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Theory of Gyromagnetic Effects and Some Related Magnetic Phenomena

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1. INTRODUCTION

THE experiment of rotating a magnet to polarize it and the converse experiment of applying a magnetic field to a freely suspended magnet in order to induce its rotation are called gyromagnetic experiments. Their history goes back as far as Maxwell,[1] who suggested and tried these types of experiments as a means of determining whether electricity is carried by a material substance. The first successful magnetization-by-rotation experiments were performed by Barnett[2] and the first successful rotation-by-magnetization experiments were carried out by Einstein and de Haas.[3] These experiments provided early measurements of the gyromagnetic ratio of electrons. The experimental work on these effects has continued[4] and

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† Work at Stanford University supported by the U. S. Air Force during 1959 and 1960.

[1] J. Clerk Maxwell, *Electricity and Magnetism* (Oxford University Press, London, 1892), pp. 574 and 575.

[2] S. J. Barnett, Phys. Rev. **6**, 239 (1915); **10**, 7 (1917); **17**, 404 (1921); **20**, 90 (1922). S. J. Barnett and J. H. Barnett, Proc. Am. Acad. Arts Sci. **60**, 125 (1925).

[3] A. Einstein and W. J. de Haas, Verhandl. deut. physik Ges. **17**, 152 (1915). A. Einstein, *ibid.* **17**, 203 (1915); **18**, 17 (1916). W. J. de Haas, Proc. Acad. Sci., Amsterdam **18**, 1280 (1916).

[4] The earlier experiments are reviewed by S. J. Barnett, Revs. Modern Phys. **7**, 136 (1935) and by L. F. Bates, *Modern Magnetism* (Cambridge University Press, New York, 1951),

very high accuracy is attained in the recent experiments, particularly those of Scott.[5]

In this paper we present a unified theory of these gyromagnetic effects and ordinary magnetic polarization. In addition, we consider the analogous nuclear gyromagnetic phenomena and polarization of nuclei by a magnetic field. This results in a unified treatment of several effects, such as the Knight shift, the Lamb diamagnetic shielding, the Ramsey chemical shift, and pseudodipolar coupling. Of these phenomena, only the nuclear gyromagnetic effects have not as yet been observed experimentally, although their existence has been suggested.[6] Our treatment of electronic effects does not include ferromagnetism.

The physical fact underlying all the gyromagnetic effects is that the nuclear spin and the electronic spin, as well as their orbital angular momenta, generate a magnetic moment parallel to the angular momentum with a magnitude fixed through a characteristic constant of proportionality, known as the gyromagnetic ratio. This fact, together with Newton's second law of motion or the Schrödinger equation, transformed to a rotating-coordinate system, leads to Larmor's theorem—that the effect of a uniform magnetic field on a system of spins or particles can be transformed away by going to a rotating coordinate system, provided the angular momentum of the system in the field direction is a constant of motion.

In Sec. 2, the quantum-mechanical Larmor theorem is derived. It is given in a generalized form including spin and orbital motion, systems of spins with differing gyromagnetic ratios, and some time-dependent magnetic fields. According to the Larmor theorem, the magnetic field produces only a periodic effect, although in fact it is well known that magnetic fields tend to produce polarization in the field direction, not just periodic Larmor precession. To analyze how polarization can take place, the behavior in a magnetic field of two spins coupled by the interaction between their magnetic dipoles is followed by an exact solution of the Schrödinger equation. The coupling is essential so as to allow the exchange of angular momentum required to produce polarization. It is shown that, if no field acts on these two spins but instead the whole system is physically caused to rotate, this rotation can cause a polarization of just the magnitude produced by a field which produces a Larmor frequency equal to the rotation frequency. Polarization does not occur for any arbitrary initial conditions, but it does occur, for example, if the initial density matrix corresponds to thermal equilibrium. This example helps reconcile in a qualitative way the exact Schrödinger-equation solution with the approximate statistical theories of magnetization or magnetic-relaxation phenomena.[7]

In Sec. 3a, the density matrix for a uniformly rotating system in thermal equilibrium is derived on the basis of maximum-entropy inference. Since one rarely sees equilibrium distributions involving the angular momentum in a role parallel to that of the energy (although they were given by Gibbs), it is of some interest to make predictions for observations on the basis of this density matrix. The application to physical systems is made by use of a perturbation theory for expectation values. The perturbation theory is derived in general terms and its properties are investigated in detail in Sec. 3b.

In Sec. 3c we obtain the magnetic moment of a piece of magnetically dilute material with a magnetic field acting on it and with the material rotating. Similarly, the electronic angular momentum is studied subject to a field and a rotation. The cross-coupling coefficients, i.e., the magnetic moment due to rotation alone or the angular momentum due to the field alone, represent the Barnett and the Einstein-deHaas effects, respectively. A summary of the comparison of experimental data with the theory of these effects is given. The present form of the theory is in agreement with some previous calculations for particular cases in the literature.[8]

In Sec. 3d, the polarization of a nuclear spin in a rotating crystal acted upon by a constant magnetic field is studied and its magnitude calculated. The corrections to the polarization due to the internal crystal field are obtained from the perturbation theory for expectation values. Many line-shift phenomena, well known from nuclear magnetic resonance experiments, are shown to result from such a treatment. These effects are usually derived separately; in some cases, the unified method given here may provide a simpler means of evaluating the effects because the

Chap. 7. Of particular importance are the experiments on paramagnetic materials performed by W. Sucksmith, Proc. Roy. Soc. (London) **A128**, 276 (1930); **A133**, 179 (1931); **A135**, 276 (1932). Measurements reported in the literature since 1951 are S. J. Barnett and G. S. Kenney, Phys. Rev. **87**, 723 (1952). A. J. P. Meyer, Compt. rend. **246**, 1294 (1958). A. J. P. Meyer and S. Brown, J. phys. radium **18**, 161 (1957). A. J. P. Meyer, G. Asch, and S. Brown, "Colloque National de Magnetisme," (Strasbourg 1957), p. 305. G. Asch, Compt. rend. **246**, 1294 (1958). G. G. Scott, Phys. Rev. **82**, 542 (1951); **99**, 1241 (1955); **99**, 1824 (1955); **103**, 561 (1956); Rev. Sci. Instr. **28**, 270 (1957); Phys. Rev. **119**, 84 (1960); **120**, 331 (1960). For a recent review of experiments see G. G. Scott, Revs. Modern Phys. **34**, 102 (1962).

[5] G. G. Scott, see reference 4.

[6] E. T. Jaynes, Phys. Rev. **106**, 620 (1957); S. P. Heims, Helv. Phys. Acta Suppl. VI (1960).

[7] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1943). R. V. Wangsness and F. Bloch, *ibid.* **89**, 728 (1953). F. Bloch, *ibid.* **102**, 104 (1956); **105**, 1206 (1957). Y. Ayant, J. phys. radium **16**, 411 (1954). U. Fano, Phys. Rev. **96**, 869 (1954). R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954). A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

[8] A. Frank, Phys. Rev. **39**, 119 (1932). J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, England, 1932). C. J. Gorter and B. Kahn, Physica **7**, 753 (1940).

[9] Reviews of such phenomena are given by G. E. Pake, in *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2; by N. F. Ramsey, *Nuclear Moments* (John Wiley & Sons, Inc., New York, 1953); and J. A. Pople, W. G. Schneider, and H. T. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

energy denominators of second-order perturbation theory can be avoided and also because the formulas are in a form independent of the representation used.

In Sec. 4, the time-dependent behavior of nuclear spins in a rotating crystal is described. We attempt there to show the relation of solutions to the Schrödinger equation for the rotating crystal to those for the case of a rotating magnetic field acting on the crystal. A statistical treatment of the spin system on a rotating crystal is given, using the formalism and the approximations of the Wangsness-Bloch theory of nuclear magnetic relaxation.

In all of the theory of rotation phenomena and induced angular momenta, it is apparent that the information to be gained from their study is of a nature similar to, but not usually identical with, that obtained from studying magnetic phenomena and magnetic moments. Thus, the measurements of gyromagnetic coefficients give as much useful information as the determination of magnetic susceptibilities, nuclear or electronic. Yet, the magnetic phenomena have been studied far more fully than the gyromagnetic ones; small wonder, in view of the greater difficulty of performing experiments of the latter type.

2. DYNAMICS OF SPIN SYSTEMS

a. Larmor's Theorem in Quantum Mechanics

According to both classical theory and quantum mechanics, the effect of a uniform magnetic field on a system of charged particles may be shown to be equivalent to a rotation of the coordinate system. In quantum mechanics, the system is described by the wave function $\psi(x,t)$, a solution to the Schrödinger equation

$$i\hbar\partial\psi/\partial t=\mathcal{H}\psi, \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian operator, x represents all the space and spin coordinates of the system of particles, and t is the time. The transformation of the wave function to a rotating coordinate system is achieved by means of a unitary operator $R(t)$. The rotated wave function is $\psi_r=R(t)\psi(x,t)$. The vector operators appearing in quantum mechanics (momentum, position, angular momentum) are rotated by the same transformation. If $\mathbf{Q}$ is such a vector operator, then $\mathbf{Q}_r=R(t)\mathbf{Q}R(-t)$ gives the operator in the rotating system. Explicitly,

$$R(t)=\exp[(i/\hbar)\mathbf{J}\cdot\omega t], \tag{2}$$

where $\mathbf{J}$ is the total angular momentum of the system and ω the angular velocity of the coordinate system. Equation (2) follows from the requirements that R be unitary, that it satisfy the relation $R(t_1)R(t_2-t_1)=R(t_2)$, and the well-known connection between infinitesimal rotations and angular-momentum operators,[10] expressed by

$$\mathbf{J}\cdot\omega=i\hbar\lim_{t\to 0}[R(t)-1]/t.$$

The Hamiltonian $\mathcal{H}$ of the system considered is assumed to be time-independent and to consist of a part $\mathcal{H}_0$ independent of the magnetic field and an additional part $\mathcal{H}_1$ due to a constant magnetic field. Without the field, the time development of the wave function is

$$\psi(x,t)=\exp[-(i/\hbar)\mathcal{H}_0 t]\psi(x,0); \tag{3}$$

with the magnetic field, it is

$$\psi_f=\exp[-(i/\hbar)(\mathcal{H}_1+\mathcal{H}_0)t]\psi(x,0). \tag{4}$$

Applying the rotation operator $R(t)$ corresponding to a uniform rate of rotation to (3), gives

$$\psi_r=\exp[(i/\hbar)\mathbf{J}\cdot\omega t]\exp[-(i/\hbar)\mathcal{H}_0 t]\psi(x,0). \tag{5}$$

Restricting consideration to a Hamiltonian $\mathcal{H}_0$ which is invariant to rotation around the direction of ω, so that $[\mathbf{J}\cdot\omega,\mathcal{H}_0]=0$, permits rewriting (5) in the form

$$\psi_r=\exp[-(i/\hbar)(-\omega\cdot\mathbf{J}+\mathcal{H}_0)t]\psi(x,0). \tag{6}$$

To obtain a Larmor theorem,[11] we compare Eqs. (4) and (6) for some particular types of systems:

For a system of spins all having the same gyromagnetic ratio γ, in a uniform magnetic field $\mathbf{H}$, $\mathcal{H}_1=-\gamma\mathbf{S}\cdot\mathbf{H}$; then by inspection ψ_f and ψ_r are identical if the field is equal to $\mathbf{H}=(1/\gamma)\omega$.

For a system of spins with differing gyromagnetic ratios and a field $\mathbf{H}_k$ acting on the kth spin, $\mathcal{H}_1=-\sum_k\gamma_k\mathbf{S}_k\cdot\mathbf{H}_k$. For a given angular velocity ω, ψ_f and ψ_r are equal only if the fields $\mathbf{H}_k$ have the values

$$\mathbf{H}_k=(1/\gamma_k)\omega; \tag{7a}$$

or if a uniform field $\mathbf{H}_k=\mathbf{H}$ is given, the theorem may be stated as requiring a different rotation frequency for each particle, so that in Eq. (6), $\omega\cdot\mathbf{J}$ becomes $\sum_k\omega_k\cdot\mathbf{S}_k$ with

$$\omega_k=\gamma_k\mathbf{H}. \tag{7b}$$

The theorem is exact for a pure spin system. Consider however the magnetic part of the Hamiltonian for the motion of an electron in a uniform magnetic field $\mathbf{H}$,

$$\mathcal{H}_1=(e/2mc)\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})+(e^2/8mc^2)H^2r^2\sin^2\theta, \tag{8}$$

[10] P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, New York, 1947), 3rd ed., p. 35.

[11] For the case of a pure spin system, I. Rabi, N. F. Ramsey, and J. Schwinger [Revs. Modern Phys. 26, 167 (1954)] give a different proof of Larmor's theorem. They consider the operator $\mathbf{J}$ and its equation of motion in the Heisenberg picture. Their proof can be readily generalized to differing γ's and to include orbital motion. However, the restriction $[\mathbf{J}\cdot\omega,\mathcal{H}_0]=0$ is also necessary. Transformation to a rotating coordinate system as a means of transforming away static fields is well known in the theory of magnetic resonance. See, for example, R. V. Wangsness and F. Bloch, Phys. Rev. 89, 728 (1953).

where θ is the angle between the position vector $\mathbf{r}$ and the magnetic field. In this case, it is necessary to assume that the quadratic term in $\mathcal{H}$ is small compared to the linear term. Then the Larmor theorem applies, the space function and spin functions being rotated with angular velocities

$$\omega_l = -\frac{e}{2mc}\mathbf{H}, \quad \text{and} \quad \omega_s = 2\omega_l, \tag{9}$$

respectively. For ordinary laboratory fields, the quadratic term in (8) is indeed very small compared to a linear term and (9) is a very good approximation. The error can be estimated by expanding (4) to first order in the neglected term to obtain

$$\psi_f(x,t) = e^A(1+\epsilon)\psi(x,0),$$

where

$$A \equiv -\frac{it}{\hbar}\left[\mathcal{H}_0 - \frac{e}{2mc}\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})\right]$$
$$\epsilon = -\frac{it}{\hbar}\frac{e^2H^2}{8mc^2}\int_0^1 d\tau e^{-A\tau}(r^2\sin^2\theta)e^{A\tau}. \tag{10}$$

Thus, (9) is valid when $|\epsilon| \ll 1$. The assumption made in deriving (6), namely, that $[\mathbf{J}\cdot\omega, \mathcal{H}_0]=0$ is fulfilled for any system on which no external torque is acting other than the constant magnetic field considered.

The Larmor theorem, Eqs. (7) and (9), may be generalized to time-dependent fields, giving a description of the wave function as the field builds up. Suppose the magnetic field varies linearly with the time[12]

$$\mathbf{H}(t) = \boldsymbol{\alpha}t + \mathbf{H}_0, \tag{11}$$

but is uniform throughout space. The vectors $\mathbf{H}_0$ and $\boldsymbol{\alpha}$ may point in arbitrary directions, so that the direction of the field $\mathbf{H}(t)$ may be a function of time. To satisfy the Maxwell equation $\text{curl}\mathbf{E} = (-1/c)\partial H/\partial t$ an electric field must accompany the growing magnetic field: $\mathbf{E} = -\boldsymbol{\alpha}\times\mathbf{r}/2c$. The other Maxwell equations for a source-free region are then also satisfied. By introducing the potentials $\mathbf{A} = \mathbf{H}(t)\times\mathbf{r}/2$ and $\phi = 0$, it is readily shown that the Hamiltonian of systems of spins and particles will differ from that of a system in a constant magnetic field only in that $\mathbf{H}(t)$ everywhere will replace $\mathbf{H}$. The time-dependent Larmor theorem is then proved by considering small rotations

$$R_n = 1 + (i/\hbar)\textstyle\sum_k \mathbf{I}_k\cdot\omega_k(t_n)\Delta t, \tag{12}$$

and the limit of the product

$$R(t) = \lim_{\substack{\Delta t\to 0 \\ N\to\infty \\ N\Delta t\to 1}} \prod_{n=1}^{N} R_n = \exp\left[\frac{i}{\hbar}\sum_k \mathbf{I}_k\cdot\int_0^t \omega_k(t')dt'\right]. \tag{13}$$

In (13), the convention must be observed that in every product of $\mathbf{I}_k\cdot\omega_k(t_n)$ and $\mathbf{I}_k\cdot\omega_k(t_m)$ that occurs, the order of writing the factors is taken to be the order of the natural time sequence. Comparing (13) to the part of the time-evolution operator involving the magnetic field and requiring that $[\mathbf{J}\cdot\omega(t), \mathcal{H}_0]=0$, gives the time-dependent Larmor theorem which differs from (7) and (9) only in that $\mathbf{H}$ and ω are time-dependent. For example, (7b) becomes

$$\omega_k(t) = \gamma_k\mathbf{H}(t) \text{ for all } t. \tag{14}$$

For magnetic fields which vary nonlinearly with the time, the accompanying electric field is only approximately given by $\mathbf{E} = -\dot{\mathbf{H}}\times\mathbf{r}/2c$. The approximation consists of neglecting displacement current. When that approximation applies, the theorem (14) and the other time-dependent expressions corresponding to (7a) and (9) can be derived.

b. A Simple Example of Polarization

The discussion of Larmor's theorem has shown that the effect of a constant magnetic field is transformed away by going to a rotating coordinate system. However, in the following sections, we are primarily concerned with the polarization of systems in the field direction, a phenomenon which is *not* transformed away by going to a rotating system. To help clarify how polarization can occur in spite of Larmor's theorem, a very simple example is treated in Appendix A by an exact integration of the Schrödinger equation. The system considered is a pair of nuclear spins, each of magnitude $\frac{1}{2}\hbar$, coupled to each other by dipole-dipole coupling. Some polarization of the spins can be brought about either by applying a magnetic field in a direction perpendicular to the line connecting the positions of the two nuclei, or by a rigid rotation of the whole system about such a direction.[13] To show that the latter problem can be reduced to the magnetic-field problem, we note that the expression for the interaction of two dipoles, if the relative position vector $\mathbf{R}$ is rotating, is

$$G(t) = \frac{\hbar^2\gamma_1\gamma_2}{2R^3}\left[\mathbf{S}_1\cdot\mathbf{S}_2 - \frac{3[\mathbf{S}_1\cdot\mathbf{R}(t)][\mathbf{S}_2\cdot\mathbf{R}(t)]}{R^2}\right]$$
$$= \exp\left(\frac{-i}{\hbar}\omega\cdot\mathbf{S}t\right)\frac{\hbar^2\gamma_1\gamma_2}{2R^3}$$
$$\times\left[\mathbf{S}_1\cdot\mathbf{S}_2 - \frac{3[\mathbf{S}_1\cdot\mathbf{R}(0)][\mathbf{S}_2\cdot\mathbf{R}(0)]}{R^2}\right]\exp\left(\frac{i}{\hbar}\omega\cdot\mathbf{S}t\right),$$

[12] Exact solutions of the Schrödinger equation for particles with spin, but without orbital motion, in a time-dependent, magnetic field have been studied by E. Majorana, Nuovo cimento 9, 43 (1932), and by F. Bloch and I. Rabi, Revs. Modern Phys. 17, 237 (1945). One may treat the case including orbital motion by means of the adiabatic approximation: If the field does not change direction, then, in the lowest approximation of a slowly varying field, the eigenvalue equation $[\mathcal{H}_0 - MH(t)]\psi_n = E_n(t)\psi_n$ is solved, yielding the Zeeman splitting but no transitions between states. The next approximation yields transition probabilities proportional to $(dH/dt)^2$.

[13] Not to be confused with the rotation of the coordinate system in Larmor's theorem. We are now talking about an actual, physical rotation.

where ω is the angular velocity of rotation and $\mathbf{S}_1$ and $\mathbf{S}_2$ the spins of the two dipoles in units of $\hbar$ and γ_1, γ_2, their gyromagnetic ratios. Transforming the Schrödinger equation $i\hbar\dot{\psi}=G(t)\psi$ by the unitary transformation $\psi'=\exp[(i/\hbar)\omega\cdot\mathbf{S}t]\psi$ gives the equation

$$i\hbar\partial\psi'/\partial t=[G(0)-\hbar\omega\cdot\mathbf{S}]\psi', \quad \mathbf{S}\equiv\mathbf{S}_1+\mathbf{S}_2. \quad (15)$$

The Schrödinger equation for the pair of coupled spins with identical gyromagnetic ratios γ is $i\hbar\partial\psi/\partial t=[G(0)-\gamma\hbar\mathbf{H}\cdot\mathbf{S}]\psi$, which is identical with (15) except in that the Larmor frequency $\omega_L\equiv\gamma\mathbf{H}$ replaces ω. We expand the solution in eigenfunctions ϕ of S^2 [eigenvalues $s(s+1)$, $|S_1-S_2|\leq s\leq|S_1+S_2|$] and S_z [eigenvalues m, $-s\leq m\leq s$]:

$$\psi(t)=\sum_k b_k(t)\phi_k^{(ms)},$$

where $k=1$ stands for $(m,s)=(1,1)$; $k=2$ for $(m,s)=(0,1)$; $k=3$ for $(m,s)=(-1,1)$; and $k=4$ for $(m,s)=(0,0)$. We take the direction of ω or $\mathbf{H}$ as the x direction, but the nuclei on a line parallel to the z direction. Assuming the field turned on at $t=0$, and averaging over oscillations, we find the following results for the expectation value of the total spin after the field (or rotation) has been on a long time:

$$\langle\bar{S}_z\rangle=\frac{3\hbar\omega E_0}{\epsilon^2}[|b_1(0)+b_3(0)|^2-2|b_2(0)|^2]+\frac{4(\hbar\omega)^2}{\epsilon^2}\langle S_z(0)\rangle, \quad (16)$$

$$\langle\bar{S}_y\rangle=\langle\bar{S}_z\rangle=0,$$

with $E_0=(\hbar\gamma)^2/2R^3$, $\epsilon=[(3E_0)^2+(2\hbar\omega)^2]^{\frac{1}{2}}$. The polarization (16) clearly depends on initial conditions and may be in either direction. If the initial density matrix $b_ib_j^*$ is a multiple of the unit matrix, the system cannot polarize because the density matrix will of necessity commute with the Hamiltonian and so will not change with time. If we have a large number of identical pairs of spins, and if initially before the field is turned on each pair is in contact with a heat reservoir at a temperature T_0, and then at $t=0$ the reservoir is removed, we find from (16) for one such pair on the average

$$\langle\langle\bar{S}_z\rangle\rangle=\frac{\hbar\omega}{kT_0}\left(\frac{3E_0}{2\epsilon}\right)^2. \quad (17)$$

The second $\langle\ \rangle$ indicates the average over the initial states. The polarization (17) is a maximum when $2\hbar\omega=3E_0$ and it falls off for $2\hbar\omega\gg3E_0$. This is to be expected, because the polarization process requires simultaneous exchange of energy $\hbar\omega$ and angular momentum $\hbar$ between the Zeeman part of the Hamiltonian and the dipole-dipole coupling. However, the latter can absorb no more than an amount of energy of the order of $\frac{3}{2}E_0$, so that when $2\hbar\omega\gg3E_0$ the two spins are effectively uncoupled and no polarization can occur. If we had included more degrees of freedom in the example, then it is expected more polarization would be possible. The spins can be polarized in this example in spite of Larmor's theorem, since the Hamiltonian G does not commute with $\mathbf{S}\cdot\omega$; the angular momentum lost or gained by the spin is transferred to the nuclear-orbital motion via the interaction G. Thus, the dipole-dipole coupling provides a mechanism for spin polarization through the exchange of angular momentum with the nuclear-position coordinates.

3. EQUILIBRIUM THEORY

a. Density-Matrix Description of Rotating-Material System

The foregoing example illustrates that Larmor's theorem (or in fact the Schrödinger equation) is not incompatible with the tendency of systems to move towards thermal equilibrium. In this section, we assume that thermodynamic equilibrium of the system is obtained, and study the equilibrium properties of general systems. Consider a macroscopic system which has a total energy $E=\langle\mathcal{H}\rangle$ and whose total, angular-momentum components are $M_i=\langle J_i\rangle$. The $\langle\ \rangle$ indicate the taking of an expectation value of an operator, i.e., the trace of the product of the operator with the density matrix describing the system. The density matrix which describes the aforementioned information is obtained by maximizing the entropy, subject to the constraints imposed by knowledge of the expectation value of energy and angular momentum.[14] The resulting density matrix is

$$\rho=\exp(-\beta\mathcal{H}-\lambda_iJ_i-\lambda_0\cdot1), \quad (18)$$

where β, λ_i, and λ_0 are introduced in the derivation as Lagrange multipliers whose physical significance is determined next.[15] The summation convention is used for the index i, which runs from 1 to 3. Normalization of ρ such that $\mathrm{Tr}\rho=1$, requires that $\lambda_0=\ln Z$, where $Z=\mathrm{Tr}\exp(-\beta\mathcal{H}-\lambda_iJ_i)$ is the partition function. The afore-mentioned expectation values are given in terms

[14] This procedure has been formulated by E. T. Jaynes, Phys. Rev. **106**, 620 (1957); **108**, 171 (1957), in a general way from considerations based on information theory.

[15] One may also wish to incorporate into ρ knowledge of the accuracy with which the energy and angular momentum are known. This can be done most easily by including $\mathcal{H}^2$ and J_i^2 in the set of operators whose expectation values are given, which would add the terms $-\omega\mathcal{H}^2-\gamma_iJ_i^2$ to the exponent in (18). In principle, whenever such information is available it should be incorporated into ρ. However, as was pointed out in the classical case already by Gibbs, the state-density function for any system which exhibits reproducible thermodynamic properties is such a rapidly varying function of the parameters $\mathcal{H}$, J_i that the variance $\langle\mathcal{H}^2\rangle-\langle\mathcal{H}\rangle^2$ or $\langle J_i^2\rangle-\langle J_i\rangle^2$ obtained from (18) is already very small compared to any reasonable mean-square, experimental error. Consequently, although the extra terms would represent a considerable redistribution of probabilities, they would not lead to any difference in prediction of reproducible phenomena. This is the basic reason for the success of the Gibbs canonical ensemble, and it is interesting to note that Gibbs also used an ensemble canonical in angular momenta, as in (18), to describe a rotating system.

of ρ and Z by

$$\langle \mathcal{H} \rangle = \mathrm{Tr}(\mathcal{H}\rho) = -\partial \ln Z/\partial\beta;$$
$$\langle J_i \rangle = \mathrm{Tr}(J_i\rho) = -\partial \ln Z/\partial\lambda_i. \tag{19}$$

The entropy corresponding to the density matrix (18) is, in conventional units,

$$S = -k\,\mathrm{Tr}(\rho \ln\rho) = k[\beta\langle\mathcal{H}\rangle + \lambda_i\langle J_i\rangle + \lambda_0], \tag{20}$$

where k is the Boltzmann constant. Differentiating (20) and noting from (19) that $-d\lambda_0 = \langle\mathcal{H}\rangle d\beta + \langle J_i\rangle d\lambda_i$, gives

$$dS = k[\beta d\langle\mathcal{H}\rangle + \lambda_i d\langle J_i\rangle]. \tag{21}$$

We now consider a macroscopic system characterized by a uniform and constant temperature T, rotating with constant and uniform angular velocity ω. The system is in thermal and rotational equilibrium, and can be described by the laws of thermodynamics. The increment of total energy is $dE = dQ + \omega_i dM_i$, from which the differential of entropy is

$$dS = dQ/T = (1/T)dE - (\omega_i/T)dM_i. \tag{22}$$

Comparison of (21) and (22) yields the physical meaning of the Lagrange multipliers,

$$\beta = 1/kT, \quad \lambda_i = -\omega_i/kT. \tag{23}$$

The density matrix (18) may thus be written as $\rho = Z^{-1}\exp -\beta(\mathcal{H} - \omega_i J_i)$. From Eq. (6), the quantity $\mathcal{H} - \omega_i J_i$ appearing in the exponent has the physical significance of the effective Hamiltonian in the rotating-coordinate system, if $\omega_i J_i$ is a constant of the motion. In this case, the density matrix remains given by (18) for all time.

If $\omega_i J_i$ is not a constant of the motion, Eq. (18) gives the density matrix only at the initial time $t=0$, for which the information $\langle\mathcal{H}\rangle$, $\langle J_i\rangle$ is given. The time dependence of any density matrix is given by $i\hbar\dot{\rho} = [\mathcal{H},\rho]$. The equilibrium-density matrix for a rotating system need not commute with the Hamiltonian and thus may have a time dependence. By "equilibrium" we mean that expectation values of observable quantities are constant in a frame of reference rotating with the system. The vector operator $\mathbf{v}$ is represented in the rotating system, for example, by the operator $\mathbf{v}_r = R(t)\mathbf{v}R(-t)$, where $R(t)$ is given by the expression (2). Its equation of motion is

$$\left\langle \frac{d\mathbf{v}_r}{dt} \right\rangle = \left\langle \frac{\partial \mathbf{v}_r}{\partial t} \right\rangle + \frac{1}{i\hbar}\langle[\mathbf{v}_r, \mathcal{H}]\rangle$$
$$= (1/i\hbar)\langle[\mathbf{v}_r, \mathcal{H} - \omega_i J_i]\rangle$$
$$= (1/i\hbar)\,\mathrm{Tr}\{\mathbf{v}_r[\rho, \mathcal{H} - \omega_i J_i]\}, \tag{24}$$

The commutator, and hence $\langle d\mathbf{v}_r/dt\rangle$, vanishes for the equilibrium-density matrix (18). Also, it is easily seen that the density matrix in the rotating frame is constant: $\dot{\rho}_r = (d/dt)[R(t)\rho R(-t)] = 0$.

In practice, one may be interested only in some small part of the macroscopic rotating system, such as the expected value of the spin angular momentum in a crystal with many other degrees of freedom. Then, in taking the trace of ρ, one can first sum over all the quantum numbers of the other degrees of freedom; what remains is a density matrix with a smaller number of rows and columns, describing only the small subsystem being studied. If the interaction energy between the subsystem and the remaining system is neglected, the only role of the larger system will be to provide an environment with a definite temperature and angular velocity. We focus attention on the expectation value of the magnetic moment of a single atom or nucleus, but assume that it is representative of a large number of identical spins in the macroscopic sample. If spin-spin interactions, either direct or indirect (through the lattice) are negligible, the condition that expected moments for a single spin correspond to a reliable prediction of total moment of N spins is $N \gg (\beta\hbar\gamma H^*)^2$, where $H^* = |H - \omega/\gamma|$ is the effective magnetic field. As spin-spin interactions become stronger, the requirements become more stringent, and when conditions for a ferromagnetic or antiferromagnetic phase change are reached, the connection between expected moment of a single spin and total moment of N spins breaks down completely. As is shown elsewhere, this breakdown of correspondence between the Boltzmann "molecular" treatment and the Gibbs "global" treatment is characteristic of any phase transition. In this paper, we limit ourselves to the case of sufficiently weak interactions so that cooperative phenomena do not appear.

Before proceeding to calculate specific gyromagnetic effects with the density matrix (18), the perturbation method to be employed is developed.

b. Perturbation Expansion[16] for Expectation Values

The expectation value of an arbitrary operator C, pertaining to a system described by a density matrix of the form (18), is $\langle C\rangle = \mathrm{Tr}(\rho C)$. If part of the exponent in (18) is small, but complicated, it may be treated as a perturbation. Since the quantity $\langle C\rangle$ is the trace of an operator, its value is independent of the representation; this invariance property is to be retained in the perturbation scheme. Not only is it convenient to work directly with the expansion for the expectation value of the observable of interest rather than an

[16] An early quantum-statistical perturbation theory, expressed in terms of perturbations on the energy levels, was given by R. Peierls, Z. Physik **80**, 763 (1933); S. Nakajima, Advances in Physics **4**, 363 (1955), has used operator techniques to obtain an expansion for the partition function. Application of similar techniques to statistical-mechanics problems has been given among others by R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954); D. Thouless, Ann. Phys. **10**, 553 (1960); W. Kohn and J. Luttinger, Phys. Rev. **118**, 41 (1960). The present approach was briefly reported at the April 15, 1961, meeting of the New England Section of The American Physical Society.

expansion for the partition function, but also, because of the normalizing denominator, the convergence of the expansion is bound to be better. Consider a quite general system described by a density matrix

$$\rho = e^{A+B}[\mathrm{Tr}(e^{A+B})]^{-1}, \tag{25}$$

where A and B are arbitrary operators. A second, simpler, density matrix, is $\rho_0 = e^A[\mathrm{Tr}e^A]^{-1}$. We assume that expectation values over ρ_0 can be evaluated directly, and express the expectation value over ρ in terms of those over ρ_0. The expectation value of an arbitrary operator C, $\langle C\rangle_\epsilon = \mathrm{Tr}Ce^{A+\epsilon B}[\mathrm{Tr}e^{A+\epsilon B}]^{-1}$, is a function of the number ϵ. When $\epsilon=0$, then $\langle C\rangle_\epsilon = \langle C\rangle_0 = \mathrm{Tr}(\rho_0 C)$. When $\epsilon=1$, then $\langle C\rangle_\epsilon = \langle C\rangle = \mathrm{Tr}\rho C$. Expanding $\langle C\rangle_\epsilon$ in a Taylor series about $\epsilon=0$,

$$\langle C\rangle_\epsilon = \sum_{n=0}^{\infty} \frac{\epsilon^n}{n!} \frac{d^n\langle C\rangle_\epsilon}{d\epsilon^n}\bigg|_{\epsilon=0}. \tag{26}$$

To evaluate the leading terms in (26), we make use of the well-known mathematical identity[17]

$$e^{A+\epsilon B} = e^A\left[1+\epsilon\int_0^1 e^{-Ax}Be^{(A+\epsilon B)x}dx\right] \tag{27}$$

to obtain, by iteration,

$$e^{A+\epsilon B} = e^A[1+\epsilon S_1+\epsilon^2 S_2+O(\epsilon^3)]$$

$$S_1 \equiv \int_0^1 dx e^{-Ax}Be^{Ax}$$

$$S_2 \equiv \int_0^1\int_0^1 xdxdx' e^{-Ax}Be^{Ax(1-x')}Be^{Axx'}, \tag{28}$$

and, thus,

$$\frac{de^{A+\epsilon B}}{d\epsilon}\bigg|_0 = e^A S_1;$$

$$\frac{d^2e^{A+\epsilon B}}{d\epsilon^2}\bigg|_0 = 2e^A S_2. \tag{29}$$

The derivatives for $\langle C\rangle_\epsilon$ are then obtained by application of (29) and the definition (26) for $\langle C\rangle_\epsilon$. The result is up to $n=2$ for $\epsilon=1$, if we define $\Gamma \equiv C - \langle C\rangle_0 \cdot 1$,

$$\langle\Gamma\rangle = \langle S_1\Gamma\rangle_0 + \langle(S_2 - S_1\langle B\rangle_0)\Gamma\rangle_0. \tag{30}$$

The subscript 0 means the average is taken over density matrix ρ_0. The higher-order terms to arbitrary order are derived in Appendix B. In the special case that A and B commute, the calculation becomes relatively simple because $S_1 = B$ and $S_2 = \frac{1}{2}B^2$. A somewhat more complicated case is the one where A and B do not commute, but A and C are commuting operators. In that case, (30) becomes

$$\begin{aligned}\langle\Gamma\rangle &= \langle B\Gamma\rangle_0 + \langle(S_2 - \langle B\rangle_0 B)\Gamma\rangle_0 \\ &= \langle B\Gamma\rangle_0 + \tfrac{1}{2}\langle(B-\langle B\rangle_0)^2\Gamma\rangle_0 + Q,\end{aligned} \tag{31}$$

where

$$Q \equiv \int_0^1\int_0^1 xdxdx'\langle e^{-Ax}[B, e^{Ax(1-x')}]Be^{Axx'}\Gamma\rangle_0. \tag{32}$$

It is seen that if the operator $A \to 0$, the commutator in Q vanishes, since every operator commutes with the unit operator. For small A, the operator Q is of order (AB^2), and is, therefore, small compared to the other terms in (31) which are of the order (B^2). So, for sufficiently small A, the operator Q may be neglected. To make this condition more precise, we introduce an explicit representation. In general, one can split A into a part a which fails to commute with B and a part a' which commutes with a and B, both a and a' commuting with Γ. Then, in a representation where a and Γ are diagonal, the complete quadratic term in (27), $\langle(S_2 - \langle B\rangle_0 B)\Gamma\rangle_0$, can be shown to be equal to $\langle\theta\Gamma\rangle_0$ with

$$\theta_{kl} \equiv \delta_{kl}\Big[\sum_n |B_{kn}|^2 f(a_n - a_k) - \langle B\rangle_0 B_{kk}\Big],$$

$$f(x) \equiv \sum_{n=2}^{\infty}\frac{x^{n-2}}{n!} = \frac{e^x - x - 1}{x^2}. \tag{33}$$

Putting $Q=0$ corresponds to replacing $f(a_n - a_k)$ by $1/2$, its limiting value for vanishing $|a_n - a_k|$. A sufficient condition for neglecting Q is that for all states n and k for which $|B_{nk}|^2$ is finite, $|a_n - a_k|$ be much less than unity. A particular case of (31) and (33) is the one in which B is a sum of terms, $B = \sum_k b^{(k)}$. Then,

$$\begin{aligned}\langle\Gamma\rangle = &\sum_k \langle b^{(k)}\Gamma\rangle_0 \\ &+ \tfrac{1}{2}\sum_k\sum_\lambda \langle(b^{(k)}b^{(\lambda)} - 2\langle b^{(k)}\rangle_0 b^{(\lambda)})\Gamma\rangle_0 + Q,\end{aligned} \tag{34}$$

and

$$\theta_{lm} = \delta_{lm}\sum_k\sum_\lambda\Big[\sum_n b_{mn}{}^{(k)}b_{nm}{}^{(\lambda)}f(a_n - a_m) - \langle b^{(k)}\rangle_0 b_{mn}{}^{(\lambda)}\Big].$$

The rapid convergence of the expansion (26) or (30) for $\langle C\rangle$ does not necessarily require that the eigenvalues of the operator B be small, even though it is an expansion in powers of B. The convergence is in part due to the effective cancellation of terms in the numerator and the denominator of $\mathrm{Tr}(Ce^{A+B})/\mathrm{Tr}(e^{A+B})$. For example, if B is a multiple of the unit operator, cancellation is complete and $\langle C\rangle = \langle C\rangle_0$; if B is a multiple of the unit operator plus a small operator, one expects convergence to be rapid because the part proportional to the unit operator has no effect.

The linear term in the expansion (30) has the property that if the roles of B and C are interchanged, it remains unchanged, even if none of the operators

[17] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948); R. P. Feynman, *ibid.* 84, 108 (1951); R. Kubo and K. Tomita, J. Phys. Soc. Japan 9, 888 (1954).

A, B, or C commute with either of the other operators:

$$\int_0^1 dx\langle e^{-Ax}Be^{Ax}C\rangle_0-\int_0^1 dx\langle e^{-Ax}Ce^{Ax}B\rangle_0=0; \quad (35)$$

for, in a representation in which A is diagonal,

$$(Z^{-1})\sum_n\sum_m(n|B|m)(m|C|n)\times\int_0^1 dx\{\exp[A_n(1-x)+A_mx]-\exp[A_m(1-x)+A_nx]\}=0,$$

because the integral vanishes identically. The other linear term $\langle S_1\rangle_0\langle C\rangle_0=\langle B\rangle_0\langle C\rangle_0$ is obviously also unchanged by an interchange of B and C. This symmetry property is shown to imply a class of reciprocity laws for measurable magnetic and gyromagnetic constants.

We illustrate some properties of the expansion (30) and at the same time obtain some formulas which are required later on by applying the perturbation scheme to some simple examples of nonrotating systems.

Magnetic Susceptibility of Free Atoms or Ions

The electrons of an atom or an ion in the presence of a static magnetic field H, may be described by a Hamiltonian of the form

$$\begin{aligned}&\mathfrak{H}=\mathfrak{H}^{(0)}+\mathfrak{H}^{(1)}H+\mathfrak{H}^{(2)}H^2,\\&\mathfrak{H}^{(1)}=-(e/2mc)(\mathbf{L}+2\mathbf{S})_z,\\&\mathfrak{H}^{(2)}=(e^2/8mc^2)\textstyle\sum_k(x_k^2+y_k^2),\end{aligned} \quad (36)$$

and $\mathfrak{H}^{(0)}$ is an operator not involving the magnetic field; $\mathbf{L}$ and $\mathbf{S}$ are orbital and spin angular momentum. The magnetic-moment operator is defined by $M_z=-\partial\mathfrak{H}/\partial H$, which in view of (36), becomes $M_z=-\mathfrak{H}^{(1)}-2H\mathfrak{H}^{(2)}$. Taking the expectation value gives the exact expression for the magnetic moment; assuming an equilibrium density matrix with no rotation,

$$\begin{aligned}\langle M_z\rangle&=\frac{-\mathrm{Tr}(\partial\mathfrak{H}/\partial H)\exp(-\beta\mathfrak{H})}{\mathrm{Tr}\exp(-\beta\mathfrak{H})},\\&=-\langle\mathfrak{H}^{(1)}\rangle-2H\langle\mathfrak{H}^{(2)}\rangle.\end{aligned} \quad (37)$$

We restrict attention to the part of the magnetic moment linear in the field strength. Let $A=-\beta\mathfrak{H}^{(0)}$, $B=-\beta(H\mathfrak{H}^{(1)}+H^2\mathfrak{H}^{(2)})$, and assume that B is small, or numerically that $\beta\mu_BH=6.4\times10^{-5}H/T\ll1$, if H is measured in gauss and T in degrees Kelvin. Expanding (37) by means of Eq. (30) and assuming zero spontaneous polarization $\langle\mathfrak{H}^{(1)}\rangle_0=0$, we obtain for the term linear in H,

$$\langle M_z\rangle=H\beta\int_0^1 dx\langle e^{-Ax}\mathfrak{H}^{(1)}e^{Ax}\mathfrak{H}^{(1)}\rangle_0-2H\langle\mathfrak{H}^{(2)}\rangle_0.$$

The susceptibility, defined by $\chi=d\langle M_z\rangle/dH$, is then

$$\chi=\beta\int_0^1 dx\langle e^{-Ax}\mathfrak{H}^{(1)}e^{Ax}\mathfrak{H}^{(1)}\rangle_0-2\langle\mathfrak{H}^{(2)}\rangle_0. \quad (38)$$

The diamagnetic (negative definite) part has the usual form,

$$\chi_d=-2\langle\mathfrak{H}^{(2)}\rangle_0=\frac{-e^2}{4mc^2}\sum_k(x_k^2+y_k^2)=\frac{-e^2}{6mc^2}\sum_k\langle r_k^2\rangle_0,$$

where the last step is permissible if in the absence of the field no direction is singled out in the atom, i.e., if its environment has cubic or isotropic symmetry. We obtain the Van Vleck expression[18] for paramagnetic susceptibility from the first part of (38) by introducing a representation in which $\mathfrak{H}^{(0)}$ is diagonal with eigenvalues E_n, and then integrating:

$$\chi_p=\beta\int_0^1 dx\langle e^{-Ax}\mathfrak{H}^{(1)}e^{Ax}\mathfrak{H}^{(1)}\rangle_0 \quad (39)$$

$$=\beta\int_0^1 dx\frac{\sum_m\sum_n(m|e^{A(1-x)}|m)(m|\mathfrak{H}^{(1)}|n)(n|e^{Ax}|n)(n|\mathfrak{H}^{(1)}|m)}{\sum_n(n|e^A|n)} \quad (39a)$$

$$=\frac{2\sum_{n\neq m}\sum_m\dfrac{\exp(-E_n\beta)}{E_m-E_n}|(m|\mathfrak{H}^{(1)}|n)|^2}{\sum_n\exp(-E_n\beta)}+\frac{\beta\sum_n\exp(-E_n\beta)|(n|\mathfrak{H}^{(1)}|n)|^2}{\sum_n\exp(-E_n\beta)}. \quad (39b)$$

An approximation to (39) suggests itself if we write

$$\chi_p=\beta\langle(\mathfrak{H}^{(1)})^2\rangle_0+\beta\int_0^1 dx\langle[e^{-Ax},\mathfrak{H}^{(1)}]e^{Ax}\mathfrak{H}^{(1)}\rangle_0$$

and neglect the commutator to obtain

$$\chi_p=\beta\mu_B^2/\hbar^2\langle(L_z+2S_z)^2\rangle_0. \quad (40)$$

The neglect of the commutator is permissible if that part of A which fails to commute with $\mathfrak{H}^{(1)}$ is sufficiently small. In an atom or ion, this is usually a single term of the form $(\zeta/\hbar^2)\mathbf{L}\cdot\mathbf{S}$, so that if $|\zeta\beta|\ll1$, the commutator may be neglected.

[18] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

From this derivation of susceptibilities, three points about the perturbation theory are noted. (1) Whereas the result (39) is obtained by using only the first term in the expansion (30), the usual derivation[18] of (39) by means of a perturbation theory for the energy levels requires a second-order perturbation calculation. Generally, the two different perturbation schemes need not run parallel, since their expansion parameters are in fact different. (2) The result (40) would not be obtained at all in the energy-level perturbation scheme. There the first-order term involves only the diagonal elements of (L_z+2S_z), whereas (40) includes both diagonal and off-diagonal elements. Thus, somewhat different approximations are suggested by the two different schemes. (3) If the energy denominator in (39b) creates a problem, an alternative method of evaluating (39) is to take the trace [e.g., carry out the sums in (39a)] before doing the integral.

Polarization of Nuclei with Hyperfine Coupling

The second example for consideration is the polarization of nuclei which are coupled to electrons via the hyperfine interaction. The system is described by the Hamiltonian

$$\mathcal{H}=\mathcal{H}_e-\gamma_e\mathbf{S}\cdot\mathbf{H}-\gamma_n\mathbf{I}\cdot\mathbf{H}-\gamma_n\sum_k a_k\mathbf{S}_k\cdot\mathbf{I}, \quad (41)$$

where $\mathcal{H}_e$ does not involve the nuclear-spin coordinates, $\mathbf{I}$ is the nuclear-spin vector, $\mathbf{S}=\sum_k\mathbf{S}_k$ is the total electronic spin, and γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively ($\hbar\gamma_e=2\mu_B$ and $\hbar\gamma_n=g\mu_n$ in terms of the Bohr and nuclear magneton). The a_k are the hyperfine-coupling constants,[19] $a_k=(8\pi/3)\gamma_e|\psi_k(0)|^2$ where $|\psi_k(0)|^2$ is the probability that the kth electron is found at the nucleus. This probability is finite for the S-state electrons in free atoms as well as for the free electrons in metals. The second and third terms of (41) give the coupling of the external field with the electronic and nuclear dipoles, respectively, and the last term is the interaction of the nuclear dipole with the electronic ones. Let us call the direction of the magnetic field the z direction, and let

$$A=\beta(\gamma_n\mathbf{I}\cdot\mathbf{H}+\gamma_e\mathbf{S}\cdot\mathbf{H}-\mathcal{H}_e),$$
$$B=\beta\gamma_n\sum_k a_k\mathbf{S}_k\cdot\mathbf{I},$$
$$C=I_z.$$

Since $[A,C]=0$, we have to first order in B from Eq. (31)

$$\langle I_z\rangle=\langle I_z\rangle_0+\beta\gamma_n\sum_k a_k\langle\mathbf{S}\cdot\mathbf{I}(I_z-\langle I_z\rangle_0)\rangle_0. \quad (42)$$

Evaluating the sums over the nuclear-spin states gives for $\beta\gamma_n\hbar H\ll 1$,

$$\langle I_z\rangle=\beta\gamma_n\hbar^2\tfrac{1}{3}I(I+1)[H+\textstyle\sum_k\langle a_k(S_z)_k\rangle]. \quad (43)$$

The only requirement for the expression (42) to be valid is that $\beta\mu_N g\sum_k a_k\ll 1$. The physical interpretation of (43) is simple. Clearly, the magnetic susceptibility for the free nucleus is

$$\chi_n=\beta(\gamma_n\hbar)^2\tfrac{1}{3}I(I+1),$$

and the effect of the hyperfine coupling is to provide an internal magnetic field of magnitude $H'=\sum_k\langle a_k(S_z)_k\rangle_0$. For the free electrons in a metal, $\sum_k\langle a_k(S_z)_k\rangle_0$ is evaluated[20] with the help of the definition of the a_k and the Pauli theory of paramagnetism in metals, to yield $H'\cong H\cdot(8\pi\mu_B^2/E_F)n(0)$, where E_F is the Fermi energy of the metal at absolute zero, and $n(0)\equiv\langle\sum_k|\psi_k(0)|^2\rangle_0$. These internal fields give rise to the Knight shift[21] in the nuclear magnetic resonance in metals. The internal field here gives a small correction to the applied field, so that the problem could as well be treated by a perturbation theory for the energy levels. On the other hand, in a hydrogen-like atom, if the electron is in its ground state, one easily finds[20]

$$H'=\langle a(S_z)\rangle_0=(\beta H\mu_B)(8/3)\mu_B Z^3/a_0^3,$$

where a_0 is the Bohr radius and Z the atomic number of the nucleus. These fields give rise to a method of polarizing nuclei suggested by Rose and Gorter.[22] At temperatures of the order of 1°K, such internal fields may be 10^4 or 10^5 times as large as the external field. Still, the present perturbation theory would be applicable and second-order terms negligible, although it would not be appropriate to use the usual perturbation theory for energy levels. As these examples indicate, the method employed here can provide a unified derivation of some phenomena which are usually treated by diverse methods.

c. Electronic Gyromagnetic Effects

The results of the preceding sections are now applied to the analysis of electronic gyromagnetic effects. We wish to evaluate the combined effect of a macroscopic rotation of a substance and of an external magnetic field on the angular momentum of the electrons and on the atomic-magnetic moment. Only the effects linear in the magnetic field and the rotation are considered, practically limiting the theory to magnetically dilute systems.

Let $\mathcal{H}_0$ be the Hamiltonian of a stationary crystal in the absence of any external field. The crystal is rotating about a fixed direction with angular velocity ω and has an external magnetic field $\mathbf{H}$ acting on it. We introduce coordinates fixed with respect to the crystal, and

[19] E. Fermi, Z. Physik 60, 320 (1930).

[20] In the evaluation of the H' for the free electrons in a metal and for the hydrogen-like atom, it was assumed that $\langle S_z\delta(\mathbf{r})\rangle_0\approx\langle S_z\rangle_0\langle\delta(\mathbf{r})\rangle_0$.

[21] W. D. Knight, Phys. Rev. 76, 1259L (1949); in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

[22] M. E. Rose, Phys. Rev. 75, 213 (1949). C. J. Gorter, Physica 14, 504 (1948). The problem is analyzed by A. Simon, M. E. Rose, and J. M. Jauch, Phys. Rev. 84, 1155 (1951).

distinguish all operators expressed in the rotating coordinates by an asterisk. More explicitly, by a vector operator A^* we mean one whose components A_i^* are found by computing the components A_j in the laboratory frame and projecting onto rotating axes. In view of (18) and (23), the density matrix of the system may be written in the form (25) with

$$A=-\beta\mathcal{H}_0^*,$$

$$B=\beta\left[\frac{e}{2mc}(\mathbf{L}+2\mathbf{S})^*\cdot\mathbf{H}^*(t) -\frac{e^2}{8mc^2}\sum_k|\mathbf{r}_k^*\times\mathbf{H}_k^*(t)|^2+\mathbf{J}\cdot\omega\right]. \quad (44)$$

The time dependence of $\mathbf{H}^*(t)$ arises because a field which is fixed in space will be seen as a rotating field in the rotating-coordinate system.

While $\mathcal{H}_0$ would be expected to have an implicit time dependence due to the rotation, the Hamiltonian $\mathcal{H}_0^*$ referred to body-fixed axes keeps the relative-position vector of particles approximately independent of the rotation, and no implicit time dependence is expected. We calculate the magnetic moment $\langle\mathbf{M}^*\rangle$ and the angular momentum $\langle\mathbf{J}^*\rangle$; these vectors, like $\mathbf{H}^*(t)$, are related to the laboratory frame, if the axis of rotation is the 3 direction, by the relation

$$\begin{pmatrix}v_1^*\\v_2^*\\v_3^*\end{pmatrix}=\begin{pmatrix}\cos\omega t & \sin\omega t & 0\\ -\sin\omega t & \cos\omega t & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}v_1\\v_2\\v_3\end{pmatrix}. \quad (45)$$

If the $\cos\omega t$ and $\sin\omega t$ are treated as C numbers, the commutation rules for vectors in the rotating system are the same as that in the fixed system; the transformation (45) is then, in fact, equivalent to the unitary transformation (2) for vector operators, although not for classical quantities such as the magnetic field. If the $\cos\omega t$ and $\sin\omega t$ are regarded as the components of a vector giving the relative orientation of physical particles (or a quasi-particle such as the center of mass of the system), they do not commute with $\mathbf{J}$. In that case, the angular-momentum, commutation rules become in the rotating system[23] $[J_x^*,J_y^*]=-iJ_z^*$, etc., instead of the usual $[J_x,J_y]=iJ_z$, etc. Note the minus sign.

Applying the perturbation expansion (30) to (44), considering only the term linear in B, yields for the expectation value of J_i^* and $M_i^*\equiv-\partial\mathcal{H}/\partial H_i$:

$$\langle M_i^*\rangle-\frac{e}{2mc}\langle L_i^*+2S_i^*\rangle_0=\sum_{j=1}^{3}\chi_{ij}H_j^*(t)+\theta_{i3},$$
$$\langle J_i^*\rangle-\langle J_i^*\rangle_0=\sum_{j=1}^{3}\theta'_{ij}H_j^*(t)+\eta_{i3}\omega, \quad (46)$$

where

$$\chi_{ij}=\beta\left(\frac{e}{2mc}\right)^2\int_0^1 dx\langle e^{-Ax}(L_j^*+2S_j^*)e^{Ax}(L_i^*+2S_i^*)\rangle_0 -\beta(e/2mc)^2\langle(L_i^*+2S_i^*)\rangle_0\langle L_j^*+2S_j^*\rangle_0 +(e^2/4mc^2)\sum_\sigma\langle x_i^{*\sigma}x_j^{*\sigma}-\delta_{ij}(r^{*\sigma})^2\rangle_0,$$

$$\theta_{i3}=\beta\frac{e}{2mc}\int_0^1 dx\langle e^{-Ax}J_3^*e^{Ax}(L_i^*+2S_i^*)\rangle_0 -\beta\frac{e}{2mc}\langle J_3^*\rangle_0\langle L_i^*+2S_i^*\rangle_0, \quad (47)$$

$$\theta'_{ij}=\beta\frac{e}{2mc}\int_0^1 dx\langle e^{-Ax}(L_j^*+2S_j^*)e^{Ax}J_i^*\rangle_0 -\beta\frac{e}{2mc}\langle J_i^*\rangle_0\langle L_j^*+2S_j^*\rangle_0,$$

$$\eta_{i3}=\beta\int_0^1 dx\langle e^{-Ax}J_3^*e^{Ax}J_i^*\rangle -\beta\langle J_3^*\rangle_0\langle J_i^*\rangle_0.$$

From the identity (35), it follows that these coefficients have certain symmetry properties:

$$\theta_{ij}=\theta'_{ji};\quad \chi_{ij}=\chi_{ji};\quad \eta_{ij}=\eta_{ji}. \quad (48)$$

In deriving (46) and (47), it was assumed that the system is in thermodynamic equilibrium; but, the system is generally in the presence of a time-dependent field $H^*(t)$ so that the assumption is not generally justified. The time-dependent behavior is discussed in Sec. 4. However, the equilibrium treatment is applicable in several important cases.

(a) The field is parallel to the axis of rotation (only the transverse components have a time dependence).
(b) The transverse components are made to rotate with the crystal, so that again there is no time dependence.
(c) The rotation is so slow that the longest relaxation time of the system is very small compared to the period of rotation. Then the system continues in a time-varying equilibrium.
(d) The rotation is so rapid that the shortest relaxation time of the system is very large compared to the period of rotation. In this case, the spins and particles do not have time to respond to the rapidly changing, transverse field, and only the field in the 3-direction should be considered in Eq. (46).

The usual Einstein-deHaas and Barnett effects[2-4] are already included in the case of a field parallel to the axis of rotation. For analysis of these effects, we require further that the system have sufficient symmetry (e.g., reflection symmetry across a plane passing through the 3 axis is sufficient), so that the off-diagonal elements

[23] J. H. Van Vleck, Revs. Modern Phys. 23, 213 (1951).

of the tensors (47) all vanish. In addition, it is assumed that the unperturbed crystal is unpolarized. Finally, diamagnetism is neglected.

The Eqs. (46) become, with these simplifications,

$$\begin{aligned}\langle M_3\rangle &= \chi_{33}H_3+\theta_{33}\omega,\\ \langle J_3\rangle &= \theta'_{33}H_3+\eta_{33}\omega,\end{aligned} \tag{49}$$

with

$$\chi_{33}=\beta\left(\frac{e}{2mc}\right)^2\int_0^1 dx\langle e^{-\lambda x}(L_3+2S_3)e^{\lambda x}(L_3+2S_3)\rangle_0,$$

$$\theta'_{33}=\theta_{33}=\beta\frac{e}{2mc}\int_0^1 dx\langle e^{-\lambda x}(L_3+2S_3)e^{\lambda x}J_3\rangle_0, \tag{50}$$

$$\eta_{33}=\beta\int_0^1 dx\langle e^{-\lambda x}J_3e^{\lambda x}J_3\rangle_0.$$

In the usual Einstein-deHaas type of experiment, a magnetic field H_3 induces a magnetic moment $\langle M_3\rangle$ in a solid which is measured, and it also induces an electronic angular momentum $\langle J_3\rangle$. This internal angular momentum must be balanced[24] by a macroscopic rotation $Q\omega_E=-\langle J_3\rangle$, with Q the moment of inertia about the 3 axis. Measurements then yield the g'_E factor

$$\begin{aligned}(e/2mc)g'_E &\equiv \langle M_3\rangle/Q\omega_E\\ &= \langle M_3\rangle/\langle J_3\rangle=\chi_{33}/\theta'_{33}.\end{aligned} \tag{51}$$

In the Barnett experiments, the angular velocity ω_B is impressed, and a resulting polarization observed. The angular velocity is compared to an equivalent field H_B which produces the same polarization. The Barnett coefficient

$$\begin{aligned}(e/2mc)g'_B &\equiv \omega_B/H_B\\ &= \frac{\langle M_3\rangle/\theta_{33}}{\langle M_3\rangle/\chi_{33}}=\frac{\chi_{33}}{\theta_{33}}.\end{aligned} \tag{52}$$

The equality $g'_B=g'_E\equiv g'$ arises from the equality of θ'_{33} and θ_{33}, which is a direct consequence of the relation (35). In the present (linear) approximation, g'_E and g'_B are independent of the field strength or angular velocity, but may have a temperature dependence.

Numerical evaluation of g' has been carried out by Van Vleck and Frank,[25] by Arajs *et al.*[26] for rare-earth salts, and by Gorter and Kahn[27] particularly for salts containing ions of the iron group. Van Vleck, Frank, and Arajs assume that J_i commutes with $\mathcal{H}^{(0)}$, so that

$$\theta_{ii}=(e/2mc)\beta\langle(L_i+S_i)(L_i+2S_i)\rangle_0. \tag{53}$$

This is a good assumption for the rare-earth salts, since the $4f$ electrons responsible for the magnetism are well inside the atoms and only very weakly coupled to other atoms with which they could exchange angular momentum; in addition, these authors assume Russell-Saunders coupling for the atom.[26] With only these assumptions, g' has been evaluated for Eu^{3+} and Sm^{3+} by Frank for various temperatures. Theory and experiment[28] are in agreement insofar as experimental data are available. For the other rare-earth ions, the calculation for room temperatures is simplified, because the multiplet splitting (same L and S, different J) is large compared to kT. If, further, the off-diagonal elements of (L_i+2S_i) are neglected in a representation where $\mathcal{H}_0$ is diagonal, it is found from (39) and (51) that $g'=g$, the usual Lande splitting factor associated with the ground state of the ion:

$$g=3/2+\frac{S(S+1)-L(L+1)}{2J(J+1)}.$$

This simple formula agrees with the experimental results quite well for all the rare-earth salts, except those involving Eu^{3+} or Sm^{3+}. To illustrate the situation, we take the case of Nd^{3+} where $g=0.73$; the evaluation of g' without assuming large multiplet splitting or negligible off-diagonal elements gives $g'=0.76$; the experiments of Sucksmith[29] on Nd_2O_3 give values of g' ranging from 0.74 to 0.83, the mean value for the experimental results being 0.77, in good agreement with Van Vleck theory. Arajs and coworkers have extended the calculations of Frank for Eu^{3+} and Sm^{3+} to higher temperatures, up to 2000°K. They also have evaluated the g' for the other tripositive rare-earth ions in the temperature range from 10°K to 2000°K. They find that Eu^{3+} (six $4f$ electrons) has by far the largest g' value at room temperature, but it falls off with increasing temperatures; the g' for Sm^{3+} (five $4f$ electrons) increases with temperature, reaches a maximum at about 1000°K, and then decreases. The g' values for the tripositive, rare-earth ions having from one to four $4f$ electrons increase monotonically with temperature, whereas those for ions with more than six $4f$ electrons are practically independent of temperature. No high-temperature experimental measurements of g' for these tripositive ions are available.

[24] The field does not give up appreciable angular momentum to the material: The angular momentum of the field,

$$G(t)=1/4\pi c\int[(\mathbf{E}\times\mathbf{H})\times\mathbf{r}]dv$$

with $\mathbf{r}$ the vector distance to the center of rotation of the crystal, is quadratic in field strength and in this respect of higher order than the right-hand side of (49). If the field increases linearly with time in the z direction, $G(t)=(1/8\pi)c^2\dot{H}H(t)\int z(y\hat{z}-x\hat{y})dv$ This quantity has no component in the field direction and vanishes for all but rather asymmetrically shaped bodies.

[25] A. Frank, Phys. Rev. **39**, 119 (1932); (see also reference 17).

[26] S. Arajs, R. V. Colvin, and R. W. Whitmore (1961 unpublished). Recently these authors have used for some cases more-exact energy levels than those given by the L-S coupling scheme.

[27] C. J. Gorter and B. Kahn, Physica **7**, 753 (1940).

[28] The comparison of theory and experiment for the g' values of salts of the iron group, given by L. F. Bates (cited in footnote 4) p. 270, does not include the only really satisfactory calculation, of the g' values, that of C. J. Gorter and B. Kahn, reference 27.

[29] W. Sucksmith, Proc. Roy. Soc. (London) **A128**, 276 (1930); **A135**, 276 (1932).

Gorter and Kahn have worked out a procedure for calculating θ_i without the simplification (53); J_i and $\mathcal{H}_0'$ need not commute. However, they assume, in analogy to the Van Vleck theory for susceptibilities, that one has Russell-Saunders coupling and that multiplet splitting is either large compared to kT or small compared to kT. In evaluating g' for salts of the iron group, it is assumed that the crystalline-field splitting is much larger than the $\mathbf{L}\cdot\mathbf{S}$ splitting; the former is in lowest approximation assumed to quench completely the magnetism due to orbital motion; then the $\mathbf{L}\cdot\mathbf{S}$ coupling is treated as a perturbation. The perturbation parameter α is a measure of the relative strength of spin-orbit coupling to the crystal field. In terms of this parameter, the magnetic susceptibility obtained is $\chi=\frac{1}{3}(e/2mc)^2\beta S(S+1)(2+\alpha)^2$, and the g' value is $g'=(2+\alpha)/(1+\alpha)$. The values of α obtained from susceptibility measurements are then employed to predict g' values. Agreement is satisfactory[27] for Cr^{3+}, Mn^{3+}, Fe^{++}, and Co^{++}, although for Co^{++} the application of perturbation theory is questionable, and α is rather large, around 0.5. The g' for Ni^{++} and Cu^{++} were evaluated by these authors, but no measurements are available.

Although the theory presented here is primarily for paramagnetic materials, for completeness we summarize the status of the theory of the gyromagnetic ratio for ferromagnetic and other materials. For ferromagnetic materials, it has been shown first by Kittel[30] and proved quite generally by Van Vleck[31] that the magneto-mechanical factor g' is related to the spectroscopic-splitting factor g which occurs in the theory of ferromagnetic-resonance experiments by the relation $g'=g/(g-1)$, or approximately $g-2=2-g'$. This is proved by assuming again that the orbital angular momentum is nearly quenched. It is irrelevant whether quenching is due to exchange coupling or due to the crystal field. If $M_z=(e/2mc)(L_z+2S_z)$, i.e., if diamagnetism may be neglected, and $J_z=L_z+S_z$, then one has $g'=(2mc/e)\langle M_z\rangle/\langle J_z\rangle=(2+\alpha)/(1+\alpha)$, where $\alpha\equiv\langle L_z\rangle/\langle S_z\rangle\ll 1$. In microwave spectroscopy, one observes energy levels $E=E_0+\mu_B gMH$, where M is an integer eigenvalue of the component of the total spin in the direction of the field. The splitting factor g is equal to 2 in the case of no orbital contribution. In Van Vleck's calculation, the spin-orbit coupling and the effect of the external field on the orbital angular momentum are treated as a perturbation. Using second-order perturbation theory, he finds $g=2+\alpha$. The result is valid even when exchange interactions, dipole interactions between spins, and any other interactions which commute with $\mathbf{S}$ are included. The available experimental data[32] are summarized in Table I.

TABLE I. Comparison of experimental g values and g' values.[a]

Material	Magnetic-resonance measurements g	Magnetic-resonance measurements $g/(g-1)$	Gyromagnetic-effect measurements g'
Fe	2.11	1.90	1.92
Co	2.20	1.83	1.85
Ni	2.21	1.83	1.84
Permalloy	2.11	1.90	1.91
Supermalloy	2.10	1.91	1.91
Heusler Alloy	2.01	1.99	1.99
Magnetite	2.20	1.83	1.93
Mn Sb	2.10	1.91	1.98

[a] See reference 32.

The data indicate satisfactory agreement with the relation $g/(g-1)=g'$, for Fe, Ni, Co, and the alloys. A few years ago it appeared that discrepancies existed for these metals and alloys. However, the recent precision measurements of the Einstein-deHaas effect[4] seem to have removed the discrepancies. For the chemical compounds Fe_3O_4 and MnSb, the experiments indicate that $g/(g-1)\neq g'$. Possible origins of deviations from this relation have been discussed by Van Vleck[31] and by Kittel and Mitchell,[33] although not specifically in connection with these compounds. Further theoretical study is needed to understand quantitatively and qualitatively the relation between g and g' for them.

For diamagnetic ionic crystals, one expects no gyromagnetic phenomena because the θ_{ij} and θ'_{ij} of Eq. (47) contain no diamagnetic contribution as the susceptibilities do. Gyromagnetism due to conduction electrons has been discussed by Broer,[34] although it is too small to be observable in ordinary metals by present techniques. However gyromagnetic experiments have been performed[35] on superconducting lead; these experiments

[30] C. Kittel, Phys. Rev. **76**, 743 (1949). See also D. Polder, Phil. Mag. **40**, 99 (1949).

[31] J. H. Van Vleck, Phys. Rev. **87**, 266 (1950).

[32] The g and g' values for Fe, Ni, Co, Permalloy, and Supermalloy are those given by G. G. Scott, Bull. Am. Phys. Soc. **5**, 178 (1960). The g' values are measured by the Einstein-deHaas effect by Scott; the g values for these substances are averages of the results of various investigators during the past ten years: G. Asch, Compt. rend. **248**, 781 (1959); **249**, 1483 (1959). D. M. S. Baggulay, Proc. Phys. Soc. (London) **A66**, 765 (1953). D. M. S. Baggulay and N. J. Harick, *ibid.* **A67**, 648 (1954). L. Barlow and K. J. Standley, *ibid.* **B69**, 1052 (1956). N. Bloembergen, Phys. Rev. **78**, 572 (1950). A. J. P. Meyer, Compt. rend. **246**, 1517 (1958). K. H. Reich, Phys. Rev. **101**, 1647 (1956). J. A. Young, Jr. and E. A. Uehling, *ibid.* **94**, 544 (1954). The agreement between the ferromagnetic g and the magneto-mechanical g' should be still better if instead of the averaged values of g, the most-recent measurements, those of Asch, would be used for comparison. The g' values for the Heussler alloy and for MnSb have been recently measured by G. G. Scott (private communication); the magnetic-resonance values are from W. A. Yager and F. R. Merritt, Phys. Rev. **75**, 318(L) (1949), and Adam and K. S. Standley, Proc. Phys. Soc. (London) **A65**, 454 (1952), respectively. The g and g' values for magnetite are from L. R. Bickford, Phys. Rev. **76**, 137(L) (1949), and W. Sucksmith (reference 29), respectively. For a summary of the earlier measurements of g and g' values, see C. Kittel, J. phys. radium **12**, 291 (1951). A very recent summary of data for Fe, Co, Ni, and their alloys is given by A. J. P. Meyer and G. Asch, J. Appl. Phys. **32**, 3305 (1961). *Added in proof.* See also G. G. Scott, Revs. Modern Phys. **34**, 102 (1962).

[33] C. Kittel and A. Mitchell, Phys. Rev. **101**, 1611 (1956). See also Kittel, reference 5.

[34] L. J. F. Broer, Physica **13**, 473 (1947).

[35] I. K. Kikoin and S. V. Goobar, Doklady Acad. Nauk S.S.S.R. **19**, 249 (1938).

give $g'=1.0$ for the conduction electrons in magnetic fields below the threshold value at which the resistivity of lead has a measurable magnitude.

Magnetomechanical effects are not necessarily restricted to solids, but would also be expected in liquids and gases, in which the atoms or molecules have a magnetic moment. Gorter and Kahn point out that molecules in a gas can exchange angular momentum through collisions with the walls of the vessel in which the gas is contained, so that we should be able to detect gyromagnetic effects in paramagnetic gases such as oxygen and nitric oxide. In the Einstein-deHaas effect, we would observe a rotation ω_E of the vessel.

d. Polarization of Nuclear Spins in a Crystal

Since most nuclei, like electrons, posses both a spin angular momentum and a parallel magnetic moment in their ground state, and since angular momentum can be exchanged between nuclear spins and lattice motion, we expect at least in principle that polarization of nuclei by the rotation of a macroscopic sample, the nuclear analog of the Barnett effect, is possible. The polarization of nuclei by a magnetic field requires a means for balancing the angular momentum acquired by the nuclei. One such means is the rotation of the whole lattice. This occurrence is the nuclear analog of the Einstein-deHaas effect. We discuss in the following the polarization of nuclei due to the simultaneous action of an external field and a rotation, thus including both effects. The coupling of the nuclear spins with the crystal environment is treated as a perturbation, whereas the action of the field and the rotation on the uncoupled nucleus are treated exactly. In evaluating the polarization of the nuclear spins, the simplifying assumption is made that in the stationary crystal the nuclei have no orbital angular momentum.

Consider a single-spin operator $\mathbf{I}$ expressed in units of $\hbar$ with moment $\mu g\mathbf{I}$ and in an external field $\mathbf{H}$ contained in a rotating crystal which is at temperature β. If the coupling between the spin and the surroundings is neglected, the density matrix, in view of (18) and (23) is

$$\rho_1=(1/Z)\exp(\beta\mu g I_i K_i), \quad \text{where} \quad K_i=H_i+\omega_1/\gamma, \tag{54}$$

the K_i are the components of the effective magnetic field due to the combined action of the external field and the angular velocity ω of the crystal. We leave off the subscript n from γ_n in the rest of this paper. The expectation value for the component I_{11} along the direction $\mathbf{K}$ is

$$\langle I_{11}\rangle=(I+\tfrac{1}{2})\coth[a(I+\tfrac{1}{2})]-\tfrac{1}{2}\coth a/2\cong\tfrac{1}{3}aI(I+1), \quad \text{if} \quad Ka\equiv\beta\mu gK\ll 1. \tag{55}$$

The expectation value $\langle I_{11}\rangle$ is time-independent; the perpendicular component has zero expectation value. I is the spin of the nucleus in its ground state. The effects of rotation and magnetic field are additive according to (55) if $a\ll 1$, and for any value of a are correctly described by a total effective field $\mathbf{K}$. The moment of inertia η_N, defined by $\hbar\langle\mathbf{I}\rangle=f_N\omega$, and the nuclear susceptibility are related:

$$\chi_N=\gamma^2\eta_N=\beta(g\mu)^2\tfrac{1}{3}I(I+1). \tag{56}$$

To include the interaction of a single nuclear spin with the internal fields due to all the rest of the crystal, we treat the uncoupled system "spin plus remainder of crystal" as the zeroth approximation, and regard the coupling between the spin and the crystalline fields as a perturbation, which must be small compared to kT. The calculation is carried out in the laboratory coordinate system in which the effective, external magnetic field $\mathbf{K}$ is constant. The perturbation Hamiltonian $\mathcal{H}_{12}$ will in general have an implicit time dependence, which is discussed further on. In applying the perturbation expansion (30), we choose

$$A=-\beta(\mathcal{H}_0-\mathbf{H}\cdot\mathbf{M}-\omega\cdot\mathbf{J}-\mu g\mathbf{K}\cdot\mathbf{I}),$$
$$B=-\beta\mathcal{H}_{12},$$
$$\mathbf{\Gamma}=\mathbf{I}-\langle\mathbf{I}\rangle_0.$$

Here, $\mathcal{H}_0$ is the uncoupled Hamiltonian of the crystal in the absence of the magnetic field and the rotation. $\langle I_z\rangle_0$ is given by (55) and $\langle I_\pm\rangle_0=0$. $\mathbf{M}$ and $\mathbf{J}$ are the magnetic-moment and angular-momentum operators for the crystal excluding the particular nuclear spin of interest. To calculate $\langle\Gamma_z\rangle$, Eq. (31) is applied, neglecting Q; to obtain $\langle I_\pm\rangle$, the corresponding approximation is made in Eq. (30). Thus one obtains,

$$\langle\Gamma_z\rangle=\beta\langle\mathcal{H}_{12}\Gamma_z\rangle_0 +\tfrac{1}{2}\beta^2(\langle\Gamma_z\mathcal{H}_{12}^2\rangle_0-2\langle\Gamma_z\mathcal{H}_{12}\rangle_0\langle H_{12}\rangle_0), \tag{57}$$

$$\langle I_\pm\rangle=-\beta(1\pm\sigma)\langle\mathcal{H}_{12}I_\pm\rangle_0+\tfrac{1}{2}\beta^2([1\mp1\mp2(\sigma/a)] \times\langle\mathcal{H}_{12}^2I_\pm\rangle_0-[1\pm\sigma]\langle\mathcal{H}_{12}I_\pm\rangle_0\langle\mathcal{H}_{12}\rangle_0), \tag{58}$$

where

$$a\equiv\beta\mu gK;\ \ \sigma=(1-e^{-a})/a-1\cong-\tfrac{1}{2}a;\ \text{ and }\ I_\pm=I_x\pm iI_y.$$

The z direction is chosen parallel to $\mathbf{K}$. To derive (58), we use the commutation relations

$$[e^{cI_z},I_\pm]=\pm(e^c-1)I_\pm e^{cI_z}, \tag{59}$$

where c is any complex number. These relations are easily verified in any explicit representation of the I_z and $I_\pm$. The Hamiltonian $\mathcal{H}_{12}$ is a sum of interactions. In the linear approximation, only those terms can make a contribution which have a dependence on the components of $\mathbf{I}$. These terms are:

1. the magnetic-dipole coupling between nuclei

$$\mathcal{H}^{(1)}=-\mu^2g\sum_\alpha\frac{g_\alpha}{R_\alpha^3}\left[\mathbf{I}_\alpha\cdot\mathbf{I}-3\frac{(\mathbf{R}_\alpha\cdot\mathbf{I})(\mathbf{R}_\alpha\cdot\mathbf{I}_\alpha)}{R_\alpha^2}\right]; \tag{60}$$

2. the coupling with electron spins of unpaired

electrons

$$\mathcal{H}^{(2)} = -(8\pi/3)g\mu\gamma_e \sum_n \delta(\mathbf{r}_n)\mathbf{I}\cdot\mathbf{S}_n - g\mu\gamma_e \sum_m \left[\frac{\mathbf{I}\cdot\mathbf{S}_m}{r_m^3} - \frac{3(\mathbf{I}\cdot\mathbf{r}_m)(\mathbf{S}_m\cdot\mathbf{r}_m)}{r_m^5}\right]; \quad (61)$$

3. the interaction due to the electric-quadrupole moment of the nucleus[36]

$$\mathcal{H}^{(3)} = \frac{1}{6}\sum_{j,k=1}^{3} Q_{jk}\left(\frac{\partial^2\phi}{\partial x_j \partial x_k}\right)_0,$$

$$Q_{jk} = C[\tfrac{3}{2}(I_jI_k + I_kI_j) - \delta_{jk}I^2] \quad (62)$$

with the constant $C = eQ/I(2I-1)$; and

4. the interaction between the nuclear magnetic moment and the orbital motion of the electrons[37] in the presence of the external field,

$$\mathcal{H}^{(4)} = -\mu g\frac{e}{mc}\sum_n \frac{\mathbf{I}}{r_n^3}\cdot\left[\mathbf{r}_n\times\mathbf{p}_n - \frac{e}{2c}(\mathbf{H}r_n^2 - \mathbf{r}_n\mathbf{H}\cdot\mathbf{r}_n)\right] + (\mu g)^2\frac{e^2}{8mc^2}\sum_n\left[\mathbf{I}\times\nabla\frac{1}{r_n}\right]^2. \quad (63)$$

The notation used is the conventional one. In the first term of (61), the sum is over S electrons and $\delta(\mathbf{r}_n)$, the Dirac delta function which vanishes unless the electron is at the nucleus; the second sum in $\mathcal{H}^{(2)}$ is over electrons other than S electrons. In (62), x_j and x_k are the Cartesian coordinates of the nuclear charge of the nucleus of interest, Q_{jk} is an operator, ϕ is the electrostatic potential, and Q is the quadrupole moment of the nucleus. $\mathcal{H}^{(4)}$ is obtained if it is assumed the nth electron is in the combined external and nuclear field $\mathbf{H}_n = \mathbf{H} + \mu g \operatorname{grad}(\mathbf{I}\cdot\nabla 1/r_n)$, and the vector potential is taken to be $\mathbf{A}_n = \frac{1}{2}\mathbf{H}\times\mathbf{r}_n - \mu g\mathbf{I}\times\nabla(1/r_n)$. The $\mathbf{r}_n$ is the position vector of the nth electron relative to the nucleus to which it is bound.

Unlike the calculation of the electronic gyromagnetic effects, we have here expressed the Hamiltonian in the stationary frame. The rotation means that the nuclear position coordinates will in fact rotate in space; if the rotation is sufficiently slow and the external field produces an effect on the electron motion which is small compared to the electrostatic crystal fields, the electron coordinates will also rotate with the same frequency ω. The nuclear-spin orientation $\mathbf{I}$ in effective, external, magnetic fields of a magnitude customary in nuclear magnetic resonance experiments is primarily determined by the effective external field and is little influenced by the changing, internal, magnetic fields. The orientation of unpaired electronic spins is again primarily determined by the effective, external-field direction rather than the relatively weak, internal, magnetic fields.[38] The fact that the spin of interest is subject to an internal magnetic field which varies systematically with time indicates that the assumption of thermodynamic equilibrium can be expected to hold only in some cases, such as any of the following:

(a) The internal magnetic field has cylindrical symmetry about the axis of rotation.
(b) The longest relaxation time is much shorter than the period of rotation. The equilibrium polarization will in that case vary slowly with time, as in the corresponding electronic case. The dominant part of $\langle I\rangle$, namely, $\langle I\rangle_0$, will remain constant.
(c) The shortest relaxation time is much longer than the period of rotation. The internal fields perpendicular to ω are effectively replaced by their average value in this case.

With these reservations, the first order to $\langle I_z\rangle$, in view of (57) and (60) to (63), are found to be

$$\langle I_z\rangle - \langle I_z\rangle_0 = \beta\mu g(H^I + H^S + H^{S'} + H^P + H^D) \times\langle I_z\Gamma\rangle_0 - \beta(D_1+D_2)\langle I_z^2\Gamma\rangle_0, \quad (64)$$

with the following expressions for the quantities in (64) (see Appendix C):

$$\langle I_z\Gamma\rangle_0 \cong I(I+1)/3;$$

and

$$\langle I_z^2\Gamma\rangle_0 \cong [aI(I+1)/45][4I(I+1)-3].$$

H^I is the average field in the z direction due to other polarized nuclear spins,

$$H^I = \mu\sum_{\text{nuclei}} g_\alpha\left\langle\frac{(I_\alpha)_z}{R_\alpha^3} - \frac{3Z_\alpha(\mathbf{R}_\alpha\cdot\mathbf{I}_\alpha)}{R_\alpha^5}\right\rangle_0. \quad (65a)$$

If all the nuclei are similar to the one of interest, and the external field is large compared to internal magnetic fields, this may be written in terms of the angle θ_α which the relative-position vector $\mathbf{R}_\alpha$ makes with the z axis:

$$H^I \cong \tfrac{1}{3}I(I+1)\beta\mu g H\sum_\alpha\langle(1-3\cos^2\theta_\alpha)/R_\alpha^3\rangle_0. \quad (65b)$$

The internal field H^S due to nearby unpaired electron

[36] See e.g., N. H. Cohen and F. Reif in *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), vol. 5.

[37] N. F. Ramsey, Phys. Rev. 78, 699 (1950); 86, 243 (1952).

[38] This time dependence arising from rotating-position vectors may be made explicit by rewriting (60) to (63) as follows

$$\mathcal{H}^{(1)}(t) = U(t)\mathcal{H}^{(1)}(0)U(-t); \quad U(t) \equiv \exp[(i/\hbar)(\mathbf{I}+\textstyle\sum_\alpha \mathbf{I}_\alpha)\cdot\boldsymbol{\omega}t],$$
$$\mathcal{H}^{(2)}(t) = V(t)\mathcal{H}^{(2)}(0)V(-t); \quad V(t) \equiv \exp[(i/\hbar)(\mathbf{I}+\textstyle\sum_m \mathbf{S}_m)\cdot\boldsymbol{\omega}t],$$
$$\mathcal{H}^{(3)}(t) = \frac{1}{6}\sum_{j,k,l,m=1}^{3} Q_{jk}\frac{\partial^2\phi}{\partial x_m^*\partial x_l^*}C_{lk}(-\omega t)C_{mj}(-\omega t),$$

with C the square matrix appearing in (45), and x_m^* the nuclear coordinates fixed relative to the crystal axes. Finally, in $\mathcal{H}^{(4)}$ the vectors $\mathbf{r}_n$ have components $\eta_i = \sum_k C_{ik}(-\omega t)\eta_k^*$, the scalar r_n has no time dependence, but the components of the gradient operator become $\partial/\partial\eta_i = \sum_k C_{ik}(-\omega t)\partial/\partial\eta_k^*$.

spins for all but s electrons is

$$H^S=\gamma_e \sum_{\text{electrons}} \left\langle \frac{(S_i)_z}{r_i^3}-\frac{3z_i(\mathbf{r}_i\cdot\mathbf{S}_i)}{r_i^5}\right\rangle_0, \tag{66}$$

and the internal field due to the s electrons,

$$H^{S'}=(8\pi/3)\gamma_e \textstyle\sum_j \langle\delta(\mathbf{r}_j)S_z^j\rangle_0. \tag{67}$$

This field $H^{S'}$ is the hyperfine field already discussed and shown to be responsible for the Knight shift in metals, and the Rose-Gorter polarization in paramagnetic ions. In the presence of the rotation as well as the external field, the expressions given there for this internal field must be generalized to $H^{S'}\approx 8\pi\mu_B n(0)\times(\mu_B H_z+\hbar\omega_z)/E_F$ for free electrons in a metal, and $H^{S'}\approx(8/3)\beta(\mu_B Z^3/a_0^3)(\mu_B H_z+\hbar\omega_z)$ for a hydrogen-like atom or ion. The magnetic moment due to orbital angular momenta $\mathbf{L}^i$ of the individual electrons gives rise through $\mathcal{H}^{(4)}$ to the internal field

$$H^D=\frac{\mu_B}{\hbar}\left\langle \sum_i \frac{L_z^i}{r_i^3}\right\rangle_0, \tag{69}$$

where, in evaluating the expectation value, it must be remembered that the electrons are in an effective external field $(\mathbf{H}+\hbar\omega/\mu_B)$. Also, from $\mathcal{H}^{(4)}$, there arises the field

$$H^D=-\frac{e^2}{2mc^2}\sum_i\left[H_x\left\langle\frac{x_iz_i}{r_i^3}\right\rangle_0-H_y\left\langle\frac{y_iz_i}{r_i^3}\right\rangle_0+H_z\left\langle\frac{x_i^2+y_i^2}{r_i^3}\right\rangle_0\right]. \tag{70}$$

For the spin of a nucleus in an atom with a spherically symmetric charge distribution, only the last term in (70) will contribute. The direction of the internal field is in this case opposite to that of $\mathbf{K}$.

For $I>\frac{1}{2}$, the D_1 and D_2 terms can contribute. D_1 depends on the nuclear quadrupole moment:

$$D_1=-\frac{eQ}{2I(2I-1)}\left\langle\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}-2\frac{\partial^2\phi}{\partial z^2}\right\rangle_0 \cong\frac{3eQ}{2I(2I-1)}\left\langle\frac{\partial^2\phi}{\partial z^2}\right\rangle_0. \tag{71}$$

The last expression is legitimate[38] because the s electrons do not contribute to the quadrupole interaction, and the charge density at the nucleus due to p or d electrons $\nabla^2\phi$ is negligibly small. The quantity D_2 has the value

$$D_2=\frac{e^2}{16mc^2}(\mu g)^2\sum_{\text{elec}}\left\langle\frac{1-3\cos^2\theta_i}{r_i^4}\right\rangle_0. \tag{72}$$

It is a small interaction of the nonspherical part of the electron cloud with the nuclear-magnetic moment.

Each of the terms in (64) is related to previously known effects, many of which have been observed and evaluated theoretically in detail.

The field H^I is known[39] to cause splitting of magnetic-resonance lines in unsymmetrical configurations. If the crystal is rotating, the vector $\mathbf{R}_\alpha$ also rotates, so that the splittings depending on the components of $\mathbf{R}_\alpha$ perpendicular to the axis of rotation will be washed out.[40]

The term H^S produces an anisotropic line shift, which is however zero in crystals with cubic symmetry. The field H^S must also include the effect of the second-order, pseudodipolar coupling, which has, for example, been studied by Bloembergen and Rowland.[41] This is shown by treating the contact interaction between the electron spin $\mathbf{S}$ and nuclear spin $\mathbf{I}_\alpha$ as a perturbation in the exponent of the density matrix ρ_0 in evaluating the expectation values (66), and by then calculating the linear term in the perturbation according to (30). In this way, we find for an electron of spin S coupled with a nuclear spin $\mathbf{I}_\alpha$ other than the spin of interest:

$$\left\langle\frac{S_z}{r^3}-\frac{3z(\mathbf{r}\cdot\mathbf{S})}{r^5}\right\rangle_0\cong\left\langle\frac{S_z}{r^3}-\frac{3z(\mathbf{r}\cdot\mathbf{S})}{r^5}\right\rangle_{00} -(4\pi/3)\mu g\mu_B\beta\langle I_z^\alpha\rangle_{00}\left\langle\frac{1-3\cos^2\theta_\alpha}{R_\alpha^3}\right\rangle_{00}+\cdots \tag{73}$$

Here, the 00 means that the expectation value is taken over the density matrix ρ_{00} unperturbed by the $\mathbf{I}_\alpha\cdot\mathbf{S}$ coupling. Comparison of the second term in (73) with (65b) shows its resemblance to a direct, nuclear, dipole-dipole interaction. Integrals over commutators of the form $[\rho_{00},\delta(\mathbf{r}-\mathbf{R}_\alpha)\mathbf{S}\cdot\mathbf{I}_\alpha]$ are neglected in deriving (73).

For the Knight shift $H^{S'}$, much detailed knowledge is available for nonrotating crystals, and values of $H^{S'}/H$ are in the literature[42] for a large number of metals. In many cases, the magnitude of $H^{S'}/H$ is of the order of 1/100. If the crystal is rotating, the correction is unchanged, except that H is replaced by $H_z+(\hbar\omega_z/\mu_B)$. If $H^{S'}$ is evaluated in just the same way as H^S in Eq. (73), with $\beta\mu g_\alpha(8\pi\gamma_e/3)\delta(\mathbf{r}_i-\mathbf{R}_\alpha)\mathbf{I}_\alpha\cdot\mathbf{S}_i$ treated as a perturbation, one finds,

$$\langle H^{S'}I_z\Gamma\rangle_0\cong(8\pi\gamma_e/3)\textstyle\sum_k\langle\delta(\mathbf{r}_k)S_z^k\rangle_{00}\langle I_z\Gamma\rangle_0 +(8\pi\gamma_e/3)^2\mu\beta g_\alpha\langle I_z^\alpha I_z\Gamma\rangle_0\sum_k\left[\langle\delta(\mathbf{r}_i-\mathbf{R}_\alpha)S_z^i\rangle_{00}\times\langle\delta(\mathbf{r}_k)S_z^k\rangle_{00}-\langle S_z^iS_z^k\delta(\mathbf{r}_k)\delta(\mathbf{r}_i-\mathbf{R}_\alpha)\rangle_{00}\right]. \tag{74}$$

The second term in (74) is, in effect, like an exchange interaction between nuclear spins $\mathbf{I}$ and $\mathbf{I}_\alpha$. Here $\mathbf{r}_k$ is

[39] G. E. Pake, J. Chem. Phys. **16**, 327 (1948); See also G. E. Pake, reference 9.

[40] H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953). H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *ibid.* **21**, 279 (1953).

[41] N. Bloembergen and T. Rowland, Phys. Rev. **97**, 1679 (1955).

[42] W. D. Knight in *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), 2nd ed.

the position vector of electron k, the nucleus of interest being taken as the origin. In a metal, if an electron has a finite probability of being at nucleus α as well as at the nucleus of interest, the effective-exchange term can give a contribution for $i=k$. This kind of pseudo-exchange effect has been derived by Rudermann and Kittel.[42] It is possible to obtain a contribution if $i\neq k$, provided the two electrons are strongly coupled to each other, as for example by an electron-exchange interaction.[44] Without any correlation between the electrons, the effective-exchange term is zero. If the electron, nuclear, dipole-dipole interaction were treated as the perturbation in evaluating $H^{S\prime}$, we should again obtain a pseudo-dipolar term something like (73).

The field H^P is seen from (69) to have the simple, physical significance of the field due to polarization of the magnetic moments due to the orbital motion of the electrons. It is closely related to the shielding effect obtained by Ramsey,[37] which is known as the chemical shift. This relation is shown by writing

$$\rho_0=\exp[-\beta(\mathcal{H}_{00}-\mu_B\mathbf{L}\cdot\mathbf{H}')]/z_0,$$

where $\mathbf{H}'=\mathbf{H}+1/\mu_B\hbar\omega$, and z_0 is the partition function, and then treating $\beta\mu_B\mathbf{L}\cdot\mathbf{H}'$ as a perturbation. If $\rho_{00}=\exp(-\beta\mathcal{H}_{00})/z_{00}$, application of (30) to (69) yields in a representation in which $\mathcal{H}_{00}$ is diagonal and has eigenvalues E_n for the term linear in $\beta\gamma_e\mathbf{L}\cdot\mathbf{H}'$,

$$H^P=\frac{\gamma_e{}^2}{2}\,\mathrm{Re}\sum_{n\neq m}\sum(\rho_{00})_{nn}\frac{\sum_i(\mathbf{L}_i\cdot\mathbf{H}')_{nm}(L_z{}^i/r_i{}^3)_{mn}}{E_n-E_m}$$

$$+\mu_B{}^2\beta\sum_n(\rho_{00})_{nn}\sum_i[(\mathbf{L}_i\cdot\mathbf{H}')L_z{}^i/r_i{}^3]_{nn};\quad(75)$$

Re means "real part of." As Ramsey points out, the calculation of this effect is very similar to that of the Van Vleck theory of paramagnetism. Ramsey's shielding correction corresponds to the double sum in (75). In obtaining (75), it is assumed that $\sum_i\langle L_z{}^i/r_i{}^3\rangle_{00}=0$, or complete quenching of the orbital angular momenta in the absence of the field. The rotation manifests itself in that H' rather than H appears, and in that energy levels may be modified by the rotation. Experimentally, without rotation, shifts of resonance lines due to chemical surroundings have been found for example to be $H^P/H\sim6\times10^{-4}$ for fluorine atoms. Measurements of chemical shifts have been made by a number of investigators.[45]

The field H^D [Eq. (70)] becomes in the limit of no rotation the diamagnetic-shielding field found by Lamb[46]: $H^D=\sigma H_z$ where

$$\sigma\equiv\frac{e^2}{2mc^2}\sum_i\left\langle\frac{x_i{}^2+y_i{}^2}{r_i{}^3}\right\rangle_0.$$

The term proportional to D_1 gives the polarization through the electric-quadrupole moment of the nucleus.[47] In the evaluation of the field gradient $\langle\partial^2\phi/\partial z^2\rangle_0$, the field gradient of the electrons of the ion containing the nuclear spin of interest must be added to the field gradient due to other ions. The contribution to the quadrupole interaction arising from the distortion of the field of the ion in which the nucleus of interest sits, due to the other ions is included in the expectation value $\langle\partial^2\phi/\partial z^2\rangle_0$, since the interaction energy between the electrons of the ion with the crystal field is contained in the exponent of ρ_0. This interaction may be treated as a linear perturbation using (30). Finally, the term proportional to D_2 has been discussed by Ramsey[48] in connection with the magnetic-resonance spectrum of molecules, and the line shift evaluated for deuterium molecules. It gives rise to an apparent quadrupole moment, since it produces the same line-splitting as the nuclear-quadrupole term D_1.

In evaluating the correction to $\langle I_z\rangle_0$, which is linear in the direct coupling of the spin to the surroundings $\mathcal{H}_{12}$, we have found actually two types of corrections: one which is really of first order, such as the Knight shift and the Lamb shielding—these line shifts would appear as a first-order perturbation of energy levels in usual quantum-mechanical, perturbation theory; the other type involves not only the coordinates q_2 coupled directly to the spin $\mathbf{I}$ of interest, through $\mathcal{H}_{12}$, but also coordinates q_3 coupled to $\mathbf{I}$ only indirectly through terms in the total Hamiltonian which contain both q_2 and q_3. These corrections are of the form $\sim\beta\langle\mathcal{H}_{12}\mathcal{H}_{23}\Gamma\rangle_{00}$ and are exemplified by the Ramsey shielding and the effective-nuclear-exchange term; the corresponding corrections to the energy levels would appear in second-order perturbation theory.

Of course, we might have employed a perturbation $\mathcal{H}'_{12}=\mathcal{H}_{12}+\mathcal{H}_{23}$ in the first place, and then the terms proportional to $(\mathcal{H}_{12}\mathcal{H}_{23})$ would appear in the second-order part of the expansion. However, the physical significance of individual terms is more clearly brought out in the present way of doing it; besides, we are assured that the $\beta^2(\mathcal{H}_{12})^2$ effect is small, whereas this may not be the case for $\beta^2(\mathcal{H}'_{12})^2$.

In Eq. (64), seven linear corrections were distinguished; we would obtain 28 types of terms from them in evaluating $(\mathcal{H}_{12})^2$. While all of these quadratic corrections are expected to be small, some of them are expected to be well within the range of observation of

[42] M. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

[44] N. Ramsey and E. Purcell, Phys. Rev. 85, 143(L) (1952) discuss this interaction in molecules.

[45] See, e.g., reference listed by G. E. Pake in reference 9, pp. 57–58; also see N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1950), pp. 162–166. J. A. Pople, W. G. Schneider, and H. T. Bernstein, *High Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959).

[46] W. E. Lamb, Phys. Rev. 60, 817 (1941); numerical values are given there and also by W. C. Dickinson, Phys. Rev. 80, 563 (1950).

[47] Nuclear-quadrupole effects are reviewed by N. H. Cohen and F. Reif, reference 36.

[48] N. F. Ramsey, Phys. Rev. 89, 527 (1953).

experiment.[9] Here, only the five quadratic terms involving the hyperfine coupling and the "internal magnetic fields" occurring in (64) are evaluated; they are corrections either to the nuclear polarization in a paramagnetic ion or to the Knight shift. At this point, it must be mentioned that the "internal fields" H^I, H^S, etc., are statistical averages of fields arising from particular internal interactions. It does not necessarily follow from this that the NMR frequency will be shifted by the Larmor frequency corresponding to the internal fields; however, (64) states that the polarization of the spin acts as if the levels were shifted by just that amount. In some cases, as for example in the lowest-order Knight shift or the Lamb shielding, it is in fact so.

We write the part of $\mathcal{H}_{12}$ giving rise to H^I, H^S, $H^{S'}$, H^P, and H^D in the form $\mathcal{H}^I+\mathcal{H}^S+\mathcal{H}^{S'}+\mathcal{H}^P$, where $\mathcal{H}^I$ gives H^I, etc. The coupling of hyperfine interaction $\mathcal{H}^{S'}$ with $\mathcal{H}^I$ gives in second order,

$$\tfrac{1}{2}(g\mu\beta)^2[(3K_z{}^{S'}H_z{}^I-\mathbf{H}^{S'}\cdot\mathbf{H}^I)\langle I_z{}^2\Gamma\rangle_0 -4H_z{}^IH_z{}^{S'}\langle I_z\rangle_0\langle I_z\Gamma\rangle_0], \quad (76)$$

where $H_{x,y}{}^I$ are obtained from (65) by replacing z by x and y, respectively; similarly, $H_{x,y}{}^{S'}$ are obtained from (67). To obtain (76), the simplifying assumption is made that the coordinates and spins of the electrons responsible for the contact interaction are not correlated to the spins of the nuclei, other than the one of interest.

The quadratic term coupling $\mathcal{H}^S$ and $\mathcal{H}^{S'}$ is of the same form, if it is assumed that the coordinates of different electrons are uncorrelated and that a particular electron either has the $\mathcal{H}^S$ type or the $\mathcal{H}^{S'}$ type of interaction, but not both:

$$\tfrac{1}{2}(g\mu\beta)^2[(3H_z{}^{S'}H_z{}^S-\mathbf{H}^{S'}\cdot\mathbf{H}^S)\langle I_z{}^2\Gamma\rangle_0 -4H_z{}^SH_z{}^{S'}\langle I_z\rangle_0\langle I_z\Gamma\rangle_0]. \quad (77)$$

If the correlation between electrons is to be included, the coefficient of $\langle I_z{}^2\Gamma\rangle_0$ in (77) is replaced by

$$(8\pi/3)(g\mu\mu_B\beta)^2 \times\sum_{n\neq n'}\sum\left\langle\delta(\mathbf{r}_n)\left[3S_z{}^n\left(\frac{S_z{}^{n'}}{r_{n'}{}^3}-\frac{3z_{n'}(\mathbf{S}^{n'}\cdot\mathbf{r}^{n'})}{r_{n'}{}^5}\right) -\left(\frac{\mathbf{S}^n\cdot\mathbf{S}^{n'}}{r_{n'}{}^3}-\frac{3(\mathbf{S}^n\cdot\mathbf{r}^{n'})(\mathbf{S}^{n'}\cdot\mathbf{r}^{n'})}{r_{n'}{}^5}\right)\right]\right\rangle_0. \quad (78)$$

The quadratic correction depending on $(\mathcal{H}^{S'})^2$ is

$$[(8\pi/3)g\mu(\mu_B/\hbar)\beta]^2\langle\Gamma_z I_z{}^2\rangle_0 \times\sum_n\sum_{n'}\langle[S_z{}^nS_z{}^{n'}-\tfrac{1}{2}(S_x{}^nS_x{}^{n'}+S_y{}^nS_y{}^{n'})] \times\delta(\mathbf{r}_n)\delta(\mathbf{r}_{n'})\rangle_0-(g\mu H^{S'}\beta)^2\langle I_z\rangle_0\langle I_z\Gamma\rangle_0. \quad (79)$$

If $n=n'$, the first term of (79) clearly vanishes; it can make a contribution only if at least two electrons have a finite probability of being at the nucleus. Even then, it can be shown to vanish, if the electron-spin space and coordinate space may be separated. For the quadratic terms coupling $\mathcal{H}^{S'}$ and $\mathcal{H}^P$, one assumes that the electrons with finite probability of being at the nucleus are in s states, to obtain

$$(8\pi/3)\left(g\mu\frac{\mu_B}{\hbar}\beta\right)^2\langle\Gamma I_z{}^2\rangle_0 \times\sum_{n\neq n'}\sum\left\langle\frac{\delta(\mathbf{r}_{n'})}{r_{n'}{}^2}(3L_z{}^nS_z{}^{n'}-\mathbf{L}^n\cdot\mathbf{S}^{n'})\right\rangle_0 -2(g\mu\beta)^2H_z{}^PH_z{}^{S'}\langle I_z\rangle_0\langle\Gamma I_z\rangle_0. \quad (80)$$

The terms arising from products of $\mathcal{H}^{S'}$ and $\mathcal{H}^D$ give rise to the quadratic correction

$$(4\pi/3)(g\mu\beta)^2(e^2/mc^2)\mu_B\langle\Gamma I_z{}^2\rangle_0 \times\sum_n\langle\delta(\mathbf{r}_n)(3S_z{}^nf_z-\mathbf{S}^n\cdot f)\rangle_0 +2(g\mu\beta)^2H_z{}^{S'}H_z{}^D\langle I_z\rangle_0\langle I_z\Gamma\rangle_0, \quad (81)$$

where f_z is the sum over electron coordinates:

$$f_z=\sum_n[y_nz_nH_y-x_nz_nH_x-(x_n{}^2+y_n{}^2)H_z]/r_n{}^5,$$

and f_x and f_y are obtained by cyclic permutation of x, y, and z. We recall that, when the crystal is not rotating, $H_x=H_y=0$. This completes the list of quadratic effects calculated here. In Eqs. (76) to (81), all of the coefficients of $\langle I_z{}^2\Gamma\rangle_0$ produce an effect on the expectation value of the z component of the nuclear spin proportional to that produced by a nuclear-quadrupole moment. For $I=1/2$, these effects are not present, since $\langle I_z{}^2\Gamma\rangle_0=0$. Ramsey[48] has discussed the pseudoquadrupolar effect contained in our Eq. (77) in connection with the deuterium molecule. He also points out that no pseudoquadrupolar contribution can come from $(\mathcal{H}^{S'})^2$, because the dot product $\mathbf{I}\cdot\mathbf{S}$ is isotropic. In solids in thermal equilibrium, a small contribution could come from this term, the first term in our Eq. (79), through the anisotropic terms in the exponent of the density matrix.

Finally, a comment on the magnitude of the nuclear gyromagnetic effects. According to Eqs. (54) and (55), the polarization produced by a crystal rotation of $\omega/2\pi$ rev/sec is equal to that produced by a magnetic field of H gauss if $\omega/2\pi=\mu gH/\hbar=762\,gH$. For a nuclear g factor of order unity, a rotation frequency of order of 1000 rev/sec is equivalent to a gauss; rotation frequencies up to 10^4 rev/sec have been achieved.[49] By the techniques of nuclear induction, one might observe not only the total polarization due to rotation, but also details of the associated relaxation phenomena. The easiest, but least interesting, observable effect of rotation would be the shift of the resonance line. The nuclear counterpart of the Einstein-deHaas effect, rotation by polarization, would, for a sample of N-

[49] J. Dreitlein and H. Kessemeier, Phys. Rev. 123, 835 (1961); see also I. Lowe, Phys. Rev. Letters 2, 285 (1959).

saturated, nuclear spins which are allowed to come to thermal equilibrium, lead to a rotation frequency of the crystal $\omega=NI(I+1)\beta g\mu H/3B$, where B is the moment of inertia of the sample. For a field of 10^4 gauss, $T=1°$K, and a cylindrical sample with radius of gyration 10^{-2} cm, we have $\omega=0.0023[I(I+1)g/A$ sec$]^{-1}$, where A is the average atomic weight of the sample.

4. TIME-DEPENDENT BEHAVIOR OF NUCLEAR SPINS IN ROTATING CRYSTALS

a. Solution of Schrödinger Equation

To generalize the example of the rotating pair of spins coupled by dipole-dipole interaction of Sec. 2b, we consider a general system of spins in a rotating crystal, acted upon by an external magnetic field $\mathbf{H}$. The interaction between spins is assumed to consist of a part A which is unaffected by the fact that the crystal is rotating, and a part $G(0)$, which if the crystal is rotating becomes

$$G(t)=U(t)G(0)U(-t)\,;\quad U(t)=\exp(i\boldsymbol{\omega}\cdot\mathbf{S}t),$$

where $\mathbf{S}$ is the total-spin vector for the system. The term A includes, for example, the contact interaction between nuclear spins and S electrons; the $G(0)$ includes, in particular, the interaction between nonoverlapping dipoles. The Hamiltonian for the spins is, thus,

$$\mathcal{H}_S=-\textstyle\sum_k \gamma_k\mathbf{H}\cdot\mathbf{S}_k+G(t)+A, \tag{83}$$

where $\mathbf{S}_k$ may be a nuclear or electronic spin. If the operator A is unchanged by the transformation U, we can put the time dependence into the Zeeman term by the transformation $\psi'=U\psi$ to give $i\hbar\dot{\psi}'=\mathcal{H}_S'\psi'$ with

$$\mathcal{H}_S'=\textstyle\sum_k \mathbf{S}_k\cdot[\mathbf{H}'(t)\gamma_k+\boldsymbol{\omega}]+G(0)+A, \tag{84}$$

where

$$H'_x=H_x\cos\omega t-H_y\sin\omega t,$$
$$H'_y=H_x\sin\omega t+H_y\cos\omega t,$$
$$H'_z=H_z,$$

if the axis of rotation is taken as the z axis. The Hamiltonian (84) is, however, just the Hamiltonian for the spin system in a stationary crystal acted on by the rotating field $\mathbf{H}_1=(H'_x,H'_y,0)$ plus a static field $\mathbf{H}_0{}^k=(0,0,H_z+\omega/\gamma_k)$ acting on the kth spin. Thus, the rotating-crystal problem can be reduced to the much-studied, rotating-field[50] problem; of course, the solution to $i\hbar\dot{\psi}'=\mathcal{H}_S'\psi'$ must finally be transformed back to the laboratory frame through $\psi=U^{-1}\psi'$.

In the particular case that the field is parallel to $\boldsymbol{\omega}$, the equivalent problem is just the stationary field H acting on the spins, but with the effective gyromagnetic ratio $\gamma_k'=(\gamma_k+\omega/H)$. In this case, the effect of the rotation on the wave function and eigenvalues is found by considering the eigenvalues E'_g and eigenfunctions φ'_g of $\mathcal{H}_S'$. Assume the φ'_g forms a complete nondegenerate set, and the g symbolizes the quantum numbers of a complete set of commuting, dynamical variables. In particular, if the magnetic-quantum number m_g, eigenvalue of $\mathbf{S}\cdot\boldsymbol{\omega}/\omega$, is a good quantum number, it too is included in the symbol g. In general, we transform the φ'_g to a representation in which $\mathbf{S}\cdot\boldsymbol{\omega}$ is diagonal by means of transformation coefficients $(g|m_gf)$, where f represents any quantum numbers besides m_g required to label the complete set of functions U_{m_gf}. Then,

$$\begin{aligned}\psi&=\exp(-i\mathbf{S}\cdot\boldsymbol{\omega}t)\psi'=\exp(-i\mathbf{S}\cdot\boldsymbol{\omega}t)\textstyle\sum_g\exp(-i/\hbar E_gt)\varphi'_g\\&=\exp(-i\mathbf{S}\cdot\boldsymbol{\omega}t)\textstyle\sum_g\exp(-i/\hbar E')_gt\sum_{f,m_g}(g|m_gf)U_{m_gf}\\&=\textstyle\sum_g\sum_{m_g}\exp[-i/\hbar(E'_g+m_g\omega)t]\sum_f(g|m_gf)U_{m_gf}.\end{aligned} \tag{85}$$

So that, in the laboratory system, the characteristic energies are $E_k(\omega)=E'_g(\omega)+m_g\omega$. If m_g is a good quantum number, then it follows from (84) that $E'_g(\omega)=E'_g(0)-m_g\omega$. Thus,

$$E_n(\omega)=E'_g(0). \tag{86}$$

The wave function is then in the laboratory frame

$$\psi=\textstyle\sum_n\exp(-i/\hbar E_nt)\varphi'_n(\Omega_k),\quad \Omega_k=\gamma_kH+\omega, \tag{87}$$

where the E_n are independent of the frequency of rotation and are given by (86); the $\varphi'_n(\Omega)$ are simultaneous eigenfunctions of $\mathcal{H}'_S$ and $\mathbf{S}\cdot\boldsymbol{\omega}$. The effect of the rotation is only to change the argument of the φ'_n from γ_kH to Ω_k. The condition that m_g is a good quantum number is satisfied if the effective external field $\gamma_kH+\omega$ is large compared to the transverse part of the internal field due to the other dipoles acting on spin k.

The effect of the rotation on the lattice motion can be seen by transforming the Hamiltonian to body-fixed axes. Presumably the rotation is slow enough so that in the rotating coordinate system the crystal electric fields are the same as those in a stationary crystal. The Hamiltonian referred to the rotating axes is, if spin-orbit coupling and external fields are neglected,[51]

$$\mathcal{H}_L{}^R=\textstyle\sum_k P_k{}^2/2m_k-\boldsymbol{\omega}\cdot\mathbf{L}+V.$$

Here, $\mathbf{L}$ is the orbital angular momentum in the rotating system. The $\mathbf{L}\cdot\boldsymbol{\omega}$ term is due to the rotation; it indicates that a particular lattice-vibration frequency may be split into frequencies differing from it by an amount of the order of the frequency of rotation of the crystal. If $\mathbf{L}\cdot\boldsymbol{\omega}/\omega$ commutes with the Hamiltonian, its integer eigenvalues are good quantum numbers, and the frequency splitting is by integer multiples of ω.

[50] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chaps. II and XII.

[51] One readily finds the classical, inertial accelerations from this Hamiltonian:

$$\begin{aligned}\ddot{\mathbf{r}}&=(1/i\hbar)[\dot{\mathbf{r}},\mathcal{H}_L{}^R]=-(1/\hbar^2)[[\mathbf{r},\mathcal{H}_L{}^R],\mathcal{H}_L{}^R]\\&=-\operatorname{grad}V-2\boldsymbol{\omega}\times\dot{\mathbf{r}}-\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r}).\end{aligned}$$

b. Statistical Treatments; Approach to Equilibrium

The approach to thermal equilibrium of nuclear spins in a rotating crystal may be studied by means of the Wangsness and Bloch[52] theory of nuclear magnetic relaxation. Consider the case of a crystal rotating with angular velocity ω; in addition, the crystal is in a constant magnetic field $\mathbf{H}_0$. Let $\mathbf{I}_1$ be the spin operator of system one, the system of interest, and $\mathbf{I}_2$ the total-spin operator of system two, the environment. The combined system is described by a Hamiltonian of the form

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+G(t), \tag{88}$$

where $\mathcal{H}_1$ and $\mathcal{H}_2$ are the Hamiltonian operators for systems one and two separately, and $G(t)$ is the coupling between them. $\mathcal{H}_1$ and $\mathcal{H}_2$ are assumed to be independent of the time while $G(t)$ will be assumed to have the time-dependence characteristic of the dipole-dipole interaction in a rotating crystal:

$$G(t)=U^{-1}G(0)U, \quad U=\exp[i(\mathbf{I}_1+\mathbf{I}_2)\cdot\omega t]. \tag{89}$$

The calculations are most easily carried out in the interaction representation, obtained by a unitary transformation S from the laboratory system. Let ρ be the density matrix in the laboratory system and ρ' in the interaction representation, then,

$$\rho'=S\rho S^{-1}, \quad S\equiv\exp[i/\hbar(\mathcal{H}_1+\mathcal{H}_2)t], \tag{90}$$

and

$$\dot{\rho}'=(1/\hbar i)[G',\rho'], \quad G'=SG(t)S^{-1}. \tag{91}$$

Applying perturbation theory to (91), keeping terms up to second order in G', and then summing over the quantum numbers of the environment, gives in the usual way[52]

$$\dot{\sigma}'+i\ \mathrm{Tr}_2[G'(t),\rho'(0)] = -\mathrm{Tr}_2\int_0^t[G'(t),[G'(t'),\rho'(0)]]dt,' \tag{92}$$

where Tr_2 means the diagonal sum over the quantum numbers of the environment, and $\sigma'\equiv\mathrm{Tr}_2\rho'$.

The eigenvalues of $\mathcal{H}_2-\mathbf{I}\cdot\omega$ will be labeled g and are assumed to be nondegenerate; one can suppose some very small perturbations to have removed all degeneracies. Now, we restrict system one to a single nuclear spin, with $(\mathbf{I}_1)_z\doteq m\hbar$. The matrix elements of σ' are

$$(m|\sigma'|m')=\sum_g(mg|\rho'|m'g).$$

Choose the z axis along the external field $\mathbf{H}_0$ and choose the y axis such that ω lies in the x-z plane at some angle θ with the z axis. Then,

$$\begin{aligned}U(t)&=\exp(i\mathbf{I}_2\cdot\omega t)\exp(i\mathbf{I}_1\cdot\omega t)\\&=\exp(i\mathbf{I}_2\cdot\omega t)\exp[-i\theta(\mathbf{I}_1)_y]\exp[-i\omega t(\mathbf{I}_1)_z]\\&\qquad\times\exp[i\theta(\mathbf{I}_1)_y]\\(mg|U(t)|m'g')&=(g|\exp(i\mathbf{I}_2\cdot\omega t)|g')\sum_{m''}\exp(-i\omega tm'')\\&\qquad\times d_{mm''}^{I_1}(\theta)d_{m''m'}^{I_1}(-\theta),\end{aligned} \tag{93}$$

where the $d_{mm'}^{I}(\theta)$ are the well-known, explicit matrix elements[53] $(m|\exp[-i\theta(\mathbf{I})_y]|m')$. The interaction $G'(t)=SU^{-1}G(0)US^{-1}$ is in this representation

$$\sum_{\substack{m'',m'''\\m'',m''}}\exp[-i\omega t(m''-m'')]\times(m'''g|G(0)|m''g')A(\theta)_{mm'}, \tag{94}$$

with $A_{mm'}=d_{mm''}^{I_1}(\theta)d_{m'''m''}^{I_1}(-\theta)d_{m''m''}^{I_1}(\theta)d^{I_1}{}_{m''m'}(-\theta)$.

In particular, we consider ω and $\mathbf{H}_0$ parallel, $\theta=0$. Since $d_{mm'}(0)=\delta_{mm'}$, (94) becomes for this case

$$(mg|G'(t)|m'g')=e^{i(m-m')\Omega t}(mg|G(0)|m'g'), \tag{95}$$

where $\Omega=\gamma H_0+\omega$. The heat bath is assumed to remain in thermal equilibrium

$$\textstyle\sum_m(gm|\rho|g'm)=(e^{-\beta g}/\sum_{g''}e^{-\beta g''})\delta_{gg'}; \tag{96}$$

further, the interaction of the spin of interest is assumed to be linear in the spin components, so that one may expand

$$G(0)=\textstyle\sum_n F^nK_n, \tag{97}$$

with $(gm|K_n|g'm')=(m|K_n|m+n)\delta_{m',m+n}\delta_{gg'}$ and F^n dependent only on the state of system two. The heat-bath action is characterized by the quantum-mechanical spectral density defined by

$$\begin{aligned}\langle F^n(\epsilon)F^{-n}(-\epsilon)\rangle&=\textstyle\sum_g(g|F^n|g+n\Omega+\epsilon)(g+n\Omega+\epsilon|F^{-n}|g)\\&\qquad\times(e^{-\beta g}/\sum_{g'}e^{-\beta g'}).\end{aligned} \tag{98}$$

We insert (95), (96), and (97) into Eq. (92), and averaging over oscillation in the usual manner[52] to obtain in the laboratory system

$$\begin{aligned}\dot{\sigma}+i[\gamma H_0J_z+\Delta E+\Gamma,\sigma]&=\pi\textstyle\sum_n\langle F^n(0)F^{-n}(0)\rangle(2e^{-\beta n\Omega}K_n\sigma K_{-n}\\&\qquad-\sigma K_nK_{-n}-K_nK_{-n}\sigma),\end{aligned} \tag{99}$$

with ΔE defined by its matrix elements

$$(m|\Delta E|m')=[\delta_{mm'}/(\textstyle\sum_{g'}e^{-\beta g'})]\sum_g e^{-\beta g}(mg|G(0)|mg),$$

[52] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1956); F. Bloch, *ibid.* **102**, 104 (1956); **105**, 1206 (1957).

[53] See, for example, M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., 1957).

and

$$\Gamma \equiv \sum_n \mathrm{P} \int (d\epsilon/\epsilon) \langle F^n(-\epsilon) F^{-n}(\epsilon) \rangle K_n K_{-n},$$

where P means the "principal part of the integral." The left-hand side of (99) describes the periodic precession of the spin. In first approximation, the precession frequency is just γH_0, independent of the rotation of the crystal. The terms in ΔE and Γ are corrections, respectively, linear and quadratic in the coupling G; these correspond to the linear and quadratic perturbations on the energy levels, which were studied in Sec. 3d in connection with the equilibrium-density matrix. The right-hand side of (99) describes the rate of relaxation towards equilibrium. Inspection shows that it depends on the quantity $\Omega = \gamma H_0 + \omega$, but does *not* depend on γH_0 and ω separately, except for the dependence of the heat-bath levels g on H_0 and ω separately. Generally, g will depend on the combination $\Omega_K' = \gamma_K H_0 + \omega$ where γ_K is the gyromagnetic ratio of spins interacting with the spin of interest. In the case of pure rotation ($H_0 = 0$), all the $\Omega_K = \Omega$; this allows transitions involving two spins of differing gyromagnetic ratio without exchanging energy with the lattice. For this reason, one should expect an enhanced cross relaxation if the total effective field $H = H_0 + \omega/\gamma$ is partly due to rotation, rather than wholly due to a static field. If we multiply (99) by the spin vector $\mathbf{I}$ for $I = \frac{1}{2}$, we obtain in the usual manner[52] the Bloch phenomenological equations with the asymptotic value

$$\langle I_z \rangle_0 = \tfrac{1}{2} \tanh \tfrac{1}{2}\beta\Omega, \quad \langle I_{x,y} \rangle_0 = 0; \tag{100a}$$

the precession frequency

$$\begin{aligned} W &= \gamma(H_0 + h' + h''), \\ \gamma h' &= (1/\textstyle\sum_{v'} e^{-\beta v'}) \sum_v e^{-\beta v} (g | F(0) | g), \\ \gamma h'' &= -\mathrm{P} \int \frac{d\epsilon}{\epsilon} [1 + e^{-\beta(\Omega+\epsilon)}] \langle F^1(\epsilon) F^{-1}(-\epsilon) \rangle; \end{aligned} \tag{100b}$$

and relaxation times

$$\begin{aligned} 1/T_2 &= 2\pi(1 + e^{-\beta\Omega}) \langle F^1(0) F^{-1}(0) \rangle, \\ 1/T_2 &= 1/2T_1 + \pi \langle F^0(0) F^0(0) \rangle. \end{aligned} \tag{100c}$$

It may be of interest to note explicitly that $\gamma h''$, if the exponent is expanded, contains a term linear in $\beta\Omega$.

It follows from (99) that, when the diagonal elements of σ are stationary, then,

$$(m | \sigma | m)/(m+n | \sigma | m+n) = e^{-\beta n \Omega}, \tag{101}$$

provided that for every value m there exist at least one value of n so that

$$\langle F^n(0) F^{-n}(0) \rangle (m | K_n K_{-n} | m) \neq 0.$$

The foregoing discussion based on the Wangsness-Bloch is limited in a number of ways.

1. We have assumed that ω and $\mathbf{H}_0$ are parallel. This simplified the analysis, permitting the use of the expression (95) instead of (94). However, the extension to the case of ω and $\mathbf{H}_0$ being in different directions can be carried through; in fact, the closely related problem of the rotating magnetic field has been treated[54] by several authors.

2. It has been assumed that the interaction G is a perturbation on the dominant energy term which has a magnitude Ω, so that m is a good quantum number. In other words, we require $\Omega \gg 1/T_2$. For CaF_2, the $1/T_2 \sim 10^4$ sec^{-1}. These are rather high frequencies for a pure rotation.

3. The most serious shortcoming is that the system of interest is taken to be a single spin, and the other nuclear spins are regarded as part of the heat bath, which is not described in detail. Thus, the correlations between neighboring spins is completely ignored. In principle, one should consider all of the spins and their dipole interaction as the system of interest. However, the solution of the coupled-spin systems in a solid lattice is prohibitively difficult. One can, however, assume that the spin system as a whole is described by a spin temperature[55] different from the lattice temperature; then, the problem becomes soluble. In many crystals indeed, $T_2 \ll T_1$, so that the assumption of a spin temperature can at least be regarded as physically plausible.

Dreitlein and Kessemeier,[4] have studied the line shape for the magnetic resonance absorption of a rotating crystal. The study is restricted to high magnetic fields and assumes a rigid lattice. The physical features obtained include (1) the narrowing of the magnetic-resonance lines which results from the time dependence of the dipole-dipole coupling $G(t)$ if the crystal rotates, and (2) the characteristic frequencies of satellite lines which appear in the presence of rotation. These phenomena occur when the rotation axis makes a finite angle with the magnetic field.

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[54] F. Bloch, Phys. Rev. **105**, 1206 (1957); R. K. Wangsness, *ibid.* **98**, 928 (1955); P. Hubbard, Revs. Modern Phys. **33**, 249 (1961).

[55] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958); R. T. Schumacher, *ibid.* **112**, 837 (1958); N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *ibid.* **114**, 445 (1959); P. S. Pershan, *ibid.* **117**, 109 (1960).

APPENDIX A. SYSTEM OF TWO COUPLED SPINS

Consider two spins, $\mathbf{S}_1$ and $\mathbf{S}_2$ attached to two nuclei located on the Z axis a distance R apart; the coupling between the associated dipoles is

$$\mathcal{H}_{12}=2E_0[\mathbf{S}_1\cdot\mathbf{S}_2-3S_{1z}S_{2z}], \text{ where } E_0\equiv\hbar^2\gamma_1\gamma_1/2R^3. \quad \text{(A1)}$$

In a representation in which $S^2=(\mathbf{S}_1+\mathbf{S}_2)^2$ and $S_z=(\mathbf{S}_1+\mathbf{S}_2)_z$ are diagonal with eigenvalues $S(S+1)$ and m, respectively, a complete set of orthonormal eigenfunctions are $\phi_k{}^{(m,s)}$:

$$\phi_1{}^{(11)}=\begin{bmatrix}1\\0\\0\\0\end{bmatrix},\quad \phi_2{}^{(01)}=\begin{bmatrix}0\\1\\0\\0\end{bmatrix},\quad \phi_3{}^{(-11)}=\begin{bmatrix}0\\0\\1\\0\end{bmatrix},\quad \phi_4{}^{(00)}=\begin{bmatrix}0\\0\\0\\1\end{bmatrix}$$

The single index k replaces the two quantum numbers m and S. The equations for the coefficients in the expansion $\psi(t)=\sum_k b_k(t)\phi_k{}^{(m,s)}$ of the Schrödinger wave function are

$$i\hbar\dot{b}_n+\sum_{m=1}^{4} b_mK_{mn}=0, \quad \text{where} \quad K_{mn}=K_{nm}. \quad \text{(A2)}$$

If the two spins are acted upon by a magnetic field $\mathbf{H}=(H_x,0,H_z)$ and are coupled through $\mathcal{H}_{12}$ of Eq. (A1), the symmetric matrix K has elements

$$\begin{aligned}&K_{11}=-E_0-\bar{\gamma}H_z;\ K_{22}=2E_0;\ K_{33}=-E_0+\bar{\gamma}H_z;\\ &K_{44}=0,\\ &K_{12}=K_{32}=-\bar{\gamma}H_x/\sqrt{2};\ K_{14}=-H_x\Delta/2;\\ &K_{24}=-H_z\Delta,\end{aligned} \quad \text{(A3)}$$

with $\bar{\gamma}=\frac{1}{2}(\gamma_1+\gamma_2)$ and $\Delta\equiv\frac{1}{2}(\gamma_1-\gamma_2)$. If a rotating pair of spins is being treated, replace $\bar{\gamma}H$ by ω expressed in energy units and put $\Delta=0$. When $\Delta=0$, no transitions between the triplet ($S=1$) and singlet ($S=0$) state are possible. We treat only this case. The eigenvalues of K are most easily expressed in terms of the angle ϕ where

$$\cos\phi=\frac{E_0(E_0{}^2+\frac{1}{2}\omega_x{}^2-\omega_z{}^2)}{(E_0{}^2+\frac{1}{2}\omega^2)^{\frac{1}{2}}}, \quad 0\leq\phi<\pi.$$

They are

$$\begin{aligned}\lambda_1&=(E_0{}^2+\tfrac{1}{3}\omega^2)^{\frac{1}{2}}[\sqrt{3}\,\sin\phi/3+\cos\phi/3],\\ \lambda_2&=(E_0{}^2+\tfrac{1}{3}\omega^2)^{\frac{1}{2}}[\sqrt{3}\,\sin\phi/3-\cos\phi/3],\\ \lambda_3&=2(E_0{}^2+\tfrac{1}{3}\omega^2)^{\frac{1}{2}}\cos\phi/3,\\ \lambda_4&=0.\end{aligned} \quad \text{(A4)}$$

Since the trace of K vanishes, $\lambda_1+\lambda_2+\lambda_3+\lambda_4=0$ even when $\Delta\neq0$. In the limiting case of $|\omega/E_0|\gg1$, the eigenvalues (A4) go into the usual Zeeman splitting $(\omega,-\omega,0,0)$, whereas in the $|\omega/E_0|\ll1$ limit, they become the eigenvalues of $\mathcal{H}_{12}$, $(-E_0,-E_0,2E_0,0)$. Assume the field is practically in the x direction, but has a very small component in the z direction, which will eventually be put equal to zero. Then,

$$\begin{aligned}\lambda_1&=\tfrac{1}{2}(E_0-\epsilon)-\Delta_1,\\ \lambda_2&=-E_0+\Delta_2,\\ \lambda_3&=-\tfrac{1}{2}(E_0+\epsilon)+\Delta_3,\\ \lambda_4&=0,\end{aligned} \quad \text{(A5)}$$

with

$$\begin{aligned}\Delta_1&=6E_0\omega_z{}^2/(\epsilon^2-3E_0\epsilon),\\ \Delta_2&=3E_0(\omega_z/\omega)^2,\\ \Delta_3&=6E_0\omega_z{}^2/(\epsilon^2+3E_0\epsilon),\\ \epsilon&\equiv(9E_0{}^2+4\omega^2)^{\frac{1}{2}}.\end{aligned}$$

The solution to (A2) reduces to

$$b_k(t)=\sum_{n=1}^{3} B_k{}^n e^{i\lambda_n t}, \quad k=1,2,3, \quad \text{(A6)}$$

where the constant $B_k{}^n$ can be expressed in terms of the initial state $b_k(0)$ by substituting (A6) into (A2) and solving the resulting linear, algebraic equations together with

$$b_k(0)=\sum_{n=1}^{3} B_k{}^n.$$

The result is

$$\begin{aligned}B_1{}^1&=-B_3{}^1=\tfrac{1}{2}[b_1(0)-b_3(0)],\\ B_1{}^2&=B_3{}^2=-\frac{\omega}{\sqrt{2}\epsilon}b_2(0)+[b_1(0)+b_3(0)]\frac{\epsilon-3E_0}{4\epsilon},\\ B_1{}^3&=B_3{}^3=\frac{\omega}{\sqrt{2}\epsilon}b_2(0)+[b_1(0)+b_3(0)]\frac{\epsilon+3E_0}{4\epsilon},\\ B_2{}^1&=0,\\ B_2{}^2&=\frac{\epsilon+3E_0}{2\epsilon}b_2(0)-[b_1(0)+b_3(0)]\frac{\omega}{\sqrt{2}\epsilon},\\ B_2{}^3&=\frac{\epsilon-3E_0}{2\epsilon}b_2(0)+[b_1(0)+b_3(0)]\frac{\omega}{\sqrt{2}\epsilon}.\end{aligned} \quad \text{(A7)}$$

The expectation value of S_x in the representation chosen is

$$\begin{aligned}(S_x)&=\psi^*(t)S_x\psi(t)\\ &=(1/\sqrt{2}\epsilon)[b_1{}^*b_2+b_1b_2{}^*+b_2{}^*b_3+b_2b_3{}^*].\end{aligned}$$

Substituting (A6) for the b_k and averaging over all periodic terms, gives a time-independent value, which

is, with the help of (A7),

$$\langle S_x\rangle_{\rm av}=(3\omega E_0/\epsilon^2)[|b_1(0)+b_3(0)|^2-2|b_2(0)|^2]+(4\omega^2/\epsilon^2\sqrt{2})[b_1(0)b_2^*(0)+b_2(0)b_1^*(0)+b_3(0)b_2^*(0)+b_2(0)b_3^*(0)]. \quad \text{(A8)}$$

Similarly, one obtains $\langle S_y\rangle_{\rm av}=\langle S_z\rangle_{\rm av}=0$. The $_{\rm av}$ indicates the time average. If the initial density matrix $b_k(0)b_l^*(0)$ is diagonal and is normalized so that

$$\sum_{k=1}^{3}|b_k(0)|^2=3/4,$$

Equation (A8) becomes

$$\langle S_x\rangle_{\rm av}=(9\omega E_0/4\epsilon^2)(1-4|b_2(0)|^2).$$

If the initial states are distributed in a Boltzmann distribution at temperature T_0, an average over initial states gives the result quoted in the text:

$$\langle\langle S_x\rangle\rangle_{\rm av}=(\omega/kT_0)(3E_0/2\epsilon)^2.$$

The same assumption gives for the squared components

$$\langle\langle S_x^2\rangle\rangle_{\rm av}=\frac{1}{2}-\frac{E_0}{8kT_0},$$

$$\langle\langle S_y^2\rangle\rangle_{\rm av}=\frac{1}{2}-\left(\frac{9E_0^2-2\omega^2}{\epsilon^2}\right)\frac{E_0}{8kT_0}, \quad \text{(A9)}$$

$$\langle\langle S_z^2\rangle\rangle_{\rm av}=\frac{1}{2}+\left(\frac{9E_0^2+\omega^2}{\epsilon^2}\right)\frac{E_0}{4kT_0}.$$

In the limit of no coupling between spins ($E_0\to 0$), $\langle\langle S_k^2\rangle\rangle_{\rm av}=1/2$. A geometrical picture of the motion of the tip of the averaged spin vector is, according to (A9), more complicated than a circular precession around the field direction, for otherwise one would have equal values for $\langle\langle S_y^2\rangle\rangle_{\rm av}$ and $\langle\langle S_z^2\rangle\rangle_{\rm av}$.

APPENDIX B. PERTURBATION THEORY TO ALL ORDERS

The perturbation expansion (30) may be extended to all orders of B, by calculating the derivatives indicated in (26).

We generalize the definitions (28) to

$$S_0\equiv 1$$

$$S_n=\int_0^1\int_0^1\cdots\int_0^1 dx'dx''\cdots \times dx^{(n)}e^{-Ax'}Be^{Ax'}e^{-Ax'x''}(Bx')e^{Ax'x''}\cdots \times e^{-Ax'x''\cdots x^{(n)}}(Bx'x''\cdots x^{(n)}) \times e^{Ax'x''\cdots x^{(n)}}, \quad n\geq 1. \quad \text{(B1)}$$

The general expansion of $\langle\Gamma\rangle$ then gives

$$\langle\Gamma\rangle=\sum_{n=1}^{\infty}\langle Q_n\Gamma\rangle_0, \quad \text{(B2)}$$

with

$$Q_n\equiv S_n-\sum_{k=1}^{n-1}\langle Q_k\rangle_0 S_{n-k}.$$

To prove (B2) one can write (27) in the form

$$e^{A+\epsilon B}=e^A\sum_{n=0}^{n}\epsilon^n S_n, \quad \text{(B3)}$$

where the S_n are defined by (B1). Consequently,

$$u(\epsilon)\equiv{\rm Tr}Ce^{A+\epsilon B}=\sum_{n=0}^{\infty}\epsilon^n\,{\rm Tr}Ce^AS_n$$

$$v(\epsilon)={\rm Tr}e^{A+\epsilon B}=\sum_{n=0}^{\infty}\epsilon^n\,{\rm Tr}e^AS_n$$

and the nth derivatives with respect to ϵ evaluated at $\epsilon=0$ are

$$u^{(n)}(0)/v(0)=n!\langle S_nC\rangle_0, \quad v^{(n)}(0)/v(0)=n!\langle S_n\rangle_0. \quad \text{(B4)}$$

We need the derivatives of $1/v$; these may be expanded in terms of the derivatives of v, to obtain by use of the second of the Eqs. (B4),

$$v(0)(v^{-1})^{(n)}(0)=-n!\langle Q_n\rangle_0. \quad \text{(B5)}$$

Equations (B4) and (B5) show that the $\langle Q_n\rangle_0$ and $\langle S_n\rangle_0$ are related to the derivatives of the partition function v. The derivatives required in (26) are

$$\frac{1}{n!}\frac{d^n\langle C\rangle_\epsilon}{d\epsilon^n}=\frac{1}{n!}\frac{d^n(uv^{-1})}{d\epsilon^n}=\sum_{k=0}^{n}\frac{u^{(k)}(v^{-1})^{(n-k)}}{k!(n-k)!},$$

as follows from the elementary rule for differentiating a product. At $\epsilon=0$, the derivatives are, with the help of (B4) and (B5),

$$\frac{1}{n!}\frac{d^n\langle C\rangle_\epsilon}{d\epsilon^n}=-\sum_{k=1}^{n}\langle Q_k\rangle_0\langle S_{n-k}C\rangle_0+\langle S_nC\rangle_0 =\langle Q_n\Gamma\rangle_0. \quad \text{(B6)}$$

Inserting the expression (B6) into (26), finally gives the theorem (B2).

APPENDIX C. SOME SIMPLE EXPECTATION VALUES

Below are given the expectation values of frequently occurring, spin operators taken over the density matrix

$$\rho_0=\frac{\exp(aI_z)}{{\rm Tr}[\exp(aI_z)]}.$$

The abbreviation $\Gamma \equiv I_z - 1 \cdot \langle I_z \rangle_0$ is used, and I is the angular momentum in units of $\hbar$.

1. $\langle I_x \rangle_0 = \langle I_y \rangle_0 = 0$

2. $\langle I_z \rangle_0 = (I+\frac{1}{2}) \coth[a(I+\frac{1}{2})] - \frac{1}{2} \coth a/2 = (a/3) I(I+1) + O(a^3)$

3. $\langle I_z I_{z,y} \rangle_0 = \langle I_{z,y} I_z \rangle_0 = 0$

4. $\langle I_z^2 \rangle_0 = I(I+1) + \frac{1}{2} \coth^2 a/2 - (I+\frac{1}{2}) \coth(a/2) \coth[a(I+\frac{1}{2})] = \frac{1}{3} I(I+1) + O(a^2)$

5. $\langle I_z \Gamma \rangle_0 = \partial \langle I_z \rangle_0 / \partial a = \frac{1}{3} I(I+1) + O(a^2)$

6. $$\langle I_z^2 \Gamma \rangle_0 = \frac{\partial \langle I_z^2 \rangle_0}{\partial a} = \frac{aI(I+1)}{45} [4I(I+1) - 3] + O(a^3)$$

7. $$\langle I_{z,y}^2 \Gamma \rangle_0 = -\frac{1}{2} \frac{\partial \langle I_z^2 \rangle_0}{\partial a} = -\frac{aI(I+1)}{90} [4I(I+1) - 3] + O(a^3)$$

8. $\langle I_{z,y} I_z \Gamma \rangle_0 = \langle I_z I_{z,y} \Gamma \rangle_0 = 0$

9. $\langle I_x I_y \Gamma \rangle_0 = -\langle I_y I_x \Gamma \rangle_0 = \frac{1}{2} i\hbar \langle I_z \Gamma \rangle_0$.