Stochastic Theory of the Resonant Scattering of Photons*

D. L. HUBER
Department of Physics, University of Wisconsin, Madison, Wisconsin
(Received 7 September 1967; revised manuscript received 12 February 1968)

The resonant scattering of photons from a perturbed two-level system is studied in detail. Adiabatic perturbations are approximated by a randomly fluctuating term in the level splitting. Off-diagonal perturbations are accounted for in the linewidth and the time dependence of the correlation functions. Explicit expressions for the cross section are obtained in the statistical and motional-narrowing limits. The detailed-balancing symmetry of the scattering is established. Minor modifications of the approximate expressions for the cross sections are proposed in order to preserve this symmetry. The effects of off-diagonal perturbations, which couple the atom to a thermal bath, are investigated at length for a model interaction.

I. INTRODUCTION

IN a recent paper[1] (hereafter referred to as I) the author discussed the resonant scattering of photons from an atom which was coupled to a crystal lattice. It was shown that the frequency spectrum of the scattered radiation is dominated by three terms: a coherent elastic component, a quasi-elastic component, and the resonance fluorescence. These results were obtained from a study of the induced dipole-moment operator. It was pointed out that the differential cross section could be written as the Fourier transform of the induced dipole-moment correlation function. An approximate expression for the cross section was obtained by expanding the induced dipole-moment operator to first order in the atom-lattice interaction. This approach, together with a phenomenological treatment of the linewidth and the population fluctuations, led directly to the three-component spectrum.

Subsequent to the appearance of I, Hizhnyakov and Tehver[2] published a general treatment of scattering from an atom-lattice system. By utilizing a different method of approximation, these authors were able to obtain an effectively nonperturbative expression for the cross section in the vicinity of the resonance.[3] In view of the fact that their analysis was limited to temperatures such that the thermal population of the upper state could be neglected and, further, was appropriate only to phonon-induced perturbations it was believed that a finite-temperature treatment of the resonant scattering based on a simple stochastic model would be of interest. The present paper outlines such a treatment. Our approach will be sufficiently general to encompass not only atom-lattice interactions but other types of perturbations as well.

Stochastic models have long been used in the calculation of the absorption line shape.[4] As will be made plain below, there are many points which are common to both the calculation of the absorption spectrum and the spectrum of scattered radiation. For this reason we will not go into detail about the situations where our particular model is appropriate. It is sufficient to say that in general the model has the same range of validity in both the absorption and scattering calculations.

The starting point in our study is the equation relating the differential cross section to the induced dipole-moment correlation function [I, Eq. (1.6)];

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\frac{\omega_1\omega_2^3}{2\pi c^4}\int_{-\infty}^{\infty} dt\,\exp(i\omega_2 t)\,\langle P_{fi}{}^\dagger P_{fi}(t)\rangle. \quad (1.1)$$

Here ω_1 is the angular frequency of the incident light, ω_2 is the angular frequency of the scattered light, c is the velocity of light, and the angular brackets indicate an ensemble average. The symbol P_{fi} denotes the induced dipole-moment operator

$$P_{fi}(t)=\exp(-i\omega_1 t)\,\exp(iHt'/\hbar)P_{fi}\exp(-iHt/\hbar), \quad (1.2)$$

with

$$P_{fi}=\frac{i}{\hbar}\int_{-\infty}^{0}[(\mathbf{d})_f,\,\exp(iHt'/\hbar)(\mathbf{d})_i\exp(-iHt'/\hbar)]\times\exp(-i\omega_1 t'+\epsilon t')\,dt'. \quad (1.3)$$

In (1.3), H is the Hamiltonian of the total system including both the atom and the perturbers. The symbol $(\mathbf{d})_i$ [or $(\mathbf{d})_f$] denotes the component of the dipole-moment operator along the direction of polarization of the incident [or scattered] light. The limit $\epsilon\to 0^+$ is understood.

As in I we view the atom as a two-level system which is characterized by the effective spin operators S_x, S_y, and S_z. The Hamiltonian of the unperturbed atom takes the form $\hbar\omega_0 S_z$, where $\hbar\omega_0$ denotes the difference in energy between the two levels. We approximate the effect of the perturbers by a fluctuating term in the level splitting, $\hbar\delta\omega_0(t)$. The full Hamiltonian is thus written

$$H(t)=\hbar\omega_0 S_z+\hbar\delta\omega_0(t)S_z. \quad (1.4)$$

* Work supported by the National Science Foundation.
[1] D. L. Huber, Phys. Rev. **158**, 843 (1967).
[2] V. Hizhnyakov and I. Tehver, Phys. Status Solidi **21**, 755 (1967).
[3] Reference 2, Eq. (46).
[4] A general discussion of the application of stochastic models to line-shape calculations is given in an article by R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh, 1962), pp. 23–68.

It is apparent that the perturbation $\hbar\delta\omega_0(t)S_z$ modulates the splitting between the two levels. In addition to perturbations of this type, which are frequently referred to as adiabatic, the atom is also subject to perturbations which induce transitions between the two levels. It is the off-diagonal perturbations, which are sometimes called diabatic, which maintain the average populations of the two atomic levels at their thermal-equilibrium value. For the moment we will not deal directly with the mechanism responsible for the transitions. Rather, as in I, we introduce relaxation effects through the time dependence of the longitudinal correlation function and by the artifice of replacing $i\omega_0 t$ by $i\omega_0 t - \Delta\omega_{\mathrm{OD}}|t|$ at appropriate points in the calculation. Here $\Delta\omega_{\mathrm{OD}}$ denotes the off-diagonal (diabatic) linewidth, which is equal to half of the inverse relaxation time $(1/2T_1)$ for a two-level system.[5] Additional comments on this approximation will be made in Sec. IV and Appendix A.

II. CALCULATION

In this section we outline the calculation of the cross section for the two-level system with the Hamiltonian given by Eq. (1.4). In the vicinity of the resonance (i.e., $\omega_1 \approx \omega_0$) the induced dipole-moment operator can be written [I, Eq. (2.5)]

$$P_{fi} = \frac{i}{\hbar}\alpha_i\alpha_f \int_{-\infty}^{0} [S_-, S_+(t')] \exp(-i\omega_1 t' + \epsilon t')\,dt', \quad (2.1)$$

where α_i and α_f denote the matrix elements of $(\mathbf{d})_i$ and $(\mathbf{d})_f$, respectively. From the equation of motion of S_+ $(=S_x + iS_y)$ we obtain the result

$$dS_+/dt = i[\omega_0 + \delta\omega_0(t)]S_+, \quad (2.2)$$

which integrates, if $[\delta\omega_0(t_1), \delta\omega_0(t_2)] = 0$ as we assume, to

$$S_+(t) = S_+ \exp\left[i\omega_0 t + i\int_0^t \delta\omega_0(t')\,dt'\right]. \quad (2.2')$$

Consequently we may write

$$P_{fi}(t) = -2\frac{i}{\hbar}\alpha_i\alpha_f S_z(t) \times \exp(-i\omega_1 t)\left\langle \int_{-\infty}^{0} \exp[i(\omega_0-\omega_1)t' - \Delta\omega_{\mathrm{OD}}|t'|] \times \exp\left[i\int_t^{t+t'} \delta\omega_0(\bar{t})\,d\bar{t}\right]\right\rangle dt', \quad (2.3)$$

after having inserted the off-diagonal linewidth. The limits on the integration of $\delta\omega_0$ are to be noted. They come about because we have

$$S_-(t) = S_- \exp\left[-i\omega_0 t - i\int_0^t \delta\omega_0(t')\,dt'\right]$$

so that the commutator $[S_-(t), S_+(t+t')]$ can be written

$$-2S_z \exp\left[i\omega_0 t' + i\int_t^{t+t'} \delta\omega_0(\bar{t})\,d\bar{t}\right].$$

It also should be pointed out that we have anticipated the effect of the off-diagonal perturbations on S_z by allowing for it to be time-dependent.

The cross section that is obtained from (2.3) takes the form

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2} = \frac{2|\alpha_i|^2|\alpha_f|^2\omega_1\omega_2^3}{\pi\hbar^2c^4}\int_{-\infty}^{\infty} dt\, \exp[i(\omega_2-\omega_1)t]\langle S_z S_z(t)\rangle \times \int_{-\infty}^{0} dt'' \int_{-\infty}^{0} dt' \exp[i(\omega_0-\omega_1)(t'-t'') - \Delta\omega_{\mathrm{OD}}(|t'|+|t''|)]\left\langle \exp\left[-i\int_0^{t''}\delta\omega_0(\bar{t})\,d\bar{t} + i\int_t^{t+t'}\delta\omega_0(\bar{t})\,d\bar{t}\right]\right\rangle, \quad (2.4)$$

after having separated the average of $S_zS_z(t)$ from the average over $\delta\omega_0$. This is permissible since the fluctuations in the frequency do not affect the populations of the atomic levels.

At this point we specialize to a Gaussian model for frequency modulation. With a Gaussian distribution we have the result[6]

$$\left\langle \exp\left[-i\int_0^{t''}\delta\omega_0(\bar{t})\,d\bar{t} + i\int_t^{t+t'}\delta\omega_0(\bar{t})\,d\bar{t}\right]\right\rangle = \exp\left\{-\frac{1}{2}\left\langle\left[\int_0^{t''}\delta\omega_0(\bar{t})\,d\bar{t} - \int_t^{t+t'}\delta\omega_0(\bar{t})\,d\bar{t}\right]^2\right\rangle\right\}$$

$$= \exp\left[-\frac{1}{2}\int_0^{t''} d\bar{t}\int_0^{t''} d\bar{\bar{t}}\langle\delta\omega_0(\bar{t})\delta\omega_0(\bar{\bar{t}})\rangle - \frac{1}{2}\int_t^{t+t'} d\bar{t}\int_t^{t+t'} d\bar{\bar{t}}\langle\delta\omega_0(\bar{t})\delta\omega_0(\bar{\bar{t}})\rangle + \int_0^{t''} d\bar{t}\int_t^{t+t'} d\bar{\bar{t}}\langle\delta\omega_0(\bar{t})\delta\omega_0(\bar{\bar{t}})\rangle\right], \quad (2.5)$$

[5] D. L. Huber and J. H. Van Vleck, Rev. Mod. Phys. **38**, 187 (1966).
[6] Reference 4, pp. 28–32.

assuming that $\langle\delta\omega_0\rangle=0$. The differential cross section is seen to depend on the autocorrelation function of the frequency fluctuations. It is convenient to consider two limiting types of behavior for this function. In the first of these it is assumed that the correlation time for the fluctuations is long compared with the smallest of the times $\Delta\omega_{OD}^{-1}$, $|\omega_0-\omega_1|^{-1}$, and $|\omega_0-\omega_2|^{-1}$. In this limit, which is sometimes called the statistical limit, we may replace $\langle\delta\omega_0(t_1)\delta\omega_0(t_2)\rangle$ with the constant $\langle\delta\omega_0^2\rangle$. As a result we obtain

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\frac{2\omega_1\omega_2^3|\alpha_i|^2|\alpha_f|^2}{\pi\hbar^2c^4}\int_{-\infty}^{\infty}dt\exp[i(\omega_2-\omega_1)t]\langle S_zS_z(t)\rangle$$
$$\times\int_{-\infty}^{0}dt'\int_{-\infty}^{0}dt''\exp[i(\omega_0-\omega_1)(t'-t'')-\Delta\omega_{OD}(|t'|+|t''|)]\exp[-\tfrac{1}{2}\langle\delta\omega_0^2\rangle(t'-t'')^2]. \quad (2.6)$$

An explicit expression for the cross section follows from approximating $\langle S_zS_z(t)\rangle$ by $(\langle S_z^2\rangle-\langle S_z\rangle^2)\exp(-|t|/T_1)+\langle S_z\rangle^2$ [I, Eq. (2.18)]. Further refinements in the treatment of longitudinal correlation function are discussed in Sec. IV. Note that the appearance of T_1 both in the linewidth and as the relaxation time for the population difference holds only for two-level systems. For systems with more than two levels the off-diagonal linewidth is half the sum of the inverse lifetimes of the two levels involved in the transition. If we also assume that $\Delta\omega_{OD}$ $(=1/2T_1)$ is much less than $\langle\delta\omega_0^2\rangle^{1/2}$, we have the result

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\frac{\omega_1\omega_2^3|\alpha_i|^2|\alpha_f|^2}{\hbar^2c^4}\left\{\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\,\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/(\pi T_1)}{(\omega_1-\omega_2)^2+(1/T_1)^2}\right\}$$
$$\times(2\pi/\langle\delta\omega_0^2\rangle)^{1/2}T_1\exp[-(\omega_0-\omega_1)^2/2\langle\delta\omega_0^2\rangle], \quad (2.7)$$

where $\beta=1/kT$, with T being the temperature and k denoting Boltzmann's constant.

On the other hand, if the condition $\Delta\omega_{OD}\gg\langle\delta\omega_0^2\rangle^{1/2}$ is satisfied we find

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\frac{\omega_1\omega_2^3|\alpha_i|^2|\alpha_f|^2}{\hbar^2c^4}\left[\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\,\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/(\pi T_1)}{(\omega_1-\omega_2)^2+(1/T_1)^2}\right][(\omega_0-\omega_1)^2+(1/2T_1)^2]^{-1}. \quad (2.8)$$

We postpone discussion of (2.7) and (2.8) until Sec. III.

In the opposite limit, when the correlation time is short compared with $\Delta\omega_{OD}^{-1}$, $|\omega_0-\omega_1|^{-1}$, and $|\omega_0-\omega_2|^{-1}$ the autocorrelation function can be approximated by a delta function;

$$\langle\delta\omega_0(\bar{t})\delta\omega_0(\bar{\bar{t}})\rangle=2\Delta\omega_D\delta(\bar{t}-\bar{\bar{t}}), \quad (2.9)$$

where $\Delta\omega_D$ denotes the diagonal linewidth. This width is on the order of $\langle\delta\omega_0^2\rangle\tau_c$, with τ_c being the correlation time.[4] In this limit, which is frequently referred to as the motional narrowing limit,[7] we have

$$\exp\left\{-\frac{1}{2}\left\langle\left[\int_0^{t''}\delta\omega_0(\bar{t})d\bar{t}-\int_t^{t+t'}\delta\omega_0(\bar{t})d\bar{t}\right]^2\right\rangle\right\}$$
$$=\exp[-\Delta\omega_D(|t'|+|t''|)-\Delta\omega_D(|t|+|t+t'-t''|-|t'+t|-|t-t''|)]. \quad (2.10)$$

The cross section can then be written

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\frac{\omega_1\omega_2^3|\alpha_i|^2|\alpha_f|^2}{\hbar^2c^4[(\omega_0-\omega_1)^2+(1/2T_1+\Delta\omega_D)^2]}\left\langle\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/(\pi T_1)}{(\omega_1-\omega_2)^2+(1/T_1)^2}+\frac{\Delta\omega_D}{1/2T_1}\right.$$
$$\left.\times\left[\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\frac{(\Delta\omega_D+1/2T_1)/\pi}{(\omega_2-\omega_0)^2+(\Delta\omega_D+1/2T_1)^2}+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{(\Delta\omega_D+3/2T_1)/\pi}{(\omega_2-\omega_0)^2+(\Delta\omega_D+3/2T_1)^2}\right]\right\rangle. \quad (2.11)$$

[7] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **69**, 37 (1946).

Although discussion of this equation is left to Sec. III we should point out that the results of Ref. 2 are obtained as the zero-temperature limit of (2.11) in which $\tanh\frac{1}{2}\beta\hbar\omega_0$ is replaced by unity and $1/2T_1$ by the natural linewidth.[3]

III. DISCUSSION

It is apparent from Eqs. (2.7) and (2.8) that the spectrum of scattered light has no fluorescent component (i.e., there is no component which as a function of ω_2 peaked about ω_0) in the statistical limit. The finite width arises only from the fluctuations in the populations of the two atomic levels. For frequencies in the visible and near-infrared part of the spectrum the condition $\beta\hbar\omega_0 \gg 1$ generally holds so that $\tanh\frac{1}{2}\beta\hbar\omega_0 \approx 1$. In this region nearly all the scattering is coherent. This result is not unexpected since the statistical limit is equivalent to having an ensemble of atoms with a static distribution of level splittings. At absolute zero, or in the absence of off-diagonal perturbations, the spectrum of light scattered by any member of the ensemble is identical to the spectrum incident upon it.[8]

In the motional-narrowing limit, Eq. (2.11), we have the same three-component spectrum as was obtained in I by applying perturbation theory to the atom-lattice interaction. The only significant difference between Eq. (2.11) of this paper and Eq. (3.1) of I is that in the former equation the fluorescence terms are multiplied by the factor $\Delta\omega_D/(1/2T_1)$. This factor has its origin in the expression

$$\exp\left[\int_0^{t''} d\bar{t} \int_t^{t+t'} d\bar{t}\langle \delta\omega_0(\bar{t})\delta\omega_0(\bar{t})\rangle\right].$$

Were we to have expanded this expression in powers of the autocorrelation function and kept only the zeroth- and first-order terms we would have obtained an equation similar to (2.11) but without the factor $\Delta\omega_D/(1/2T_1)$. It is apparent that the integrated intensity of the fluorescence differs from the sum of the integrated intensities of the elastic and quasi-elastic components by the same factor. This result has a simple physical interpretation.[9]

We note that the integrated intensity of the fluorescence is independent of the relative populations of the upper and lower states, except insofar as they affect $\Delta\omega_{OD}$. This happens because the fluorescence can occur in either of two ways:

(a) An atom in the ground state absorbs a photon and makes a transition to the upper state. While in the upper state it is perturbed and then emits a photon and returns to the ground state.

(b) An atom in the upper state emits a photon while making a transition to the ground state. While it is in this state it is perturbed and then subsequently absorbs a photon.

The intensity of the fluorescence, measured relative to the sum of the integrated intensities of the coherent and quasi-elastic peaks, is then given by the relative number of atoms which are perturbed by the frequency fluctuations compared with the number which undergo the absorption-emission process without being perturbed. This fraction may be inferred from the following argument.

The number of atoms undergoing fluorescence via process (a) is proportional to the number of atoms which have absorbed a photon and have then been perturbed. Under steady-state conditions this number is obtained from a consideration of the relevant transition rates. The number of coherent systems which are brought to the upper state is equal to the population factor of the lower state, $[1+\exp(-\beta\hbar\omega_0)]^{-1}$, multiplied by N_c, the total number of systems responding coherently to the field. The rate at which they are perturbed is $\Delta\omega_D$. The rate at which the incoherent systems are removed from the upper state is determined by the transition rate from the upper to the lower state. This we designate by $A_{+-}(\beta)$. Then under steady-state conditions the number of incoherent systems which are created per unit time equals the number which are lost through transitions to the ground state, i.e.,

$$\frac{\Delta\omega_D N_c}{1+\exp(-\beta\hbar\omega_0)} = A_{+-}(\beta) N_I^+, \tag{3.1}$$

where N_I^+ is the number of incoherent systems in the upper state.

A similar argument for the lower state yields

$$\frac{\Delta\omega_D N_c \exp(-\beta\hbar\omega_0)}{1+\exp(-\beta\hbar\omega_0)} = A_{-+}(\beta) N_I^-, \tag{3.2}$$

where $A_{-+}(\beta)$ is the transition rate from the lower to the upper state and N_I^- is the number of incoherent systems in the lower state. The total number of fluorescing systems, $N_I^+ + N_I^-$, is thus given by

$$N_I^+ + N_I^- = N_c\Delta\omega_D\{[(1+\exp(-\beta\hbar\omega_0))A_{+-}(\beta)]^{-1} + [(1+\exp(\beta\hbar\omega_0))A_{-+}(\beta)]^{-1}\}. \tag{3.3}$$

The arguments of detailed balance, when applied to the transition rates, show that

$$A_{+-}(\beta) = A(\beta)\exp(\beta\hbar\omega_0), \qquad A_{-+}(\beta) = A(\beta), \tag{3.4}$$

where $A(\beta)$ is an arbitrary function of β. Hence we have

$$N_I^+ + N_I^- = \frac{2N_c\Delta\omega_D}{A(\beta)[1+\exp(\beta\hbar\omega_0)]} = \frac{\Delta\omega_D N_c}{1/2T_1}, \tag{3.5}$$

[8] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, London, 1954), 3rd ed., p. 302.

[9] A similar argument, appropriate to the zero-temperature limit, has been given by T. Holstein, Phys. Rev. **72**, 1212 (1947), Appendix.

where we have made use of the result[5]

$$1/2T_1=\tfrac{1}{2}[A_{+-}(\beta)+A_{-+}(\beta)]$$
$$=\tfrac{1}{2}A(\beta)[1+\exp(\beta\hbar\omega_0)]. \qquad (3.6)$$

Since the number of systems which scatter via the elastic and quasi-elastic processes is N_c, we conclude on the basis of these arguments that the integrated (over ω_2) intensity of the fluorescence differs from the sum of the integrated intensities of the elastic and quasi-elastic components by the factor $\Delta\omega_D/(1/2T_1)$, in agreement with Eq. (2.11). Implicit in this analysis is the assumption that the lifetime in the upper state is limited by relaxation processes rather than radiative processes—as must be the case if the populations of the upper and lower levels follow the Boltzmann distribution.

We note that when $\Delta\omega_D=\Delta\omega_{OD}$ or, equivalently, when the relaxation rate equals the linewidth, the integrated intensity of the coherent and quasi-elastic peaks equals the integrated intensity of the fluorescence. In the limit of zero temperature this result agrees with the findings of Holstein, who studied the resonant scattering from a classical oscillator perturbed by totally quenching collisions.[10,11] After a totally quenching collision the atom is returned to the ground state. Hence in this case the collision rate equals the relaxation rate. The analogy is completed by the identification of the collision rate with the (transverse) linewidth.

IV. FURTHER REFINEMENTS

In this section we discuss modifications of Eqs. (2.7), (2.8), and (2.11) which arise from a more rigorous treatment of relaxation effects. We begin by establishing a general symmetry property of the cross section for photon scattering from systems in thermal equilibrium. We write the expression for the cross section in the form [I, Eq. (1.1)]

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\omega_1\omega_2{}^3c^{-4}Z^{-1}$$
$$\times\sum_{n,n'}\exp(-\beta E_n)\left|\sum_{n''}\frac{\langle n'\,|\,(\mathbf{d})_f\,|\,n''\rangle\langle n''\,|\,(\mathbf{d})_i\,|\,n\rangle}{E_n+\hbar\omega_1-E_{n''}}+\sum_{n''}\frac{\langle n'\,|\,(\mathbf{d})_i\,|\,n''\rangle\langle n''\,|\,(\mathbf{d})_f\,|\,n\rangle}{E_n-\hbar\omega_2-E_{n''}}\right|^2\delta(\omega_2+E_{n'}/\hbar-\omega_1-E_n/\hbar), \qquad (4.1)$$

where $Z[=\sum_n\exp(-\beta E_n)]$ is the partition function of the scatterer whose energy levels are designated by E_n. We make use of the restrictions imposed by the delta function and the Hermitian character of the dipole-moment operators to rewrite (4.1) in the form

$$\frac{d^2\sigma(\omega_1)}{d\Omega d\omega_2}=\omega_1\omega_2{}^3c^{-4}\exp[-\beta\hbar(\omega_2-\omega_1)]Z^{-1}$$
$$\times\sum_{n,n'}\exp(-\beta E_{n'})\left|\sum_{n''}\frac{\langle n\,|\,(\mathbf{d})_i\,|\,n''\rangle\langle n''\,|\,(\mathbf{d})_f\,|\,n'\rangle}{E_{n'}+\hbar\omega_2-E_{n''}}+\sum_{n''}\frac{\langle n\,|\,(\mathbf{d})_f\,|\,n''\rangle\langle n''\,|\,(\mathbf{d})_i\,|\,n'\rangle}{E_{n'}-\hbar\omega_1-E_{n''}}\right|^2$$
$$\times\delta(\omega_2+E_{n'}/\hbar-\omega_1-E_n/\hbar)$$
$$=\frac{\omega_2{}^2}{\omega_1{}^2}\exp[-\beta\hbar(\omega_2-\omega_1)]\frac{d^2\sigma(\omega_1)^T}{d\Omega d\omega_2}. \qquad (4.2)$$

Here $d^2\sigma(\omega_2)^T/d\Omega d\omega_1$ denotes the cross section characterizing the time-reversed scattering process where the incoming photon has frequency ω_2 and wave vector $-\mathbf{k}_2$, and has associated with it the dipole-moment operator $(\mathbf{d})_f$, while the scattered photon has frequency ω_1, wave vector $-\mathbf{k}_1$, and dipole-moment operator $(\mathbf{d})_i$.[12]

The physical significance of Eq. (4.2) can be inferred from the conditions necessary for maintaining a state of thermal equilibrium between the scattering system and a photon gas having a blackbody frequency distribution. In an equilibrium situation the rate of scattering from photon state 1 to photon state 2 is the same as the rate for the time-reversed process from 2 to 1. The rate of scattering from 1 to 2, R_{12}, is given by

$$R_{12}=(2\pi)^{-3}c$$
$$\times[\exp(\beta\hbar\omega_1)-1]^{-1}k_1{}^2dk_1d\Omega_1[d^2\sigma(\omega_1)/d\Omega d\omega_2]d\Omega_2d\omega_2$$
$$\times\exp(\beta\hbar\omega_2)/[\exp(\beta\hbar\omega_2)-1], \qquad (4.3a)$$

[10] See Ref. 9.
[11] Resonant scattering from a perturbed harmonic oscillator has also been studied by D. Towne, thesis, Harvard University, 1954 (unpublished).
[12] In the case of circularly polarized light, the sense of polarization is reversed in the time-reversed scattering process.

where the factor preceding the cross section is the flux of photons with frequencies between ω_1 and $\omega_1+d\omega_1$ heading in the solid angle $d\Omega_1$ determined by the wave vector $\mathbf{k}_1$. We have also included the factor $\exp(\beta\hbar\omega_2)/[\exp(\beta\hbar\omega_2)-1]$ to account for the enhancement of the scattering which comes from induced emission. The rate for the reverse process can be written

$$R_{12}{}^T=(2\pi)^{-3}c \times[\exp(\beta\hbar\omega_2)-1]^{-1}k_2{}^2dk_2d\Omega_2[d^2\sigma(\omega_1)^T/d\Omega d\omega_2]d\Omega_1 d\omega_1 \times\exp(\beta\hbar\omega_1)/[\exp(\beta\hbar\omega_1)-1]. \quad (4.3b)$$

Equating R_{12} and $R_{12}{}^T$ leads directly to a result which is equivalent to the second line of (4.2). It is apparent that (4.2) displays the detailed balancing symmetry of the scattering process.[13]

An examination of (2.7), (2.8), and (2.11) indicates that these equations fail to satisfy Eq. (4.2) when the frequencies ω_1 and ω_2 are interchanged. The origin of the failure lies in the approximate treatment of the off-diagonal perturbations. As a first step towards remedying this defect we will replace our previous expressions for the cross section by the symmetrized combinations

$$\tfrac{1}{2}\{d^2\sigma(\omega_1)'/d\Omega d\omega_2+(\omega_2/\omega_1)^2 \times\exp[-\beta\hbar(\omega_2-\omega_1)]d^2\sigma(\omega_1)^{T'}/d\Omega d\omega_2\},$$

where the prime indicates that it is to be evaluated with (2.7), (2.8), (2.11) and their time-reversed counterparts.

Although having the proper symmetry the revised expressions for the cross sections have the undesirable feature that they become infinite in the limit as β approaches infinity whenever ω_1 is greater than ω_2. This feature is corrected by an improved calculation of the Fourier transform of $\langle S_zS_z(t)\rangle$. By assuming an exponential decay in $S_z(t)$, as in Sec. II, we obtain the result

$$\frac{2}{\pi}\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle S_zS_z(t)\rangle=\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/\pi T_1}{\omega^2+(1/T_1)^2}. \quad (4.4)$$

An alternative method of obtaining this transform is with the help of Green's functions. It is shown in Appendix B that an analysis based on Green's functions leads to the result

$$\frac{2}{\pi}\int_{-\infty}^{\infty}dt\, e^{i\omega t}\langle S_zS_z(t)\rangle=\frac{2}{\exp(\beta\hbar\omega)+1}\left[\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\ \delta(\omega)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/\pi T_1}{\omega^2+(1/T_1)^2}\right]. \quad (4.5)$$

Equations (4.4) and (4.5) differ only in the factor $2/(e^{\beta\hbar\omega}+1)$. This result suggests that we alter the approximate expressions for the cross section a second time in the manner suggested by Eq. (4.5). We thus obtain the modified cross section

$$\frac{d^2\sigma(\omega_1)_{\rm M}}{d\Omega d\omega_2}=\left[\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}^{-1}\frac{d^2\sigma(\omega_1)'}{d\Omega d\omega_2}+\frac{\omega_2{}^2}{\omega_1{}^2}\exp[-\beta\hbar(\omega_2-\omega_1)]\{\exp[-\beta\hbar(\omega_2-\omega_1)]+1\}^{-1}\frac{d^2\sigma(\omega_1)^{T'}}{d\Omega d\omega_2}\right]$$
$$=\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}^{-1}\left[\frac{d^2\sigma(\omega_1)'}{d\Omega d\omega_2}+\frac{\omega_2{}^2}{\omega_1{}^2}\frac{d^2\sigma(\omega_1)^{T'}}{d\Omega d\omega_2}\right]. \quad (4.6)$$

The modified counterparts of (2.7), (2.8), and (2.11) take this form:

A. Statistical limit, $\langle\delta\omega_0{}^2\rangle^{1/2}\gg1/2T_1$:

$$\frac{d^2\sigma(\omega_1)_{\rm M}}{d\Omega d\omega_2}=\frac{\omega_1\omega_2{}^3\,|\,\alpha_i\,|^2\,|\,\alpha_f\,|^2}{\hbar^2c^4\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}}\left[\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/T_1\pi}{(\omega_1-\omega_2)^2+(1/T_1)^2}\right]$$
$$\times\left(\frac{2\pi}{\langle\delta\omega_0{}^2\rangle}\right)^{1/2}T_1\{\exp[-(\omega_0-\omega_1)^2/2\langle\delta\omega_0{}^2\rangle]+\exp[-(\omega_0-\omega_2)^2/2\langle\delta\omega_0{}^2\rangle]\}; \quad (2.7')$$

B. Statistical limit, $\langle\delta\omega_0{}^2\rangle^{1/2}\ll1/2T_1$:

$$\frac{d^2\sigma(\omega_1)_{\rm M}}{d\Omega d\omega_2}=\frac{\omega_1\omega_2{}^3\,|\,\alpha_i\,|^2\,|\,\alpha_f\,|^2}{\hbar^2c^4\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}}\left(\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/\pi T_1}{(\omega_1-\omega_2)^2+(1/T_1)^2}\right)$$
$$\times\{[(\omega_0-\omega_1)^2+(1/2T_1)^2]^{-1}+[(\omega_0-\omega_2)^2+(1/2T_1)^2]^{-1}\}. \quad (2.8')$$

[13] Detailed balancing symmetry in neutron scattering has been discussed by P. Schofield, Phys. Rev. Letters **4**, 239 (1960).

C. Motional-narrowing limit:

$$\begin{aligned}\frac{d^2\sigma(\omega_1)_{\mathrm{M}}}{d\Omega d\omega_2} &= \frac{\omega_1\omega_2^3|\alpha_i|^2|\alpha_f|^2}{\hbar^2c^4\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}}\Bigg\{\Bigg[\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\,\delta(\omega_1-\omega_2)+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/\pi T_1}{(\omega_1-\omega_2)^2+(1/T_1)^2}\Bigg]\\
&\quad\times\{[(\omega_1-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2]^{-1}+[(\omega_2-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2]^{-1}\}+\Delta\omega_{\mathrm{D}}/(1/2T_1)\\
&\quad\times\Bigg\langle(2\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{[(\omega_2-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2]^{-1}[(\Delta\omega_{\mathrm{D}}+1/2T_1)/\pi]}{(\omega_1-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2}+(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{\Delta\omega_{\mathrm{D}}+3/2T_1}{\pi}\\
&\quad\times\Bigg[\frac{[(\omega_2-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+3/2T_1)^2]^{-1}}{(\omega_1-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2}+\frac{[(\omega_1-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+3/2T_1)^2]^{-1}}{(\omega_2-\omega_0)^2+(\Delta\omega_{\mathrm{D}}+1/2T_1)^2}\Bigg]\Bigg\rangle\Bigg\}. \qquad (2.11')\end{aligned}$$

There are several features of Eqs. (2.7′), (2.8′), and (2.11′) which deserve further comment. First, under typical experimental conditions ($\omega_1\approx\omega_2\approx\omega_0$, $\beta\hbar|\omega_2-\omega_1|\ll 1$) the difference between the modified cross sections and the original expressions is slight. Second, in the limit $\beta\hbar|\omega_2-\omega_1|\ll 1$ the expression $(\omega_1\omega_2^3)^{-1}d^2\sigma(\omega_1)_{\mathrm{M}}/d\Omega d\omega_2$ is symmetric under the interchange of ω_1 and ω_2. This symmetry is classical in origin and is related to the conditions necessary for equilibrium between a classical radiation field and the scattering system. Third, at absolute zero the cross section vanishes for $\omega_2>\omega_1$. This latter result has a simple physical interpretation. At absolute zero the scattering system is in its lowest energy state and hence the photon cannot carry away more energy than it brings to the system.

V. SUMMARY

To summarize, we have outlined a stochastic theory of resonance scattering based on a Gaussian approximation for the frequency fluctuations. Explicit expressions have been obtained for the differential cross section in the statistical and motional narrowing limits. It should be pointed out that the Gaussian model, while appropriate for many solid-state phenomena (e.g., phonon modulation, which corresponds to the motional-narrowing limit[14]) is unsatisfactory for the simulation of the effects of collisions in gases. As emphasized by Kubo,[4] the perturbations acting on atoms in a gas are better approximated by a Poisson rather than a Gaussian distribution of frequencies. Resonant scattering in gases, including kinematical effects, will be dealt with in a separate paper.

APPENDIX A

This Appendix is devoted to a discussion of the effects of off-diagonal perturbations, with the aim of justifying our treatment of them in the calculation of the cross section. We use as a model an off-diagonal atom-lattice interaction of the form $S_x\sum_v A_v(a_v+a_v^\dagger)$, where the a_v and $a_v^\dagger$ are phonon annihilation and creation operators which obey the usual Bose commutation relations and A_v is a coupling constant. The effects of such an interaction on the absorption spectrum have been studied in detail.[5] It contributes to the width of the absorption line and to the fluctuations in S_z. It is apparent that both effects appear in the scattering cross section. The influence of the off-diagonal perturbations on the fluorescence which is present in the motional narrowing limit comes about mainly through the $1/2T_1$ term in the linewidth, with population fluctuations having only a small effect. This is to be contrasted with the quasi-elastic scattering, which comes entirely from the fluctuations in S_z.

The justification for our approximate treatment of the $1/2T_1$ term in the linewidth comes from a study of the operator $S_+(t)=\exp(iHt/\hbar)S_+\exp(-iHt/\hbar)$. For the purpose of illustration we will neglect the diagonal perturbations. The Hamiltonian H can then be written H_0+H_1, where H_0 is the sum of the unperturbed atom and lattice Hamiltonians and H_1 is the coupling. Using standard techniques,[15] we may expand $S_+(t)$ in powers of H_1. Thus to second order we have

$$\begin{aligned}S_+(t)&=\Bigg[1+\frac{i}{\hbar}\int_0^t\hat{H}_1(\bar{t})d\bar{t}\\
&\qquad-\Big(\frac{1}{\hbar}\Big)^2\int_0^t d\bar{t}\int_0^{\bar{t}}d\bar{\bar{t}}\,\hat{H}_1(\bar{\bar{t}})\hat{H}_1(\bar{t})\Bigg]S_+\exp(i\omega_0t)\\
&\quad\times\Bigg[1-\frac{i}{\hbar}\int_0^t\hat{H}_1(\bar{t})d\bar{t}-\Big(\frac{1}{\hbar}\Big)^2\int_0^t d\bar{t}\int_0^{\bar{t}}d\bar{\bar{t}}\,\hat{H}_1(\bar{t})\hat{H}_1(\bar{\bar{t}})\Bigg],\end{aligned}\qquad (A1)$$

where $\hat{H}_1(t)=\exp(iH_0t/\hbar)H_1\exp(-iH_0t/\hbar)$.

The terms in (A1) which are linear in H_1, when included in the cross section, give rise to the quasi-elastic scattering which is discussed below. These we

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

[15] J. Hamilton, *Theory of Elementary Particles* (Oxford University Press, London, 1959), pp. 186–187.

will neglect for the moment. Thus we have

$$S_+(t)\approx S_+e^{i\omega_0 t}\Bigg[1-\left(\frac{1}{2\hbar}\right)^2\sum_{v,v'}A_vA_{v'}\int_0^t d\bar{t}\int_0^{\bar{t}}d\bar{\bar{t}}\exp[i\omega_0(\bar{\bar{t}}-\bar{t})]\times\{[a_v\exp(-i\omega_v\bar{t})+a_v{}^\dagger\exp(i\omega_v\bar{t})][a_{v'}\exp(-i\omega_{v'}\bar{\bar{t}})+a_{v'}{}^\dagger\exp(i\omega_{v'}\bar{\bar{t}})]+[a_v\exp(-i\omega_v\bar{\bar{t}})+a_v{}^\dagger\exp(i\omega_v\bar{\bar{t}})][a_{v'}\exp(-i\omega_{v'}\bar{t})+a_{v'}{}^\dagger\exp(i\omega_{v'}\bar{t})]\}\Bigg], \quad (A2)$$

where the ω_v are the frequencies of the lattice oscillators. In writing (A2) we have omitted terms of the form $\hat{H}_1(t_1)S_+\hat{H}_1(t_2)$ which do not contribute to the resonance cross section since they commute with S_-. Since the cross section involves the ensemble average of the induced dipole-moment operator, we replace the products of the lattice operators in (A2) by their ensemble averages;

$$S_+(t)\approx S_+e^{i\omega_0 t}\left[1-\left(\frac{1}{2\hbar}\right)^2\sum_v A_v{}^2\int_0^t d\bar{t}\int_0^{\bar{t}}d\bar{\bar{t}}\exp[i\omega_0(\bar{\bar{t}}-\bar{t})]\coth\tfrac{1}{2}\beta\hbar\omega_v\{\exp[i\omega_v(\bar{\bar{t}}-\bar{t})]+\exp[-i\omega_v(\bar{\bar{t}}-\bar{t})]\}\right]. \quad (A3)$$

In the resonance region with $t>0$ we may evaluate the integrals in (A3) by first introducing the variable $u=\bar{\bar{t}}-\bar{t}$ and then extending the lower limit in the u integration to $-\infty$ with the convergence factor $e^{\epsilon u}$ ($\epsilon\to 0^+$).[16] As a result we find

$$S_+(t)\approx S_+\exp(i\omega_0 t)\left[1-t\left(\frac{1}{2\hbar}\right)^2\sum_v A_v{}^2\coth\tfrac{1}{2}\beta\hbar\omega_v\times\left(\frac{1}{i(\omega_0+\omega_v)+\epsilon}+\frac{1}{i(\omega_0-\omega_v)+\epsilon}\right)\right]$$
$$\approx S_+\exp(i\omega_0 t)(1-t/2T_1)$$
$$\approx S_+\exp(i\omega_0 t-t/2T_1), \quad (A4)$$

in agreement with the approximations made in Sec. II since we have

$$\frac{1}{T_1}=2\pi\left(\frac{1}{2\hbar}\right)^2\sum_v A_v{}^2\coth\tfrac{1}{2}\beta\hbar\omega_v\delta(\omega_0-\omega_v), \quad (A5)$$

which is the standard expression for the spin-lattice relaxation time.[17] In obtaining (A4) we have made use of the symbolic identity $(\omega\pm i\epsilon)^{-1}=P/\omega\mp i\pi\delta(\omega)$, where P denotes the principal value. In addition we have neglected the small shift in frequency,

$$\left(\frac{1}{2\hbar}\right)^2 P\sum_v A_v{}^2\coth\tfrac{1}{2}\beta\hbar\omega_v[(\omega_0+\omega_v)^{-1}+(\omega_0-\omega_v)^{-1}]$$

coming from H_1.

We may justify our calculation of the quasi-elastic and coherent scattering by comparing the limiting expressions obtained from (2.7′), (2.8′), and (2.11′) with the results of perturbation theory. If we neglect adiabatic effects we may write the cross section in the resonance region as a sum of n-phonon cross sections, with $n=0, 1, 2\cdots$. The zero-phonon cross section is written

$$\frac{d^2\sigma(\omega_1)^0}{d\Omega d\omega_2}=\frac{|\alpha_i|^2|\alpha_f|^2\omega_1\omega_2{}^3\delta(\omega_1-\omega_2)}{\hbar^2c^4(\omega_0-\omega_1)^2}, \quad (A6)$$

which agrees with the sum of the coherent and quasi-elastic terms in (2.7′), (2.8′) and (2.11′) in the limit $T_1\to\infty$. Note that it is independent of temperature.

The one-phonon cross section is easily calculated as a third-order process involving two photons and one phonon. Neglecting nonresonant contributions we obtain the result

$$\frac{d^2\sigma(\omega_1)^1}{d\Omega d\omega_2}=\frac{\omega_1\omega_2{}^3|\alpha_i|^2|\alpha_f|^2N_-}{c^4\hbar^4(\omega_1-\omega_0)^2(\omega_1-\omega_2)^2}\times\sum_v n_vA_v{}^2\delta(\omega_1+\omega_v-\omega_2-\omega_0)+\frac{\omega_1\omega_2{}^3|\alpha_i|^2|\alpha_f|^2N_+}{c^4\hbar^4(\omega_2-\omega_0)^2(\omega_1-\omega_2)^2}\times\sum_v(n_v+1)A_v{}^2\delta(\omega_1+\omega_0-\omega_2-\omega_v). \quad (A7)$$

where N_+ is the fraction of atoms in the upper state, $\exp(-\beta\hbar\omega_0)[1+\exp(-\beta\hbar\omega_0)]^{-1}$, N_- is the fraction in the lower state $[1+\exp(-\beta\hbar\omega_0)]^{-1}$, and n_v is the phonon occupation number $(e^{\beta\ \omega_v}-1)^{-1}$. If we ignore $\omega_2-\omega_1$ in comparison with ω_0, we obtain the result

$$\frac{d^2\sigma(\omega_1)^1}{d\Omega d\omega_2}=\frac{\omega_1\omega_2{}^3|\alpha_i|^2|\alpha_f|^2(1/\pi T_1)}{2c^4\hbar^2(\omega_1-\omega_2)^2}\times\left[\frac{1}{(\omega_1-\omega_0)^2}+\frac{1}{(\omega_2-\omega_0)^2}\right](1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)), \quad (A8)$$

where T_1 is again given by (A5).

It is evident that (A8) very nearly agrees with the leading term in the expansion of the quasi-elastic scattering cross section in (2.7′), (2.8′), and (2.11′) in powers of $1/T_1$ as long as $\omega_1\neq\omega_2$. The difference arises solely in the presence of the factor $2/\{\exp[\beta\hbar(\omega_2-\omega_1)]+1\}$. The presence of this factor in our approximate cross sections is necessary in order that the symmetry condition Eq. (4.2) be satisfied. It is worthwhile pointing out in this regard that although the cross section given in (A8) does not satisfy (4.2), the one-phonon cross section from which it was obtained, (A7), does have the property symmetry.

We thus conclude that our treatment of the off-diagonal perturbations is essentially correct in that it

[16] The linewidth treatment that we are following is discussed, for example, in Ref. 4, pp. 59–64.

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

incorporates the correct linewidth while at the same time reproducing of the results of perturbation theory through first order. Although the justification we have given here is based on a particularly simple interaction, it is plausible that our treatment is satisfactory for other types of off-diagonal perturbations as well.

APPENDIX B

In this Appendix we outline a calculation of the Fourier transform of $\langle S_z S_z(t)\rangle$ which is carried out with the help of Green's functions. The main results presented here are implicit in Ref. 5, to which the reader is referred for further details. The Fourier transform of the longitudinal correlation function can be written in the form[18]

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle S_z S_z(t)\rangle = \left.\frac{i[G(\omega+i\epsilon)-G(\omega-i\epsilon)]}{e^{\beta\hbar\omega}+1}\right|_{\epsilon\to 0+}. \quad \text{(B1)}$$

Here $G(\omega)$ denotes the Fourier transform of the retarded Green's function $-i\theta(t)\langle S_z(t)S_z+S_zS_z(t)\rangle$, where $\theta(x)$ is the unit step function. As shown in Ref. 5, the use of spin-phonon interaction as an off-diagonal perturbation leads in lowest order to a Green's function of the form[19]

$$G(\omega\pm i\epsilon)=\frac{1}{4\pi}\frac{1\pm i(1/T_1\omega)\tanh^2\frac{1}{2}\beta\hbar\omega_0}{\omega\pm i/T_1} \mp (i/4)\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega). \quad \text{(B2)}$$

Hence we have

$$\frac{2}{\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle S_z S_z(t)\rangle = \frac{2}{e^{\beta\hbar\omega}+1} \times\left[(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/(\pi T_1)}{\omega^2+(1/T_1)^2}+\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\delta(\omega)\right], \quad \text{(B3)}$$

in agreement with (4.5). As is the case in Appendix A, the calculation was carried out for a model interaction but is expected to hold for a wider class of off-diagonal perturbations.

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

[19] Reference 5, Eq. (II, 22), in the limit $E\to\omega\pm i\epsilon$. In the one-phonon approximation a coupling of the form $S_z\Sigma_v B_v(a_v+a_v^\dagger)$ does not contribute significantly to $\langle S_z S_z(t)\rangle$.

PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Theory of Indirect Nuclear Interactions in Rubidium and Cesium Metals*

S. D. Mahanti and T. P. Das
Department of Physics, University of California, Riverside, California
(Received 14 September 1967)

A quantitative evaluation has been made of the Ruderman-Kittel and pseudodipolar parameters A_{ij} and B_{ij} for Rb^{85} and Cs^{133} nuclei in the respective metals using one-orthogonalized-plane-wave functions and calculated band structures. All the possible mechanisms that contribute to A_{ij} and B_{ij} have been considered. For A_{ij}, about 90.54 and 92.25 % of the total contribution for rubidium and cesium, respectively, are found to arise from the second-order effect of the contact hyperfine interaction. For B_{ij}, the corresponding figures are 89.95 and 88.84 %, arising from one order each in the electron-nuclear contact and dipole interactions. For each mechanism, the calculation involves an integration over the region of **k** space within the Fermi surface. The integrand is composed of three **k**-dependent factors, an expectation value over the wave functions, a density-of-states term, and a phase factor which depends on the distance between the nuclei. The final result depends sensitively on the k dependence of these factors, and in some cases there is a cancellation between positive and negative contributions from different regions of **k** space. In the light of this, a critical analysis is made of earlier approximations, where some of the **k**-dependent factors were replaced by their values at the Fermi surface. Self-consistency and correlation effects are explicitly included, and produce less than 10% correction for A_{ij} and B_{ij} in both metals. Our calculated values for A_{ij} are 22.73 and 124.65, respectively, for rubidium and cesium, as compared to recent experimental values 51±5 and 200±10 cps. For B_{ij}, the calculated values are 0.398 and 2.330, as compared to experimental values 11.80 and 35.00 cps. Possible sources for the discrepancies, and additional factors whose inclusion could lead to improved agreement with experiment, are discussed.

I. INTRODUCTION

THE role of conduction electrons in producing indirect coupling between two localized moments or between nuclear moments in a metal was first realized by Fröhlich and Nabarro.[1] For transition metals, Zener[2] proposed that this indirect exchange interaction between localized d-electron magnetic moments can lead to ferromagnetism. These authors only considered the diagonal contribution to the coupling, which is nonzero for the case of metals because of their Pauli paramagnetism. They did not take into account the contributions from second-order polarization effects

* Supported by the National Science Foundation.

[1] H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1949).

[2] C. Zener, Phys. Rev. **81**, 440 (1951).