Effects of diffusion and surface interactions on the line shape of electron paramagnetic resonances in the presence of a magnetic field gradient

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In an evanescent wave magnetometer the Zeeman polarization is probed at micrometer to submicrometer distances from the cell surface. The electron paramagnetic resonance lines of an evanescent wave magnetometer in the presence of a magnetic field gradient exhibit edge enhancement seen previously in nuclear magnetic resonance lines. We present a theoretical model that describes quantitatively the shape of the magnetic resonance lines of an evanescent wave magnetometer under a wide range of experimental conditions. It accounts for diffusion broadening in the presence of a magnetic field gradient as well as interactions of spin polarized Rb atoms with the coated Pyrex glass surfaces. Depending on the field gradient, cell thickness, and buffer gas pressure, the resonance line may have the form of a single asymmetric peak or two peaks localized near the front and back surfaces in frequency space. The double-peaked response depends on average characteristics of the surface interactions. Its shape is sensitive to the dwell time, relaxation probability, and average phase shift of adsorbed spin polarized Rb atoms.

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I. INTRODUCTION

Nuclear magnetic resonances in the presence of magnetic field gradients have been studied extensively in connection with magnetic resonance imaging [1]. Diffusion of spin polarized atoms in an inhomogeneous magnetic field causes line broadening [2–7] and is associated with edge enhancement in nuclear magnetic resonances [8–10].

Due to their small penetration depth, evanescent waves have been used in many studies of atom-surface interactions. Relaxation of sodium atoms on cell surfaces, for example, was studied by probing the magnetic resonances by an evanescent wave in a homogeneous magnetic field [11]. We recently demonstrated the operation of a type of atomic magnetometer, an evanescent wave magnetometer, that uses evanescent waves to probe the Zeeman polarization in the vicinity (\(\sim 10^{-5}\) cm) of cell surfaces [12]. Since the Zeeman polarization is measured at micrometer to submicrometer distances from the cell surface, the magnetic resonance lines of the evanescent wave magnetometer are influenced by the interactions of spin polarized alkali-metal atoms with the cell surface. We find that in the presence of a magnetic field gradient the electron paramagnetic resonance (EPR) lines of the evanescent wave magnetometer have features not observed in conventional atomic magnetometers that probe the Zeeman polarization in the bulk. Depending upon the field gradient, cell thickness, and buffer gas pressure, the resonance line may have the form of a single asymmetric peak or consist of two peaks, one near the front and one near the back surface in frequency space. A similar enhancement of the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the free precession signal due to edges was predicted for the...
FIG. 1. Schematic experimental setup. Laser beams A and B are circularly polarized ($\sigma^+$) by a Glan-Thompson linear polarizer (LP) and a quarter-wave plate ($\lambda/4$). The laser power of beam A and of beam B is 20 $\mu$W and 2.7 mW, respectively. A round Alnico bar magnet in combination with three orthogonal pairs of Helmholtz coils produces a magnetic field along the z axis with a field gradient $\nabla B_z$ in the positive direction of the $z$ axis. A pair of coils generates a radio field at a frequency $\omega$. Both beams are in the same direction and propagate in the same direction. The laser beams are 45 MHz. The 1 $P_1/2$ laser operated in the free-running mode. The linewidth of the 1 $P_1/2$ laser is 20 MHz and that of beam $B$ is 0.7 mW. A round Alnico bar magnet in combination with three orthogonal pairs of Helmholtz coils produces a magnetic field along the y axis. A pair of coils generates a radio field at a frequency $\omega$. Both beams are in the same direction and propagate in the same direction. The laser beams are 45 MHz. The 1 $P_1/2$ laser operated in the free-running mode. The linewidth of the 1 $P_1/2$ laser is 20 MHz and that of beam $B$ is 0.7 mW.

A. EPR in the presence of surface interactions and a magnetic field gradient

The interaction of a Rb atom with the time-dependent radio frequency field is described by the Hamiltonian

$$H_{rf} = \cos(\Omega t/2)[S_y, \cos(\omega t) - S_z, \sin(\omega t)].$$  \hspace{1cm} (1)

where $S_y$ and $S_z$ are respectively the $y$ and $z$ components of the Rb electronic spin operator and $\omega$ is the rf frequency. The amplitude modulation of the rf field at the frequency $\Omega \ll \omega$ is simulated by beating two unmodulated rf radiations of angular frequencies $\omega \pm \Omega/2$. The rf field causes transitions among Zeeman levels and depolarizes the Rb atoms. The absorption of the probe beam is proportional to the density of depolarized Rb atoms in the measurement volume at the front surface.

We follow the position of the polarized spin from its creation near the evanescent-wave pump laser at time $t_0$ to the time $T$ at which it may absorb a photon from the evanescent-wave probe laser. On any given diffusion path $\{x\}_D = \{x, t_0 < t < t_D\}$ over this time interval, the probability $p(\{x\}_D, \omega, \Omega)$ that the spin has been depolarized by the rf radiation (to first order in $H_{rf}$) is expressed by

$$p(\{x\}_D, \omega, \Omega) \propto e^{-\tau} \int_{t_0}^{T} dt_2 \int_{t_0}^{T} dt_1 \cos(\Omega t_2/2) \cos(\Omega t_2/2)$$

$$\times \exp \left[ -\frac{\Gamma}{2} |t_2 - t_1| + i \int_{t_1}^{t_2} [\omega - \omega_L(x)] dt \right].$$  \hspace{1cm} (2)

In Eq. (2) $\Gamma + 2 \tau^{-1}$ is the full width of the spectral line measured in the bulk in a homogeneous magnetic field. It is assumed to be Lorentzian and $\omega_L(x)$ is the local Larmor frequency of the spin. Due to its narrow linewidth, our laser probes only the $F=2$ ground state hyperfine level. Hyperfine relaxation from the $F=2$ to the $F=1$ level, due to spin exchange collisions, thus renders the electron spin undetectable. We account for this loss of polarized electron spins by an attenuation factor characterized by the decay time $\tau$.

Replacing the spin Hamiltonian by its local eigenvalues in Eq. (2) is permissible if the spin can adiabatically follow the inhomogeneous magnetic field. For a diffusion path characterized by the diffusion constant $D$, the adiabatic approximation requires that

$$|\nabla \omega_L \cdot \Delta x| \sim |\nabla \omega_L| \sqrt{D/\omega_L} \ll \omega_L,$$

or equivalently

$$|D|\nabla \omega_L|^{2} \ll \omega_L,$$

a condition that is well satisfied in the experiments.

The lock-in signal and its quadrature due to the polarization created by the pump beam at time $t_0$ are the real and imaginary parts of the complex signal $S_y(\omega, \Omega)$, where

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\[ S_0(\omega, \Omega) \approx \int_{t_0}^{\infty} dT e^{-i\Omega T} \int_V d^3\mathbf{x}_0 \int_V d^3\mathbf{x}_T P_{\text{probe}}(\mathbf{x}_T) \times \langle \rho(\{\mathbf{x}\}_D, \omega, \Omega) \rangle P_{\text{source}}(\mathbf{x}_0). \]  
\( (3) \)

Here \( \langle \cdots \rangle \) denotes the average over diffusion paths \( \{\mathbf{x}\}_D \). \( P_{\text{source}}(\mathbf{x}) \) is the probability that a polarized spin is created at \( \mathbf{x}_0 \), and is proportional to the intensity of the profile of the pump beam, which is assumed to be similar in form to that of the pump beam,

\[ P_{\text{source}}(\mathbf{x}) = \frac{e^{-r_p^2/\pi\sigma^2}}{\pi\sigma^2} \sim \frac{e^{-r_p^2/\pi\sigma^2}}{\pi\sigma^2} \delta(z + l/2). \]  
\( (4) \)

The parameter \( r_p \) is the radius of the source laser beam and \( \lambda_p \) the penetration depth of its evanescent wave. The probability that a depolarized spin is detected is proportional to the profile of the probe beam, which is assumed to be in similar form to that of the pump beam,

\[ P_{\text{probe}}(\mathbf{x}) = \frac{e^{-r_p^2/\pi\sigma^2}}{\pi\sigma^2} \sim \frac{e^{-r_p^2/\pi\sigma^2}}{\pi\sigma^2} \delta(z + l/2), \]  
\( (5) \)

where \( r_p \) is the radius of the probe laser beam and \( \lambda_p \) the penetration depth of its evanescent wave. The \( \delta \)-function approximation in Eq. (4) and Eq. (5) is justified because the penetration depth of the evanescent wave is negligible compared to the cell dimensions, and the polarization in the vicinity \( (\sim 10^{-5} \text{ cm}) \) of a coated cell surface is constant \( [15] \).

Note that in contrast to the cylindrical symmetry of the profiles, taking the limit of an evanescent wave of vanishing penetration depth is not essential to the analysis below.

We separate the dependence of \( S_0(\omega, \Omega) \) on the absolute time \( t_0 \) by shifting the time variable by \( t_0 \) on all diffusion paths and parametrizing the diffusion paths in terms of the time that has elapsed since the spin was created by the pump laser. We then have

\[ \int_{t_0}^{\infty} dT e^{-i\Omega T} \rho(\{\mathbf{x}\}_D, \omega, \Omega) \]

\[ \approx \int_{0}^{\infty} dT e^{-i(\Omega + \Gamma)T} \int_{0}^{T} dt_2 \int_{0}^{T} dt_1 \]

\[ \times \left\{ \exp \left( -\frac{\Gamma}{2} |t_2 - t_1| \right) \right\} \]

\[ + i \int_{t_1}^{t_2} \left[ \omega - \omega_L(\mathbf{x}_1) \right] dt \}

\[ \times \cos \left( \frac{\Omega t_1 + \Omega t_2}{2} \right) \cos \left( \frac{\Omega t_2 + \Omega t_1}{2} \right) e^{-i\Omega t_0}, \]  
\( (6) \)

where \( \langle \cdots \rangle_{t_0 \leq t \leq T} \) denotes the average over all diffusion paths that start at \( t=0 \) near the pump and are probed at a time \( T>0 \) later. This average does not depend on the absolute time \( t_0 \) given by the phase of the lock-in amplifier and rf modulation.

The measured lock-in signal \( S(\omega, \Omega) \) is obtained by averaging \( S_0(\omega, \Omega) \) over \( t_0 \). Averaging over the absolute time \( t_0 \) \( \text{the spins are created, the last factor in Eq.} \) becomes

\[ \cos \left[ \Omega (t_1 + t_2)/2 \right] \cos \left[ \Omega (t_2 + t_0)/2 \right] \exp(-i\Omega t_0) \]

\[ = \frac{1}{4} \exp \left[ i\Omega (t_1 + t_2)/2 \right] \]  
\( (7) \)

Thus the measured lock-in signal is given by

\[ S(\omega, \Omega) \]

\[ \approx \int_V d^3x_T \int_V d^3x_0 P_{\text{probe}}(\mathbf{x}_T) P_{\text{source}}(\mathbf{x}_0) \int_{0}^{\infty} dT e^{-i(\Omega + \Gamma)T} \]

\[ \times \int_{0}^{T} dt_2 \int_{0}^{T} dt_1 \exp \left( -\frac{\Gamma}{2} |t_2 - t_1| + i\Omega \frac{t_1 + t_2}{2} \right) \]

\[ + i \omega(t_2 - t_1) \left( e^{-i\frac{\omega_L(x_1)}{2}} \right)_{t_0 \leq t \leq T} \]  
\( (8) \)

Note that the lock-in signal detects only the fundamental modulation frequency. For square-wave modulation used in the experiment the signal is proportional to \( S(\omega + \Omega/2, \Omega) + S(\omega - \Omega/2, \Omega) \). In essence the line shape does not depend on the type of modulation as long as \( \Omega \ll \Gamma \) (see the discussion in Sec. III D).

Let us denote the expectation value of the phase \( \exp(-i\frac{\omega_L(x_1)}{2}) \) for a diffusion path originating at the pump \( \{x_0 \sim (\rho=0,z=-l/2)\} \) at \( t=0 \) and ending at the probe after a time \( T \{x_T \sim (\rho=0,z=-l/2)\} \) by

\[ G(0 \leq t_1 \leq t_2 \leq T; \rho_L) \]

\[ := \langle e^{-i\frac{\omega_L(x_1)}{2}} \rangle_{t_0 \leq t \leq T}. \]  
\( (9) \)

We take only the ordering \( 0 \leq t_1 \leq t_2 \leq T \) in Eq. (9). Since the diffusion is real, the ordering \( 0 \leq t_2 \leq t_1 \leq T \) corresponds to taking the complex conjugate \( G^* \). In terms of \( G \) defined by Eq. (9), the signal in Eq. (8) can be written as

\[ S(\omega, \Omega) \]

\[ \approx \int_V d^3x_T \int_V d^3x_0 P_{\text{probe}}(\mathbf{x}_T) P_{\text{source}}(\mathbf{x}_0) \int_{0}^{\infty} dT e^{-i(\Omega + \Gamma)T} \]

\[ \times \int_{0}^{T} dt_2 \int_{0}^{T} dt_1 \exp \left( -\frac{\Gamma}{2} |t_2 - t_1| + i\Omega \frac{t_1 + t_2}{2} \right) \]

\[ \times \Re \left[ e^{i\omega_L(z)} G(0 \leq t_1 \leq t_2 \leq T; \rho_L) \right]. \]  
\( (10) \)

As the phase accumulates only in the time interval \( t_1 < t < t_2 \), it is convenient to separate \( G \) into three parts,

\[ G(0 \leq t_1 \leq t_2 \leq T; \rho_L) \]

\[ = \int_V d^3x_T \int_V d^3x_0 g(x_T, x_2; T-t_2) \]

\[ \times g_{\rho_L}(x_2, x_1; t_2-t_1) \]  
\( (11) \)

The Green’s function \( g_{\rho_L} \) in Eq. (11),

\[ g_{\rho_L}(y, x; t) = \langle e^{-i\frac{\omega_L(\mathbf{x}_1)}{2}} \rangle_{t_0 \leq t \leq t_0}, \]  
\( (12) \)

is a complex weighted average of diffusion paths within the cell that proceed from \( x \) to \( y \) in time \( t > 0 \), and \( g_{0}(y, x; t) \) is
the probability that a spin diffuses from \( x \) to \( y \) in time \( t > 0 \). It can be shown (see Sec. III C) that the expectation in Eq. (16) satisfies the partial differential equation,

\[
\partial_t g_{\alpha}(y;x,t) = \left[ D \Delta_y - i \omega_L(y) \right] g_{\alpha}(y;x,t),
\]

subject to suitable boundary conditions. We will neglect surface interactions on the rather distant cylindrical surface of the cell and, in particular, ignore polarization losses on that surface. Only interactions of the spins with the front and back faces of the cell will be included. Although this simplification may be removed without much effort, it is justified, since the radius of the cylindrical cells used in the experiments is more than one order of magnitude larger than the radii of the probe and pump beams. No spin flux through the cylindrical surface implies the boundary condition

\[
\vec{n} \cdot \nabla g_{\alpha}(y;x,t)|_{\text{cylindrical cell boundary}} = 0.
\]

In Sec. III C we show that the surface interactions of a spin polarized Rb atom at the front and back faces of the cell may be described by boundary conditions of the form

\[
\left[ \vec{n} \cdot \nabla_y + \eta(\vec{n} \cdot \nabla)_y \right]^2 + \mu g_{\alpha}(y;x,t)|_{\text{face}} = 0,
\]

where the constants \( \mu \) and \( \eta \) depend upon properties of the coated surfaces. The unit vector \( \vec{n} \) in Eq. (14) and Eq. (15) is normal to the cell surface and always points out of the cell. Finally, causality provides the initial condition,

\[
g_{\alpha}(y;x,0) = \delta(y - x).
\]

To obtain a spectral representation for \( g_{\alpha}(y;x,t) \), consider the set of solutions \( \{ \Psi_n(y;\omega_L) \} \) to the eigenvalue equations

\[
\left[ D \Delta_y - i \omega_L(y) + \beta_n \right] \Psi_n(y;\omega_L) = 0
\]

that satisfy the same boundary conditions, Eq. (14) and Eq. (15), as \( g_{\alpha} \) does. Since the boundary condition of Eq. (15) is of second order, solutions of Eq. (17) for different eigenvalues \( \beta_n \) are not orthogonal, but nevertheless are linearly independent. We can expand \( g_{\alpha}(y;x,t) \) in terms of \( \{ \Psi_n(y;\omega_L) \} \),

\[
g_{\alpha}(y;x,t) = \sum_n \Psi_n(y;\omega_L) \overline{\Psi}_n(x;\omega_L) e^{-\beta_n}. \tag{18}
\]

Equation (16) gives the set of linear equations

\[
\sum_m N_{nm} \overline{\Psi}_m(x;\omega_L) = \Psi_n(x;\omega_L), \tag{19}
\]

where

\[
N_{nm} = \int_R d^3 x \overline{\Psi}_m(x;\omega_L) \Psi_n(x;\omega_L).
\]

When the normalization matrix \( N_{nm} \) is nonsingular, Eq. (19) uniquely defines the \( \overline{\Psi}_n \) of any finite model space.

To proceed further, we make extensive use of the cylindrical symmetry of the cell and of the pump and probe configuration. Separation in cylindrical coordinates is possible if the Larmor frequency depends only upon the \( z \) coordinate \( (\omega_L(x) = \omega_L(z)) \), i.e., we assume the magnetic field gradient throughout the cell is perpendicular to the cell faces (see, however, the discussion in Sec. III B). For the radially symmetric pump and probe profiles of Eq. (4) and Eq. (5), we have contributions with vanishing angular momentum only, and \( \Psi_n \) is then of the (regular) form

\[
\Psi_m(x;\omega_L) = \frac{J_0(\kappa_j R)}{\sqrt{\pi R J_0(\kappa_j R)}} \psi_n(z;\omega_L), \tag{21}
\]

where \( J_0 \) is the cylindrical Bessel function of zero order. The boundary condition, Eq. (14), at the cylindrical surface of radius \( R \) determines \( \kappa_j \),

\[
J_0(\kappa_j R) = -J_1(\kappa_j R) = 0 \Rightarrow \kappa_j = z_j/R, \tag{22}
\]

where \( z_j \) is the \( j \) zero of the cylindrical Bessel function \( J_1 \). Note that \( z_0=0 \) corresponds to a diffusion mode that does not depend on \( \rho \). Writing the eigenvalues of Eq. (17) as

\[
\beta_n = D \kappa_j^2 + \alpha_n = z_j^2 D/R^2 + \alpha_n, \tag{23}
\]

the longitudinal modes \( \psi_n(z;\omega_L) \) are solutions to the ordinary differential equation

\[
\left( D \frac{d^2}{dz^2} - i \omega_L(z) + \alpha_n \right) \psi_n(z;\omega_L) = 0. \tag{24}
\]

The conditions of Eq. (15) translate to boundary conditions at \( z = \pm 1/2 \),

\[
\pm \psi_n'(\pm 1/2;\omega_L) + \eta \psi_n'(\pm 1/2;\omega_L) + \mu \psi_n(\pm 1/2;\omega_L) = 0, \tag{25}
\]

where the constants \( \eta \) and \( \mu \) characterize the interactions of the electronic spin with the front (−) and back (+) surfaces of the cell.

The transverse modes in Eq. (21) are orthonormal and complete for the set of functions with no flux through the radial surface of the cell,

\[
2 \int_0^R \rho d\rho J_0(\kappa_j R) J_0(\kappa_{j'} R) = \delta_j \delta_{j'} J_0^2(\kappa_j R),
\]

\[
\sum_{j=0}^{\infty} J_0(\kappa_j R) J_0(\kappa_{j'} R) = \frac{\delta(\rho - \rho')}{2 \pi \rho}. \tag{26}
\]

The initial condition of Eq. (16) thus requires that

\[
\sum_n \overline{\psi}_n(z;\omega_L) \psi_n(z';\omega_L) = \delta(z - z'), \tag{27}
\]

which implies that the \( \overline{\psi}_n(z;\omega_L) \) solve the linear system

\[
\sum_m N_{nm} \overline{\overline{\psi}}_m(z;\omega_L) = \psi_n(z;\omega_L), \tag{28}
\]

with

\[
N_{nm} = \int_{-1/2}^{1/2} dz \overline{\overline{\psi}}_n(z;\omega_L) \overline{\overline{\psi}}_m(z;\omega_L). \tag{29}
\]
We note that for $r \ll R$,

$$\int_0^R e^{-r^2/4z^2} F_0(k\rho) \sim \int_0^\infty e^{-\rho^2/2} J_0(\rho) = \frac{r^2}{2} e^{-\kappa^2 l^2/4}. \quad (29)$$

Using Eq. (29), the orthogonality and completeness relations of Eq. (26) and the special forms of the pump and probe profiles of Eq. (4) and Eq. (5), we can perform the integrals over transverse cylindrical coordinates in Eq. (10),

$$S(\omega, \Omega) \approx \int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^{t_2} dt_2 \int_0^{l/2} dz \bar{\psi}_m(z_1; \omega_L) \psi_m(z_1; 0) \bar{\psi}_n(0) - \frac{i}{2} :0 \bigg] \bigg\} \bigg\}, \quad (30)$$

where $\alpha_n^{(0)}$ are the eigenvalues of Eq. (24) for $\omega_L = 0$.

We now are in a position to evaluate all the time integrals. The prototypical time integral can be evaluated by successive partial integration,

$$\int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^{t_2} dt_2 e^{i(\Omega + \Gamma - \omega)\tau} D\kappa^2 + \tau^2 + i\Omega + a_m^{(0)}$$

$$= \frac{(D\kappa^2 + \tau^2 + i\Omega + a_m^{(0)})^{-1}}{D\kappa^2 + \tau^2 + \frac{\Gamma}{2} + \alpha_L + i\left(\frac{\Omega}{2} - \omega\right)} \int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau}$$

$$= \frac{(D\kappa^2 + \tau^2 + i\Omega + a_m^{(0)})^{-1}(D\kappa^2 + \tau^2 + \alpha_n^{(0)})^{-1}}{D\kappa^2 + \tau^2 + \frac{\Gamma}{2} + \alpha_L + i\left(\frac{\Omega}{2} - \omega\right)} \int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau}$$

$$= \frac{(D\kappa^2 + \tau^2 + i\Omega + a_m^{(0)})^{-1}(D\kappa^2 + \tau^2 + \alpha_n^{(0)})^{-1}}{D\kappa^2 + \tau^2 + \frac{\Gamma}{2} + \alpha_L + i\left(\frac{\Omega}{2} - \omega\right)} \int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau}$$

$$= \frac{(D\kappa^2 + \tau^2 + i\Omega + a_m^{(0)})^{-1}(D\kappa^2 + \tau^2 + \alpha_n^{(0)})^{-1}}{D\kappa^2 + \tau^2 + \frac{\Gamma}{2} + \alpha_L + i\left(\frac{\Omega}{2} - \omega\right)} \int_0^\infty d\tau e^{-i(\Omega + \Gamma - \omega)\tau} \int_0^T dt_1 e^{-i(\Omega + \Gamma - \omega)\tau}$$

The dependence of Eq. (31) on the mode numbers $n$ and $m$ can be neatly factorized and we define the matrix elements as follows:

$$\mathcal{M}_m(a) = \int_{-l/2}^{l/2} dz \bar{\psi}_m(z; \omega_L) \phi_a(z, -\frac{l}{2})$$

solves a diffusion equation with a source at $z = z'$,

and

$$\tilde{\mathcal{M}}_m(a) = \int_{-l/2}^{l/2} dz \psi_m(z; \omega_L) \phi_a(z, -\frac{l}{2}, z) \quad (32)$$

while satisfying the same boundary conditions at $z = \pm l/2$ as the $\psi_m(z; 0)$ [see Eq. (25)]. Solving Eq. (34) explicitly with the boundary conditions of Eq. (25) yields

$$\phi_a(z, z') = D \sum_{n=\infty}^\infty \frac{\psi_a(z, 0) \bar{\psi}_n(z'; 0)}{Da^2 + \alpha_n^{(0)}}$$

Here
The matrix element \( M_k \) may be interpreted to be the projection of the equilibrium polarization distribution \( \phi_{\delta}(z, -l/2) \) established by the pump in the absence of an rf field on the diffusion mode \( \psi_j(z; \omega_j) \) in the presence of the rf field. The matrix element \( M_k = \sum \lambda_j \lambda_{j'} M_{jk} \), on the other hand, describes the modulated signal arising from \( \phi_{\delta}(z; \omega_k) \).

Using Eq. (31), one can recast Eq. (30) in terms of the matrix elements of Eq. (32),

\[
S(\omega, \Omega) \approx \sum_{j=0}^{\infty} \frac{e^{-\kappa_j^2 \tau^2 \rho^2}}{\tilde{J}_0(\zeta_j)} \sum_k \tilde{M}_k \left( \frac{1}{D\tau} + \kappa_j^2 \right) \times \left( \frac{\kappa_j^2}{D\tau} + \frac{1}{\tau} + \frac{\Omega}{D} + \kappa_j^2 \right) + \frac{\kappa_j^2}{D\tau} + \frac{1}{\tau} + \frac{\Omega}{D} + \kappa_j^2
\]

\[
(36)
\]

where \( \tilde{M}_k^* \) is the complex conjugate of \( \tilde{M}_k \) and the two terms in brackets of Eq. (36) arise from the real part in Eq. (10). Note that the sign of \( \Omega \) in the argument of \( \tilde{M}_k^* \) is opposite to that in the argument of \( \tilde{M}_k \).

The \( j=0 \) contribution to the signal in Eq. (36) can be described by a simpler, one-dimensional model, since the eigenvalue \( \kappa_0 = 0 \) corresponds to a transverse mode that is uniform in the radial direction [see Eq. (22)]. For \( R^2/(D\tau) \ll 1 \), this constant transverse mode is the only one with a significant matrix element and the problem indeed is one dimensional since the equilibrium distribution in this limit does not depend on the radial distance from the source. For \( \tau \) of the order of milliseconds, \( D \sim 30 \text{ cm}^2/\text{Hz} \) and a cell radius of the order of a centimeter, \( R^2/(D\tau) \sim 30 \gg 1 \), and the one-dimensional case is not a very good approximation. However, the summation over transverse modes converges rapidly, and none of the cells we studied required more than the lowest 8 transverse modes for an accurate description. Note that the number of relevant transverse modes depends only on \( R^2/(D\tau) \) and not on the cell thickness \( l \).

**B. Solution of the longitudinal diffusion problem**

It remains for us to determine the longitudinal modes \( \psi_j(z; \omega_j) \) and the corresponding eigenvalues \( \alpha_n \) of the reduced diffusion problem given by Eq. (24), Eq. (25), and Eq. (27) for \( \omega_j(z) > 0 \). For a general function \( \omega_j(z) \), numerical methods must be used to solve Eq. (24). However, for the thin cells used in the experiment, the Larmor frequency can be well approximated by a linear function,

\[
\omega_L(z) = \omega_L(0) + \alpha z, \quad (37)
\]

where \( \omega_L(0) \) is the Larmor frequency at the center of the cell, and \( \alpha = 2\pi\gamma\rho B(0)/\partial z \) is the Larmor frequency gradient, with \( \gamma = g_s \mu_B/(2I+1) h = 700 \text{ kHz/G} \) being the gyromagnetic ratio of the \(^{87}\text{Rb} \) atoms.

Experimentally, the magnetic field gradient is provided by a long thin magnet outside the cell, oriented along the \( x \) direction. We assume the \( B \) field is in the \( zx \) plane. Because the static magnetic field is rotation-free, a nonvanishing gradient of the holding field \( (B_x) \) along the \( z \) axis implies a gradient of the transverse field \( B_z \) along the \( x \) axis. We thus have \( \partial B_x(0)/\partial z = \partial B_z(0)/\partial x = \sigma/2 \pi \gamma \). The gradient in the transverse magnetic field leads to an additional line broadening of \( \approx 1 \text{ kHz} \). Therefore it is better to use larger holding fields as long as the splitting between different Zeeman components is insignificant.

Using Eq. (37) the general solution to Eq. (24) is a superposition of the two linearly independent Airy functions \( A(x) \) and \( B(x) \) [16],

\[
\psi_j(x = 2z/l; \omega_j) = a_n A(e_n - isx) - b_n B(e_n - isx), \quad (38)
\]

where

\[
s = \frac{1}{2}(\sigma l/D)^{1/3}, \quad (39)
\]

and the dimensionless eigenvalue \( e_n \) is related to \( \alpha_n \) through

\[
\alpha_n = (D\sigma^2)^{1/3} e_n + i\omega_L(0). \quad (40)
\]

The coefficients \( a_n, b_n \) and dimensionless eigenvalues \( e_n \) are determined by the boundary conditions of Eq. (25). Up to an overall normalization factor the boundary conditions for the front surface (–) imply that [17]

\[
a_n = B'(e_n + is) + [\bar{\mu}_+ + (e_n + is) \bar{\eta}_+] B(e_n + is),
\]

\[
b_n = A'(e_n + is) + [\bar{\mu}_- + (e_n + is) \bar{\eta}_+] A(e_n + is), \quad (41)
\]

with

\[
\bar{\mu}_s = \frac{1}{2s} \mu_s \quad \text{and} \quad \bar{\eta}_s = \frac{2s}{l} \eta_s. \quad (42)
\]

Requiring that both boundary conditions of Eq. (25) be satisfied implies that the \( e_n \) are solutions to the transcendental equation,
We note that for a polarized spin at site \( \mathbf{x} \), the spin on the cell surface hops to an adjacent interior site will be excluded in this binomial model. We found it useful to turn on the complex boundary conditions adiabatically and consider the flow \( \mathbf{e}_{n}(0,0,0,0) \rightarrow \mathbf{e}_{n}(\mu_{+},\mu_{-},\eta_{+},\eta_{-}) \) from the simpler case of vanishing flux at the boundary. This adiabatic procedure is numerically stable as long as the eigenvalues are well separated, but one has to resort to additional considerations when eigenvalues approach each other, i.e., near “level crossings.”

C. Derivation of the partial differential equation and boundary conditions using a binomial model for diffusion

In this section we derive the partial differential equation and boundary conditions satisfied by the average accumulated phase [Eq. (12)],

\[
g_{a_{t}}(\mathbf{y}, t) = \langle e^{-i\int_{0}^{t} g_{a}(\mathbf{y}, t')dt'} \rangle_{\mathbf{y}, t'},
\]

along diffusion paths that begin at \( \mathbf{x}_{0} = \mathbf{x} \) and reach \( \mathbf{x}_{t} = \mathbf{y} \) at time \( t \). As in Sec. III B, \( g_{a}(\mathbf{x}) \) is the linear function of \( z \) given by Eq. (37). Equation (44) thus has the form

\[
g_{a_{t}}(\mathbf{y}, t) = e^{-i\int_{0}^{t} g_{a}(\mathbf{y}, t')dt'} g_{a}(\mathbf{y}, t),
\]

with

\[
g_{a}(\mathbf{y}, t) = \langle e^{-i\int_{0}^{t} g_{a}(\mathbf{y}, t')dt'} \rangle_{\mathbf{y}, t'},
\]

We model the diffusion with a discrete isotropic binomial walk. The interior of the cell is represented by a regular cubic lattice of sites with spacing \( a \). Each site in the cell is thus labeled by a vector \( \mathbf{k} \) of integer components, with \( a \mathbf{k} = \mathbf{x}_{k} \) representing its position. In the discrete time interval \( \Delta t \), a polarized spin at an interior site is assumed to hop to any one of the \( 6 \) neighboring lattice sites with equal probability \( 1/6 \). (The possibility that the atom does not move during \( \Delta t \) is excluded in this binomial model.) Sites on the coating surface are taken to be a distance \( a_{s} \) from interior sites. To account for effects such as the finite thickness of coatings, \( a_{s} \), in general, may differ from the lattice spacing \( a \) in the interior. In the time interval \( \Delta t \), the probability that a polarized spin on the cell surface hops to an adjacent interior site will be denoted by \( p \); consequently, \( 1 - p \) is the probability that the polarized spin remains on the surface in this interval. The exit probability \( p \), therefore, is related to the mean sticking time \( \tau_{e} \) by

\[
\tau_{e} = \sum_{n=0}^{\infty} p(1 - p)^{n} \Delta t = \frac{1 - p}{p} \Rightarrow p = \frac{\Delta t}{\Delta t + \tau_{e}}.
\]

Note that this sticking time differs both conceptually and numerically [see Eq. (73)] from that defined by Masnou-Seeuws and Bouchiat [13].

To compute the expectation value in Eq. (44), one has to consider the phase \( e^{-i\phi_{k}} \) accumulated during the time interval \( \Delta t \) by a polarized spin at site \( \mathbf{k} \). If we decompose the vector \( \mathbf{k} = (x_{k}, y_{k}) \) into its transverse \((x, y)\) and longitudinal \((z)\) components, then, for any link pointing away from an interior site of the lattice, \( \phi_{k} = \sigma_{k} \Delta t \), i.e., the phase \( \phi_{k} \) depends only on the \( z \) component of the vector \( \mathbf{k} \). This is the case because we assume that the Larmor frequency has the simple form given in Eq. (37).

We take into account that owing to interaction with the coated cell walls, a polarized spin may relax or become unobservable with a probability differing from that in the bulk of the cell. The change in relaxation rate will be denoted by \( \delta \). We also include the possibility of a frequency shift \( \delta \omega \Delta t \) at surface sites due to interaction of the Rb atoms with the coating. Possible contributions to this frequency shift are (1) changes in the average Larmor frequency caused by the magnetic fields of protons in the coating [18], and (2) a change in the \( g \) factor of the ground state Rb atom induced by deformation of the Rb wave function while it is adsorbed. Note that additional phase accumulation due to the finite thickness of coatings occurs only in the presence of a magnetic field gradient.

By defining \( g_{k}(t) = g_{a}(\mathbf{k}, \mathbf{x}_{k}; t) \), where \( a \mathbf{k}_{0} \) is the position at time \( t = 0 \), one arrives at the following set of discrete equations,

\[
g_{a_{t}}(\mathbf{y}, t) = \sum_{j=k} g_{a_{t}}(\mathbf{y}, t) \omega_{jk}.
\]

where the complex weights \( \omega_{jk} \) for hopping from lattice site \( j \) at time \( t \) to the adjacent site \( k \) at time \( t + \Delta t \) depend only on the \( z \) components of the vectors and are given by

\[
\omega_{jk} = \begin{cases} 
\frac{(1 - p)}{4} \alpha_{e} \alpha_{s} \beta_{s}, & \text{if } k = j = N, \\
\frac{(1 - p)}{4} \alpha_{e} \alpha_{s} \beta_{s}, & \text{if } j = k + 1 = N, \\
\frac{1}{6} \alpha_{e}, & \text{if } -N < j < N, \\
\frac{1}{6} \alpha_{e}, & \text{if } -N < j = N, \\
\frac{1}{6} \alpha_{e} \beta_{s}, & \text{if } k = -1 = N, \\
\frac{1}{6} \alpha_{e} \beta_{s}, & \text{if } k = -N, \\
0, & \text{in all other cases}.
\end{cases}
\]

Here \( k = \pm N \) corresponds to lattice sites on the back and front surfaces at \( z = \pm t/2 \) of the cylindrical cell, i.e., \( (N-1)a + a_{s} = l/2 \). In Eq. (49) we have introduced factors

\[
\alpha_{e} = e^{-i\alpha_{e} \Delta t}, \\
\alpha_{s} = e^{-i\alpha_{s} \Delta t},
\]

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\[ \beta_s = e^{-(\delta s + \delta a)\Delta t}. \]  

(52)

Note that \( \beta_s \) is associated with the phase accumulation and relaxation due to surface interactions at the back and front surfaces, and \( \alpha_s \) is associated with an additional phase shift \( \sigma(a_s - a) \) at surface sites because these sites are assumed to be at a distance \( a_s \) from the bulk.

In the continuum limit the problem separates in cylindrical coordinates. To first order in \( \Delta t \) the discrete model also separates. This can be shown as follows. Writing \( g_k(t) = g_{k_\perp}(t)g_{k_z}(t) \) we have that

\[ g_{k_\perp}(t + \Delta t) = g_k(t)[g_{k_\perp}(t + \Delta t) - g_{k_\perp}(t)] \]

\[ + g_{k_\perp}(t)g_k(t + \Delta t) + O(\Delta t^2), \]

(53)

and Eq. (48) becomes

\[ g_k(t + \Delta t) = g_k(t)\omega_{kk} \sum_{j \sim k_\perp} g_{j_\perp}(t) + g_{k_z}(t) \sum_{j \sim k_z} g_j(t)\omega_{jk} \]

\[ = g_k(t)\omega_{kk} \sum_{j \sim k_\perp} [g_{j_\perp}(t) - g_{k_\perp}(t)] \]

\[ + g_{k_\perp}(t)\left(4g_k(t)\omega_{kk} + \sum_{j \sim k_z} g_j(t)\omega_{jk}\right) \]

The last assertion in Eq. (54) follows from the fact that \( \sum_{j \sim k_\perp} [g_{j_\perp}(t) - g_{k_\perp}(t)] = O(a^2 - \Delta t) \) for a diffusion process, and \( \omega_{kk} = \frac{1}{6} + O(\Delta t) \). A comparison with Eq. (52) reveals that motion in the transverse direction is described by a simple random walk,

\[ g_{k_\perp}(t + \Delta t) = \begin{cases} 
\frac{1}{3} g_{k_\perp}(t) + \frac{1}{6} \sum_{j \sim k_\perp} g_{j_\perp}(t), & \text{for } k_\perp \in \text{cell}, \\
0, & \text{for } k_\perp \notin \text{cell},
\end{cases} \]

(55)

and the motion in the \( z \) direction is described by

\[ g_{k_z}(t + \Delta t) = 4\omega_{kk}g_k(t) + \sum_{j} \omega_{jk}g_j(t). \]

(56)

Equation (56) denotes the following set of trinomial equations,

\[
\begin{align*}
g_k(t + \Delta t) &= \alpha^k \left( \begin{array}{l}
\frac{1}{6} g_{N+1}(t) + (1 - p)\alpha \beta_s g_N(t), \\
p \alpha \beta_s g_N(t) + \frac{1}{6} g_{N-2}(t) + \frac{2}{3} g_{N-1}(t), \\
\frac{1}{6} g_{N+1}(t) + \frac{1}{3} g_{N+2}(t) + \frac{2}{3} g_{N-1}(t), \\
\frac{1}{6} g_{N+1}(t) + (1 - p)\beta_s g_{N-1}(t), \\
\frac{1}{6} g_{N+1}(t) + \frac{1}{3} g_{N+2}(t) + \frac{2}{3} g_{N-1}(t), \\
\frac{1}{6} g_{N+1}(t) + (1 - p)\beta_s g_{N-1}(t), \\
\end{array} \right),
\end{align*}
\]

(57)

To first order in \( \Delta t \) and lowest (quadratic) order in the lattice spacing \( a \), Eq. (55) corresponds to free and isotropic two-dimensional diffusion,

\[ \frac{\partial}{\partial t} g_{k_\perp}(x_\perp, t) = D_{k_\perp} \Delta_{k_\perp} g_{k_\perp}(x_\perp, t), \]

(58)

where \( \Delta_{k_\perp} \) is the two-dimensional Laplace operator in the transverse directions and the effective diffusion constant of the model is

\[ D = \frac{a^2}{6\Delta t}. \]

(59)

Neglecting spin relaxation and any additional phase shifts at the coated cylindrical boundary of the cell, we can solve Eq. (58) with Neumann boundary conditions at \( \rho = R \), which in cylindrical coordinates \( (\rho, \theta, z) \) is

\[ \left. \frac{\partial}{\partial \rho} g_{k_\perp}(\rho, t) \right|_{\rho = R} = 0. \]

(60)

The dynamics of greater interest is in the longitudinal direction, i.e., along the \( z \) axis. One cannot directly cast the set of discrete equations of Eq. (57) in differential form because interpolation between the boundary layer at \( k = \pm N \) and the bulk with \( |k| < N \) is not smooth when \( a \) and \( \Delta t \) vanish while \( a^2/\Delta t \) remains finite. Numerical simulation of Eq. (57)
confirms that the density of polarized Rb atoms in this model generally is discontinuous at the boundary. We can circumvent this problem by replacing the model values \( \bar{g}_k(t) \) by fictitious ones that smoothly interpolate toward the cell faces. The field \( \bar{g}_k(t) \) that achieves this and coincides with \( g_k(t) \) in the bulk is given by

\[
\bar{g}_k(t + \Delta t) = \alpha^{k}\begin{cases} 
(1 - p)\alpha_k \beta_k \bar{g}_k(t) + \frac{p \alpha_k \beta_k}{\alpha} \bar{g}_{k-1}(t), & \text{if } k = N, \\
\frac{\alpha}{6} \bar{g}_{k+1}(t) + \frac{1}{6\alpha} \bar{g}_{k-1}(t) + \frac{2}{3} \bar{g}_k(t), & \text{if } |k| < N, \\
(1 - p)\frac{\beta_k}{\alpha_k} \bar{g}_{k+1}(t) + \frac{p \beta_k}{\alpha_k} \bar{g}_{k-1}(t), & \text{if } k = -N.
\end{cases}
\]  

One can now derive the diffusion equation and boundary condition to which this discrete model corresponds by positing a twice differentiable smooth function \( g(z,t) \), which coincides with the field \( \bar{g}_k(t) \) at all mesh points of the (now everywhere regular) lattice, that is, with \( g(ka,t) = \bar{g}_k(t) \), for all \( |k| \leq N \). Expanding Eq. (62) to first order in \( \Delta t \) and noting that the exit probability \( p \) in Eq. (47) is itself of order \( \Delta t \), one obtains

\[
\frac{\partial}{\partial t} g(z,t) = \begin{cases} 
-i\sigma \bar{g}(z,t) - i\delta \omega - \delta_\xi, & \text{for } z = \frac{-l}{2}, \\
D \frac{\partial^2}{\partial z^2} g(z,t) - i\sigma g(z,t), & \text{for } |z| < \frac{-l}{2}, \\
i\sigma \bar{g}(z,t) + i\delta \omega - \delta_\xi, & \text{for } z = \frac{+l}{2}, \\
\frac{\partial}{\partial z} g(z,t) + \frac{a}{\tau_z} \bar{g}(z,t), & \text{for } z = \frac{+l}{2},
\end{cases}
\]  

where \( l/2 = l/2 + a \). In Eq. (63) the diffusion constant \( D \) is again the ratio of the model parameters given in Eq. (59) and we have retained terms of order \( a^2/\tau_z \) while ignoring corrections of order \( a^3 = 6D\Delta t \). Note that the boundary conditions of Eq. (63) are not at \( z = \pm l/2 \), where the surface of the coating is, but are imposed at \( z = \pm l/2 \), which is at a distance \( a - a \), beneath the coating surface. Thus \( a - a \), could be interpreted as the effective coating thickness in this model. The continuity of \( \partial g(z,t)/\partial t \) at \( |z| = l/2 \) yields boundary conditions of the form given in Eq. (25). 

\[
\pm \frac{\partial}{\partial z} g(z,t) + \mu g(z,t) + \eta g(z,t) \bigg|_{z = \frac{-l}{2}} = 0,
\]  

with 

\[
\eta = \frac{D}{a} \frac{1}{\tau_z} \bigg|_{z = \frac{-l}{2}} \quad \text{and} \quad \mu = \frac{1}{a} (\xi + i\phi), \bigg|_{z = \frac{-l}{2}} \]  

Here \( \xi = \delta_\xi a \), is the average relaxation probability and \( \phi = \delta_\phi (a - a) \), the average phase accumulated during the dwell time \( \tau_z \) on the front (–) or back (+) surfaces of the cylindrical cell. In principle, we can allow the front and back surfaces to have different properties, i.e., different values of \( \tau_z \), \( \xi \), and \( \phi \). For a physical interpretation of the lattice spacing \( a \), we note that in this model, a spin is assumed to move with equal probability to any of six adjacent lattice sites in the time interval \( \Delta t \). The mean speed of a Rb atom, therefore, is simply

\[
\bar{v} = a / \Delta t.
\]  

Since the diffusion constant expressed by the average speed \( \bar{v} \) and mean free path \( \lambda \) of the atoms is \( D = \lambda \bar{v}/3 \), Eq. (59) and Eq. (66) relate the lattice spacing \( a \) of this discrete model to the mean free path of Rb atoms in the bulk as

\[
a = 2\lambda.
\]  

Equation (63) thus implies that \( g(z,t) \) satisfies the partial differential equation

\[
\frac{\partial}{\partial t} g(z,t) = D \frac{\partial^2}{\partial z^2} g(z,t) - i\sigma g(z,t)
\]  

with boundary conditions given by Eq. (64) and the initial condition
g(z,0)=δ(z−z0). \quad (69)

The parameters \( \mu_a \) and \( \eta_a \) in Eq. (64) are determined by the average microscopic properties of the surface and the gas,

\[
\eta_a = \left. \frac{\tau D}{2\lambda} \right|_{z=\lambda/2} = \left. \frac{\tau \tilde{\vartheta}}{6} \right|_{z=\lambda/2} \\
\mu_a = \left. \frac{1}{2\lambda} (\xi_i + i\phi_i) \right|_{z=\lambda/2}.
\]

Neither the average phase shift \( \phi \) nor the relaxation probability \( \xi \) of an adsorbed spin polarized Rb atom have been studied much. Both parameters may depend strongly on the quality, thickness, and type of coating. Estimates of the sticking time \( \tau \) for different coats and atoms range from \( \tau \sim 10^{-9} \) s for Rb on paraffin coated surfaces [13] to \( \tau \sim 10^{-5} \) s for \( ^{129}\text{Xe} \) on Surfassil-coated surfaces [19]. In our experiment, a representative value of \( \tau_a \) for Rb atoms on Surfassil-coated Pyrex glass surfaces is \( \sim 1 \) \( \mu \)s. Studying the line shape of the magnetic resonance lines of an evanescent wave magnetometer in the presence of a magnetic field gradient thus might yield interesting information on the parameters that characterize the interaction of the electronic spin with the coated cell surfaces [20].

Mixed boundary conditions with \( \eta = 0 \) were used by Maxwell to describe the phenomenon of viscous slip [21]. The same boundary conditions for diffusion (with \( \sigma = 0 \)) were used by Masnou-Seeuws and Bouchiat to describe Rb surface interactions in spherical paraffin-coated cells [13]. Similar boundary conditions, but with the normal gradient coefficient \( \mu \) being treated as an operator, were used to describe coherent quadrupole surface interactions of \( ^{131}\text{Xe} \) [14]. The term proportional to the second normal derivative in Eq. (64) was ignored by Masnou-Seeuws and Bouchiat in their study of the interactions of Rb atoms with paraffin-coated glass surfaces [13]. This was justifiable because their measured dwell time \( \tau \) was far too short for this correction to be relevant. For sufficiently short dwell times and \( \sigma = \phi = 0 \), one can in fact use Eq. (68) to replace the second derivative term in the boundary condition of Eq. (64) by the time derivative. Equation (64) can then be rewritten as a relation between time-delayed polarized spin fluxes \( J_\perp \) and \( J_\parallel \) which enter and leave the surface,

\[
J_\perp(t+\tau_a)=\left(1-\alpha_i\right)J_\perp(t), \quad (71)
\]

where \( \alpha_i \) is the relaxation probability of Rb atoms on the surface as defined in [13]. Its relation to \( \xi_i \) is given by

\[
\xi_i = \frac{3\alpha_i}{2-\alpha_i}, \quad (72)
\]

and \( \tau_a \) is the dwell time as defined in [13], related to \( \tau \) through the expression

\[
\tau_a = \frac{2-\alpha_i}{3} \tau. \quad (73)
\]

We also note the following relation between the quantities used by Masnou-Seeuws and Bouchiat [13] and those defined here, \( \alpha_i/\tau_a^B=\xi_i/\tau=\delta \xi \). The main difference between our description and theirs lies in the definition of the sticking times \( \tau_a^B \) and \( \tau_a \). We assumed a Poisson process in which a Rb atom leaves the surface in any equal time interval with equal probability, and \( \tau_a \) is the average sticking time of the Poisson distribution. Masnou-Seeuws and Bouchiat, on the other hand, used a model in which the spin-polarized Rb atoms, on average, leave the surface after a relatively sharp time delay \( \tau_a^B \), such that Eq. (71) is satisfied.

Note that for a positive sticking time \( \tau_a \), the second derivative term in the boundary condition, Eq. (64), also gives rise to a meniscuslike increase in the equilibrium density near the cell surfaces. For sizable “sticking” this surface effect could, perhaps, be observed in an evanescent-wave magnetometer.

**D. Some limiting cases**

We shall now consider some physically interesting limiting cases of Eq. (68) with boundary conditions Eq. (64). The dynamics is considerably simpler in the following situations: (1) when the lowest diffusion modes are localized near the front or back surface, and, therefore, one of the boundary conditions can be moved to \( z=\pm \infty \) with impunity, and (2) when the term proportional to \( \delta \) in Eq. (68) may be ignored, i.e., the magnetic field gradient is small. The relevant dimensionless parameter that governs these limits is the scale \( s \) defined in Eq. (39).

### 1. Localized modes

The localized modes can be analyzed most easily in the special case \( \eta_a=\mu_a=0 \), where analytical solutions are available. For \( \eta_a=\mu_a=0 \) and \( s > \sqrt{\frac{3}{2}} \beta^2/3-1 \) [see Eq. (39)], the lowest eigenmodes of Eq. (68) are localized at one of the two faces of the cell. The corresponding eigenvalues are complex conjugate to each other. Thus \( s > 1 \) corresponds to the case where one of the boundaries may essentially be ignored. The eigenfunctions come in conjugate pairs \( \psi_i^a(z) = \psi_i^\ast(-z) \) and can be approximated by Airy functions localized at the front (−) and back (+) surfaces of the cell, respectively.

Localized modes correspond to eigenfunctions that are vanishingly small at the distant surface. The asymptotic behavior of the derivatives of the Airy functions for large imaginary values of their argument \( \text{lim}_{y \to -\infty}B'(a \pm ib)/A'(a \pm ib) \sim \pm i \) implies that localized eigenfunctions to Eq. (68) are of the form [see Eq. (38) and Eq. (41)]

\[
\psi_i^a(z) \propto A(e_n^a - 2izs/l) \pm iB(e_n^a - 2izs/l) \propto A[(2isz/l - e_n^a) e^{i\pi/3}]. \quad (74)
\]

The last expression stems from the identity \( A(y) = iB(y) = 2e^{a+i\pi/3}A(y e^{+7\pi/3}) \) [16]. The corresponding pair of complex conjugate eigenvalues \( e_n^a = e_n^\ast \) is found by requiring that the eigenfunctions of Eq. (74) also satisfy the boundary condition at the surface near which they are localized. For no flux boundary conditions one has


\[ e^{\pm i\pi/3} = \frac{\sqrt{3}}{2} \pm i \frac{1}{2} \left( \frac{\sigma}{D} \right)^{1/3} \],

(75)

where \{-z_n; n=0, 1, 2, \ldots\} are the real roots of the first derivative of the Airy function. To a good approximation, these are asymptotically given by \[ z_n = \frac{3\pi}{2} \left( n + \frac{1}{4} \right)^{2/3}, \quad n = 0, 1, 2, \ldots . \]

(76)

Equation (75) provides the criterion that complex conjugate pairs of localized states occur only when

\[ z_n < \frac{l}{\sqrt{3}} \left( \frac{\sigma}{D} \right)^{1/3} = \frac{2s}{\sqrt{3}} \text{ or } n < \frac{4\sqrt{2}}{3^{7/4}\pi} - 1 . \]

(77)

Setting \( n=0 \) in the last expression, we find that for ideal cell walls (\( \eta_k = \mu_s = 0 \)), localized states can occur only for \( s > \frac{\sqrt{3}}{2} (l_3)^{2/3} \sim 1 \).

2. Nonlocalized modes

When \( s < 1 \), there is no strong localization at either cell wall. For \( \sigma=0 \), the problem reduces to the diffusion between two boundaries that are a distance \( l \) apart. In this technically interesting case, the diffusion modes for symmetrical boundaries with \( \eta_k = \mu_s = \eta \) and \( \mu_s = \mu_s = \mu \) are proportional to \( \cos(kx) \) and \( \sin(kx) \). They correspond to eigenvalues \( \alpha_n(\sigma=0) = Dk_n^2 \). Substituting in Eq. (64), we find the wave numbers \( k_n = 2\eta/s \) to be the solution of

\[ \tan\left( \frac{x_n - \frac{\pi}{2}}{n \frac{\pi}{2}} \right) = \frac{1}{2} \frac{\eta}{\frac{2}{x_n}} \]

with \( (n-1)\pi < x_n < (n+1)\pi \); \( x_0 > 0 \).

(78)

Graphical analysis of Eq. (78) shows that for \( l_3^2 \mu > \eta \pi^2 \) the next-to-smallest wave number \( k_1 \) has a value \( k_1 > \pi/\lambda \). For cells with \( \xi_0/\tau_s > D_0^2/\mu^2 \Gamma > \Gamma \), higher diffusion modes with \( n > 0 \) thus too broad to contribute significantly. However, the lowest wave number \( k_0 \) depends upon the boundary condition, Eq. (64), in an interesting and nontrivial way. We estimate it by expanding the tangent in Eq. (78) for small values of \( x_0 \). To leading order, the lowest eigenvalue in this approximation is

\[ \alpha_0(\sigma=0) = Dk_0^2 \sim \frac{\bar{v}(\xi_0 + i\phi_s)}{3l + \tau_s \bar{v}} . \]

(79)

Thus, the increase in the linewidth of an ultrathin cell due to surface interactions in a homogeneous magnetic field is given by

\[ \delta \Gamma = \text{Re}(\alpha_0) \sim \frac{\bar{v}\xi_0}{3l + \tau_s \bar{v}} . \]

(80)

Note that this increase does not depend upon the mean free path \( \lambda \). Equation (80) remains valid even when the mean free path \( \lambda \) exceeds \( l \), as long as \( s + l(\sigma/D)^{1/3} / 2 < 1 \) is satisfied. The dependence of Eq. (80) on cell thickness and temperature possibly allows one to measure \( \tau_s \) and \( \xi_0 \) directly in ultrathin cells. However, the phase shift \( \phi_s \) cannot be determined from the line shape of ultrathin cells.

In deriving Eq. (80) we have assumed \( \sigma=0 \). To first order, a nonzero \( \sigma \) does not broaden or shift the line and our analysis of the line broadening for ultrathin cells remains valid as long as the field gradient is small enough for the phase change due to the field gradient being neglected; that is, \( \Delta \phi \sim \Delta \omega_0 \Delta t \sim (\sigma l^2)/D = 8s^3 < 1 \) rad.

From a theoretical point of view it is also interesting to consider the limit of Eq. (36) in which the rf modulation frequency \( \Omega \) vanishes. Although this limit cannot be realized experimentally because the lock-in amplifier must average over at least one cycle, the signal shape would not depend on the type of modulation, making this theoretical limit “universal” in this sense. In practice, the observed signal becomes essentially independent of the modulation frequency and approaches the limiting steady state when \( \Omega < 1/\tau \). At modulation frequencies that exceed the homogeneous linewidth, separate sideband peaks are observable. These depend on the type of modulation used. For example, simple beating produces only two peaks separated by \( \Omega \), while square wave modulation results in three peaks separated by \( \Omega \). Most of the experiments were carried out at intermediate modulation frequencies \( 1/\tau < \Omega < \Gamma \), where some influence of the modulation on the width and shape of the peaks was observable but sidebands were not resolved.

E. Discussion

In the following, we compare the theoretical model to our experimental data. A more detailed experimental investigation will be presented elsewhere [20]. Figures 2 and 3 show two representative EPR curves of the evanescent wave magnetometer in the presence of a magnetic field gradient \( (\sigma/2\pi) = 400 \text{ kHz/cm} \) that show nonlocalized and localized modes. The data in Fig. 2 was obtained with a 0.15-mm thick cell filled with 5 Torr \( N_2 \) as a buffer gas. The relevant scale parameter \( s \) [defined in Eq. (39)] has the value \( s = 0.33 < 1 \) and the response of this cell has a single peak showing no
localization. Figure 3 shows the response of a 0.8 mm thick cell filled with N\textsubscript{2} buffer gas at 5 Torr and a temperature of 105 °C. Dots represent experimental data (with insignificant statistical error). The data is best reproduced by Eq. (36) (solid line) with \( 1.7 \mu \text{s}, \xi = 10 \text{ mrad}, \phi = 27 \text{ mrad} \). Two resolved localized peaks are clearly visible. The dashed and dotted lines correspond to theoretical response curves assuming dwell times of 0.7 \( \mu \text{s} \) and 2.7 \( \mu \text{s} \), respectively, all other parameters remaining unchanged. All calculated line shapes are normalized to the height of the first peak. Note that as the dwell time increases, the central frequencies of the localized peaks shift closer toward those corresponding to the front and back surfaces.

To demonstrate the sensitivity of the theoretical curves to changes in the surface parameter \( \xi \), we focus on the EPR in Fig. 3. The experimental data is best reproduced with a dwell time \( 1.7 \mu \text{s} \) of the Rb atom on the Surfasil-coated Pyrex surface and a spin disorientation probability \( \xi = 10 \text{ mrad} \) and phase shift \( \phi = 27 \text{ mrad} \) while it is adsorbed. In addition to our best fit to the data, Fig. 3 also shows two curves calculated for less optimal values of \( \tau \). The sensitivity of the theoretical description to surface parameters \( \xi \) and \( \phi \) can be observed in Fig. 4 and Fig. 5.

In Fig. 6 we plot the half-width in kHz of the homogeneous side of the front surface peak against \( (\sigma D)^{1/3} / 2\pi \) for three Surfasil-coated cells. The cells contain N\textsubscript{2} as a buffer gas at various pressures.

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**FIG. 3.** The EPR curve of a 0.8-mm thick Surfasil-coated cell filled with N\textsubscript{2} buffer gas at 5 Torr and a temperature of 105 °C. Dots represent experimental data (with insignificant statistical error). The data is best reproduced by Eq. (36) (solid line) with \( 1.7 \mu \text{s} \), \( \xi = 10 \text{ mrad} \), and \( \phi = 27 \text{ mrad} \). Two resolved localized peaks are clearly visible. The dashed and dotted lines correspond to theoretical response curves assuming dwell times of 0.7 \( \mu \text{s} \) and 2.7 \( \mu \text{s} \), respectively, all other parameters remaining unchanged. All calculated line shapes are normalized to the height of the first peak. Note that as the dwell time increases, the central frequencies of the localized peaks shift closer toward those corresponding to the front and back surfaces.

**FIG. 4.** Sensitivity of the theoretical line shape to change in the surface relaxation parameter \( \xi \). The data (dots) is the same as in Fig. 3. Dashed and dotted lines correspond to \( \xi = 5 \text{ mrad} \) and \( \xi = 15 \text{ mrad} \), respectively, with all other parameters remaining unchanged.

**FIG. 5.** Sensitivity of the theoretical line shape to change in the frequency shift \( \phi \). The data (dots) is the same as in Fig. 3. Dashed and dotted lines correspond to \( \phi = 14 \text{ mrad} \) and \( \phi = 40 \text{ mrad} \), respectively, with all other parameters remaining unchanged. Note that, in this example, with a larger magnetic field at the back surface, a positive (equal for both surfaces) phase shift \( \phi \) enhances the front surface peak and shifts it to higher frequencies, i.e., away from the front surface.

**FIG. 6.** The half-width at half maximum \( \Delta \omega / 2\pi \) of the Lorentzian side of the magnetic resonance curve as a function of \( (\sigma D)^{1/3} / 2\pi \) for three Surfasil-coated cells. The cells contain N\textsubscript{2} as a buffer gas at various pressures.
We have presented a theoretical model that quantitatively describes the magnetic resonance lines of an evanescent wave magnetometer in a magnetic field with gradient under a variety of experimental conditions. The unique feature of these magnetic resonance lines is that they consist of two peaks localized in frequency space near the front and back surfaces of the cell when \( s = \frac{I}{2} \). This localization of the magnetic resonance response is not generally associated with any physical localization of the Rb atoms near the surfaces and is not observable for \( s < 1 \). The localized peaks can be used to study surface interactions of spin polarized alkali-metal atoms. The line shape of the electron paramagnetic resonances depends on nine parameters: the thickness of the cell \( l \sim 1 \) mm, the Larmor frequency gradient \( 200 \text{ kHz/cm} < \sigma/2\pi < 700 \text{ kHz/cm} \), the rf modulation frequency \( \Omega/2\pi \sim \text{a few hundred Hz} \), the line width in the homogeneous magnetic field \( (\Gamma/2\pi) \sim 1 \text{ kHz} \), the mean thermal velocity of Rb atoms \( v \sim 3 \times 10^4 \text{ cm s}^{-1} \), the mean-free path of Rb atoms in the N\(_2\) buffer gas \( \lambda \sim 1 - 30 \mu \text{m} \), the average dwell time of Rb atoms on the coated-glass surface \( \tau \sim 1.7 \times 10^{-6} \text{ s} \), the probability of disorientation of the Rb atom \( \xi \sim 10 \text{ mrad} \), and the average phase shift of the Rb atom while it is adsorbed on the surface \( \phi_s \sim 27 \text{ mrad} \). The numerical values of the parameters in parenthesis are representative of the experimental data shown in Fig. 3.

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[17] For modes that are small at the front face, it is numerically advisable to solve the boundary conditions at the back face.