Coherent interactions of the polarized nuclear spins of gaseous atoms with the container walls

Z. Wu, S. Schaefer, G. D. Cates, and W. Happer
Department of Physics, Princeton University, Princeton, New Jersey 08544
(Received 24 August 1987)

We have developed a general perturbative theory which describes how coherent wall interactions affect the NMR spectrum of nuclear-spin-polarized gases in containers of any shape. The important practical case of cylindrical containers with quadrupolar wall interactions has been worked out completely. The basic results are quite simple. The frequency shift and damping of the NMR spectrum depend on seven fundamental parameters: \( v \), the mean thermal velocity of spin polarized atoms; \( \lambda \), the mean-free path of spin-polarized atoms in the gas; \( l \), a characteristic linear dimension of the container; \( A \), an asymmetry parameter of the container; \( \langle \theta \rangle \), the mean twist angle experienced by the nuclear polarization of an atom as a result of a collision with the wall; \( \langle \theta^2 \rangle \), the mean-squared twist angle experienced by the nuclear polarization of an atom as a result of a collision with the wall; and \( \beta \), the angle between the symmetry axis of the container and the direction of the quantizing magnetic field.

I. INTRODUCTION

Gaseous samples of nuclear-spin-polarized diamagnetic atoms exhibit a number of unusual phenomena because of their interactions with the container walls. Simpson et al. observed that the relaxation of the nuclear spins of \(^{201}\text{Hg}\) depends on the orientation of the cell with respect to the external magnetic field.\(^2\)\(^3\) Similar effects due to cell orientation were observed for \(^{85}\text{Kr}\) and \(^{131}\text{Xe}\) by Volk et al.\(^4\) No dependence on cell orientation has been observed for \(^{199}\text{Hg}\) or \(^{129}\text{Xe}\), which do not have quadrupole moments. The most obvious explanation for these effects is that the coherent interaction between the nuclear quadrupole moment and the electric field gradient at the cell walls contributes to the relaxation of the nuclear spins. The coherent quadrupole interactions at the cell wall are also believed to be responsible for the beating signal first observed by Simpson\(^2\) in \(^{201}\text{Hg}\) and by Volk et al.\(^4\) for \(^{85}\text{Kr}\) and \(^{131}\text{Xe}\). A typical beat signal, observed in our laboratory with experimental methods similar to those described in Refs. 5 and 6, is shown in Fig. 1(a). The data were obtained from a cylindrical pyrex glass cell, 12.8 mm in diameter and 6.8 mm in height, which contained natural Rb metal, 5 Torr of \(^{131}\text{Xe}\) and 49.4 Torr of \(^{2}\text{N}\). The \(^{131}\text{Xe}\) nuclei were driven by a small magnetic field, oscillating at the Larmor frequency of the nuclei. The signal is proportional to the longitudinal magnetization of \(^{131}\text{Xe}\) nuclei in a fixed, laboratory coordinate system, or to a component of the transverse magnetization in a rotating coordinate system. The Fourier transform of the signal is shown in Fig. 1(b). As indicated in the figure, the three different frequencies which contribute to the transient come from the three \( \Delta m = 1 \) transitions between the nuclear spin sublevels in the rotating coordinate system. The three transition frequencies are split because of the small, ensemble-averaged, quadrupole interaction of the nuclei with the cell walls.

Following a suggestion by Happer, Volk et al. have given a semiquantitative theory of coherent wall interaction.\(^3\) This simple theory, in which the nuclei are assumed to continuously experience the ensemble-averaged electric field gradients of every surface site in the cell, gives a satisfactory description of the dependence of the beat period on the cell orientation in an external magnetic field, but the theory does not address the important question of how fast the atoms must diffuse to effectively sample the entire inner surface of the cell. The purpose of this paper is to present a more complete, perturbative theory of the interaction between the nuclear spins and the cell wall. We apply the theory to the important practical case of a cylindrical cell with quadrupolar wall interactions, and we present simple formulas which allow one to use data like that of Fig. 1 to obtain precise, quantitative information about the mean quadrupole interaction and the mean-squared quadrupole interaction experienced by the nuclei of adsorbed atoms. Important information about the microscopic nature of the surface can be deduced from such data.

II. BASIC THEORY

We consider a gas of diamagnetic atoms, e.g., mercury or noble-gas atoms, contained in a glass cell. The cell is in a static magnetic field \( B \), which is in the \( z \) direction. The nuclear spin of the diamagnetic atom is \( K \). The nuclear spin Hamiltonian of the diamagnetic atoms is

\[
H = H_b + H_w .
\]  

(1)

Here

\[
H_b = g_K \mu_B B K_z = \hbar \Omega K_z
\]  

(2)

is the gas phase or bulk interaction and \( \Omega = g_K \mu_B B / \hbar \) is the Larmor frequency. Although the subsequent discussion assumes a fixed, laboratory coordinate system,
FIG. 1. (a) The transient NMR signal of a gaseous sample of $^{131}$Xe nuclei in a cylindrical Pyrex glass cell. (b) The Fourier transform of the transient signal. The three resonances are peaked at the Bohr frequencies of the three $\Delta m = 1$ transitions between the nuclear-spin sublevels. The unequal energy splittings of the four Zeeman sublevels of the $^{131}$Xe nuclei are due to the ensemble averaged quadrupole interaction, which is proportional to the parameter $\Delta \Omega_0$ of the nuclei with the electric field gradients at the cell walls. The Larmor frequency of the $^{131}$Xe nuclei in the rotating coordinate system is $\Omega$. The quadrupole interactions at the cell walls are also responsible for the damping of the transient signal. See Ref. 6.

Averaging over all possible wall interaction histories, we get

$$\rho_f = \langle \rho(\tau) \rangle = \mathcal{E} \rho_i = (1 + e^{(1)} + e^{(2)} + \cdots) \rho_i ,$$

where $\rho_f$ is the final density matrix after the collision and $\rho_i = \rho(0)$ is the density matrix before the collision. We use the notation $\langle \rho(\tau) \rangle$ to indicate an average over the adsorption time $\tau$ on the wall and also over the microscopic spin interaction history of an atom while it is adsorbed on the wall. The terms in the series expansion of the operator $\mathcal{E}$ of (7) follow from (6) and are completely analogous considerations hold for the rotating coordinate systems used to describe situations like those of Fig. 1, where an oscillating magnetic field is used for experimental convenience.

The wall interaction $H_w$ can be written as

$$H_w = g_k \mu_B B_w \cdot \mathbf{K} + \frac{1}{2} \sum_{\mathbf{i},\mathbf{j}} Q_{ij} \frac{\partial^2 V_w}{\partial x_i \partial x_j} + \cdots .$$

Here $B_w$ is the microscopic local field experienced by the nucleus of the diamagnetic atom while the atom is adsorbed on the surface. The nuclear electric quadrupole moment tensor $Q_{ij}$ couples to the microscopic electric field gradient tensor $\partial^2 V_w / \partial x_i \partial x_j$. The magnetic field is produced by free electrons in dangling bonds, by unpaired conduction band electrons near the Fermi level of metal surfaces, by the nuclear magnetic moments of atoms in the wall, etc. The electric field gradients are produced by polar groups near the surface, e.g., $- \text{OH}$, or $- \text{ONa}$, by conduction-band electrons at metal surfaces, etc. The field gradient at the nucleus of the diamagnetic atom may be strongly enhanced because of Sternheimer shielding or antishielding by the surrounding electrons. These microscopic fields will fluctuate in time due to the relative motions of the adsorbed atom and the atoms of the surface.

A. The normal gradient operator

The evolution of the density matrix of the noble-gas atoms in the bulk is given by

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

where $D$ is the diffusion coefficient. We neglect gas-phase spin relaxation. The evolution of the density matrix while an atom is adsorbed on the wall is given by

$$\frac{\partial \rho}{\partial t} = \frac{1}{i \hbar} [H_w(t) + H_b(t), \rho] .$$

We assume that $H_b$ is small enough to be neglected during the short adsorption time $\tau$ on the wall, and that $H_w \tau$ is small enough that we may solve (5) by iteration to obtain

$$\rho(t) = \rho(0) + \frac{1}{i \hbar} \int_0^t dt [H_w(t), \rho(0)] + \frac{1}{(i \hbar)^2} \int_0^t dt \int_0^t dt' [H_w(t), [H_w(t - t'), \rho(0)]] \cdots .$$

$$e^{(1)} \rho_i = \frac{1}{i \hbar} \left( \int_0^t dt [H_w(t), \rho_i] \right) ,$$

$$e^{(2)} \rho_i = \frac{1}{(i \hbar)^2} \left( \int_0^t dt \int_0^t dt' [H_w(t), [H_w(t'), \rho_i]] \right).$$

Let $n$ be the normal to the surface of the cell wall, pointing out of the cell. Let $j_+$ be the current of the polarized noble gas atoms into the wall and $j_-$ the current out of the wall. From kinetic theory we have

$$j_+ = \frac{N_v}{4} \rho_0 \frac{ND}{2} \frac{\partial \rho}{\partial n} ,$$

where $v$ is the velocity of the wall.
where $N$ is the density of the noble gas atoms, $v$ is the mean atomic velocity, and $\partial / \partial n = n \cdot \nabla$. We assume that every atom which hits the wall returns as an evolved atom. Then the return current $j_-$ of the polarized atoms is

$$j_- = \varepsilon j_+ = \frac{1}{2} N v \varepsilon \rho - \frac{1}{2} N D \frac{\partial}{\partial n} \varepsilon \rho .$$

(11)

Assume that the net current to the wall is given by the usual law of diffusion for atoms in the bulk:

$$j_+ - j_- = - N D \frac{\partial \rho}{\partial n} .$$

(12)

Substituting (10) and (11) into (12) we get

$$\frac{N v}{4} (\rho - \varepsilon \rho) = - N D \frac{\partial}{\partial n} (\rho + \varepsilon \rho) .$$

(13)

From kinetic theory we have

$$D = \frac{1}{2} v \lambda ,$$

(14)

where $\lambda$ is the mean-free path, and $v = (8kT / \pi m)^{1/2}$ is the mean thermal velocity of a polarized atom of mass $m$. Substituting (14) and (7) into (13) we get

$$(2 + \varepsilon^{(1)} + \varepsilon^{(2)} + \cdots) \frac{\partial}{\partial n} \rho = \frac{3}{2\lambda} \varepsilon^{(1)} + \varepsilon^{(2)} + \cdots \rho .$$

(15)

Inverting (15) we find

$$\frac{\partial}{\partial n} \rho = - \mu \rho ,$$

(16)

where the normal gradient operator $\mu$ is given to second order in $H_0$ by

$$\mu \rho = - \frac{3}{4\lambda} \varepsilon^{(1)} + \varepsilon^{(2)} - \frac{1}{2} \varepsilon^{(1)} \varepsilon^{(1)} + \cdots \rho .$$

(17)

Boundary conditions formally similar to (16) were first used by Maxwell to discuss the phenomenon of "viscous slip" discovered by Kundt and Warburg in 1875. Masnou-Seeuws and Bouchiat used a boundary condition like (16) to discuss wall induced spin relaxation. In this paper, however, the normal gradient coefficient $\mu$ is the operator defined by (17) and not a simple scalar as was assumed in the earlier work. This generalization of $\mu$ is essential for the treatment of coherent wall interactions.

B. The eigenpolarizations $P_i$ and their amplitudes $f_i$

We see by inspection that the solution to the bulk Schrödinger equation is

$$H_0 \left| m \right> = \hbar \Omega m \left| m \right> ,$$

(18)

where $m$ is the azimuthal quantum number of the eigenvector $\left| m \right>$, i.e.,

$$K_z \left| m \right> = m \left| m \right> .$$

(19)

We use the eigenvectors of (18) to construct basis polarizations

$$P_i = P_{mn} = \left| m \right> \left< n \right| .$$

(20)

The basis polarizations are orthonormal since

$$\text{Tr}(P_i^* P_j) = \delta_{ij} .$$

(21)

We note also that the basis polarizations are eigenpolarizations of the bulk Hamiltonian in the sense that

$$[H_0, P_i] = \hbar \Omega P_i. P_i = \hbar \Omega (m-n) P_{mn} .$$

(22)

We expand the density matrix $\rho$ in terms of the eigenpolarizations

$$\rho = \sum_i P_i f_i .$$

(23)

We seek an exponentially decaying solution for $\rho$, i.e.,

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

(24)

Then (4) becomes

$$\sum_i (D \nabla^2 + \gamma - i \Omega_i) P_i f_i = 0 .$$

(25)

Since the $P_i$ are orthonormal, (25) is equivalent to a set of equations

$$(D \nabla^2 + \gamma - i \Omega_i) f_i = 0 ,$$

(26)

with $i = 0, 1, 2, \ldots$, which must be solved subject to the boundary condition (16).

C. Nonperturbative solutions

One can find nonperturbative solutions for simple cell geometries and simple normal gradient operators. Consider a cell bounded by two infinite parallel planes located at $z = \pm h / 2$. Suppose that some bulk eigenpolarization $P_i$ is also an eigenpolarization of $\mu$. Then (17) can be written as

$$\mu P = \frac{3 \alpha e^{i\delta}}{4\lambda} P ,$$

(27)

where we have expressed the eigenvalue in terms of the mean free path $\lambda$ of a polarized atom in the cell, and a complex accommodation coefficient $\alpha \exp i \delta$ with a real, positive amplitude $\alpha$ and a real phase angle $\delta$. We will assume that $\alpha \ll 1$ for situations of practical interest. The amplitude $f$ of $P$ can be chosen to be a function of $z$ alone so that (26) becomes

$$\left[ D \frac{d^2}{dz^2} + \gamma - i \Omega \right] f = 0 .$$

(28)

This has the symmetric solution

$$f = \cos(k z) ,$$

(29)

and the boundary condition (16) becomes

$$w \tan w = e^{i\delta} p / p^* ,$$

(30)

where

$$w = kh / 2 ,$$

(31)

and the characteristic pressure $p^*$ is defined by

$$p / p^* = 3h \alpha / 8 \lambda .$$

(32)
Substituting (29) into (28) we find
\[ \gamma = i\Omega + \frac{\alpha v}{2h}(w^2p^*/p) . \]  
(33)

We will be interested in the solution \( w \) of (30) which approaches zero as \( p/p^* \) approaches zero. To lowest order in \( p/p^* \) we find
\[ w^2 = e^{i\theta}p/p^* - \frac{1}{2}(e^{i\theta}p/p^*)^2 + \cdots . \]  
(34)

Substituting (34) into (33) we find for the uniform mode
\[ \gamma = i\Omega + \frac{\alpha v}{2h} \left[ \cos\delta - \frac{p}{3p^*}\cos(2\delta) \right] 
+ i \left[ \sin\delta - \frac{p}{3p^*}\sin(2\delta) \right] + \cdots . \]  
(35)

We note that the damping rate \( \gamma \) is expressed in terms of the characteristic damping rate \( \alpha v/2h \) of a low-pressure cell with a real accommodation coefficient \( \alpha \).

The damping rate \( \gamma \) obtained from (33) by numerically solving (30) for \( \delta = 0 \) is shown in Fig. 2(a). This is basically the same as Fig. 4 of Masson-Seeuw and Bouchiat, who thoroughly discussed the situation of wall relaxation with normal operating conditions. There is no frequency shift, and the relaxation rate decreases monotonically from the low-pressure value to zero as the gas pressure becomes high enough to hinder the diffusion of polarized atoms to the cell walls. Of course any bulk-phase relaxation caused by high-pressure gas has been neglected in Fig. 2(a). In Fig. 2(b) we show the relaxation and frequency shift for a cell in which \( \tan\delta = 10 \). The complex equation (30) was solved numerically to obtain values of \( w^2 \) for various values of \( p/p^* \). The pressure dependence is quite different from that of Fig. 2(a). The damping rate at first increases with increasing pressure before reaching a maximum, and decreases as the pressure becomes high enough to hinder the diffusion of the atoms to the cell walls. The frequency shift due to the coherent wall interaction decreases monotonically with pressure. The maximum damping, which is a kind of inhomogeneous broadening, occurs when the frequency shift has dropped by about a factor of 2. Also shown in Fig. 2(b) are the linear approximations (35) to the complex damping rate \( \gamma \). The linear approximations are seen to be quite accurate for low gas pressures.

In the next section we will show how perturbation theory can be used to obtain linear approximations like those of (35) for more realistic cell geometries and for more complicated and realistic normal gradient operators \( \mu \), where the nonperturbative methods sketched above do not work. These low-pressure, perturbative approximations are adequate for analyzing all experiments on coherent wall interactions which have been carried out so far.

D. Perturbation theory

As mentioned in Sec. I, the wall interaction for the noble-gas nuclear spin is generally very weak, i.e., we can solve for the effects due to wall collisions by regarding \( H_w \) as a small perturbation of a cell with no wall relaxation at all. Following the standard procedures of perturbation theory, we introduce an expansion parameter \( \eta \) which we will eventually set equal to 1, and write \( H_w \) as \( \eta H_w \).

We expand \( \gamma \) and \( f_i \) as a power series of \( \eta \),
\[ \gamma = \gamma^{(0)} + \eta\gamma^{(1)} + \eta^2\gamma^{(2)} + \cdots , \]  
(36)

\[ f_i = f_i^{(0)} + \eta f_i^{(1)} + \eta^2f_i^{(2)} + \cdots . \]  
(37)

Substituting (36) and (37) into (26) and equating the coefficients of \( \eta^l (l = 0,1,2, \ldots) \), we get
\[ (D\nabla^2 - i\Omega_{j} + \gamma^{(0)}j_{i}^{(0)})f_{i}^{(0)} = 0 , \]  
(38)

\[ (D\nabla^2 - i\Omega_{j} + \gamma^{(0)}j_{i}^{(1)} + \gamma^{(1)}j_{i}^{(0)})f_{i}^{(1)} = 0 , \]  
(39)

\[ (D\nabla^2 - i\Omega_{j} + \gamma^{(0)}j_{i}^{(2)} + \gamma^{(1)}j_{i}^{(1)} + \gamma^{(2)}j_{i}^{(0)})f_{i}^{(2)} = 0 . \]  
(40)

![Fig. 2.](image)

(a) Nonperturbative predicted damping rate \( \gamma' \) of the free precession NMR signal for a parallel-plate cell with a real accommodation coefficient \( \alpha \) or a phase angle of \( \delta = 0 \). The walls cause no frequency shift in this case. The plate separation is \( h \) and the mean thermal velocity of the spin-polarized atoms is \( v \). The characteristic pressure \( p^* \) is defined in (32). The gas is assumed to hinder the diffusion of spin-polarized atoms to the walls but to cause no bulk-phase relaxation. (b) Nonperturbative predicted damping rate \( \gamma' \) and frequency shift, \( \gamma'' - \Omega \), for a parallel-plate cell with a complex accommodation coefficient and a phase angle given by \( \tan\delta = 10 \). In contrast to the situation in (a), increasing the gas pressure causes the damping rate to increase. The low-pressure, straight-line approximations to the frequency shift and damping rates are shown with the dashed line and can be calculated for any cell geometry or wall interaction by perturbation theory.
To solve (38)–(40) we need to know the boundary conditions which follow from (16) for \( f_i^{(0)}, f_i^{(1)}, \ldots \) at the cell surface. We define the matrix element \( \mu_{ij} \) of the normal gradient operator \( \mu \) by

\[
\mu P_j = \sum_i P_i \mu_{ij} .
\]  

(41)

Using (21) and (41) we find

\[
\mu_{ij} = \text{Tr} (P^+ \mu P_j) = \eta \mu_{ij}^{(1)} + \eta^2 \mu_{ij}^{(2)} + \cdots ,
\]

(42)

where from (17) we find

\[
\mu_{ij}^{(1)} = -\frac{3}{4\eta} \epsilon_{ij}^{(1)} ,
\]

(43)

\[
\mu_{ij}^{(2)} = -\frac{3}{4\eta} \left[ \epsilon_{ij}^{(2)} - \frac{1}{k} \sum_k \epsilon_{ik}^{(1)} \epsilon_{kj}^{(1)} \right] ,
\]

(44)

and from (8) and (9)

\[
\epsilon_{ij}^{(1)} = \text{Tr} \left[ P^+ \frac{1}{i\hbar} \int_0^T \text{d} t \{ H_{\omega}(t), P_j \} \right] ,
\]

(45)

\[
\epsilon_{ij}^{(2)} = \text{Tr} \left[ P^+ \frac{1}{i\hbar} \int_0^T \int_0^T \text{d} t \text{d} t' \{ H_{\omega}(t), [H_{\omega}(t'), P_j] \} \right] .
\]

(46)

One can verify from (42)–(46) that

\[
\mu_{ij}^{(1)*} = -\mu_{ji}^{(1)} ,
\]

(47)

and for the usual case that \( \langle [H_{\omega}(t), H_{\omega}(t')] \rangle = 0 , \)

\[
\mu_{ij}^{(2)*} = \mu_{ji}^{(2)} .
\]

(48)

That is, \( \mu^{(1)} \) is anti-Hermitian and \( \mu^{(2)} \) is Hermitian. The matrix element \( \mu_{ij} \) is a function of position on the cell wall.

Substituting (23), (37), (41), and (42) into (16) and equating the coefficients of each power of \( \eta \), we get

\[
\frac{\partial f_i^{(0)}}{\partial n} = 0 ,
\]

(49)

\[
\frac{\partial f_i^{(1)}}{\partial n} = -\sum_j \mu_{ij}^{(1)} f_j^{(0)} ,
\]

(50)

\[
\frac{\partial f_i^{(2)}}{\partial n} = -\sum_j (\mu_{ij}^{(1)} f_j^{(1)} + \mu_{ij}^{(2)} f_j^{(0)}) .
\]

(51)

We may write the zeroth-order diffusion equation (38) as

\[
(\nabla^2 + k^2) f_i^{(0)} = 0 ,
\]

(52)

where

\[
D k^2 = \gamma^{(0)} - i \Omega_i .
\]

(53)

Given the boundary condition (49), Eq. (52) has solutions only for certain real, non-negative eigenvalues \( k^2 \), which we denote by \( k_\alpha^2 \) with \( \alpha = 0, 1, 2, \ldots \) and with the magnitude of \( k_\alpha^2 \) increasing with \( \alpha \). We denote a solution of (52) corresponding to eigenvalue \( k_\alpha^2 \) by \( \phi_\alpha \), i.e.,

\[
(\nabla^2 + k_\alpha^2) \phi_\alpha = 0 .
\]

(54)

Equations (52) and (49) ensure that the diffusion modes \( \phi_\alpha \) can be chosen to be orthonormal, i.e.,

\[
\int_V dV \phi_\alpha^* \phi_\beta = \delta_{\alpha\beta} ,
\]

(55)

where the integral extends over the entire cell volume \( V \).

We will be particularly interested in the uniform mode, which is given for any cell of volume \( V \) by

\[
\phi_0 = \frac{1}{\sqrt{V}} .
\]

(56)

This mode has zero spatial frequency,

\[
k_0 = 0 .
\]

(57)

The polarization of interest to us in cells with weakly relaxing 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 Bouchiat⁸ refer to this situation as that of "orientation non confinée."

We will also be interested in cells with sufficiently low gas pressures and magnetic fields that for all \( \alpha \neq 0 \)

\[
D k_\alpha^2 >> \Omega_k .
\]

(58)

Equation (58) implies that the polarized atoms diffuse easily throughout the cell in one Larmor period of the polarization.

### E. Diffusion modes of a cylinder

For practical applications we will be interested in the diffusion modes of a circular cylinder of diameter \( d \) and height \( h \) with its base centered in the \( (x,y) \) plane of a Cartesian coordinate system as sketched in Fig. 3. Then the spatial modes defined by (54) are separable and can be written as

\[
\phi_\alpha = Z_\alpha(z) R_\alpha(r) \Phi_\alpha(\varphi) ,
\]

(59)

FIG. 3. The cylindrical container after it has been rotated through the Euler angles \( \alpha \) and \( \beta \). A point \( P \) on the side of the cylinder is specified by its height \( z \) above the base and by an azimuthal angle \( \varphi \). The outwardly directed normal unit vector at the point \( P \) is \( n \).
where \( \alpha \) represents the set of quantum numbers, \( a, l, n, \) and \( \Lambda \). The azimuthal function is

\[
\Phi_{\alpha} = \frac{e^{i \lambda \hat{\alpha}}}{\sqrt{2 \pi}},
\]

where \( \Lambda = \pm l \). The axial function is

\[
Z_{\alpha}(z) = \left( \frac{2}{h} \right)^{1/2} \cos \frac{a \pi x}{h},
\]

where \( a = 1, 2, 3, \ldots \). The uniform axial function is

\[
Z_0(z) = 1/\sqrt{h}.
\]

The radial function is a Bessel function\(^9\)

\[
R_\alpha(r) = \frac{N_{\alpha}}{d} J_l \left( \frac{2x_{\alpha}r}{d} \right), \tag{63}
\]

where \( l = 0, 1, 2, \ldots \), \( n = 1, 2, 3, \ldots \). The number \( x_{\alpha n} \) is the \( n \)-th solution, counting upward from the smallest \( x \), of

\[
d x J_l(x) = 0. \tag{64}
\]

For example, \( x_{01} = 3.83, x_{02} = 7.02, x_{11} = 1.84 \), etc. The uniform radial function is

\[
R_{00} = 2\sqrt{2}/d. \tag{65}
\]

The requirement that \( \int_0^d R_\alpha^2 r \, dr = 1 \) determines the normalization constant \( N_\alpha \), and for \( \alpha \neq 0 \) one can show that

\[
N_{\alpha}^2 = \frac{8}{J_1^2(x_{\alpha}) - J_{\alpha - 1}(x_{\alpha}) J_{\alpha + 1}(x_{\alpha})}. \tag{66}
\]

The spatial frequency of the function (59) is given by

\[
k_{\alpha}^2 = \left( \frac{a \pi}{h} \right)^2 + \left( \frac{2x_{\alpha}}{d} \right)^2, \tag{67}
\]

with \( a = 0 \) if the axial mode is uniform and \( x_{00} = 0 \) if the radial mode is uniform. Analogous expressions for \( \phi_\alpha \) and \( k_\alpha \) can be found for any other cell geometry.

Thus for nonrelaxing cell walls there is a solution to (24) of the form

\[
f^{(0)}_{\alpha;ag} = \phi_\alpha \delta_{\alpha g}, \tag{68}
\]

for every combination of a diffusion index \( \alpha \) and a polarization index \( g \). The corresponding decay rates are given by (53) as

\[
\gamma^{(0)}_{\alpha g} = D k_{\alpha}^2 + i \Omega_g. \tag{69}
\]

Each unperturbed state of polarized atoms in the cell is labeled by a diffusion quantum number \( \alpha \) and a polarization quantum number \( g \).

**F. Expansion of \( \gamma \) in powers of \( H_w \) and the gas pressure \( p \)**

We will derive real and imaginary corrections to the zeroth-order damping rate (69) which are linear in the gas pressure \( p \) and are of sufficiently high order in \( H_w \) to be nonvanishing. In all experiments on coherent wall interactions performed to date the dependence of the results on the gas pressure is so slight and the wall interactions are so weak that these linear corrections should be completely adequate to analyze the experimental results. Assuming that \( \lambda \propto p^{-1} \), we note for future reference that from (42) we have

\[
\mu^{(n)} \propto \rho. \tag{70}
\]

From (14) we have

\[
D \propto p^{-1}, \tag{71}
\]

and from (69) and for the condition (58) of rapid diffusion we have for \( k_\alpha > 0 \)

\[
\gamma^{(0)}_{\alpha g} \propto p^{-1}. \tag{72}
\]

Let us consider the first-order correction to the zeroth-order solution (68). Substituting (68) and (69) into (39) we find

\[
[D (\nabla^2 + k_\alpha^2) + i (\Omega_{\alpha} - \Omega_{\alpha})] f^{(1)}_{\alpha;ag} + \gamma^{(0)}_{\alpha g} \delta_{\alpha g} = 0. \tag{73}
\]

We may regard (73) as an inhomogeneous wave equation, which together with the boundary condition (50) determines \( f^{(1)}_{\alpha;ag} \). In the spirit of perturbation theory we multiply (73) by the spatial mode function \( \phi_{\alpha g} \) and integrate over the cell volume to find, after integration by parts and the use of boundary condition (50),

\[
\gamma^{(1)}_{\alpha g} \delta_{\alpha g} = \frac{DS}{V} \langle \beta | \mu^{(1)}_{\alpha g} | \alpha \rangle + (\gamma^{(0)}_{\beta g} - \gamma^{(0)}_{\alpha g}) a^{(1)}_{\beta;ag}. \tag{74}
\]

The surface matrix element is defined by

\[
\langle \beta | \mu^{(n)}_{\alpha g} | \alpha \rangle = V \int_S dS \phi_{\beta g}^{(n)} \phi_{\alpha g}, \tag{75}
\]

and the integral extends over all elements of the cell surface area \( S \). The \( n \)-th order mixing coefficient is

\[
a^{(n)}_{\beta;ag} = \int_V dV \phi_{\beta g}^{(n)}, \tag{76}
\]

If we set \( \beta = \alpha \) and \( i = g \) in (74) we find the first-order correction to the relaxation rate to be

\[
\gamma^{(1)}_{\alpha g} = \frac{DS}{V} \langle \alpha | \mu^{(1)}_{gg} | \alpha \rangle. \tag{77}
\]

For the important case of uniform polarization \( (\alpha = 0) \) we find from (77), (75), and (56)

\[
\gamma^{(1)}_{0 g} = \frac{D}{V} \int_S dS \phi^{(1)}_{gg}. \tag{78}
\]

In view of (70) and (71) we see that (78) is independent of gas pressure. Since \( \mu^{(1)} \) is anti-Hermitian, (78) implies that \( \gamma^{(1)}_{0 g} \) is a purely imaginary number, i.e., to first order \( H_w \) causes a shift in the magnetic resonance frequencies of the diamagnetic atom. The frequency shift (78) can also be described in an elementary way by adding to the bulk Hamiltonian \( H_b \) an effective perturbation

\[
H_{\text{ef}} = \frac{uS^2}{4V} \int_S dS' \int_0^t \frac{dt}{r} H_w, \tag{79}
\]

where

\[
u = \text{const}.
\]
which is the mean value of the wall interaction $H_w$ for a spatially uniform distribution of atoms in the cell. The more systematic, perturbative analysis, of which (78) is a part, is needed to account for the interplay of diffusion in the bulk and wall interactions, which lead to higher-order contributions to the frequency shift and damping of the spin-polarized atoms.

Equation (74) determines the mixing coefficient for nondegenerate states, i.e., states with $\gamma_{\beta_i}=\gamma_{\alpha g}$. We find
\[
a_{\beta_i;\alpha g}^{(1)} = \frac{DS}{\nu} \langle \alpha | \mu_{\beta i}^{(1)} | \alpha \rangle . \tag{80}
\]
The mixing parameters (80) need to be much less than unity to ensure rapid convergence of the perturbation formulas discussed here. For the experiment illustrated in Fig. 1, the mixing parameter is on the order of $10^{-2}$. For degenerate states (74) implies that
\[
\langle \beta | \mu_{\beta i}^{(1)} | \alpha \rangle = 0 \quad \text{if} \quad \gamma_{\beta_i}^{(0)} = \gamma_{\alpha g}^{(0)} \quad \text{and} \quad (\beta_i) \neq (\alpha g). \tag{81}
\]
Degeneracies such as those envisaged in (81) naturally occur for states with the same diffusion mode, $\beta = \alpha$, but with different polarization modes, $i \neq g$, with the same Larmor frequencies $\Omega_i = \Omega_g$. Orthogonal linear combinations of the degenerate polarization states can always be chosen to ensure the validity of (81). The mixing coefficients $a_{\beta_i;\alpha g}^{(1)}$ for degenerate states with $\gamma_{\beta_i}^{(0)} = \gamma_{\alpha g}^{(0)}$, and the self-mixing coefficient $a_{\alpha g;\alpha g}^{(1)}$ are not determined by (74).

We now consider the second-order corrections. Substituting (68) into (40) we find
\[
[D \left( \nabla^2 + k_0^2 \right) + i (\Omega_\alpha - \Omega_\beta)] f_{i;\alpha g}^{(2)} = \gamma_{\alpha g}^{(1)} f_{i;\alpha g}^{(1)} + \gamma_{\alpha g}^{(0)} \phi_\alpha \delta_{i} = 0 . \tag{82}
\]
We may regard (82) as an inhomogeneous wave equation which together with the boundary condition (51) determines $f_{i;\alpha g}^{(2)}$. We multiply (82) by $\phi_\beta^{*}$ and integrate over the cell volume to find, after integrating by parts and using boundary condition (51)
\[
\gamma_{\alpha g}^{(2)} \phi_\alpha \phi_\beta = \frac{DS}{\nu} \langle \beta | \mu_{\beta i}^{(1)} | \alpha \rangle + (\gamma_{\beta_i}^{(0)} - \gamma_{\alpha g}^{(0)}) a_{\beta_i;\alpha g}^{(1)}
\]
\[
-\gamma_{\alpha g}^{(1)} a_{\beta_i;\alpha g}^{(1)} + \frac{DS}{\nu} \sum_{k} \langle \beta | \mu_{\beta i}^{(1)} | \kappa \rangle a_{\alpha k;\alpha g}^{(1)} . \tag{83}
\]
If we set $\beta = \alpha$ and $i = g$ in (83) we find the second-order damping rate to be
\[
\gamma_{\alpha g}^{(2)} = \frac{DS}{\nu} \langle \alpha | \mu_{\beta g}^{(1)} | \alpha \rangle - \frac{DS}{\nu} \left( \sum_{k} \langle \alpha | \mu_{\beta g}^{(1)} | \kappa \rangle \langle \kappa | \mu_{\beta g}^{(1)} | \alpha \rangle \right)
\]
\[
\times \left( \frac{DS}{\nu} \sum_{k} \langle \alpha | \mu_{\beta g}^{(1)} | \kappa \rangle \langle \kappa | \mu_{\beta g}^{(1)} | \alpha \rangle \right) , \tag{84}
\]
where the prime means that terms with $\gamma_{\alpha g}^{(0)} = \gamma_{\alpha g}^{(0)}$ are to be excluded from the sum. In view of (70)–(72) we see that the first term in (84) is real and independent of the gas pressure. The second term in (84) contains contributions with $\kappa \neq \alpha$ which, under the conditions (58) of extreme motional narrowing, are very nearly real and proportional to the gas pressure, and a pressure-independent, imaginary contribution from states with $\kappa = \alpha$.

For degenerate states with $\gamma_{\beta_i}^{(0)} = \gamma_{\alpha g}^{(0)}$, (83) can be used to determine the first-order mixing coefficients, which are
\[
a_{\beta_i;\alpha g}^{(1)} = -\frac{DS}{\nu} \left\{ \frac{1}{\gamma_{\beta_i}^{(1)} - \gamma_{\alpha g}^{(1)}} \right\} \left[ \sum_{k} \langle \beta | \mu_{\beta i}^{(1)} | \kappa \rangle \frac{DS}{\nu} \sum_{k} \langle \kappa | \mu_{\beta i}^{(1)} | \alpha \rangle \right] . \tag{85}
\]
This is analogous to (80). If the degeneracy is not lifted to first order and $\gamma_{\beta_i}^{(1)} = \gamma_{\alpha g}^{(1)}$, it is necessary to choose linear combinations of the degenerate polarizations to ensure that the effective second-order matrix element between degenerate states, i.e., the quantity in square brackets in (85), is zero.

One can also use (83) to determine the mixing coefficients $a_{\beta_i;\alpha g}^{(2)}$ for nondegenerate states for which $\gamma_{\beta_i}^{(0)} \neq \gamma_{\alpha g}^{(0)}$. These coefficients can be used to calculate higher-order corrections to the damping rates in a way similar to that outlined above. The most important higher-order terms, which are proportional to the pressure and are therefore needed to calculate the linear approximations of Fig. 2, are
\[
y^{(2,4)} = -\left\{ \frac{DS}{\nu} \right\} \left[ \sum_{k} \langle \alpha | \mu_{\beta i}^{(1)} | \kappa \rangle \langle \kappa | \mu_{\beta i}^{(1)} | \alpha \rangle + \langle \alpha | \mu_{\beta i}^{(2)} | \kappa \rangle \langle \kappa | \mu_{\beta i}^{(2)} | \alpha \rangle + \langle \alpha | \mu_{\beta i}^{(2)} | \kappa \rangle \langle \kappa | \mu_{\beta i}^{(2)} | \alpha \rangle \right] . \tag{86}
\]
In summary, the lowest-order corrections to $\gamma_{\alpha g}^{(0)}$ which are linear in the gas pressure are given by the sum of (77), (84), and (86), which we write for future reference as
\[
\Delta \gamma_{\alpha g} = \frac{DS}{\nu} \langle \alpha | \mu_{\beta g} | \alpha \rangle - \frac{DS}{\nu} \left( \sum_{k} \langle \alpha | \mu_{\beta g} | \kappa \rangle \langle \kappa | \mu_{\beta g} | \alpha \rangle \right)
\]
\[
-\frac{DS}{\nu} \langle \alpha | \mu_{\beta g} | \alpha \rangle + \frac{DS}{\nu} \sum_{j} \langle \alpha | \mu_{\beta g} | \Delta f_{j;\alpha g} \rangle , \tag{87}
\]
where to this order of approximation we set
\[ \mu = \mu^{(1)} + \mu^{(2)} , \]
and we represent the admixture of nondegenerate states into the diffusion mode amplitude by
\[ \Delta f_{f_{ag}} = -\frac{DS}{V} \sum_{k} \phi_{k} (\kappa | \mu_{ag} | \alpha) \gamma_{k}^{(0)} \gamma_{ag}^{(0)} . \]
We note that the expressions for \( \gamma^{(1)} \) and \( \gamma^{(2)} \) as given by (77) and (84), respectively, are analogous to the first- and second-order corrections to the energy of a quantum mechanical system in perturbation theory.

### III. APPLICATION TO QUADRUPOLE WALL INTERACTIONS

Now we will apply the theory developed above to a situation of practical importance, the damping and frequency shift due to the electric quadrupole interaction between the cell wall and the nuclei of diamagnetic atoms with nuclear spin \( K \geq 1 \). We will discuss the spatially uniform polarization modes with quantum numbers \((\alpha, \gamma) = (0, g)\).

The wall interaction can be written as
\[ H_{w} = \frac{1}{2} \sum_{ij} Q_{ij} \frac{\partial^{2} V_{w}}{\partial x_{i} \partial x_{j}} , \]
where \( K \) is the angular momentum quantum number, \( e \) is the (positive) elementary charge, and \( Q \) (an area) is the nuclear quadrupole moment. While the diamagnetic atom is adsorbed on the cell wall, the atomic nucleus will experience an electric field gradient \( \frac{\partial^{2} V_{w}}{\partial x_{i} \partial x_{j}} \). The field gradient will fluctuate in time because of the vibrational and hopping motion of the adsorbed atom and because of the motion of the atomic constituents of the surface.

To simplify subsequent algebra, we will find it convenient to express \( H_{w} \) in terms of irreducible basis tensors, defined in terms of the uncoupled polarizations (20) by
\[ T_{JM} = \left( \frac{2J + 1}{2K + 1} \right)^{1/2} \sum_{m} | m + M \rangle \langle m | C(KJK; m, M) , \]
with analogous formulas for the other irreducible spherical tensor components of the nuclear quadrupole moment operator. Then the wall interaction (90) becomes
\[ H_{w} = H_{2} T_{2} = \sum_{M} (-1)^{M} H_{2, -M} T_{2M} , \]
where the multipole coefficient \( H_{20} \) of (94) is
\[ H_{20} = \frac{\hbar \delta_{zz}}{4 \pi K (K + 1)(2K + 1)(2K + 3)} \left( \frac{2K - 1}{4(2K - 1)} \right)^{1/2} . \]
The corresponding formulas for the other multipole coefficients are given by analogous formulas. The twist-rate tensor \( \delta_{ij} \) is defined by
\[ \delta_{ij} = \frac{3eQ}{4K \hbar} \left( \frac{\partial^{2} V_{w}}{\partial x_{i} \partial x_{j}} - \frac{\delta_{ij}}{3} \nabla^{2} V_{w} \right) . \]

#### A. Evaluation of \( \mu^{(1)} \)

By symmetry we can be sure that the ensemble averaged value of the wall interaction has axial symmetry about the direction \( \mathbf{n} \) of the outwardly directed unit vector, normal to the macroscopic surface, which we specify with the polar angles \( \psi \) and \( \chi \), i.e.,
\[ \mathbf{n} = x \sin \psi \cos \chi + y \sin \psi \sin \chi + z \cos \psi , \]
where \( x, y, \) and \( z \) are unit vectors along the coordinate axes. Thus the mean value of the wall interaction can be written as
\[ \left\langle \int_{0}^{t} dt H_{w} \right\rangle = \left( \frac{\hbar}{2K - 1} \right) \left( \frac{(K - 1)^{3}}{3} \right) \]
\[ = \left( \frac{\hbar}{15} \right) \left( \frac{4\pi K (K + 1)(2K + 1)(2K + 3)}{(2K - 1)} \right)^{1/2} \times \sum_{M} T_{2M} Y_{2M}^{*}(\psi, \chi) . \]
Here \( Y_{2M} \) denotes a spherical harmonic, and
\[ \left\langle \theta \right\rangle = \left( \int_{0}^{t} dt \delta_{\theta} \right) , \]
where \( \delta_{\theta} \) is given by (96). Substituting (98) into (45) and (43) we readily find
\[ \mu_{m'n'; mn}^{(1)} = \left( \frac{\pi K (K + 1)(2K + 3)}{20(2K - 1)} \right)^{1/2} \]
\[ \times \left\{ \delta_{nn'} Y_{2m'}^{*}(-\psi, \chi) C(K2K; m, m' - m) \right. \]
\[ \left. - \delta_{mm'} Y_{2n'}^{*}(-\psi, \chi) C(K2K; n', n - n') \right\} . \]

Consider a point of the side of a vertical cylinder. Let the polar angles of the surface normal \( \mathbf{n}_{0} \) of the point be \( \chi_{0} = \pi/2 \). If the cylinder is rotated through the Euler angles \((\alpha, \beta, 0)\) as sketched in Fig. 3(b), the polar
angles of the rotated surface normal \( n \) will be \( \psi \) and \( \chi \). Because of the tensor properties of the spherical harmonics we can use a Wigner \( D \) function\(^{(10)}\) to write

\[
Y_{2M}(\psi, \chi) = \sum_{\Lambda} D_{M\Lambda}^* (\alpha, \beta, 0) Y_{2\Lambda}(\pi/2, \phi). \quad (101)
\]

Substituting (101) into (100) we find for a point on the side of the cylinder

\[
\mu_{m', m; n}^{(1)}(s) = \sum_{\Lambda} \mu_{m', m; n}^{(1)}(\Lambda)e^{i\Lambda \phi}, \quad (102)
\]

where

\[
\mu_{m', m; n}^{(1)}(\Lambda) = \begin{pmatrix} \frac{\pi K}{4(2K + 1)(2K - 1)} \right)^{1/2} Y_{2\Lambda}(\pi/2, 0) \left[ \delta_{m'n'} - C(K 2K; m, m' - m) D_{m, -m}^{2} (\alpha, \beta, 0) - \delta_{m'n'} C(K 2K; n, -n') D_{n', -n'}^{2} (\alpha, \beta, 0) \right]. \quad (103)
\]

We note that

\[
[\mu_{m', m; n}^{(1)}(\Lambda)]^* = -\mu_{m; m', n}^{(1)}(-\Lambda), \quad (104)
\]

and also that \( \mu_{m'; m; n}^{(1)}(\pm 1) = 0 \).

### B. Evaluation of \( \mu_{l}^{(2)} \)

We now consider the matrix elements of \( \mu_{l}^{(2)} \). There is good experimental evidence that the magnitudes of the fluctuating field gradients at the wall are quite large compared to the mean value of the field gradients, and we therefore assume that

\[
\langle \begin{pmatrix} \partial^2 V_{w} \\ \partial x \partial x \\ \partial x \partial y \end{pmatrix} \rangle^2 \gg \langle \begin{pmatrix} \partial^2 V_{w} \\ \partial x \partial y \end{pmatrix} \rangle^2. \quad (105)
\]

For this reason we will ignore the terms proportional to \( e^{(1)} e^{(1)} \) and write (44) as

\[
\mu_{l}^{(2)} P_{i} = \frac{3}{4\lambda R} \int_{0}^{s} \frac{d\tau_{s}}{\tau_{s}} e^{-\tau_{s}/\tau_{c}} \int_{0}^{t} \int_{0}^{t'} dt' (H_{w}(t)H_{w}(t')P_{i} + P_{i}H_{w}(t')H_{w}(t) - H_{w}(t)P_{i}H_{w}(t') - H_{w}(t')P_{i}H_{w}(t)), \quad (106)
\]

where we have assumed that the adsorption time \( \tau \) of the atoms on the wall has an exponential probability distribution with a mean sticking time \( \tau_{c} \). We will make the plausible assumption that the fluctuations are nearly isotropic, i.e., we assume that the microscopic structure of the wall is sufficiently rough that any tensor component of the field gradient will have approximately the same mean-squared amplitude as any other, and that correlations between different irreducible tensor components are zero. We further assume that the correlation in time of the fluctuating gradients falls off exponentially with a time constant \( \tau_{c} \). Thus we write for the ensemble-averaged correlation function

\[
\langle H_{2M}(t)H_{2M}(t') \rangle = \delta_{-M, M'}(-1)^{M} \langle (H_{20})^{2} \rangle \exp \left[ -\frac{t - t'}{\tau_{c}} \right]. \quad (107)
\]

Substituting (94) and (107) into (106) and carrying out the time integrals we find

\[
\mu_{l}^{(2)} = \frac{3}{2\lambda R^{2}} \tau_{c} \int_{0}^{t} \frac{5}{2K + 1} - P_{i} - \sum_{M} (-1)^{M} T_{2,-M} P_{i} T_{2M}. \quad (108)
\]

To write down (108) we have made use of the identity

\[
T_{2} = \frac{5}{2K + 1}. \quad (109)
\]

The matrix elements of \( \mu_{l}^{(2)} \) between the polarization states \( | m \rangle \langle n | \) of (20) are found to be

\[
\mu_{m, m', n}^{(2)} = \text{Tr}(|m \rangle \langle n | \mu_{l}^{(2)} | m' \rangle \langle n' |) = \frac{1}{30\lambda} \langle \theta^{2} \rangle \left( K(1 + 2K + 3) \right)^{-1} \left[ \delta_{m'n'} - C(K 2K; m, m' - m) C(K 2K; n, n' - n) \delta_{m', -m, -n'} \right], \quad (110)
\]

where we define a mean-squared twist angle by

\[
\langle \theta^{2} \rangle = 5\langle \dot{\theta}^{2} \rangle \frac{\tau_{c} \tau_{s}}{\tau_{c} + \tau_{s}}. \quad (111)
\]
Since we have assumed near isotropy of the fluctuating field gradients we will have \( \langle \theta_{xx}^2 \rangle \approx \langle \theta_{yy}^2 \rangle \approx \langle \theta_{zz}^2 \rangle \).

C. The pressure-independent frequency shift and damping

We begin by evaluating the first term from (87). Using (100) we find that the contribution from \( \mu^{(1)} \) is

\[
\Delta \gamma_{0;mn}^{(1)} = \frac{DS}{V} \langle 0 | \mu_{mn;mn}^{(1)} | 0 \rangle = i \frac{DS}{V} \frac{3}{4\lambda} \frac{m^2 - n^2}{2K - 1} \int_s \frac{dS'}{S'} \left[ \frac{3}{2} \cos^2 \psi - \frac{1}{2} \right].
\]

For the cylindrical cell orientation of Fig. 3(b) one can readily show that

\[
\int_s \frac{dS}{S} \left[ \frac{3}{2} \cos^2 \psi - \frac{1}{2} \right] = A \left[ \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right],
\]

where the asymmetry parameter of the cylinder is

\[
A = \frac{d - h}{d + 2h}.
\]

We also define a characteristic length \( l \) of the cell by

\[
\frac{1}{l} = \frac{S}{2V} = \frac{1}{2h} + \frac{1}{d}
\]

such that the mean rate at which an atom in the cell collides with the walls is

\[
\frac{1}{\tau_0} = \frac{\nu}{l}.
\]

Substituting (113) into (112) we find

\[
\Delta \gamma_{0;mn}^{(1)} = \frac{i\nu A \langle \theta \rangle}{l} \frac{m^2 - n^2}{2K - 1} \left[ \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right].
\]

Since (117) is purely imaginary it describes a pressure-independent shift in the Larmor frequency of the polarization \( | m \rangle \langle n | \).

The contribution to the first term of (87) of the matrix element (110) of \( \mu^{(2)} \) is

\[
\Delta \gamma_{0;mn}^{(2)} = \frac{DS}{V} \langle 0 | \mu_{mn;mn}^{(2)} | 0 \rangle
\]

\[
= \frac{2\nu}{45l} \langle \theta^2 \rangle \left[ \frac{K(K+1)(2K+3)}{2K-1} - \frac{3m^2-K(K+1)}{2K-1} \right] \left[ \frac{3n^2-K(K+1)}{2K-1} \right].
\]

Since (118) is purely real, it describes a pressure-independent damping of the polarization \( | m \rangle \langle n | \). In particular, for the polarizations \( | \frac{1}{2} \rangle \langle \frac{1}{2} | \), \( | \frac{1}{2} \rangle \langle - \frac{1}{2} | \), and \( | - \frac{1}{2} \rangle \langle - \frac{1}{2} | \), which contribute to the transverse magnetization \( K_+ \) of a spin-I nucleus we find

\[
\Delta \gamma_{0;3/2,1/2} = \Delta \gamma_{0;-3/2,-1/2} = \frac{1}{2} \Delta \gamma_{0;1/2,-1/2} = \frac{3\nu}{5l} \langle \theta^2 \rangle.
\]

We conclude this section with a discussion of modes which are degenerate to order \( \mu^{(1)} \). According to (53) the uniform modes with the same azimuthal quantum number \( M = m - n \) have the same zeroth-order damping rate

\[
\gamma_{0g}^{(0)} = i\Omega_g = iM\Omega.
\]

This degeneracy is lifted to first order according to (117) for states with \( M \neq 0 \) provided that the cell is not effectively spherical (i.e., \( A \neq 0 \)) and provided that the cell is not oriented at the magic angle \( \beta = \cos^{-1}3^{-1/2} = 54.74^\circ \). In case the polarizations with the same \( M \) remain degenerate, which is always true if \( M = 0 \) and true for special geometries or cell orientations for \( M \neq 0 \), we must take linear combinations of the degenerate polarizations to ensure that the quantity in square brackets in (85) is zero. If we neglect the terms in (85) proportional to \( \mu^{(1)} \mu^{(1)} \) in comparison to the terms proportional to \( \mu^{(2)} \), the correct linear combinations\(^{11} \) are in fact the irreducible basis tensors (92). Then (108) becomes

\[
\mu^{(2)} T_{JM} = \mu^{(2)}_{JM} T_{JM} ,
\]

where the matrix element can be written in terms of a Racah coefficient \( W \) as

\[
\mu^{(2)}_{JM} = \frac{\langle \theta^2 \rangle}{30\lambda} \frac{K(K+1)(2K+3)}{2K-1} \times [1 - (2K+1)W(KKJ;KK)] .
\]

In evaluating (122) we have made use of the identity

\[
\sum_M T_{LM} T_{LM'}^{+} = (2L + 1)W(LKKJ;KK) T_{JM} .
\]
Substituting (122) into the first term of (87) we find the multipole damping damping rates \( \gamma_j \) for spin-\( \frac{1}{2} \) nuclei to be
\[
\gamma_1 = \frac{1}{2} \gamma_2 = \gamma_3 = \frac{2v}{5l} \langle \theta^2 \rangle .
\] (124)

Of course we find \( \gamma_0 = 0 \) for the monopole damping rate, which ensures that there is no damping of the total number of atoms. The multipole damping rates (124) for a spin-\( \frac{1}{2} \) nucleus subject to an isotropic, fluctuating quadrupole interaction seem to have been first calculated by Cohen-Tannoudji.\(^\text{12}\)

D. The pressure-dependent damping

We turn now to consider the contributions from the second term of (87), which describes damping due to virtual excitation of different polarization-diffusion modes. In this section we will consider virtual excitations of diffusion modes with nonzero spatial frequencies and with the same or different polarization states. Virtual excitations to polarization states of zero spatial frequency, i.e., the uniform modes, are a special case which give a pressure-independent frequency shift. We will discuss this special case in Sec. III F.

The modes are excited by the normal gradient operator \( \mu \) at the cell surface. We write \( \mu \) as a sum of a contribution from the two ends which we denote as \( \mu(e) \) and a contribution from the side wall of the cylinder, which we denote by \( \mu(s) \).
\[
\mu = \mu(e) + \mu(s) .
\] (125)

Because of the assumed form (100) of \( \mu^{(1)} \) and (110) of \( \mu^{(2)} \) we see that \( \mu \) has the same constant value on both ends of the cylinder. Thus, \( \mu(e) \) will excite purely axial modes, which according to (59) have the form
\[
\phi_k = \left[ \frac{2}{k} \right]^{1/2} \cos \frac{apz}{h} .
\] (126)

The matrix element (75) becomes
\[
\langle \kappa | \mu_k | 0 \rangle = \frac{\mu_k(e) V\sqrt{2}}{S_h} \left[ 1 + (-1)^\kappa \right] .
\] (127)

From (89) we find that the first-order correction to the spatial function is
\[
\Delta \gamma_{j;0g}(e) = -\frac{h \mu_k(e)}{6\sqrt{V}} \int \frac{1}{h} \left( \Omega_j - \Omega_g \right) h^2 \left[ \frac{1}{D} \right] .
\] (128)

The sum over nonuniform diffusion modes is described by the function
\[
\Delta \gamma_{j;0g}(e) = \frac{D}{\sqrt{V}} \sum \int dS \mu_{jl}(e) \Delta f_{j;0g}(e) .
\] (131)

We readily evaluate (131) to be
\[
\Delta \gamma_{j;0g}(e) = \frac{D}{3} \sum \mu_{jl}(e) \mu_{jk}(e) Z \left[ 1, \frac{(\Omega_j - \Omega_g) h^2}{D} \right] .
\] (132)

We evaluate (132) for the special case of a spin-\( \frac{1}{2} \) nucleus. As initial polarizations we consider \( \mid \frac{1}{2}; \frac{1}{2} \rangle \), \( \mid \frac{1}{2}; \frac{1}{2} \rangle \), and \( \mid -\frac{1}{2}; -\frac{1}{2} \rangle \). The nonzero matrix elements of \( \mu^{(1)} \) which contribute to (132) correspond to the virtual transitions indicated in Fig. 4, which connect unperturbed polarization states \( g \) to perturbing polarization states \( j \). Each line in Figs. 4(b)–4(d) represents a set of virtual transitions to nonuniform diffusion modes of the perturbing polarization states indicated by the arrow. We will be interested in situations for which \( \mu^{(1)} \ll \mu^{(2)} \) so we approximate \( \mu(e) \) in (132) by \( \mu^{(1)} \) from (100) with \( \psi = \beta \) and \( \chi = \alpha \) to get

\[
\Delta \gamma_{0;1/2, -1/2}(e) = \frac{v}{16\lambda} \left[ \cos \theta \right]^2 \left[ \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right] + \frac{3}{8} \sin^2(2\beta) Z \left[ \frac{1}{1, -\Omega h^2}{D} \right]
\]
\[
+ \frac{3}{16} \sin^4 \beta Z \left[ 1, \frac{2\Omega h^2}{D} \right] + Z \left[ 1, \frac{-2\Omega h^2}{D} \right] \right] ,
\] (133)

\[
\Delta \gamma_{0;1/2, -1/2}(e) = \frac{3v}{128\lambda} \left[ \sin^2(2\beta) Z \left[ 1, \frac{\Omega h^2}{D} \right] \right]
\]
\[
+ \sin^4 \beta Z \left[ 1, \frac{-2\Omega h^2}{D} \right] \right] .
\] (134)

We now consider the radial-azimuthal excitations which are caused by the cylinder sides. According to (59) the spatial wave functions are
\[
\phi_e = \frac{N_m}{d \sqrt{2\pi h}} J_l \left[ \frac{2r}{d} \right] e^{iA} .
\] (135)
From (135) and (102) we find that the matrix element for excitation of a diffusion mode with azimuthal quantum number $\Lambda$ is

$$\langle k | \mu_{jk}(s) | 0 \rangle = \frac{\sqrt{2} V_{j}^{(1)}(\Lambda)}{Sd} N_{m} J_{1}(x_{m}) .$$  \hspace{1cm} (136)$$

From (89) we find that the first-order correction to the spatial function is

$$\Delta f_{j; 0}^{{\text{a}}}(s) = - \sum_{\Lambda} \mu_{jk}(\Lambda) e^{iA} \mathcal{R}_{\Lambda} \left[ \frac{2r}{d^2}, \frac{(\Omega_{j} - \Omega_{k})^2}{4D} \right] .$$  \hspace{1cm} (137)$$

where the sum over nonuniform diffusion modes is described by the functions

$$\mathcal{R}_{j}(\xi, \eta) = \sum_{n=0}^{\infty} \frac{(N_{m})^{2} J_{1}(x_{m})}{{(x_{m})}^2 + i\eta} .$$  \hspace{1cm} (138)$$

We evaluate (138) with (103) and again we include the contributions from all virtual transitions indicated in Figs. 4(b)–4(d) to find

$$\Delta\gamma_{0; 3/2, 1/2}(s) = \Delta\gamma_{0; -1/2, -3/2}(s) = \frac{3\nu(\theta)^2}{256\lambda} (5 - 12\cos^2 \beta + 9\cos^4 \beta)$$

$$+ \frac{9\nu(\theta)^2}{2048\lambda} \left[ \sin^2 \beta \cos^2 \beta \mathcal{R}_{0} \left[ 1, -\frac{\Omega d^2}{4D} \right] + \sin^2 \beta(1 + \cos^2 \beta) \mathcal{R}_{2} \left[ 1, -\frac{\Omega d^2}{4D} \right] \right]$$

$$+ \frac{9\nu(\theta)^2}{2048\lambda} \left[ \sin^4 \beta \mathcal{R}_{0} \left[ 1, \frac{2\Omega d^2}{4D} \right] + \mathcal{R}_{0} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right]$$

$$+ \frac{1 + 6\cos^2 \beta + \cos^4 \beta}{2} \left[ \mathcal{R}_{2} \left[ 1, \frac{2\Omega d^2}{4D} \right] + \mathcal{R}_{2} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right] ,$$  \hspace{1cm} (143)$$

and

$$\Delta\gamma_{1/2, -1/2}(s) = \frac{9\nu(\theta)^2}{1024\lambda} \left[ \sin^2 \beta \cos^2 \beta \mathcal{R}_{0} \left[ 1, \frac{\Omega d^2}{4D} \right] + \sin^2 \beta(1 + \cos^2 \beta) \mathcal{R}_{2} \left[ 1, \frac{\Omega d^2}{4D} \right] \right]$$

$$+ \frac{9\nu(\theta)^2}{1024\lambda} \left[ \sin^4 \beta \mathcal{R}_{0} \left[ 1, -\frac{2\Omega d^2}{4D} \right] + \frac{1 + 6\cos^2 \beta + \cos^4 \beta}{2} \mathcal{R}_{2} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right] .$$  \hspace{1cm} (144)$$

The total damping is the sum of (133) and (143) for the polarizations $|\frac{1}{2}\rangle \langle \frac{1}{2}|$ and $|\frac{1}{2}\rangle \langle \frac{1}{2} |$ or the sum of (134) and (144) for the polarization $|\frac{3}{2}\rangle \langle \frac{3}{2}|$.

When the condition (58) of rapid diffusion is satisfied, (130), (139), and (140) imply that the coefficients $\mathcal{R}_{0}, \frac{1}{2}\mathcal{R}_{2},$ and $Z$, which occur in the formulas for the damping rates, are all very nearly unity. Then the total damping rates are

$$\Delta\gamma_{0; 3/2, 1/2} = \Delta\gamma_{0; -1/2, -3/2} = \frac{\nu(\theta)^2}{\lambda} \left[ \frac{77}{512} - \frac{15}{128}\cos^2 \beta + \frac{63}{512}\cos^4 \beta \right] ,$$  \hspace{1cm} (145)$$

We note that for $\eta = 0$ the sums are the Bessel-Fourier series representation on the interval $0 \leq \xi \leq 1$ of the functions

$$2\xi^2 - 1 = \mathcal{R}_{0}(\xi, 0)$$  \hspace{1cm} (139)$$

and

$$2\xi^2 = \mathcal{R}_{2}(\xi, 0) .$$  \hspace{1cm} (140)$$

The damping due to (137) is given by the second term in (87) and is

$$\Delta\gamma_{0; 3/2, 1/2} = \frac{D}{\sqrt{V}} \sum_{j} \int ds \mu_{jk}(s) \Delta f_{j; 0}^{{\text{a}}}(s) .$$  \hspace{1cm} (141)$$

Substituting (102) and (137) into (141) we find

$$\Delta\gamma_{0; 3/2, 1/2} = \frac{D}{\sqrt{V}} \sum_{j} \int ds \mu_{jk}(s) \left[ \frac{2r}{d^2}, \frac{(\Omega_{j} - \Omega_{k})^2}{4D} \right] .$$  \hspace{1cm} (142)$$

We evaluate (142) with (103) and again we include the contributions from all virtual transitions indicated in Figs. 4(b)–4(d) to find

$$\Delta\gamma_{0; 3/2, 1/2} = \frac{9\nu(\theta)^2}{256\lambda} \left[ \sin^2 \beta \cos^2 \beta \mathcal{R}_{0} \left[ 1, -\frac{\Omega d^2}{4D} \right] + \sin^2 \beta(1 + \cos^2 \beta) \mathcal{R}_{2} \left[ 1, -\frac{\Omega d^2}{4D} \right] \right]$$

$$+ \frac{9\nu(\theta)^2}{2048\lambda} \left[ \sin^4 \beta \mathcal{R}_{0} \left[ 1, \frac{2\Omega d^2}{4D} \right] + \mathcal{R}_{0} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right]$$

$$+ \frac{1 + 6\cos^2 \beta + \cos^4 \beta}{2} \left[ \mathcal{R}_{2} \left[ 1, \frac{2\Omega d^2}{4D} \right] + \mathcal{R}_{2} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right] ,$$  \hspace{1cm} (143)$$

and

$$\Delta\gamma_{1/2, -1/2} = \frac{9\nu(\theta)^2}{1024\lambda} \left[ \sin^2 \beta \cos^2 \beta \mathcal{R}_{0} \left[ 1, \frac{\Omega d^2}{4D} \right] + \sin^2 \beta(1 + \cos^2 \beta) \mathcal{R}_{2} \left[ 1, \frac{\Omega d^2}{4D} \right] \right]$$

$$+ \frac{9\nu(\theta)^2}{1024\lambda} \left[ \sin^4 \beta \mathcal{R}_{0} \left[ 1, -\frac{2\Omega d^2}{4D} \right] + \frac{1 + 6\cos^2 \beta + \cos^4 \beta}{2} \mathcal{R}_{2} \left[ 1, -\frac{2\Omega d^2}{4D} \right] \right] .$$  \hspace{1cm} (144)$$

The rates (145) and (146) are independent of the cell shape or volume, and they depend weakly on the cell orientation angle $\beta$.

**E. The pressure-dependent frequency shift**

In the nonperturbative example discussed in Sec. II C the frequency shift exhibited a linear dependence on the gas pressure in the low-pressure limit. For perturbation
theory the lowest-order pressure dependence of the frequency shift comes from the imaginary parts of (133), (134), (143), and (144), which are proportional to the square of the pressure and are negligible when the condition (58) for rapid diffusion is satisfied, and from the products of $\mu^{(1)}$ and $\mu^{(2)}$ in (132) and (142), which are directly proportional to the pressure. Because of the special symmetries we have assumed for the wall interactions, it is possible for both $p_{1}'$ and $p_{2}'$ to be nonzero only if $m' = m$ and $n' = n$. For the case of a spin-$\frac{1}{2}$ nucleus we have from (100)

$$
\mu_{3/2,1/2,3/2,1/2}^{(1)}(e) = \frac{i3}{8\lambda}(3\cos^2\beta - 1),
$$

and from (110)

$$
\mu_{3/2,1/2,3/2,1/2}^{(2)}(e) = \frac{9}{20\lambda}(\theta^2).
$$

The contribution from (132) which involves products of (147) and (148) is

$$
\Delta\gamma_{0,3/2,1/2}(e) = -\frac{i3v(\theta)(\theta^2)}{80\lambda}(3\cos^2\beta - 1).
$$

For the cylinder sides we have from (103)

$$
\mu_{3/2,1/2,3/2,1/2}^{(1)}(0) = \frac{i3}{16\lambda}(3\cos^2\beta - 1).
$$

The contribution from (142) which involves products of (150) and (148) is

$$
\Delta\gamma_{0,3/2,1/2}(s) = -\frac{i3v(\theta)(\theta^2)}{320\lambda}(3\cos^2\beta - 1).
$$

The total pressure-dependent frequency shift, the sum of (149) and (151), is

$$
\Delta\gamma_{0,3/2,1/2} = -\frac{i3v(\theta)(\theta^2)}{320\lambda}(3\cos^2\beta - 1).
$$

Since $\mu_{1/2,-1/2,1/2,-1/2}$ is zero, there is no frequency shift of the polarization $|\frac{1}{2}\rangle e^{-\frac{1}{2}}$.

F. The second-order effects of $H_{eff}$

In the calculations of Secs. III D and III E we did not include the effects of virtual transitions to states of uniform polarization. One can readily show that the contribution of this type of virtual transition to (87) can be written in terms of the effective Hamiltonian (79) as

---

**FIG. 4.** (a) The polarization states $|m\rangle \langle n|$ of a nucleus with spin $K = \frac{3}{2}$. The azimuthal quantum numbers $M = m - n$ of the polarization states are also indicated. (b) The allowed virtual transitions from the uniform diffusion mode of polarization states with $M = 1$ to nonuniform diffusion modes of the same polarization state. (c) The allowed virtual transitions from the uniform diffusion mode of polarization states with $M = 1$ to nonuniform diffusion modes of polarization states with azimuthal quantum numbers $M \pm 1$. (d) The allowed virtual transitions from the uniform diffusion mode of states with $M = 1$ to nonuniform diffusion modes of polarization states with azimuthal quantum numbers $M \pm 2$. 
TABLE I. Dependence of NMR frequency shift and damping on basic parameters.

<table>
<thead>
<tr>
<th>Shift or damping rate</th>
<th>Dependence on $v, \lambda, l, A, \langle \theta \rangle, \langle \theta^2 \rangle$</th>
<th>Representative equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure-independent frequency shift</td>
<td>$v \langle \theta \rangle \omega^{-1}$</td>
<td>(117)</td>
</tr>
<tr>
<td>Pressure-independent damping</td>
<td>$v \langle \theta^2 \rangle I^{-1}$</td>
<td>(124)</td>
</tr>
<tr>
<td>Pressure-dependent frequency shift</td>
<td>$v \langle \theta \rangle \langle \theta^2 \rangle \lambda^{-1}$</td>
<td>(152)</td>
</tr>
<tr>
<td>Pressure-dependent damping</td>
<td>$v \langle \theta \rangle \langle \theta^2 \rangle \lambda^{-1}$</td>
<td>(145)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$\lambda$</td>
<td>(146)</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

We have developed a general perturbative theory which describes how coherent wall interactions affect the NMR spectrum of nuclear-spin–polarized gases in containers of any shape. The important practical case of cylindrical containers with quadrupolar wall interactions has been worked out completely. The basic results are quite simple. The frequency shift and damping of the NMR spectrum depend on seven fundamental parameters, which we list below.

1. $v \approx 2.4 \times 10^4$ cm sec$^{-1}$, the mean thermal velocity of spin-polarized atoms.
2. $\lambda \approx 10^{-3}$ cm, the mean free path of a spin-polarized atom in the gas; $\lambda$ is related to the diffusion constant $D$ and the mean velocity $v$ by (14).
3. $l \approx 0.5$ cm, a characteristic linear dimension of the container, given by (115).
4. $A \approx 0.2$, an asymmetry parameter of the container, which is given by (114).
5. $\langle \theta \rangle \approx 4 \times 10^{-5}$ rad, the mean twist angle experienced by the nuclear polarization of an atom as a result of a collision with the wall. $\langle \theta \rangle$ is given by (99).
6. $\langle \theta^2 \rangle \approx 3 \times 10^{-6}$ rad$^2$, the mean-squared twist angle experienced by the nuclear polarization of an atom as a result of a collision with the wall. $\langle \theta^2 \rangle$ is given by (111).
7. $\beta \approx \pi/2$ rad, the angle between the symmetry axis of the cylinder and the direction of the quantizing magnetic field.

The approximate numerical values of the parameters are representative of those for the experimental data of Fig. 1. The dependence of the frequency shift and damping on these basic parameters is summarized in Table I. Also listed in Table I are representative equation numbers where one can find the exact formulas for the shifts and damping rates and their dependence on the tilt angle $\beta$. The expansion parameter (80) is on the order of $l \lambda^{-1} \langle \theta \rangle$, so we recognize that this perturbation theory works best for small cells (small $l$), small gas pressure (small $\lambda^{-1}$), and small wall interactions (small $\langle \theta \rangle$).

ACKNOWLEDGMENT

This work was supported by the U.S. Air Force Office of Scientific Research under Grant No. 81-0104-C.


9E. Jahnke and F. Emde, Tables of Functions with Formulae and Curves (Dover, New York, 1945).


12C. Cohen-Tannoudji, J. Phys. (Paris) 24, 653 (1963). We have made the following corrections to formulas in this reference: The right-hand side of (2) should be multiplied by \(-\frac{1}{2}\). The right-hand side of (5b) should be multiplied by \((4\pi)^{-1}\). The right-hand side of (12) should be multiplied by \((16\pi \hbar^2)^{-1}\).