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THERMODYNAMICS AND STATISTICAL MECHANICS
OF A THREE-LEVEL MASER

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ABSTRACT

The population distribution and the associated thermodynamic properties of a three-level MASER are calculated. By treating the three spin states as individual chemical species, it is possible to write the partition function, free energy, internal energy, entropy, and chemical potential for each species. The principle of minimum entropy production is used to derive an equation of reaction equilibrium. This equation is used in separate thermodynamic and statistical mechanical calculations to obtain the normalized population distribution. This result agrees in first order with that obtained by means of the customary rate equations. Competitive relaxation processes and partial saturation effects are discussed in detail. The saturation parameter used is the one defined in the treatment of the Overhauser effect. An explicit expression is obtained for this parameter in terms of the various transition probabilities and its effect on MASER performance is discussed.

I. INTRODUCTION

The MASER, RASER, LASER, and IRASER are amplifiers which operate by stimulated emission of radiation in the microwave, radiofrequency, visible, and infrared regions of the electromagnetic spectrum, respectively. These devices depend, for their operation, on some scheme for changing the equilibrium Boltzmann population distribution among two or more discrete quantum mechanical energy levels.

It is the purpose of this paper to present several different techniques for calculating the steady-state population distribution and related thermodynamic quantities.

In order to fix our ideas we will consider a three-level solid state MASER subjected to a radiation field which "pumps" between the first and the third energy levels.

In Section II, the normalized population distribution is calculated by the customary kinetic method by means of the rate equations. A saturation parameter is defined to take into account incomplete saturation of levels 1 and 3. An explicit expression for this parameter is obtained, and its effect on MASER performance is discussed.

In Section III, a simple diagrammatic scheme is presented by which the relative (unnormalized) population distributions may be obtained.

In Section IV, a thermodynamic argument based on an equation of reaction equilibrium, the law of mass action, and the Van't Hoff equation is used to obtain the population distribution.

In Section V, a statistical mechanical method is developed which enables one to calculate the population distribution, internal energy, free energy, entropy, and heat capacity of a MASER.

In Section VI, the principle of minimum entropy production is used to demonstrate that the equation of reaction equilibrium used in Sections IV and V is justified from the point of view of the thermodynamics of irreversible processes.

II. THE RATE EQUATIONS

A. Notation

The energy level diagram for a three-level MASER is given in Fig. 1. The energy of the i^{th} level is denoted by E_i . The pump frequency is indicated by $\nu_{31} = (E_3 - E_1)/h$, the signal frequency by $\nu_{32} = (E_3 - E_2)/h$, and the idler frequency by $\nu_{21} = (E_2 - E_1)/h$. The radiative transition probabilities associated with the pump and signal frequencies are W_{13} and W_{23} , respectively, with $W_{ij} = W_{ji}$.

Fig. 1. Energy Level Diagram for a Three-level MASER

The thermal transition probability associated with relaxation between the i^{th} and j^{th} levels is represented by w_{ij} , but $w_{ij} \neq w_{ji}$. The thermal relaxation rates are related by the appropriate Boltzmann factor:

$$\begin{aligned} w_{21} &= w_{12}e^{\Delta} \\ w_{32} &= w_{23}e^{\delta} \\ w_{31} &= w_{13}e^{\Delta+\delta} \end{aligned} \tag{1}$$

where $\Delta \equiv h\nu_{21}/kT$ and $\delta \equiv h\nu_{32}/kT$ are convenient abbreviations. The steady-state operating occupation number of the i^{th} level is denoted by n_i and the equilibrium occupation number by N_i . This notation is standard in MASER literature.

The energy values, wave functions, and transition probabilities of a three-level solid-state MASER depend on the interaction of the paramagnetic ion with its crystalline environment and with the external magnetic field which has both static and time-varying components. We shall not be concerned in this paper with the explicit quantum mechanical calculation of these quantities, which have been discussed thoroughly in previous papers.⁽¹⁾

B. Approximations

Two approximations are made in the following treatment of the steady-state population distribution. The rate equations themselves are valid only when the electronic gyromagnetic ratio times the amplitude of the pumping field is small in comparison with the electronic spin-spin relaxation time.⁽²⁾ For mathematical simplicity, Δ and δ are assumed small compared with unity, although this condition is not satisfied experimentally at microwave frequencies and temperatures near 1°K.

C. Saturation Parameter

Overhauser⁽³⁾ introduced a saturation parameter in his paper on nuclear polarization, which is both instructive and convenient in this discussion of the three-level MASER:

$$s \equiv 1 - \frac{n_1 - n_3}{N_1 - N_3} \tag{2}$$

The parameter s ranges from 0, in the absence of a time-varying field, to 1, when the populations of levels one and three are equalized in the limit of a very large pumping field. Although the Overhauser effect provided some of the inspiration for Bloembergen's proposal for a solid-state MASER,⁽⁴⁾ this parameter has not to my knowledge been employed in papers on MASERS.⁽⁵⁾

D. Solution to the Rate Equations

The rate equation for the population of the i^{th} level may be written in the form

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij}) + \sum_j W_{ij} (n_j - n_i) \quad i, j = 1, 2, 3 \quad (3)$$

which, together with

$$N = \sum_i n_i = \text{total number of paramagnetic ions}, \quad (4)$$

comprise a set of three independent equations.

An explicit expression for s and for each of the n_i in terms of s is obtained from Eqs. (1) through (4) by somewhat tedious algebra.

$$s = \frac{W_{13}(w_{21} + w_{23} + W_{23}) + \frac{\nu_{32}}{\nu_{31}} W_{23} w_{21}}{W_{13}(w_{21} + w_{23} + W_{23}) + W_{23}(w_{13} + w_{21}) + w_{13} w_{21} + w_{13} w_{23} + w_{21} w_{23}} \quad (5)$$

$$\begin{aligned} n_1 &= \frac{N}{3} \left[1 + \frac{C}{3} + \frac{2D}{3} \right] \\ n_2 &= \frac{N}{3} \left[1 - \frac{2C}{3} - \frac{D}{3} \right] \\ n_3 &= \frac{N}{3} \left[1 + \frac{C}{3} - \frac{D}{3} \right] \quad , \end{aligned} \quad (6)$$

where

$$\begin{aligned} C &\equiv \frac{h}{kT} \left\{ \frac{s \nu_{31} w_{21} - \nu_{32} (w_{21} + w_{23})}{w_{21} + w_{23} + W_{23}} \right\} \\ D &\equiv \frac{h}{kT} \left\{ \frac{s \nu_{31} w_{21} (w_{23} + W_{23}) - \nu_{32} w_{21} W_{23}}{(w_{13} + W_{13})(w_{21} + w_{23} + W_{23})} + \frac{\nu_{31} w_{13}}{(w_{13} + W_{13})} \right\} . \end{aligned} \quad (7)$$

If neither the pumping nor the detection field is turned on, $W_{13} = W_{23} = 0$ and the saturation parameter $s = 0$. In this limit, Eqs. (6) go over, as they should, to the normal Boltzmann distribution:

$$\begin{aligned}
n_1 &= \frac{N}{3} \left\{ 1 + \frac{2\Delta}{3} + \frac{\delta}{3} \right\} = N_1 \\
n_2 &= \frac{N}{3} \left\{ 1 - \frac{\Delta}{3} + \frac{\delta}{3} \right\} = N_2 \\
n_3 &= \frac{N}{3} \left\{ 1 - \frac{\Delta}{3} - \frac{2\delta}{3} \right\} = N_3 \quad .
\end{aligned} \tag{8}$$

On the other hand, if the pumping field is large and if the transition $1 \rightarrow 3$ is not completely forbidden, W_{13} will dominate the relaxation rates and W_{23} . In this limit,

$$s = 1$$

$$D = 0$$

$$C = \frac{h}{kT} \left\{ \frac{\nu_{31}w_{21} - \nu_{32}(w_{21} + w_{23})}{w_{21} + w_{23} + W_{23}} \right\}$$

$$n_1 = n_3 = \frac{N}{3} \left(1 + \frac{C}{3} \right)$$

$$n_2 = \frac{N}{3} \left(1 - \frac{2C}{3} \right) \quad . \tag{9}$$

Suppose the signal transition probability is small compared with the pumping transition probability and with the various thermal relaxation rates, a situation often encountered experimentally. Then s takes the useful form

$$s \simeq \frac{1}{1 + \frac{w_{13}}{W_{13}} + \frac{w_{21}w_{23}}{(w_{21} + w_{23})W_{13}}} \quad . \tag{10}$$

From Eq. (10) we see that complete saturation of levels 1 and 3 is not guaranteed by $W_{13} \gg w_{13}$, since transitions may take place from level 3 to level 1 via level 2.

It is important to note that $s \neq 0$ when $W_{13} = 0$. In fact, in this case,

$$s = \frac{\frac{\nu_{23}}{\nu_{31}} W_{23}w_{21}}{W_{23}(w_{13} + w_{21}) + w_{13}w_{21} + w_{13}w_{23} + w_{21}w_{23}} \quad . \tag{11}$$

In the limit of large W_{23} , Eq. (11) becomes

$$s = \frac{\nu_{23}}{\nu_{31}} \frac{w_{21}}{w_{13} + w_{21}} \quad , \tag{12}$$

which is always less than unity.

If we denote by s_1 the saturation parameter in the presence of the pumping field but in the absence of the detection field, and by s_2 the saturation parameter when both fields are switched on, we see that the second field has the effect of reducing s_1 somewhat:

$$s_1 - s_2 = \left[\frac{1}{1 + \frac{3w}{W_{13}}} - \frac{\left(1 + \frac{W_{23}}{w} + \frac{\nu_{23}}{\nu_{31}} \frac{W_{23}}{W_{31}} \right)}{\left(1 + \frac{3w}{W_{13}} + \frac{W_{23}}{w} + \frac{2W_{23}}{W_{13}} \right)} \right], \quad (13)$$

where all the thermal relaxation times have been set equal to one another for simplicity.

E. MASER Performance

The gain band-width product and the noise temperature are among the most important figures of merit of an amplifier. These two quantities are related in a rather simple fashion to the population difference

$$n_3 - n_2 = \frac{NC}{3} = \frac{Nh}{3kT} \left\{ \frac{s \nu_{31} w_{21} - \nu_{32} (w_{21} + w_{23})}{w_{21} + w_{23} + W_{23}} \right\} \quad (14)$$

and the population ratio

$$\frac{n_2}{n_3} = 1 - C, \quad (15)$$

respectively. Now

$$G\Delta\nu \approx \frac{2 \nu_{32}}{|Q_M|}, \quad (16)$$

where G is the voltage gain, $\Delta\nu$ the band width, and Q_M is the magnetic Q :

$$Q_M \equiv - 2 \pi \nu_{32} E / P_{32}. \quad (17)$$

Here E is the energy stored in the principal cavity mode and P_{32} is the signal power emitted by the paramagnetic material:

$$P_{32} = (n_3 - n_2) h \nu_{32} W_{32}. \quad (18)$$

The noise temperature

$$T_N \approx |T_M|, \quad (19)$$

where T_M is the "spin temperature" associated with levels 2 and 3, i.e.,

$$\frac{n_2}{n_3} \equiv \exp \frac{h\nu_{32}}{kT_M} \approx 1 + \frac{\delta T}{T_M} \quad . \quad (20)$$

Expressions (16) and (19) are good approximations⁽⁶⁾ providing $Q_0^{-1} \ll Q_e^{-1} = |Q_M^{-1}|$, where Q_0 is the unloaded cavity Q and Q_e is the external Q . The gain band width as given in Eq. (16) holds for a reflection cavity. The factor of two should be omitted for a transmission cavity.

Combining Eqs. (14) through (20) enables one to write $G\Delta\nu$ in several equivalent forms:

$$G\Delta\nu \approx \frac{2\nu_{32}}{|Q_M|} = \frac{|P_{32}|}{\pi E} = \frac{N(h\nu_{32})^2}{3\pi EkT_N} W_{32} \quad . \quad (21)$$

Hence a large gain band-width product and a low noise temperature are mutually compatible.

The signal power emitted by the paramagnetic material is

$$P_{32} = \frac{Nh^2\nu_{32}}{3kT} \left\{ \frac{s\nu_{31}W_{21} - \nu_{32}(W_{21} + W_{23})}{W_{21} + W_{23} + W_{23}} \right\} W_{23} = -\frac{N(h\nu_{32})^2}{3kT_M} W_{23} \quad , \quad (22)$$

and the spin temperature is

$$T_M = -\frac{\delta T}{C} = \frac{\nu_{32}(W_{21} + W_{23} + W_{23})T}{\nu_{23}(W_{21} + W_{23}) - s\nu_{31}W_{21}} \quad . \quad (23)$$

It is instructive to consider several limiting cases of P_{32} and T_M .

For $s = 0$, we find $C = -\delta$ and $T_M = T$, as they should. Strictly speaking, $s = 0$ only when both W_{13} and W_{23} are zero, in which case $P_{32} = 0$.

If $W_{13} = 0$ and W_{23} is small, $P_{32} \approx -\frac{N(h\nu_{32})^2}{3kT} W_{23} = -(N_2 - N_3)h\nu_{32}W_{23}$, and we have absorption in the amount expected. As s increases, T_M approaches $+\infty$, for

$$s_C = \nu_{23}(W_{21} + W_{23})/\nu_{31}W_{21} \quad . \quad (24a)$$

In this case, $P_{32} = 0$; the two levels are equally occupied and the signal is lost completely in the noise, that is, the noise temperature is infinite. As s increases beyond the critical value s_C , the value of T_M goes immediately over to $-\infty$ and then to smaller negative values. The smallest negative value of T_M is, for $s = 1 > s_C$, when

$$T_M = \frac{\nu_{23}(w_{21} + w_{23} + W_{23})}{\nu_{23}(w_{21} + w_{23}) - \nu_{31}w_{21}} T \quad . \quad (25)$$

This gives an optimum value for the noise temperature and for P_{32} , which becomes

$$P_{32} = \frac{Nh^2\nu_{32}}{3kT} \left\{ \frac{\nu_{31}w_{21} - \nu_{32}(w_{21} + w_{23})}{w_{21} + w_{23} + W_{23}} \right\} W_{23} \quad , \quad (26)$$

which agrees with Weber's⁽¹⁾ Eq. (13).

The condition that $P_{32} > 0$ is given, in general, by the simple relation

$$1 \geq s > s_c \quad . \quad (24b)$$

If s reaches unity before it exceeds s_c , no emission is possible between levels 3 and 2. In this event, emission between levels 2 and 1 is possible, a situation which can be investigated by studying $n_2 - n_1$. However, in this case s will depend on W_{21} rather than on W_{23} .

If (24b) is satisfied and $w_{21} = w_{23}$, as is often the case, the condition for induced emission may be written as

$$(E_3 - E_1) > \frac{2(E_3 - E_2)}{s} \quad , \quad (24c)$$

which tells us that the pump frequency must be at least twice as large as the signal frequency, a familiar result.

Suppose that $w_{21} \gg w_{23}$, W_{23} , and $W_{13} \gg W_{23}$. These conditions lead to a very desirable situation, namely: $\nu_{31} > \nu_{32}/s$ guarantees emission, a less stringent condition than (24c);

$$s = \frac{1}{\left(1 + \frac{W_{13}}{W_{23}}\right)} \quad ,$$

which means saturation is easier; and

$$T_N = \frac{\nu_{23}}{\nu_{21}} T \quad ,$$

a low noise temperature.

In general, it is possible to say that complete saturation of levels 1 and 3 corresponding to an infinite $T_{M(13)}$ improves the noise temperatures of the MASER, a result discussed in detail by J. Weber.⁽⁷⁾ However, if levels 1 and 3 are only partially saturated, the noise temperature can be very large.

It is interesting to note that MASER performance can be improved by "artificially" shortening the relaxation time connecting levels 1 and 2 in order to satisfy the condition $w_{21} \gg w_{32}$. Such a scheme was used by Scovil, Feher, and Seidel,⁽⁸⁾ who succeeded in making one relaxation rate 10 times faster than another by putting 0.2% cerium ions in 0.5% gadolinium-doped, hydrated lanthanum ethyl sulfate.

III. RELATIVE POPULATION DISTRIBUTION DIAGRAMS

In the absence of a radiation field, the thermal relaxation rates w_{31} , w_{32} , and w_{21} establish a Boltzmann distribution between all three sets of levels, as shown in Fig. 2.

Fig. 2. Normal Boltzmann Population Distribution

Suppose now that levels 1 and 3 are saturated by a large W_{13} , i.e., $n_1 = n_3$. Suppose also that $w_{32} = 0$ but $w_{21} \neq 0$. In this case, a Boltzmann distribution is maintained between levels 1 and 2

$$n_1/n_2 = e^{\Delta} \approx 1 + \Delta \quad , \quad (27)$$

and the relative populations are given in Fig. 3a. Amplification between levels 3 and 2 is possible:

$$n_3 - n_2 \approx \frac{N}{3} \frac{h\nu_{21}}{kT} \quad . \quad (28)$$

Suppose, again, that levels 1 and 3 are saturated such that $n_1 = n_3$ by virtue of a large pumping field at frequency ν_{31} , but that $w_{21} = 0$ and $w_{32} \neq 0$. In this case, a Boltzmann distribution is maintained between levels 3 and 2:

$$n_2/n_3 = e^{\delta} \approx 1 + \delta \quad , \quad (29)$$

and the relative populations are given in Fig. 4a. Amplification between levels 2 and 1 is possible:

$$n_2 - n_1 \approx \frac{N}{3} \frac{h\nu_{32}}{kT} \quad . \quad (30)$$

In cases of practical interest, s may not be unity, and neither w_{21} nor w_{32} can be neglected. The effect of saturation may be introduced as follows. Let

$$n_1/n_3 = e^{\gamma} \approx 1 + \gamma \quad , \quad (31)$$

where γ is a parameter which includes the effect of saturation. The relationship between γ and s is easily found with the aid of Eqs. (2) and (8):

$$\gamma = (\Delta + \delta) (1 - s) \quad . \quad (32)$$

Partial saturation is indicated in the relative population distributions of Figs. 3b and 4b. Competitive relaxation may be treated by introducing the fractions

$$f_1 = \frac{w_{21}}{w_{21} + w_{23}}$$

and

$$f_2 = \frac{w_{23}}{w_{21} + w_{23}} \quad . \quad (33)$$

Fig. 3a. Complete Saturation $w_{32} = 0$

Fig. 3b. Partial Saturation $w_{32} = 0$

Fig. 4a. Complete Saturation $w_{12} = 0$

Fig. 4b. Partial Saturation $w_{12} = 0$

The relative populations for partial saturation and competitive relaxation may be found by multiplying f_1 times the relative populations of Fig. 3b, f_2 times the relative population of Fig. 4b, and adding. The result is indicated in Fig. 5, in which the relative n_i include all the idealized situations as special cases.

For $s = 0$; $n_1 \sim 1$, $n_2 \sim 1 - \Delta$, $n_3 \sim 1 - \Delta - \delta$ as in Fig. 2

For $s = 1$; $f_1 = 1$, and $f_2 = 0$; $n_1 \sim 1$, $n_2 \sim 1 - \Delta$, $n_3 \sim 1$ as in Fig. 3a

For $s = 1$, $f_2 = 1$, and $f_1 = 0$; $n_1 \sim 1$, $n_2 \sim 1 + \delta$, $n_3 \sim 1$ as in Fig. 4a

For $0 < s < 1$, $f_1 = 1$, and $f_2 = 0$; $n_1 \sim 1$, $n_2 \sim 1 - \Delta$, $n_3 \sim 1 - (\Delta + \delta)(1 - s)$ as in Fig. 3b

For $0 < s < 1$, $f_2 = 1$, and $f_1 = 0$; $n_1 \sim 1$, $n_2 \sim 1 - (\Delta + \delta)(1 - s) + \delta$, $n_3 \sim 1 - (\Delta + \delta)(1 - s)$ as in Fig. 4b.

Fig. 5. Partial Saturation. Competitive Relaxation

Using $\sum n_i = N$ and the relative distribution indicated in Fig. 5, one finds the following difference in population between levels 3 and 2:

$$\begin{aligned} n_3 - n_2 &= \frac{N}{3} \left\{ s(\Delta + \delta)(1 - f_2) - \delta \right\} = \frac{Nh}{3kT} \left[s \nu_{31} f_1 - \nu_{32} \right] \\ &= \frac{Nh}{3kT} \left[\frac{s \nu_{31} W_{21} - \nu_{32} (W_{21} + W_{32})}{W_{21} + W_{23}} \right] \end{aligned} \quad (34)$$

This result agrees with Eq. (14) obtained from the rate equations, except that it lacks W_{23} in the denominator. This is to be expected, since the foregoing scheme has not taken into account the effect of the detection field. Further, this method does not give an explicit value for s . Consequently, in Eq. (34) s must be interpreted as due to W_{13} and the thermal relaxation rates alone, as given by Eq. (10).

The procedure outlined in this section for computing the steady-state population distribution of a three-level MASER is modeled after similar calculations made by Pake⁽⁹⁾ for the Overhauser effect and by Jeffries⁽¹⁰⁾ for dynamic nuclear polarization.

IV. POPULATION DISTRIBUTION FROM A THERMODYNAMIC ARGUMENT

A. Thermodynamic Equilibrium

Let B_i denote the i^{th} chemical species of energy E_i , concentration n_i , and chemical potential μ_i . The chemical reactions which may take place between the three chemical species of the MASER are

In thermodynamic (mechanical, thermal, and chemical) equilibrium at temperature T , the chemical potentials for the three species are equal:

$$\mu_1 = \mu_2 = \mu_3 \quad . \quad (36)$$

From the equations of reaction equilibrium [Eq. (36)], for each of these three reactions we can derive the corresponding law of mass action:⁽¹¹⁾

$$\prod_{i=1}^3 n_i^{f_{ij}} = K_j \quad , \quad (37a)$$

above f_{ij} is the stoichiometric coefficient for the i^{th} species in the j^{th} reaction. It is taken as positive for quantities on the left-hand side and negative for quantities on the right-hand side of the reaction equation. The equilibrium constant for the j^{th} reaction is K_j , and this may be evaluated by integrating the Van't Hoff equation:

$$\frac{d}{dT} \ln K_j = \frac{\Delta U_j}{RT^2} \quad , \quad (38a)$$

where ΔU_j is the change in internal energy per mole during the j^{th} process and R is the gas constant. Writing out (37) and (38) explicitly, we have

$$\frac{n_1}{n_2} = K_1; \quad \frac{n_2}{n_3} = K_2; \quad \frac{n_1}{n_3} = K_3; \quad (37b)$$

$$\frac{d}{dT} \ln K_1 = -\frac{h\nu_{21}}{kT^2}; \quad \frac{d}{dT} \ln K_2 = -\frac{h\nu_{32}}{kT^2}; \quad \frac{d}{dT} \ln K_3 = -\frac{h\nu_{31}}{kT^2} \quad . \quad (38b)$$

After integrating (38b) and combining with (37b), we have

$$\frac{n_1}{n_2} = C_1 e^{h\nu_{21}/kT}; \quad \frac{n_2}{n_3} = C_2 e^{h\nu_{23}/kT}; \quad \frac{n_1}{n_3} = C_3 e^{h\nu_{31}/kT} \quad . \quad (39)$$

The constants of integration, C_j , may be found by the condition that, at $T \rightarrow \infty$, we have $n_1 = n_2 = n_3$, which gives $C_j = 1$ for all j . Thus we obtain

$$\frac{n_1}{n_2} = e^{\Delta} = \frac{N_1}{N_2}; \quad \frac{n_2}{n_3} = e^{\delta} = \frac{N_2}{N_3}; \quad \frac{n_1}{n_3} = e^{\Delta+\delta} = \frac{N_1}{N_3} \quad , \quad (40)$$

which is the normal Boltzmann distribution.

B. Steady-state Distribution in the Presence of a Radiation Field

We now suppose that there is a radiation field switched on, which completely saturates levels 1 and 3 such that $n_1 = n_3$. This is a constraint on the system which forces reaction (3) out of chemical equilibrium: $\mu_1 \neq \mu_3$. However, we assume that reactions (1) and (2) do come to chemical equilibrium. This they may not do independently, however, because then we would find that $\mu_1 = \mu_3$ and $n_1/n_3 = e^{\Delta+\delta}$, which is inconsistent with the constraint assumed.

We note that f_1 moles of B_2 is involved in reaction (1) and f_2 moles of B_2 in reaction (2), where f_1 and f_2 are given by Eq. (33). We now write a single reaction equation representing this situation:

or

The corresponding equation of reaction equilibrium is

$$\mu_2 = f_1 \mu_1 + f_2 \mu_3 \quad , \quad (42)$$

from which we write the law of mass action:

$$\frac{n_2}{\frac{f_1 f_2}{n_1 n_3}} = K \quad . \quad (43a)$$

For complete saturation, $n_1 = n_3$ and, using $f_1 + f_2 = 1$, Eq. (43a) becomes

$$n_2/n_3 = K \quad . \quad (43b)$$

As before, K is determined by integrating the Van't Hoff equation with

$$\Delta U = N_0 f_1 h \nu_{21} - N_0 f_2 h \nu_{32} \quad , \quad (44)$$

where N_0 is Avogadro's number. The result is

$$n_2/n_3 = \exp [-f_1 \Delta + f_2 \delta] \approx 1 - f_1 \Delta + f_2 \delta. \quad (45)$$

The population difference becomes

$$n_3 - n_2 \approx \frac{N h}{3 k T} [f_1 \Delta - f_2 \delta] = \frac{N h}{3 k T} \left[\frac{w_{21} \nu_{21} - w_{32} \nu_{32}}{w_{21} + w_{32}} \right] . \quad (46)$$

This agrees with Eq. (34), for $s = 1$ if we use $\nu_{31} = \nu_{21} + \nu_{32}$.

C. Partial Saturation

This thermodynamic argument may be readily extended to the case of partial saturation. In this case, $n_1/n_3 = e^\gamma$, and $\gamma = (\Delta + \delta)(1-s)$ from Eqs. (31) and (32). The equation of reaction equilibrium, (42), is not changed, but the law of mass action, (43a), does not reduce to the simple form given by (43b). Instead, we have

$$\frac{n_2}{n_3 e^{f_1 \gamma}} = K \quad . \quad (43c)$$

Again, $K = C \exp(f_2 \delta - f_1 \Delta)$, from which we find

$$n_2/n_3 = \exp[f_1(\gamma - \Delta) + f_2 \delta] \quad (47)$$

by means of the condition that $n_2 = n_3$ at $T = \infty$ to evaluate C as unity. Writing this out in the linear approximation, we find that

$$n_3 - n_2 \approx \frac{Nh}{3kT} [f_1 s(\Delta + \delta) - \delta] = \frac{Nh}{3kT} \left[\frac{sw_{21}\nu_{31} - (w_{21} + w_{32})\nu_{32}}{w_{21} + w_{32}} \right], \quad (48)$$

in agreement with Eq. (34)

The argument used in this section was inspired by a paper of Brovetto and Cini,⁽¹²⁾ who use the same method to discuss the Overhauser effect.

V. STATISTICAL MECHANICS OF A THREE-LEVEL MASER

A. Assumptions

Consider N paramagnetic ions in a crystalline environment and in an external magnetic field. The only energy values we consider are those associated with the interaction of the spin magnetic moment of each ion with the combined magnetic and crystal field. We assume that there are three such levels and divide the N ions into three corresponding chemical species. We assume that these three chemical species are in thermal equilibrium at temperature T with the lattice, but that they are not necessarily in chemical equilibrium with one another. The total partition function for a single ion with spin energy E_i may be written as the product of z_i and z_ℓ where $z_i = e^{-E_i/kT}$ and z_ℓ is a factor associated with all other contributions to the energy of the ion. We assume z_ℓ is the same for all three chemical species and focus our attention on the partial partition function z_i . The corresponding partition function⁽¹³⁾ for N_i identical

ions of energy E_i is

$$Z_i = \frac{(e^{-E_i/kT})^{n_i}}{n_i!} \quad (49)$$

The free energy F_i associated with the i^{th} species is given by

$$F_i = -k n_i T \ln Z_i = -k n_i T \ln z_i + kT \ln n_i! = n_i E_i + kT \ln n_i! \quad (50)$$

The internal energy, entropy, and chemical potential for the i^{th} species may be found from F_i as follows:

$$U_i = -T^2 \frac{\partial}{\partial T} \frac{F_i}{T} = n_i E_i \quad (51)$$

$$S_i = - \left(\frac{\partial F_i}{\partial T} \right)_{n_i} = -k \ln n_i! \quad (52)$$

$$\mu_i = \left(\frac{\partial F_i}{\partial n_i} \right)_T = E_i + kT \ln n_i \quad (53)$$

The expression for μ_i is obtained with the aid of Stirling's approximation:

$$\ln n_i! \approx n_i \ln n_i - n_i \quad (54)$$

From Eqs. (50), (51), and (52), it is clear that

$$F_i = U_i - TS_i \quad (55)$$

An essential assumption to the remainder of this statistical mechanical argument is the validity of the equation of reaction equilibrium:

$$\mu_2 = f_1 \mu_1 + f_2 \mu_3 \quad (42)$$

which has already been used in Section IV and which will be justified in Section VI.

B. Equilibrium

In thermodynamic equilibrium all the chemical potentials are equal. Using this condition with Eq. (53), we find that

$$n_1 = \exp\left(\frac{\mu - E_1}{kT}\right); \quad n_2 = \exp\left(\frac{\mu - E_2}{kT}\right); \quad n_3 = \exp\left(\frac{\mu - E_3}{kT}\right) \quad (56)$$

from which

$$\frac{n_1}{n_2} = e^{\Delta} = \frac{N_1}{N_2}; \quad \frac{n_2}{n_3} = e^{\delta} = \frac{N_2}{N_3}; \quad \text{and} \quad \frac{n_1}{n_3} = e^{\Delta+\delta} = \frac{N_1}{N_3} \quad .$$

C. Steady-state Distribution in the Presence of a Radiation Field

With a partially saturating field turned on,

$$n_1/n_3 = e^{\gamma}, \text{ where } \gamma \cong (\Delta + \delta)(1-s),$$

which means that $\mu_1 \neq \mu_3$. Using Eq. (53) we find that

$$\mu_3 - \mu_1 = E_3 - E_1 + kT \ln (n_1/n_3) = h\nu_{31} - kT\gamma = sh\nu_{31} \quad . \quad (57)$$

Now

$$\frac{n_3}{n_2} = \exp \left\{ \frac{(\mu_3 - \mu_2) - (E_3 - E_2)}{kT} \right\} \quad , \quad (58)$$

which, together with (42) and (57), gives

$$\frac{n_3}{n_2} = \exp \left(\frac{f_1 sh\nu_{31} - h\nu_{32}}{kT} \right) \quad . \quad (59)$$

If we take the linear term in the expansion of (59) and write out f_1 , Eq. (59) reduces to the previous result, Eq. (34).

D. Internal Energy, Heat Capacity, and Entropy of a Three-level MASER

This statistical mechanical approach has provided us with the population distribution obtained from the rate equations for the special case of no signal field ($W_{32} = 0$) and s given by Eq. (10). Explicit expressions for the various thermodynamics quantities associated with a three-level MASER may be calculated by means of Eqs. (50)-(52), inclusive, in conjunction with Eqs. (6) and (7). Thus

$$U = \sum_i U_i = n_1 E_1 + n_2 E_2 + n_3 E_3 \quad (60)$$

$$C_H = \left(\frac{\partial U}{\partial T} \right)_H \quad (61)$$

$$S = \sum_i k n_i (1 - \ln n_i) = Nk - k \sum_i n_i \ln n_i \quad . \quad (62)$$

Let us treat the special case of $s = 1$ and compare the internal energy and heat capacity of a fully saturated MASER with the same quantities in the absence of a pumping field. In these limits,

$$n_1 = \frac{N}{3} \left(1 + \frac{C}{3}\right); \quad n_2 = \frac{N}{3} \left(1 - \frac{2C}{3}\right); \quad n_3 = \frac{N}{3} \left(1 + \frac{C}{3}\right) \quad , \quad (63)$$

with $C = \Delta f_1 - \delta f_2$ for $s = 1$ and

$$N_1 = \frac{N}{3} \left[1 + \frac{2\Delta}{3} + \frac{\delta}{3}\right]; \quad N_2 = \frac{N}{3} \left[1 - \frac{\Delta}{3} + \frac{\delta}{3}\right]; \quad N_3 = \frac{N}{3} \left[1 - \frac{\Delta}{3} - \frac{2\delta}{3}\right] \quad (64)$$

for $s = 0$. We take $E_1 = 0$, $E_2 = \Delta kT$, $E_3 = (\Delta + \delta)kT$ and find

$$U_1 = \frac{N}{3} (\nu_{31} + \nu_{21}) - \frac{Nh^2}{9kT} (\nu_{21} - \nu_{32}) \left(\frac{\nu_{21}w_{21} - \nu_{32}w_{23}}{w_{21} + w_{23}} \right) \quad (65)$$

$$U_0 = \frac{N}{3} (\nu_{31} + \nu_{21}) - \frac{2Nh^2}{9kT} (\nu_{21}^2 + \nu_{21}\nu_{32} + \nu_{32}^2) \quad (66)$$

$$\frac{\partial U_1}{\partial T} = \frac{Nh^2}{9kT^2} (\nu_{21} - \nu_{32}) \left(\frac{\nu_{21}w_{21} - \nu_{32}w_{23}}{w_{21} + w_{23}} \right) + \phi(T) \quad (67)$$

$$\frac{\partial U_0}{\partial T} = \frac{2Nh^2}{9kT^2} (\nu_{21}^2 + \nu_{21}\nu_{32} + \nu_{32}^2) \quad . \quad (68)$$

In Eq. (67), $\phi(T)$ is added to take into account the temperature dependence of the thermal relaxation rates:

$$\phi(T) = - \frac{Nh^2}{9kT} (\nu_{31} - \nu_{32}) \left(\nu_{21} \frac{\partial f_1}{\partial T} - \nu_{32} \frac{\partial f_2}{\partial T} \right) \quad . \quad (69)$$

From Eqs. (65) and (66), we see that, when $w_{21} = w_{23}$, the internal energy of a fully saturated MASER exceeds that of an unsaturated MASER by $(Nh^2/6kT)\nu_{31}^2$. From Eqs. (67) and (68), we see that when $w_{21} = w_{23}$ and $\frac{\partial w_{21}}{\partial T} = \frac{\partial w_{23}}{\partial T}$ the heat capacity of a saturated MASER is less than that of an unsaturated MASER by $(Nh^2/6kT^2)\nu_{31}^2$.

The entropy difference for a partially saturated and an unsaturated MASER is given from Eq. (62) by

$$S_s - S_0 = k \sum_i (N_i \ell_n N_i - n_i \ell_n n_i) \quad . \quad (70)$$

For the special case $s = 1$, and $w_{21} = w_{23}$,

$$S_1 - S_0 \approx \frac{Nk}{6} \ln \left[\frac{N}{3} \left(\frac{h\nu_{31}}{kT} \right)^2 \right] \quad . \quad (71)$$

The point of view expressed in Section V closely parallels Desloge's⁽¹³⁾ statistical treatment of the Overhauser effect in metals.

VI. MINIMUM ENTROPY PRODUCTION

A. Notation

Consider the five reactions among the three chemical species:

The first three reactions are thermal relaxation processes in which the lattice supplies or receives energy from the paramagnetic system. The last two reactions are radiative transitions induced by the presence of time-varying magnetic fields of the proper frequencies.

Two quantities of considerable use in this discussion are the chemical affinities A_j ($j = 1, 2, 3$) and the differential degrees of advancement $d\xi_k$ ($k = 1, 2, 3, 4, 5$):

$$\begin{aligned} A_1 &\equiv \mu_2 - \mu_1 \\ A_2 &\equiv \mu_3 - \mu_2 \\ A_3 &\equiv \mu_3 - \mu_1 \end{aligned} \quad (73)$$

$$\begin{aligned} d\xi_1 &\equiv d_1 n_1 = -d_1 n_2 \\ d\xi_2 &\equiv d_2 n_2 = -d_2 n_3 \\ d\xi_3 &\equiv d_3 n_1 = -d_3 n_3 \\ d\xi_4 &\equiv d_4 n_1 = -d_4 n_3 \\ d\xi_5 &\equiv d_5 n_2 = -d_5 n_3 \end{aligned} \quad (74)$$

In Eq. (74), $d_k n_i$ means the change in n_i due to the k^{th} reaction:

$$dn_i \equiv \sum_{k=1}^5 d_k n_i \quad . \quad (75)$$

B. The Gibbs Relation

We assume the validity of the Gibbs relation when the system is not necessarily in thermodynamic equilibrium:

$$TdS = dU - \sum_i \mu_i dn_i + dW \quad , \quad (76)$$

and set $dW = 0$ on the assumption that the sample volume and the static magnetic field are held constant.

With the aid of Eqs. (73), (74), and (75), Eq. (76) may be rewritten as follows:

$$TdS = dU + \sum_{j=1}^3 A_j d\xi_j + A_3 d\xi_4 + A_2 d\xi_5 \quad . \quad (77)$$

The quantity of interest is the internal entropy production associated with the irreversible relaxation processes:

$$\frac{d_i S}{dt} = \frac{1}{T} \sum_{j=1}^3 A_j \frac{d\xi_j}{dt} \quad . \quad (78)$$

The $\frac{d\xi_j}{dt}$'s and the A_j 's are related as follows:

$$\begin{aligned} \frac{d\xi_1}{dt} &= \frac{d_1 n_1}{dt} = n_2 w_{21} - n_1 w_{12} \cong \frac{w_{21} N}{3kT} A_1 \\ \frac{d\xi_2}{dt} &= \frac{d_2 n_2}{dt} = n_3 w_{32} - n_2 w_{23} \cong \frac{w_{32} N}{3kT} A_2 \\ \frac{d\xi_3}{dt} &= \frac{d_3 n_1}{dt} = n_3 w_{31} - n_1 w_{13} \cong \frac{w_{13} N}{3kT} A_3 \\ \frac{d\xi_4}{dt} &= \frac{d_4 n_1}{dt} = (n_3 - n_1) W_{13} \cong \frac{W_{13} N}{3kT} (A_3 - h \nu_{31}) \\ \frac{d\xi_5}{dt} &= \frac{d_5 n_2}{dt} = (n_3 - n_2) W_{23} \cong \frac{W_{23} N}{3kT} (A_2 - h \nu_{23}) \quad . \end{aligned} \quad (79)$$

An important approximation is made in obtaining Eq. (79):

$$A_j \ll kT \quad j = 1, 2, 3 \quad . \quad (80)$$

Combining Eqs. (79) and (78)

$$\begin{aligned} \frac{d_i S}{dt} &\cong \frac{N}{3kT^2} [w_{21}A_1^2 + w_{23}A_2^2 + w_{13}A_3^2] \\ &\cong \frac{N}{3kT^2} [w_{21}A_1^2 + w_{23}(A_1^2 - 2A_1A_3 + A_3^2) + w_{13}A_3^2] \quad . \end{aligned} \quad (81)$$

The second form for Eq. (81) follows from the fact that the A_j are not independent:

$$A_2 = A_3 - A_1 \quad . \quad (82)$$

In thermodynamic equilibrium $\frac{d_i S}{dt} = 0$, in which case we see from (81) that $A_1 = A_2 = A_3 = 0$, $\mu_1 = \mu_2 = \mu_3$, and we obtain the normal Boltzmann population distribution.

In the presence of a pumping field but without a signal field, A_3 is held fixed at a nonzero value and $W_{23} = 0$. The principle of minimum entropy production now requires that

$$\frac{\partial}{\partial A_1} \left(\frac{d_i S}{dt} \right) = 0 \quad . \quad (83)$$

Carrying out the indicated differentiation of the second form of Eq. (81) leads to the simple condition

$$A_1 w_{21} = A_2 w_{23} \quad . \quad (84)$$

Using the definition of the chemical affinities, Eq. (73), and the definition of the f 's, Eq. (33), this condition is equivalent to the equation of reaction equilibrium:

$$\mu_2 = \mu_1 f_1 + \mu_3 f_2 \quad . \quad (85)$$

What happens to the power P_{13} absorbed by the MASER system?

$$P_{13} = (n_1 - n_3) h \nu_{13} W_{13} \cong \frac{N}{3} \frac{(h \nu_{13})^2}{kT} (1-s) W_{13} \quad . \quad (86)$$

A fraction s of this power increases the internal energy of the MASER without an increase in temperature. This is represented by the third term on the right-hand side of Eq.(77):

$$-A_3 \frac{d\xi_4}{dt} = s(n_1 - n_3)h\nu_{13}W_{13} = sP_{13} \quad . \quad (87)$$

The balance, $(1-s)P_{13}$, increases the temperature of the sample without an increase in the internal energy of the spin system. If the MASER material is kept at constant temperature T , this power boils off some of the liquid helium or nitrogen coolant. In the steady state, the rate of increase in internal energy is exactly compensated by the power lost due to thermal relaxation. This latter is represented by

$$+T \left(\frac{d_i S}{dt} \right)_{\min} = \frac{N}{3kT} A_3^2 \left\{ w_{31} + \frac{w_{21}w_{32}}{w_{21} + w_{32}} \right\} \quad . \quad (88)$$

Equation (88) follows from Eqs. (81), (82), and (84). Using Eqs. (73), (53), and (57),

$$A_3 = sh\nu_{13} \quad , \quad (89)$$

from which

$$+T \left(\frac{d_i S}{dt} \right)_{\min} = \frac{N}{3kT} (h\nu_{13})^2 s^2 \left\{ w_{31} + \frac{w_{21}w_{32}}{w_{21} + w_{32}} \right\} \quad . \quad (90)$$

By equating Eqs. (87) and (90) for the steady state, we find an explicit expression for the saturation parameter:

$$s = \frac{W_{13}(w_{32} + w_{21})}{W_{13}(w_{32} + w_{21}) + w_{31}w_{21} + w_{31}w_{32} + w_{21}w_{32}} \quad , \quad (91)$$

in agreement with Eq. (10).

As the saturation is increased to higher levels, less of the input power is used to increase the sample temperature and more is used to increase the internal energy of the MASER system. In fact, in the limit that $s = 1$, when $W_{13} \gg w_{ij}$, we see from Eqs. (86), (87), (90), and (91) that

$$P_{13} = \frac{N}{3kT} (h\nu_{13})^2 \left\{ w_{31} + \frac{w_{32}w_{21}}{w_{32} + w_{21}} \right\} = T \left(\frac{d_i S}{dt} \right)_{\min} \quad . \quad (92)$$

This discussion, using the thermodynamics of irreversible processes, has been guided by the work of Barker and Mencher⁽¹⁴⁾ on the Overhauser effect and by Desloge's⁽¹³⁾ Ph. D. dissertation, which, in turn, relied heavily on the excellent treatises on this important branch of thermodynamics by S. R. de Groot⁽¹⁵⁾ and I. Prigogine.⁽¹⁶⁾

CONCLUSION

It has been shown in this paper that the principle of minimum entropy production leads to an equation of reaction equilibrium which may be used either by a thermodynamic or a statistical mechanical argument to calculate the population distribution of a three-level MASER. This result of the thermodynamics of irreversible processes is subject to the restriction that all three of the chemical affinities be small in comparison with kT . This means in particular that

$$A_1 = h\nu_{21} \left(1 - \frac{T}{T_{M(12)}} \right) \ll kT \quad (93)$$

$$A_2 = h\nu_{32} \left(1 - \frac{T}{T_{M(23)}} \right) \ll kT \quad (94)$$

$$A_3 = sh\nu_{31} = h\nu_{31} \left(1 - \frac{T}{T_{M(13)}} \right) \ll kT \quad , \quad (95)$$

where $T_{M(ij)}$ is the "spin temperature," a convenient parameter, associated with the nonequilibrium population ratio n_i/n_j

$$\left[\frac{n_i}{n_j} \equiv \exp \frac{h\nu_{ij}}{kT_{M(ij)}} \right] .$$

The population distribution calculated by means of the rate equations uses the approximation that $h\nu_{31}$, $h\nu_{21}$, and $h\nu_{32}$ are small compared to kT .

The principal conclusion is that the minimum entropy production population distribution and the steady-state population distribution are found to agree in lowest order where comparable approximations are made.

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