

Relaxation at Cell Walls in Optical-Pumping Experiments*

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(Received 4 May 1972; revised manuscript received 28 July, 1972)

Franzen's approximation for the relaxation time of an optically pumped vapor is shown to yield effective values of diffusion coefficients and relaxation cross sections which differ by small predictable amounts from the true values of these parameters. The appropriate correction factors have been calculated. Relaxation at cell walls is shown to be approximated well by an additive relaxation rate, allowing a simple description of the relaxation of the electronic spin polarization of atoms subject to collisions both with cell walls and with buffer-gas atoms.

I. INTRODUCTION

Spin relaxation in an optically pumped vapor can be induced both by collisions of the pumped atoms with the walls of the cell and by collisions of the pumped atoms with foreign (buffer) gas atoms. The rate of change of any particular observable of the system thus is governed by a diffusion equation. The solution of this equation is an infinite sum of exponential terms, each of which is a function of the diffusion coefficient D_0 and of the cross section for relaxation σ of the pumped atoms in the buffer gas. Franzen suggested a simple approximation in which only the first term of the series solution is considered to contribute significantly to the relaxation.¹ Franzen's approximation, which since has been widely used, permits a convenient and straightforward determination of D_0 and of σ from the experimentally measured dependence of the relaxation time upon buffer-gas pressure. Legowski² and Masnou-Seeuws and Bouchiat³ have extended Franzen's treatment to consider also the second most important diffusion mode. Minguzzi, Strumia, and Violino made an extensive evaluation of the diffusion problem, deriving in detail the relative weights of all diffusion modes.⁴ Their calculations have been utilized recently by Beverini, Minguzzi, and Strumia in analyzing data on the collisional relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$ in cesium.⁵ The approach employed by these authors goes far beyond Franzen's approximation: It involves the fitting of more than 100 terms of the series solution to the experimental data. While analyses such as these may be necessary in cases where experimental cells cannot be considered optically thin, or in cases where extreme accuracy can be sought, in many situations they introduce an unwelcome complexity which would be desirable to avoid.

In this paper we report on detailed studies of the limits of accuracy of Franzen's approximation compared to the exact solution of the diffusion equation. We show how the approximation may be used to extract highly accurate determinations of

D_0 and of σ from experimental data on the relaxation of observables such as $\langle \vec{S} \cdot \vec{I} \rangle$. We show that the effects of wall relaxation can indeed be approximated by a simple additive relaxation rate, as Franzen's approximation suggests. Finally, we show how the effects of wall relaxation can be treated in more complicated situations, such as in the relaxation of the electronic spin polarization $\langle S_z \rangle$.

II. DIFFUSION EQUATION AND FRANZEN'S APPROXIMATION

Assume that the relaxation of the observable θ of an optically pumped vapor can be described by a single rate constant R . The relaxation of $\langle \vec{S} \cdot \vec{I} \rangle$ induced by collisions of pumped atoms with buffer-gas atoms satisfies this criterion. When the contribution to relaxation arising from diffusion to the walls of the cell is included, the relaxation equation becomes¹

$$\frac{\partial}{\partial t} \langle \theta \rangle = D \nabla^2 \langle \theta \rangle - R \langle \theta \rangle, \quad (1)$$

where $D = D_0(p_0/p)$ and $R = n_0 \sigma v_{\text{rel}} p/p_0$. p is the buffer-gas pressure in Torr, D_0 is the diffusion coefficient of the alkali metal in the buffer gas at atmospheric pressure, n_0 is Loschmidt's number corrected to the actual temperature of the cell, v_{rel} is the mean relative velocity, and σ is the cross section for the collisional relaxation of the observable θ . The solution of Eq. (1), for cylindrical symmetry, and subject to the boundary condition that $\theta = 0$ at the walls of the cell, is^{4,5}

$$\theta(t) = \theta_0 \sum_{\substack{\nu=0, \infty \\ i=1, \infty}} B_{i\nu} e^{-t/\tau_{i\nu}}, \quad (2a)$$

where

$$\tau_{i\nu}^{-1} = [\pi^2(2\nu+1)^2/L^2 + \mu_i^2/r^2]D + R \quad (2b)$$

and

$$B_{i\nu} = \tau_{i\nu} J_1(\mu_i r_b/r) J_1(\mu_i r_a/r) / [\pi \mu_i (2\nu+1) J_1(\mu_i)]^2. \quad (2c)$$

μ_i is the i th zero of $J_0(x)$, L is the length of the cell, r is the radius of the cell, r_b is the radius of

the pumping beam, and r_a is the radius of the detection beam. Equations (2b) and (2c) are strictly valid only for small polarizations (see Appendix). For simplicity in subsequent discussions we shall assume that $r_p = r_a = r$, a common experimental situation.

In Franzen's approximation, one assumes that only the first term of Eq. (2) contributes significantly to the relaxation. Thus,

$$\tau_{\text{eff}}^{-1} = [\pi^2/L^2 + \mu_1^2/r^2]D + R. \quad (3)$$

If Franzen's approximation were strictly valid, the relaxation equation for θ would reduce to the following form:

$$\frac{\partial \theta}{\partial t} = -R\theta - R'\theta, \quad (4a)$$

with the solution

$$\theta = \theta_0 e^{-Rt} e^{-R't}. \quad (4b)$$

Relaxation due to wall collisions thus would be described by the simple additive rate constant R' , where

$$R' = (\pi^2/L^2 + \mu_1^2/r^2)D_0 p_0/p. \quad (4c)$$

We now examine Eq. (2) in closer detail. This equation is factorable into the following form:

$$\theta(t) = \theta_0 \exp(-Rt)$$

$$\times \left(\sum_{i\nu} B_{i\nu} \exp\{-t[\pi^2(2\nu+1)^2/L^2 + \mu_i^2/r^2]D\} \right). \quad (5)$$

Comparing Eq. (5) to (4b), we find that Franzen's approximation is, in effect, that the infinite sum of exponentials in Eq. (5) can be approximated by a single "average" or "effective" exponential. That is,

$$\sum_{i\nu} B_{i\nu} \exp\{-t[\pi^2(2\nu+1)^2/L^2 + \mu_i^2/r^2]D\} \approx \exp(-R't), \quad (6)$$

ultimately yielding the same time dependence for θ as that given in Eqs. (4a) and (4b). Equations (5) and (6) suggest that if experimental transient signals closely approximate single exponentials, then Franzen's approximation should yield reasonably accurate determinations of R and of R' , and therefore of D_0 and of σ . The situation is muddled, however, by the fact that both the time constants and their relative weights depend upon buffer-gas pressure. Thus, even if the single-exponential approximation were found to hold, the effective values of D_0 and of σ necessary to fit the data still might vary considerably as a function of buffer-gas pressure. Fortunately, as we shall show below, such a situation does not exist in practice.

III. COMPUTER ANALYSES AND RESULTS

We have investigated the problems described above with the aid of extensive computer analyses

of Eqs. (2a)–(2c). We have used these equations to generate simulated experimental data, to which we fit single-exponential functions, determining effective decay times. We then fit Franzen's approximation to the pressure dependence of the effective decay times. Comparison of the "evaluated" values of D_0 and σ with the input values provides an exact measure of the error associated with the use of Franzen's approximation. We have found that over a wide range of geometries (L/r ratios) and over a wide range of buffer-gas-wall relaxation-rate ratios both that the relaxation of $\theta(t)$ is well approximated by a single exponential, and that the application of Franzen's approximation to the analysis of experimental data yields effective values of D_0 and of σ that differ from the "true" values by small *predictable* amounts. A full discussion of this analysis follows below.

For convenience, we rewrite Eq. (2b) in the following form:

$$\tau_{i\nu}^{-1} = \left(\frac{\pi^2(2\nu+1)^2}{(L/r)^2} + \mu_i^2 \right) \frac{A}{p} + A\alpha p, \quad (7)$$

where

$$A = D_0 p_0 / r^2$$

and

$$\alpha = n_0 \sigma v_{\text{rel}} r^2 / p_0^2 D_0.$$

We have simulated experimental data for the following values of the parameters A , L/r , and α : $A = 10$; $L/r = 0.5, 1, 2, 3$; $\alpha = 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}$. These values encompass virtually all commonly encountered geometries and relaxation-rate ratios. For each combination of L/r and α and for a wide range of p , we used Eqs. (2a), (2c), and (7) to calculate $\theta(t)$ at 100 values of t equally distributed over the interval $t = 0$ to $t = 4\tau_{10}$.⁶ We then fit a single exponential to each set of "data," using a standard least-mean-squares technique, and obtained an effective relaxation time τ_{eff} . One of the poorer examples of such a fit is shown in Fig. 1, where the \times 's represent some of the generated values of $\theta(t)$ and the solid line represents the best fit of a single exponential to the data. The only strong nonexponential behavior occurs near $t = 0$, as evidenced by the intercept of the fitted curve falling lower than the exact data. This discrepancy varies from a negligibly small amount at high pressures to about 6% of $\theta(0)$ at low pressures.

Having demonstrated the validity of the effective-single-exponential approximation, we proceeded to fit Franzen's approximation to the appropriate calculated values of $\tau_{\text{eff}}(p)$. We provided a rather stringent test by including data at pressures relatively far out on both sides of the relaxation-time-vs.-buffer-gas-pressure curve. Specifically, we included data at the pressure $\frac{1}{16}p_m$, $\frac{1}{8}p_m$, $\frac{1}{4}p_m$, $\frac{1}{2}p_m$,

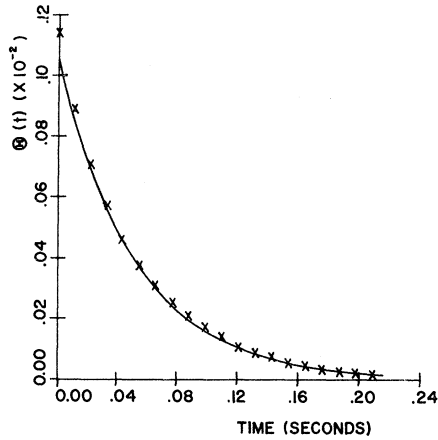


FIG. 1. Sample fit of a single exponential (solid line) to the simulated data (x's) obtained from Eqs. (2a), (2c), and (7) for $A=100$, $\alpha=0.001$, $L/r=2$, and $p=90.7$. Fits for all other sets of parameters were of comparable or better quality.

p_m , $2p_m$, $4p_m$, $8p_m$, and $16p_m$, where p_m is the pressure at which τ_{10} is a maximum. For convenience we wrote Franzen's approximation in the form

$$\tau_{\text{eff}}^{-1} = \left[\left(\frac{\pi^2}{(L/r)^2} + \mu_1^2 \right) C_1 \frac{A}{p} + C_2 A \alpha p \right]; \quad (8)$$

A , L/r , and α are the original input parameters, while C_1 and C_2 are variable parameters determined by the best fit to the data. The deviations of C_1 and C_2 from unity yield the errors in the determination of D_0 and σ associated with the use of Franzen's approximation. We found that, for a given L/r ratio, C_1 and C_2 are virtually unaffected by changes in α . A summary of the relevant results is given in Table I. C_1 and C_2 do, however, depend somewhat on the L/r ratio. We summarize the relevant results in Table II. We make the following conclusions. For optically thin cells,

TABLE I. Variation of the correction factors C_1 and C_2 as a function of α ($=n_0 \sigma v_{\text{rel}} r^2 [\rho_0^2 D_0]^{-1}$) for a cylindrical cell with $L/r=2$. The table indicates that Franzen's approximation yields an effective value of D_0 which is approximately 3.4% higher than the true value, and an effective value for σ which is 7.4% higher than the true value.

α	C_1	C_2
1.0	1.032	1.074
0.1	1.034	1.074
0.01	1.036	1.073
0.001	1.034	1.074
0.0001	1.035	1.074

TABLE II. Variation of the average values of the correction factors C_1 and C_2 as a function of L/r ratio for a cylindrical cell.

L/r	C_1 (av)	C_2 (av)
0.5	1.061	1.052
1.0	1.046	1.069
2.0	1.034	1.074
3.0	1.040	1.070

and for small polarizations, Franzen's approximation may be used with confidence to evaluate D_0 and σ from experimental data. For a cell with $L/r=2$ geometry, and for data distributed in the manner described above, Franzen's approximation will yield a value of D_0 which is 3.4% higher than the true value, and a value of σ that is 7.4% higher than the true value. These percentage differences are unaffected by the volume of the cell, and by the actual magnitudes of the diffusion coefficient and relaxation cross section. The correction factors depend somewhat, however, on the distribution of data points with respect to pressure. If, for example, Franzen's approximation is fit only to data on the low-pressure side of the τ_{eff} -vs- p curve, best values of $C_1=1.018$ and $C_2=1.088$ are obtained for a $L/r=2$ cell. These values of C_1 and C_2 differ by less than 2% from the values calculated including the data at higher pressures. The difference is small compared to typical experimental uncertainties. Similarly, if only extremely high pressure ($p \gg 16p_m$) data are analyzed, C_2 approaches unity. Such a situation is very seldom encountered in practice.

An interesting test of our results can be made by fitting Franzen's approximation to the published data of Beverini *et al.*⁵ The solid curves in the data graphs in their article represent the best fits of the series solution to the experimental data. These curves can be reproduced by Franzen's approximation with values for σ that are 7% to 9% higher than those reported by Beverini *et al.*, and by values for D_0 that are 9 to 14% higher. The correction factors for σ are almost exactly those that we would predict. The apparent discrepancies of the D_0 correction factors from our predictions are due primarily the fact that the data of Beverini *et al.* represent the times at which $\theta(t)$ falls to $(1/e)$ of its value at $t=0$, rather than the time constants of single exponentials fit to the experimental transients. Differences between these two representations of data are most pronounced on the low-pressure side of the relaxation-time [τ_{eff} or $\tau(1/e)$] vs buffer-gas-pressure curve, with $\tau_{\text{eff}} > \tau(1/e)$ in that region. The correction factor C_1 for the $\tau(1/e)$ curve should be about 6% larger than that which we calculated for the τ_{eff} curve, thus re-

moving the apparent discrepancy. It may be worth mentioning that the τ_{eff} representation of data, now that the appropriate correction factors are known, promises in practice to yield more accurate data than the $\tau(1/e)$ approach. The accuracy of the $\tau(1/e)$ representation depends heavily on the accuracy with which a single point, the amplitude of the signal at $t=0$, is known. In the τ_{eff} approach, an analytic expression can be fit to a large number of data points, which need not include points near $t=0$, nor at $t \rightarrow \infty$.

IV. RELAXATION OF THE ELECTRONIC SPIN POLARIZATION

We have shown that relaxation caused by diffusion to the walls of the cell can, to a good approximation, be described by an additive relaxation rate. We now utilize this fact to describe the relaxation of the electronic spin polarization $\langle S_z \rangle$, a task that would be almost hopelessly complex if a complete solution to the diffusion equation were required. The complexity arises from the fact that the relaxation of $\langle S_z \rangle$ is coupled to the relaxation of $\langle I_z \rangle$, the nuclear spin polarization. For simple binary "fly-by" alkali-buffer-gas collisions, the relevant relaxation equations are, in the case of cesium ($I = \frac{7}{2}$),⁷⁻⁹

$$\frac{d\langle S_z \rangle}{dt} = -R\langle S_z \rangle + \left(\frac{R}{32}\right)\langle I_z \rangle, \quad (9a)$$

$$\frac{d\langle I_z \rangle}{dt} = -\left(\frac{R}{32}\right)\langle I_z \rangle. \quad (9b)$$

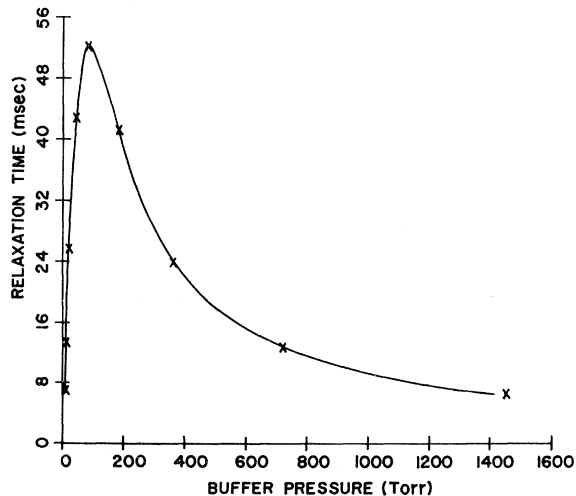


FIG. 2. Sample fit of Franzen's approximation (solid line) to calculated values τ_{eff} (\times 's). The input parameters were $A=100$, $\alpha=0.001$, and $L/r=2$. The evaluated correction factors were $C_1=1.034$ and $C_2=1.074$. Fits for all other sets of parameters were of comparable quality.

To include the effects of wall relaxation, we take advantage of the fact that relaxation at a glass or quartz surface is "uniform"; that is, any Zeeman sublevel can be reached with equal probability in a single relaxation event. This fact allows us to use the same additive relaxation rate to describe the effect of diffusion to the walls on both $\langle S_z \rangle$ and $\langle I_z \rangle$ as that which was used for $\langle \vec{S} \cdot \vec{I} \rangle$. We thus obtain the following approximate equations, which include the effects of both wall relaxation and buffer-gas relaxation:

$$\frac{d\langle S_z \rangle}{dt} = -(R' + R)\langle S_z \rangle + \left(\frac{R}{32}\right)\langle I_z \rangle, \quad (10a)$$

$$\frac{d\langle I_z \rangle}{dt} = -\left(R' + \frac{R}{32}\right)\langle I_z \rangle. \quad (10b)$$

The solution of these equations yields the result that the relaxation of $\langle S_z \rangle$ is approximated by a sum of two exponentials with time constants

$$\tau_1^{-1} = (R' + \frac{1}{32}R), \quad (11a)$$

$$\tau_2^{-1} = (R' + R), \quad (11b)$$

a result which has been verified in our laboratory.

ACKNOWLEDGMENTS

I am grateful to both Peter Bender and Judy Franz for stimulating discussions and helpful critical comments, and to Ron Lipton for invaluable assistance in making a number of extensive calculations.

APPENDIX

We have stressed the point that our calculations have been made under the assumption of small polarizations, i. e., small values of $\theta(0)$. This restriction stems from the fact that a similar assumption was implicit in the derivation of the "exact" equations (2a), (2b), and (2c). We now briefly indicate how that derivation may be broadened to include arbitrary polarizations.

In order to calculate the weighting factors, $B_{i\nu}$, of the various diffusion modes, the distribution of polarization at $t=0$ must be known. Minguzzi *et al.*⁴ attacked this problem by solving the pumping equation, for which $\theta=0$ at $t=0$, to determine the distribution of polarization in the optically pumped equilibrium. This same distribution then served as the initial distribution of polarization when the pumping light was turned off, that is, at the start of the measurement of the relaxation transient. Minguzzi *et al.* wrote the pumping equation as¹⁰

$$D\nabla^2 P - kP + I(r, z) = 0, \quad (A1)$$

where $I(r, z)$ is the pump rate and P corresponds to our θ and k to our R . Equation (A1) is valid only for small pump-rate to relaxation-rate

ratios, that is, for $P \approx 0$. The correct general equation is

$$D\nabla^2 P - [k + I(r, z)]P + I(r, z) = 0. \quad (\text{A2})$$

The result of the change indicated by Eq. (A2) is that the $\tau_{i\nu}$ in our Eq. (2c) no longer are the $\tau_{i\nu}$ of Eq. (2b), but now include the pumping rate: Let us call these modified constants $\tau'_{i\nu}$ and understand that they must be substituted into Eq. (2c) for the $\tau_{i\nu}$:

$$\tau'_{i\nu} = [\pi^2(2\nu + 1)^2/L^2 + \mu_i^2/r^2]D + R + I(r, z). \quad (\text{A3})$$

The $\tau_{i\nu}$ in Eq. (2b), remain, of course, unchanged. While it may seem strange at first that a pumping rate now appears in an equation describing relaxation in the dark, it must be remembered that this parameter enters because of the dependence of the initial polarization upon it. Referring again to Ref. 4, we write the initial polarization in the form

$$\theta(z, r, t=0) = \sum_{i\nu} \left[\frac{4I_0 \tau'_{i\nu} J_1(\mu_i) [1 - (-1)^\nu]}{\mu_i J_1^2(\mu_i) \pi \nu} \right]$$

*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace, USAF, under Grant No. AFOSR 69-1686

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⁴P. Minguzzi, R. Strumia, and P. Violino, Nuovo Cimento **46**, 145 (1966).

$$\times J_0\left(\frac{\mu_i r}{a}\right) \sin\left(\frac{\nu \pi z}{L}\right) \Big], \quad (\text{A4})$$

where we have assumed that, in terms of the notation of Ref. 4, $\lambda=0$, $\alpha=1$, and $I_0=I(r, z)$. In the limit of extremely strong pumping, $I \rightarrow \infty$. In that case the z dependence of the polarization has the form

$$P \approx \sum_{\nu \text{ odd}} \frac{1}{\nu} \sin \frac{\nu \pi z}{L},$$

which is just the Fourier series for the function $P(z) = \text{const}$ for $0 \leq z \leq L$. Total polarization thus exists throughout the volume of the cell, the limiting case which is expected. Relaxation starting from such a state of polarization is radically different from that described in the main section of this paper, as inspection of the relevant equations will reveal. Higher-order diffusion modes play a much more significant role.

⁵N. Beverini, P. Minguzzi, and F. Strumia, Phys. Rev. A **4**, 550 (1971).

⁶The sum in Eq. (2) was taken from $\nu=0$ to 9 and from $i=1$ to 10, thus including the first 100 terms.

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¹⁰Reference 4, Eq. (4.1).

Interaction of Electrons with Cavities*

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(Received 16 December 1971; revised manuscript received 19 May 1972)

The radiation emitted by an electron traversing an output cavity tuned to a single frequency after having traversed an excited input cavity is calculated using quantum field theory. It is found that the emission has maxima when the output cavity is tuned to a harmonic of the input-cavity frequency, the result being very similar to classical klystron theory. The emitted power is independent of the state of the field in the input cavity under any realizable conditions, so that this provides no mechanism for determining the state of this field.

I. INTRODUCTION

The classical description of the interaction of an electron beam with the field of a resonant cavity is straightforward. For beams which are not too intense the space-charge interaction may be neglected, and the motion of the individual electrons may be treated independently. An electron traversing a gap in an excited cavity, such as the input gap of a klystron, is accelerated by the electric

field in the gap by an amount depending on the amplitude and phase of the cavity field. A succession of electrons passing through the gap is velocity modulated and forms bunches at a distance from the gap.¹ This bunching is a many-electron effect, even in the absence of any electron-electron interaction, and becomes less pronounced relative to statistical fluctuations in the beam as the beam gets weaker.

It is our purpose to give a quantum-mechanical