

$$\mathbf{K}=a\frac{3(\mathbf{I}\cdot\mathbf{J})^2+\frac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)}{2J(2J-1)2I(2I-1)},$$

where $\mathbf{J}$ is the angular momentum of the electronic shell of the atom, if the gas is monatomic, or that of the electronic shell plus the rotational moment in a gaseous molecule.

For atoms, where the total angular momentum F is a good quantum number, Goertzel's treatment of the correlation and Alder's formulas (33) and (34) of reference 4 remain valid. There is only a trivial change in the energy differences $E_F-E_{F'}$.

The same statement applies to molecules if $\mathbf{F}=\mathbf{I}+\mathbf{J}$ remains a good quantum number; that is to say, if no other nuclear spins in the molecule are coupled to the moment J. (The magnetic couplings between the different nuclear spins themselves are always much smaller than the quadrupole interaction and can be disregarded.) If this is not the case, the treatment is more complicated. The general formulas, Eqs. (15) and (16′), have to be used.

It is important to point out that these considerations are valid only if the collision time in the gas is so much longer than the nuclear lifetime τ_N that the gas molecules can really be considered as isolated during the decay process. Incidentally, this also applies to Goertzel's treatment of the atomic hyperfine structure.

We have seen that observations of correlations perturbed only by quadrupole interactions do not give the sign of the quadrupole interaction. The sign of the nuclear quadrupole moment is even more important than its magnitude for an understanding of nuclear structure. If a measurement of perturbed correlation in a free atom, where magnetic and quadrupole interaction are both present, could ever be so precise as to detect the departure from the Landé interval rule due to the presence of a quadrupole interaction, the relative sign of the magnetic and quadrupole moments (or the absolute sign of the quadrupole moment if the sign of the magnetic moment is known) could be obtained. Such an experiment seems hardly feasible in the present stage of experimental techniques. A possible suggestion of such an experiment is made in Sec. VII.

V. TIME DEPENDENT ELECTRIC QUADRUPOLE INTERACTIONS

Several experimenters have found that liquid sources, usually aqueous solutions, give much more nearly the expected theoretical correlations than do solid sources of the same chemicals. Steffen has found that molten metallic indium, for the γ-γ scheme following K capture in In^{111}, gives nearly five times the anisotropy of the solid metal.[15] The improved performance of liquid sources has been attributed to rapid disappearance of magnetic electronic states previously invoked to explain the disturbance in solids, or to the smallness of electric fields in liquids. In terms of the effect of the nuclear electric quadrupole moment an explanation that can reveal the limitations as well as the utility of liquid sources can be constructed.

Liquids possess, instantaneously, certain local configurations characteristic of their particular composition not very dissimilar to local configurations in solids. The work of Bernal and Fowler on x-ray diffraction of water,[23] for example, demonstrates that a pseudocrystalline structure exists in the liquid state. On the other hand, it is clear that no given configuration, and so no preferred direction, can exist for very long at the position of any particular constituent of the liquid. The local configuration of a given nucleus, and so any electric quadrupole interaction resulting from it, is in a state of continual change, in a random manner. Particularly significant is the resultant continual reorientation of the direction of the normal axes of the interaction relative to external coordinates. If many uncorrelated directions of the axes occur in the nuclear lifetime τ_N, we can say that the nature of the source

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[23] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933).

imposes no preferred direction at any particular nucleus and the direction of the first particle in the cascade decay can, then, be taken as an axis of quantization of the nuclear spin.

Under this condition, detection of the first decay establishes the probabilities of occupancy of the various intermediate substates relative to the axis to the counter at the instant of the first decay. Then, as usual, the angular correlation function is just the angular distribution of the second decay from such a distribution over the intermediate substates, if they are not disturbed before the second decay. However, because of the Brownian motion and its accompanying fluctuating electric quadrupole interaction, transitions between these substates can result. Eventually, the nucleus must become likely to be found in any one substate with equal probability. Thus, if τ_N were sufficiently long, the second emission would become isotropic and the correlation would be completely destroyed. The mechanism described is the direct analog of that giving rise to thermal equilibrium between spins and the liquid in nuclear paramagnetism. (The corresponding effect is usually far less rapid in solid sources and, in them, it would usually be negligible in any of the lifetimes τ_N we are considering.) Although the effect of the random fluctuations in direction of the axes of the interaction would be to reduce its influence as compared to a static one of the same magnitude, unlike the static effect, no recovery after a time delay and no hard core should exist.

A. Formal Treatment

The time dependent angular correlation $w(t)$ in liquids can be obtained from the general formulas, Eqs. (12) and (13). Choosing as the z axis the direction to the first counter makes μ_1 equal to zero and, accordingly, μ_2 is also zero because there is no other privileged direction associated with the source. Equations (12) and (13) become

$$w(t)=\mathrm{I}(k_1)\mathrm{II}(k_2)\mathrm{III}(k_1k_2,\,00,\,t)Y_{k_1}{}^0(0)Y_{k_2}{}^0(\boldsymbol{\Omega}_2), \tag{44}$$

and

$$\mathrm{III}(k_1k_2,\,00,\,t)=(Ik_1m0|Ik_1Im)\times(Ik_2m'0|Ik_2Im')|(m'|\mathbf{U}(t)|m)|^2, \tag{45}$$

where $|(m'|\mathbf{U}(t)|m)|^2$ is the probability $W_{mm'}(t)$ that if the nucleus were in the state m at $t=0$, it would be in the state m' at the time t. Equations (44) and (45) may also be used to describe the behavior of a crystalline powder. However, in that case it is more convenient to use Eq. (21) where the z axis of quantization is referred to the axes of each microcrystal.

The Hamiltonian $\mathbf{K}$ describing the quadrupole interaction of the nuclear spin with its surroundings can be most generally written

$$\mathbf{K}=\textstyle\sum_\mu T_{2\mu}(X)T_2{}^{\mu*}(I_x,\,I_y,\,I_z), \tag{46}$$

where the functions $T_2{}^\mu$ are tensor operators defined by Racah[24] and the quantities X are parameters describing the local electric field at the nucleus. In accordance with the above model for a liquid, they are randomly fluctuating functions of time.

The ensemble average, taken over all the nuclear sites at a given time, given by

$$G=\langle f(t)f^*(t-\tau)\rangle_{\mathrm{Av}}, \tag{47}$$

we call the correlation function of the random function f.[25] If the ensemble is stationary, this quantity is independent of t and can be written $G(\tau)$. The function $G(\tau)$ can be shown to be a real, positive, even function of τ decreasing to zero with increasing $|\tau|$. For $\tau=0$, $G(0)=\langle|f|^2\rangle_{\mathrm{Av}}$. The Fourier transform of $G(\tau)$,

$$J(\omega)=\int_{-\infty}^{\infty}e^{-i\omega\tau}G(\tau)d\tau, \tag{48}$$

may be termed the spectral density of the random function f. We define somewhat loosely the correlation time τ_c as the time τ such that for $\tau=\tau_c$, $G(\tau)$ is appreciably smaller than $G(0)$. One often assumes

$$G(\tau)=G(0)e^{-|\tau|/\tau_c}. \tag{49}$$

As a consequence of the above assumption of random rotation of the axes of the electric field,

$$\langle T_2{}^\mu(X)T_2{}^{\mu*}\rangle_{\mathrm{Av}}=d^2\delta(\mu,\,\mu'),$$

where the constant d^2 is independent of μ. It then follows from the properties of the tensor operators that

$$\langle(m|\mathbf{K}|m')(m|\mathbf{K}|m'')^*\rangle_{\mathrm{Av}}=b^2\delta(m',\,m'')(I2m'\mu|I2Im)^2. \tag{50}$$

With the usual notations, the constant b^2 is given as

$$b^2=\frac{1}{80}\frac{(I+1)(2I+3)}{I(2I-1)}(eQ)^2\left\langle\left(\frac{\partial^2V}{\partial z'^2}\right)^2\right\rangle_{\mathrm{Av}}, \tag{51}$$

where z' is the direction of largest field gradient in coordinates moving with the fluctuation. The Hamiltonian $\mathbf{K}$ induces transitions between different magnetic substates of the nucleus. According to first-order perturbation theory the probability of transition in a time t from a state m to a state m', for a single spin, is given by

$$W_{mm'}(t)=(1/\hbar^2)\left|\int_0^t K_{mm'}(t')e^{-i\omega_{mm'}t'}dt'\right|^2, \tag{52}$$

where $\omega_{mm'}$ is the angular frequency corresponding to the energy difference between the two states m and m' in the absence of the perturbing random field.

In order to display the properties of the random

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[24] G. Racah, Phys. Rev. **62**, 438 (1942).

[25] See, for example, Ming Chen Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945).

functions $K_{mm}(t')$ we rewrite Eq. (52) as

$$W_{mm'}(t)=(1/\hbar^2)\int_0^t dt'\int_0^t dt''K_{mm'}(t')\times K_{mm'}^*(t'')e^{-i\omega_{mm'}(t'-t'')}. \quad (53)$$

Introducing $t'-t''=\tau$, this can be rewritten as

$$W_{mm'}(t)=(1/\hbar^2)\biggl[\int_0^t d\tau e^{-i\omega_{mm'}\tau}\times\int_\tau^t K_{mm'}(t')K_{mm'}^*(t'-\tau)dt' +\int_{-t}^0 d\tau e^{-i\omega_{mm'}\tau}\times\int_0^{t+\tau} K_{mm'}(t')K_{mm'}^*(t'-\tau)dt'\biggr]. \quad (54)$$

If we take the ensemble average of Eq. (54), we get

$$\langle W_{mm'}(t)\rangle_{\text{Av}}=(1/\hbar^2)\biggl[\int_0^t d\tau e^{-i\omega_{mm'}\tau}(t-\tau)G_{mm'}(\tau) +\int_{-t}^0 d\tau e^{-i\omega_{mm'}\tau}(t+\tau)G_{mm'}(\tau)\biggr], \quad (55)$$

where

$$G_{mm'}(\tau)=\langle K_{mm'}(t')K_{mm'}(t'-\tau)\rangle_{\text{Av}}.$$

Equation (55) is equivalent to

$$\langle W_{mm'}(t)\rangle_{\text{Av}}=(1/\hbar^2)\biggl[t\int_{-t}^t e^{-i\omega_{mm'}\tau}G_{mm'}(\tau)d\tau -2\int_0^t \cos(\omega_{mm'}\tau)\tau G_{mm'}(\tau)d\tau\biggr]. \quad (56)$$

If t is large compared with the correlation time τ_c, the ratio of the two integrals is approximately t/τ_c, and the second can be neglected compared with the first. In the first integral, the integration limits can be replaced by $+$ and $-\infty$. The result is

$$\langle W_{mm'}(t)\rangle_{\text{Av}}=(t/\hbar^2)J(\omega_{mm'}). \quad (57)$$

A transition probability per unit time can be defined as

$$Q_{mm'}=\langle W_{mm'}(t)\rangle_{\text{Av}}/t=(1/\hbar^2)J_{mm'}(\omega_{mm'}). \quad (58)$$

Taking $G(\tau)$ as $G(0)\exp(-|\tau|/\tau_c)$, the result becomes

$$Q_{mm'}=\frac{2\tau_c}{\hbar^2}\frac{G_{mm'}(0)}{1+(\omega_{mm'}\tau_c)^2}=\frac{2\tau_c}{\hbar^2}\frac{\langle|K_{mm'}|^2\rangle_{\text{Av}}}{1+(\omega_{mm'}\tau_c)^2}. \quad (59)$$

Frequently for nonviscous liquids $\omega_{mm'}\tau_c\ll 1$ and

$$Q_{mm'}=(2\tau_c/\hbar^2)\langle|K_{mm'}|^2\rangle_{\text{Av}}. \quad (60)$$

In Eq. (56), for $t\ll\tau_c$, on the other hand, the quantity (τ) in both integrals can be replaced by $G(0)=\langle|K_{mm'}|^2\rangle_{\text{Av}}$. For $\omega_{mm'}=0$, this is precisely the case of the crystalline powder ($\omega_{mm'}$ is the distance between levels m and m' *in the absence* of the quadrupole interaction) which should obviously correspond to an infinitely viscous liquid (long τ_c). Equation (56) gives then

$$\langle W_{mm'}(t)\rangle_{\text{Av}}=(1/\hbar^2)t^2\langle|K_{mm'}|^2\rangle_{\text{Av}}. \quad (61)$$

As a consequence, for times much larger than τ_c but still so small that $\langle|K_{mm'}|^2\rangle t\tau_c/\hbar^2\ll 1$, the time dependent correlation $w(t)$ for a liquid can be obtained by expanding the suitable formulas of Eqs. (25)–(33) as a power series in t and replacing in the first term, which is the square, t^2 by $2t\tau_c$. This is equivalent to replacing $\tau_N{}^2$ by $\tau_N\tau_c$ in the series expansion of the time independent correlation

$$W=\int_0^\infty \exp(-t/\tau_N)w(t)dt/\tau_N,$$

and explains why in many cases liquid sources give better correlations than solids.

For the intermediate situation between Eq. (60) and Eq. (61), when t is neither large nor small compared with τ_c but $\langle|K_{mm'}|^2\rangle_{\text{Av}}t\tau_c/\hbar^2$ is still small, the transition probability is given by the general formula, Eq. (56).

If $\langle W_{mm'}\rangle_{\text{Av}}$, given by $Q_{mm'}$ of Eq. (60) multiplied by t, is not small compared with unity, it is not correct to use that expression for $\langle|(m|\mathbf{U}|m')|^2\rangle_{\text{Av}}$ in Eq. (46). $\langle W_{mm'}\rangle_{\text{Av}}$ must then be calculated as follows. If the probabilities of occupancy of the different states $|m)$ are called $P_m(t)$, these quantities obey the usual differential equations for a relaxation process,

$$\frac{dP_m}{dt}=\sum_{m'=-I}^{I} Q_{mm'}(P_{m'}-P_m), \quad (62)$$

where $Q_{mm'}$ are the transition probabilities per unit time defined in Eqs. (59) and (60). In order for the system of equations described by Eq. (62) to be valid, the condition that $Q_{m'm}\tau_c\ll 1$ must be satisfied. If it is, the passage from the ordinary quantum-mechanical equation for the probability amplitudes C_m,

$$\frac{\hbar}{i}\frac{dC_m}{dt}=\sum_{m'} K_{mm'}e^{-i\omega_{mm'}t}C_m, \quad (63)$$

to Eqs. (62) can be jusified, formally, using arguments analogous to the derivation of Eq. (57) from Eq. (52).

The function $W_{mm'}(t)$ is now defined as the solution $P_{m'}(t)$ of the system, Eqs. (62), corresponding to the initial conditions $P_{m'}(0)=\delta_{mm'}$. From Eqs. (50), (51), and (60) it is found that

$$Q_{mm'}=a(I2m'\mu|I2Im)^2, \quad (64)$$

where

$$a=\frac{\tau_c}{40}\frac{(I+1)(2I+3)}{I(2I-1)}\left(\frac{eQ}{\hbar}\right)^2\left\langle\left(\frac{\partial^2 V}{\partial z'^2}\right)^2\right\rangle_{\mathrm{Av}}. \tag{65}$$

Remembering that $\sum_{m'}(I2m'\mu|I2Im)^2=1$, (62) can be written:

$$\frac{1}{a}\frac{dP_m}{dt}+1=\sum_{m'}(I2m'\mu|I2Im)^2P_{m'}. \tag{66}$$

If the substitution $P_m(t)=P_me^{-\lambda/t}$ is made,

$$(1-\lambda/a)P_m=\sum_{m'}(I2m'\mu|I2Im)^2P_{m'}. \tag{67}$$

Equation (67) is an eigenvalue linear system of the type

$$\mathbf{AX}=\mu\mathbf{X},$$

where $\mathbf{X}$ is a vector with $(2I+1)$ components. The matrix element $A_{mm'}$ is $(I2m'\mu|I2Im)^2$, and the eigenvalue is $\mu=(1-\lambda/a)$.

Using Racah's formula for the reduction of a product of three Clebsch-Gordan coefficients, it can be shown that the $(2I+1)$ eigenvectors $\mathbf{V}^{(k)}$ of Eq. (67) are given by

$$V_m^{(k)}=(Ikm0|IkIm),$$

and the eigenvalues μ_k are

$$\mu_k=(2I+1)W(I2kI/II), \tag{68}$$

where W is the Racah function.

The function $\langle W_{mm'}(t)\rangle_{\mathrm{Av}}$ is then easily seen to become

$$\langle W_{mm'}(t)\rangle_{\mathrm{Av}}=\frac{1}{2I+1}\sum_k(Ikm0|IkIm)(Ikm'0|IkIm')\times(2k+1)e^{-a(\mu_k-1)t}. \tag{69}$$

Equation (69), introduced in Eq. (45), shows that $\mathrm{III}(k_1k_2,00)$ vanishes unless $k_1=k_2$ and

$$\mathrm{III}(kk,0)=\frac{2I+1}{2k+1}e^{-\lambda_kt}, \tag{70}$$

where[26]

$$\lambda_k=a(1-\mu_k)=\frac{3}{80}\left(\frac{eQ}{\hbar}\right)^2\left\langle\left(\frac{\partial^2V}{\partial_{z'}{}^2}\right)^2\right\rangle_{\mathrm{Av}}\times\tau_c\frac{k(k+1)[4I(I+1)-k(k+1)-1]}{I^2(2I-1)^2}. \tag{71}$$

The time-dependent attenuation coefficients are

$$G_k(t)=e^{-\lambda_kt}, \tag{72}$$

and the integrated coefficients are

$$G_k=\int_0^\infty e^{-t/\tau_N}G_k(t)dt/\tau_N=\frac{1}{1+\lambda_k\tau_N}. \tag{73}$$

B. Applications of the Results for Liquids

The foregoing results appear capable of explaining for at least some cases the discrepancies remaining between the angular correlations expected and those observed from liquid sources. As an example, reported briefly previously,[27] the γ-γ correlation of Pd^{106}, following the 2.44-Mev β emission of Rh^{106} shows, from the results of Kraushaar and Goldhaber,[28] relative to a $0-E2\rightarrow2-E2\rightarrow0$ decay scheme, a G_2 of 0.779 and a G_4 of 0.864. The values of the quantity

$$[(eQ)^2\langle(\partial^2V/\partial z'^2)^2\rangle_{\mathrm{Av}}/\hbar^2]\tau_N\tau_c$$

required to give these values of G_2 and G_4 are, respectively, 2.66 and 2.53. The consistency of these two independent determinations of the same quantity seems to be strong evidence for attributing the discrepancy to this cause.

Neither τ_N nor τ_c are known for this example. From nuclear paramagnetism and from Debye's studies of polar liquids, it seems reasonable to take a value of about 10^{-11} sec for the τ_c of water molecules themselves in dilute aqueous solutions at room temperatures. Sufficient information to allow estimates of values for τ_c appropriate to the ions in the solution is not available but it might be supposed that the same 10^{-11} sec applies for the Pd^{106} ion or atom. If the lifetime τ_N is taken as less than 5×10^{-9} sec, then $\Delta\nu_Q'=eQ\langle(\partial^2V/\partial z'^2)^2\rangle_{\mathrm{Av}}^{\frac{1}{2}}/h$ must be larger than 1160 Mc/sec. Any interaction of that scale would, in the solid state, cause attenuation nearly to the "hard core," thus explaining Steffen's failure to observe differences among various solid sources of differing composition.[29] If the nuclear lifetime were only 5×10^{-10} sec, a three times larger $\Delta\nu_Q'$ would be required to explain the liquid results and the remark about solid sources still holds. It should be kept in mind that the Zürich group's ability to obtain an essentially unperturbed correlation from Cd^{111} in thick silver films probably results from the fitting of the parent In^{111} into and retention of the daughter Cd^{111} at a

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[26] The procedure used to calculate the inverse time constants λ_k is a generalization of a procedure that can be used to calculate in liquids the inverses of the well-known relaxation times T_1 and T_2 of nuclear paramagnetism. One, then, is normally concerned with the rate of approach to a Boltzmann distribution over the substates $|m)$ from a distribution initially uniform, because an applied field splits the substates. The procedure used here relates to the inverse process of the disappearance of nonuniform distributions. If ω_L is 2π times the Larmor frequency $g_NH/\hbar$ and if $\omega_L\tau_c\ll1$, $T_1=T_2$ and the value obtained from Eq. (71) by putting $k=1$ is just $(T_1)^{-1}$ or $(T_2)^{-1}$ for nuclei of spin I in a liquid when the relaxation results from fluctuating electric quadrupole interactions. An analogous calculation for relaxation by local, continuously reorienting, magnetic interactions, such as an $\mathbf{I}\cdot\mathbf{J}$ interaction in a tumbling molecule, can easily be made by using 1 for 2 in Eq. (46), Eq. (64), and following, and using $k=1$ for relaxation of magnetic moments or $k=2, 4, \cdots$ for effects on angular correlations. The expression for the paramagnetic relaxation $\lambda_1=(T_1)^{-1}$ derived from Eq. (71) for quadrupole relaxation is identical to that found by R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953), using a different approach.

[27] R. V. Pound and A. Abragam, Phys. Rev. **90**, 903 (1953).

[28] J. J. Kraushaar and M. Goldhaber, Phys. Rev. **89**, 1081 (1953).

[29] R. M. Steffen, Phys. Rev. **86**, 632 (1952).

normal lattice site of the cubic silver lattice. That evidence is not sufficient to allow the inference that other "double stream" metal sources would have similar qualities in general, independently of the nature and energy of the decay from parent to daughter and of the chemistry of the three metal atoms involved. Relevant to the difference is the fact that the Cd^{111} nucleus has much smaller recoil energy than that of Pd^{106}.

As to the magnitude of $\Delta\nu_Q'$, probably greater than 1160 Mc/sec, the value of 2500 Mc/sec for $\Delta\nu_Q$ for I^{127} with a single pure p bond may be compared.[30] The electronic state of the Pd^{106} is not known but it is unlikely that $\langle(\partial^2V/\partial z'^2)^2\rangle_{\mathrm{Av}}^{\frac{1}{2}}$ is as large as that of the p electron in iodine. Thus it seems likely that the magnitude of Q is at least as large as 0.2×10^{-24} cm^2.

If the magnitude of the electric quadrupole interaction is such that $2\pi\Delta\nu_Q'\tau_c\gg1$, in spite of limitations on the realm of validity of the quantitative formulas, the behavior of the factors G_k as functions of τ_c can be seen qualitatively on physical grounds. They start from unity and decrease toward zero as τ_c increases from zero since λ_k is proportional to τ_c. For τ_c of the order of magnitude of τ_N, the values of the G_k begin to rise again and approach the "hard core" values of the static quadrupole interaction as τ_c becomes large compared to τ_N because the liquid is then indistinguishable from a crystalline solid except, perhaps, with respect to the uniformity of the magnitudes of the interactions.

Measurement of the attenuation factors G_k for liquid sources can be seen to allow determination of $\Delta\nu_Q'(\tau_N\tau_c)^{\frac{1}{2}}$. If τ_N is known, a determination of τ_c would result in evaluation of $\Delta\nu_Q'$. Some information on τ_c can be found from studies of nuclear paramagnetic resonance of stable isotopes in similar solutions or liquids because of the analogy between the mechanism causing the attenuation G_k and that producing the line width and the thermal equilibrium in paramagnetic resonance. This comparison could be safely made only for γ-γ cascades not immediately preceded by a chemical change like that accompanying K capture or α or β emission, because the chemical behavior must be known to be identical for the isotopes compared in the two experiments. If a stable isotope of known quadrupole moment is available for the comparison, a direct elimination of τ_c and $\langle(\partial^2V/\partial z'^2)^2\rangle_{\mathrm{Av}}^{\frac{1}{2}}$ can be made to obtain the ratio of the magnitudes of the quadrupole moments of the short-lived intermediate isomer and of the stable nucleus. Unfortunately the scale of effects that make the attenuation coefficients G_k appreciably less than unity is such as to make the paramagnetic resonance very difficult to detect unless either τ_N is quite large or the quadrupole moment of the isomer is much larger than that of the stable isotope.

The result to be expected from the application of a static magnetic field to liquid sources that show some attenuation because of the rapidly fluctuating electric quadrupole interaction can now easily be seen. The description of the behavior of an ensemble of spins in the presence of a static applied field is frequently much simplified if it is considered relative to a system of coordinates that rotates about its z axis, taken parallel to the direction of the applied field, with the angular velocity of Larmor precession $\omega_L=g_NH_0/\hbar$, where g_N is the nuclear gyromagnetic ratio. With respect to the rotating coordinates the field H_0 can be ignored and any other interactions present must be suitably transformed. The rapidly fluctuating electric fields that act on the nucleus through its quadrupole moment, with respect to the rotating coordinates, appear essentially unchanged provided that the frequencies characteristic of them, measured by $1/\tau_c$, are large compared to ω_L, or, thus, $\omega_L\tau_c\ll1$. This restriction is analogous to the earlier one $\omega_{mm'}\tau_c\ll1$. For ordinary nuclear magnetic moments and fields up to 20 kilogauss this condition is satisfied for $\tau_c<10^{-9}$ sec. This approach shows in a simple way that a field applied along the direction to a counter can have no influence on the attenuations of the correlations, so long $\omega_L\tau_c\ll1$, because the correlation is independent of rotation about that direction. For a magnetic field applied normal to the plane of the counters, the correlation function becomes

$$w(\theta,t)=1+\textstyle\sum_k G_k(t)A_kP_k[\cos(\theta-\omega_Lt)],\qquad(74)$$

where $G_k(t)$ is given in Eq. (72).

If the coincidence rate at, say, 180° is observed as a function of a variable time delay with a small resolving time compared to $1/\omega_L$, and multiplied by $\exp(t/\tau_N)$, the result $w(180,t)$ is an oscillating function of time with the fundamental frequency $2\omega_L$, just as in the absence of a quadrupole interaction, but the various harmonics of the fundamental frequency are damped. The damping factor of each harmonic k is a linear combination of terms $\exp(-\lambda_{k'}t)$ with $k'\geqslant k$. On the other hand, for observation of the coincidence rates without time delay and with resolving times greater than τ_N, as in the usual experiments, the interpretation is more complicated.

If, however, only A_2 is significant a rather simple result obtains. In that case $w(\theta,t)$ can be written

$$w(\theta,t)=1+\tfrac{1}{4}A_2e^{-\lambda_2t}+\tfrac{3}{4}A_2e^{-\lambda_2t}\cos[2(\theta-\omega_Lt)].\qquad(75)$$

The correlation integrated over all nuclear lifetimes is obtained as before as

$$W(\theta)=\int_0^\infty w(\theta,t)e^{-t/\tau_N}dt/\tau_N,$$

which gives

$$W(\theta)=1+\frac{A_2}{2(1+\lambda_2\tau_N)}+\frac{3A_2}{4(1+\lambda_2\tau_N)}\times\frac{\cos(2\theta)+[2\omega_L\tau_N/(1+\lambda_2\tau_N)]\sin(2\theta)}{1+[2\omega_L\tau_N/(1+\lambda_2\tau_N)]^2}\qquad(76)$$

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[30] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

if the two counters distinguish between the first and second radiations. It is interesting to note that, without independent knowledge of A_2 or of λ_2, the correlation might be considered unperturbed and the quantity $A_2'=A_2/(1+\lambda_2\tau_N)$ would be mistaken for A_2. In that event the effect of the field, measured by the quantity $[2\omega_L\tau_N/(1+\lambda_2\tau_N)]$ would be mistaken for the quantity $2\omega_L\tau_N$. Thus the Larmor frequency would be mistaken for $\omega_L A_2'/A_2$. For this example, then, an error identical to that in the coefficient A_2 itself would be made in the nuclear magnetic moment so measured. The argument also holds if the counters do not distinguish between the two decays.

VI. ANGULAR CORRELATIONS PERTURBED BY MAGNETIC FIELDS

The influence of an applied magnetic field on angular correlations has been considered by Goertzel[3] and by Alder.[4] Alder's treatment assumed that the coupling of the nuclear spin to the applied field is the only perturbation present. Because of the frequent presence of quadrupole interactions, often much larger than the magnetic coupling, this assumption is fulfilled only under special circumstances. For moderately large nuclear quadrupole moments the quadrupole coupling could be ignored only when it is greatly reduced by either cubic symmetry of the crystal structure in solids or by Brownian motion in liquids. The influence of applied fields in liquid sources has been considered in Sec. V(B).

A. The Quadrupole Coupling Small Compared to the Magnetic

In solids, when the quadrupole interaction is much smaller than the coupling of the nuclear magnetic moment to the applied field, it can be treated using first order perturbation theory, i.e., taking into account the small changes, due to the quadrupole coupling, in the eigenvalues of the magnetic coupling but neglecting the changes in the eigenvectors.

If the direction of the applied field is chosen as the axis of quantization, the correlation can be written

$$W=\mathrm{I}(k_1)\mathrm{II}(k_2)Y_{k_1}{}^{\mu}(\mathbf{\Omega}_1)Y_{k_2}{}^{\mu *}(\mathbf{\Omega}_2)\times(Ik_1m'\mu|Ik_1Im)(Ik_2m'\mu|Ik_2Im)\times\frac{1}{1-i\mu\omega_L\tau_N-i(m^2-m'^2)\omega_q\tau_N\cos^2\delta},\qquad(77)$$

where ω_q is ω_0 of Eq. (34) for integral spins and $\omega_0/2$ of Eq. (35) for half-odd integral spins. In Eq. (77), δ is the angle of the axis of symmetry of the crystalline field with respect to the direction of the magnetic field and ω_L is 2π times the Larmor frequency of the nuclear magnetic moment in the applied field. We can rewrite the denominator of Eq. (77) as

$$[1-i\mu\omega_L\tau_N]\left[1-\frac{i(m^2-m'^2)\omega_q\tau_N\cos^2\delta}{1-i\mu\omega_L\tau_N}\right],\qquad(78)$$

and expand W as a power series of $\omega_q\tau_N$. In this series the interpretation of terms in $(\omega_q\tau_N)^p$ with $p>0$ is complicated because they contain interference terms with $k_1\neq k_2$, which do not exist either in the unperturbed theoretical correlation or, if the substance is a powder, in the zero field correlation perturbed by the quadrupole interaction only.

When $\mu\omega_L\tau_N$ becomes significantly larger than unity, we take the second bracket equal to 1, remembering that $\omega_q\ll\omega_L$, and the correlation perturbed by both the magnetic field and the quadrupole interaction is the same as if the latter did not exist. As a consequence, if the field is perpendicular to the plane of the counters and the correlation is expanded as

$$W=\textstyle\sum_k B_k e^{ik\phi},\qquad(79)$$

the coefficients B_k are given by

$$B_k=b_k/(1-ik\omega_L\tau_N).\qquad(80)$$

Here b_k is the corresponding coefficient in the completely unperturbed correlation, rather than the one which is observed in zero magnetic field where an effect by the quadrupole interaction is present. The simplified view that it is the coefficients b_k' in the expansion analogous to Eq. (79) for the correlation in zero field, rather than the completely unperturbed coefficients b_k, which are reduced by the factors $[1-ik\omega_L\omega_N]^{-1}$ leads to a nuclear magnetic moment in error by a factor b_k'/b_k for $(b_k-b_k')/b_k\ll 1$. This error is reduced to $(b_k'/b_k)^{\frac{1}{2}}$ if the counters do not distinguish between the two radiations. In Cd^{111}, if we regard the anisotropy of, say, 0.23, as observed by the Zurich group,[7] in experiments on a single crystal of indium metal, as completely unperturbed, a value for the magnetic moment obtained by assuming that the unperturbed anisotropy is 0.20,[8] should be increased by about 7 percent. This last statement applies only if the value of the magnetic moment has been extracted from the measurement of magnetic fields so strong that $(2\omega_L\tau_N)^2$ is much larger than unity.

B. The Quadrupole Coupling Large Compared to the Magnetic

When the quadrupole interaction is much larger than the applied field, we consider the latter as a perturbation and choose the axis of the crystal as axis of quantization. The correlation can be written with the same notation as Eq. (77).

$$W=\mathrm{I}(k_1)\mathrm{II}(k_2)Y_{k_1}{}^{\mu}(\mathbf{\Omega}_1)Y_{k_2}{}^{\mu *}(\mathbf{\Omega}_2)\times(Ik_1m'\mu|Ik_1Im)(Ik_2m'\mu|Ik_2Im)\times\frac{1}{1-i\omega_q(m^2-m'^2)\tau_N-i\omega_L\mu\cos\delta}.\qquad(81)$$

In writing Eq. (81) we have again assumed that the small perturbation, in this case the magnetic field, changes only the eigenvalues but not the eigenvectors of the principal Hamiltonian which is now the quadrupole interaction, and that I_z quantized along the axis of the crystal, remains a good quantum number. This assumption may be questioned since, in the quadrupole interaction, the states $\pm m$ are degenerate and may not be the right zero-order states in a perturbation by a magnetic field making an angle with the quadrupole axis. Since the magnetic coupling $g_N\mathbf{H}\cdot\mathbf{I}$ has only matrix elements $\Delta m=0, \pm1$, the question only arises for the states $m=\pm\frac{1}{2}$ of half-odd integral spins. It is well known that there the right zero-order states are two linear combinations, $|b)$ and $|b')$, of the $\pm\frac{1}{2}$ states with coefficients depending on the angle δ. The more general formula, Eq. (16), must be used to calculate the contribution of these states but it is easy to show that, because of the properties of the Clebsch-Gordan coefficients, the contribution of the states $|b)$ and $|b')$ to W in Eq. (16) is the same as if the magnetic field did not exist. Equation (81) can therefore be used quite generally. We can rewrite the denominator of Eq. (81) as

$$[1-i\omega_q(m^2-m'^2)\tau_N]\left[1-\frac{i\omega_L\tau_N\mu\cos\delta}{1-i\omega_q(m^2-m'^2)\tau_N}\right],$$

and expand W as a power series of $\omega_L\tau_N$. If the source is a powder and if the quadrupole interaction is so strong, or the lifetime so long, that $\omega_q\tau_N\gg1$ and the correlation in zero magnetic field is reduced to its minimum value or "hard core," Eq. (81) shows that the effect of the magnetic field is greatly reduced except for the terms $m^2=m'^2$, $\mu\neq0$, i.e., for $m=-m'$. The situation is different depending on whether the nuclear spin I is integral or not. If it is not integral the Clebsch-Gordan coefficients $(Ik;-m,2m|IkIm)$ vanish and the hard core is practically unaffected by the applied field. On the other hand, for integral spins, these coefficients do not vanish and the magnetic field may change the angular correlation appreciably. If the magnetic field is so strong that $\omega_L\tau_N$, although still much smaller than $\omega_q\tau_N$, is much larger than unity, the only terms which give an appreciable contribution to Eq. (81) are those for which $m=m'$, except if $\cos\delta$ is so small that $\omega_L\tau_N\cos\delta$ is not much larger than one. If $\omega_L\tau_N$ is sufficiently large, the proportion of microcrystals in a powder for which this is true is small and their contribution to the average correlation $\bar{W}$ may be neglected. Then $\bar{W}$ becomes

$$\bar{W}=\sum\frac{1}{2k+1}A_kP_k(\cos\psi),$$

where the A_k are the coefficients of the completely unperturbed correlation. This result is independent of the direction of the magnetic field with respect to the counters.

C. The Quadrupole and the Magnetic Couplings of Comparable Strength

Finally, when the coupling to the applied magnetic field and the quadrupole interaction are of comparable magnitude, the treatment becomes complicated and the general formulas, Eqs. (15) and (16), have to be used. These are used after the secular equation, giving the eigenvectors and the eigenvalues of the Hamiltonian $\mathbf{K}$, the sum of the magnetic and electric couplings, has been solved. This must be done numerically except in special cases.[22] As already mentioned in Sec. II, there is no need to solve the secular equation if the correlation is only little perturbed because of short nuclear lifetime or because both the quadrupole and the magnetic couplings are small.

If the source is a crystalline powder, the simplified treatment of Sec. III cannot be applied since the perturbing Hamiltonian is different for two microcrystals differently oriented with respect to the applied magnetic field. The correlation has to be calculated by the general formulas, Eqs. (15) and (16) and averaged over the orientations of the microcrystals, taking into account the angular dependence of the energy levels E_b themselves. Until the results of a specific experiment can be discussed there seems little to be gained by going beyond these general considerations in this complicated case.

D. Static, Anisotropic Magnetic Hyperfine Structure

The perturbation by an atomic magnetic hyperfine structure has been discussed by Goertzel[3] and Alder[4]. Goertzel showed that an applied magnetic field directed toward one of the counters, and sufficiently strong to decouple the nuclear and electronic spins could restore the full correlation otherwise perturbed by the hyperfine structure. Both Goertzel and Alder have considered only the isotropic hyperfine structure described by the coupling $a\mathbf{I}\cdot\mathbf{J}$ which exists in free atoms. In solids, however, this description is inadequate in general. In the iron group of paramagnetic elements, where the hyperfine structure has been most extensively studied experimentally[31] and theoretically,[32] this coupling can be represented by the expression

$$\mathbf{K}=\mathbf{I}\cdot\mathbf{T}\cdot\mathbf{S}, \tag{82}$$

where $\mathbf{T}$ is a symmetrical tensor and $\mathbf{S}$ the spin of the electronic shell. Reduced to its principal axes, Eq. (82) can be written

$$\mathbf{K}=AI_zS_z+BI_xS_x+CI_yS_y. \tag{83}$$

A correlation perturbed by such a Hamiltonian can be described by the general formulas, Eqs. (15) and (16′), after determination of the eigenstates and eigenvalues

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[31] B. Bleaney, Physica **17**, 175 (1951).

[32] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

of **K**. If no external field is applied and if the substance is a powder, the somewhat simpler formulas, Eqs. (17) and (22) can be used.

We consider in some detail the simple example of a crystalline powder where one of the coefficients A, B, and C in Eq. (83), say A, is so much larger than the other two that **K** can be approximately taken as AI_zS_z. This case is physically significant. It occurs both in copper and cobalt Tutton salts where A is several times larger than B and C, and is the basis of Bleaney's method for aligning nuclear spins at low temperatures.[33]

Formula (22) is then simplified, since both I_z and S_z are good quantum numbers, and leads, for $S=\frac{1}{2}$, to the following expression for the attenuation coefficients.

$$G_k=\frac{1}{2k+1}\sum_{\mu=-k}^{k}[1-i\mu A\tau_N/2\hbar]^{-1}. \tag{84}$$

If $A\tau_N/\hbar$ is large compared with 1,

$$G_k(\text{lim})=1/(2k+1). \tag{85}$$

The magnetic hyperfine structure is usually several times larger than the quadrupole interaction, and we can, as a first approximation, disregard the latter. An interesting feature of this example is that, even in the absence of quadrupole interaction, an external magnetic field, however strong, applied toward one of the counters cannot restore the correlation perturbed by **K**. This can be shown as follows.

Let us consider one microcrystal. We call $0z$ the direction of the magnetic field, which is also the direction toward the counter, and $0z'$ the axis of the microcrystal, making with $0z$ the angle θ. The total Hamiltonian **K** can be written

$$\mathbf{K}=g\beta_0HS_z+AI_{z'}S_{z'},$$

or

$$\mathbf{K}=g\beta_0HS_z+AI_{z'}(S_z\cos\theta+S_x\sin\theta). \tag{86}$$

Here g and β_0 are, respectively, the gyromagnetic ratio of the paramagnetic ion and the Bohr magneton. (We neglect the direct coupling of the applied field with the nuclear moment.) If the Zeeman interaction $g\beta_0HS_z$ is much larger than the hyperfine coupling $AI_{z'}S_{z'}$, which is the condition required for the decoupling, we can in Eq. (86) treat the second part of **K** as a perturbation and replace there S_z and S_x by their expectation values. The expectation value of S_x in an eigenstate of S_z is zero. For this particular microcrystal there is an effective Hamiltonian which is

$$\mathbf{K}_{\text{eff}}=AI_{z'}S_z\cos\theta. \tag{87}$$

If $A\tau_N/\hbar$ is so much larger than unity that the coefficients G_k given by Eq. (84) are practically reduced to their limiting values $1/(2k+1)$, the Hamiltonian $AS_zI_{z'}\cos\theta$ of Eq. (87) will have practically the same effect as $AI_{z'}S_z$ except for the small proportion of microcrystals for which $\cos\theta\ll1$.

Because the energy levels of $\mathbf{K}_{\text{eff}}$ depend on the orientation of the microcrystal, Eq. (22) cannot be used as it was in the absence of the applied field. However, because of the linear dependence of these energy levels on the magnetic numbers $I_z=m$, and because of the orthogonality properties of the Clebsch-Gordan coefficients, the correlation $\overline{W}$ averaged over all microcrystals can still be represented by Eq. (17), where the attenuation coefficients G_k are defined by

$$G_k=\frac{1}{2k+1}\sum_{\mu=-k}^{k}\int\frac{|Y_k^{\mu}(\theta,\psi)|^2d\Omega}{1-(i\mu A\tau_N\cos\theta)/2\hbar}. \tag{88}$$

The attenuation coefficients G_k in Eq. (88) are larger than those given by Eq. (84), but still smaller than unity and, when A becomes very large, they decrease toward $1/(2k+1)$, although more slowly than in Eq. (84).

If we introduce $\beta=\hbar/A\tau_N$, we find

$$G_2=\frac{1}{5}+\frac{27}{4}\beta^2+\frac{189}{4}\beta^4-24\beta^3(4\beta^2+1)\arctan(1/2\beta)$$
$$+\frac{3\beta}{4}(1+\beta^2)\arctan(1/\beta). \tag{89}$$

This can be compared to

$$G_2=\frac{1}{5}\left\{1+\frac{8\beta^2}{1+4\beta^2}+\frac{32\beta^2}{1+16\beta^2}\right\} \tag{90}$$

in the absence of the decoupling field.

As an order of magnitude, in copper Tutton salts $A\sim0.01$ cm^{-1}. If $\tau_N=10^{-7}$, $\beta\sim1/200$ and G_2 is practically $\frac{1}{5}$ even in the presence of the applied field.

E. The Influence of Electronic Paramagnetic Relaxation

The discussion of the attenuations caused by magnetic hyperfine structure interactions in Sec. VI(D) supposed that entirely stationary electronic states, at least over times comparable to τ_N, exist. There must always be present some coupling of those states to the thermal vibrations of the lattice which, for most ions that show spin-only paramagnetism, is a result of spin-orbit coupling. A relaxation time for the electron moment can be defined and this can, in some cases, be so short as to require a different approach to be taken to the treatment of the effect on angular correlations. In electronic paramagnetic resonance it is necessary to work at temperatures as low as 4°K, in some cases, in order to obtain lifetimes of the electronic states sufficiently long to allow detection of the resonance lines.

The methods applied to the discussion of the electric quadrupole effect in liquid sources, Sec. V, can be used in some circumstances to analyze this effect. The effect of the spin-lattice coupling would mainly be to cause

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[33] B. Bleaney, Phil. Mag. **42**, 441 (1951).

continual random changes in the orientation of the electronic spin angular momentum **S**. The result of this would be equivalent to a continuously reorienting classical magnetic field at the nucleus and the resulting time dependent behavior of the nuclear spin can be calculated in a manner analogous to the calculations of Sec. V. If the interaction energy is $\hbar\omega_S \mathbf{I}\cdot\mathbf{S}$ and $\omega_S\tau_S \ll 1$, where τ_S is the relaxation time of the electron spin, the effect on the angular correlation is expressible by attenuation coefficients

$$G_k = (1+\lambda_k'\tau_N)^{-1},$$

where, here, the λ_k' are calculated as in Sec. V, but in Eq. (46) $T_1{}^\mu$ is used and corresponding changes are made in the expressions leading to Eq. (71). Expressions for the λ_k' are then

$$\lambda_k' = a'[1-(2I+1)W(I1kI/II)] \tag{91}$$

and

$$a' = \tfrac{2}{3}\tau_S\omega_S{}^2 I(I+1)S(S+1). \tag{92}$$

It is apparent that the attenuation considered here can be arbitrarily complete for sufficiently large values of the quantities $\lambda_k'\tau_N$.

Because τ_S, in general, shortens as the temperature increases, the correlation largely destroyed by such an effect would improve as the temperature is raised. The quantitative formula is not valid for $\tau_S \sim \tau_N$ or for $\omega_S\tau_S$ not much smaller than unity but, nevertheless, if τ_S becomes greater than τ_N, as it must at sufficiently low temperatures, the effect goes into that of the isotropic static hyperfine structure interaction for which a "hard core" remains no matter how strong the interaction. There is, thus, for a large ω_S, a maximum disturbance somewhere between a very small τ_S and one longer than τ_N.

A sufficiently strong magnetic field applied along the direction to the first counter can completely restore the correlation. The condition for that is for $g\beta_0 H/\hbar$, the angular Larmor frequency of the electron in the field H, to be made sufficiently large compared to the larger of ω_S and $1/\tau_S$. In effect, the spectral density of the fluctuating component of local magnetic field in the plane normal to the direction to the counter must be reduced and this results only if the above condition is satisfied. The g factor of the electron is such that a field of 10 kilogauss would be sufficient to partially restore the correlation unless τ_S were shorter than 5×10^{-12} sec. At room temperatures shorter relaxation times than this do occur for some ions.

VII. RESONANCE METHODS

If angular correlations are to be used to measure nuclear moments of the intermediate state the improvement over the observation of the effect of static fields obtained by inducing resonant transitions by an rf field, analogous to that gained by Rabi in molecular beams, might be considered. Several difficulties present themselves as discussed for a couple of examples below.

A. Nuclear Magnetic Resonance

It has already been stated that in a double decay cascade the first radiation can be considered as creating in the intermediate state of the nucleus unequally populated magnetic states quantized along the direction of emission of this radiation. The existence of an angular correlation between the two radiations, i.e., of an anisotropy in the direction of emission of the second radiation with respect to the first, is precisely due to these inequalities of population.

If resonant transitions between the magnetic substates can be induced by an applied rf field, their effect will be to decrease these inequalities of population and therefore to decrease the anisotropy of the angular correlation, thus providing a means of detecting the resonance. If there is no static quadrupole interaction or magnetic hyperfine structure, a uniform magnetic field H applied along the direction to the first counter splits the magnetic substates without affecting the correlation and the resonance frequency for an rf field in the plane normal to H is the Larmor frequency $\omega_L/2\pi$ of the intermediate nucleus in the static field.

In order for a resonance experiment to provide an accurate measurement of the nuclear magnetic moment, the following conditions must be realized.

(a) The natural width of the magnetic levels due to the finite lifetime of the intermediate state of the nucleus must be much smaller than the spacings between these levels. The ratio of the spacing between two adjacent levels to the line width is $\omega_L\tau_N$ which, thus, should be much larger than unity. This is equivalent to saying that the uniform field, if applied perpendicular to the plane of the counters, should destroy the correlation completely. As an example, for Cd^{111} where $\tau_N \sim 10^{-7}$ and $g_n \sim 0.3$ nuclear magneton, $\omega_L\tau_N \simeq 2$ in a field of 15 000 gauss, which makes this type of experiment for this particular nucleus relatively unrewarding.

(b) The amplitude of the rf field should be sufficiently large for the resonant transitions to have an appreciable probability during the nuclear lifetime. This requires that $\omega_1\tau_N \simeq 1$ where ω_1 is 2π times the Larmor frequency of the nucleus in a constant field equal to the amplitude of the rf field. It is equivalent to say that such a constant field, if applied perpendicular to the plane of the counters, should have a detectable effect on the correlation. This rules out this experiment for Cd^{111}, since rf fields so large would be extremely difficult to produce. More conventional resonance experiments seldom utilize rf fields larger than about 10 gauss.

(c) The lifetime of the nucleus should be shorter than the relaxation time of the nuclear spin in the source. Since, in order for the resonant experiment to be feasible, rather long nuclear lifetimes are required, this may be a limitation in liquid sources. with strong quadrupole relaxation, but probably is not a limitation in solid sources. In the latter a crystal structure of cubic symmetry is required in order to avoid perturbation by the static quadrupole interaction.

To sum up, it can be said that a resonance experiment is probably feasible for a nucleus for which the product $g_n\tau_N$ is as large as for a free proton with a lifetime of one microsecond. No such nucleus is known at present.

The time-dependent correlation $w(t)$ in the presence of the rf field is given by the general formulas of Eq. (12) and Eq. (13). If the z axis is parallel to the direction of the applied magnetic field $\mu_1=\mu_2=0$. In Eq. (13), $(m|\mathbf{U}^+|m'')(m'''|\mathbf{U}|m')$ becomes $|(m''|\mathbf{U}|m)|^2$, which is the well-known Majorana function $P(I, m'', m, t)$,[34] expressing the probability of finding the spin in the state m'' at time t if it was in the state m at $t=0$. The integrals

$$\int_0^\infty e^{-t/\tau_N}P(t)dt/\tau_N$$

have been calculated and tabulated by Bitter and Brossel for several values of the spin.[35]

In principle, the resonance method could also apply to the quadrupole interaction in a single crystal with its axis parallel to the applied field, or to a crystalline powder.

B. Resonance in Magnetic Atoms

If the atom containing the radioactive nucleus has a magnetic moment and therefore a hyperfine structure, $A\mathbf{I}\cdot\mathbf{J}$, a somewhat different resonance experiment might be attempted.

If a strong magnetic field parallel to one of the counters restores the correlation perturbed by the hyperfine structure interaction as already discussed, the correlation could again be disturbed by an rf field. The energy levels of the system are given by $K=g\beta_0HJ_z+AJ_zI_z$, and transitions $\Delta J_z=0$, $\Delta I_z=\pm1$ can be induced between the levels $J_z=M$, $I_z=m$ and $J_z=M$, $I_z=m\pm1$, whose separation is AM. The point of these remarks is that AM, which measures the hyperfine structure of the atom, can be orders of magnitude larger than the Zeeman splittings of the nuclear moment in an applied field, thus relaxing the limitation (a) of the resonance method. The limitation (b), however, remains unchanged and especially difficult to meet because the frequency is high.

Perhaps a better method is to induce transitions between different eigenstates of the total atomic moment F, where $\mathbf{F}=\mathbf{I}+\mathbf{J}$, in zero applied field. Alder has shown that, even if $(E_F-E_{F'})\tau_N/\hbar$ is very large, which is precisely the condition (a), the correlation does not disappear completely but leaves a "hard core." A resonant rf field could produce a detectable change in this hard core. The important point here is that in these transitions the rf field flips the electronic moment but since the electronic moment is coupled to the nuclear spin both flip and the angular correlation is altered. Since the coupling of the rf field to the electronic spin is thousands of times larger than its coupling to the nuclear spin, the probability of a transition during the time τ_N is considerably increased and condition (b) can be met.

The measurement of the hyperfine structure in a stable isotope of known nuclear moment by conventional methods would, by comparison, give the magnetic moment of the radioactive nucleus.

As remarked in Sec. IV(D), by measuring the departures from Landé's interval rule in the energy differences $E_F-E_{F'}$, the sign and magnitude of the quadrupole interaction could be measured if $J>\frac{1}{2}$.

These considerations apply most directly to free atoms such as those in a gaseous source. It is clear that a condition that should be met by the source is that collisions between atoms or against the walls, which result in changes in $\mathbf{F}$, must not occur, on the average, in times shorter than, or of the order of, τ_N.

VIII. CONCLUSION

It has been shown that static electric quadrupole interations in polycrystalline sources can reduce the angular correlation. For both axially symmetric and rhombic fields, no matter how strong the interaction, there remains some anisotropy.

In liquid sources, the electric quadrupole moment interacts with a randomly fluctuating field and the resulting attenuations are expressed as $G_k=(1+\lambda_k\tau_N)^{-1}$, where the λ_k are given in Eq. (71). Here the correlation, although usually less disturbed than in solid sources, can be completely destroyed for sufficiently long τ_N. A similar effect is possible if the electronic shell is magnetic with a short lifetime of a given magnetic substate. The application of magnetic fields in the first of these cases should have little effect if directed toward either counter. In the second, unless the relaxation time τ_S is very short, it should be possible to reduce the disturbance by application of such a field.

The explanation of the observation by the Zürich group and by Stefen of correlations from the γ-γ cascade from the Cd^{111} daughter of In^{111} in solid compounds of indium remains unclear. It would appear that a purely static interaction in the intermediate state could not be the sole effect unless the crystallites of the source were preferentially oriented, which seems unlikely. Instead, the existence of a magnetic shell, following the K capture, in compounds is a possibility. In that event, the most likely mechanism for the disturbance would be that associated with relaxation of the electron spin. Even more speculative would be the suggestion that the recoil energy accompanying K capture excites vibrations of a complex or molecule in

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[35] F. Bitter and J. Brossel, Technical Report No. 176, Research Laboratory of Electronics, Massachusetts Institute of Technology, 1950 (unpublished).

which the Cd^{111} is contained. The vibrations might, in turn, cause reorientations of the spin in times shorter than τ_N. Such vibrations, on the other hand, should be very short lived and this, too, seems an unlikely mechanism.

It should be emphasized that for γ-γ cascades following almost instantaneously after K capture, the electronic configuration during the lifetime of the intermediate state of the nucleus is less clearly defined than it would be for a γ-γ cascade from a long-lived isomer, such as 48-min Cd^{111}. In such a case, the radiation from the isomer could be observed in a normal chemical environment. For all other correlations than pure γ-γ and γ-conversion electron, the surroundings of the nucleus in its intermediate state are not well known and it is difficult to draw quantitative conclusions from observed perturbations of the correlation.

IX. ACKNOWLEDGMENTS

Our interest in this subject was aroused through discussion of a related subject with Professor N. Bloembergen. We wish to thank him and also Professor H. Brooks, Professor M. Deutsch, Dr. M. Goldhaber, and Professor E. M. Purcell for helpful discussions. One of us (A.A.) wishes to thank the Shell Oil Company for support through a research grant.

PHYSICAL REVIEW VOLUME 92, NUMBER 4 NOVEMBER 15, 1953

Nuclear Spin Relaxation by Translational Diffusion*

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(Received July 21, 1953)

The general theory of Bloembergen, Purcell, and Pound of nuclear spin relaxation has been extended to a more quantitative study of relaxation by translational diffusion. It has been found necessary to treat the problem by the theory of random walk. In the case of isotropic diffusion two cases have been studied: one in which the flight distance has a probability distribution, and the other in which it is constant. The problem of random walk to nearest neighbor sites in a lattice is also treated and quantitative results are obtained for a face-centered cubic lattice.

I. INTRODUCTION

Bloembergen, Purcell, and Pound have given a general solution to the problem of nuclear spin relaxation.[1,2] An important and prevalent mechanism has been shown to be the coupling of spin orientation with nuclear thermal motion via the dipolar magnetic interaction of the nuclear moments. This influence and the corresponding relaxation are particularly strong whenever the nuclei perform random diffusive motions such as occur in liquids of appropriate viscosity. Such diffusive motions may occur also in the solid phase particularly in the case of solid solutions; for example, hydrogen in palladium, but also in the case of self-diffusion. Bloembergen[2] has applied his theory to diffusive motions. His treatment of translational diffusion is, however, admittedly crude and must be regarded as only semiquantitative. It is the purpose of this paper to present a more quantitative theory and in particular to emphasize the possibility of examining certain microscopic details of the diffusion process which cannot be ascertained from a study of gross diffusion phenomena alone. In Bloembergen's treatment only the diffusion constant D enters as a parameter. Thus his theory gives no basis for a closer study of the diffusion mechanism than can be obtained by conventional measurements of macroscopic diffusion. Nuclear spin relaxation is however essentially microscopic in character. The magnetic field of one nucleus at the position of another depends on the inverse cube of the distance and the influence of nearest neighbors is thus relatively strong. It is apparent from this that one needs to consider the individual motions of neighboring spins, that is to say, the process of random flights of which, as is well known, the phenomenon of diffusion is only the limiting macroscopic approximation. Thus it may be expected that certain details of random flights such as $\langle r^2\rangle$, the mean squared flight distance, and τ, the mean time between flights, will enter into the description of relaxation in other ways than merely in the familiar combination:

$$D=\langle r^2\rangle/6\tau. \tag{1}$$

This is indeed the case and leads at least in principle to the possibility of independent measurement of these parameters in certain cases.

II. APPLICATION OF THE THEORY OF RANDOM FLIGHTS

We start from the general formula derived by Bloembergen[1,2] for the relaxation time T_1:

$$T_1^{-1}=\tfrac{3}{4}\gamma^4\hbar^2 I(I+1)[S_2(2\omega_0)+2S_1(\omega_0)]. \tag{2}$$

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* Supported by the joint program of the U. S. Office of Naval Research and U. S. Atomic Energy Commission, by the Radio Corporation of America, and by the Rutgers Research Council.

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