PHYSICAL REVIEW VOLUME 128, NUMBER 5 DECEMBER 1, 1962

Statistical Theory of Spin Resonance Saturation

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(Received July 27, 1962)

In the high-temperature limit for a macroscopic spin system the equivalence of canonical and microcanonical averages is shown to imply that a diagonal element of any extensive operator is simply related to the corresponding energy eigenvalue. This relation permits a steady-state solution of the density matrix transport equation appropriate to spin resonance saturation in the limit of weak spin-lattice relaxation, strong saturation, and homogeneous broadening. The solution corresponds to a thermal distribution with respect to the transformed Hamiltonian in the rotating coordinate system, as had been conjectured previously.

INTRODUCTION

A STARTING point for much of statistical physics is the assumption that the value of any extensive variable in a macroscopic system having a definite energy is equal to the average value of the same variable for a canonical ensemble of systems having the same average energy, independent of the initial state of the system. There are really two steps involved in this assumption: The first is expressed, classically, as the hypothesis that in the course of time a system will pass arbitrarily close to all points in phase space having the same energy. The second step is a more or less rigorous proof of the mathematical equivalence of canonical and microcanonical averages, and of the relative disappearance of fluctuations of extensive quantities as the volume is increased. The physical reasoning underlying these ideas is well known and will not be repeated here.[1] A consequence of this assumption is that a macroscopic system can always be described by a temperature under reversible conditions, so that reversible variations of such systems can be treated according to thermodynamics.

This assumption naturally applies to spin systems[2,3] provided that no part of the system is isolated from the rest of the system as a result of unequal single-spin level splittings,[4] and provided the system is not in a ferromagnetic state. In fact, a nuclear spin system provides a model *par excellence* for statistical mechanics, since it is possible and realistic to formally divide it into a large number of weakly interacting subsystems, each containing in turn many spins; thus a macroscopic spin system is a simple realization of a canonical ensemble. Furthermore, the energy spectrum of a spin system has an upper bound, so that at laboratory temperatures one can make expansions in $(kT)^{-1}$, keeping only the first term.

Spin systems are of interest because of the variety of experiments which can be performed on them and because they are tractable theoretically in the high-temperature limit.

We restrict our attention to a coupled nuclear spin system having a Hamiltonian $\mathcal{H}$ which contains a Zeeman interaction with an external field $\mathbf{H}$, and a spin-spin interaction characterized by an interaction field H_{ss} not much less than H. Such a system has no obvious *extensive* constants of the motion other than the energy;[5] we will assume that there are no others whatsoever. It is well known that if $H \gg H_{ss}$, Zeeman and spin-spin energy are each effectively constants of the motion, and that similar problems arise when two or more spin species are present. We do not wish to worry about such problems but we feel they offer no insurmountable difficulty.

We always use a representation in which $\mathcal{H}$ is diagonal, and we denote its eigenstates by α, β. We will be interested in knowing the diagonal elements $U_{\alpha\alpha}$ of an operator whose expectation value is assumed to be an extensive quantity. The element $U_{\alpha\alpha}$ is the expectation value for the system if it has a definite energy $\mathcal{H}_{\alpha\alpha}$, so by the assumption stated in the first sentence

$$U_{\alpha\alpha} = \mathrm{Tr}U \exp(-\mathcal{H}/kT_\alpha)/\mathrm{Tr} \exp(-\mathcal{H}/kT_\alpha), \quad (1)$$

where T_α is implicitly determined by

$$\mathcal{H}_{\alpha\alpha} = \mathrm{Tr}\mathcal{H} \exp(-\mathcal{H}/kT_\alpha)/\mathrm{Tr} \exp(-\mathcal{H}/kT_\alpha). \quad (2)$$

It should be remembered that $U_{\alpha\alpha}$ is, by definition, the expectation value of U for a *particular* eigenstate α, not an average over many eigenstates. Equation (1) states our assumption that this expectation value is equal to a certain canonical average expectation value. We assume, therefore, that differences in the expectation value of U between different states α and α' having the same energy are negligible for a macroscopic system. This assumption is contained in the last phrase of the first sentence, and is made reasonable by arguments

[1] See, for example, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1958), Chap. 1.

[2] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947) and references therein.

[3] A. Abragam, *Nuclear Magnetism* (Clarendon Press, Oxford, 1961), Chap. V.

[4] A. Abragam and W. G. Proctor, Phys. Rev. 81, 278 (1951).

[5] The expectation value of $\mathcal{H}^3$, for example, is a constant of the motion but is not extensive. An extensive variable is one whose macroscopic equilibrium value is proportional to the volume. Evidently, it must be a quantity which can be specified in such a way that it is well defined for different systems of different volume. We will not attempt a more formal definition of the term "extensive," though it may be interesting to do so. We do not include entropy in this discussion as entropy is not represented by an operator in the usual sense.

concerning fluctuations in reference 1. We could express more precisely these ideas concerning the vanishing of fluctuations, but we feel that it is not useful to do so.

In the limit of high temperature we expand (1) and (2) in powers of T_α^{-1} and retain first terms. We choose our energy zero so that $\mathrm{Tr}\mathcal{H}=0$, and we also assume that $\mathrm{Tr}U=0$; the latter assumption is not essential but it simplifies what follows with no loss of generality. Then we have

$$U_{\alpha\alpha}=u\mathcal{H}_{\alpha\alpha}, \tag{3}$$

where u is a constant depending on U but independent of α:

$$u=\mathrm{Tr}\mathcal{H}U/\mathrm{Tr}\mathcal{H}^2. \tag{4}$$

Equation (3) must not be taken too literally: Presumably it fails for a negligible set of states for a macroscopic system, such as low-energy ordered states. Equation (3) was derived for the high-temperature limit, yet temperature is absent from the final result. Thus, α must be limited to states of nearly zero energy or, in other words, small spin order.

So far we have found a simple mathematical relation (3) based on rather general assumptions. We have not introduced a canonical ensemble of systems explicitly, but have used it implicitly in order to elucidate the mathematical properties of extensive operators. This reasoning has been based only on the fact that we are dealing with a macroscopic system. So far we have said nothing about what the system is, or what experiments we are performing on it. In the next section we specifically introduce an ensemble of systems (since we use the density matrix) in order to treat relaxation and kinetics.

SATURATION

A. The Problem

We now apply (3) to the problem of the steady state of a spin system irradiated with a radio-frequency magnetic field at a frequency ω near resonance.[6] The spin system is assumed to be in a dc magnetic field $\mathbf{H}_0$ which is large compared to the rf and spin-spin interaction fields H_1 and H_{ss} and the system is thermally relaxed by some spin-lattice interaction. Such a system appears to violate the conditions stated in the introduction, and is also complicated by the presence of the strong near-resonant rf field; perturbation theory is not applicable. However, in a previous publication[7,8] we pointed out that under a canonical transformation corresponding to rotation around H_0 at the rf frequency ω, the time dependence of the spin Hamiltonian is effectively eliminated except for rapidly varying terms which can be neglected as nonsecular.[9] The remaining Hamiltonian $\mathcal{H}$ consists[10] of a truncated[9] spin-spin interaction and a Zeeman interaction with a field $\mathbf{H}_{\mathrm{eff}}$ which is the vector sum of a component $H_0-\omega/\gamma$ parallel to $\mathbf{H}_0$ plus a component H_1 perpendicular to $\mathbf{H}_0$. The *transformed* Hamiltonian $\mathcal{H}$ thus has the properties specified in the introduction, and the transformed equation of motion of the spin-system density matrix ρ in the rotating frame of reference is

$$d\rho/dt=-(i/\hbar)[\mathcal{H},\rho]-W(\rho-\rho_T), \tag{5}$$

where $\rho_T=\exp(-\mathcal{H}_z/kT)/\mathrm{Tr}\exp(-\mathcal{H}_z/kt)$ and W is a fourth rank matrix

$$(W\rho)_{\alpha\alpha'}=\sum_{\beta\beta'}W_{\alpha\alpha'\beta\beta'}\rho_{\beta\beta'}. \tag{6}$$

W expresses the rate of spin-lattice relaxation;[11,12] in many problems we can replace W by T_1^{-1} where T_1 is the spin-lattice relaxation time. In general, however, we assume that W has the property that if U is an extensive variable operator, WU is also extensive. This assumption is valid for all relaxation processes and all simple extensive operators encountered in practice. Also, $W\mathbf{1}=0$, where $\mathbf{1}$ is the unit matrix, and if $\mathrm{Tr}U=0$ then $\mathrm{Tr}WU=0$. The simple form of the last term in Eq. (5) is valid only in the high-temperature approximation.

$\mathcal{H}_z$ is the Hamiltonian of the spin system in the *fixed* coordinate system; it is an excellent approximation to include only the Zeeman interaction with the large static field $\mathbf{H}_0$ in $\mathcal{H}_z$, and, thus, to ignore the effect of the spin-spin and rf field interaction on the relaxation process, provided $H_0>H_{ss}$ and H_1.

Having made these approximations which make $\mathcal{H}$, W, and ρ_T time independent, we can hope to find a steady-state solution of (5)

$$(i/\hbar)[\mathcal{H},\rho]=-W(\rho-\rho_T). \tag{7}$$

The solution of (7) is difficult because $\mathcal{H}$ and $\mathcal{H}_z$ do not commute, and because we are dealing with a many-spin system.

B. The Solution

We expand ρ in increasing powers of W.

$$(i/\hbar)[\mathcal{H},\rho_0]=0; \tag{8}$$

$$(i/\hbar)[\mathcal{H},\rho_1]=-W(\rho_0-\rho_T); \tag{9}$$

$$(i/\hbar)[\mathcal{H},\rho_{N+1}]=-W\rho_N \quad (N>1). \tag{10}$$

The zeroth-order equation (8) is easily soluble; it requires only that ρ_0 be diagonal. (We use, as always, the representation in which $\mathcal{H}$ is diagonal. We assume for simplicity that there are no degenerate energy levels; this restriction is easily removed without changing the final result.)

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[6] This problem has also been treated theoretically by K. Tomita, Progr. Theoret. Phys. (Kyoto) **19**, 541 (1958), and B. N. Provotorov, Soviet Phys.—JETP **14**, 1126 (1962).
[7] A. Redfield, Phys. Rev. **98**, 1787 (1955), Sec. B.
[8] Reference 3, Chap. XII, part II.
[9] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[10] The Hamiltonian $\mathcal{H}$ in the present section is the same as $\mathcal{H}_{er}$ in reference 7. $\mathcal{H}_z$ corresponds to $\mathcal{H}_s$ or the first term thereof.
[11] Reference 3, Chap. IX.
[12] A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

To completely specify ρ_0 we have to go to (9); since $[\rho_1,\mathcal{H}]$ has no diagonal elements, (9) requires that

$$[W(\rho_0-\rho_T)]_{\alpha\alpha}=0. \tag{11}$$

We now show that this equation can be satisfied by a diagonal matrix ρ_0 of the form

$$\rho_0=\exp(-\mathcal{H}/kT^*)/\mathrm{Tr}\exp(-\mathcal{H}/kT^*). \tag{12}$$

This matrix corresponds to a thermal distribution in the rotating coordinate system, and T^* is the temperature in this system. T^* will be determined using (11) and (3). Expanding ρ_0 and ρ_T in $(kT)^{-1}$ and $(kT^*)^{-1}$ and retaining the first term, (11) becomes

$$[W(\mathcal{H}/kT^*-\mathcal{H}_z/kT)]_{\alpha\alpha}=0. \tag{13}$$

Since $\mathcal{H}$ and $\mathcal{H}_z$ are extensive, the left-hand side of (13) is the diagonal element of an extensive operator. From (3) and (4) we have

$$[W(\mathcal{H}/kT^*-\mathcal{H}_z/kT)]_{\alpha\alpha}=\mathcal{H}_{\alpha\alpha}\mathrm{Tr}\mathcal{H}W(\mathcal{H}/kT^*-\mathcal{H}_z/kT)/\mathrm{Tr}\mathcal{H}^2. \tag{14}$$

Since, in general, $\mathcal{H}_{\alpha\alpha}\neq0$, Eqs. (13) and (14) can be satisfied for all α only if

$$\mathrm{Tr}\mathcal{H}W(\mathcal{H}/kT^*-\mathcal{H}_z/kT)=0. \tag{15}$$

This condition determines T^*, which can be positive or negative and is usually smaller in magnitude than T.

It should be realized that we have found a detailed zeroth-order solution of (8) and (9). That is, if the assumptions of the introduction are correct, then (12) solves (8) and (11) *element* by *element*. Previously,[7] the matrix (12) had been used as a trial solution of (6) and T^* was determined[8] by an equation like (15) which is a statement of conservation of "effective energy" $\langle\mathcal{H}\rangle$ in the rotating system. What is new here is that we show that (12) is an *exact* solution in the macroscopic and high-temperature limit. The extension to low temperatures is probably difficult; for one thing, the relaxation term of (5) becomes more complicated.

We have not studied the higher order terms ρ_1, ρ_2, etc., in detail, though they are perfectly well determined in principle from (9) and (10), because the eigenvalues of $\mathcal{H}$ are unknown. From the detailed properties of $\mathcal{H}$ and $W(\rho_0-\rho_T)$, we conclude from (9) that $\rho_1\ll\rho_0$ if

$$(H_1^2+H_{ss}^2)^{1/2}/\gamma H_1^2T_1\ll1, \tag{16}$$

which is the usual condition that H_1 be well above saturation. There seems little doubt that (16) also insures convergence of the series. When relaxation proceeds via spin diffusion the convergence is doubtful, however, and the situation is complicated.

We may ask if our procedure is unique. Certainly the solution of (11) is unique. Our choice of solution (12) was determined by a desire to make $W(\rho_0-\rho_T)$ extensive. Evidently the choice is unique provided that there are no U such that WU is extensive and U commutes with $\mathcal{H}$. There is no obvious operator other than $\mathcal{H}$ satisfying these conditions, but a rigorous proof of uniqueness appears impossible.

The predictions of (13) and (15) are discussed in detail elsewhere[7,8] and are confirmed by experiment, although there are few quantitative experiments[13] in which relaxation plays an essential part.[14,15]

CONCLUSION

Starting from simple hypotheses about the Hamiltonian of a spin system in the rotating frame of reference, we have shown that the state of the system is described by a temperature in the rotating reference frame. This solution to the equation of motion has the peculiar property that it is correct to zeroth order in the relaxation rate (in the limit T_1 infinite), yet the final result depends on the *details* of the relaxation process (ratios of relaxation rates for different kinds of energy). The method used is unusual in that explicit use is made of the macroscopic nature of the spin system.

I would like to thank Peter Price for reading and commenting on the manuscript; and T. D. Schultz, D. Mattis, and P. Marcus for their comments.

[13] W. Goldburg, Phys. Rev. **122**, 831 (1961); R. Blume and A. Redfield (to be published).

[14] Other experiments which give reasonable qualitative agreement, but for which the relaxation process is too complicated or the data only qualitative, are described by A. Landesman and M. Goldman, Compt. rend. **252**, 263 (1961); D. Holcomb, Phys. Rev. **112**, 1599 (1958); N. Bloembergen and P. P. Sorokin, *ibid.* **110**, 865 (1958); and I. Solomon, and J. Ezraty, *ibid.* **127**, 78 (1962).

[15] Related experiments in which lattice relaxation plays no essential role are described by C. P. Slichter and W. P. Holton, Phys. Rev. **122**, 1701 (1961) and A. G. Anderson and S. Hartmann, *ibid.* **128**, 2023 (1962). The article of Slichter and Holton, in particular, is recommended as an introduction to this subject.