Simple Solutions of the Torrey–Bloch Equations in the NMR Study of Molecular Diffusion

V. M. Kenkre, Eiichi Fukushima,[1] and D. Sheltraw

Center for Advanced Studies, Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

A simple technique for solving the Torrey–Bloch equations appearing in the calculation of the NMR signal under gradient fields is presented. It is applicable to arbitrary time dependence of the gradient field to arbitrary initial distribution of spins, and to spin motion on discrete lattices as well as in the continuum under conditions of unrestricted diffusion. Known results are recovered as particular cases and new results are presented. The discrete lattice results are shown to be similar to known results for restricted diffusion in the continuum. Also presented is a surprising equivalence between results for a simple two-site hopping model and earlier expressions for the NMR signal for spins undergoing restricted diffusion in a continuum. © 1997 Academic Press

1. INTRODUCTION

There has been a recent revival of interest in pulsed gradient and constant gradient NMR studies of nuclear spins in unconfined as well as confined geometries. The aims of these studies are varied. The externally applied gradient can provide information about the diffusion coefficient. Alternatively, if the diffusion coefficient is known, one may obtain information about the confinement of the diffusing particles (*1*). Externally applied gradients have also been used to provide useful diffusion-related contrast in magnetic resonance imaging (*1–4*).

The purpose of this paper is to present some alternative methods of solving the Torrey–Bloch equations in order to derive expressions for the NMR signal containing explicit information about the diffusion of spins, their initial distribution, and, where applicable, their confinement. The results we present include exact calculations under the condition of no confinement and approximate calculations for confined geometry, i.e., restricted diffusion. They have the advantage that the solutions are available for arbitrary time dependence of the applied gradient and for arbitrary initial spin distribution. We first present a useful transformation technique which allows us to obtain exact solutions for the NMR signal

in unconfined geometry. We obtain an expression for the signal which contains explicit information about the initial distribution of spins and show that it reduces to well-known expressions in particular cases. For instance, we show that the contribution of the initial spin distribution factor cancels for a bipolar pulse experiment such as the usual Stejskal–Tanner diffusion experiment. We apply our result to relatively new situations such as a slow turn-on of the gradient, sinusoidal gradient, and also calculate the time dependence of the signal that would arise in nonstandard experiments which would be sensitive to nonuniform initial magnetization density such as the Gaussian and the square distribution. We give a generalization of our transformation technique to spin motion in *discrete* space as among Wannier states in a lattice and examine particular cases of our result. Finally, we analyze confined systems through an exact solution of a representative two-state system which we find, surprisingly, to be completely equivalent, or simply related, to earlier analysis (*5–7*).

2. EXACT SOLUTIONS IN THE CONTINUUM

The Torrey–Bloch equation for the magnetization density $M(\mathbf{r}, t)$ arising from spins diffusing with diffusion coefficient D and an arbitrary time-dependent linear gradient field is (*8*)

$$\frac{\partial M(\mathbf{r}, t)}{\partial t} = -igf(t)xM(\mathbf{r}, t) + D\nabla^2 M(\mathbf{r}, t), \quad [1]$$

where g denotes the product of the gyromagnetic ratio γ and the gradient strength, the gradient field has the temporal shape function $f(t)$ and is taken to be in the x direction, and $\mathbf{r}$ is the position vector of the spin. For motion in one dimension Eq. [1] becomes

$$\frac{\partial M(x, t)}{\partial t} = -igf(t)xM(x, t) + D\frac{\partial^2 M(x, t)}{\partial x^2}. \quad [2]$$

Our method of solution consists of obtaining and solving

[1] Also the Lovelace Institutes, 2425 Ridgecrest Dr. S.E., Albuquerque, NM 87108.

the equation obeyed by the spatial Fourier transform $M(k, t)$ of Eq. [2]. The definition of the Fourier transform is

$$\hat{M}(k, t) = \int_{-\infty}^{\infty} M(x, t)e^{-ikx}dx. \qquad [3]$$

From Eq. [2], the evolution equation for Fourier-transformed magnetization density is

$$\frac{\partial \hat{M}(k, t)}{\partial t} = gf(t)\frac{\partial \hat{M}(k, t)}{\partial k} - Dk^2\hat{M}(k, t). \qquad [4]$$

To solve Eq. [4], we employ the transformation

$$J(k, t)$$
$$= \hat{M}(k, t)\exp\left\{D\int_0^t dt'\left(k + g\int_{t'}^t f(s)ds\right)^2\right\} \qquad [5]$$

and obtain, for the evolution of the transformed quantity $J(k, t)$, the simple one-sided wave equation in k space:

$$\frac{\partial J(k, t)}{\partial t} = gf(t)\frac{\partial J(k, t)}{\partial k}. \qquad [6]$$

It is trivial to solve Eq. [6] since it results in the ballistic displacement of the initial k dependence of $J(k, 0)$ at the time-dependent velocity $gf(t)$. The solution of [6] is, thus,

$$J(k, t) = J\left(k + g\int_0^t f(s), 0\right), \qquad [7]$$

where the right-hand side equals the initial displacement with the k replaced by $k + g\int_0^t f(s)ds$. According to the transformation given by Eq. [5], we obtain the explicit solution for the magnetization in k space to be

$$\hat{M}(k, t) = \hat{M}\left(k + g\int_0^t f(s)ds, 0\right)$$
$$\times \exp\left\{-D\int_0^t dt'\left(k + g\int_{t'}^t f(s)ds\right)^2\right\}. \qquad [8]$$

While it is a straightforward matter in principle to invert Eq. [8] to obtain $M(x, t)$, it is convenient to notice that $M(t)$, the NMR signal normalized to its initial value, is given by

$$M(t) = \int_{-\infty}^{\infty} M(x, t)dx = \lim_{k\to 0} \hat{M}(k, t) \qquad [9]$$

as is evident from Eq. [3]. Thus, the NMR signal can be obtained without performing the inversion of the Fourier transform, and we are able to write, directly from Eq. [8],

$$M(t) = \hat{M}\left(g\int_0^t f(s)ds, 0\right)$$
$$\times \exp\left\{-D\int_0^t\left(g\int_{t'}^t f(s)ds\right)^2 dt'\right\}. \qquad [10]$$

Equation [10] is a general result for the NMR signal as it develops in the presence of a time-dependent magnetic field gradient. Our derivation above is simple and transparent. The expression obtained contains two factors. The second (exponential) factor is identical to the signal obtained in past derivations (*4, 9*). The preexponential factor in our expression describes the effect of the initial distribution of spins. This distribution affects the dephasing of the spins in the presence of the magnetic field gradient. We see that it is independent of the spin diffusion constant. In a standard pulsed gradient spin echo experiment, one arranges for complete rephasing of spins to occur, i.e., for the time integral of $f(t)$ to vanish. It is obvious from Eq. [10] that the preexponential factor we display is of no importance to such experiments. However, the factor is of value in the context of observations in which complete rephasing is not utilized. A possible example is the situation where the diffusion constant is known and the initial magnetization density is under investigation.

Equation [10] is implicit in earlier analyses in the literature. Relatively little use has been made, however, of its ability to predict the NMR signal for arbitrary time dependence of the gradient. Furthermore, the effect of nonuniform magnetization density, which is treated easily from our result Eq. [10], appears not to have been analyzed earlier. Therefore, we present a few examples of the application of Eq. [10] to demonstrate its versatility.

Case (i): Time-Dependent Turn-on of the Gradient

Because we are not interested in this case in the effect of the preexponential factor, we will take the initial placement of the spin to be localized so that $M(k, 0) = 1$. Our interest is in describing the result of a slow turn-on of the gradient field. We model the time dependence of the turn-on through $f(t) = (1 - \exp(-t/\tau))$, where τ is the turn-on time. We obtain from Eq. [10]

$$M(t) = \exp(-Dg^2t^3/3)\exp[-Dg^2\tau^3 h(t/\tau)], \qquad [11]$$

where the function h is given by

$$h(t/\tau) = (t/\tau + 3/2)e^{-2t/\tau}$$
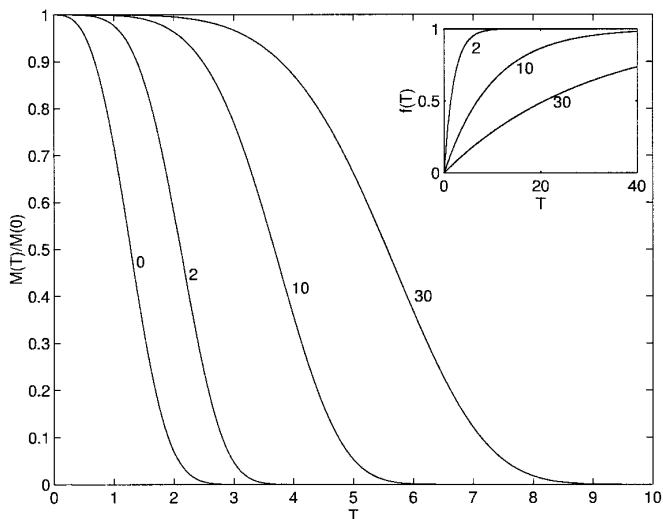$$+ [(t/\tau)^2 - 4]e^{-t/\tau} + (5/2 - 2t/\tau). \qquad [12]$$

FIG. 1. The NMR signal $M(t)/M(0)$ for the slow turn-on case $f(t) = (1 - \exp(-t/\tau))$ as a function of the dimensionless time $T = t(Dg^2)^{1/3}$. The four curves are labeled by the respective values (0, 2, 10, and 30) of the parameter $\tau(Dg^2)^{1/3}$ which is the ratio of the turn-on time of the applied gradient to the magnetization decay time for the full applied gradient. The time dependence of the applied gradient is shown in the inset.

Notice that the slow turn-on process introduces a multiplicative factor into the signal which results in a relative period of quiescence of the signal. An expansion of $h(t/\tau)$ in ascending powers of its argument shows that the constant, linear and quadratic terms in the expansion vanish identically. This corresponds to the quiescence. The larger the turn-on time τ, the larger the period of quiescence. This is shown in Fig. 1 where the signal is plotted for several values of the dimensionless parameter $(Dg^2)^{1/3}\tau$ which equals the ratio of the gradient turn-on time τ to the magnetization decay time $(Dg^2)^{-1/3}$ in the presence of the full gradient. The leftmost curve represents a sudden turn-on ($\tau = 0$).

Case (ii): Sinusoidal Gradient

The case of sinusoidal gradients is of relevance to recent experiments performed by Callaghan and Stepisnik (*10*) to analyze the frequency dependence of coherent and incoherent motion of spins. We consider two cases of a sinusoidal gradient. For $f(t) = \cos \omega t$, we get, for the same initial condition as in case (i),

$$M(t) = \exp\{-(Dg^2/\omega^3)[\omega t - (\omega t/2)\cos 2\omega t$$
$$+ (3/4)\sin 2\omega t - 2 \sin \omega t]\}, \qquad [13]$$

whereas, for $f(t) = \sin \omega t$, we get

$$M(t) = \exp\{-(Dg^2/\omega^3)(\omega t + (\omega t/2)\cos 2\omega t$$
$$- (3/4)\sin 2\omega t)\}. \qquad [14]$$

Figures 2a and 2b show the time dependence of the signals given by Eq. [13] and Eq. [14], respectively, for various values of the quantity $(Dg^2)^{1/3}/\omega$ which is the ratio of the gradient period to the magnetization decay time. In both cases, the oscillating fields give rise to extrema in the signal. It is clear from Eq. [13] and Eq. [14] that the location of the extrema is independent of the diffusion coefficient and the gradient strength. However, the magnitude of the signal at an extremum is dependent on both the diffusion coefficient and the gradient strength. We also see that the NMR signal in both cases follows the standard cubic exponential at short times but that the envelope decays exponentially (linear exponential) with the characteristic time given by ω^2/Dg^2.

Case (iii): Nonuniform Initial Density

As explained above, a novel feature of our general result is the ability to incorporate the effect of an arbitrary initial spin distribution. We consider an initial Gaussian distribution as well as an initial square distribution, and treat only the case of a constant gradient for simplicity. In the case of an initial Gaussian distribution of spread L, Eq. [8] leads to

$$M(t) = \exp[-(g^2t^3/3)(D + 3L^2/4t)] \qquad [15]$$

and shows that a finite initial spread results in the logarithm of the signal being quadratic rather than cubic at short times. The effective diffusion constant is increased by a term proportional to the square of the initial spread and inversely proportional to the time. At long times, the well-known cubic dependence is restored. These results are depicted in Fig. 3a where the signal for various values of the dimensionless constant $L^2(g/D)^{2/3}$ is given.

An initial distribution which is uniform over a distance L centered on the zero of the gradient leads to

$$M(t) = \left[\frac{\sin(gtL/2)}{gtL/2}\right]\exp(-Dg^2t^3/3) \qquad [16]$$

which, as in the Gaussian case, shows a quadratic rather than cubic initial dependence on time. These results are depicted in Fig. 3b for various values of the dimensionless parameter $(g/D)^{1/3}L$.

3. SOLUTIONS IN DISCRETE SPACE

Spins may move not only continuously in space as described above but also discretely among localized states such as Wannier states in a crystal. An example is triplet excitons moving via exchange interactions among the molecules in an aromatic hydrocarbon crystal such as anthracene or tetrachlorobenzene. Such systems underwent considerable experimental scrutiny in the 1970s through the ODMR (optically
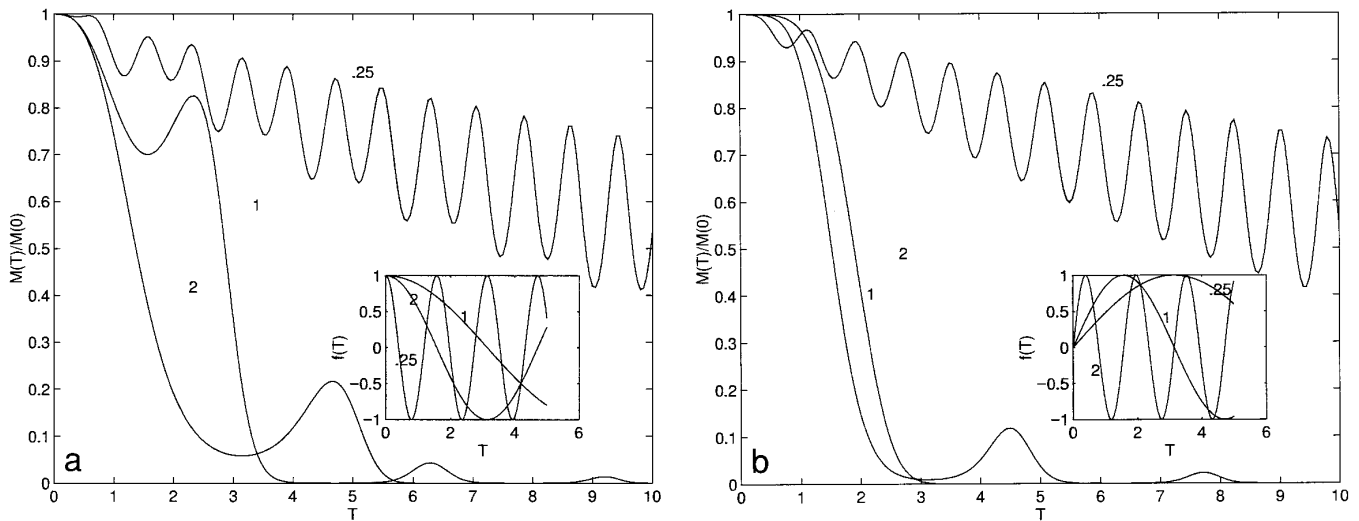
FIG. 2. The NMR signal $M(t)/M(0)$ for the sinusoidal time dependence of the gradient field as a function of the dimensionless time $T = t(Dg^2)^{1/3}$. The time dependence of the applied gradient is shown in the insets and is given by $f(t) = \cos \omega t$ in (a) and by $f(t) = \sin \omega t$ in (b). The three curves are labeled by the respective values (0.25, 1, and 2) of the parameter $(Dg^2)^{1/3}/\omega$. This parameter is a measure of the ratio of the period of the applied gradient to the magnetization decay time for the full applied gradient.

detected magnetic resonance) probe fashioned particularly to study fundamental issues such as exciton coherence (11, 12). For such a system, the diffusion term $D\partial^2 M(x, t)/\partial x^2$ is represented by a gain–loss expression of the form $\Sigma_n [F_{mn}M_n(t) - F_{nm}M_m(t)]$, where M_m represents the contribution to the NMR signal from the mth spin, m and n denote vectors in the appropriate number of dimensions, and F_{mn} is the hopping rate from state n to state m. The general problem involves the diagonalization of a transition matrix related to the F matrix. In the case of one-dimensional hopping motion via nearest neighbors with hopping rate F, the Torrey–Bloch equation takes the form

$$\frac{dM_m}{dt} = -ibgf(t)mM_m + F(M_{m+1} - 2M_m + M_{m-1}), \quad [17]$$
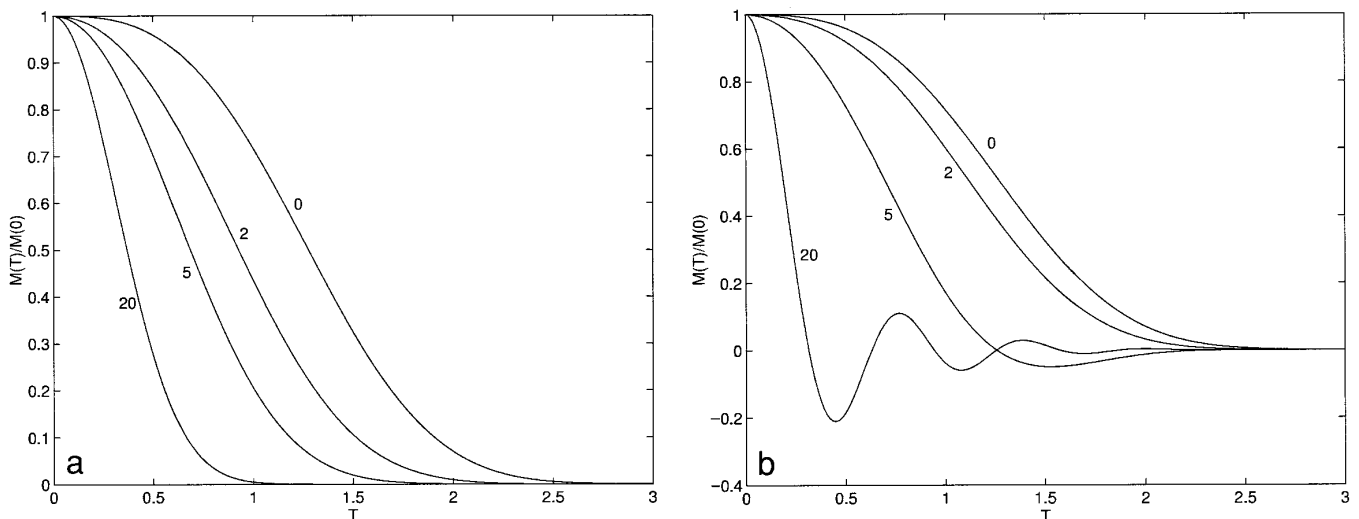

FIG. 3. The NMR signal $M(t)/M(0)$ as a function of the dimensionless time $T = t(Dg^2)^{1/3}$ for a constant gradient and nonuniform initial distribution of spins. This initial distribution, denoted by $M(x, 0)$, is Gaussian with half-width L in (a) and is a square distribution of width L in (b). The four curves in each case are labeled by the respective values (20, 5, 1, and 0) of the parameter $(g/D)^{1/3}L$. This parameter is the square of the ratio of the spread of the initial distribution of spins to the distance the spins diffuse in the time representing the maximum difference in the precession periods due to the applied gradient field.

where b is the distance between neighboring sites. We solve this equation by employing the method of *discrete* Fourier transforms. With the definition $M(k, t) = \sum_{m=-\infty}^{m=\infty} M_m(t)e^{ikm}$, Eq. [17] is converted into

$$\frac{\partial M(k, t)}{\partial t}$$

$$= -bgf(t)\frac{\partial M(k, t)}{\partial k} - 2FM(k, t)(1 - \cos k). \quad [18]$$

We modify our method of solution for the continuum equation by using the related transformation.

$$J(k, t) = M(k, t)\exp\left\{2F\int_0^t dt'\right.$$

$$\times \left.\left[1 - \cos\left(k + bg\int_{t'}^t f(s)ds\right)\right]\right\}, \quad [19]$$

and obtain

$$M(t) = M\left(bg\int_0^t f(s)ds, 0\right)\exp\left\{-2F\int_0^t dt'\right.$$

$$\times \left.\left[1 - \cos\left(bg\int_{t'}^t f(s)ds\right)\right]\right\}. \quad [20]$$

Equation [20] is our result for discrete lattices and constitutes a generalization of Eq. [10] which is valid for the continuum. It can be shown that, in the limit of vanishing b, Eq. [20] reduces to Eq. [10]. We now show three particular cases of the discrete result. While it is possible to explore with its help the effect of initial spin distributions, we concentrate here only on the exponential factor, i.e., consider a localized initial condition so that the preexponential factor equals 1.

Case (i): Constant Gradient

For a constant gradient, the signal becomes

$$M(t) = \exp\{-F[t - (1/gb)\sin gbt]\}. \quad [21]$$

Notice that this spin diffusion result differs from the well-known continuum result $M(t) = \exp(-Dg^2t^3/3)$ but reduces to it for small gb/F as one can see by retaining terms up to the cubic in the expansion for the sine in Eq. [21] and identifying Fb^2 with D. In the opposite limit of large gb/F the signal becomes a simple exponential. This is quite unlike the unrestricted continuum result. For a given value of the parameters, the time dependence of the signal starts out as the cubic exponential $\exp(-Fb^2g^2t^3/3)$ at short times but
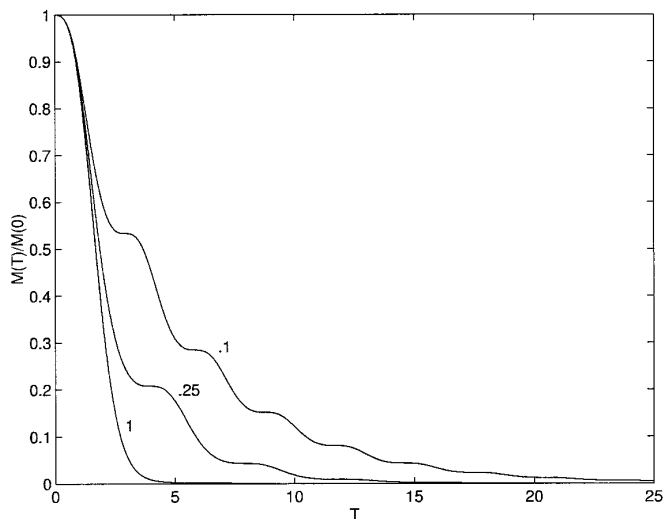

FIG. 4. The NMR signal $M(t)/M(0)$ as a function of the dimensionless time $T = t(Fb^2g^2)^{1/3}$ for a constant gradient and localized initial density. The value of the parameter F/gb, which measures the ratio of the difference between spin precession times under the applied gradient field at locations separated by the intersite distance b to the time taken by the spin to hop that distance, is taken to be 0.1, 0.25, and 1.0, respectively.

ends up at long times with an envelope essentially following the linear exponential $\exp(-Ft)$. It appears that the spacing of the discrete lattice introduces a quasi-confinement in this unconfined system. The results of this quasi-confinement can be seen in Fig. 4. Oscillations with respect to time appear with a frequency which is proportional to b, the site spacing.

Case (ii): Two-Pulse Gradient

The standard two-pulse gradient experiment (1) is represented by

$$f(t) = \Theta(t) - \Theta(t - \delta) - \Theta(t - \Delta)$$

$$+ \Theta(t - [\Delta + \delta]), \quad [22]$$

where δ is the pulse duration and Δ is the pulse separation. The NMR signal is observed at the peak of the spin echo occurring at $t = 2\Delta$. For the discrete lattice one gets

$$M(2\Delta) = \exp\{-2F(\Delta + \delta - (2/bg)\sin bg\delta$$

$$- (\Delta - \delta)\cos bg\delta)\}. \quad [23]$$

One may envision an experiment in which the lattice constant b is unchanged and the pulse duration δ and interval Δ are also constant but $g\delta$ is varied. Figures 5a and 5b show that the discrete nature of the lattice gives rise to oscillations of the signal with respect to the quantity $g\delta b$. The positions of the extrema bq_{ex} in Figs. 5a and 5b satisfy

$$2r\frac{\cos bq_{ex}}{bq_{ex}} - 2r\frac{\sin bq_{ex}}{(bq_{ex})^2} - \sin \overline{bq_{ex}} = 0, \quad [24]$$
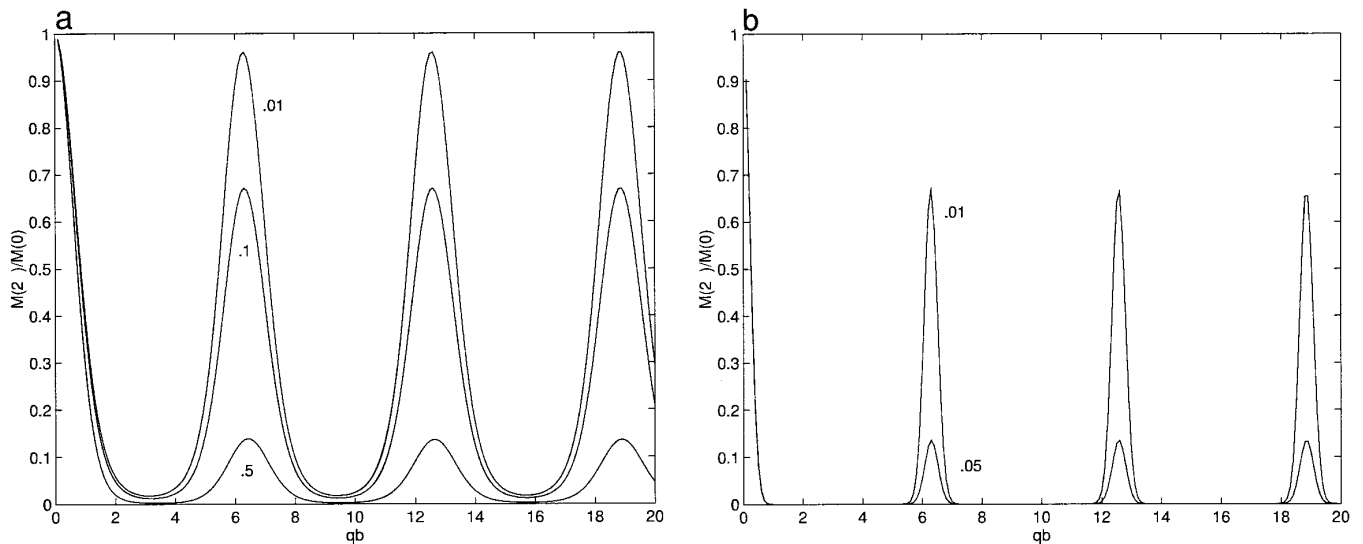
FIG. 5. The NMR signal $M(2\Delta)$ as a function of qb for the PGSE experiment for spin motion on the discrete lattice. The value of $F(\Delta - \delta)$, the ratio of the difference between the pulse interval and pulse duration to the time the spin takes to hop between neighboring sites, is 1 in (a) and 10 in (b). The value of $r = \delta/(\Delta - \delta)$, which, for a large pulse interval relative to the pulse duration, is the ratio of the duration to the interval, equals 0.01, 0.1, and 0.5, respectively, as shown in (a) and 0.01 and 0.05 in (b).

where $r = \delta/((\Delta - \delta))$ and q_{ex} equals $g\delta$ at the extrema. Therefore, for large $g\delta b$, the minima are separated by π. With a magnetic field gradient of sufficient strength, one might experimentally determine b from $b = \pi/(q_2 - q_1)$, where q_2 and q_1 are the values of $g\delta$ for adjacent minima. We see again that the discrete locations of the spins in this *unconfined* system give rise to behavior which is similar to that of spins diffusing in the presence of confinement (*7*) and is highly reminiscent of pore hopping solutions for diffusion in a rectangular lattice obtained earlier (*13*).

Case (iii): Sinusoidal Gradient

If the gradient is sinusoidal in time, we get

$$M(t) = \exp(-2Ft)\exp\left\{ 2F \int_0^t dt' \right.$$
$$\left. \times \cos[(bg/\omega)(\sin \omega t - \sin \omega t')] \right\} \quad [25]$$

for the case that $f(t) = \cos \omega t$, and

$$M(t) = \exp(-2Ft)\exp\left\{ 2F \int_0^t dt' \right.$$
$$\left. \times \cos[(bg/\omega)(\cos \omega t - \cos \omega t')] \right\} \quad [26]$$

for the case that $f(t) = \sin \omega t$. In both cases we see the appearance of a cosine of cosines or of sines which can be

expanded in terms of Bessel functions through well-known identities such as

$$\cos[(bg/\omega)\sin \omega t]$$
$$= J_0(bg/\omega) + 2 \sum_{n=1}^{\infty} J_{2n}(bg/\omega)\cos 2n\omega t. \quad [27]$$

Approximations to the NMR signal involving low-order Bessel functions are easily developed for large ω by using the fact that, if the neglect of fast oscillations is justified, the LHS of Eq. [27] is given by its average value $J_0(bg/\omega)$. This value vanishes whenever bg/ω equals a zero of the Bessel function. We do not display these approximations here but merely remark that the parameter bg/ω thus controls the signal in a crucial way: oscillations will occur with increasing gradient strength, specifically with increasing bg/ω, exactly as in the confined continuum case. This parameter bg/ω is a measure of the ratio of the period of the applied gradient to the characteristic time bg. The period of the gradient in this case is analogous to the duration δ of the pulse in case (ii) analyzed above. Once again we see that b, the lattice spacing, plays the role of a confining distance in this unconfined system.

4. SOLUTIONS FOR A REPRESENTATIVE TWO-STATE SYSTEM

The above analysis holds only for systems of infinite extent where translational invariance is not broken by end walls. The NMR technique is, however, of particular sig-

nificance for the study of systems involving confining geometries. A simple calculation with a surprising range of applicability can be given in the context of a representative two-state system. The system consists of a spin hopping between just two sites which we label by 1 and -1. The Torrey–Bloch equations are then

$$\frac{dM_1}{dt} = -F(M_1 - M_{-1}) - ibg f(t)M_1$$

$$\frac{dM_{-1}}{dt} = F(M_1 - M_{-1}) + ibg f(t)M_{-1}. \qquad [28]$$

We now define the quantities $M_{\pm}(t) = M_1(t) \pm M_{-1}(t)$ whose evolution is given by

$$\frac{dM_+(t)}{dt} = -ibg f(t)M_-(t)$$

$$\frac{dM_-(t)}{dt} = -2FM_-(t) - ibg f(t)M_+(t). \qquad [29]$$

The NMR signal $M(t)$, which is the sum of the contributions from both sites, is obviously given by $M_+(t)$, a closed equation for which is obtained from Eq. [29]:

$$\frac{d^2M(t)}{dt^2} + \left[2F - \frac{1}{f(t)} \frac{df(t)}{dt} \right] \frac{dM(t)}{dt}$$
$$+ b^2g^2f^2(t)M(t) = 0. \qquad [30]$$

Equation [30] can be easily rewritten as

$$\frac{dM(t)}{dt} + f(t) \int_0^t dt' f(t')\phi(t - t')M(t') = 0, \qquad [31]$$

where $\phi(t - t') = b^2g^2e^{-2F(t-t')}$. This is identical to the memory equation given by Sheltraw and Kenkre (7), which goes beyond earlier treatments (6, 14) based on truncated cumulants. These memory effects are known to be real (15, 16) and, as explained in Ref. (7), are inaccessible to approaches which, explicitly or otherwise, incorporate the assumption of Gaussian behavior. Those Gaussian results can be derived, however, from the more general and more accurate two-state result [31]. Thus, to reobtain the analysis of Wang et al. (6) we approximate Eq. [31] by taking $M(t)$ outside the integral sign under the supposition that it is a slow variable. We obtain, as an *approximate* version of our full result [31],

$$M(t) = \exp\left\{ -b^2g^2 \int_0^t dt' \int_0^{t'} dt'' \right.$$
$$\left. \times f(t')f(t'')\phi(t' - t'') \right\}, \qquad [32]$$

which is identical to the Stepisnik expression (14) used by Wang et al. (6) where $\phi(t)$ is proportional to the autocorrelation function of the spin displacement. Thus, all the results of Wang et al. (6) can be recovered from our exact simple two-state diffusion result through the above slow-$M(t)$ approximation. The necessary correspondence of the parameters as given by Sheltraw and Kenkre (7) is that the two-state system distance b equals the actual confinement length a except for a proportionality constant ($b = a/2\sqrt{3}$), and the two-state hopping time $1/F$ equals the diffusion time also except for a proportionality constant ($1/F = a^2/5D$), where D is the diffusion constant of the spins in the *actual* system. In a certain sense, the two states of the two-state system represent two halves of the confined region under consideration.

The essence of many of the results obtained earlier can be understood from the fact that there is an exact equivalence between our two-state diffusion system and a damped harmonic oscillator. Indeed, Eq. [30] represents the displacement of a harmonic oscillator with a time-dependent frequency $g(t)$ and a time-dependent damping rate $2F - (1/f(t))(df(t)/dt)$. In the case of a constant gradient or of the experimentally common two-pulse gradient, g is a constant and we have a normal damped harmonic oscillator with a frequency which is either zero or nonzero according to the time under consideration. Phenomena such as motional narrowing, wherein increasing D can have opposite effects according to the range of system parameters, or the various useful regime clarifications given by Wang et al. (6), are then understood transparently.

Whereas the two-state system gives the Stepisnik (14) or Wang et al. (6) results under the slow-$M(t)$ approximation, it is equivalent *without any approximations* to the memory results of Sheltraw and Kenkre. This means that the various oscillatory features of the NMR signal, both with respect to time in the constant gradient case and with respect to the gradient strength in the two-pulse experiment, present in the analysis of Sheltraw and Kenkre (7), are also immediately obtainable from the two-state analysis given in the present paper. The *determination* of the quantities b and F from system parameters requires, however, a first-principles treatment such as that given in Ref. (7).

5. SUMMARY

We have given a simple method for calculating the NMR signal of spins diffusing in the presence of a linear gradient. The method easily incorporates arbitrary initial conditions as well as an arbitrary time dependence of the gradient. The method has been applied to obtain old as well as new results for the case of continuum as well as hopping type diffusion in the absence of confinement. We have seen that results for the discrete unconfined system exhibit features characteristic of the continuum confined system, the confinement length

being related in the latter to the lattice constant (intersite distance) in the former. We have also shown that predictions from a simple two-site model are equivalent to the results of previous work for the case of motion in a continuum under confinement.

ACKNOWLEDGMENTS

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