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The Role of Boltzmann Factors in Line Shape

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A study is made of the effect of temperature and environment on the absorption spectra of simple systems. In part I the longitudinal and transverse susceptibilities of a two-level system are analyzed in terms of simple stochastic models. Particular attention is paid to the different roles played by the phase-interruption and frequency-modulation mechanisms. A calculation is given of the susceptibility of a harmonic oscillator perturbed by interaction with other oscillators. In part II the same systems are studied using Green's function methods. It is assumed that the two-level system is coupled to a crystal lattice by an isotropic interaction that is linear in the lattice displacement. Expressions are obtained for the longitudinal and transverse susceptibilities and comparison is made with the results of part I. The susceptibility of the harmonic oscillator is calculated and found to be identical to the susceptibility obtained by more elementary methods.

INTRODUCTION

Although there are innumerable papers on the subject of line shape, there has been very little written on one particular aspect of this subject, viz., how the temperature affects the line contour in case the Boltzmann factor cannot be treated as constant over the profile. With the increasing amount of spectroscopic work at exceedingly low temperatures, this aspect is no longer academic, and so an article on the subject seems in order. Many of our results are not new, but the existing presentations are rather fragmentary and sometimes not entirely correct. Also, quite irrespective of the role of Boltzmann factors, we discuss and contrast how one calculates line shapes for rapid interactions both without (part I) and with (part II) the use of Green's functions.

If N_r and N_s denote the number of atoms in the upper state and lower states, respectively (both supposed nondegenerate), then the rate of spontaneous radiation is $A(\omega, T)=N_rA_{r\rightarrow s}$ and that of absorption is

$$B(\omega, T)=B_{r\rightarrow s}(N_s-N_r)\rho(\omega),$$

where $\rho(\omega)$ is the radiation energy density. If the atoms are in thermal equilibrium at a temperature T, then $N_r/N_s=\exp(-\hbar\omega/kT)$ and the absorption coefficient $B(\omega, T)$ is connected with $A(\omega, T)$ by the relation[1]

$$A(\omega, T)=F(\omega)B(\omega, T)/[\exp(\hbar\omega/kT)-1], \quad (0.1)$$

with[2]

$$F(\omega)=2\hbar\omega^3/\pi c^3 \quad (0.2)$$

since then absorption and emission balance when $\rho(\omega)$ has the Planck form. In Einstein's classic derivation of (0.1), and for most practical purposes, the distinction between the impressed frequency ω (measured in angular units) and the atomic resonance frequency ω_0 is disregarded. In other words, $A(\omega, T)$ and $B(\omega, T)$ are considered to be delta functions of $(\omega-\omega_0)$. The present article, however, is concerned with situations where this procedure is not allowable In problems of line structure, what is sometimes done is to calculate a shape $f(\omega)$ that is independent of temperature, and assume that the net absorption is proportional to $f(\omega)N_s[1-\exp(\hbar\omega_0/kT)]$ and the emission to $f(\omega)N_s\exp(-\hbar\omega_0/kT)$. Then a relation of the type (0.1) is not satisfied, since a factor $[\exp(\hbar\omega_0/kT)-1]^{-1}$ occurs in place of $[\exp(\hbar\omega/kT)-1]^{-1}$ which is required in order for there to be equilibrium between absorption and emission over the entire line profile when $\rho(\omega)$ has the Planck form. The anomaly has arisen because when the line shape is not ideally monochromatic, the atomic levels are "fuzzed out," be it by interaction with other molecules through collision, phonon coupling, or even coupling to the radiation field itself. Consequently $A(\omega, T)$ and $B(\omega, T)$ are not simply decomposable into thermal and line-shape factors, or in other words, ω and T are scrambled together so that the problem ceases to be an elementary one. In principle it should be possible to treat the entire system, i.e., the given atom plus other molecules, phonons, etc., as one big glorified atom, and then each line should be monochromatic, since all disturbances have been incorporated in the "inner" system. Actually, however, the

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[1] A. Einstein, Phys. Z. **18**, 121 (1917).

[2] The absorption coefficient $B(\omega)$ as we use it is defined as the quotient of rate of absorption of energy to field energy, both computed per unit volume. The value of $F(\omega)$ given in (0.2) is on the assumption of an isotropic radiation field. The appropriate value of $F(\omega)$ for other cases can be deduced from purely geometrical considerations as long as the field can be described by harmonic oscillators, as then generally $F(\omega)=2\pi\hbar\omega K_\omega$, where $K_\omega V$ is the density of these oscillator states in ω space. This general formula for $F(\omega)$ applies regardless of whether the transitions are caused by interactions of our atomic system with radiation, magnons, or phonons, since any of these can be described by the oscillator model. With longitudinal isotropic phonons, for example, $F(\omega)$ has half the value given in (0.2) (with c now an acoustic velocity) as there are not two directions of polarization. The fact that electromagnetic fields carry equal amounts of electric and magnetic energies is the counterpart of the fact that the kinetic and potential energies are equal for a harmonic oscillator. Oftentimes one has situations where there is only an alternating magnetic field without an appreciable electric one or vice versa, rather than both equal as in the radiation "wave zone." Then the harmonic-oscillator model is inapplicable, and the factor $F(\omega)$ has double the value (0.2) since the energy density is halved.

internal dynamics are so complicated that this procedure is usually not feasible.

Fortunately, other methods are available in particular the Green's function technique which has come into vogue in recent years. It is possible to give satisfactory answers to the problem for special cases, viz., the two-level system (especially the spin system $S=\frac{1}{2}$) and the harmonic oscillator, to the extent that essentially the Lorentzian or stochastic model is used. In the extreme wings of the line this model fails completely, yielding even an infinite second moment, i.e., an infinite mean square of the deviation of the frequency from its average value. In this region one should instead use the so-called statistical model, in which the perturbations are regarded as static, and one averages over all possible distributions weighted with the proper probability of occurrence.[3] This procedure is equivalent to treating collisions as infinitely slow, rather than infinitely short as in the stochastic model. Since the statistical model is essentially static in character, the role of temperature poses no additional problem, as each static configuration is weighted according to its appropriate Boltzmann factor.

Although Green's functions furnish the most refined approach, they do not provide the most intuitive one, and so in the first part of the paper (Secs. I.1–I.6) we derive most of the results in a less rigorous fashion based essentially on rudimentary examination of the correlation function for the two level system, and of the work done in the case of the harmonic oscillator. In the second part (Secs. II.1–II.8) we use the Green's function formalism. In part I the accent is on the stochastic model, equivalent to taking the Fourier components of the broadening mechanism as independent of frequency. In part II this specialization is not made, and instead the calculation is pointed particularly towards spin–lattice coupling, where the phonon spectrum is not flat.

PART I. ELEMENTARY METHODS

1. Relation between the Complex Susceptibility, the Correlation Function, and Absorption

In calculating line shapes or absorption, it is convenient and customary to introduce a complex, frequency-dependent atomic susceptibility tensor, defined by

$$\langle P_\beta \rangle = \chi_{\beta\alpha} F_\alpha \exp(i\omega t) \qquad (\alpha, \beta = x, y, z), \quad \text{(I.1)}$$

where the real part (Re) of $F_\alpha \exp(i\omega t)$ is the impressed rf field, and the real parts of P_x, P_y, P_z are the components of moment, electrical or magnetic, as appropriate to the problem. The symbol $\langle\ \rangle$ denotes the statistical average over the ensemble of atoms. If we write $\chi=\chi'-i\chi''$, then if there are N atoms/cc, the absorption coefficient per unit volume is

$$B(\omega)=4\pi\omega\chi''(\omega)N \qquad \text{(I.2)}$$

since this expression is[4] the time average of the product $(\text{Re}\ \dot{P}_\alpha)\cdot[\text{Re}\ F_\alpha \exp(i\omega t)]N$ divided by the energy density $|F_\alpha|^2/8\pi$.

The starting point of practically all modern calculations of line shape is a formula, apparently first given by Kubo,[5] relating the imaginary part of the diagonal components of the susceptibility tensor to the transform of the correlation function. This formula is

$$\chi_{\alpha\alpha}''(\omega)=\frac{1}{2\hbar}\tanh\left(\frac{\hbar\omega}{2kT}\right) \times\int_{-\infty}^{\infty}\cos(\omega t)\,\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle\,dt. \quad \text{(I.3)}$$

Here and elsewhere, $\langle\ \rangle$ denotes the thermodynamic average or expectation value, i.e.,

$$\langle P_\alpha(0)P_\alpha(t)\rangle=\frac{\text{Tr}\,[P_\alpha(0)P_\alpha(t)\exp(-\mathcal{H}/kT)]}{\text{Tr}\exp(-\mathcal{H}/kT)}. \quad \text{(I.4)}$$

The Heisenberg representation is to be understood throughout, so that

$$P_\alpha(t)=\exp(i\mathcal{H}t/\hbar)P_\alpha(0)\exp(-\mathcal{H}t/\hbar). \quad \text{(I.5)}$$

The Boltzmann factors entering in (I.4) are to be evaluated at $t=0$. It is not necessary to include the impressed field $F_\alpha \exp(i\omega t)$ to evaluate the correlation function (I.4) involved in (I.3). Consequently, the Hamiltonian $\mathcal{H}$ entering in (I.5) is to be taken as exclusive of this field, but inclusive of the atomic system's interaction with the collision agency (e.g., phonons or colliding gas molecules) responsible for the line broadening, and also this agency's self-energy, so that $\mathcal{H}$ is a constant of the motion when $F_\alpha=0$. If this self energy is omitted, then time-dependent perturbation theory must be used, and $\mathcal{H}t$ replaced by

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[3] For references on the statistical model, as well as to the literature of line breadths generally, see the review article by R. G. Breene, Jr., Rev. Mod. Phys. 29, 94 (1957).

[4] In (I.2) we have assumed the radiation case, where the electric and magnetic energy densities are equal. If the incident field is purely electrical or magnetic, the factor in the right-hand side of (I.2) is 8 instead of 4. Cf. end of footnote 2.

[5] R. Kubo, *Lectures in Theoretical Physics*, edited by W. E. Britten and L. G. Dunham (Interscience Publishers, Inc., New York, 1959), Vol. I, p. 151. The relation (I.3) is also implicitly contained in an earlier paper by R. Kudo and K. Tomita, Proc. Phys. Soc. Japan **9**, 888 (1954). For a good discussion of the Heisenberg representation used in connection with (I.3) see Chap. VIII, especially sections 10, 14, 19 of A. Messiah's *Quantum Mechanics* (English transl.) (North-Holland Publishing Co., Amsterdam, 1961).

$\int \mathcal{H} dt$ in (I.5), making the exponentials become time-development operators.

The derivation of (I.3), which is now fairly standard and best achieved by use of the density matrix, is given in Appendix A.

2. Longitudinal Susceptibility of a Two-Level System

We will now restrict our calculations to a two-level system. Without any essential loss of generality we may suppose this to be a spin system $S=\frac{1}{2}$. We then have $P_\alpha=-g\beta S_\alpha$, where β is the Bohr magneton, and in order to allow the spin to be real or fictitious, we do not specialize the g factor to the value 2. We assume that there is a large constant magnetic field along the z axis. We examine separately the longitudinal and the transverse susceptibilities as they must be handled in somewhat different fashions. With obvious, appropriate changes in notation, our calculations apply to any two-level system if we understand by *longitudinal* and *transverse* the absorption stemming from the part of the moment, respectively, diagonal and nondiagonal in the index specifying the two energy levels.

We first consider the longitudinal case $\alpha=z$, i.e., the aperiodic absorption studied so extensively by Gorter and his school at Leiden.

At $t=0$ the eigenvalues of S_z are $\pm\frac{1}{2}$, with probabilities

$$p_-=\tfrac{1}{2}+\tfrac{1}{2}\tanh(\hbar\omega_0/2kT),\quad p_+=1-p_-,\quad (\hbar\omega_0=g\beta H_0) \tag{I.6}$$

and the thermodynamic mean of the two eigenvalues is

$$\langle S_z\rangle=\tfrac{1}{2}(p_+-p_-)=-\tfrac{1}{2}\tanh(\hbar\omega_0/2kT).$$

We now assume that the transition between the two eigenvalues of S_z occurs by a purely random, stochastic process. If τ is the mean free time between switches between the two eigenvalues, the mean lives τ_-, τ_+ in the states $S_z=-\frac{1}{2}$, $+\frac{1}{2}$ are, respectively,

$$\tau_-=2p_-\tau,\qquad \tau_+=2p_+\tau. \tag{I.7}$$

[The factor 2 occurs in (I.7) because half of the collisions end life in a given state.] One cannot disregard correlations after a switch, as the product of the two eigenvalues of S_z before and after a switch is $-\frac{1}{4}$. However, one can avoid the necessity of following through the correlations by imagining partially dummy collisions to take place such that in the + state a fraction p_+ remain in the +, and a fraction p_- change over into the − state. Similarly in the − state a fraction p_- of the imaginary collisions do nothing and a fraction p_+ are real. The frequency of occurrence $1/\tau_1$ of such artificially defined collisions is the same in either state since

$$\tau_1^{-1}=[(p_-+p_+)/p_+]\tau_-^{-1}=[(p_-+p_+)/p_-]\tau_+^{-1}$$
$$=(2\tau p_-p_+)^{-1} \tag{I.8}$$

by (I.6) and (I.7). After such an artificially defined collision the mean value of $S_z-\langle S_z\rangle$ is zero regardless of whether one is starting from $+\frac{1}{2}$ or $-\frac{1}{2}$. Thus one has a simple decay of $S_z-\langle S_z\rangle$ to zero with time constant τ_1. We can write

$$4\int_{-\infty}^{\infty}\langle S_z(0)\,S_z(t)\rangle\cos\omega t\,dt=\int_{-\infty}^{\infty}p_+(1-\bar{\sigma})(2S_+(t)-\bar{\sigma})\cos\omega t\,dt+\int_{-\infty}^{\infty}p_-(-1-\bar{\sigma})[2S_-(t)-\bar{\sigma}]\cos\omega t\,dt$$
$$+\int_{-\infty}^{\infty}\bar{\sigma}^2\cos\omega t\,dt, \tag{I.9}$$

where $\bar{\sigma}=2\langle S_z\rangle=p_+-p_-$ and $S_+(t)$, $S_-(t)$ are the values of $S_z(t)$ emanating, respectively, from $S_z=\frac{1}{2}$ and $S_z=-\frac{1}{2}$ at $t=0$. In virtue of what has been said above, the first two integrals on the right-hand side of (I.9) involve a simple exponential decay with the same constant, and so the right-hand side of (I.7) is

$$[p_+(1-\bar{\sigma})^2+p_-(-1-\bar{\sigma})^2]\int_{-\infty}^{\infty}\exp(-|t|/\tau_1)\cos\omega t\,dt+\bar{\sigma}^2\int_{-\infty}^{\infty}\cos\omega t\,dt=[1-\bar{\sigma}^2]\frac{2\tau_1}{1+\tau_1^2\omega^2}+2\bar{\sigma}^2\pi^{-1}\,\delta(\omega). \tag{I.10}$$

Because of the factor $\tanh(\hbar\omega/2kT)$ in (I.3) we can safely drop the term involving the Dirac delta function $\delta(\omega)$ (really a limiting operator) with singularity at $\omega=0$. Since our calculation is a semiclassical one, we do not need[6] to distinguish between $S_z(0)\,S_z(t)$ and $S_z(t)\,S_z(0)$, and so we can identify the integral in (I.3) with $\frac{1}{2}g^2\beta^2/\hbar$ times the expression (I.10). Thus (I.3) becomes

$$\chi_z''(\omega)=\frac{g^2\beta^2}{2\hbar}\tanh\left(\frac{\hbar\omega}{2kT}\right)\frac{\tau_1}{1+\tau_1^2\omega^2}\operatorname{sech}^2\left(\frac{\hbar\omega_0}{2kT}\right), \tag{I.11}$$

where $\hbar\omega_0=g\beta H_0$.

This equation is to be compared with the equation for the nonresonant susceptibility obtained by Casimir

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[6] In adapting semiclassically quantum-mechanical formulas involving the correlation function one must select a form which is symmetric in $P_\alpha(0)$ and $P_\alpha(t)$. If one were naively to use the alternative form, for instance, which involves the antisymmetric combination one would get zero. The proper transcription of the antisymmetric form would involve a complicated consideration of Poisson brackets.

and du Pré,[7] viz.,

$$\chi_z''(\omega)=\tfrac{1}{4}(g^2\beta^2/kT)\{\tau_1\omega/[1+(\tau_1\omega)^2]\}. \qquad (I.12)$$

Equation (I.12) differs from (I.11) in two respects. The first of these is the factor of $\frac{1}{2}\omega/kT$ as compared to $\hbar^{-1}\tanh(\hbar\omega/2kT)$. This difference is indicative of the fact that the Casimir–du Pré analysis is valid only in the quantum-mechanical adiabatic limit $\omega=0$. It is usually of little importance in conventional experiments.

Of greater significance is the factor $\mathrm{sech}^2(\hbar\omega_0/2kT)$. Its existence apparently was explicitly pointed out for the first time by Van Vleck and Orbach.[8] It is intimately connected with the fact that in the limit of zero temperature, the population of the spin system remains entirely in the ground state, and so is unaffected by the alternating field. As a consequence, $\chi_z''(\omega)$ becomes exponentially small as $T\rightarrow 0$. The same factor could have been obtained from a thermodynamic analysis if the Curie susceptibility $g^2\beta^2/4kT$ is replaced by the static susceptibility evaluated in a finite field:

$$\chi_{H_0}=\frac{d}{dH}M(H)\bigg|_{H=H_0}=\tfrac{1}{2}g\beta\frac{d}{dH}\tanh\left(\frac{g\beta H}{2kT}\right)$$

$$=\frac{g^2\beta^2}{4kT}\,\mathrm{sech}^2\left(\frac{\hbar\omega_0}{2kT}\right).$$

A more or less equivalent procedure was used by Van Vleck and Orbach to obtain the sech² factor, though in connection with a somewhat different problem, viz., the effect of anisotropy in the aperiodic susceptibility of rare earth impurities on the ferrimagnetic resonance of iron garnets.

3. Effect of Phase Interruptions on the Resonant Absorption of a Two-Level System

We now proceed to treat the case that the rf field is perpendicular to the dc field that splits the energy levels. This is the case involved in the usual experiments in magnetic resonance of a system $S=\frac{1}{2}$. Also the analysis applies more generally to any two-level system, or system with two singled-out "effective levels" if the broadening due to interaction with other levels is not important, and if by N in (I.2) we understand the sum total of atoms in the two particular levels under consideration.

We note first of all that in the transverse case the matrix elements of, say, S_x for the transition $\frac{1}{2}\rightarrow-\frac{1}{2}$ are of the form

$$(\tfrac{1}{2}\mid S_x\mid-\tfrac{1}{2})=\int\psi_{\frac{1}{2}}{}^*S_x\psi_{-\frac{1}{2}}\,d\tau, \qquad (I.13)$$

where the wave function is inclusive of spin. The wave function ψ has a phase factor ϵ in the sense that $\psi=\mid\psi\mid\exp(-iEt/\hbar)\exp(-i\epsilon)$. There is no question of persistence of phase at collision, as the new phases are random. The situation is different from the longitudinal or diagonal case, where the same phase enters fore, and, with reversed sign, aft in the formula for the matrix element, so that the phase cancels out in the expression for the matrix element. Consequently in treating longitudinal absorption, correlation could not be ignored when one switches from one eigenvalue to another, and only by introducing the artifice of fake collisions were we able to disregard correlations.

If there were no interruptions caused by collisions, the product of spin operators involved in the integrand of (I.3) for the transverse case would be simply

$$[P_x(0)P_x(t)+P_x(t)P_x(0)]=\tfrac{1}{2}g^2\beta^2\cos\omega_0 t \qquad (I.14)$$

regardless of the initial conditions, inasmuch as

$$(\tfrac{1}{2}\mid P_x(t)\mid-\tfrac{1}{2})=(-\tfrac{1}{2}\mid P_x(t)\mid\tfrac{1}{2})^*=\tfrac{1}{2}g\beta\exp[i(\omega_0 t+\epsilon)].$$

The value of ω_0 is $g\beta H_0/\hbar$ for the particular case that the decomposition is due to an applied magnetic field.

Since in the transverse case there is no "hang-over effect" and the coherence is lost whenever there is an interruption of either the initial or final state, at first sight, it appears that allowance can be made for the gradual loss of correlation by multiplying (I.14) by $\exp(-\mid t\mid/\tau_2')$ with $1/\tau_2'=(1/\tau_-)+(1/\tau_+)$, where τ_-, τ_+ are the mean lifetimes in the initial and final states associated with (I.13). However, a little reflection will convince one that the proper value of the constant in the exponent is instead

$$1/\tau_2'=\tfrac{1}{2}(\tau_-^{-1}+\tau_+^{-1}). \qquad (I.15)$$

The appropriateness of the additional factor $\frac{1}{2}$ involved in (I.15) can be seen in a variety of ways. In the first place, in classical theory the appropriate decay factor associated with a mean life τ is $\exp(-t/\tau)$, and considerations of symmetry require that in quantum mechanics $1/\tau$ be apportioned symmetrically between the initial and final states. Alternatively or essentially equivalently, one can say that in quantum mechanics, the life time of a state is determined by the rate of decay of the squared modulus of its probability amplitude (i.e., $\mid c_i\mid^2$ in an expansion of the form $\sum_i c_i\psi_i$), whereas a matrix element is represented by $c_ic_j^*$, and c_i, of course, decays half as fast as $\mid c_i\mid^2$. All this is rather heuristic, but for more rigorous confirmation of the factor $\frac{1}{2}$, appeal can be made to the results of Wigner and Weisskopf,[9] or to our calculation by means of Green's functions in part II. In virtue of (I.7) and

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[7] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).

[8] J. H. Van Vleck and R. Orbach, Phys. Rev. Letters **11**, 65, 303 (E) (1963).

[9] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930); **65**, 18 (1930).

(I.8), Eq. (I.15) reduces to

$$1/\tau_2'=\tfrac{1}{2}\tau_1^{-1}. \tag{I.16}$$

When we multiply (I.14) by the exponential factor to allow for the loss of correlation and substitute in (I.3) we obtain for the transverse absorptive susceptibility the expression

$$\chi_{xx}''(\omega)=\tfrac{1}{4}g^2\beta^2\int_{-\infty}^{\infty}\cos(\omega_0 t)\cos(\omega t)\exp(-|t|/\tau_2')\,dt \times\hbar^{-1}\tanh(\hbar\omega/2kT). \tag{I.17}$$

Evaluation of the integral in (I.17) gives

$$\chi_{xx}''(\omega)=\tfrac{1}{4}g^2\beta^2\hbar\tanh\left(\frac{\hbar\omega}{2kT}\right) \times\left[\frac{1/\tau_2}{(\omega-\omega_0)^2+(1/\tau_2)^2}\quad\frac{1/\tau_2}{(\omega+\omega_0)^2+(1/\tau_2)^2}\right] \tag{I.18}$$

if we take $\tau_2=\tau_2'$. We use different notations τ_2, τ_2' because it will later turn out that (I.16) is not really the correct value of the transverse damping constant $1/\tau_2$ which should be used in (I.18).

4. Effect of Frequency Modulation on the Resonant Absorption of a Two-Level System

If we identify the damping constant $1/\tau_2$ in (I.18) with the expression $1/\tau_2'$ given in (I.16) the line-breadth constant $1/\tau_2$ for transverse resonance is half as large as that $1/\tau_1$ entering in the longitudinal case [Eq. (I.11)]. It is clear that something is wrong or incomplete, since it is well known that under certain circumstances the transverse relaxation time τ_2 is equal to the longitudinal one τ_1. In fact, if the collision mechanism is an isotropic one, then in the limit $\omega_0\rightarrow 0$ there is no possible way of distinguishing between the transverse and longitudinal situations, and this, of course, demands equal relaxation times or line-breadth constants for the two cases.

The difficulty is due to the fact that there are two mechanisms responsible for broadening in the transverse case, viz., phase interruption and frequency modulation, and we have considered only the first of these. The existence of the two mechanisms was recognized in the early work of Bloembergen, Purcell, and Pound,[10] and to distinguish between the two of them, they introduced the notation $1/\tau_2'$ and $1/\tau_2''$, which we follow, for the two corresponding line-breadth constants, with a combined total

$$1/\tau_2=(1/\tau_2')+(1/\tau_2''). \tag{I.19}$$

The phase interruptions are caused by the involvement of S_x, S_y in the perturbing mechanism, and the frequency modulations by that of S_z. The reason is that for a system of spin $\frac{1}{2}$, the most general Hamiltonian is a linear function of S_x, S_y, S_z. The terms in S_x, S_y in the collision Hamiltonian are nondiagonal in the magnetic quantum number, and so induce collisions, with attendant phase interruptions, whereas the terms in S_z represent, so to speak, a noise field and merely alter the precession in a wobbly fashion. The term noise field is a catch-all for any kind of disturbance which adds to the Hamiltonian function a term linear in S_z, and may represent interactions with magnons, phonons, forces present at collision in gases, or even coupling to radiation. Our analysis is general, since we simply incorporate any of these effects in a time-dependent perturbation theory.

Because of the noise field, the time-dependent phase factor associated with, say, S_x+iS_y is $\exp[i\omega_0 t+i\phi(t)]$ instead of $\exp(i\omega_0 t)$. The excursion in phase $\phi(t)$ caused by the wobbles in the precession rate can be either positive or negative. We suppose that the longitudinal noise field is the sum

$$H_{nz}=\sum_k A_{kz}\exp(i\omega_k t) \tag{I.20}$$

of Fourier components without correlation except for the reality condition $A_{-k}{}^*=A_k$. Note that since the phase factor ϵ_k in $A_k=|A_k|\exp(i\epsilon_k)$ is random we have

$$\langle A_{kz}A_{k'z}\rangle_{\mathrm{Av}}=|A_{kz}|^2\delta_k{}^{-k}. \tag{I.21}$$

Because the noise field is random, the addition of the various Fourier components is a random-walk affair, and, in accordance with rudimentary statistical theory, the excursion in phase after a sufficiently long time t has a Gaussian disturbation[11]

$$P(\phi)=(1/2\pi)^{\frac{1}{2}}\exp(-\phi^2/2\Delta)$$

with the mean-square excursion Δ a linear function of time. To compute Δ we note that

$$\phi(t)=g\beta\hbar^{-1}\int_0^t H_{nz}\,dt$$

so that

$$\Delta=g^2\beta^2\hbar^{-2}\{\sum_k[\exp(i\omega_k t)-1]A_{kz}/i\omega_k\}^2{}_{\mathrm{Av}}. \tag{I.22}$$

If we use (I.21) and replace the sum by an integral (I.22) becomes

$$\Delta=2g^2\beta^2\hbar^{-2}\int_{-\infty}^{\infty}\rho_\omega|A_z(\omega)|^2\left(\frac{1-\cos\omega t}{\omega^2}\right)d\omega,$$

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[10] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[11] The present treatment of the broadening due to frequency modulation as a random-walk process parallels closely that previously given by J. H. Van Vleck in a review article on nuclear relaxation times in Ned. T. Natuurk. **27**, 1 (1961). This previous treatment, however, was primarily for high temperatures.

where ρ_ω is the density of k values in ω space and we now use the notation $A_z(\omega)$ rather than A_{kz}. For large t, all the contribution to the integral comes from the vicinity of the origin, so that $A_z(\omega)$ may be replaced by $A_z(0)$ and taken outside the integration sign, giving

$$\Delta = 2\pi g^2\beta^2 t\hbar^{-2}\rho_0 \,|\, A_z(0)\,|^2. \tag{I.23}$$

The extra factor in the integrand of the correlation function because of the frequency modulation effect is thus

$$\left(\frac{1}{2\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{\infty} \exp\,(i\phi)\,\exp\,(-\phi^2/2\Delta)\;d\phi = \exp\,(-\,|\,t\,|/\tau_2''), \tag{I.24}$$

where

$$1/\tau_2'' = \pi\hbar^{-2}g^2\beta^2\rho_0 \,|\, A_z(0)\,|^2. \tag{I.25}$$

When now the extra factor (I.24) is inserted in the integrand of (I.17) the absorptive susceptibility is still given by (I.18), but now τ_2 is given by (I.19).

We must now examine the conditions under which $\tau_2'' = \tau_2'$ so as to make $(1/\tau_2') + (1/\tau_2'') = 1/\tau_1$ [of (I.16)], i.e., the longitudinal and transverse relaxation times equal to each other.

Let us first consider the case of high temperatures, so that the mean lives τ_+, τ_- in the upper and lower states are equal. Then by (I.15) the part $1/\tau_2'$ of the transverse relaxation rate is the mean decay rate out of either state. By the "golden rule," if the perturbation is

$$g\beta\sum_k [A_{kx}S_x + A_{ky}S_y]\,\exp\,(i\omega t), \tag{I.26}$$

this rate is

$$\frac{1}{\tau_2'} = \frac{1}{2}\left(\frac{1}{\tau_-} + \frac{1}{\tau_+}\right) = 2\pi\hbar^{-2}g^2\beta^2(\tfrac{1}{4})[\,|\,A_x(\omega_0)\,|^2 + \,|\,A_y(\omega_0)\,|^2]\rho_{\omega_0}. \tag{I.27}$$

For an isotropic milieu, the averages for the x, y, and z components will all be the same. Also if, in addition, the broadening and frequency modulation are ideally stochastic, in other words if the spectrum of the disturbance is independent of frequency, corresponding to infinitely rapid collision times, then

$$|\,A_z(0)\,|^2\rho_0 = \,|\,A_x(\omega_0)\,|^2\rho_{\omega_0} = \,|\,A_y(\omega_0)\,|^2\rho_{\omega_0}, \tag{I.28}$$

and one does indeed have $\tau_2' = \tau_2''$ and $\tau_1 = \tau_2$, so that the longitudinal and transverse relaxation times are equal. Of course, the Fourier spectrum cannot extend to infinity, as supposed in the ideally stochastic model, but the cutoff may be well above ω_0, in which case no harm is done in assuming that it extends to infinity.

To extend the proof to the case that ω_0 is not small compared to $kT/\hbar$, i.e., that $\tau_- \neq \tau_+$ in (I.15) requires some more quantum theory. The square modulus of an x-Fourier component in (I.26) as applied to the spin state $-\frac{1}{2}$ corresponds in quantum mechanics to a factor of the form $\langle|(j\,|\,A_x\,|\,j')\,|^2 N_j\rangle_{\text{Av}}$, where N_j is the population factor for the perturbing agency: phonons, magnons, or what-have-you, before it is changed by interaction with the spin system. The corresponding square for the state $\frac{1}{2}$ is $\langle|(j'\,|\,A_x\,|\,j)\,|^2 N_{j'}\rangle_{\text{Av}}$. The state j exceeds j' in energy by an amount $\hbar\omega_0$ in order to ensure conservation and a thermal average is to be understood over the various states of the perturbing agency. The Hermitian property and detailed balancing require that

$$(j\,|\,A_x\,|\,j') = (j'\,|\,A_x\,|\,j)^*, \qquad N_{j'}/N_j = p_-/p_+,$$

where p_-, p_+ are the thermal or probability factors defined in (I.5). Hence, using (I.15), we see that (I.27) is replaced by

$$\tfrac{1}{4}g^2\beta^2\hbar^{-2}\pi\{[\,|(j\,|\,A_x\,|\,j')\,|^2 + |(j\,|\,A_y\,|\,j')\,|^2](N_j + N_{j'})\}_{\text{Av}}\,\rho_{\omega_0}.$$

Similarly Eq. (I.25) transcribes quantum mechanically into

$$1/\tau_2'' = \tfrac{1}{2}\pi\hbar^{-2}g^2\beta^2\{|(j\,|\,A_z\,|\,j')\,|^2(N_j + N_{j'})\}_{\text{Av}}\,\rho_0,$$

where the energy difference between the states j and j' is negligible. The isotropic and stochastic assumption means that $\{|(j\,|\,A_q\,|\,j')\,|^2(N_j + N_{j'})\}_{\text{Av}}$ is independent of q or of the energy difference between the states j and j', also that $\rho_0 = \rho_{\omega_0}$ giving us again $\tau_1 = \tau_2$. This proof can be criticized on grounds of rigor, and skeptics can refer to the treatment by means of Green's functions in part II. It is doubtful, anyway, if the stochastic model has much meaning except when $\hbar\omega_0 \ll kT$ and then we do not need to worry about the distinction between τ_- and τ_+.

5. Discussion of the Final Formula for the Transverse Absorptive Susceptibility

The final bracketed factor in (I.18), our expression for the transverse absorptive susceptibility, yields the same line shape as that given by Kronig,[12] Van Vleck and Weisskopf,[13] Fröhlich,[14] Karplus and Schwinger,[15] Garstens,[16] and others. It can be derived in a variety of ways, among them transitions between smeared out initial and final energy levels,[12] or Fourier analysis of spontaneous emission with absorption obtained from detailed balancing.[17] If the absorption is calculated directly[13,15] from the equations of motion without use

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[12] R. de L. Kronig, Physica **5**, 65 (1938).

[13] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

[14] H. Frohlich, Nature **157**, 478 (1946).

[15] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

[16] M. A. Garstens, Phys. Rev. **93**, 1228 (1954).

[17] J. H. Van Vleck and H. Margenau, Phys. Rev. **76**, 1211 (1949).

of correlation functions, it is necessary to take into account the fact that after collisions the assumed spatial distribution conforms to the Boltzmann law appropriate to the instantaneous value of the rf field, rather than being random.[18] Otherwise an expression is obtained which is correct only near resonance—in fact the antiresonant term—that in $\omega+\omega_0$ even has the wrong sign. In Lorentz's[19] original work he was interested only in the behavior near resonance, and so his assumption of randomness was warranted.

Our primary interest, however, is the way that the temperature enters. If one refers to the papers by Van Vleck,[20] Karplus and Schwinger,[15] etc., it is found that they used a factor

$$(\omega/\omega_0)\tanh(\hbar\omega_0/2kT)$$

in place of $\tanh(\hbar\omega/2kT)$ in (I.18). If one has both

$$(\hbar\omega/kT)\ll 1, \qquad (\hbar\omega_0/kT)\ll 1 \qquad \text{(I.29)}$$

then there is no distinction between the two expressions. This is also true near resonance, where

$$\hbar\,|\,\omega-\omega_0\,|/kT\ll 1, \qquad |\,\omega-\omega_0\,|/\omega\ll 1 \qquad \text{(I.30)}$$

even though $\hbar\omega$ may not be negligible compared with kT. Fortunately, in most cases one of the conditions (I.29) or (I.30) is satisfied, e.g., (I.30) is well-tuned resonance experiments and (I.29) in the propagation of radar or far-infrared waves, or in conventional studies of nuclear magnetization. However, with the modern techniques of very low temperatures achieved by adiabatic demagnetization, one can think of situations where the distinction is important. Also, from the sheer logic of the situation, it is desirable to know which form is correct, and there is no doubt that the proper factor is $\tanh(\hbar\omega/2kT)$. This conclusion is not a new one, since the correct factor has long been used in the fluctuation dissipation theorem, as adapted from Nyquist to the quantum-mechanical case by Callen and Welton[21] in connection with the study of the Johnson noise in circuits. This theorem is frequently used by workers on many-body problems.

It should be emphasized that the relation $\tau_1=\tau_2$ holds only under the particular condition that the perturbations responsible for the broadening are isotropic and the noise spectrum is independent of frequency. If one uses for a solid instead of the stochastic model a more realistic mechanism in which the perturbations are due to interaction with either phonons or magnons, then the spectral density ρ_0 at zero frequency is zero (i.e., $\rho\sim\omega^2$ for the well-known Debye law). In such cases we expect that $1/\tau_2''=0$ and $1/\tau_2=\frac{1}{2}(1/\tau_1)$, as already emphasized by McCumber.[22] The other extreme is where the noise spectrum is so narrow that it is largely cut off for the $1/\tau_1$ and $1/\tau_2'$ effects, which depend on perturbations being able to bridge the gap between $S_z=-\frac{1}{2}$ and $S_z=\frac{1}{2}$. Then the broadening is caused almost entirely by the FM effect, and we expect $1/\tau_2''\gg 1/\tau_1$. Under such circumstances the line shape must be calculated by the statistical rather than stochastic model. The classic experiments of Bloembergen, Purcell, and Pound[10] on nuclear resonance in liquid mixtures reveal vividly how $1/\tau_2$ begins to deviate from and exceed $1/\tau_1$ as the viscosity is increased and the perturbations by collisions become slower and more nearly static.

Finally it should be noted that as long as the surroundings are isotropic even if the noise spectrum is not flat, the formulas for the transverse and longitudinal susceptibilities should become identical when the static applied field is made to approach zero and the resonance frequency ω_0 hence is small compared to the impressed frequency ω. This is an obvious consequence of symmetry, for in the limit $\omega_0=0$ there can be no distinction between the longitudinal and transverse situations. This requirement is fulfilled by our formulas, for in the limit $\omega\rightarrow 0$ there can be no distinction between τ_1 and τ_2 inasmuch as $A_x(\omega)\rightarrow A_z(0)$ if there is isotropy, and if $\tau_1=\tau_2$, $\omega_0=0$, the longitudinal and transverse expressions (I.11) and (I.18) both reduce to a common expression

$$\chi''=\tfrac{1}{2}g^2\beta^2\hbar^{-1}\tanh(\hbar\omega/2kT)[\tau_1/(1+\tau_1^2\omega^2)]. \qquad \text{(I.31)}$$

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[18] It is an advantage of the Kubo approach based on correlation functions that it gives the spectral shape without the necessity of investigating how the rf field affects the distribution after collision as it is a little hard to see what is implied in the assumption that the collisions readjust themselves to conform to the instantaneous value of a rapidly oscillating field. It should, however, be mentioned that if it assumed that such adjustment takes place, it is possible to show that for the stochastic model one has $\tau_1=\tau_2$ without the need of isolating the two kinds of contribution to τ_2. This was done by one of the present authors (V.V.) in J. Appl. Phys. **35**, 882 (1964), footnote 13. He assumed following Van Vleck and Weisskopf, or Karplus and Schwinger, that each collision restores the distribution to that appropriate to the instantaneous value of the total field. If τ' be the interval between such collisions, then the work of Karplus and Schwinger (Ref. 15) shows that τ_2 is the same as the transverse damping constant τ'. Elementary considerations such as given in our Sec. I.2, and not elaborated in the original article of Van Vleck, show that the τ_1 is the same as τ'. It is at first sight rather surprising that with this approach one obtains the full value of $1/\tau_2$ without ostensibly invoking the frequency modulation effect. The explanation is a rather subtle one. Adjustment to the proper orientation relative to the applied transverse field can be obtained by rephasing without changing the eigenvalues of s_z. Thus what looks like a "do-nothing" collision as far as s_z is concerned is a real one as regards s_x, s_y and such rephasing is another way of looking at the FM effect.

[19] H. A. Lorentz, Proc. Amst. Akad. Sci. **8**, 591 (1906), or *The Theory of Electrons* (Teubner, Leipzig, 1909, or Dover Publications, New York, 1952, note 57).

[20] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947); an attempt by the same author [Conference on the Broadening of Spectral Lines, Pittsburgh, (1955)] to improve on the thermal factor he originally used is not satisfactory.

[21] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

[22] D. E. McCumber, Phys. Rev. **133**, A163 (1964).

6. Line Shape for a Perturbed Harmonic Oscillator

We now turn to a completely different problem—a harmonic oscillator X perturbed by interactions with other systems x_1, x_2, $\cdots$. We assume that these other systems are themselves harmonic oscillators, and that the interaction is linear in the coordinates which it couples. These conditions are met if, for example, the perturbing systems are phonons, magnons, or even photons. We assume that the applied field E acts only on x, so that the Hamiltonian function is

$$\mathcal{H}_E=\tfrac{1}{2}m[(p_X/m)^2+\omega_0^2X^2]+\sum_k\tfrac{1}{2}\mu_k[(p_k/\mu_k)^2+\omega_k^2x_k^2]$$
$$+X\sum_k c_kx_k-eXE_0\cos\omega t. \quad \text{(I.32)}$$

We attach a subscript E to $\mathcal{H}$ in order to emphasize that the Hamiltonian (I.32) is inclusive of the interaction $-eXE_0\cos\omega t$ with the impressed rf field, and in order to distinguish it clearly from the Hamiltonian exclusive thereof which we throughout denote by $\mathcal{H}$ and which we use generally in evaluating the correlation function [cf. e.g., Eqs. (I.3)–(I.5)].

We suppose we are dealing with a one-dimensional problem, but the extension to the isotropic three-dimensional problem occasions no difficulty. For concreteness we assume that we are dealing with a harmonically bound electric charge e of mass m. Without resorting to any mathematical analysis, one can immediately conclude how the temperature enters in absorption and emission. If we take $E_0=0$, the dynamical problem is simply that of a system of coupled harmonic oscillators whose Hamiltonian is a quadratic form. In either classical or quantum mechanics, it is possible to introduce normal coordinates ξ_j such that the Hamiltonian is reduced to a sum of squares $\frac{1}{2}\sum_j(\alpha_jp_j^2+\beta_j\xi_j^2)$. The extra term from the perturbing field acquires the form $\sum_j\gamma_j\xi_jE_0\cos\omega t$. In other words a fraction of the perturbing field acts on each of the new, uncoupled harmonic oscillators that correspond to the normal coordinates. The absorption by a harmonic oscillator in thermal equilibrium is independent of temperature in both classical and quantum mechanics. Its emission is proportional to $1/[\exp(\hbar\omega/kT)-1]$ in quantum theory and to kT classically. The absorption coefficient $B(\omega)$ for our system is thus independent of temperature and the corresponding coefficient associated with spontaneous radiation is

$$A(\omega)=F(\omega)B(\omega)/[\exp(\hbar\omega/kT)-1], \quad \text{(I.33)}$$

where $F(\omega)$ has the value $2\hbar\omega^3/\pi c^3$ if the electric field arises from isotropic radiation. The form of the temperature-independent function $F(\omega)$ for other cases is discussed in footnote 2.

The absorption $B(\omega)$ is the net difference between the true upwards absorption $B_+(\omega, T)$ and the stimulated emission $B_-(\omega, T)$, which are connected with $B(\omega)$ by the relations

$$B_+(\omega,T)=\frac{\exp(\hbar\omega/kT)}{\exp(\hbar\omega/kT)-1}B(\omega),$$

$$B_-(\omega,T)=\frac{B(\omega)}{\exp(\hbar\omega/kT)-1}.$$

Only the difference B_+-B_- is independent of temperature. It is particularly to be noted that the thermal factor for the spontaneous emission is

$$[\exp(\hbar\omega/kT)-1]^{-1}$$

and not

$$[\exp(\hbar\omega_0/kT)-1]^{-1}.$$

Consequently the low frequency tail of the line can be emitted when $\hbar\omega/kT\sim1$ even though $\hbar\omega_0/kT\ll1$ provided only that $F(\omega)B(\omega)$ is not negligible. If the oscillator X was uncoupled to other oscillators, the absorption coefficient would be a line-strength factor times a delta function located at $\omega=\omega_0$. Because of the interaction terms $X\sum_kc_kx_k$ the myriads of other oscillators x_1, x_2, $\cdots$ steal a fraction of the line strength otherwise associated purely with X, and it is this stealing effect which is responsible for the line shape. We allow the ensemble of perturbing oscillators to become more and more closely spaced, and in the limit the absorption becomes a continuum rather a discrete set of closely spaced delta functions. The original oscillator X has then lost its identity and contributed all its line strength to the ensemble, as some of the oscillators x_k fall so close to X in frequency that in this region there is complete scrambling.

Our problem is now to determine how the absorption intensity is distributed among the various new eigenfrequencies. It turns out to be remarkably easy to solve.

Instead of using correlation functions, it is easiest to compute directly the work done by the impressed field $E_0\cos\omega t$. All the coordinates will oscillate in phase with the field, i.e., have time factors $\cos\omega t$. The equation of motion

$$\mu_k(\ddot{x}_k+\omega_k^2x_k)+c_kX=0$$

for the coordinate x_k gives immediately

$$x_k=[c_k/\mu_k(\omega^2-\omega_k^2)]X \quad \text{(I.34)}$$

and substitution of (I.34) into the equation for X yields

$$X=eE_0\cos\omega t/f(\omega), \quad \text{(I.35)}$$

where

$$f(\omega)=m(\omega_0^2-\omega^2)+\sum_k[c_k^2/\mu_k(\omega^2-\omega_k^2)]. \quad \text{(I.36)}$$

We now assume that the values of ω_k, the original frequencies of the perturbing oscillators, are closely spaced at intervals ϵ_k which are small compared with ω, and which vary only slowly with the region of the spectrum so that they can be regarded as sensibly constant in the vicinity of a given ω_k. The denominator (I.36) of (I.35) has one simple zero $\omega_{k'}$ in the interval ω_k+0 to $\omega_{k+1}-0$ as it seings from $+\infty$ to $-\infty$ in this interval. (There are no higher order zeros, as we will later find a non-vanishing derivative at each root.) The expression (I.35) can thus be written in the form

$$X=\sum_k[g_k(\omega)/(\omega_k'-\omega)], \tag{I.37}$$

where ω_k' is not quite the same as ω_k, and $g_k(\omega)$ is finite at $\omega=\omega_k'$. There is absorption only if the impressed frequency is accurately tuned to one of the poles ω_k'. Actually, however, any impressed field is not strictly monochromatic, and will have a practically uniform intensity over the small region separating two roots, which in the limit becomes negligible as they finally contract together to make the perturbing agency (magnons, phonons, etc.) have a continuous spectrum. If instead of being monochromatic, the electric energy has a spectral distribution described by

$$\tfrac{1}{2}E_0^2=\int K(\omega)\,d\omega \tag{I.38}$$

the absorption arising from a given term of (I.37) is proportional to $g(\omega_k')K(\omega_k')$. The proportionality factor is most readily determined by comparison with the time-honored and familiar result that an undamped harmonic oscillator of frequency ω_0 absorbs radiation from a field of the form (I.38) at a rate[23]

$$dW/dt=(e^2/4m)\cdot 2\pi K(\omega_0). \tag{I.39}$$

The response of a harmonic oscillator near resonance is

$$X=\frac{eE_0\cos\omega t}{m(\omega_0^2-\omega^2)}\sim\frac{eE_0\cos\omega t}{2m\omega_0(\omega_0-\omega)}. \tag{I.40}$$

Each member of (I.37) is evidently equivalent to a fictitious harmonic oscillator having an apparent e/m value $2\omega_k'g_k(\omega_k')$. Any one term of (I.37) therefore absorbs energy at a rate

$$dW/dt=\pi e\omega_k'g_k(\omega_k')K(\omega_k'). \tag{I.41}$$

If, instead of being strictly monochromatic, the intensity in (I.35) is spread uniformly over a band wide enough to include n roots of (I.36), then $K(\omega_k')=\frac{1}{2}E_0^2/\epsilon_k n$. The factor n cancels out of the formula for dW/dt, in terms of E_0, since an extra factor n must be inserted in the right side of (I.41) to allow for the fact that there is now absorption from n resonances of approximately equal strength. The absorptive susceptibility χ'' is $(dW/dt)/\frac{1}{2}E_0^2\omega$ and is consequently

$$\chi_\omega''=\pi g_k(\omega)\rho_k e, \tag{I.42}$$

where $\rho_k=1/\epsilon_k$ is the density of the roots of (I.36) in ω space and we use a value of k such that ω_k is near ω. Since the coefficients c_k are very small, and the roots crowd very close together, we do not need to distinguish between the spacing between consecutive infinities (the ω_k) and that between consecutive zeros (the ω_k') of (I.36).

Our problem is now to compute the pole strength $g_k(\omega)$, which by (I.35), (I.36), and (I.37) is

$$g_k=-e/[df/d\omega]_{\omega=\omega_k'}. \tag{I.43}$$

To evaluate the derivative needed in (I.43) we write the function f defined in (I.36) near some particular root ω_k' in the form

$$f(\omega)=m(\omega_0^2-\omega^2)+\Delta+Q, \tag{I.44}$$

where

$$\Delta=\sum_k[c_k^2/\mu_k(\omega^2-\omega_k^2)]-Q, \tag{I.45}$$

$$Q=\frac{c_k{}^2}{\mu_k{}'}\frac{\Omega}{\omega_{k'}}\left[\frac{1}{\Omega^2-(\frac{1}{2}\epsilon)^2}+\frac{1}{\Omega^2-(\frac{3}{2}\epsilon)^2}+\frac{1}{\Omega^2-(\frac{5}{2}\epsilon)^2}+\cdots\right], \tag{I.46}$$

where $\epsilon=\epsilon_k'$ and where $\Omega=\omega-\frac{1}{2}(\omega_k+\omega_{k+1})$ is the frequency measured relative to the midpoint of the interval which is bounded by two adjacent infinities of $f(\omega)$ and which contains the particular zero of $f(\omega)$ that is being studied. If we let ϵ_k gradually contract towards zero, we can ultimately replace the sum in (I.45) [but not in (I.46)] by an integral that can be written in the convenient form

$$\Delta=\mathcal{P}\int_0^\infty\frac{c_k^2}{\mu_k(\omega^2-\omega_k^2)}\rho_k\,d\omega_k, \tag{I.47}$$

where $\mathcal{P}$ denotes the principal part. The validity of the expression (I.47) for Δ is a consequence of the fact that the pole of the second term of (I.45) just cancels that of the first one, and the principal part of the integral associated with the second (Q) term is zero. (Strictly speaking this is true only if the lower limit of integration is $-\infty$, but the resulting error is inconsequential.) Were it not for the fact that c_k, μ_k, ρ_k are

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[23] Cf., for instance, M. Planck, *Vorlesungen Uber die Theorie der Warmestrahlung* (Barth, Leipzig, 1921), 4th ed., part IV, Chap. 1.

slowly varying functions of k, the entire expression (I.45) could also be set equal to zero. The displacement of the resonance maximum which will later turn out to be a consequence of the nonvanishing Δ is thus an expression of the nonuniformity of the perturbing spectrum.

Thanks to a mathematical formula[24] tailor-made for our purposes, the series in brackets in (I.46) can be summed exactly, and has the value

$$-(\pi/2\epsilon\Omega)\tan(\pi\Omega/\epsilon).$$

The expression (I.44) is consequently

$$f(\omega)=m(\omega_0^2-\omega^2)+\Delta-(c_{k'}^2\pi/2\mu_{k'}\omega_{k'}\epsilon)\tan(\pi\Omega/\epsilon). \tag{I.48}$$

In evaluating $df/d\omega$, we need only consider the term coming from the differentiation of the tangent, as this throws down a factor $1/\epsilon$, which is large compared to $1/\omega$. Hence

$$\left.\frac{df}{d\omega}\right|_{\omega=\omega_{k'}}=-\frac{c_{k'}^2\pi^2}{2\mu_{k'}\omega_{k'}\epsilon^2}\left[1+\tan^2\left(\frac{\pi\Omega}{\epsilon}\right)\right]. \tag{I.49}$$

Since (I.49) is to be evaluated at a root of (I.48) we see, using (I.43), that formula (I.42) becomes

$$\chi_\omega''=\frac{2\pi e^2\rho_{k'}(c_{k'}^2/\omega_{k'}\mu_k)}{4[m(\omega_0^2-\omega^2)+\Delta]^2+(c_{k'}^2\pi\rho_{k'}/\mu_{k'}\omega_{k'})^2}, \tag{I.50}$$

where $\rho_k'=1/\epsilon$ and k' is determined by $\omega_{k'}=\omega$. Equation (I.50) is also obtained in part II by a different method. The contrast between the two approaches yielding the same result is quite striking.

In conclusion we should mention that the model that we have used, in which the perturbing mechanism is an ensemble of harmonic oscillators, is somewhat specialized, and does not portray the most general stochastic or collision process. Since even after the coupling our system remained harmonic, any light scattered from incident monochromatic radiation should be coherent and have the same frequency as the latter. On the other hand, Holstein[25] and Towne[26] have shown that an oscillator excited by a monochromatic beam interrupted by strong collisions can reradiate part of the energy absorbed from the beam as light which is not monochromatic or coherent, and is centered around the resonance rather than the impressed frequency. To yield this effect, essentially a Raman process involving the states of the atomic + colliding system, something more general than a completely harmonic total system is required.

II. GREEN'S FUNCTION APPROACH

1. Preliminaries

In this and the following sections we attack the line-shape problem using powerful, but more formal, Green's function techniques. Seven of the remaining eight sections are devoted to the treatment of a two-level (spin-$\frac{1}{2}$) system interacting with a crystal lattice. In the final section we discuss the behavior of a harmonic oscillator which is also coupled to a lattice.

To a certain extent our treatment of the two-level system parallels the recent work of McCumber.[27] He discusses the influence of the spin–phonon coupling on the optical spectrum. There are, however, important differences between optical- and magnetic-resonance phenomena which are relevant to the line shape analysis. First, because of the enormous separation between optical levels, population effects arising from thermal excitation can usually be neglected. Second, there is no optical analog of the longitudinal susceptibility, where the absorption is measured with the alternating field parallel to the static field. Our analysis also overlaps somewhat with a study of the influence of the spin–phonon coupling on the magnetic-resonance spectrum that has been made by Aminov and Kochelaev.[28] They, however, were mainly interested in determining the magnitude of the shifts arising from the interaction.

Prior to introducing the Hamiltonian appropriate to the spin problem it will be convenient to rewrite (I.3) in terms of the Fourier transforms of the spin–spin correlation functions. The Fourier transform (or spectral intensity function) associated with $\langle S_zS_z\rangle$ is defined by

$$\langle S_z(t)\,S_z(t')\rangle=\int_{-\infty}^{\infty}J^{zz}(\omega)\exp[-i\omega(t-t')]\,d\omega. \tag{II.1}$$

By making use of (II.1) we can rewrite $\chi_{zz}''(\omega)$ in the following fashion (specializing to the magnetic dipole):

$$\chi_{zz}''(\omega)=(\pi g^2\beta^2/\hbar)\tanh(\hbar\omega/2kT)(J^{zz}(\omega)+J^{zz}(-\omega)). \tag{II.2}$$

In the case of the xx and yy components of χ'' we introduce the spectral functions associated with the operators $S_+=S_x+iS_y$ and $S_-=S_x-iS_y$ by means of

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[24] Knopp, *Unendliche Reihen* (Springer-Verlag, Berlin, 1922), p. 197; quoted by O. K. Rice in Phys. Rev. **33,** 755 (1929).

[25] T. Holstein, Phys. Rev. **72,** 1212 (1947), Appendix IA.

[26] D. Towne, Ph.D. thesis, Harvard, 1954 (unpublished).

[27] D. E. McCumber, J. Math. Phys. **5,** 222 (1964); **5,** 508 (1964).

[28] L. K. Aminov and B. I. Kochelaev, Fiz. Tverd. Tela **4,** 1604 (1962) [English transl.: Soviet Phys.—Solid State **4,** 1175 (1962)].

the equations

$$\langle S_-(t)S_+(t')\rangle$$
$$=\int_{-\infty}^{\infty} J^{-+}(\omega)\exp(\hbar\omega/kT)\exp[-i\omega(t-t')]\,d\omega, \tag{II.3}$$

$$\langle S_+(t')\,S_-(t)\rangle=\int_{-\infty}^{\infty} J^{-+}(\omega)\exp[-i\omega(t-t')]\,d\omega, \tag{II.4}$$

$$\langle S_+(t)\,S_+(t')\rangle=\int_{-\infty}^{\infty} J^{++}(\omega)\exp[-i\omega(t-t')]\,d\omega, \tag{II.5}$$

$$\langle S_-(t)\,S_-(t')\rangle=\int_{-\infty}^{\infty} J^{--}(\omega)\exp[-i\omega(t-t')]\,d\omega. \tag{II.6}$$

It should be noted that Eqs. (II.3) and (II.4) showing the interdependence of $\langle S_+S_-\rangle$ and $\langle S_-S_+\rangle$ follow from the definition of the correlation function and the cyclic properties of the trace.[29]

Upon inserting (II.3)–(II.6) into (I.3) we obtain the result

$$\chi''_{xx,yy}(\omega)=(\pi g^2\beta^2/4\hbar)\tanh(\hbar\omega/2kT)$$
$$\times\{[1+\exp(\hbar\omega/kT)]J^{-+}(\omega)$$
$$+[1+\exp(-\hbar\omega/kT)]J^{-+}(-\omega)\pm J^{++}(\omega)$$
$$\pm J^{++}(-\omega)\pm J^{--}(\omega)\pm J^{--}(-\omega)\}, \tag{II.7}$$

where the plus and minus signs refer to the xx and yy components, respectively. Equations (II.2) and (II.7) from the basis for our subsequent discussion. We emphasize that the expressions for χ''_{zz} and $\chi''_{xx,yy}$ are completely general. No assumptions have been made about the nature of the interaction of the spin with its environment.

2. Hamiltonian

We consider a system having spin $\frac{1}{2}$ that is coupled to the crystal lattice by terms that are linear in the lattice displacement. If we take the direction of the static magnetic field to define the z axis, then the Hamiltonian, in its general form, is written

$$\mathcal{H}=\hbar\omega_0S_z+\sum_{\mathbf{k}p}\hbar\omega_{\mathbf{k}p}a_{\mathbf{k}p}{}^+a_{\mathbf{k}p}+\sum_{\mathbf{k}p}(A_x(\mathbf{k}p)\,S_x$$
$$+A_y(\mathbf{k}p)\,S_y+A_z(\mathbf{k}p)\,S_z)(a_{\mathbf{k}p}{}^++a_{-\mathbf{k}p}). \tag{II.8}$$

Here $\hbar\omega_0(=g\beta H)$ is the splitting between the upper and lower spin levels, and $\hbar\omega_{\mathbf{k}p}$ is the energy of a phonon having wave vector $\mathbf{k}$ and polarization p. The $a_{\mathbf{k}p}$ and $a_{\mathbf{k}p}{}^+$ are phonon annihilation and creation operators with the commutation relations

$$[a_{\mathbf{k}p},a_{\mathbf{k}'p'}]=0;$$
$$[a_{\mathbf{k}p}{}^+,a_{\mathbf{k}'p'}{}^+]=0;$$
$$[a_{\mathbf{k}p},a_{\mathbf{k}'p'}{}^+]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{pp'}. \tag{II.9}$$

The $A_\alpha(\mathbf{k}p)$ are coupling constants which depend on the detailed properties of the magnetic ion and its crystalline environment.

Rather than work with the general Hamiltonian we will find it convenient to consider a simplified isotropic approximation to (II.8) which we write in the form

$$\mathcal{H}_{\text{iso}}=\hbar\omega_0S_z+\sum_{\mathbf{k}p}\hbar\omega_{\mathbf{k}}a_{\mathbf{k}p}{}^+a_{\mathbf{k}p}$$
$$+\sum_{\mathbf{k}p}A_{\mathbf{k}}\mathbf{S}\cdot\boldsymbol{\varepsilon}(\mathbf{k}p)\,(a_{\mathbf{k}p}{}^++a_{-\mathbf{k}p}), \tag{II.10}$$

where we assume $\omega_{\mathbf{k}}=\omega_{-\mathbf{k}}$ and $A_{\mathbf{k}}=A_{-\mathbf{k}}$. Here $\boldsymbol{\varepsilon}(\mathbf{k}p)$ is the polarization vector associated with the mode designated by $\mathbf{k}$ and p. Our reasons for choosing to work with the model interaction are twofold. First, the isotropic nature of the coupling makes possible a direct comparison of the effects of the spin–lattice interaction with the effects of analogous broadening mechanisms in liquids and gases. Second, the use of an interaction involving the scalar product of the polarization and spin vectors leads to a considerable simplification in the calculation of the spectral functions. Although there is an accompanying loss in generality, we will relate the results obtained with $\mathcal{H}_{\text{iso}}$ to what would have been obtained with a more general Hamiltonian in the situations which are of experimental interest.

3. Green's Function Formalism

Having specified the Hamiltonian we are left with the problem of calculating the correlation functions. A convenient way of doing this is to make use of the double-time thermodynamic Green's functions introduced by Zubarev.[29] We define the Green's function $\langle\langle A(t);B(t')\rangle\rangle_\pm$ associated with the operators A and B by means of equation

$$\langle\langle A(t);B(t')\rangle\rangle_\pm$$
$$=-i\theta(t-t')[\langle A(t)B(t')\rangle\pm\langle B(t')A(t)\rangle]. \tag{II.11}$$

Here $\theta(t-t')$ is the unit step function with the property

$$\theta(t-t')=1,\quad t>t';\qquad \theta(t-t')=0,\quad t<t'. \tag{II.12}$$

It is shown in Ref. 29 that $\langle\langle A(t);B(t')\rangle\rangle_\pm$ satisfies

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[29] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Uspekhi **3**, 320 (1960)].

the equation of motion

$$i\hbar(d/dt)\,\langle\langle A(t)\,;B(t')\rangle\rangle_{\pm}$$
$$=\hbar\delta(t-t')[\langle A(t)B(t)\pm B(t)A(t)\rangle]$$
$$+\langle\langle(A(t)\mathcal{H}(t)-\mathcal{H}(t)A(t));\quad B(t')\rangle\rangle_{\pm},\quad \text{(II.13)}$$

where $\mathcal{H}(t)$ is the Hamiltonian.

For the most part we will work with the Fourier transform of $\langle\langle A(t)\,;B(t')\rangle\rangle_{\pm}$ which we define by the integral

$$\langle\langle A\,;B\rangle\rangle_{\pm}(E)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left(\frac{iEt}{\hbar}\right)\langle\langle A(t)\,;B(0)\rangle\rangle_{\pm}\,dt. \quad \text{(II.14)}$$

The transform of (II.13) is then written

$$E\langle\langle A\,;B\rangle\rangle_{\pm}(E)=(1/2\pi)[\langle AB\pm BA\rangle]$$
$$+\langle\langle[A,\mathcal{H}];B\rangle\rangle_{\pm}(E).\quad \text{(II.13')}$$

In Ref. 29 it is demonstrated that the correlation functions $\langle A(t)B(t')\rangle$ and $\langle B(t')A(t)\rangle$ can be expressed in the following form

$$\langle A(t)B(t')\rangle=\int_{-\infty}^{\infty}\exp\left(\frac{\hbar\omega}{kT}\right)J_{\pm}{}^{AB}(\omega)\exp[-i\omega(t-t')]\,d\omega, \quad \text{(II.15)}$$

$$\langle B(t')A(t)\rangle=\int_{-\infty}^{\infty}J_{\pm}{}^{AB}(\omega)\exp[-i\omega(t-t')]\,d\omega, \quad \text{(II.16)}$$

where the spectral function $J_{\pm}{}^{AB}(\omega)$ is defined in terms of the limiting values of $\langle\langle A\,;B\rangle\rangle_{\pm}(E)$ as E approaches the real axis. That is, we have

$$J_{\pm}{}^{AB}(\omega)=\frac{i\hbar}{\exp(\hbar\omega/kT)\pm1}$$
$$[\langle\langle A\,;B\rangle\rangle_{\pm}(\hbar\omega+i\epsilon)-\langle\langle A\,;B\rangle\rangle_{\pm}(\hbar\omega-i\epsilon)], \quad \text{(II.17)}$$

where the limit $\epsilon\rightarrow0+$ is understood.

In the spin-$\frac{1}{2}$ problem we are led to consider the Green's functions $\langle\langle S_-;\ S_+\rangle\rangle_+$ and $\langle\langle S_z;\ S_z\rangle\rangle_+$. In the subsequent sections we will solve equations for these functions. With the aid of (II.17) we will obtain expressions for the spectral functions which appear in the formal definitions of the susceptibility. In order to obtain closed expressions for the Green's functions it is necessary to employ a simple decoupling approximation similar to that used in Ref. 29. The details and significance of this approximation are discussed at appropriate places in the calculation.

4. Calculation of χ_{zz}''

From the analysis given in the preceding sections it is evident that the Fourier transform of the Green's function $\langle\langle S_z(t);\ S_z(t')\rangle\rangle_+$ can be directly related to the longitudinal susceptibility. In this section we will outline the calculation of $\langle\langle S_z;\ S_z\rangle\rangle_+$. The application of (II.13') together with the Hamiltonian (II.10) leads to the equation

$$E\langle\langle S_z;\ S_z\rangle\rangle_+(E)=1/4\pi+\tfrac{1}{2}\sum_{\mathbf{k}p}A_{\mathbf{k}}(\epsilon_x(\mathbf{k}p)-i\epsilon_y(\mathbf{k}p))(\langle\langle S_+a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+(E)+\langle\langle S_+a_{-\mathbf{k}p};\ S_z\rangle\rangle_+(E))$$
$$-\tfrac{1}{2}\sum_{\mathbf{k}p}A_{\mathbf{k}}(\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p))(\langle\langle S_-a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+(E)+\langle\langle S_-a_{-\mathbf{k}p};\ S_z\rangle\rangle_+(E)). \quad \text{(II.18)}$$

It is evident that the equation for $\langle\langle S_z;\ S_z\rangle\rangle_+$ involves the Green's functions $\langle\langle S_{\pm}a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+$ and $\langle\langle S_{\pm}a_{-\mathbf{k}p};\ S_z\rangle\rangle_+$. Following Zubarev[29] we are led to consider the equations of motion for these higher-order functions. We will discuss in detail only $\langle\langle S_+a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+$ since a nearly identical analysis can be made for the other functions. The equation of motion for $\langle\langle S_+a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+$ is written

$$(E+\hbar\omega_0+\hbar\omega_{\mathbf{k}})\,\langle\langle S_+a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+(E)=\sum_{\mathbf{k}'p'}A_{\mathbf{k}'}(\epsilon_x(\mathbf{k}'p')+i\epsilon_y(\mathbf{k}'p'))\,\langle\langle S_z(a_{\mathbf{k}'p'}{}^++a_{-\mathbf{k}'p'})\,a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+(E)$$
$$-\sum_{\mathbf{k}'p'}A_{\mathbf{k}'}\epsilon_z(\mathbf{k}'p')\,\langle\langle S_+(a_{\mathbf{k}'p'}{}^++a_{-\mathbf{k}'p'})\,a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+(E)-\tfrac{1}{2}A_{\mathbf{k}}(\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p))$$
$$\times(\langle\langle S_z;\ S_z\rangle\rangle_+(E)+\tfrac{1}{2}\langle\langle 1;\ S_z\rangle\rangle_+(E))+\tfrac{1}{2}A_{\mathbf{k}}\epsilon_z(\mathbf{k}p)\,\langle\langle S_+;\ S_z\rangle\rangle_+(E). \quad \text{(II.19)}$$

We see that the equation for $\langle\langle S_+a_{\mathbf{k}p}{}^+;\ S_z\rangle\rangle_+$ has in it still higher order Green's functions. It follows that an exact expression for $\langle\langle S_z;\ S_z\rangle\rangle_+$ can only be obtained by solving an infinite set of coupled equations. In order to reduce the problem to manageable size we introduce an approximate decoupling scheme. We replace the products of phonon operators appearing on the right-hand side of (II.19) by their thermal averages taken in the absence of a spin–phonon interaction

$$(a_{\mathbf{k}'p'}{}^+(t)+a_{-\mathbf{k}'p'}(t))a_{\mathbf{k}p}{}^+(t)\rightarrow\langle(a_{\mathbf{k}'p'}{}^++a_{-\mathbf{k}'p'})\,a_{\mathbf{k}p}{}^+\rangle=\delta_{\mathbf{k}-\mathbf{k}'}\delta_{pp'}(n_{\mathbf{k}}+1). \quad \text{(II.20)}$$

Here $n_{\mathbf{k}}[=[\exp(\hbar\omega_k/kT)-1]^{-1}]$ is the Bose–Einstein occupation number. The significance of the approximation will become more clear in the subsequent discussion. At present it suffices to say that the approximation takes into account only one-phonon processes in which a single lattice mode is created or destroyed. Making use of (II.20) Eq. (II.19) is written

$$\begin{aligned}(E+\hbar\omega_0+\hbar\omega_{\mathbf{k}})\langle\langle S_+a_{\mathbf{k}p}{}^+;\,S_z\rangle\rangle_+(E)&=\tfrac{1}{2}A_{\mathbf{k}}(\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p))(2n_{\mathbf{k}}+1)\langle\langle S_z;\,S_z\rangle\rangle_+(E)\\&\quad-\tfrac{1}{4}A_{\mathbf{k}}(\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p))\langle\langle 1;\,S_z\rangle\rangle_+(E)-\tfrac{1}{2}A_{\mathbf{k}}\epsilon_z(\mathbf{k}p)(2n_{\mathbf{k}}+1)\langle\langle S_+;\,S_z\rangle\rangle_+(E).\qquad\text{(II.19}'\text{)}\end{aligned}$$

Analogous equations for the functions $\langle\langle S_-a_{\mathbf{k}p}{}^+;\,S_z\rangle\rangle_+$ and $\langle\langle S_\pm a_{-\mathbf{k}p};\,S_z\rangle\rangle_+$ can also be derived in a straightforward fashion with the help of the decoupling approximation. Insertion of the expressions thus obtained into (II.18) leads to an inhomogeneous equation for $\langle\langle S_z;\,S_z\rangle\rangle_+$. The algebra is especially simplified when the orthogonality properties of the polarization vectors are taken into account

$$\sum_p\epsilon_\alpha(\mathbf{k}p)\epsilon_\beta(\mathbf{k}p)=\delta_{\alpha\beta}.\qquad\text{(II.21)}$$

For this reason the terms involving $\epsilon_z(\mathbf{k}p)$ in the equations for the higher order functions do not appear in the equation for $\langle\langle S_z;\,S_z\rangle\rangle_+$. This simplification is a particular feature of the isotropic interaction and the assumption that the phonon energies are independent of polarization. The resulting expression for the longitudinal Green's function is written

$$\begin{aligned}E\langle\langle S_z;\,S_z\rangle\rangle_+(E)&=1/4\pi+\tfrac{1}{2}\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2(2n_{\mathbf{k}}+1)\\&\quad\times[(E+\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}+(E+\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}+(E-\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}+(E-\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}]\langle\langle S_z;\,S_z\rangle\rangle_+(E)\\&\quad+\tfrac{1}{4}\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2[(E-\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}+(E+\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}-(E+\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}-(E-\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}]\langle\langle 1;\,S_z\rangle\rangle_+(E).\qquad\text{(II.22)}\end{aligned}$$

The function $\langle\langle 1;\,S_z\rangle\rangle_+$ can be evaluated from its equation of motion

$$\langle\langle 1;\,S_z\rangle\rangle_+(E)=\langle S_z\rangle/\pi E=-(1/2\pi E)\tanh(\hbar\omega_0/2kT).\qquad\text{(II.23)}$$

Here we have made the approximation of replacing $\langle S_z\rangle$ by its value in the absence of a spin–phonon coupling, $-\tfrac{1}{2}\tanh(\hbar\omega_0/2kT)$.

The spectral function $J^{zz}(\omega)$ is obtained from Eqs. (II.22) and (II.23) and the defining equation, (II.17). Insertion of the expression for $J^{zz}(\omega)$ into (II.2) leads to an equation for $\chi_{zz}''(\omega)$. Omitting a number of intermediate steps we arrive at the result

$$\begin{aligned}\chi_{zz}''(\omega)&=\frac{1}{2\hbar}g^2\beta^2\tanh\frac{\hbar\omega}{2kT}\\&\quad\times\frac{[(\Gamma(\omega+\omega_0)+\Gamma(\omega-\omega_0))(1-[\Lambda(\omega)/\omega]\tanh(\hbar\omega_0/2kT))-[\Psi(\omega)/\omega]\tanh(\hbar\omega_0/2kT)(\omega-\mathrm{K}(\omega-\omega_0)-\mathrm{K}(\omega+\omega_0))]}{(\omega-\mathrm{K}(\omega-\omega_0)-\mathrm{K}(\omega+\omega_0))^2+(\Gamma(\omega-\omega_0)+\Gamma(\omega+\omega_0))^2},\end{aligned}\qquad\text{(II.24)}$$

where[30]

$$\Gamma(\omega)=(\pi/2\hbar)\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2\coth(\hbar\omega_{\mathbf{k}}/2kT)(\delta(\hbar\omega_{\mathbf{k}}+\hbar\omega)+\delta(\hbar\omega_{\mathbf{k}}-\hbar\omega)),\qquad\text{(II.25)}$$

$$\mathrm{K}(\omega)=(\mathcal{P}/2\hbar)\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2\coth(\hbar\omega_{\mathbf{k}}/2kT)[(\hbar\omega_{\mathbf{k}}+\hbar\omega)^{-1}-(\hbar\omega_{\mathbf{k}}-\hbar\omega)^{-1}],\qquad\text{(II.26)}$$

since

$$2n_{\mathbf{k}}+1=\coth(\hbar\omega_{\mathbf{k}}/2kT).\qquad\text{(II.27)}$$

Also, we have

$$\Psi(\omega)=(\pi/2\hbar)\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2(\delta(\hbar\omega-\hbar\omega_{\mathbf{k}}+\hbar\omega_0)+\delta(\hbar\omega+\hbar\omega_{\mathbf{k}}-\hbar\omega_0)-\delta(\hbar\omega-\hbar\omega_{\mathbf{k}}-\hbar\omega_0)-\delta(\hbar\omega+\hbar\omega_{\mathbf{k}}+\hbar\omega_0)),\qquad\text{(II.28)}$$

$$\Lambda(\omega)=(\mathcal{P}/2\hbar)\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2[(\hbar\omega-\hbar\omega_{\mathbf{k}}+\hbar\omega_0)^{-1}+(\hbar\omega+\hbar\omega_{\mathbf{k}}-\hbar\omega_0)^{-1}-(\hbar\omega-\hbar\omega_{\mathbf{k}}-\hbar\omega_0)^{-1}-(\hbar\omega+\hbar\omega_{\mathbf{k}}+\hbar\omega_0)^{-1}].\qquad\text{(II.29)}$$

We defer discussion of these rather formidable expressions to the following section.

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[30] In obtaining (II.25)–(II.29) we have made use of the symbolic identity $(\omega+i\epsilon)^{-1}=\mathcal{P}/\omega-i\pi\delta(\omega)$, where $\mathcal{P}$ denotes the principal part [Ref. 29, Eq. (3.29)].

5. Discussion of the Longitudinal Susceptibility

In typical experiments measuring $\chi_{zz}''(\omega)$ the frequency of the alternating field is much less than the precession frequency. Thus in evaluating (II.24) we are justified in neglecting ω in comparison with ω_0. In which case we have

$$\Gamma(\omega_0)+\Gamma(-\omega_0)$$
$$=(\pi/\hbar)\sum_{\mathrm{k}}A_{\mathrm{k}}^2\delta(\hbar\omega_{\mathrm{k}}-\hbar\omega_0)\ \coth\ (\hbar\omega_{\mathrm{k}}/2kT)=\tau_1^{-1}, \tag{II.30}$$

$$\mathrm{K}(\omega_0)+\mathrm{K}(-\omega_0)=0, \tag{II.31}$$

$$\Psi(0)=(\pi/\hbar)\sum_{\mathrm{k}}A_{\mathrm{k}}^2\delta(\hbar\omega_{\mathrm{k}}-\hbar\omega_0)=\tau_1^{-1}\tanh\ (\hbar\omega_0/2kT), \tag{II.32}$$

$$\Lambda(0)=0, \tag{II.33}$$

where τ_1 is the spin–lattice relaxation time for the direct process.[31] With the help of (II.30)–(II.33) we obtain the following equation for $\chi_{zz}''(\omega)$ $(\omega\ll\omega_0)$

$$\chi_{zz}''(\omega)=\frac{g^2\beta^2}{2\hbar}\tanh\frac{\hbar\omega}{2kT}\frac{\tau_1}{1+(\omega\tau_1)^2}\operatorname{sech}^2\frac{\hbar\omega_0}{2kT}, \tag{II.34}$$

which is identical to Eq. (I.11). Although our expression for $\chi_{zz}''(\omega)$ was obtained from a particularly simple Hamiltonian, a similar but more lengthy analysis based on (II.8) shows that (II.34) is still valid in the limit $\omega\ll\omega_0$ provided the value of τ_1 appropriate to the more general interaction is used.

Examination of the steps in the calculation of $\chi_{zz}''(\omega)$ indicates that the terms in the interaction which couple the z component of the spin to the lattice make no contribution to the susceptibility. The linewidth arises solely from the phase-interrupting (S_x and S_y) terms. This last result is rigorously true for the model Hamiltonian. In the case of a more general Hamiltonian it is valid to the extent to which Green's functions of the form $\langle\langle S_\pm;\ S_z\rangle\rangle_+$ can be neglected in the equation for $\langle\langle S_z;\ S_z\rangle\rangle_+$. A rough calculation shows that $\langle\langle S_+;\ S_z\rangle\rangle_+\approx(1/\omega_0\tau_1)\langle\langle S_z;\ S_z\rangle\rangle_+$ in the region of interest. The dropping of these terms is justified as long as $\omega_0\tau_1\gg1$, a condition which is nearly always satisfied.

The presence of the relaxation time for the direct process in the expression for $\chi_{zz}''(\omega)$ reflects the fact that the decoupling approximation takes into account only one-phonon transitions. Transitions involving multiple phonon emission are neglected. General phase space considerations show that these higher order effects are negligible in comparison with the direct process as long as there are lattice modes with energies comparable to $\hbar\omega_0$.

6. Calculation of the Transverse Susceptibility

The spectral functions for the transverse susceptibilities are obtained from Green's functions associated with the operators S_+ and S_-. From the symmetry of the model Hamiltonian it is evident that $\chi_{xx}''=\chi_{yy}''$ so that we need solve only for $\langle\langle S_-;\ S_+\rangle\rangle_+$. The terms in (II.7) involving $J^{--}(\omega)$ and $J^{++}(\omega)$ make no contribution as long as the two transverse susceptibilities are equal. The equation of motion for $\langle\langle S_-;\ S_+\rangle\rangle_+$ is written

$$(E-\hbar\omega_0)\langle\langle S_-;\ S_+\rangle\rangle_+(E)=1/2\pi-\sum_{\mathbf{k}p}A_{\mathrm{k}}\big(\epsilon_x(\mathbf{k}p)-i\epsilon_y(\mathbf{k}p)\big)\big(\langle\langle S_za_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+(E)+\langle\langle S_za_{-\mathbf{k}p};\ S_+\rangle\rangle_+(E)\big)$$
$$+\sum_{\mathbf{k}p}A_{\mathrm{k}}\epsilon_z(\mathbf{k}p)\big(\langle\langle S_-a_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+(E)+\langle\langle S_-a_{-\mathbf{k}p};\ S_+\rangle\rangle_+(E)\big). \tag{II.35}$$

As before we are faced with the problem of calculating higher order Green's functions involving products of spin and lattice operators. In order to do this we make use of the decoupling approximation introduced previously. Because of the orthogonality of the polarization vectors we need keep only terms having the factor $\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p)$ in the equations for $\langle\langle S_za_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+$ and $\langle\langle S_za_{-\mathbf{k}p};\ S_+\rangle\rangle_+$. By the same token we keep only terms proportional to $\epsilon_z(\mathbf{k}p)$ in the equations for $\langle\langle S_-a_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+$ and $\langle\langle S_-a_{-\mathbf{k}p};\ S_+\rangle\rangle_+$. The results of the calculation are as follows

$$(E+\hbar\omega_{\mathrm{k}})\langle\langle S_za_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+(E)=-\tfrac{1}{4}A_{\mathrm{k}}\big(\epsilon_x(\mathbf{k}p)+i\epsilon_y(\mathbf{k}p)\big)(2n_{\mathrm{k}}+1)\langle\langle S_-;\ S_+\rangle\rangle_+(E),$$
$$=(E-\hbar\omega_{\mathrm{k}})\langle\langle S_za_{-\mathbf{k}p};\ S_+\rangle\rangle_+(E), \tag{II.36}$$

$$(E-\hbar\omega_0+\hbar\omega_{\mathrm{k}})\langle\langle S_-a_{\mathbf{k}p}{}^+;\ S_+\rangle\rangle_+(E)=(1/2\pi)\langle a_{\mathbf{k}p}{}^+\rangle+\tfrac{1}{2}A_{\mathrm{k}}\epsilon_z(\mathbf{k}p)(2n_{\mathrm{k}}+1)\langle\langle S_-;\ S_+\rangle\rangle_+(E), \tag{II.37}$$

$$(E-\hbar\omega_0-\hbar\omega_{\mathrm{k}})\langle\langle S_-a_{-\mathbf{k}p};\ S_+\rangle\rangle_+(E)=(1/2\pi)\langle a_{-\mathbf{k}p}\rangle+\tfrac{1}{2}A_{\mathrm{k}}\epsilon_z(\mathbf{k}p)(2n_{\mathrm{k}}+1)\langle\langle S_-;\ S_+\rangle\rangle_+(E). \tag{II.38}$$

The functions $\langle a_{\mathbf{k}p}{}^+\rangle$ and $\langle a_{-\mathbf{k}p}\rangle$ can be calculated by making use of the time-independence of the expectation value[29]

$$i\hbar(d/dt)\langle\cdots\rangle=0=\langle[\cdots,\ \mathcal{H}]\rangle. \tag{II.39}$$

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[31] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

We have

$$i\hbar(d/dt)\,\langle a_{\mathbf{k}p}{}^{+}\rangle=0=-\hbar\omega_{\mathbf{k}}\,\langle a_{\mathbf{k}p}{}^{+}\rangle+\tfrac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,\epsilon_z(\mathbf{k}p)\,A_{\mathbf{k}}, \tag{II.40}$$

$$i\hbar(d/dt)\,\langle a_{-\mathbf{k}p}\rangle=0=\hbar\omega_{\mathbf{k}}\,\langle a_{-\mathbf{k}p}\rangle-\tfrac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,\epsilon_z(\mathbf{k}p)\,A_{\mathbf{k}}, \tag{II.41}$$

where we have kept only terms proportional to $\epsilon_z(\mathbf{k}p)$.

With the help of (II.36)–(II.41) we obtain the following equation for $\langle\langle S_-;\,S_+\rangle\rangle_+$:

$$\begin{aligned}(E-\hbar\omega_0)\,\langle\langle S_-;\,S_+\rangle\rangle_+(E)&=(2\pi)^{-1}+\tfrac{1}{2}\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2(2n_{\mathbf{k}}+1)\\ &\quad\times[(E-\hbar\omega_{\mathbf{k}})^{-1}+(E+\hbar\omega_{\mathbf{k}})^{-1}+(E-\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}+(E-\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}]\,\langle\langle S_-;\,S_+\rangle\rangle_+(E)\\ &\quad+\frac{\tanh\,(\hbar\omega_0/2kT)}{4\pi}\sum_{\mathbf{k}}(A_{\mathbf{k}}{}^2/\hbar\omega_{\mathbf{k}})[(E-\hbar\omega_0-\hbar\omega_{\mathbf{k}})^{-1}+(E-\hbar\omega_0+\hbar\omega_{\mathbf{k}})^{-1}].\end{aligned} \tag{II.42}$$

From (II.42) we obtain the spectral function $J^{-+}(\omega)$ by means of the limiting procedure described in Sec. II.3. Inserting the expression thus obtained into (II.7) leads to the following equation for the transverse susceptibility

$$\begin{aligned}\chi_{xx}''(\omega)=\chi_{yy}''(\omega)=\frac{g^2\beta^2}{4\hbar}\tanh\frac{\hbar\omega}{2kT}\Bigg[&\frac{(\Gamma(\omega)+\Gamma(\omega-\omega_0))(1+\frac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,\Theta(\omega-\omega_0))}{(\omega-\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega-\omega_0))^2+\Gamma((\omega)+\Gamma(\omega-\omega_0))^2}\\ &+\frac{\frac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,(\omega-\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega-\omega_0))\Phi(\omega-\omega_0)}{(\omega-\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega-\omega_0))^2+(\Gamma(\omega)+\Gamma(\omega-\omega_0))^2}\\ &+\frac{(\Gamma(\omega)+\Gamma(\omega+\omega_0))(1-\frac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,\Theta(\omega+\omega_0))}{(\omega+\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega+\omega_0))^2+(\Gamma(\omega)+\Gamma(\omega+\omega_0))^2}\\ &-\frac{\frac{1}{2}\tanh\,(\hbar\omega_0/2kT)\,(\omega+\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega+\omega_0))\Phi(\omega+\omega_0)}{(\omega+\omega_0-\mathrm{K}(\omega)-\mathrm{K}(\omega+\omega_0))^2+(\Gamma(\omega)+\Gamma(\omega+\omega_0))^2}\Bigg],\end{aligned} \tag{II.43}$$

where $\Gamma(\omega)$ and $\mathrm{K}(\omega)$ are defined by Eqs. (II.25) and (II.26), respectively. The functions $\Theta(\omega)$ and $\Phi(\omega)$ have as their defining equations

$$\Theta(\omega)=(\mathcal{P}/\hbar)\sum_{\mathbf{k}}(A_{\mathbf{k}}{}^2/\hbar\omega_{\mathbf{k}})[(\hbar\omega+\hbar\omega_{\mathbf{k}})^{-1}+(\hbar\omega-\hbar\omega_{\mathbf{k}})^{-1}], \tag{II.44}$$

$$\Phi(\omega)=(\pi/\hbar)\sum_{\mathbf{k}}(A_{\mathbf{k}}{}^2/\hbar\omega_{\mathbf{k}})[\delta(\hbar\omega+\hbar\omega_{\mathbf{k}})+\delta(\hbar\omega-\hbar\omega_{\mathbf{k}})]. \tag{II.45}$$

We postpone discussion of (II.43) until the following section.

7. Discussion of the Transverse Susceptibility

In typical paramagnetic resonance experiments only the values of $\chi_{xx}''(\omega)$ in the neighborhood of $\omega=\omega_0$ are of interest. In this region the equation for χ_{xx}'' simplifies considerably. Because of the vanishing volume of phase space accessible to phonons of zero energy we have

$$\Gamma(0)=(\pi/\hbar)\sum_{\mathbf{k}}A_{\mathbf{k}}{}^2\delta(\hbar\omega_{\mathbf{k}})\coth\,(\hbar\omega_{\mathbf{k}}/2kT)=0, \tag{II.46}$$

$$\Phi(0)=(2\pi/\hbar)\sum(A_{\mathbf{k}}{}^2/\hbar\omega_{\mathbf{k}})\,\delta(\hbar\omega_{\mathbf{k}})=0, \tag{II.47}$$

as well as

$$\Theta(0)=\mathrm{K}(0)=0. \tag{II.48}$$

Neglecting the second-order shift, $\mathrm{K}(\omega_0)$, in comparison with ω_0 we obtain the result ($\omega\approx\omega_0$)

$$\chi_{xx}''(\omega)=\frac{g^2\beta^2}{4\hbar}\tanh\frac{\hbar\omega}{2kT}\left(\frac{1/2\tau_1}{(\omega-\omega_0)^2+(1/2\tau_1)^2}\right). \tag{II.49}$$

We note that the susceptibility has a Lorentzian profile with a width $1/2\tau_1$. As was pointed out in part I, this width reflects the absence of a contribution from the frequency modulation terms in the Hamiltonian. Indeed such terms are represented in the factor $\Gamma(\omega-\omega_0)$ in (II.43) which vanishes at resonance in virtue of (II.46). [In the stochastic case, where the spectrum is flat, one has $\Gamma(\omega)=\Gamma(\omega-\omega_0)$ and $1/\tau_1$ appears in place of $1/2\tau_1$ in (II.49) and the transverse and longitudinal relaxation times become equal, in agreement with Sec. I.6, where the situation is discussed more fully.] Our expression for $\chi_{xx}''(\omega)$ in the vicinity of the resonance is easily modified to include the effects of an anisotropic interaction. As in the case of χ_{zz}'' it is only necessary to replace the expression for τ_1 by the corresponding relaxation time calculated from the more general Hamiltonian.

An interesting limiting case of (II.43) is obtained when we take the doublet splitting to be much greater than the maximum phonon energy. Since there are no phonons "on speaking terms" with the spins we have $\Gamma(\omega_0)=0$. The resulting expression for the susceptibility has the approximate form

$$\chi_{xx}''(\omega)\approx\frac{g^2\beta^2}{4\hbar}\tanh\frac{\hbar\omega}{2kT}\,\frac{\Gamma(x)+\frac{1}{2}x\tanh(\hbar\omega_0/2kT)\Phi(x)}{x^2}$$

$$=\frac{g^2\beta^2}{4\hbar x^2}\tanh\frac{\hbar\omega}{2kT}$$

$$\times\left\{\frac{\pi}{\hbar}\sum_{\mathrm{k}}A_{\mathrm{k}}^2\left[(n_{\mathrm{k}}+\tfrac{1}{2})+\tfrac{1}{2}\tanh\left(\frac{\hbar\omega_0}{2kT}\right)\right]\delta(\hbar\omega_{\mathrm{k}}-\hbar x)\right.$$

$$\left.+\frac{\pi}{\hbar}\sum_{\mathrm{k}}A_{\mathrm{k}}^2\left[(n_{\mathrm{k}}+\tfrac{1}{2})-\tfrac{1}{2}\tanh\left(\frac{\hbar\omega_0}{2kT}\right)\right]\delta(\hbar\omega_k+\hbar x)\right\},\tag{II.50}$$

where $x=\omega-\omega_0$. The terms in the numerator of (II.50) arise from the FM part of the interaction. They characterize vibrational sidebands associated with the simultaneous creation or destruction of phonon–photon pairs. In the zero-temperature limit $n_{\mathrm{k}}=0$ and $\tanh(\hbar\omega_0/2kT)=1$ so that χ_{xx}'' differs from zero only for $\omega>\omega_0$. These sidebands have been extensively studied in recent years in connection with the optical spectra of magnetic ions imbedded in insulating crystals.[32]

A check on the consistency of our analysis can be made by setting ω_0 equal to zero. We then find

$$\chi_{xx}''(\omega)=\frac{g^2\beta^2}{2\hbar}\tanh\frac{\hbar\omega}{2kT}\,\frac{2\Gamma(\omega)}{(\omega-2\mathrm{K}(\omega))^2+(2\Gamma(\omega))^2},\tag{II.51}$$

$$=\chi_{zz}''(\omega),$$

as can be seen from (II.24). The equality of χ_{xx}'' and χ_{zz}'' in the limit of zero field is to be expected in view of the isotropy of the model interaction.

Finally we would like to point out that although we have explicitly considered a system having $S=\frac{1}{2}$ the Green's function techniques can be applied equally well to a system having arbitrary spin. However for $S>\frac{1}{2}$ the analysis becomes complicated. One encounters Green's functions of the form $\langle\langle S_\alpha S_\beta;\, S_\gamma\rangle\rangle_+$ which do not appear in the spin $\frac{1}{2}$ problem. The simplification for $S=\frac{1}{2}$ results from there being only three linearly independent spin operators. Any product $S_\alpha S_\beta S_\gamma\cdots$ can be expressed in terms of the operators S_x, S_y, S_z and the unit operator.

8. Harmonic Oscillator

In this section we use the Green's function formalism to calculate the susceptibility of a harmonic oscillator coupled to the lattice by a term linear in the lattice displacement. We take as the Hamiltonian [cf. (I.32)]

$$\mathcal{H}=\tfrac{1}{2}m[(P_x/m)^2+\omega_0^2X^2]+\sum_k\tfrac{1}{2}\mu_k[(P_k/\mu_k)^2+\omega_k^2x_k^2]$$

$$+X\sum_k c_kx_k.\tag{II.52}$$

The imaginary part of the susceptibility, $\chi''(\omega)$, can be written in terms of the Fourier transform of the electric dipole-moment correlation function

$$\chi=\frac{e^2}{2\hbar}\tanh\frac{\hbar\omega}{2kT}\int_{-\infty}^{\infty}\cos\omega t[\langle X(t)X(0)+X(0)X(t)\rangle]\,dt.\tag{II.53}$$

We introduce the spectral function $J_{xx}(\omega)$ through the equation

$$\langle X(t)X(t')\rangle=\int_{-\infty}^{\infty}J_{xx}(\omega)\exp[-i\omega(t-t')]\,d\omega,\tag{II.54}$$

so that $\chi''(\omega)$ is expressed as

$$\chi''(\omega)=(\pi e^2/\hbar)\tanh(\hbar\omega/2kT)\,(J_{xx}(\omega)+J_{xx}(-\omega)).\tag{II.55}$$

The spectral function can be obtained from the Green's function $\langle\langle X(t);\, X(0)\rangle\rangle_-$. By making use of the commutation relations $[X,P_x]=i\hbar$, $[x_k,P_{k'}]=i\hbar\delta_{kk'}$ we find the following equations for $\langle\langle X;\, X\rangle\rangle_-$.

$$-(d^2/dt^2)\langle\langle X(t);\, X(0)\rangle\rangle_-=$$

$$[\hbar\delta(t)/m]+\omega_0^2\langle\langle X(t);\, X(0)\rangle\rangle_-$$

$$+m^{-1}\sum_k c_k\langle\langle x_k(t);\, X(0)\rangle\rangle_-,\tag{II.56}$$

$$-(d^2/dt^2)\langle\langle x_k(t);\, X(0)\rangle\rangle_-=\omega_k^2\langle\langle x_k(t);\, X(0)\rangle\rangle_-$$

$$+c_k\langle\langle X(t);\, X(0)\rangle\rangle_-/\mu_k.\tag{II.57}$$

The equations are readily solved without approximation for the transformed functions $\langle\langle X;\, X\rangle\rangle_-(E)$ and $\langle\langle x_k;\, X\rangle\rangle_-(E)$. In particular we have

$$\langle\langle X;\, X\rangle\rangle_-(E)$$

$$=\frac{(1/2\pi m)}{(E/\hbar)^2-\omega_0^2-\sum(c_k^2/m\mu_k)\,((E/\hbar)^2-\omega_k^2)^{-1}}.\tag{II.58}$$

The spectral function can be obtained from (II.58) with the help of (II.17). Omitting several intermediate steps we arrive at the result

$$\chi''(\omega)=\frac{e^2}{m}\,\frac{\operatorname{Im}G(\omega)}{[\omega_0^2-\omega^2+\operatorname{Re}G(\omega)]^2+[\operatorname{Im}G(\omega)]^2},\tag{II.59}$$

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[32] For example, G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).

where

$$\operatorname{Re} G(\omega)=(\mathcal{P}/m\mu_k)\sum_k c_k^2(\omega^2-\omega_k^2)^{-1},$$

$$=\frac{\mathcal{P}}{m\mu_k}\int_0^\infty \rho_k c_k^2(\omega^2-\omega_k^2)^{-1}\,d\omega_k=\frac{\Delta}{m}, \qquad \text{(II.60)}$$

with the symbols ρ_k and Δ having the same meaning as in Sec. I.6. Also, we have

$$\operatorname{Im} G(\omega)=(\pi/m\mu_k)\sum_k (c_k^2/2\omega_k)[\delta(\omega-\omega_k)-\delta(\omega+\omega_k)],$$

$$=(\pi/m\mu_{k'})(c_{k'}^2\rho_{k'}/2\omega_{k'}), \qquad \text{(II.61)}$$

where k' is fixed by the equation $\omega_{k'}=\omega$. If we rewrite (II.59) using (II.60) and (II.61) we obtain the expression

$$\chi''(\omega)=\frac{e^2(\pi c_{k'}^2\rho_{k'})/2\omega_{k'}\mu_{k'}}{(m(\omega_0^2-\omega^2)+\Delta)^2+(\pi c_{k'}^2\rho_{k'}/2\omega_{k'}\mu_{k'})^2}, \qquad \text{(II.62)}$$

in agreement with (I.50).

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APPENDIX A: RELATIONS BETWEEN THE CORRELATION FUNCTION AND THE SUSCEPTIBILITY

The change in the component of moment P_α along the αth direction, which arises from the interaction $-P_\alpha F_\alpha \exp(i\omega t)$, is given by

$$\delta P_\alpha(t)=(i/\hbar)\times\int_{-\infty}^{t}\langle P_\alpha(t)P_\alpha(t')-P_\alpha(t')P_\alpha(t)\rangle F_\alpha \exp(i\omega t')\,dt'. \qquad \text{(A1)}$$

This formula can be established as follows by a method slightly different from that of Kubo,[5] or of Kadanoff and Martin,[33] whose procedure we follow in the main in this appendix. Let us imagine the field F_α to be first applied at a large negative time $-t_A$. Since there is no outstanding polarization prior to the application of the field, one has

$$\delta P_\alpha(t)=\int_{-t_B}\operatorname{Tr}\left[\rho\frac{dP_\alpha(t'')}{dt''}\right]dt'',$$

where $-t_B$ is some time prior to $-t_A$, and the Boltzmann factor or density matrix

$$\rho=\exp[-\mathcal{H}_0/kT/\operatorname{Tr}(\exp[-\mathcal{H}_0/kT])$$

is to be evaluated at $t=-t_A$ and so involves only the Hamiltonian function $\mathcal{H}$ exclusive of the field. The equation of motion for P_α is

$$dP_\alpha/dt=i\hbar^{-1}[\mathcal{H}P_\alpha-P_\alpha\mathcal{H}]$$

inasmuch as P_α commutes with the part $-P_\alpha F_\alpha \exp(i\omega t)$ of the Hamiltonian that arises from the applied field. From the fact that the change in inner energy just equals the work done by the applied field, we have

$$d\mathcal{H}/dt=(dP_\alpha/dt)F_\alpha\exp(i\omega t).$$

Since $\delta P_\alpha=0$ for $t<-t_A$, we can write

$$\delta P_\alpha=i\hbar^{-1}\int_{-t_B}^{t}dt''\int_{-t_A}^{t''}\Theta(t',t'')F_\alpha\exp(i\omega t')\,dt', \qquad \text{(A2)}$$

where

$$\Theta(t',t'')=\operatorname{Tr}\rho\left[\frac{dP_\alpha(t')}{dt'}P_\alpha(t'')-P_\alpha(t'')\frac{dP_\alpha(t')}{dt'}\right].$$

We now utilize the fact that we wish an expression for δP_α that is correct only to the first power of F_α. This means that the factor $\Theta(t',t'')$ can be evaluated as though the field were not there, and $\mathcal{H}$ treated as a constant. In the unperturbed condition, any expression of the form $\langle A(t')B(t'')\rangle$ is a function only of the argument $t'-t''$ since the equilibrium distribution is a stationary one. This permits us to replace $\Theta(t',t'')$ by $\Theta(t'',t')$, and after this permutation, the integration over t'' in (A2) can immediately be performed. (It is really a partial integration, but the portion coming from the fact that the upper limit of the t' integral involves t'' makes no contribution because of a cancellation of terms when $t'=t''$.) Such terms as $\langle P_\alpha(-t_B)P_\alpha(t)\rangle$ resulting from the integration can be dropped since $-t_B$ can be taken an arbitrarily long time before $-t_A$, and $\lim_{-t_B\to-\infty}\langle P_\alpha(-t_B)P_\alpha(t)\rangle=0$ if there is no mean polarization in the absence of the applied field—in other words, all correlation is lost if the time interval is sufficiently long. The integration over t'' when $t_B\to-\infty$ thus reduces (A2) to (A1), which we wished to establish.

On introducing the integral representation of the unit step function $\theta(t-t')$, by means of the equation

$$\theta(t-t')=\frac{i}{2\pi}\int_{-\infty}^{\infty}\frac{\exp[-i\omega(t-t')]\,d\omega}{\omega+i\epsilon},$$

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[33] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) **24**, 419 (1963), particularly Secs. I and II and Appendix A.

(with $\epsilon \to 0+$) we can rewrite (A1) as follows:

$$\delta P_\alpha(t) = \Big(-\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d\omega' dt'}{\omega'+i\epsilon}\exp\left[-i(\omega'+\omega)(t-t')\right]\langle P_\alpha(t)P_\alpha(t')-P_\alpha(t')P_\alpha(t)\rangle\Big)F_\alpha \exp(i\omega t). \tag{A3}$$

In view of the definition of $\chi_{\alpha\beta}$, (I.1), we have

$$\chi_{\alpha\alpha}(\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d\omega' dt \exp(i\omega' t)}{\omega'-\omega+i\epsilon}\langle P_\alpha(t)P_\alpha(0)-P_\alpha(0)P_\alpha(t)\rangle. \tag{A4}$$

In obtaining (A4) we have made use of the fact that $\chi_{\alpha\alpha}$ is independent of t so that we can set t equal to zero in the bracketed factor of (A3). Noting that

$$\int_{-\infty}^{\infty}\exp(i\omega t)\langle P_\alpha(0)P_\alpha(t)\rangle dt = \mathrm{Tr}\int_{-\infty}^{\infty}\exp\left[-\mathcal{H}/kT\right]P_\alpha \exp\left[i\mathcal{H}t/\hbar\right]P_\alpha \exp\left[-i\mathcal{H}t/\hbar\right]\exp\left[i\omega t\right]dt, \tag{A5}$$

and making use of the cyclic property of the trace, Tr ABC = Tr BCA = Tr CAB, we see that the right-hand side of (A5) can be written as follows:

$$\begin{aligned}\int_{-\infty}^{\infty}\exp(i\omega t)\langle P_\alpha(0)P_\alpha(t)\rangle dt &= \mathrm{Tr}\int_{-\infty}^{\infty}\exp\left[-\mathcal{H}/kT\right]\exp\left[i\mathcal{H}(t-(i\hbar/kT))/\hbar\right]P_\alpha \\ &\qquad \times \exp\left[-i\mathcal{H}(t-(i\hbar/kT))/\hbar\right]P_\alpha \exp(i\omega t)\, dt, \\ &= \exp\left(-\frac{\hbar\omega}{kT}\right)\int_{-\infty}^{\infty}\exp(i\omega t)\langle P_\alpha(t)P_\alpha(0)\rangle dt. \end{aligned} \tag{A6}$$

With the help of (A6) $\chi_{\alpha\alpha}$ becomes

$$\chi_{\alpha\alpha}(\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d\omega' \, dt \exp(i\omega' t)}{\omega'-\omega+i\epsilon}\tanh\frac{\hbar\omega'}{2kT}\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle. \tag{A7}$$

Upon expanding $\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle$ in terms of the eigenstates of $\mathcal{H}$

$$\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle = 2\sum_{n,n'}\exp(-E_n/kT)\,|\langle n\mid P_\alpha\mid n'\rangle|^2\cos\left[(E_n-E_{n'})t/\hbar\right], \tag{A8}$$

it is evident that the bracketed expression in (A7) is both real and an even function of t. Utilizing these properties together with the symbolic identity, $(\omega+i\epsilon)^{-1} = \mathcal{P}/\omega - i\pi\delta(\omega)$, we infer that the real and imaginary parts of the susceptibility, $\chi_{\alpha\alpha} = \chi_{\alpha\alpha}' - i\chi_{\alpha\alpha}''$, can be written

$$\chi_{\alpha\alpha}'(\omega) = \frac{1}{2\pi\hbar}\mathcal{P}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{d\omega' \, dt \cos\omega' t}{\omega'-\omega}\tanh\frac{\hbar\omega'}{2kT}\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle, \tag{A9}$$

$$\chi_{\alpha\alpha}''(\omega) = \frac{1}{2\hbar}\tanh\frac{\hbar\omega}{2kT}\int_{-\infty}^{\infty}\cos\omega t\langle P_\alpha(0)P_\alpha(t)+P_\alpha(t)P_\alpha(0)\rangle dt. \tag{A10}$$

Comparing (A10) with (A9) we immediately deduce the Kramers–Kronig relation

$$\chi_{\alpha\alpha}'(\omega) = \frac{\mathcal{P}}{\pi}\int_{-\infty}^{\infty}\frac{\chi_{\alpha\alpha}''(\omega')\, d\omega'}{\omega'-\omega}, \tag{A11}$$

relating the real and imaginary parts of the susceptibility.