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Implications of radiative equilibrium in neoclassical theory

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We discuss some implications of the description of spontaneous emission of radiation which has been offered by Jaynes and his collaborators in their "neoclassical" extension of semiclassical electrodynamics. In particular, we examine the thermal-equilibrium condition of radiation interacting with a tenuous gas of atoms. We argue that rate equations may be used to describe the interaction of such atoms with the chaotic thermal radiation field. For this situation the neoclassical spontaneous emission rate is incompatible with the well-secured laws of Boltzmann and Planck. Experimental evidence bearing on the accuracy of those laws as well as on the accepted level population dependence of the induced emission rate is reviewed.

I. INTRODUCTION

The interaction of electromagnetic radiation with material atomic systems has occupied a central location among the problems of physics. The energy exchanges between material systems and the radiation field were quantized in order to explain the spectrum of blackbody radiation. The quantum theory of atomic systems was invented to explain their absorption and emission spectra, and to account for the important fact that their ground states are stable against radiative decay. Finally, the radiation field was quantized in order to provide a satisfactory description of both wave- and particle-like phenomena such as might be represented by the interference of light and the photoelectric effect.

Unfortunately, the resulting quantum electrodynamics (QED) is still beset by many theoretical divergences, such as the infinite zero-point energy of the radiation field, and some of these are not so easily neglected. For this reason some physicists feel that QED must eventually be modified in some rather fundamental way.

In recent years Jaynes and his collaborators have looked for clues to such modification through examination of the predictions of a theory which they have termed "neoclassical" (NCT), in which the radiation field remains unquantized. The usual semiclassical theory[1] of radiation (SCT) describes the influence (induced emission and absorption) of an external *classical* radiation field upon a system of *quantal* atoms. It does not normally include any description of spontaneous emission. Jaynes *et al.*[2-5] have extended and modified the SCT by including the effects of the classical radiation reaction field on the atoms. The scope of their resultant NCT covers spontaneous emission and resonance frequency shifts. Thus, semiclassical theory is projected into a realm which is generally thought to be the exclusive purview of QED.

The neoclassical theory recommends[2] that, for an atom in a general pure quantum state $\psi=\sum a_n\psi_n$, the quantum expectation values of certain observables, including dipole moment and energy, be reinterpreted as exact true values. The interaction of the neoclassical atom with the electromagnetic field is then treated classically in accord with Maxwell's equations. Several important aspects of quantum theory, namely the discrete exact values imposed on certain observables (energy, for example), and the associated quantum fluctuations (i.e., uncertainty) are thereby eliminated. Thus, in the above state ψ, if the ψ_n represent energy levels, the quantum theory requires that an exact energy measurement yield one or another of the energy eigenvalues E_n, but it retains an essential uncertainty about which E_n will result, while the neoclassical theory suggests that the result will with certainty be the value $\sum |a_n|^2 E_n$, i.e., the quantum expectation value.

On this basis, one may expect to find experimental evidence either supporting or contesting a broad validity for NCT in areas where the discrete exact values of observables and/or their quantum fluctuations are accessible. Such areas which come to mind, including some that are favorite subjects for discussion in the context of SCT and NCT, include the photoelectric effect (evidence for field energy fluctuations), the experiment of Franck and Hertz (evidence for discreteness of atomic energy), the experiment of Stern and Gerlach (evidence for discreteness of the components of magnetic moment), and spontaneous emission (evidence for dipole-moment fluctuations), along with related areas such as noise in maser amplifiers and Planck's law of blackbody radiation.

In this paper we explore certain implications of the NCT with regard to the thermal-equilibrium condition of radiation and matter. The NCT eliminates the quantization of energy exchange between atoms and field, since in the NCT the energy of an atom can take on a continuous range of values, as can that of the field. The NCT therefore invalidates the usual derivations of Planck's law. In addition, the form of Boltzmann's law appropriate to the NCT has not previously been reported.

The distinctive feature of the NCT which evoked our present work is simply that the NCT predicts a smaller rate of spontaneous emission from an atom in any given state than does QED. At the same time, it is well known that the SCT (hence also the NCT) and QED yield identical energy-transfer rates when only induced emission and absorption processes are invoked. Since the thermal-equilibrium state implies a balance of spontaneous emission and net induced absorption, it seemed almost inevitable that the NCT would predict a thermal-equilibrium condition distinct from that predicted by QED.

In the following pages we argue, from consideration of a simple model and the universality of the required results, that rate equations similar to those introduced by Einstein[6] give a sufficient basis for examination of this problem. We then review the more recent experimental evidence bearing on the validity of the rates of induced processes in addition to that bearing on the validity of Planck's law and Boltzmann's law. Such evidence overwhelmingly supports the QED result for the spontaneous-emission rate, and supports other recent evidence that the neoclassical theory of Jaynes and his collaborators has extended the semiclassical theory beyond its limits of validity.

II. REVIEW OF EINSTEIN'S EQUATIONS AND RADIATIVE EQUILIBRIUM

The rate equations postulated by Einstein[6] in his derivation of Planck's law can serve as a convenient starting point for our work. He proposed that for a system of N two-level atoms, the rates of change of the upper-state population density N_2 due to spontaneous and induced radiative processes are given by

$$\left(\frac{dN_2}{dt}\right)_{\text{spont}} = -AN_2 \tag{2.1}$$

and

$$\left(\frac{dN_2}{dt}\right)_{\text{ind}} = -\rho(\nu)(B_{21}N_2 - B_{12}N_1), \tag{2.2}$$

where N_1 is the lower-state population density, $N_1 + N_2 = N$, A, B_{12}, and B_{12} are the familiar Einstein coefficients, and $\rho(\nu)$ is the spectral energy density of the radiation field near the transition frequency ν. These equations, which are in accord[7] with QED, were presumed to hold for thermal equilibrium and those nonequilibrium situations where rate equations are applicable. In particular, radiative equilibrium demands that (2.1) and (2.2) sum to zero, i.e.,

$$AN_2 = \rho(\nu)(B_{12}N_1 - B_{21}N_2). \tag{2.3}$$

The spectral energy density is given by Planck's radiation law:

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\left(\frac{h\nu}{\exp(h\nu/kT) - 1}\right). \tag{2.4}$$

The expectation number of atoms, N_i, in an equilibrium state with energy E_i, is given by Boltzmann's law from statistical mechanics,[8]

$$N_i \propto \exp(-E_i/kT), \tag{2.5}$$

where k is Boltzmann's constant and T is the absolute temperature. This expression applies[9] for our two-level quantum system of distinguishable particles, so that

$$N_1/N_2 = (g_1/g_2)\exp(h\nu/kT), \tag{2.6}$$

where we have used the Bohr condition

$$E_2 - E_1 = h\nu \tag{2.7}$$

to relate the level energies to the transition frequency ν which characterizes emission or absorption. To allow for the fact that several different quantum states may have the same energy, we have included the statistical weights g_1 and g_2. By applying (2.4) and (2.6) to (2.3) one finds, upon considering the limit $kT \gg h\nu$, the principle of detailed balance,

$$g_1B_{12} = g_2B_{21}, \tag{2.8}$$

which in turn yields

$$A/B_{21} = 8\pi h\nu^3/c^3. \tag{2.9}$$

The very simplicity of this derivation of the ratios of the rate coefficients makes clear our present concern. How can one alter only the spontaneous emission rate, as it seems the NCT does, and hope to maintain the experimentally verified laws of Boltzmann and Planck?

III. SPONTANEOUS AND INDUCED EMISSION IN THE NCT

In this section we discuss the descriptions of spontaneous and induced emission offered by the NCT, and on the basis of a simple model we derive rate equations which form the basis for our later comparisons with experimental results.

The NCT extends the SCT by treating spontaneous emission as well as induced emission from a semiclassical viewpoint. If an atom is in some general state $|\psi\rangle$, it has a semiclassical electric dipole moment (for example) which will have components oscillating at the various allowed transition frequencies of the atom. This semiclassical moment is identified in both the SCT and the NCT with the expectation value of the quantal moment, namely, $\langle\psi|e\vec{r}|\psi\rangle$. In both the SCT and the NCT, this semiclassical moment, summed over the various atoms, yields the polarization which is used in Maxwell's equations to describe the dynamics of the field. However, while the usual SCT uses only the external field in the Hamiltonian which describes the motion of each atom, the NCT in a sense completes the SCT by including the classical radiation reaction field, so that in the NCT an atom undergoes spontaneous decay in a self-consistent way as it radiates.

The crucial difference between the NCT and QED, whose consequences we shall examine, involves the nature of the emitted field and the atomic moment. The NCT assumes that the emitted field is completely determined by the semiclassical atomic moment through Maxwell's equations. In QED, the emitted field is similarly related to the quantum atomic moment, but both field and moment have quantum statistical fluctuations (uncertainty). For a given state of an atom, the emitted field in the NCT is equal to the expectation value of the emitted field in QED, but as a result of the quantum fluctuations of the dipole moment, the emitted power in the NCT is always less than the expectation value of the emitted power in QED. This is essentially a result of the fact that the mean square of a random variable is always larger than the square of its mean. As a result, QED always predicts a larger spontaneous-emission rate than does the NCT. To complete the QED picture, the quantum fluctuations of the emitted energy are nicely correlated with the quantum fluctuations of the atom's energy so as to conserve total energy in the spontaneous-emission process.

Let us now examine these matters quantitatively. Our line of argument will proceed in the following manner. First, we examine the case of a single sharply resonant atom subject to a blackbody radiation field, and find its time (or ensemble) average behavior with respect to spontaneous and induced radiation processes. Then we consider a tenuous gas of such atoms and argue that in the limit of high dilution the atoms must behave independently. This result can be strengthened in a possibly important way by the introduction of some extra line-broadening mechanism which imparts some width to the atom's resonance line in addition to its natural width. This can be done without appreciably affecting energy decay or transfer rates. Finally, we add up the individual atom results to obtain rate equations appropriate to the NCT's description of the gas. In the later sections of this paper we investigate whether such rate equations are compatible with the existing data regarding the validity of Planck's law, Boltzmann's law, and the induced transition rates.

Consider the component $E(t)$ of the electric field parallel to the dipole matrix element $\vec{\mu}_{12}\equiv\langle 1|e\vec{r}|2\rangle$ connecting atomic energy states $|1\rangle$ and $|2\rangle$. Since the blackbody field is stationary, the autocorrelation function $[E(t)E(t+\tau)]_{av}$ (the average may be a time or ensemble average) must be a symmetric function of τ only, and hence may be represented by

$$[E(t)E(t+\tau)]_{av}=\frac{4\pi}{3}\int_0^\infty \rho(\nu)\cos(2\pi\nu\tau)\,d\nu\,. \qquad (3.1)$$

By setting $\tau=0$, $\rho(\nu)$ may be identified as the blackbody spectral energy density, as we have taken into consideration that the electric and magnetic energy densities are equal and that there are three independent orthogonal field polarizations. At $\tau=\tau_c$, the autocorrelation time of $E(t)$, (3.1) drops to $1/e$ of its value at $\tau=0$. We now observe that because of the breadth of the blackbody spectrum, particularly because that spectrum broadly surrounds the assumed narrow spectrum of the atomic transition $1\leftrightarrow 2$ under consideration, τ_c is extremely short compared to the time required for the atom to change its state (i.e., absorb or emit an amount of energy comparable to $h\nu_{12}$ or have the phase of its transition dipole perturbed by an angle of order 1 radian). This means that in considering the interaction of the atom with the ambient blackbody field, distinct time intervals of duration somewhat greater than τ_c may be considered independently, and further that during any such time interval the state of the atom changes only slightly. This in turn means that a perturbation method is appropriate for handling the interaction problem, and indeed perturbation theory carried to second order in the field strength E yields the Einstein induced-rate result in straightforward fashion, namely,

$$\left(\frac{dz}{dt}\right)_{ind,av}=-2B\rho(\nu)(z)_{av}, \qquad (3.2)$$

where, if an atom is in a state

$$\psi = a_1|1\rangle + a_2|2\rangle, \tag{3.3}$$

then z is proportional to energy and is defined as

$$z \equiv |a_2|^2 - |a_1|^2, \tag{3.4}$$

and B is the Einstein coefficient $2\pi|\vec{\mu}_{12}|^2/3\hbar^2$ which was introduced in Sec. II. Since (3.2) seems to be a crucial result, we call attention to the accompanying paper,[10] hereafter referred to as I, where the corresponding result [Eq. (2.23) of I] is derived for a multilevel atom from the NCT.[3] Again, the average indicated in (3.2) may be a time average or an ensemble average for a stationary situation. Note that $(dz/dt)_{\text{ind}}$ may have a finite time average for a stationary system where $(dz/dt)_{\text{total}}$ vanishes.

Consider spontaneous emission in the NCT at this point. The spontaneous emission process proceeds independently of the induced process (3.2), except for appropriate changes (i.e., power broadening) in spectral shapes. The reason is that both rates are established in times much shorter than the inverse transition rate. The semiclassical dipole $\vec{\mu}$ corresponding to the state ψ of (3.3) is

$$\vec{\mu} = a_1^* a_2 \vec{\mu}_{12} + a_2^* a_1 \vec{\mu}_{21}, \tag{3.5}$$

and the power P_{spont} which this dipole radiates spontaneously at frequencies near ν_{21} according to classical theory is

$$P_{\text{spont}} = \frac{4\omega_{21}^4}{3c^3}|\vec{\mu}_{12}|^2|a_1|^2|a_2|^2. \tag{3.6}$$

The establishment of this emission rate requires a time only of the order of a few cycles of the emission frequency. While the exact frequency spectrum of the emission can be and is perturbed by the ambient blackbody field, according to (3.6) this does not appreciably influence the emission power in our limit of a narrow resonance line.

Conservation of energy, with which the NCT concurs, requires, by virtue of the radiation reaction field, that the atom lose energy equal to that spontaneously emitted as radiation. Since the energy of the atom, W_{atom} is given by

$$W_{\text{atom}} = \hbar\omega_{21}|a_2|^2, \tag{3.7}$$

where level 2 is the upper level, we see that, from (3.6), conservation of energy requires the result

$$\left(\frac{d|a_2|^2}{dt}\right)_{\text{spont}} = -A|a_1|^2|a_2|^2, \tag{3.8}$$

where A is the appropriate Einstein coefficient

$$A = 4\omega_{21}^3|\vec{\mu}_{12}|^2/3\hbar c^3. \tag{3.9}$$

Comparison with B [following (3.4)] yields the correct ratio (2.9) of the coefficients.

Let us pause to examine (3.8) briefly. The standard QED result for spontaneous emission is

$$\left(\frac{d|a_2|^2}{dt}\right)_{\text{spont}} = -A|a_2|^2, \tag{3.10}$$

the change from (3.8) being interpretable as due to quantum fluctuations of the dipole moment. The two rates differ by a factor $|a_1|^2$, with the NCT rate being always the smaller in absolute value. For a model "two-state" atom, where $|a_1|^2 + |a_2|^2 = 1$, the two rates approach one another when the atom is only slightly excited, with $|a_2|^2 << |a_1|^2 \approx 1$. A great deal has been made of this fact in the literature. However, for a multilevel atom, and particularly if the atom is considerably excited, the individual $|a_1|^2$ will generally be very small, and so the NCT spontaneous emission rate may be expected to depart very greatly from the QED rate. Also, if the ground state is degenerate, one might expect the two rates to disagree markedly even in the low-temperature limit. This is in fact a result we have derived in I. However, many-level effects are inessential complexities to our present purpose. Let us assume a model two-state atom, and use the relation

$$|a_1|^2 + |a_2|^2 = 1. \tag{3.11}$$

We can then express $|a_1|^2$ and $|a_2|^2$ individually in

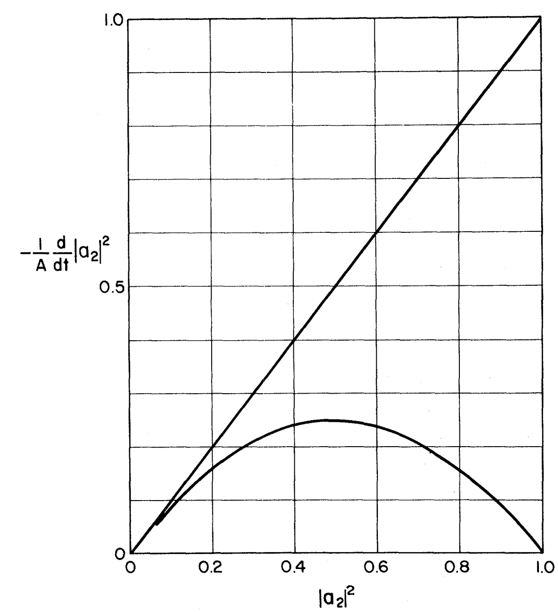

FIG. 1. Plot of the normalized spontaneous-emission rates for a single atom as given by QED [Eq. (3.10)] and the NCT [Eq. (3.8)] vs the probability of finding a two-level atom in its upper state. The two rates are equal only when the atom is close to the ground state. The straight line is the QED result.

terms of the quantity z of (3.4), obtaining

$$\left(\frac{dz}{dt}\right)_{\text{spont}} = \tfrac{1}{2}A(z^2-1). \quad (3.12)$$

This expression was given in a basic paper[4] on the NCT. A plot of the two spontaneous-emission rates (3.8) and (3.10) is shown in Fig. 1. Note that the NCT rate has a maximum at $|a_2|^2=0.5$, where it is just one-half of the QED rate. Figure 1 implies that in the thermal-equilibrium problem the greatest departures between the predictions of the two theories are to be expected in the high-temperature limit, where the atoms do not remain near the ground state. This is precisely what we find. It now remains to extend these results for single atoms to apply to a set of N atoms. To this end, we define the quantities

$$N_1 \equiv \sum_{i=1}^{N} |a_{1i}|^2, \quad N_2 \equiv \sum_{i=1}^{N} |a_{2i}|^2. \quad (3.13)$$

These quantities, which may simply be called level populations, have somewhat different significances in QED and in the NCT. In QED they represent ensemble mean values of the level populations which would be found by suitable exact measurement of those populations. In the NCT they can have no particularly well-defined physical meanings; however, various intrinsic properties of the set of atoms depend on them as though they were level populations. For example, the energy W of the set of atoms, which is simply the sum of the energies of the individual atoms so long as the interactions among the atoms can be neglected, may be expressed [see (3.7)] as

$$W = \hbar\omega_{21} N_2, \quad (3.14)$$

and of course we have

$$N_1 + N_2 = N. \quad (3.15)$$

In order to proceed from this point to any quantitative ideas and results it is helpful to have a model system in mind. It is easy to create a sufficiently complicated model (after all, the real world is very complicated) that further progress is quite difficult to make or to be sure of in retrospect. We argue, however, that the conditions of thermal equilibrium are most probably universal, so it is useful to look for the simplest model from which one can derive the desired results. Let us therefore consider a set of N atoms tenuously distributed in space so that their most important interactions are through the radiation field, and further let us suppose that these atoms couple to the total radiation field sufficiently weakly that the whole sample is optically "thin." Let us suppose that these atoms find themselves in a blackbody enclosure surrounded by distant absorbing walls at temperature T. In the absence of the atoms the enclosure must then be occupied by a "blackbody" field (at temperature T). We argue now that one can simply add the induced and spontaneous rates for the individual atoms to find the corresponding rates for the set of atoms. This simplicity is model dependent; particularly, it depends on independent behavior of the individual atoms. Both assumptions of our model lead toward independent behavior. The atoms of our tenuous gas may be arbitrarily far apart. As the atoms get farther apart, the fields they see become less correlated, since these fields result from the addition of many waves coming from many directions. Correspondingly, the spontaneous-emission rates of the individual atoms become more nearly additive, with different phase relations among the various dipoles resulting simply in different directionality of the radiation pattern. In addition, the extra line breadth we invoked earlier aids in this matter. Whether homogeneous or inhomogeneous, its effect is to remove any phase coherence among the atomic dipoles in a time of the order of the inverse linewidth. This must enhance the independence of the individual atoms. Coming back to the generality argument, we feel confident of proceeding on the assumption of effective independence, because any residual correlations among the atoms are dependent upon density and linewidth, whereas the equilibrium properties of the gas which we seek should be independent of those parameters.

With this model in mind we can forge ahead. The *linear* QED spontaneous rate equation (3.10) for a single atom is simply transformed to read

$$\left(\frac{dN_2}{dt}\right)^{\text{QED}}_{\text{spont}} = -AN_2, \quad (3.16)$$

which is identical to (2.1). However, the *nonlinear* NCT equation (3.8) becomes, after substitution of (3.13),

$$\left(\frac{dN_2}{dt}\right)^{\text{NCT}}_{\text{spont}} = -A\left(N_2 - \sum_{i=1}^{N} |a_{2i}|^4\right). \quad (3.17)$$

We may describe any distribution of the $|a_{2i}|^2$ in terms of its mean and variance, and so express the sum in (3.17) as

$$\sum_{i=1}^{N} |a_{2i}|^4 = \frac{N_2^2}{N} + N\xi_2^2, \quad (3.18)$$

where ξ_2^2 is the variance

$$N\xi_2^2 \equiv \sum_{i=1}^{N}\left(|a_{2i}|^2 - \frac{N_2}{N}\right)^2, \quad (3.19)$$

so that spontaneous emission in the NCT is given by

$$\left(\frac{dN_2}{dt}\right)^{\text{NCT}}_{\text{spont}} = -AN_2 f, \qquad (3.20)$$

$$f = \frac{N_1}{N} - \frac{N}{N_2}\xi_2^2 . \qquad (3.21)$$

Since $\xi_2^2 \geq 0$, one may set up the inequality

$$\frac{N_1}{N} \geq \frac{N_1}{N} - \frac{N}{N_2}\xi_2^2, \qquad (3.22)$$

where the equality is obtained only if $\xi_2^2 = 0$. The limiting form of (3.20) is

$$\left(\frac{dN_2}{dt}\right)^{\text{NCT}}_{\text{spont,max}} = -AN_2\frac{N_1}{N} . \qquad (3.23)$$

The significance of (3.23) is the fact that no matter what the particular distribution is, the discrepancy factor between NCT and QED spontaneous emission rates is *at least* N_1/N, which for $kT >> h\nu$ is $f = \frac{1}{2}$. This factor of $\frac{1}{2}$ figures prominently in the implications of (3.23) in the limit $kT >> h\nu$. Toward the end of this paper we will consider an explicit distribution which has been derived in I for the condition of thermal equilibrium and which for our case results in $\xi_2^2 \neq 0$ and $f = \frac{1}{3}$, i.e., an even larger discrepancy.

The inclusion of level degeneracies modifies (3.23), generally reducing the NCT spontaneous-emission rate further. If one includes degeneracy in the NCT formalism (for a case in which the Einstein A coefficient is the same for all the degenerate states of the upper level), one finds corresponding to (3.23) the result

$$\left(\frac{dN_2}{dt}\right)^{\text{NCT}}_{\text{spont,max}} = -AN_2\frac{N_1}{g_1 N} . \qquad (3.24)$$

That is, the NCT spontaneous-emission rate is inversely proportional to the degeneracy of the lower level. To see qualitatively how this comes about, we recall that in QED the spontaneous decay of the upper-level probability proceeds independently of the lower-level configuration of the wave function. In NCT, on the other hand, the form of the lower-level part of the wave function is important, and if the lower-level degeneracy is large, only a few of the possible lower-level configurations (at most three independent ones) are coupled to a particular upper-level configuration by the dipole operator. By "level configuration" we mean a particular choice of the amplitudes of the degenerate states which comprise the level. Other lower-level configurations may be coupled to the upper level by higher multipole operators, but these do not give rise to appreciable radiation. Thus, as the lower-level degeneracy increases, a decreasing fraction of the lower-level population remains effective in NCT for the generation of spontaneous emission.

Apart from the fact that the introduction of degeneracies makes the discrepancy worse at $kT >> h\nu$, it also introduces discrepancy at the other extreme, $h\nu >> kT$, where previously there has been agreement. We recall that with no degeneracy and $\xi_2^2 = 0$, $f = \frac{1}{2}$ for $kT >> h\nu$ and $f = 1$ for $h\nu >> kT$. Now we find that for $\xi_2^2 = 0$,

$$f = \frac{N_1}{g_1 N} = \frac{1}{g_1(1 + N_2/N_1)},$$

so that when $kT >> h\nu$, $f = 1/(g_1 + g_2)$, and when $h\nu >> kT$, $f = 1/g_1$; there is no limit in which NCT agrees with QED. A more sophisticated analysis in I affirms this conclusion.

We shall use (3.24) as an important base for the remainder of the paper. However, lest the reader become too concerned with the appearance of the degeneracy factor in (3.24) and with whether this is a proper result of neoclassical theory, we note that our basic conclusions do not depend on how level degeneracies might be handled in NCT. The simplest case $g_1 = g_2 = 1$ is sufficient.

In Secs. IV–VI we shall be concerned with the implications of the NCT spontaneous-emission rate (3.24) in the light of existing experimental results. The procedure will be to substitute (3.24) for the quantum rate, (2.1) or (3.16), in the rate equation for radiative equilibrium whose quantal form is (2.3). Starting with NCT equations,[3] Gordon[10] has derived the equivalent rate equation for NCT; in Appendix A we indicate the transformation into a form appropriate for our use. In accord with our comments in Sec. I, the average induced absorption and emission rates turn out to be identical with the Einstein rates (2.2).

After a summary of the conclusions to be drawn from these three experimentally oriented sections, we shall consider the actual probability distribution ($\xi_2^2 \neq 0$) for thermal equilibrium as derived by Gordon[10] and indicate how the results corresponding to $\xi_2^2 = 0$ must be modified. Section IX examines the work of others.

It will be convenient at this point to introduce a shorthand notation. Thus, let $E_s \equiv$ Einstein's spontaneous-emission law (2.1); $J_s \equiv$ the neoclassical spontaneous-emission law (3.24); $E_i \equiv$ Einstein's induced-emission-and-absorption law (2.2); $B_o \equiv$ Boltzmann's distribution law; and $P \equiv$ Planck's radiation law. The requirement of radiative equilibrium for a system of atoms and field at a common temperature interrelates these laws, so that the substitution of J_s for E_s requires alteration of at least one of the other laws. Of the three possibly suspect laws, B_o, E_i, and P, we shall in each of the next three sections assume that only one must be altered, and find the alteration required by the existence of equilibrium. The revised suspect laws are then examined in the light of existing experimental evidence. We find that *independent* experimental verifications of B_o, E_i, and P are each sufficiently accurate so that the drastic modifications required by J_s (particularly in the high-temperature limit) are not permissible, nor indeed is any combination of such modifications. It may seem odd that we have included E_i in the list of suspect laws, since it has been demonstrated in I (see also Appendix A), that E_i is also a prediction of the NCT. The inclusion is made for the sake of completeness, and because there exists some nice experimental evidence favoring E_i which we wanted to call attention to.

IV. IMPLICATIONS OF A MODIFICATION OF BOLTZMANN'S LAW

A. Theoretical inconsistencies

We shall commence by applying E_i (2.2) with the associated expressions (2.8) and (2.9), P (2.4), together with J_s (3.24) to a situation of radiative equilibrium. We seek the modified form of B_o. Since we shall be making comparisons with the results of experiments performed on paramagnetic solids and gases wherein the presence of a magnetic field removes energy-level degeneracies, we shall set $g_1 = g_2 = 1$. Equilibrium demands that $(N_1/N_2)'$ satisfy

$$n(N_1/N_2)'^2 - (N_1/N_2)' - n = 0, \qquad (4.1)$$

where

$$n = 1/[\exp(h\nu/kT) - 1]. \qquad (4.2)$$

In QED parlance, n is just the average number of photons per mode. [Note that throughout the paper, all quantities characterized by primes denote modifications of the conventional expressions which stem directly from a use of (3.24).] Since (3.24) reduces to (2.1) when $h\nu >> kT$ and $g_1 = 1$, we require $(N_1/N_2)'$ to be equal to (2.6) in the same limit. Thus the (−) solution of the quadratic equation (4.1) is unacceptable. The solutions to (4.1) are then

$$(N_1/N_2)' \approx N_1/N_2 = \exp(h\nu/kT), \quad h\nu >> kT, \qquad (4.3)$$

$$(N_1/N_2)' \approx 1 + \tfrac{1}{2}h\nu/kT, \quad h\nu << kT. \qquad (4.4)$$

B_o (2.6) in the latter limit gives

$$N_1/N_2 \approx 1 + h\nu/kT, \quad h\nu << kT. \qquad (4.5)$$

Thus, with $\Delta N \equiv N_1 - N_2$, we see that $(\Delta N/N_2)'$ is one-half of $\Delta N/N_2$. Equation (4.4) disagrees with the conclusions of quantum statistical mechanics.[9] There is clearly an implied disagreement as well with classical statistical mechanics[8] as might be represented by Maxwell's velocity distribution in the kinetic theory of gases.

Before we examine experimental results, we wish to make a useful observation. Regardless of the correct form for B_o [(2.6) *or* (4.3) and (4.4)], it must be independent of the type of interaction which established atomic equilibrium. To see this, we consider a paramagnetic atomic species embedded in a crystalline lattice where it interacts not only with the electromagnetic radiation field but also with the elastic modes of the crystal host. If the separate interactions of the lattice and free-space fields with the atoms produced *different* Boltzmann distributions when the entire system was at equilibrium, then one field would supply energy to the other and the concept of an equilibrium temperature would be invalidated. Thus, not only would the zeroth law of thermodynamics be violated but the second law as well.

B. Experimental results

For molecular beam experiments, the normal Maxwell velocity distribution must be multiplied by an additional factor[11] equal to the velocity v, so that the intensity of molecules in the beam between v and $v + dv$ is $\propto v^3 \exp(-mv^2/2kT)$. This expression has been verified in detail for a wide range of values of the exponential Boltzmann factor by many experiments.[12] However, since (4.4) was derived in connection with a quantum system, it is important to examine evidence which directly disproves (4.4) and which was also obtained for systems with discrete states.

In particular, we shall consider the simplest case of a two-level system, a single spin with no orbital moment ($S = \frac{1}{2}$, $L = 0$). If the magnetic moment associated with the atom is μ, then in a magnetic field H, there will be two energy levels. The upper level has an energy $E_2 = +\mu H$ and a population density N_2, while the lower level is characterized by $E_1 = -\mu H$, and N_1. The magnetic moment for the entire system is $M = (N_1 - N_2)\mu$. If we use B_o (2.6) and, as before, set $N = N_1 + N_2$, we find $M = N\mu \tanh(\mu H/kT)$. In the limit $kT >> h\nu$ ($= 2\mu H$), we find $M = N\mu^2 H/kT$ which, in terms of the susceptibility $\chi = M/H$, becomes

$$\chi = \mu^2 N/kT, \quad kT >> h\nu. \qquad (4.6)$$

The $1/T$ dependence is known as Curie's Law. Clearly, the form of B_o (4.5) appropriate in this limit could also have been used in the derivation. If, instead, (4.4) had been used, we would have

$$\chi' = \tfrac{1}{2}\mu^2 N/kT, \quad kT >> h\nu. \qquad (4.7)$$

An experiment[13,14] has been performed on the paramagnetic ion Cu^{+2} (two-level system) in $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$ (copper Tutton salt) in which χ was measured from 1.6–290°K where $kT >> h\nu$

throughout. The number density N of paramagnetic ions may be determined from $N=\rho N_0/\mathrm{MW}$, where N_0 is Avogadro's number (molecules/mole), ρ is the density ($\mathrm{g/cm^3}$), and MW is the molecular weight (g/mole). Not only was χ found to be inversely proportional to T, but the absolute value of

$$(\chi T/\rho)_{\mathrm{exp}}=1.03\times10^{-3}\quad \text{(CGS units)} \tag{4.8}$$

was also given for a powdered sample. By using (4.6), which is based upon B_0, and setting $\mu=\mu_B$ (Bohr magneton), we compute

$$\chi T/\rho = N_0\mu_B^2/k\,\mathrm{MW}=0.85\times10^{-3}\quad \text{(CGS units)}. \tag{4.9}$$

Using instead (4.7), we have

$$\chi' T/\rho = \tfrac{1}{2}N_0\mu_B^2/k\,\mathrm{MW}=0.43\times10^{-3}\quad \text{(CGS units)}. \tag{4.10}$$

The difference between (4.8) and (4.9) arises because of incomplete quenching of the orbital angular momentum. In the limit $kT \gg h\nu$, the correct quantum-mechanical expression for arbitrary angular momentum for ions of the iron group is given[15] by multiplying (4.6) by a factor $\frac{1}{3}[L(L+1)+4S(S+1)]$, where L and S are the orbital and spin quantum numbers. When the orbital angular momentum is *quenched* ($L=0$) and $S=\frac{1}{2}$, then this factor is unity. If, as is the case with Cu^{+2} in a Tutton salt,[15] the orbital angular momentum is not completely quenched, then the factor will exceed unity, and the susceptibility will be increased somewhat. Thus, while χ_{exp} is 20% *larger* (which is in the right direction) than the theoretical value of χ, the value of χ' (based upon a modification of B_0) is a factor of two *smaller* than χ, and this must be viewed as a serious disagreement.

There are examples of *complete* quenching ($L=0$) in paramagnetic crystals for multilevel systems Cr^{+3} ($S=\frac{3}{2}$), Fe^{+3} ($S=\frac{5}{2}$), and Gd^{+3} ($S=\frac{7}{2}$), where careful measurements of the temperature dependence of χ have been made.[16] For arbitrary values of $h\nu/kT$ the susceptibility is proportional to the Brillouin function[14,15] whose argument is $h\nu/kT$. (In a later section of the paper we will use the probability distribution derived by Gordon[10] to calculate the NCT equivalent of the Brillouin function.) For the three ions just mentioned, this function has been *accurately* verified (to within ~3%) for *all* values of $h\nu/kT$. These results are inconsistent with the modified Boltzmann distribution (4.4) and provide striking confirmation of the validity of (2.6) in quantum applications.

For the atomic systems in the experimental examples just cited, interaction is primarily with the elastic waves of the solid. However, there have been measurements performed on paramagnetic gases which reach thermal equilibrium by means of collisions. In the case of monatomic potassium vapor, (4.6) is applicable. Using for μ the value of the Bohr magneton and Avogadro's number N_0, we compute the molar susceptibility to be $N_0\chi/N=0.375/T$. The experimental value,[17] which had an uncertainty of ~10%, was determined to be $0.38/T$, in excellent agreement with expectations. For the oxygen molecule (O_2), (4.6) applies, multiplied by the factor $\frac{1}{3}[4S(S+1)+\Lambda^2]$ where Λ is a molecular quantum number. For $S=1$, $\Lambda=0$, appropriate for O_2, and 20 °C (293 °K), $N_0\chi/N=3.42\times10^{-3}$. The average result[17] of the experimental findings of seven different groups of workers was $(3.38\pm0.06)\times10^{-3}$. Again, we have superb agreement and again confirmation of B_0.

We note that the experimental verifications of B_0 did *not* involve E_s, E_i, or P in any way.

V. IMPLICATIONS OF A MODIFICATION OF EINSTEIN'S INDUCED EMISSION AND ABSORPTION EQUATIONS

A. Theoretical inconsistencies

In this section we pretend that P (2.4) and B_0 (2.6) are correct, and together with J_s (3.24) investigate the implied changes in E_i (2.2) and the associated equations (2.8) and (2.9). We preserve the form of E_i and simply replace B_{12} and B_{21} by B'_{12} and B'_{21}. Since the modified B's will be temperature dependent, we cannot properly examine the high-temperature limit of the equation of radiative equilibrium in order to find a relationship between the B's. However, for the purposes of illustration we shall assume that the principle of detailed balance still applies, i.e.,

$$g_1B'_{12}=g_2B'_{21}, \tag{5.1}$$

so that

$$\frac{A}{B'_{21}}=\frac{A}{B_{21}}\frac{Ng_1}{N_1}=\frac{8\pi h\nu^3}{c^3}[1+\exp(-h\nu/kT)]. \tag{5.2}$$

Since the values of A which appear in (2.1) and (3.24) are identical and equal to $64\pi^4\nu^3(er_{21})^2/3hc^3$, where er_{21} is three times the dipole matrix element, we see from (5.2) that B'_{21} must be temperature dependent. This result is inconsistent with[1] the SCT (and therefore the NCT also), which shows that B_{21}, like A, is dependent *only* upon internal properties peculiar to a given atomic transition (frequency and dipole matrix element) and independent of any external parameters such as temperature. Solving (5.2), we find

$$B'_{21}=B_{21}N_1/Ng_1\,. \tag{5.3}$$

Since a similar expression holds for B'_{12}, we are led directly to a modification of E_i which consists of multiplication of the right-hand side of (2.2) by

N_1/Ng_1. This result (5.3) is inconsistent with the common prediction (2.2) of all the theories under present consideration (the SCT, the NCT, and QED), which are based on Schrödinger's equation. We include it in part because of the existence of some experimental evidence strikingly in favor of the usual level-population dependence of the induced-emission rate and therefore at variance with (5.3).

B. Experimental results

The measurements made by Geusic and Scovil,[18] employing ruby as a three-level optical maser amplifying medium, provide a dramatic confirmation of the dependence of the induced emission and absorption rates upon the population densities as given in (2.2). The usual single-pass, low-signal (decibel) gain is proportional to (2.2), i.e., $G \propto [N_2 - (g_2/g_1)N_1]$, using (2.8). N_2 is the population density of the upper amplifier level, and N_1 is the density of the lower level (ground state). The populations of all three levels, including the one above the upper amplifier level, were known

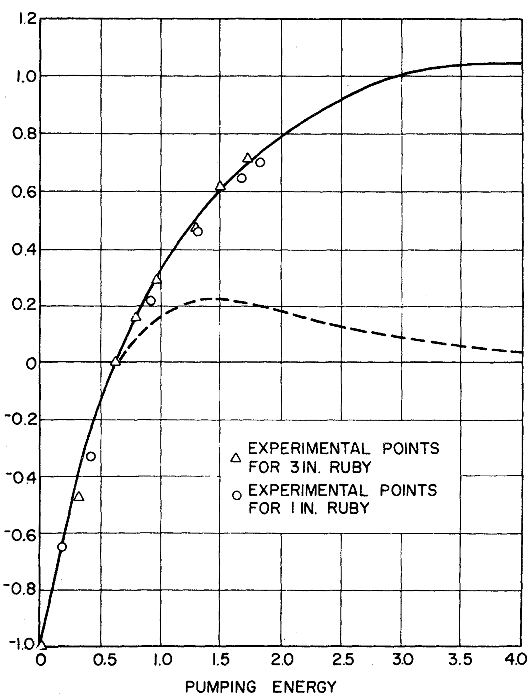

FIG. 2. The solid curve represents the normalized gain based upon the Einstein equations for stimulated emission and absorption [Eq. (2.2)]. This curve, as well as the experimental points for two ruby-laser amplifier lengths, was taken from the work of Geusic and Scovil (Ref. 18). The dashed curve represents the gain if one were to accommodate the spontaneous-emission rate of the NCT [Eq. (3.24)] in radiative equilibrium by modifying Eq. (2.2) while preserving Planck's law and Boltzmann's law. The experimental results do not favor this modification.

as functions of the pumping energy. The single-pass, unpumped loss L is the magnitude of G when all atoms are in the ground state, i.e., $L \propto (g_2/g_1)N$. In Fig. 2, the experimental values of G/L are plotted against the pumping energy. The solid line, which corresponds to

$$\frac{G}{L} = \frac{N_2 - (g_2/g_1)N_1}{(g_2/g_1)N}, \tag{5.4}$$

is seen to agree very well with the experimental points. If the modified form of (2.2) prevails, then $G' = [(N_1/g_1)/(N_1+N_2)]G$ and $L' = (1/g_1)L$, so that

$$\frac{G'}{L'} = \frac{N_1}{N_1+N_2}\,\frac{G}{L}. \tag{5.5}$$

This is plotted in Fig. 2 as a dashed line. Derivations of the explicit forms of (5.4) and (5.5) are presented in Appendix B. [Note that the additional factor in (5.5) contains in its denominator the populations of the two amplifying levels, $N_1 + N_2$, which is *not* equal to the total population, $N = N_1 + N_2 + N_3$, in a three-level case; in the previously discussed two-level case the factor is, of course, just (N_1/N).] G'/L', unlike G/L, has its maximum value when $N_1 \neq 0$. We conclude that the dependence of the stimulated emission and absorption equations of Einstein upon population density has been well verified experimentally throughout the normal and well into the region of inverted populations.

From the calculations in Appendix B, we have seen that the evaluation of the solid curve in Fig. 2 required the use of B_0. Our contention is that (2.2) [where B_{12} and B_{21} are given by (2.8) and (2.9)] has been accurately verified because (i) B_0 has previously been shown (Sec. IV) to be independently established as correct, and (ii) even if the modified B_0 (4.4) were used in Appendix B, the change in the values of G/L given by Eq. (B5) would be less than 10%, i.e., while the experiment of Geusic and Scovil is extremely sensitive to the detailed form for (2.2), it is very insensitive to the form of B_0 in the limit $kT \gg h\nu$.

VI. IMPLICATIONS OF A MODIFICATION OF PLANCK'S RADIATION LAW

A. Theoretical inconsistencies

Our final alternative is to retain E_i and B_0 and gauge the change in P demanded by (3.24) for radiative equilibrium. This is perhaps the most natural approach for an assault on QED because it was with Debye's[19] derivation of (2.4) that second quantization (quantizing the state of excitation of the radiation modes; the quantizing of the modes themselves had previously been done by Rayleigh and Jeans) was introduced. Second quantization is the heart of QED and is a procedure which the NCT circumvents. However, it is well to note that P is theoretically well established within a quantum framework, i.e., in addition to the derivations by Debye,[19] Einstein,[6] and several different formulations by Planck,[20] there are a great many others.[21,22]

Proceeding as before, we find that equilibrium for a two-level system requires

$$\rho' = \rho N_1/Ng_1 \tag{6.1}$$

or

$$\rho' = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{g_2[1-\exp(-h\nu/kT)]+g_1[\exp(h\nu/kT)-1]}, \tag{6.2}$$

where ρ is given by (2.4). An interesting feature of (6.2) is its dependence upon the degeneracy factors g_1 and g_2, which are peculiar to some particular two-level atomic system. This dependence conflicts with the laws of thermodynamics. To see this we imagine a two-level system (e.g., a paramagnetic gas) in equilibrium with the radiation field in some large highly multimode cavity. Equation (6.2) is the equilibrium energy density corresponding to the gas. The walls, however, will favor a *different* energy density ρ'', which is a function of T and the degeneracy factors for the manifold of energy levels associated with the atoms in the walls. Thus, the spin system cannot be in equilibrium with the walls. This is inconsistent with the definition of temperature and violates the zeroth law of thermodynamics. If, for example, $\rho'' > \rho'$, the spin system would be pumped by the radiation field associated with the walls, and its temperature will be increased. The subsequent flow of energy from the colder body (walls) to the hotter body (gas) constitutes a perpetual motion machine of the second kind, which violates the second law of thermodynamics. (One violation is just a corollary of the other, since it has recently been shown that the zeroth and second laws of thermodynamics are equivalent.[23]) The conclusion to which we are forced is that the equilibrium radiation field depends neither upon the nature of the system to which it is coupled nor to the strength of that coupling, so that (6.2) must be incorrect.

B. Experimental results

In the two decades following its introduction, P (2.4) has been painstakingly confirmed by many experiments.[24] By using the thermodynamic reasoning of Sec. VI A, one concludes that (2.4) is true for *all* systems (classical or quantum) which are in equilibrium with a radiation field. However, for convenience and interest, we shall now discuss several somewhat more recent experiments.

In the realm of radio engineering, Nyquist[25] established an expression for the noise power, for a single transverse mode within a bandwidth $\Delta\nu$, emitted from a resistance maintained at a temperature T into a matched transmission line, to be

$$P_{\text{noise}} \approx kT\Delta\nu, \tag{6.3}$$

which is just the high-temperature limit of the more general form based upon P,

$$P_{\text{noise}} = \frac{h\nu\Delta\nu}{\exp(h\nu/kT)-1}. \tag{6.4}$$

Equation (6.3) was accurately verified by the experimental work of Johnson,[26] who used (6.3) to determine a value for Boltzmann's constant k which was within 8% of the accepted value. The modified noise expression based upon (3.24) is

$$P'_{\text{noise}} = \frac{h\nu\Delta\nu}{g_2[1-\exp(-h\nu/kT)]+g_1[\exp(h\nu/kT)-1]}, \tag{6.5}$$

whose limit for $kT \gg h\nu$,

$$P'_{\text{noise}} \approx kT\Delta\nu/(g_1+g_2), \tag{6.6}$$

is in serious disagreement with (6.3) and the classical equipartition limit. When $g_1 = g_2 = 1$, the discrepancy is least and equals the factor of $\frac{1}{2}$ which we encountered earlier.

It is also instructive to consider noise measurements performed on manifestly quantum systems (laser amplifiers). Equation (6.4) represents the noise power emitted by a lumped-circuit loss. We may convert[27] this for the case of distributed gain, $G \gg 1$, by multiplying (6.4) by $-G$ and allowing $T \to -T_i$, where T_i is the temperature of the inverted levels. Thus

$$P_{\text{noise}} = \frac{Gh\nu\Delta\nu}{1-\exp(-h\nu/kT_i)}, \tag{6.7}$$

which by B_0 (2.6) becomes

$$P_{\text{noise}} = Gh\nu\Delta\nu\left(\frac{N_2}{N_2 - g_2/g_1 N_1}\right). \tag{6.8}$$

Paananen *et al.*[28] measured the noise power from the high-gain, 3.39-μm transition in a He-Ne discharge tube, and found agreement, to within 4%, with (6.8). In the NCT framework,

$$P'_{\text{noise}} = Gh\nu\Delta\nu\left(\frac{N_2}{g_1N_2 - g_2N_1}\right)\left(\frac{N_1}{N_1+N_2}\right), \tag{6.9}$$

which by (2.6) may be expressed as

$$P'_{\text{noise}} = \frac{Gh\nu\Delta\nu}{g_1[1-\exp(-h\nu/kT_i)]+g_2[\exp(h\nu/kT_i)-1]}. \tag{6.10}$$

Knowing the experimentally deduced value[28] for the bracketed factor in (6.8) and the degeneracies, $g_1 = 5$ and $g_2 = 3$, one calculates that $N_1/(N_1+N_2)g_1 = \frac{1}{13}$, which would predict a value for P'_{noise} that was a factor of 13 times smaller than the measured value. Strictly speaking, this discrepancy cannot be used to demonstrate that (3.16) is incorrect, *instead*, only that the results[28] actually obtained are consistent with (2.1). This occurs because of the experimental determination of the bracketed factor in (6.8). The factor was deduced from measurements of the separate spontaneous-emission intensities from the two levels involved, in light emitted from the side of the laser tube. The intensities were assumed to be proportional only to the populations of the *emitting* levels, in accord with (2.1). If instead one assumed (3.16) to be correct, then the intensity data recorded by Paananen *et al.*[28] would be insufficient to determine the factor in (6.8), since the populations of the *receiving* levels, those to which levels 1 and 2 decay spontaneously, remain unknown.

Klüver[29] has made detailed noise measurements using the 3.5-μm transition in He-Ne. He found excellent agreement between his measurements of gain and saturated noise versus input signal intensity *and* a detailed theory predicated upon (2.1) and (2.2). From this work he was able to deduce a value for the unsaturated population factor in (6.8). He also calculated this factor by using (6.8) in conjunction with his low-signal noise measurements. The two determinations agreed to within 7%.

In the summary of this section we would like to emphasize several points. The early experiments,[24] to which we referred only in passing, and also the one measuring the Johnson-Nyquist noise,[26] were made on *classical* systems. Thermodynamic arguments reveal that this work has in fact confirmed P for *all* systems in equilibrium with a radiation field. The confirmation of (2.4) is thus the disproof of (6.2). This conclusion has in no way depended upon E_i or B_o. The quantum noise measurements[28,29] that we have cited cannot strictly be used to disprove (3.24), but they make it highly unlikely that (3.24) is correct. The reason for this in both cases[28,29] is related to a lack of experimental information about the populations of other atomic levels, which is needed if (3.24) is to be tested directly. The accurate consistency checks provided by these experiments[28,29] are of two types. One derivation of the expression for P_{noise} (6.8) starts with P (which may be derived[25,27] from transmission-line considerations) and then uses B_o. Since B_o has been previously shown to be accurate independently (Sec. IV), these experiments show P to be consistent. Another derivation[30] of (6.8) starts with E_s and uses E_i. Since E_i has been shown to be accurate independently (Sec. V), the same experiments thus show E_s to be consistent as well.

VII. SUMMARY

We should like to summarize the steps by which we have been led to conclude that the description of spontaneous emission offered by the NCT is incorrect. Our primary purpose has been to show that the implications of the NCT in radiative equilibrium violate not only existing theory, but stand opposed, in every instance, to the results of experiments. If equilibrium is to exist upon adoption of (3.24), then at least one of the following must be rejected: (a) B_o, Boltzmann's law; this has been well verified by molecular-beam experiments and the measurements of paramagnetic susceptibilities, and its modification conflicts with statistical mechanics; (b) E_i, the equations of Einstein for induced emission and absorption and the associated equations for detailed balance and the A/B ratio; these have been accurately confirmed by laser amplifier experiments, and their modification suggests revision either of Schrödinger's equation or time-dependent perturbation theory, which constitute the SCT; (c) P, Planck's law; this has been carefully checked by measurements of blackbody radiation spectra and classical and quantum noise measurements, and the altered form would violate the zeroth and second laws of thermodynamics. Since (a)–(c) have been independently and accurately confirmed, we conclude that the spontaneous-emission rate of the NCT cannot be correct.

The particular evaluations of the discrepancies which appeared in Secs. IV–VI were derived on the basis of a "maximum" NCT spontaneous-emission rate. This in turn applies only when every atom is assumed to have the same level probabilities (as defined in QED), $\xi_2^2 = 0$. Any more realistic (i.e., more random) statistical choice of level probabilities further reduces the spontaneous-emission rate of the NCT, as indicated in Sec. III, and hence makes the difficulty that the thermal-equilibrium condition is even more prohibitive for the NCT. We shall examine a distribution appropriate for thermal equilibrium in Sec. VIII.

VIII. IMPLICATIONS OF A PROBABILITY DISTRIBUTION FOR THERMAL EQUILIBRIUM ($\xi_2^2 \neq 0$)

A. Derivation of distribution

In examining the implications of NCT in radiative equilibrium, we have employed the spontaneous-emission rate

$$\left(\frac{dN_2}{dt}\right)^{\text{NCT}}_{\text{spont}} = -AN_2 f, \tag{8.1}$$

where

$$f = N_1/N - (N/N_2)\xi_2^2, \tag{8.2}$$

in its limiting form for the variance $\xi_2^2 = 0$. Under these circumstances, the spontaneous-emission rate in NCT assumes it maximum value, since f is maximized. For $kT \gg h\nu$, we saw that $f = \frac{1}{2}$, which factor appeared in implied modifications of Boltzmann's law (4.4) and Planck's law (6.6).

In an accompanying paper (I), the incorporation of the spontaneous-emission rate in NCT into suitably derived rate equations is considered. For thermal equilibrium, a probability distribution is derived which is actually a composite of the NCT equivalents of the laws of Boltzmann and Planck. Equation (3.13) of I gives this distribution for a multilevel atom in terms of the diagonal components of the atomic density matrix σ_{ii}. For a two-level nondegenerate atom, the appropriate probability distribution, $P(\sigma_{11}, \sigma_{22})$ may be integrated over σ_{11} to give

$$P(\sigma_{22}) = (1/Z)\exp(-\eta\sigma_{22}), \tag{8.3}$$

where Z is the normalizing factor (partition function), and

$$\eta = h\nu/\epsilon(\nu), \tag{8.4}$$

with the equipartition energy per mode of the radiation field given by the usual expression

$$\epsilon(\nu) = (c^3/8\pi\nu^2)\rho(\nu). \tag{8.5}$$

Since $\int_0^1 P(\sigma_{22})\,d\sigma_{22} = 1$, we may derive Z, and hence

$$P(\sigma_{22}) = [\eta/(1-e^{-\eta})]\exp(-\eta\sigma_{22}). \tag{8.6}$$

The composite nature of $P(\sigma_{22})$ derives from its dependence upon both σ_{22} and η [i.e., $\rho(\nu)$].

B. Modifications of the laws of Boltzmann and Planck

Since $\sigma_{22} = |a_{2i}|^2$, we find that the expression for the variance may be rewritten as

$$\xi_2^2 = \langle\sigma_{22}^2\rangle - \langle\sigma_{22}\rangle^2, \tag{8.7}$$

where

$$\langle\sigma_{22}^n\rangle = \int_0^1 \sigma_{22}^n P(\sigma_{22})\,d\sigma_{22}. \tag{8.8}$$

Integration yields

$$\xi_2^2 = 1/\eta - e^\eta/[(e^\eta - 1)^2]. \tag{8.9}$$

If η is given by Planck's law we find in the limit $kT \gg h\nu$ that

$$\xi_2^2 = \tfrac{1}{12} \tag{8.10}$$

and

$$f = \tfrac{1}{3}. \tag{8.11}$$

Previously, for $\xi_2^2 = 0$, $f = \frac{1}{2}$ for $kT \gg h\nu$. The discrepancy between NCT and QED is now larger.

It is also straightforward to show that this factor of $\frac{1}{3}$ carries over into the previously derived modifications of the laws of Planck and Boltzmann. From (8.8) we find

$$\langle\sigma_{22}\rangle = 1/\eta - 1/(e^\eta - 1), \tag{8.12}$$

with $\langle\sigma_{11}\rangle = 1 - \langle\sigma_{22}\rangle$. If we assume Boltzmann's law to be valid, then

$$\langle\sigma_{11}\rangle/\langle\sigma_{22}\rangle = N_1/N_2 = \exp(h\nu/kT), \tag{8.13}$$

whereupon, in the limit $kT \gg h\nu$, one finds $\eta = 3h\nu/kT$ and, with $\rho(\nu) = (8\pi\nu^2/c^3)\epsilon$, we find

$$\rho'(\nu) = \tfrac{1}{3}(8\pi\nu^2/c^3)kT, \tag{8.14}$$

which is one-third of the conventional Rayleigh-Jeans expression. Similarly, if one assumes Planck's law to be valid, then the limiting case, $kT \gg h\nu$ (Rayleigh-Jeans law), gives

$$\langle\sigma_{11}\rangle/\langle\sigma_{22}\rangle = (N_1/N_2)' = 1 + \tfrac{1}{3}h\nu/kT, \tag{8.15}$$

where again the requisite $\frac{1}{3}$ factor appears. We conclude that a consideration of the specific function describing the thermal-equilibrium probability converts the $\frac{1}{2}$ discrepancy factor of previous sections into $\frac{1}{3}$.

C. Modification of the Brillouin function

As a result of the calculations by Gordon,[10] we can also derive the implied modification of the Brillouin function which makes its appearance in the quantum theory of paramagnetism. For an N-level system (in the context of I we are considering a single atom with N levels; N does not represent the number of atoms) without degeneracy, Gordon[10] has shown that the mean energy referred to the lowest level is given by [Eq. (4.9) of I]

$$W_0 = (N-1)h\nu\left(\frac{1}{\eta} - \frac{1}{e^\eta - 1}\right). \tag{8.16}$$

However, in considering paramagnetic systems whose levels are split by the application of dc magnetic fields, it is convenient to reference energy to the zero-magnetic-field level, in which case (8.16) becomes

$$W = (N-1)h\nu\left(\frac{1}{\eta} - \frac{1}{e^\eta - 1} - \frac{1}{2}\right). \tag{8.17}$$

The mean magnetic moment is given by $W = -MH$, where H is the magnetic field, and so

$$M = \mu_B gJB', \tag{8.18}$$

where the modified Brillouin function is given by

$$B' = 1 + 2/(e^\eta - 1) - 2/\eta, \quad \eta = \exp(h\nu/kT) - 1. \tag{8.19}$$

In deriving (8.18) and (8.19), we have made use of the fact that the separation between the equally spaced energy levels in a magnetic field H is $h\nu = g\mu_B H$, where g is the Landé factor and μ_B is the Bohr magneton. The total-angular-momentum quantum number J is related to N by $N = 2J+1$.

If Boltzmann's law is valid, we have the conventional expression for the mean moment[14]

$$M = \mu_B g J B, \tag{8.20}$$

where the Brillouin function is given by

$$B = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2}\frac{h\nu}{kT}\right) - \frac{1}{2J}\coth\left(\frac{1}{2}\frac{h\nu}{kT}\right). \tag{8.21}$$

In the limit $h\nu \gg kT$, $B = B' = 1$ and, as we found in Sec. IV, the NCT equivalent expression reduces to the QED dependence. In the other limit ($kT \gg h\nu$), however, we find

$$B' = \tfrac{1}{6} h\nu/kT \tag{8.22}$$

and

$$B = \tfrac{1}{3}(h\nu/kT)(J+1), \tag{8.23}$$

where for a two-level system, $J = \frac{1}{2}$, we find that $B' = \frac{1}{3}B$, which agrees with previous findings in this section.

The significant feature of this exercise is Eq. (8.19) which can be compared with Henry's results[16] which give experimental mean moments throughout the range $0 \leq h\nu/kT \leq 5.4$. As we indicated in Sec. IV, this experimental study was conducted for three paramagnetic ion samples where $S = J = \frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$ $(L=0)$. We have also noted that the agreement between the experimental results and (8.21) was within 3% throughout the entire range of variation of $h\nu/kT$. To indicate the significance of the discrepancy between (8.21) and (8.19), we will only examine the $kT \gg h\nu$ limit, where we find for $S = \frac{3}{2}$, $B' = \frac{1}{5}B$; for $S = \frac{5}{2}$, $B' = \frac{1}{5}B$; and for $S = \frac{7}{2}$, $B' = \frac{1}{9}B$; the disagreement is substantial.

IX. DISCUSSION

Up to this point, we have limited our consideration to a particular extension of semiclassical electrodynamics, which has been labeled "neoclassical," and have found it incompatible with the established properties of the thermal-equilibrium state of radiation and matter. This is a direct and simple consequence of the fact that the spontaneous-emission rate predicted by NCT is different from that predicted by QED. Nesbet[31] has also noted the apparent violation of Planck's law implied by NCT. He suggested a possible remedy involving appeal to complex material systems; however, his remedy has untenable thermodynamic implications and does not survive critical analysis. Clauser[32] has pointed to the derivation of the blackbody radiation law as one of a number of successes of the neoclassical theory. Among the group of references quoted by Clauser are two which discuss blackbody radiation, the above mentioned work by Nesbet[31] and that by Eberly.[33] Eberly[33] did derive Planck's law, but only after evaluating the *mean-square* atomic dipole moment using quantum theory. As discussed in Secs. I and III, such an evaluation includes a contribution from quantum dipole fluctuations which NCT purposefully omits. Since the spontaneous-emission rate is proportional to the square of the atomic dipole moment, a spontaneous-emission rate different from the NCT's rate is implied by Eberly's work. In an alternative derivation, which unlike the one just mentioned was conducted *entirely* within the framework of the NCT, Eberly[33] derived an expression for the energy density of the field which is identical with our Eq. (6.2) in the case $g_2 = g_1 = 1$, and which is thus quite different from Planck's law (2.4); in Sec. VI we have demonstrated this modified law to be inconsistent with experimental findings.

Nesbet[34] has pointed to another experiment, namely Raman scattering, which is incorrectly characterized by NCT. Raman scattering can be regarded as spontaneous emission from a three-level system perturbed by an applied off-resonance classical field. In quantum theory the intensities of the Stokes and anti-Stokes components of the scattering are proportional to the population of the initial level of the transition involved, which is, respectively, the lowest and next-lowest level. Hence the intensity ratio (Stokes/anti-Stokes) reflects the Boltzmann ratio of those two-level populations. This is a common experimental result. The neoclassical theory, on the other hand, finds both intensities proportional to the product of the two-level populations, just as it does for ordinary spontaneous emission, and hence does *not* yield the observed Boltzmann ratio. We believe that Crisp's criticism[35] of this work[34] is incorrect, the mistake occurring in his use of an improper (for NCT) initial atomic density matrix.

The broader question of how accurately *any* extension of semiclassical theory, which leaves the radiation field unquantized, can describe the real world, has also been reexamined recently. For example, Boyer[21] has discussed some benefits gained by taking seriously the zero-point field (energy $\frac{1}{2}h\nu$ per field mode). It is of interest in this regard that Eberly[33] found Planck's law to contain the zero-point field energy. Perhaps a short examination of this idea in our present context will be instructive. If we denote by $\hat{\rho}$ the blackbody energy density including the zero-point energy, and by ρ the same quantity excluding the zero-point energy, then using (2.9) one finds the relation

$$B_{21}\rho = B_{21}\hat{\rho} - \tfrac{1}{2}A. \tag{9.1}$$

By inserting (9.1) into (2.3) and using (2.8), one discovers a modified thermal-equilibrium relation,

$$\tfrac{1}{2}A[(g_2/g_1)N_1 + N_2] = B_{21}\hat{\rho}[(g_2/g_1)N_1 - N_2]. \tag{9.2}$$

Equation (9.2) suggests that a "spontaneous" emission rate proportional to $\frac{1}{2}[N_2 + (g_2/g_1)N_1]$ would be consistent with the laws of Boltzmann and Planck. Such a spontaneous-emission rate is also consistent with Eberly's evaluation[33] of the mean-square atomic dipole moment. Note that (9.2) suggests *spontaneous emission from ground-state atoms*! This emission is necessary, however, to balance those atom's absorption of the zero-point field. Note also that the spontaneous-emission rate of (9.2) is again larger than the NCT's rate (3.20). To achieve this increased rate, the semiclassical atomic dipole must be augmented by a fluctuation just as the field is augmented by its zero-point fluctuation. While such dipole fluctuations are a natural result of the quantum theory, we are not aware of how they are to be understood in semiclassical theory, except for the case of the harmonic oscillator (Boyer[21]).

To get back to the broader question, while it may be possible by further examination of the thermal-equilibrium state to discard all semiclassical theories, this is most probably a difficult task. As discussed by Clauser,[32] this task is best left to experiments which probe the essentially quantal correlations exemplified[36] in the "paradox" of Einstein, Rosen, and Podolski. The present evidence[32,34,36–43] already argues in disfavor of any semiclassical theory based on Maxwell's field.

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APPENDIX A

From Eq. (2.25) of I we find, for a two-level system, that the density-matrix rate equation derived from NCT equations[3] is

$$\frac{d}{dt}\langle\sigma_{22}\rangle = -A\langle\sigma_{22}\sigma_{11}\rangle + B\rho(\nu)\langle\sigma_{11} - \sigma_{22}\rangle, \tag{A1}$$

where A and B are the Einstein coefficients. With

$$\langle\sigma_{ii}\rangle = N_i/N, \quad i = 1 \text{ or } 2, \tag{A2}$$

we find

$$\frac{dN_2}{dt} = -AN\langle\sigma_{22}\sigma_{11}\rangle + B\rho(\nu)(N_1 - N_2), \tag{A3}$$

and that the stimulated emission and absorption rates (second term on the right-hand side) are identical with (2.2), the Einstein equations. The spontaneous term may be transformed by

$$N\langle\sigma_{22}\sigma_{11}\rangle = N\langle\sigma_{22}(1-\sigma_{22})\rangle = N_2 - N\langle\sigma_{22}^2\rangle.$$

Since

$$\xi^2 = \langle\sigma_{22}\rangle^2 - \langle\sigma_{22}^2\rangle,$$

$$N\langle\sigma_{22}\sigma_{11}\rangle = N_2[N_1/N - (N/N_2)\xi_2^2], \tag{A4}$$

which gives a rate identical to the earlier-derived (3.20) and (3.21).

APPENDIX B

In this section, we shall compute the explicit forms of the gain equations plotted in Fig. 2. For the system employed, pumping power conveys atoms from the ground-state level 1 up to level 4. In an extremely short time, the population of level 4 is transfered downward to the metastable levels 3 and 2. Amplification occurs at the transition connecting levels 2 and 1. Thus, the population equations are

$$N_1 + N_2 + N_3 = N, \tag{B1}$$

$$N_3 = \gamma N_2, \tag{B2}$$

and the pumping equation is

$$\frac{dN_1}{dt} = -fP_pN_1. \tag{B3}$$

γ is the Boltzmann factor, f is a pumping efficiency factor, and P_p is the pumping power. Note that (B3) is a rate equation describing induced absorption, which is the type of equation under examination in Sec. V. Equation (B3) may be integrated to give

$$N_1 = Ne^{-fE}, \tag{B4}$$

where $E = \int P_p\,dt$. The quantity fE is the abscissa of Fig. 2, and is called the "pumping energy." Substitution of (B1)–(B3) in (5.5) yields

$$\frac{G}{L} = \frac{1}{(g_2/g_1)(1+\gamma)}\left[1 - \left(1 + \frac{g_2}{g_1}(1+\gamma)\right)e^{-fE}\right], \tag{B5}$$

which is plotted in Fig. 2 as the solid line.

If induced processes are to be modified, then as we have seen, (5.5) must be used in place of (5.4). Additionally, (B3) becomes

$$\frac{dN_1}{dt} = -f P_p N_1 \left(\frac{N_1}{N_1 + N_4}\right), \qquad \text{(B6)}$$

where the denominator of the multiplying factor contains the populations of the two levels in pumping. However, since the lifetime in the pumping band (level 4) is so short, $N_4 \approx 0$, so that (B6) reduces to (B4). The modified gain expression becomes

$$\frac{G'}{L'} = \frac{\gamma + 1}{\gamma + e^{fE}} \frac{G}{L}, \qquad \text{(B7)}$$

which is plotted in Fig. 2 as a dashed line.

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