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Relaxation of spins due to field inhomogeneities in gaseous samples at low magnetic fields and low pressures

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We have developed a theory for the effect of magnetic-field inhomogeneities on the spin relaxation of gases in cells with negligible relaxation at the walls. There is a characteristic pressure p^* at which the time τ_d required for an atom to diffuse across the cell is equal to the time τ_l required for the spin to precess by one radian in the mean magnetic field. For "high pressures," $p \gg p^*$, the longitudinal spin-relaxation time T_1 is inversely proportional to the pressure. This is the classic pressure dependence discussed in the literature. The new results reported in this paper are that at "low pressures," $p \ll p^*$, the pressure dependence changes and the longitudinal relaxation time becomes directly proportional to the pressure; that is, motional narrowing occurs. We show that the transverse relaxation time T_2 will ordinarily be proportional to the pressure at both low and high pressures, but with different coefficients. There is also a small, pressure-dependent shift of the Larmor frequency associated with the field inhomogeneity.

I. INTRODUCTION

For many years it has been known that inhomogeneous magnetic fields can contribute to the transverse and longitudinal relaxation rates of spin-polarized atoms in a gas. This has been a particularly important phenomenon for spin-polarized ^{3}He gas, and in two early papers by groups working on ^{3}He the following remarkably simple and widely quoted formula for the longitudinal spin-relaxation rate was derived[1,2]

$$\frac{1}{T_1} = D\frac{|\vec{\nabla}B_x|^2 + |\vec{\nabla}B_y|^2}{B_0^2} . \tag{1}$$

Here D, the diffusion constant for the polarized spins, is inversely proportional to the gas pressure. The mean magnetic field is assumed to lie along the z axis of a coordinate system and have a magnitude B_0. The components of the magnetic field along the x and y axes of the coordinate system are B_z and B_y, and their spatial gradients $|\vec{\nabla}B_x|$ and $|\vec{\nabla}B_y|$ are assumed to be independent of position in the cell. We have omitted from the right side of (1) a factor $(1+\Omega_0^2\tau_c^2)^{-1}$ given in the original papers[1,2] to account for the rotation of the spins at the Larmor frequency Ω_0 about B_0 during the time interval τ_c between gas kinetic collisions. This factor will be essentially unity for the experimental conditions of interest in this paper.

We shall show that the validity of (1) depends on the magnitude of the parameter

$$\frac{\Omega_0 R^2}{D} = \frac{p}{p^*} = \frac{\tau_d}{\tau_l} , \tag{2}$$

which can be thought of as the ratio of a characteristic diffusion time $\tau_d = R^2/D$, required for the spins to diffuse across the cell, to a characteristic precession time $\tau_l = \Omega_0^{-1}$. Here Ω_0 is the Larmor frequency of the spins in a field B_0, and R is a characteristic length of the cell which contains the gas. In the case of a spherical cell, R would be the cell radius. As indicated in (2), we can also think of the parameter $\Omega_0 R^2/D$ as the "relative pressure," that is, the ratio of the gas pressure p to the characteristic pressure, $p^* = D_0\Omega_0^{-1}R^{-2}$ for which the parameter is unity. Here D_0 is the diffusion constant at unit pressure, usually one atmosphere.

Equation (1) is a correct limiting expression for the spin-relaxation rate when the gas pressure and magnetic field are sufficiently large that

$$\frac{\Omega_0 R^2}{D} = \frac{p}{p^*} = \frac{\tau_d}{\tau_l} \gg 1 , \tag{3}$$

that is, when the precession time is short compared to the diffusion time.

The criterion (3) is not satisfied, and (1) is not valid for experiments at low pressures and low magnetic fields. In fact, one often finds that the experiments are carried out under conditions such that

$$\frac{\Omega_0 R^2}{D} = \frac{p}{p^*} = \frac{\tau_d}{\tau_l} \ll 1 . \tag{4}$$

For example, in recent experiments with nuclear-spin-polarized isotopes of Xe carried out in our laboratory,[3] we had (in the rotating coordinate system) $D \approx 6$ cm^2 s^{-1}, $R \approx 0.3$ cm, $\Omega_0 \approx 3$ s^{-1}, so that $p/p^* \approx 0.05$. Experiments at low pressure (4) have been reported by several other groups.[4,5]

In this paper we obtain expressions for the relaxation due to field inhomogeneities which are valid for a large range of the relative pressure, including both high pressures (3) and low pressures (4). The basic results of this work are summarized in Fig. 1.

We note that at high pressures (3) the longitudinal relaxation rate scales as

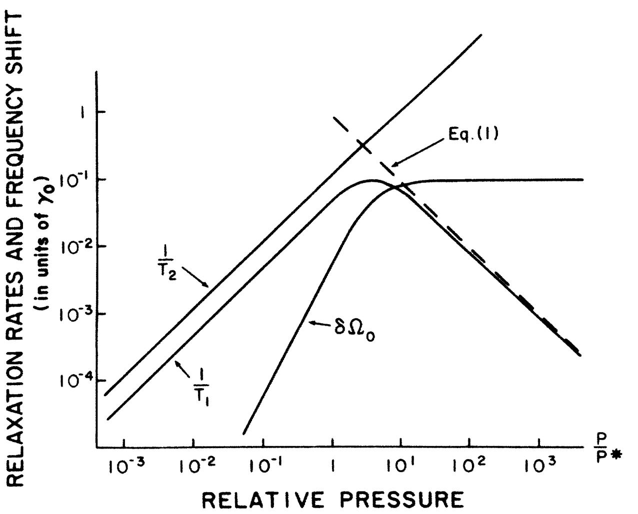

FIG. 1. The longitudinal relaxation rate $1/T_1$, the transverse relaxation rate $1/T_2$, and the frequency shift $\delta\Omega_0$ due to magnetic-field inhomogeneities. These are plotted as a function of the relative pressure p/p^* of (2). The rates and the frequency shift are computed from (57), (60), and (56) in units of the characteristic rate $\gamma_0=(|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2)R^2/\Omega_0$, and we have assumed an axially symmetric field inhomogeneity $\vec{\nabla}\boldsymbol{\Omega}_1=[2\mathbf{zz}-\mathbf{xx}-\mathbf{yy}]\Omega_1/R$. The classic formula Eq. (1) is also sketched and is seen to be a good approximation at high pressures.

$$\frac{1}{T_1}\approx\frac{\Omega_\perp^2}{\Omega_0}\frac{p^*}{p}, \tag{5}$$

and at low pressures (4) the longitudinal relaxation rate scales as

$$\frac{1}{T_1}\approx\frac{\Omega_\perp^2}{\Omega_0}\frac{p}{p^*}. \tag{6}$$

Here $\Omega_\perp$ is an rms Larmor frequency associated with the transverse inhomogeneous field.

The expression for relaxation rates and frequency shifts developed in this paper are based on perturbation theory, which sets an upper limit on the relative pressure p/p^* for which the results are valid, and the use of the diffusion equation, which sets a lower limit of the relative pressure p/p^*. The limits are found to be

$$\frac{R\Omega_0}{v}\ll\frac{p}{p^*}\ll\frac{\Omega_0}{\Omega_\perp}. \tag{7}$$

One can understand the scaling of the relaxation rates in the two regimes (5) and (6) from the following plausibility arguments, which we will justify in the body of the paper. Consider a longitudinal spin which is subject to a fluctuating, transverse magnetic field with a Larmor frequency ω and a correlation time τ. In a correlation time τ the spin will precess in a random direction by an angle $\delta\theta\approx\omega\tau\ll1$. On the average, a net precession angle of one radian will accumulate after the spin has completed a random walk in angle space with $\delta\theta^{-2}$ steps. Since each step takes a time τ, the relaxation time will be on the order of $T_1\approx\tau\delta\theta^{-2}\approx\omega^{-2}\tau^{-1}$, so we expect the longitudinal relaxation rate to scale in the well-known way

$$\frac{1}{T_1}\approx\omega^2\tau. \tag{8}$$

At high pressures (3) the spins diffuse so slowly through the gas and they precess so rapidly that their "natural" quantization axis is along the local direction of the inhomogeneous magnetic field. In moving at a velocity v from one location to another between gas kinetic collisions, the spins will perceive the field to be rotating at a rate $\omega\approx v\Omega_\perp/R\Omega_0$. This rotation rate will act like the Larmor frequency ω of the randomly fluctuating perturbation assumed in (8), and the correlation time will be the time between gas kinetic collisions $\tau\approx\lambda/v$. Substituting these estimates of ω and τ into (8) we obtain the high-pressure scaling law (5), since $D=v\lambda/3$.

At low pressures (4), the spins diffuse so rapidly through the gas and they precess so slowly that their "natural" quantization direction is the direction of the mean magnetic field. The correlation time is therefore on the order of the diffusion time $\tau\approx\tau_d=R^2/D$ and the fluctuating Larmor frequency is $\omega\approx\Omega_\perp$. Substituting these estimates of ω and τ into (8) we obtain the low-pressure scaling law (6).

Of course, the pressure dependence of the relaxation rate due to field inhomogeneities is related to other line-narrowing phenomena involving frequency-modulated oscillators. Examples are spin-exchange narrowing in paramagnetic resonance,[6] Dicke narrowing[7] of Doppler-broadened linewidths, or Mössbauer narrowing[8] of γ-ray spectra. The phenomenon discussed here is perhaps most closely related to the classical motional narrowing of nuclear magnetic resonance spectra in viscous liquids, and our Fig. 1 is qualitatively the same as Fig. 4.2 of Bloembergen's thesis.[9] However, in classical motional narrowing, the magnetic-field inhomogeneities are caused by the nuclei of molecules separated by at most a few molecular diameters from the spin of interest. The magnetic-field inhomogeneities discussed here extend through the entire macroscopic volume of the cell, and the low-pressure relaxation rates depend explicitly on the cell volume and geometrical shape. The motional narrowing is an important practical reason to use low pressures and low magnetic fields in experiments designed to exploit the long relaxation times of spin-polarized noble gas nuclei.[3-5]

II. THEORY

We consider a gas of atoms with intrinsic spin $\mathbf{K}$, confined to a sample cell. The cell is in a static magnetic field $\mathbf{B}(\mathbf{r})$, which we shall assume has a slight dependence on the position $\mathbf{r}$ of the spin within the cell. The spin Hamiltonian of the atoms is

$$H=g_K\mu_B\mathbf{K}\cdot\mathbf{B}(\mathbf{r})=H^{(0)}+H^{(1)}. \tag{9}$$

To define an unperturbed part of the Hamiltonian $H^{(0)}$ and a perturbation $H^{(1)}$, we introduce a mean field

$$\mathbf{B}_0=\frac{1}{V}\int\mathbf{B}(\mathbf{r})dV, \tag{10}$$

which is averaged over the volume V of the container. We also introduce an inhomogeneous field

$$\mathbf{B}_1=\mathbf{B}(\mathbf{r})-\mathbf{B}_0 \ . \tag{11}$$

The mean value of the inhomogeneous field is zero. We let $\mathbf{B}_0=\mathbf{z}B_0$ define a unit vector $\mathbf{z}$ along the z axis of our coordinate system, and we define the unperturbed Hamiltonian

$$H^{(0)}=\hbar\boldsymbol{\Omega}_0\cdot\mathbf{K} \ , \tag{12}$$

where the unperturbed Larmor frequency is $\boldsymbol{\Omega}_0=g_K\mu_B\mathbf{B}_0/\hbar$. The Bohr magneton is μ_B and the g factor of the spin is g_K. The eigenvectors $| m \rangle$ of the unperturbed Hamiltonian are given by

$$H^{(0)}| m \rangle=\hbar\Omega_0 m \ | m \rangle \ , \tag{13}$$

where Ω_0 is the spatially-independent magnitude of $\boldsymbol{\Omega}_0$, and m is the azimuthal quantum number, i.e.,

$$K_z \,| m \rangle = m \ | m \rangle \ . \tag{14}$$

The perturbation is

$$H^{(1)}=\hbar\boldsymbol{\Omega}_1\cdot\mathbf{K} \ , \tag{15}$$

where the perturbed Larmor frequency $\boldsymbol{\Omega}_1=g_K\mu_B\mathbf{B}_1/\hbar$, depends on the position $\mathbf{r}$ within the cell and has a mean value of zero.

The evolution of the density matrix of the noble gas atoms in the volume of the cell is given by

$$\frac{\partial\rho}{\partial t}=\frac{1}{i\hbar}[H,\rho]+D\nabla^2\rho \ , \tag{16}$$

where D is the diffusion coefficient, and the square brackets denote a commutator. We neglect collisional relaxation in the gas phase. The evolution equation (16) is valid if conditions are such that one can neglect the rotation of the spin during a mean free path of a diffusing atom, that is, if $\Omega_0\lambda/v \ll 1$, and if the mean free path is much smaller than the size R of the container, $\lambda \ll R$.

We can always express the density matrix as a superposition of the eigenpolarizations $P_i \equiv |\, i)$ of the unperturbed Hamiltonian which are defined by

$$[H^{(0)},P_i]=\hbar\Lambda_i P_i \ . \tag{17}$$

The eigenpolarizations can be chosen to be orthonormal, that is

$$\mathrm{Tr}P_i^{\dagger}P_j \equiv (i \,|\, j)=\delta_{ij} \ , \tag{18}$$

where Tr denotes a trace. For this problem it will be convenient to choose the eigenpolarizations to be irreducible basis tensors,[10] which we define in terms of the eigenvectors of (14) by

$$|\, LM) \equiv T_{LM} = \left[\frac{2L+1}{2K+1}\right]^{1/2} \sum_m | m+M \rangle\langle m \,|\, C(KLK;m,M) \ , \tag{19}$$

where $C(KLK;m,M)$ is a Clebsch-Gordan coefficient.[11]

Then (17) becomes

$$[H^{(0)},T_{LM}]=\hbar M\Omega_0 T_{LM} \ , \tag{20}$$

and thus $\Lambda_i \equiv \Lambda_{LM}=M\Omega_0$. We may define matrix elements of the perturbation (15) between eigenpolarizations by

$$H_{ij}^{(1)}=\mathrm{Tr}P_i^{\dagger}[H^{(1)},P_j] \ . \tag{21}$$

In the case considered here where the eigenpolarizations are given by (19) one can readily show that

$$H^{(1)}_{LM,L'M'}=\delta_{L,L'}\hbar\boldsymbol{\Omega}_1\cdot(LM' \,|\, \mathbf{L} \,|\, LM) \ , \tag{22}$$

that is, the perturbation operator (15) assumes the form $H^{(1)}=\hbar\boldsymbol{\Omega}_1\cdot\mathbf{L}$ in polarization space and the angular momentum operator $\mathbf{L}$ has the conventional effect on the basis states $|\, LM)$ of (19), that is,

$$L_{\pm} \,|\, LM)=\sqrt{(L \mp M)(L \pm M+1)}\,|\, L,M\pm 1)$$

and $L_z \,|\, LM)=M \,|\, LM)$. We seek an exponentially decaying solution for ρ, i.e.,

$$\rho(\mathbf{r},t)=\sum_i P_i f_i(\mathbf{r})e^{-\gamma t} \ . \tag{23}$$

Substituting (23) into (16) and equating the coefficients of the eigenpolarizations P_i to zero, we find the set of equations

$$(D\nabla^2+\gamma-i\Lambda_i)f_i+\frac{1}{i\hbar}\sum_j H_{ij}^{(1)}f_j=0 \ , \tag{24}$$

for all values of the polarization index $i=LM$.

To find unique solutions of (24) it is necessary to specify boundary conditions at the surface of the cell. Since we are considering cells with nearly nonrelaxing walls, we will set the normal derivative of the density matrix equal to zero at the cell surface

$$\frac{\partial f_i}{\partial n}=0 \tag{25}$$

where $\partial/\partial n=\mathbf{n}\cdot\vec{\nabla}$ and $\mathbf{n}$ is a unit vector, normal to the cell wall and pointing out of the gas. Physically, (25) amounts to neglecting any loss of atoms or of spin polarization due to collisions with the cell walls.

We note that one can carry out analogous calculations of the effects of magnetic field inhomogeneities for cells in which the walls do cause spin relaxation. Then the boundary condition (25) must be replaced by $\partial f_i/\partial n=-\sum_j \mu_{ij}f_j$, where μ_{ij} is the normal gradient matrix of the wall.[12] For walls with large, coherent quadrupole interactions,[3,12] the uncoupled operators $| m \rangle\langle n |$ are the appropriate basis polarizations rather than the irreducible tensors (19).

Since we have assumed that the magnetic field is nearly uniform, we will regard the inhomogeneity as a small perturbation of a perfectly homogeneous magnetic field equal to $\mathbf{B}_0$. Following the standard procedures of perturbation theory, we introduce an expansion parameter η which we will eventually set equal to 1, and write $\boldsymbol{\Omega}_1$ as $\eta\boldsymbol{\Omega}_1$.

We expand γ and f_i as a power series of η,

$$\gamma=\gamma^{(0)}+\eta\gamma^{(1)}+\eta^2\gamma^{(2)}+\cdots \ , \tag{26}$$

$$f_i=f_i^{(0)}+\eta f_i^{(1)}+\eta^2 f_i^{(2)}+\cdots \ . \tag{27}$$

Substituting (26) and (27) into (24) and equating the coefficients of $\eta^l (l=0,1,2,\dots)$, we get

$$(D\nabla^2-i\Lambda_i+\gamma^{(0)})f_i^{(0)}=0 \ , \tag{28}$$

$$(D\nabla^2-i\Lambda_i+\gamma^{(0)})f_i^{(1)}+\gamma^{(1)}f_i^{(0)}+\frac{1}{i\hbar}\sum_j H_{ij}^{(1)}f_j^{(0)}=0 \ , \tag{29}$$

$$(D\nabla^2-i\Lambda_i+\gamma^{(0)})f_i^{(2)}+\gamma^{(1)}f_i^{(1)}+\gamma^{(2)}f_i^{(0)}+\frac{1}{i\hbar}\sum_j H_{ij}^{(1)}f_j^{(1)}=0 \ . \tag{30}$$

We may regard (28), (29), etc., as inhomogeneous wave equations, which, together with the boundary condition (25), determine the mode amplitudes of various orders in terms of mode amplitudes of lower orders.

We may write the zeroth-order diffusion equation (28) as

$$(\nabla^2+k^2)f_i^{(0)}=0 \ , \tag{31}$$

where

$$Dk^2=\gamma^{(0)}-i\Lambda_i \ . \tag{32}$$

Given the boundary condition (25), Eq. (31) has solutions only for certain real, nonnegative eigenvalues k^2, which we denote by k_α^2 with $\alpha=0,1,2,\dots$, and with the magnitude of k_α^2 increasing with α. We denote a solution of (31) corresponding to eigenvalue k_α^2 by ϕ_α, i.e.,

$$(\nabla^2+k_\alpha^2)\phi_\alpha=0 \ . \tag{33}$$

Equations (31) and (25) ensure that the diffusion modes $\phi_\alpha=f_i^{(0)}$ can be chosen to be orthonormal, i.e.,

$$\int_V dV'\,\phi_\alpha^*\phi_\beta=\delta_{\alpha\beta} \ , \tag{34}$$

where the integral extends over elements dV' of the cell volume V. We will be particularly interested in the *uniform* mode, which is

$$\phi_0=\frac{1}{\sqrt{V}} \ . \tag{35}$$

This mode has zero spatial frequency

$$k_0=0 \ . \tag{36}$$

The polarization of interest to us in cells with "good" walls will be very nearly described by the uniform mode, since the polarized atoms can diffuse freely throughout the cell with little relaxation on the walls, and they will therefore tend to fill the cell uniformly. Masnou-Seeuws and Bouchiat[13] refer to this situation as that of *"orientation non confinée"* (unconfined orientation).

For definiteness we will pause to discuss the explicit form of the diffusion modes for the simple case of a spherical cell of radius R. The normalized solutions to (33) are

$$\phi_\alpha=\frac{N_{ln}}{R^{3/2}}j_l(k_{ln}r)Y_{l\mu}(\theta\phi) \ , \tag{37}$$

where the spherical Bessel junction j_l is related to the conventional cylindrical Bessel function $J_{l+1/2}$ of half-integer order by

$$j_l(x)=\left[\frac{\pi}{2x}\right]^{1/2}J_{l+1/2}(x) \ ,$$

and $Y_{l\mu}$ is a spherical harmonic. In order to satisfy the boundary condition (25), the spatial frequencies k_{ln} must be given by

$$k_{ln}=\frac{x_{ln}}{R} \ , \tag{38}$$

where the positive dimensionless numbers x_{ln}, $n=1,2,\dots$ define, in order of increasing magnitude, the zeros of the normal derivative [see (A7) of the Appendix, where more details about the diffusion modes of a spherical cell are discussed]. The normalization coefficients N_{ln} are given by (A8) of the Appendix.

Thus for a spherical cell in a perfectly homogeneous magnetic field, there is a solution to (23) of the form

$$f_{i;\alpha g}^{(0)}=\phi_\alpha\delta_{ig} \ , \tag{39}$$

for every combination of a diffusion index α, which represents the spatial quantum numbers $l\mu n$ of the mode (37), and a polarization index g which represents the multipole quantum numbers LM of the irreducible basis tensors (19). The corresponding decay rates are given by (32) as

$$\gamma_{\alpha g}^{(0)}=Dk_\alpha^2+i\Lambda_g \ . \tag{40}$$

The uniform mode (35) is an exceptional case of (37) which corresponds to the vanishing spatial frequency (36).

Let us consider the higher-order corrections to the zeroth-order solution (39). Substituting (39) and (40) into (29) we find

$$[D\nabla^2+\gamma_{\alpha g}^{(0)}-i\Lambda_i]f_{i;\alpha g}^{(1)}+\gamma_{\alpha g}^{(1)}\phi_\alpha\delta_{ig}+\frac{1}{i\hbar}H_{ig}^{(1)}\phi_\alpha=0 \ . \tag{41}$$

We may write the nth-order corrections to the polarization amplitudes as a superposition of the zeroth-order diffusion modes, which form a complete set of functions

$$f_{i;\alpha g}^{(n)}=\sum_\beta \phi_\beta a_{\beta i;\alpha g}^{(n)} \ . \tag{42}$$

Substituting (42) into (41) and equating coefficients of ϕ_β to zero we find

$$[\gamma_{\alpha g}^{(0)}-\gamma_{\beta i}^{(0)}]a_{\beta i;\alpha g}^{(1)}+\gamma_{\alpha g}^{(1)}\delta_{\beta\alpha}\delta_{ig}+\frac{1}{i\hbar}\langle\beta|H_{ig}^{(1)}|\alpha\rangle=0 \ , \tag{43}$$

where the matrix element of the inhomogeneity (22) is

$$\langle\beta|H_{ig}^{(1)}|\alpha\rangle=\int_V dV'\,\phi_\beta^*H_{ig}^{(1)}\phi_\alpha \ . \tag{44}$$

If we set $\beta=\alpha$ and $i=g$ in (43) we find the first-order correction to the relaxation rate to be

$$\gamma_{\alpha g}^{(1)}=\frac{i}{\hbar}\langle\alpha\,|\,H_{gg}^{(1)}\,|\,\alpha\rangle\ . \tag{45}$$

For the important special case of uniform zeroth-order polarization (45) implies that

$$\gamma_{0g}^{(1)}=\frac{i}{\hbar V}\int dV\,H_{gg}^{(1)}=0\ , \tag{46}$$

since the mean value of the inhomogeneity in the cell is zero.

Equation (43) determines the mixing coefficient for nondegenerate states, i.e., states with $\gamma_{\beta i}^{(0)}\neq\gamma_{\alpha g}^{(0)}$. We find

$$a_{\beta i;\alpha g}^{(1)}=\frac{\langle\beta\,|\,H_{ig}^{(1)}\,|\,\alpha\rangle}{i\hbar[\gamma_{\beta i}^{(0)}-\gamma_{\alpha g}^{(0)}]}\ . \tag{47}$$

For degenerate states (43) implies that

$$\langle\beta\,|\,H_{ig}^{(1)}\,|\,\alpha\rangle=0\quad\text{if }\gamma_{\beta i}^{(0)}=\gamma_{\alpha g}^{(0)}\text{ and }(\beta i)\neq(\alpha g)\ . \tag{48}$$

Degeneracies such as those envisaged in (48) naturally occur for states with the same diffusion mode $\beta=\alpha$, the same azimuthal quantum number M for the polarization index, but different multipolarity indices L. The irreducible basis terms (19) were chosen as the appropriate zeroth-order polarizations to ensure the validity of (48).

We now consider the second-order corrections. Substituting (39) and (42) into (30) we find

$$[\gamma_{\alpha g}^{(0)}-\gamma_{\beta i}^{(0)}]a_{\beta i;\alpha g}^{(2)}+\gamma_{\alpha g}^{(1)}a_{\beta i;\alpha g}^{(1)}$$
$$+\frac{1}{i\hbar}\sum_{\sigma,j}\langle\beta\,|\,H_{ij}^{(1)}\,|\,\sigma\rangle a_{\sigma j;\alpha g}^{(1)}+\gamma_{\alpha g}^{(2)}\delta_{\beta\alpha}\delta_{ig}=0\ . \tag{49}$$

Setting $\beta=\alpha=0$ and $i=g$ in (49), and noting from (46) that $\gamma_{0g}^{(1)}=0$, we find the second-order damping of the uniform mode to be

$$\gamma_{0g}^{(2)}=\sum_{\beta,j}{}'\,\frac{\langle 0\,|\,H_{gj}^{(1)}\,|\,\beta\rangle\langle\beta\,|\,H_{jg}^{(1)}\,|\,0\rangle}{\hbar^2[\gamma_{\beta j}^{(0)}-\gamma_{0g}^{(0)}]}\ , \tag{50}$$

where the prime means that terms with $\gamma_{\alpha g}^{(0)}=\gamma_{\beta j}^{(0)}$ are to be excluded from the sum.

Since the inhomogeneity is assumed to be small and has zero mean value we will consider only a linear variation of $\mathbf{\Omega}_1$

$$\mathbf{\Omega}_1=\mathbf{r}\cdot\vec{\nabla}\mathbf{\Omega}_1\ , \tag{51}$$

where $\vec{\nabla}\mathbf{\Omega}_1$ is a constant, traceless, symmetric tensor. We may regard (51) as the first term, a P wave, in a partial wave expansion of $\mathbf{\Omega}_1$, or as the first term in a power series expansion in $\mathbf{r}$. The subsequent steps can be readily generalized to take into account higher partial waves, in case the lowest-order term (51) vanishes because of symmetry. For example, the magnetic-field inhomogeneity near the center of Helmholtz coils is described by a G wave ($l=4$).

We note that

$$\mathbf{r}=r\left[\frac{4\pi}{3}\right]^{1/2}\sum_{\mu}(-1)^{\mu}\mathbf{x}_{-\mu}Y_{1\mu}(\theta\phi)\ , \tag{52}$$

where the spherical unit vectors are defined in terms of the Cartesian unit vectors $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ in the conventional way by

$$\mathbf{x}_{\pm 1}=\mp\frac{\mathbf{x}\pm i\mathbf{y}}{\sqrt{2}},\quad \mathbf{x}_0=\mathbf{z}\ . \tag{53}$$

To calculate the second-order damping (50) we need the matrix elements which couple the uniform mode to excited diffusional modes. Using (22), (37), and (44) we find that the only nonzero matrix elements are

$$\langle 1\mu n\,|\,H_{LM',LM}^{(1)}\,|\,0\rangle$$
$$=N_{1n}\frac{j_1(x_{1n})}{x_{1n}^2}\hbar R(\mathbf{x}_\mu\cdot\vec{\nabla}\Omega_{1,M'-M})^*$$
$$\times\sqrt{L(L+1)}C(L1L;M,M'-M)\ , \tag{54}$$

where C denotes a Clebsch-Gordan coefficient. We have made use of (A11) and (A12) in evaluating the matrix element (54). Since the zeroth-order damping rates of the coupled modes are $\gamma_{1\mu n;LM'}^{(0)}=Dx_{1n}^2R^{-2}+i\Omega_0M'$ and $\gamma_{0;LM}^{(0)}=i\Omega_0M$, we may substitute (54) into (50) and use (A9) and (A20) to find the real part of the damping to be

$$\mathcal{R}\gamma_{0,LM}^{(2)}=\frac{8M^2R^4\,|\,\vec{\nabla}\Omega_{1z}\,|^2}{175D}$$
$$+D[L(L+1)-M^2]\frac{|\,\vec{\nabla}\Omega_{1x}\,|^2+|\,\vec{\nabla}\Omega_{1y}\,|^2}{\Omega_0^2}$$
$$\times\sum_n\frac{1}{[x_{1n}^2-2][1+D^2x_{1n}^4\Omega_0^{-2}R^{-4}]}\ . \tag{55}$$

The imaginary part of the damping (a frequency shift) is

$$\mathcal{J}\gamma_{0,LM}^{(2)}=M\delta\Omega_0$$
$$=\frac{MR^2}{\Omega_0}(\,|\,\vec{\nabla}\Omega_{1x}\,|^2+|\,\vec{\nabla}\Omega_{1y}\,|^2)$$
$$\times\sum_n\frac{1}{x_{1n}^2[x_{1n}^2-2][1+D^2x_{1n}^4\Omega_0^{-2}R^{-4}]}\ . \tag{56}$$

The polarization with quantum numbers $L,M=1,0$ is the longitudinal spin polarization, which is of great importance in magnetic resonance experiments. We may use (55) to write the longitudinal spin relaxation rate as

$$\frac{1}{T_1}=\gamma_{0,10}^{(2)}$$
$$=2D\frac{|\,\vec{\nabla}\Omega_{1x}\,|^2+|\,\vec{\nabla}\Omega_{1y}\,|^2}{\Omega_0^2}$$
$$\times\sum_n\frac{1}{[x_{1n}^2-2][1+D^2x_{1n}^4\Omega_0^{-2}R^{-4}]}\ . \tag{57}$$

For high pressures, where (3) is valid, we may use (A18) to write

$$\frac{1}{T_1}\approx D\frac{|\,\vec{\nabla}\Omega_{1x}\,|^2+|\,\vec{\nabla}\Omega_{1y}\,|^2}{\Omega_0^2}\ . \tag{58}$$

The relaxation rate is proportional to the diffusion constant D or is inversely proportional to the gas pressure in the cell. This is the same as the classic formula (1), but we see that it applies only at high pressures.

At low pressure, where (4) is valid, we find that (57) becomes

$$\frac{1}{T_1} \approx \frac{8R^4}{175D}(|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2) . \tag{59}$$

That is, the relaxation rate is inversely proportional to the diffusion constant D or directly proportional to the gas pressure in the cell. Motional narrowing occurs because the spins diffuse rapidly through the inhomogeneous field.

The polarization with quantum numbers $L,M=1,\pm 1$ is the transverse spin polarization, which is so important in determining the linewidth or free precession signal of a magnetic resonance experiment. From (55) we find that the transverse damping rate is

$$\begin{aligned}\frac{1}{T_2} &\equiv \mathcal{R}\gamma^{(2)}_{0,11}\\ &= \frac{8R^4|\vec{\nabla}\Omega_{1z}|^2}{175D} + D\frac{|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2}{\Omega_0^2}\\ &\quad \times \sum_n \frac{1}{[x_{1n}^2-2][1+D^2x_{1n}^4\Omega_0^{-2}R^{-4}]} .\end{aligned} \tag{60}$$

At high pressures (3) we find that (60) approaches the limiting value

$$\frac{1}{T_2} \approx \frac{8R^4|\vec{\nabla}\Omega_{1z}|^2}{175D} . \tag{61}$$

In contrast to the longitudinal relaxation rate (58) which, at high gas pressures, decreases inversely with the pressure (increases directly with D), the transverse relaxation rate (61) is directly proportional to the gas pressure (decreases inversely with D), provided that $\vec{\nabla}\Omega_{1z}\neq 0$. Should the inhomogeneity be purely transverse, $\vec{\nabla}\Omega_{1z}=0$, one would have $T_2=2T_1$ for all pressures. From physical considerations, we know that the transverse relaxation rate cannot exceed, in order of magnitude, the maximum field inhomogeneity Ω_{1z}. This implies that (61) ceases to be valid at pressures so high that it predicts damping rates comparable to Ω_{1z}. The corresponding limit on the pressure turns out to be the same as the upper limit on the relative pressure Ω_0/Ω_1 mentioned in (7).

At low pressures (4) we use (A20) with (60) to show that the transverse relaxation rate is

$$\frac{1}{T_2} \approx \frac{4R^4}{175D}(|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2+2|\vec{\nabla}\Omega_{1z}|^2) . \tag{62}$$

At low pressures (4), the regime of motional narrowing, the transverse relaxation rate (62), like the longitudinal relaxation rate, is proportional to the gas pressure.

At high pressures (3) the frequency shift $\delta\Omega_0$ is independent of the pressure and is given by (56) and (A19) as

$$\delta\Omega_0 \approx \frac{R^2}{10\Omega_0}(|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2) . \tag{63}$$

It is interesting to note that the frequency shift (63) is equal, to order $|\vec{\nabla}\Omega_{1i}|^2$, to the difference in the volume-averaged magnitude of the local Larmor frequency, $\langle|\mathbf{\Omega}|\rangle=\langle|\mathbf{\Omega}_0+\mathbf{\Omega}_1|\rangle$, and the magnitude $\mathbf{\Omega}_0$ of the mean Larmor frequency.

At low pressures (4) we may use (A21) together with (56) to write

$$\delta\Omega_0 \approx \frac{83\Omega_0 R^6}{15\,750D^2}(|\vec{\nabla}\Omega_{1x}|^2+|\vec{\nabla}\Omega_{1y}|^2) . \tag{64}$$

At low pressures, the frequency shift is proportional to D^{-2}, that is, the shift is proportional to the square of the pressure.

III. DISCUSSION

Some insight into the physics of the situation can be gained by considering the polarization $\sum_i P_i f_i(\mathbf{r})$ associated with the exponentially decaying solutions (23). To first order in the field inhomogeneity we may use (27), (39), (42), and (47) to write the state which evolves from the polarization state $|LM)$ of the spatially uniform mode as

$$\begin{aligned}\sum_i P_i f_i(\mathbf{r}) &\approx \frac{|LM)}{\sqrt{V}} + \sum_{M'} |LM')f^{(1)}_{LM';0,LM}\\ &= \left[1-i\sum_{M'}|LM')(LM'|\sum_n \frac{R}{r}\frac{N_{1n}^2}{x_{1n}^2}\frac{j_1(x_{1n})j_1\left[\dfrac{x_{1n}r}{R}\right]}{\dfrac{Dx_{1n}^2}{R^2}+i\Omega_0(M'-M)}\mathbf{\Omega}_1\cdot\mathbf{L}\right]\frac{|LM)}{\sqrt{V}}\\ &\approx e^{-i\delta\mathbf{\Phi}\cdot\mathbf{L}}\frac{|LM)}{\sqrt{V}} .\end{aligned} \tag{65}$$

From (65) we see that the effect of the field inhomogeneity is to introduce an infinitesimal rotation of the polarization $|LM)$ by a spatially-dependent angle $\delta\Phi$ which we will write as the sum of three components

$$\delta\Phi=\delta\Phi_1+\delta\Phi_2+\delta\Phi_3 \; . \tag{66}$$

The transverse rotation angles are

$$\delta\Phi_1=\sum_n \frac{R}{r}\frac{2}{[x_{1n}^2-2]j_1(x_{1n})}j_1\left[\frac{x_{1n}r}{R}\right] \times\frac{1}{1+\frac{D^2x_{1n}^4}{\Omega_0^2R^4}}\frac{\mathbf{z}\times\mathbf{\Omega}_1}{\Omega_0} \; , \tag{67}$$

and

$$\delta\Phi_2=\frac{R^3\Omega_0}{rD}\sum_n \frac{2}{x_{1n}^2[x_{1n}^2-2]j_1(x_{1n})}j_1\left[\frac{x_{1n}r}{R}\right] \times\frac{1}{1+\frac{\Omega_0^2R^4}{D^2x_{1n}^4}}(\mathbf{xx}+\mathbf{yy})\cdot\frac{\mathbf{\Omega}_1}{\Omega_0} \; . \tag{68}$$

The longitudinal rotation angle is

$$\delta\Phi_3=\frac{3R^2-r^2}{10D}\Omega_0\mathbf{zz}\cdot\frac{\mathbf{\Omega}_1}{\Omega_0} \; . \tag{69}$$

In writing out (69) we made use of (A17).

At high pressures (3) one can show that, over most of the cell volume,

$$\delta\Phi_2\approx\frac{D}{R^2\Omega_0}\delta\Phi_1\ll\delta\Phi_1 \; ,$$

so that the transverse rotation angle at high pressures is almost completely determined by $\delta\Phi_1$. One can also show that

$$\delta\Phi_3\approx\frac{\Omega_0R^2}{D}\delta\Phi_1\gg\delta\Phi_1$$

so that the longitudinal rotation angle greatly exceeds the transverse rotation angle at high pressures. Thus, at high pressures (3), we may use (A13) to show that (66) becomes

$$\delta\Phi\approx\delta\Phi_1+\delta\Phi_3 \approx\frac{\mathbf{z}\times\mathbf{\Omega}_1}{\Omega_0}+\frac{3R^2-r^2}{10D}\Omega_0\mathbf{zz}\cdot\frac{\mathbf{\Omega}_1}{\Omega_0} \; . \tag{70}$$

The geometric significance of the high-pressure rotation angle (70) is illustrated in Fig. 2. As one might surmise from Fig. 2, there are some advantages to choosing irreducible basis tensors which are quantized along the local direction of the magnetic field when one is interested in high pressures. We have carried through the analysis of the problem with these spatially-dependent basis tensors, and of course the same results for the damping rates and frequency shift were found. However, the spatially-independent basis tensors (19) are more convenient.

At low pressures we find that

$$\delta\Phi_1\approx\frac{\Omega_0R^2}{D}\delta\Phi_2\ll\delta\Phi_2 \; ,$$

so the transverse rotation angle at low pressures is almost completely dominated by $\delta\Phi_2$, which is perpendicular to $\delta\Phi_1$. Then we may use (68), (A17), and (69) to write

$$\delta\Phi\approx\delta\Phi_2+\delta\Phi_3\approx\frac{3R^2-r^2}{10D}\mathbf{\Omega}_1 \; . \tag{71}$$

At low pressures the rotation angle is proportional to the gas pressure (inversely proportional to D). The rotation of the spin polarization at a given spatial location in the cell is far less than the rotation of the magnetic field at the same location, and the spins are rotated at right angles to the direction of rotation of the magnetic field. A qualitative sketch of the spatial variation of the spin polarization at low pressures is shown in Fig. 3.

The rotation angles (69) and (71) satisfy the boundary condition (25), which implies no flux of polarization into the walls or $(\partial/\partial r)\delta\Phi(R,\theta,\phi)=0$. This boundary condition is not satisfied by the high-pressure approximation

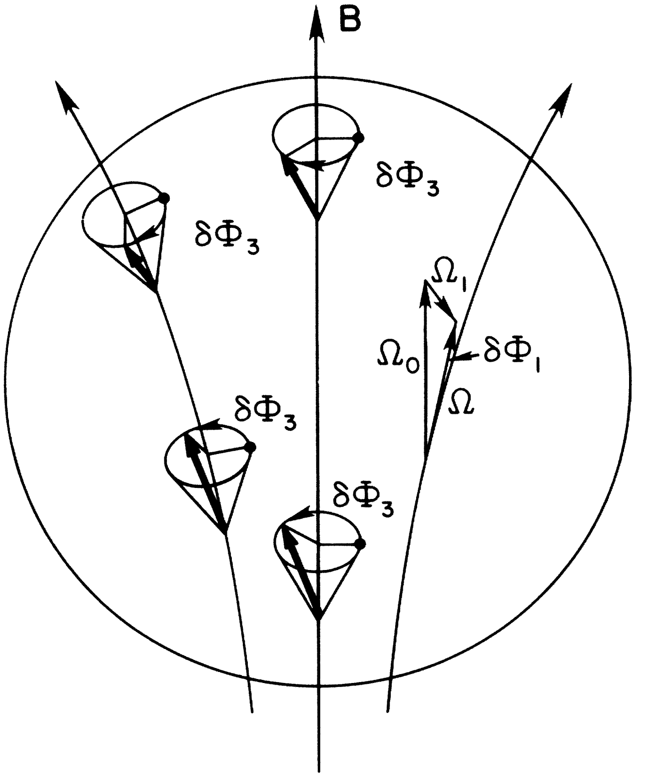

FIG. 2. The slowest spin-relaxation modes in a spherical cell with an inhomogeneous magnetic field $\mathbf{B}(\mathbf{r})$ at high gas pressure. The transverse rotation $\delta\Phi_1\approx\mathbf{\Omega}_0\times\mathbf{\Omega}_1/\Omega_0^2$ brings the spin polarization very nearly into alignment with the local direction of the magnetic field. The longitudinal rotation $\delta\Phi_3$ causes the transverse spin polarization at the bottom of the cell, where the field is stronger, to be advanced with respect to the transverse spin polarization at the top of the cell, where the magnetic field is weaker. For the high pressures depicted here, the classical expression (1) for T_1 is valid.

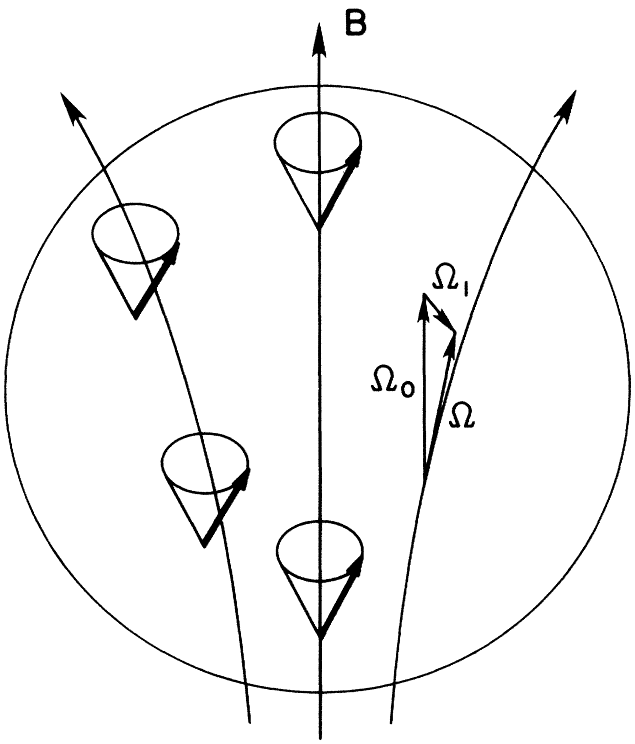

FIG. 3. The slowest spin-relaxation modes in a spherical cell with an inhomogeneous magnetic field $\mathbf{B}(\mathbf{r})$ at low gas pressure. At low pressures the spin polarization remains very nearly aligned along the mean magnetic field. The rotation $\mathbf{\Omega}_0\times\mathbf{\Omega}_1/\Omega_0^2$ of the magnetic field is large compared to the spin rotation $\delta\mathbf{\Phi}$, which is too small to show here. This is the regime (4) of motional narrowing.

(70). In writing down the high-pressure approximation $\delta\mathbf{\Phi}_1\approx\mathbf{z}\times\mathbf{\Omega}_1/\Omega_0$, we assumed that we could neglect $D^2x_{1n}^4\Omega_0^{-2}R^{-4}$ compared to one for all values of n and thereby replace the sum on n in (67) with (A13). This is clearly wrong for $n\geq\pi^{-1}D^{-1/2}\Omega_0^{1/2}R$, and it amounts to keeping terms with unphysically high-spatial frequencies which could be supported in the cell only if D were rigorously zero, which is possible only at infinite pressure. The suppression of these high-spatial-frequency terms in (67) ensures that the radial dependence of $\delta\mathbf{\Phi}_1$ is "rounded off" within a distance $D^{1/2}\Omega_0^{-1/2}$ of the walls. This is a negligibly thin skin compared to R for sufficiently high pressures.

The perturbation theory developed above will be a good approximation provided that the mixing coefficients (47) are always much less than unity. From (54) we see that the numerator of (47) is on the order of Ω_1, and from (40) we see that the denominator of (47) cannot be smaller, in order of magnitude, than D/R^2. Thus, the theory will be valid if $\Omega_1\ll D/R^2$, or equivalently, if $p/p^*\ll\Omega_0/\Omega_1$. At low pressures the theory will be valid as long as it is possible to use the diffusion equation, that is, as long as $\lambda\ll R$, or equivalently, as long as $p/p^*\gg R\Omega_0/v$. These are the limits on the relative pressure given by Eq. (7).

ACKNOWLEDGMENT

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APPENDIX

Several identities involving the spherical Bessel functions $j_1(x)$ were needed to evaluate expressions in the body of this paper. Since there seems to be no convenient reference for these identities, we will sketch their derivation here. We will make use of several standard formulas from the convenient reference work *Handbook of Mathematical Functions*,[14] which we shall refer to as AS (Abramowitz and Stegun). From 10.1.21 of AS we find

$$\frac{l+1}{x}j_l(x)+\frac{d}{dx}j_l(x)=j_{l-1}(x)\ . \tag{A1}$$

From 10.1.22 of AS we find

$$\frac{l}{x}j_l(x)-\frac{d}{dx}j_l(x)=j_{l+1}(x)\ . \tag{A2}$$

From 10.1.23 of AS with $m=1$ and $n=l+1$ we find

$$\frac{d}{dx}x^{l+2}j_{l+1}(x)=x^{l+2}j_l(x)\ . \tag{A3}$$

By use of (A1) and (A2) one can readily show that

$$x^2j_l^2(x)=\frac{d}{dx}\frac{x^3}{2}[j_l^2(x)-j_{l-1}(x)j_{l+1}(x)]\ . \tag{A4}$$

The normalization constant N_{ln} of (37) is determined by

$$\frac{N_{ln}^2}{R^3}\int_0^R r^2dr\,j_l^2\left[\frac{x_{ln}r}{R}\right]=1\ . \tag{A5}$$

Here the numbers x_{ln} are the zeros of the derivatives of the spherical Bessel functions

$$\frac{d}{dx}j_l(x_{ln})=0\quad\text{for } n=1,2,3\ldots\ . \tag{A6}$$

For future reference we note that

$$\begin{aligned}
x_{11}&=2.081\,575\,978\ ,\\
x_{12}&=5.940\,369\,991\ ,\\
x_{13}&=9.205\,840\,143\ ,\\
x_{14}&=12.404\,445\,02\ ,\\
x_{15}&=15.579\,236\,41\ ,\\
x_{1n}&\approx n\pi\quad\text{for } n\gg1\ .
\end{aligned} \tag{A7}$$

Making use of (A4) in evaluating (A5) we readily find that

$$N_{ln}^2=\frac{2}{j_l^2(x_{ln})-j_{l-1}(x_{ln})j_{l+1}(x_{ln})}\ . \tag{A8}$$

Substituting (A1) and (A2) into (A8) we find

$$N_{ln}^2=\frac{2x_{ln}^2}{j_l^2(x_{ln})[x_{ln}^2-l(l+1)]}\ . \tag{A9}$$

For the lowest-order perturbation theory discussed in this paper, we are concerned only with *P*-wave diffusion modes, so we limit our discussion to $l=1$ from now on. In the simple derivations which follow, we will always use (A1) and (A2) to reduce expressions involving $j_l(x_{1n})$ with $l>1$ to expressions involving $j_1(x_{1n})$. The functions $j_1(x_{1n}r/R)$ form a complete set onto which we may expand functions of r on the interval $0\le r\le R$. In particular, we may write

$$r=\sum_n a_n \frac{N_{1n}}{R^{3/2}} j_1\left(\frac{x_{1n}r}{R}\right) , \tag{A10}$$

where the expansion coefficients a_n are determined by

$$a_n=\int_0^R r^3 dr \frac{N_{1n}}{R^{3/2}} j_1\left(\frac{x_{1n}r}{R}\right) . \tag{A11}$$

We may readily evaluate (A11) with the aid of (A3) and (A2) to find

$$a_n=\frac{R^{5/2}N_{1n}}{x_{1n}^2} j_1(x_{1n}) . \tag{A12}$$

Substituting (A12) back into (A10) and making use of (A9) we find

$$\frac{r}{R}=\sum_n \frac{2}{[x_{1n}^2-2]j_1(x_{1n})} j_1\left(\frac{x_{1n}r}{R}\right) . \tag{A13}$$

In like manner we expand r^3 as

$$r^3=\sum_n b_n \frac{N_{1n}}{R^{3/2}} j_1\left(\frac{x_{1n}r}{R}\right) , \tag{A14}$$

where the expansion coefficient b_n is given by

$$b_n=\int_0^R r^5 dr \frac{N_{1n}}{R^{3/2}} j_1\left(\frac{x_{1n}r}{R}\right) . \tag{A15}$$

The integral (A15) can be evaluated by using (A3) to integrate by parts. The expansion coefficient is found to be

$$b_n=\left(\frac{R}{x_{1n}}\right)^6 \frac{N_{1n}}{R^{3/2}} (3x_{1n}^4-10x_{1n}^2) j_1(x_{1n}) . \tag{A16}$$

Substituting (A16) back into (A14) and making use of (A13) we find

$$\frac{3R^2r-r^3}{R^3}=\sum_n \frac{20}{x_{1n}^2[x_{1n}^2-2]j_1(x_{1n})} j_1\left(\frac{x_{1n}r}{R}\right) . \tag{A17}$$

In the special case of $r=R$ we find from (A13)

$$\sum_n \frac{1}{x_{1n}^2-2}=\frac{1}{2} . \tag{A18}$$

In the special case of $r=R$ we find from (A17)

$$\sum_n \frac{1}{x_{1n}^2[x_{1n}^2-2]}=\frac{1}{10} . \tag{A19}$$

We multiply both sides of (A17) by $\int_0^R r^3 dr$ and use (A11) and (A12) to find

$$\sum_n \frac{1}{x_{1n}^4[x_{1n}^2-2]}=\frac{4}{175} . \tag{A20}$$

Finally, we multiply both sides of (A17) by $\int_0^R r^5 dr$ and we use (A15), (A16), and (A19) to find

$$\sum_n \frac{1}{x_{1n}^6[x_{1n}^2-2]}=\frac{83}{15\,750} . \tag{A21}$$

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[1] R. L. Gamblin and T. R. Carver, Phys. Rev. A **138**, 946 (1965).

[2] L. D. Schearer and G. K. Walters, Phys. Rev. A **139**, 1398 (1965).

[3] Z. Wu, W. Happer, and J. M. Daniels, Phys. Rev. Lett. **59**, 1480 (1987).

[4] C. H. Volk, J. G. Mark, and B. Grover, Phys. Rev. A **20**, 2381 (1979).

[5] T. G. Vold, F. J. Raab, B. Heckel, and E. N. Fortson, Phys. Rev. Lett. **52**, 2229 (1984).

[6] George E. Pake, *Paramagnetic Resonance* (Benjamin, New York, 1962).

[7] R. H. Dicke, Phys. Rev. **89**, 472 (1953).

[8] R. L. Mössbauer, Science **137**, 731 (1962).

[9] N. Bloembergen, *Nuclear Magnetic Relaxation* (Benjamin, New York, 1961).

[10] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).

[11] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[12] Z. Wu, S. R. Schaefer, G. D. Cates, and W. Happer, Phys. Rev. A **37**, 1161 (1988).

[13] F. Masnou-Seeuws and M. Bouchiat, J. Phys. (Paris) **28**, 406 (1967).

[14] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. Stegun (Dover, New York, 1965).