Multipole Relaxation Times of a Weakly Perturbed Spin System*

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Simple, general formulas for the multipole relaxation times of a weakly perturbed spin system are derived. A simple formula for the Zeeman splittings of multipole relaxation times has been derived for a magnetic perturbation.

I. INTRODUCTION

THE relaxation of an ensemble of spins is often characterized by a number of longitudinal and transverse relaxation times.[1] Only in the case of spin-$\frac{1}{2}$ particles is there a single longitudinal and a single transverse relaxation time. Although the different longitudinal and transverse relaxation times are often of negligible importance in conventional nuclear magnetic resonance experiments, they play a very important role in studies of the relaxation of optically pumped vapors. For instance, Cohen-Tannoudji[2] has shown that the relaxation of polarized Hg^{201} vapor is due largely to the interaction of the quadrupole moment of the Hg^{201} nucleus with the fluctuating electric-field gradients experienced by the atom while it is stuck to the walls of a quartz container. One of the most important pieces of evidence in support of this view is that two distinct transverse relaxation times are observed experimentally. One relaxation rate, which corresponds to transverse components of the quadrupole moment of the vapor, is twice as large as a second relaxation rate, which corresponds to the transverse components of the dipole moment of the vapor. If the relaxation had been caused by the coupling of the magnetic dipole moment of the atom to a fluctuating magnetic field, one would have expected the quadrupole relaxation rate to be three times as great as the dipole relaxation rate.

The purpose of this paper is to present certain simple formulas [i.e., (12) and (17)] that relate the relaxation rates of a spin system to the strength, multipolarity, and correlation time of a weak, fluctuating perturbation. After this paper was completed we discovered that very similar results have already been obtained by Gabriel[3] in a study of the influence of the environment on angular correlations of nuclear radiations. We feel that our work is still useful, since our derivation is simpler and since we bring attention to several important examples of the role of multipole relaxation times in optical pumping experiments.

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[2] C. Cohen-Tannoudji, J. Phys. Radium **24**, 653 (1963).
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II. THEORY

Consider an ensemble of atoms of spin K. The atoms are situated in a static field H, which defines the z axis of a coordinate system. We assume that each atom is subject to a weak, fluctuating perturbation V, which varies in a random way from atom to atom. Then the Hamiltonian of an individual atom is

$$\mathcal{H}=\omega K_z+V, \tag{1}$$

where $\omega=\gamma H$ is the Larmor frequency of the atoms in the static field, and γ is the gyromagnetic ratio. We represent the state of the ensemble with a density matrix ρ or with an interaction picture density matrix σ:

$$\sigma=e^{i\omega K_z t}\rho e^{-i\omega K_z t}. \tag{2}$$

We shall expand the density matrix and all other atomic operators in terms of sperical basis operators[4] T_{LM}:

$$\sigma=\sum_{L,M}(-1)^M\sigma_{L-M}T_{LM}, \tag{3}$$

where

$$T_{LM}=\sum_m |K,m\rangle\langle K,m-M|(-1)^{m-M-K} \times C(KKL;m,M-m). \tag{4}$$

The coefficient $C(KKL;m,M-m)$ is a Clebsch-Gordan coefficient, and the basis functions $|Km\rangle$ are eigenfunctions of K_z.

$$K_z|Km\rangle=m|Km\rangle. \tag{5}$$

Our phase conventions and notation correspond to those of Rose.[5]

According to the general theory of relaxation,[6] for a sufficiently weak perturbation, the density matrix obeys the equation

$$\frac{d}{dt}\sigma=-\left\langle\int_0^\infty [V^*(t),[V^*(t-\tau),\sigma(t)]]d\tau\right\rangle_{\rm av}. \tag{6}$$

Here,

$$V^*(t)=e^{i\omega K_z t}V(t)e^{-i\omega K_z t} \tag{7}$$

is the perturbation in the interaction picture. The symbol $\langle\ \rangle_{\rm av}$ denotes an average over all atoms of the

[4] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).
[5] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).
[6] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. VIII.

ensemble. We assume that the temperature can be considered infinite so that at statistical equilibrium all atomic sublevels will be equally populated.

Let us assume that the perturbation V has a well-defined multipolarity l:

$$V(t)=\sum_m(-1)^m V_{l-m}(t)T_{lm}\ . \tag{8}$$

For instance, if $l=1$, Eq. (8) would represent the interaction of the magnetic dipole moment of the atom with a fluctuating magnetic field. If $l=2$, Eq. (8) would represent the interaction of the electric quadrupole moment of the atom with a fluctuating electric-field gradient.

We also assume that V is isotropic and has an exponential correlation function:

$$\langle V_{lm}(t)V_{lm'}(t-\tau)\rangle_{\rm av}=\frac{\delta_{m',-m}(-1)^m v^2 e^{-\tau/\tau_c}}{2l+1}\ . \tag{9}$$

Here v is the root-mean-square amplitude of the perturbation, and τ_c is the correlation time of the perturbation.

In order that Eq. (6) be valid, we must assume that the perturbation is weak, i.e., that

$$(v\tau_c)^2\ll 1\ . \tag{10}$$

A. Isotropy; Multipole Relaxation Times

Suppose that the external magnetic field is zero. Then the atoms are subject to an isotropic environment and (6) reduces to

$$(d/dt)\sigma_{LM}=-\gamma_L(l)\sigma_{LM}\ . \tag{11}$$

That is, all $(2L+1)$ components of the density matrix of multipolarity L relax at the same rate (see Appendix):

$$\gamma_L(l)=2v^2\tau_c[(2K+1)^{-1}-W(LKKl;KK)]\ . \tag{12}$$

Excluding the monopole relaxation rate, $\gamma_0(l)=0$, which must be zero if no atoms are added or removed from the ensemble, there are $2K$ potentially different relaxation times. Because of the isotropy there is no distinction between longitudinal and transverse relaxation times.

For illustrative purposes we have sketched the multipole relaxation times for several different values of the spin K and for all allowed multipolarities of the interaction (see Fig. 1). It is interesting to note that the multipole relaxation rates are closely analogous to the zero-field hyperfine intervals of an atom with nuclear spin $I=K$ and atomic spin $J=K$. It is well known that if $\boldsymbol{I}$ and $\boldsymbol{J}$ are coupled by an interaction of multipolarity l, the zero-field energy displacements of energy levels of total angular momentum F are[7]

$$E_F=\text{const}\times W(FKKl;KK)\ . \tag{13}$$

Comparison of (13) with (12) shows that the relative spacings of the multipole relaxation rates are identical to the relative spacings of the hyperfine energies of an atom with $I=J=K$. For instance, if the relaxation is caused by a fluctuating magnetic field (multipolarity $l=1$), then the spacing between the relaxation rates obeys the Landé interval rule

$$\gamma_L(1)-\gamma_{L-1}(1)=\text{const}\times L\ . \tag{14}$$

Just as one can determine the hyperfine coupling

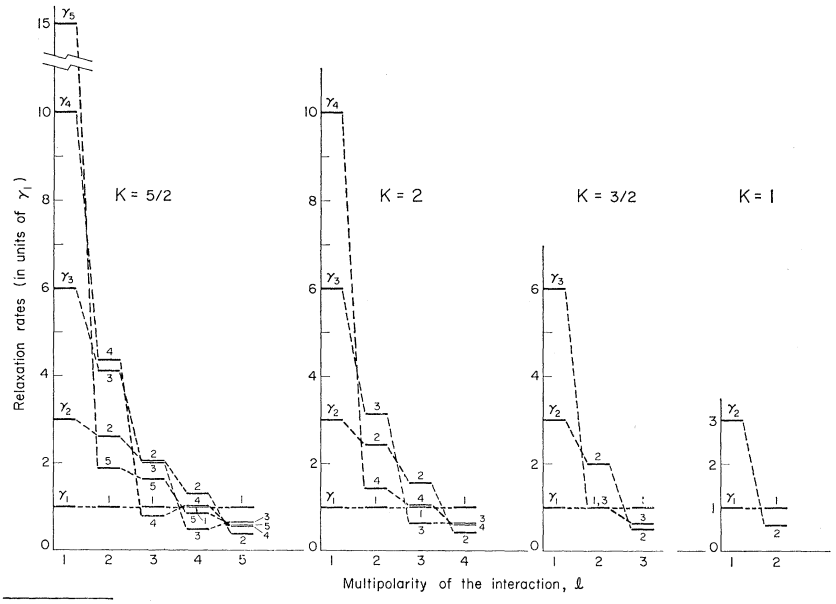

FIG. 1. Zero-field relaxation rates. For each interaction multipolarity the relaxation rates have been normalized to the dipole relaxation rate. The relaxation rates are analogous to the zero-field hyperfine energies of an atom that is subject to an interaction of multipolarity l.

[7] C. Schwartz, Phys. Rev. **97**, 380 (1955), Eq. (2).

constants of an atom from the energy intervals at zero field, one can determine the multipolarity of the interactions that are responsible for the relaxation of a spin system by measuring the relative sizes of the different relaxation rates at zero field. For instance, in optically pumped Hg^{201} ($K=\frac{3}{2}$), the quadrupole relaxation rate is found to be twice as large as the dipole relaxation rate,[2] while in optically pumped Cd^{109} ($K=\frac{5}{2}$), the quadrupole relaxation rate is found to be 2.6 times greater than the dipole relaxation rate.[8] From Fig. 1 we see that the observed ratios strongly suggest that in both Hg^{201} and Cd^{109} relaxation is caused by the coupling of the electric quadrupole moment of the nucleus to fluctuating electric-field gradients.

B. Axial Symmetry: Zeeman Splitting of Relaxation Rates in a Magnetic Field

In the presence of a large static field, the environment of a spin system is no longer isotropic. However, axial symmetry around the magnetic field is maintained. Consequently, we can expect a kind of Zeeman splitting of the multipole relaxation rates into a number of different transverse and longitudinal relaxation rates. Before discussing this problem in more general terms, we first consider an instructive special case.

1. Zeeman Splitting of Relaxation Rates Caused by a Fluctuating Magnetic Field

Let us assume that the relaxation of the atom is due to the interaction of its dipole moment with a small, fluctuating magnetic field whose root-mean-square amplitude is h, and whose correlation time is τ_c [see Eq. (9)]. Then from (12) we find that the zero-field relaxation rates are [compare Eq. (4) of Ref. 9]

$$\gamma_L(1)=\tfrac{1}{3}[(h\gamma)^2\tau_c L(L+1)], \tag{15}$$

where γ is the gyromagnetic ratio of the atom.

Now let a static magnetic field define an axis of symmetry (z axis) and a Larmor frequency ω for the atoms. Equation (6) becomes (see Appendix)

$$(d/dt)\sigma_{LM}=-\gamma_{LM}\sigma_{LM}, \tag{16}$$

where

$$\gamma_{LM}=\gamma_L(1)J_{LM}(\omega\tau_c), \tag{17}$$

and the function $J_{LM}(x)$ is defined by

$$J_{LM}(x)=\frac{1}{L(L+1)}\left\{M^2+\frac{L^2-M^2+L}{1+x^2}\right\}+\frac{-iMx}{L(L+1)(1+x)^2}. \tag{18}$$

We note that

$$J_{LM}(0)=1. \tag{19}$$

[8] M. Leduc and J. Brossel, Compt. Rend. **266**, 287 (1968).
[9] M. A. Bouchiat and J. Brossel, Phys. Rev. **147**, 41 (1966).

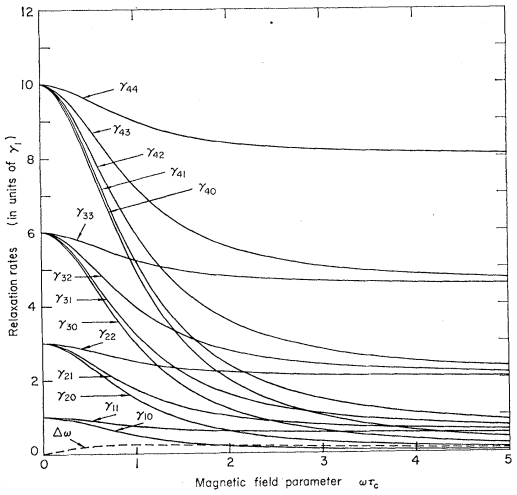

FIG. 2. High-field relaxation rates for a magnetic interaction ($l=1$). The rates have been normalized to the dipole relaxation rate at zero field. The splitting of the relaxation rates is analogous to the Zeeman splitting of atomic hyperfine structure.

At finite magnetic fields ($\omega\neq 0$), the multipole relaxation rates are no longer independent of M. We call $\gamma_{LM}(1)$ a longitudinal relaxation rate if $M=0$ and a transverse relaxation rate if $M\neq 0$. Except at zero magnetic field, the transverse relaxation rates are complex. The imaginary part of the relaxation rate gives rise to frequency shifts in the magnetic resonance spectrum of the atoms.

The real parts of the relaxation rates have been plotted as a function of $\omega\tau_c$ in Fig. 2. Note that the longitudinal rates approach zero at high magnetic fields, while the transverse relaxation rates approach a finite limit

$$\gamma_{LM}\rightarrow\tfrac{1}{3}[(h\gamma)^2\tau_c M^2] \tag{20}$$

as $\omega\rightarrow\infty$. The high-field limits can be understood fairly easily on physical grounds. Consider a coordinate system rotating with the Larmor frequency ω around the z axis. In the high-field limit, the transverse components of V^* will be rotating backward too rapidly [see (7)] to have any effect on the spins. Only the longitudinal components of V^* continue to fluctuate at low frequencies. The fluctuating longitudinal components cannot cause transitions between the different sublevels of the atoms, and consequently, no transfer of population or longitudinal relaxation can occur. However, over a time interval τ_c, random phase errors on the order of

$$h\gamma M\tau_c/\sqrt{3}$$

will be produced between the amplitudes a_m and a_{m+M} of a superposition state

$$a_m|Km\rangle+a_{m+M}|Km+M\rangle.$$

A simple random-walk calculation then leads to (20) for the relaxation time of $\langle a_m a_{m+M}\rangle_{\text{av}}$.

The imaginary components of the relaxation rates are

$$\mathrm{Im}\gamma_{LM}=-\tfrac{1}{3}(h\gamma)^2\tau_c\frac{\omega\tau_c}{1+(\omega\tau_c)^2}M. \tag{21}$$

This is equivalent to a simple shift

$$\Delta\omega=\tfrac{1}{3}(h\gamma)^2\tau_c\frac{\omega\tau_c}{1+(\omega\tau_c)^2} \tag{22}$$

in the Larmor frequency of the spin system. The frequency shift is also plotted in Fig. 2.

2. *Zeeman Splitting of Relaxation Rates Caused by Fluctuating Electric-Field Gradients and Higher-Order Interactions*

For quadrupole and high-order interactions the problem of finding high-field relaxation times becomes more complex. The relaxation of the density matrix is governed by the coupled equations

$$\frac{d}{dt}\sigma_{LM}=\sum_{L'}R_{LL'}(M)\sigma_{L'M},\quad L'=L,L\pm2,\ldots,L\pm(2l-2). \tag{23}$$

The elements of the relaxation matrix are

$$R_{LL'}(M)=-\tau_c v^2[1+(-1)^{L+L'}]\sum_{\lambda}[1-(-1)^{l+L+\lambda}]\times(2\lambda+1)W(l\lambda KK;LK)W(l\lambda KK,L'K)\times\sum_{\mu}\frac{C(l\lambda L;\mu,M-\mu)C(l\lambda L';\mu,M-\mu)}{1+i\omega\mu\tau_c}. \tag{24}$$

Several selection rules reduce the number of coupled equations somewhat. Because of the axial symmetry, the relaxation matrix couples only those components σ_{LM} and $\sigma_{L'M}$ of the density matrix that have the same azimuthal quantum number M and satisfy the condition

$$(-1)^{L+L'}=1. \tag{25}$$

Furthermore, (24) implies that $R_{LL'}(M)$ is zero unless

$$|L-L'|\leq 2l-2. \tag{26}$$

Unfortunately, (24) is still rather cumbersome, and although it is possible to transform it into a number of equivalent forms by the application of sum rules, we have been unable to reduce it to a simple formula, except for the special case $l=1$, which has already been discussed.

Once the relaxation matrix (24) has been evaluated, it is a straightforward matter to solve (23) by assuming an exponential solution and solving the secular equation that results. Although the longitudinal relaxation rates are real, the transverse relaxation rates will, in general, be complex. An example of the calculation of high-field relaxation rates for $l=2$ can be found in Ref. 2.

III. CONCLUSIONS

We have shown that in the limit of a small magnetic field the relaxation of a spin system by a weak, fluctuating perturbation can be described by a set of multipole relaxation rates. These rates are given by the simple formulas (12) and (15). If the atoms are subject to a static magnetic field of arbitrary size, and relaxation is caused by a small, fluctuating magnetic field, the longitudinal and transverse relaxation rates are given by the formulas (15), (17), and (18). We have been unable to find analogous, simple formulas for high-field relaxation rates caused by fluctuating electric-field gradients or by higher-order interactions. However, we do present a formula for the relaxation matrix, from which relaxation rates can be calculated for any specific case. Finally, we mention that all of these results can be generalized to the case where several interactions of different multipolarities or correlation times are simultaneously present. Some of these results also have close analogs for atoms with hyperfine structure.

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APPENDIX

In order to evaluate (6), we make use of the commutation relation

$$[T_{LM},T_{L'M'}]=\sum_{L''}T_{L'',M+M'}[(2L+1)(2L'+1)]^{1/2}\times W(LL'KK;L''K)C(LL'L'';MM')\times[(-1)^{L+L'+L''}-1], \tag{27}$$

which can be proved from the definition (4) by recoupling of angular momentum. We note that

$$V^*(t)=\sum_{\mu}e^{i\omega\mu t}V_{l-\mu}T_{l\mu}(-1)^{\mu}. \tag{28}$$

Applying (27) twice and making use of (9), we obtain

$$\left\langle\int_0^{\infty}d\tau[V^*(t)[V^*(t-\tau)T_{LM}]]\right\rangle=v^2\tau_c\sum_{\lambda,L'}[(-1)^{l+\lambda-L}-1][(-1)^{l+\lambda-L'}-1]T_{L'M}\times(2\lambda+1)W(l\lambda KK;LK)W(l\lambda KK;L'K)\times\sum_{\mu}\frac{C(l\lambda L;\mu,M-\mu)C(l\lambda L';\mu,M-\mu)}{1-i\omega\mu\tau_c}, \tag{29}$$

which leads to (24).

In the limit $\omega\tau_c \to 0$, Eq. (24) becomes

$$R_{LL'}(M) = -\delta_{LL'} 2v^2\tau_c \sum_{\lambda} [1-(-1)^{l+L+\lambda}] \times(2\lambda+1)W^2(l\lambda KK; LK). \quad (30)$$

Noting that

$$(-1)^{l+L+\lambda} = [(2l+1)(2L+1)]^{1/2} W(llLL; 0\lambda) \quad (31)$$

and making use of the sum rules 6.13 and 11.11 of Rose,[5] we obtain (12). For the special case $l=1$, we must have $L'=\lambda=L$ in (24), since a magnetic field simply rotates the atoms of an ensemble and does not couple different multipole moments. Then one can use tabulated Clebsch-Gordan coefficients (Rose,[5] p. 225) to obtain (17) from (24).

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Conduction-Electron Spin Polarization around a Magnetic Impurity*

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The spatial distribution of the conduction-electron spin polarization has been calculated for the Anderson model using the Hartree-Fock approximation. An expression for low temperatures has been obtained. The long-range behavior of spin polarization at absolute zero temperature is compared with the Ruderman-Kittel-Kasuya-Yosida result.

I. INTRODUCTION

THERE are two models (the Anderson and the Wolff-Clogston)[1–3] based on Friedel's picture[4] of virtual states to explain the appearance of localized magnetic moments (henceforth called local moments) in a dilute alloy of magnetic atoms in a nonmagnetic host. Both of these models are capable of predicting qualitatively the appearance of local moments in many cases. Several recent review papers[5–7] have discussed various attempts to get the exact solution of the problem of the local moments in different models.

Recently, Schrieffer, and Wolff[8] have shown that under a certain transformation the Anderson Hamiltonian goes over to the exchange Hamiltonian form, used by Kondo to show the Kondo effect.[9] The spin polarization for an exchange Hamiltonian has already been studied and the results are known as Ruderman-Kittel-Kasuya-Yosida (RKKY) polarization.[10–13] Several authors[14,15] have made calculations for spin polarization due to a magnetic impurity in different models.

The present paper is aimed at deriving conduction-electron spin polarization around a magnetic impurity in the Anderson model, under the Hartree-Fock (HF) approximation, as a function of the distance from the impurity. An expression for spin polarization at low temperatures is obtained. The long-range behavior at absolute zero temperature is compared with the RKKY result,[10–13] to see if Anderson's description of the magnetic impurity conforms to the expected exchange form of the conduction-electron-impurity interaction.

The magnitude of spin polarization is calculated for the most favorable case for the appearance of the local moments,[1] in which the levels for spin-up and spin-down electrons are close to each other and lie symmetrically about the Fermi level. A comparison of the magnitudes in our case and in the corresponding RKKY limit is made.

II. THEORY

In the Anderson model we take an extra d orbital for the impurity. The overcompleteness of the resulting set has been discussed by Anderson and McMillan.[16] They have shown that such a description gives essentially identical results with the case in which the impurity d orbital is orthogonalized to the conduction band states. In the present paper we calculate polarization in the region beyond the range of the d orbital. Irrespective of whether we start with an overcomplete set or an orthog-

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