Eqs. (4a) and (20) gives the following predictions for the magnitude of the optical-rectification coefficient:

From Carpenter's electro-optic data,

$$(X^0{}_{xyz}+X^0{}_{xzy})=(1.22\pm0.023)\times10^{-7}\ \text{esu}; \quad (22a)$$

and from Ott and Sliker's electro-optic data,

$$(X^0{}_{xyz}+X^0{}_{xzy})=(1.43\pm0.026)\times10^{-7}\ \text{esu}. \quad (22b)$$

V. CONCLUSION

The measured magnitude of an optical-rectification coefficient in $NH_4H_2PO_4$ at 27°C and 6943 Å is

$$(X^0{}_{xyz}+X^0{}_{xzy})=(1.32\pm0.18)\times10^{-7}\ \text{esu}.$$

The 15% uncertainty represents an improvement by a factor of 20 over the previous absolute measurement of an optical-rectification coefficient.[5]

The validity of the theoretical relationship, Eq. (3), between the optical-rectification and linear electro-optic coefficients may now be tested. Magnitudes of optical-rectification coefficients predicted from electro-optic data by Eq. (3), or more particularly, Eq. (4a), are as follows:

From Carpenter's electro-optic data,

$$(X^0{}_{xyz}+X^0{}_{xzy})_{\text{predicted}}=(1.22\pm0.023)\times10^{-7}\ \text{esu};$$

and from Ott and Sliker's electro-optic data,

$$(X^0{}_{xyz}+X^0{}_{xzy})_{\text{predicted}}=(1.43\pm0.026)\times10^{-7}\ \text{esu}.$$

The measured magnitude agrees with each of the predicted values to within experimental error. We conclude that these data are consistent with the validity of Eq. (3).

ACKNOWLEDGMENTS

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Theoretical Discussion of the Inverse Faraday Effect, Raman Scattering, and Related Phenomena*

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The inverse Faraday effect (IFE) occurs when circularly polarized light incident on a nonabsorbing crystal induces a magnetic moment proportional to the Verdet constant of that material, the proportionality constant being independent of the material. Some experimental details relating to the observation and proof of the IFE are presented. A microscopic, or quantum-mechanical, explanation of the IFE which also demonstrates its connection with the Faraday effect is given in terms of an optically induced "effective Hamiltonian" $\mathcal{H}_{\text{eff}}$. Conventional calculations of the optical constants like the Verdet constant compute optical-frequency polarizabilities for a given electronic configuration. It is shown here that these same constants are obtained by computing the average effects that optical fields have on the atomic configuration. The optically induced $\mathcal{H}_{\text{eff}}$ is linearly dependent on the low-frequency components of $E(t)E(t)$ and one can show the thermal average $\langle\mathcal{H}_{\text{eff}}\rangle_{\text{thermal}}$ is equal to the temporl average $\langle\mathbf{E}(t)\cdot\boldsymbol{\varepsilon}\cdot(\mathbf{E}t)\rangle_{\text{time}}$. Both the Verdet constant and the IFE coefficient arise from a thermal average of the same term in $\mathcal{H}_{\text{eff}}$. Similarly the Cotton-Mouton effect and its inverse arise from one other term in $\mathcal{H}_{\text{eff}}$. Definition of $\mathcal{H}_{\text{eff}}$ is one technique for linearizing some nonlinear optical problems. Following linearization one obtains Kramers-Kronig-type dispersion relations between constants of seemingly different phenomena. For example, a Kramers-Kronig relation is obtained between the Verdet constant and the gain coefficient for stimulated Raman scattering by paramagnetic ions in a large dc magnetic field. The effective Hamiltonian is explicitly evaluated from some illustrative examples and its general phenomenological form for a paramagnetic ion in cubic symmetry is written down and discussed.

1. INTRODUCTION

THE application of high-intensity laser radiation to various materials has resulted in observation of new effects which arise from the nonlinear response of media to optical-frequency fields.[1] A number of authors[2–4] have discussed different nonlinear optical effects phenomenologically in terms of a potential function F, whose derivatives with respect to various fields

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[1] These effects are reviewed by N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin Inc., New York, 1965), or P. S. Pershan, *Progress in Optics*, edited by E. Wolf (to be published), Vol. V.

[2] D. A. Kleinman, Phys. Rev. **126**, 1977 (1962).

[3] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[4] P. S. Pershan, Phys. Rev. **130**, 919 (1963).

[e.g., $\partial^2 F/\partial\mathcal{E}_i^*(\omega)\partial\mathcal{E}_j(\omega)$ etc.] are expected to yield nonlinear equivalents of the dielectric tensors. Although such a potential function is both plausible and useful, its existence is not generally proven. Prior to the work to be discussed here, experimental evidence on this point consisted of observation on effects of electric rather than magnetic origin. Consider electric fields $\boldsymbol{\mathcal{E}}(\omega_1)$, $\boldsymbol{\mathcal{E}}(\omega_2)$, and $\boldsymbol{\mathcal{E}}(\omega_3)$ at frequencies ω_1, ω_2, and ω_3, respectively ($\omega_1+\omega_2=\omega_3$). Experiments have shown[1] that if in some material one beats ω_1 and ω_2 to obtain a polarization at ω_3 and this effect is described by a tensor relation $\mathbf{P}(\omega_3)=\boldsymbol{\chi}:\boldsymbol{\mathcal{E}}(\omega_2)\boldsymbol{\mathcal{E}}(\omega_1)$, where $\boldsymbol{\chi}$ is a material constant, this same tensor will describe the beating of ω_3 and ω_2 to obtain ω_1; $\mathbf{P}(\omega_1)=\boldsymbol{\mathcal{E}}(\omega_3)\cdot\boldsymbol{\chi}\cdot\boldsymbol{\mathcal{E}}^*(\omega_2)$.

In a brief communication the present authors[5] have experimentally demonstrated that a similar relationship exists when one of the fields is magnetic rather than electric, and thus increased the generality of the experimental evidence for the existence of this potential function. A reciprocal relationship was demonstrated between Faraday rotation and the induction of a magnetization in the same *nonabsorbing material* when illuminated by circularly polarized laser light. This effect was named the inverse Faraday effect (IFE).

The phenomenological considerations from which the IFE was first predicted are reviewed in Sec. 2. In Sec. 3 these phenomenological results are justified from quite general quantum-mechanical considerations. It is shown there that one can define an "effective Hamiltonian" ($\mathcal{H}_{\text{eff}}$) which linearizes the original nonlinear optical problem, and that the thermal average of $\mathcal{H}_{\text{eff}}$ is equal to the general potential function F mentioned above. One term in $\mathcal{H}_{\text{eff}}$ is responsible for the IFE but others describe a variety of different phenomena.

Since the main purpose of this paper is to explain the IFE, most of the results will deal explicitly with magnetic systems but the exisetnce of $\mathcal{H}_{\text{eff}}$ is much more general and it should be a useful technique for other problems.

Sections 4 and 5 illustrate the origin of several types of terms that appear in $\mathcal{H}_{\text{eff}}$. In Sec. 6 the general form of $\mathcal{H}_{\text{eff}}$ will be presented in terms of microscopic phenomenological constants as distinct from the macroscopic ones appearing in F.

Section 7 will describe how time-dependent terms in $\mathcal{H}_{\text{eff}}$ can induce Raman transitions and demonstrate that through $\mathcal{H}_{\text{eff}}$ the Raman cross section can be obtained from macroscopic measurements of other phenomena. The linearization accomplished by means of $\mathcal{H}_{\text{eff}}$ allows the establishment of Kramers-Kronig relations between different nonlinear effects. These will be discussed in Sec. 8 and illustrated with a stimulated Raman effect from a Kramers doublet.

2. INVERSE FARADAY EFFECT

A. Phenomenological Discussion

Consider the E field of a plane wave at an optical frequency ω

$$E(t)=2\,\mathrm{Re}(\tilde{x}\mathcal{E}_x+\tilde{y}\mathcal{E}_y)\exp i(\omega t-kz)$$
$$=2\,\mathrm{Re}[2^{-1/2}(\tilde{x}+i\tilde{y})\mathcal{E}_R+2^{-1/2}(\tilde{x}-i\tilde{y})\mathcal{E}_L]\times\exp i(\omega t-kz)\,, \quad (2.1)$$

where

$$\mathcal{E}_R=(2)^{-1/2}(\mathcal{E}_x-i\mathcal{E}_y)\,, \quad (2.2)$$
$$\mathcal{E}_{\mathrm{L}}=(2)^{-1/2}(\mathcal{E}_x+i\mathcal{E}_y)\,.$$

The IFE follows from the assumption of a potential function F, which for cubic or isotropic media have the form,

$$F=\chi H(\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*)=i\chi H(\mathcal{E}_x\mathcal{E}_y^*-\mathcal{E}_y\mathcal{E}_x^*)\,, \quad (2.3)$$

where H is the component of dc magnetic field along the direction of propagation, the z direction. One can prove that F exists for cubic or isotropic materials and that χ is a real number.[4] Faraday rotation can thus be shown[4,5] to follow from

$$\begin{aligned}\Delta\epsilon_R&=-4\pi\partial^2F/\partial\mathcal{E}_R\partial\mathcal{E}_R^*=-4\pi\chi H\,,\\ \Delta\epsilon_L&=-4\pi\partial^2F/\partial\mathcal{E}_L\mathcal{E}_L^*=4\pi\chi H\,,\end{aligned} \quad (2.4)$$

where $\Delta\epsilon_R$ and $\Delta\epsilon_L$ are the contribution of this potential to the dielectric constant for right and left circularly polarized light. Equivalently one can describe the Faraday effect by

$$\Delta\epsilon_{xy}=-\Delta\epsilon_{yx}=-4\pi\partial^2F/\partial\mathcal{E}_x^*\partial\mathcal{E}_y=i4\pi\chi H\,. \quad (2.5)$$

The Verdet constant V is

$$V=-4\pi^2\chi/n_0\lambda_0[\text{rad Oe}^{-1}\text{ cm}^{-1}]\,, \quad (2.6)$$

where n_0 is the index of refraction of the medium in the absence of a dc field and λ_0 is the vacuum wavelength of the light.

In zero magnetic field the magnetization is given by[4]

$$M=-\partial F/\partial H=-\chi(\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*) \quad (2.7)$$

or in terms of measurable quantities

$$M=\lambda_0 V(2\pi c)^{-1}[I_R-I_L]\,, \quad (2.8)$$

where I_R and I_L are the intensities of right and left circularly polarized light, respectively, in cgs units and M is in Gauss per cubic centimeter.[5] The experiments described in Ref. 5 verified the relationship expressed by Eq. (2.8). The IFE thus consists of a magnetization induced by circularly polarized light in a *nonabsorbing material.*

B. Experimental Review

The IFE has been observed and Eqs. (2.6), (2.7), and (2.8) have been experimentally verified.[5] The experimen-

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[5] J. P. van der Ziel, P. S. Pershan, and L. D. Malmstrom, Phys. Rev. Letters **15**, 190 (1965); P. S. Pershan, J. P. van der Ziel, and L. D. Malmstrom, in *Proceedings of the Physics of Quantum Electronics Conference, San Juan, Puerto Rico, 1965* (to be published).

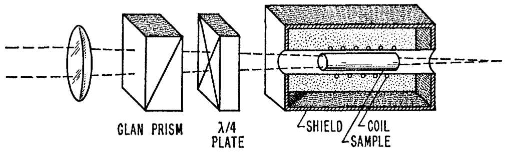

FIG. 1. Schematic illustration of the experimental geometry for observation of the IFE.

tal geometry is shown schematically in Fig. 1. Light from a Q-switched ruby laser is focused on the cylindrically shaped sample by means of a long-focal-length lens ($f\sim 1$ m). A polarizing Glan prism and a $\frac{1}{4}\lambda$ plate oriented to create circularly polarized light were placed between the lens and the sample. A voltage pulse proportional to dM/dt was induced in the coil surrounding the sample (see Eq. 2.8) by the short pulse of circularly polarized laser radiation (pulse width $\sim 30\times 10^{-9}$ sec). The voltage was amplified by a broad-band, low-noise amplifier[6] and displayed on an oscilloscope. Typical signals were from 100 μV to 1 mV at the coil. Figure 2 shows typical traces of signals induced in 3.1% Eu^{2+}: CaF_2 at 4.2°K. The lower trace is a monitor of the laser intensity and the upper curves are the signal. On the left is shown the signal for left-hand circularly polarized light and on the right for right-hand circularly polarized light. Note the change of sign for dM/dt. The second laser pulse is considerably slower than the primary pulse and the second dM/dt signal, reduced by both the intensity of the laser and slower rise time, has a much lower signal-to-noise ratio.

The electrostatic shield shown in Fig. 1 was necessary in order to eliminate pickup signals from the laser system. Spurious signals were detected whenever the laser light struck the sample coil. The long focal length lens reduced the laser cross section to a diameter smaller than the sample diameter, so that with careful alignment it was possible to eliminate some spurious signals. Other signals resulted whenever the ends of the samples were contaminated, or if small "bubbles" and inclusions were present in the sample. Some of these spurious signals could be distinguished by their time dependence (different from dM/dt) and by comparison with different samples.

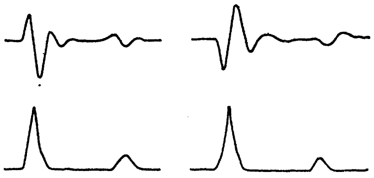

FIG. 2. Typical IFE signals observed in Eu^{++}: CaF_2 at 4.2°K. The signals are on top and the laser power is shown below. On the left is the signal for left circularly polarized light and on the right for right circularly polarized light.

As discussed in Ref. 5 the IFE was observed in a paramagnetic sample, Eu^{++}: CaF_2, a number of diamagnetic glasses, and a variety of liquids. The $1/T$ dependence characteristic of paramagnetic systems was observed in Eu^{++}: CaF_2 and correlated with measurements on the Verdet constant. The effect was shown to satisfy Eq. (2.8) independent of the material used. Thus a plot of (M/I_R) versus V fell on a straight line for all of the solid samples measured (Eu^{++}: CaF_2 as well as the diamagnetic glasses). Comparison between liquids and solids was made difficult by different sample geometries but there was substantial agreement between these too.

3. THE EFFECTIVE HAMILTONIAN

In this section we will derive an effective Hamiltonian that completely describes the effects of light on the lowest lying states of a general quantum-mechanical system. The main assumption will be that the optical frequency is not resonant with any atomic frequency and consequently there are no "first-order" absorption processes.

Consider the total Hamiltonian $\mathcal{H}=\mathcal{H}_0+V(t)$, where $\mathcal{H}_0$ represents the Hamiltonian in the absence of a light field and $V(t)$ can be written in its most general form

$$V(t)=v(t)\exp(i\omega t)+v^*(t)\exp(-i\omega t)\,, \qquad (3.1)$$

where ω is the mean angular frequency of the optical field and $v(t)$, $v^*(t)$ describe the fact that the radiation is not necessarily monochromatic. Assume $\langle v(t)v^*(t+\tau)\rangle_{\text{av}}$ independent of t and vanishingly small for $|\tau|>\tau_c$, where $\tau_c\omega\gg 1$. In the interaction representation the wave equation becomes

$$-(\hbar/i)(\partial/\partial t)\bar{\psi}(t)=\bar{V}(t)\bar{\psi}(t)\,, \qquad (3.2)$$

where

$$\bar{\psi}(t)=\exp i(\mathcal{H}_0 t/\hbar)\psi(t)\,, \qquad (3.3)$$

and

$$\bar{V}(t)=\exp i(\mathcal{H}_0 t/\hbar)V(t)\exp(-i\mathcal{H}_0 t/\hbar)\,. \qquad (3.4)$$

The general solution to Eq. (3.2) is

$$\bar{\psi}(t)=\bigg[1-\frac{i}{\hbar}\int_0^t \bar{V}(t')\,dt' -\frac{1}{\hbar^2}\int_0^t \bar{V}(t')\,dt'\int_0^{t'} \bar{V}(t'')\,dt''+\cdots\bigg]\psi(0)\,. \qquad (3.5)$$

Since we are interested solely in the effects of $V(t)$ on the lowest lying states, i.e., the states of the ground multiplet, we can introduce an effective Hamiltonian $\mathcal{H}_{\text{eff}}(t)$ such that if $|a\rangle$ and $|b\rangle$ are eigenstates of the

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[6] The amplifier design was provided by Professor A. van der Ziel. Equivalent commercial units are now available.

ground multiplet

$$\langle a|1-\frac{i}{\hbar}\int_0^t \mathcal{H}_{\text{eff}}(t')\,dt'+\cdots|b\rangle$$
$$=\langle a|1-\frac{i}{\hbar}\int_0^t \bar{V}(t')\,dt'$$
$$-\frac{1}{\hbar^2}\int_0^t \bar{V}(t')\,dt'\int_0^{t'} \bar{V}(t'_{\,\prime})\,dt''+\cdots|b\rangle. \quad (3.6)$$

Taking $\langle a|\bar{V}(t')|b\rangle=0$

$$\langle a|\mathcal{H}_{\text{eff}}(t)|b\rangle$$
$$=-\frac{i}{\hbar}\sum_n\langle a|\bar{V}(t)|n\rangle\int_0^t\langle n|\bar{V}(t')|b\rangle\,dt', \quad (3.7)$$

where the summation extends over all the excited states $|n\rangle$ of the system. Furthermore we are only interested in the low-frequency terms on the right-hand side. Physical effects due to high-frequency terms appear only when $\mathcal{H}_{\text{eff}}$ is taken to higher order in the perturbation $\bar{V}(t)$. On the assumption that $|\omega\pm\omega_{nb}|\tau_c\gg1$, where $\omega_{nb}=(E_n-E_b)/\hbar$, one can carry out the integration to obtain $\mathcal{H}_{\text{eff}}(t)$ or, in the Schrödinger representation, $[\mathcal{H}_{\text{eff}}(t)]_{ab}=\exp[-i(\omega_{ab})t]\mathcal{H}_{\text{eff}}(t)_{ab}$

$$\mathcal{H}_{\text{eff}}(t)_{ab}=-\hbar^{-1}\sum_n\left[\frac{v_{an}(t)v_{nb}^*(t)}{\omega_{nb}-\omega}+\frac{v_{an}^*(t)v_{nb}(t)}{\omega_{nb}+\omega}\right]. \quad (3.8)$$

The effects of any high-frequency, nonresonant, perturbation on the ground states of a quantum-mechanical system can always be described in terms of an effective Hamiltonian. For example, in addition to the magnetic effects to be discussed here, the effects of high-frequency phonons on the quadrupole levels of nuclei in a solid are described by Eq. (3.8) when v is taken to be the phonon-quadrupole interaction. There are numerous other phenomena to which Eq. (3.8) could also be applied; in fact, this partially parallels the list of phenomena for which the generalized potential functions would be useful.[1,4] For our purposes, however, let us specialize to the optical case. Taking[7]

$$V(t)=-2\,\text{Re}[e\mathbf{r}\cdot\boldsymbol{\mathcal{E}}(t)\exp i(\omega t-\mathbf{k}\cdot\mathbf{r})]$$

yields a dielectric tensor, without local-field corrections, of the form

$$\frac{(\epsilon-1)_{ij}}{4\pi}=\sum_{ab}\chi_{ab}{}^{ij}\rho_{ba}, \quad (3.9)$$

where $\chi_{ab}{}^{ij}$ are given by well-known expressions for the polarizability and ρ_{ba} is the density matrix for the atomic system. On substitution of the above form of $V(t)$ into Eq. (3.8) one can easily show that if $|\omega_{nb}-\omega_{na}|\ll|\omega_{nb}\pm\omega|$

$$\mathcal{H}_{\text{eff}}(t)_{ab}=-\sum_{ij}\chi_{ab}{}^{ij}\mathcal{E}_i{}^*\mathcal{E}_j \quad (3.10)$$

or defining the potential function

$$F=+\sum_{ab}\mathcal{H}_{\text{eff}}(t)_{ab}\rho_{ba}=-\sum_{i,j,a,b}\chi_{a,b}{}^{ij}\mathcal{E}_i{}^*\mathcal{E}_j\rho_{ba} \quad (3.11)$$

one has $(\epsilon-1)_{ij}/4\pi=-\partial^2F/\partial\mathcal{E}_i{}^*\partial\mathcal{E}_j$ as asserted in the phenomenological theory.[4] Furthermore if one includes in $\mathcal{H}_0$ the effects of a dc magnetic field, then, since F is a thermal average of the real Hamiltonian $\mathcal{H}_{\text{eff}}$, conventional thermodynamics justifies Eq. (2.7) for $M(t)$ when $\mathcal{E}(t)\mathcal{E}^*(t)$ changes slowly compared to thermal relaxation times of the system.

We have thus demonstrated the existence of $\mathcal{H}_{\text{eff}}$ and for a particular perturbation illustrated how its thermal average is related to the high-frequency response functions, i.e., ϵ_{ij}. We have further shown from microscopic considerations that in cases of thermal equilibrium the phenomenological relations epitomized by Eq. (2.7) are correct.

4. EVALUATION OF $\mathcal{H}_{\text{eff}}(H_{\text{dc}}=0)$

Evaluation of $\mathcal{H}_{\text{eff}}$ is equivalent to calculating ϵ_{ij} and although the general expressions for the dielectric constants are well known, it is almost always impossible to compute a numerical value for ϵ_{ij} since one does not know the excited states and their energies in sufficient detail. Nevertheless it will be of some interest to demonstrate the qualitative features of the calculation.

Taking the electric field of Eq. (2.1)

$$v(t)=+e(r_+\mathcal{E}_R-r_-\mathcal{E}_L), \quad (4.1)$$

where $r_\pm=\mp(2)^{-1/2}(x+iy)$, Eq. (3.8) can be written

$$(\mathcal{H}_{\text{eff}})_{ab}=e^2\hbar^{-1}[\mathcal{E}_R\mathcal{E}_R{}^*-\mathcal{E}_L\mathcal{E}_L{}^*]\sum_n\frac{\omega}{\omega_{nb}{}^2-\omega^2}[(r_+)_{an}(r_-)_{nb}-(r_-)_{an}(r_+)_{nb}]$$
$$+e^2\hbar^{-1}[\mathcal{E}_R\mathcal{E}_R{}^*+\mathcal{E}_L\mathcal{E}_L{}^*]\sum_n\frac{\omega_{nb}}{\omega_{nb}{}^2-\omega^2}[(r_+)_{an}(r_-)_{nb}+(r_-)_{an}(r_+)_{nb}]$$
$$-2(e^2\hbar^{-1})\mathcal{E}_R\mathcal{E}_L{}^*\sum_n\frac{\omega_{nb}}{\omega_{nb}{}^2-\omega^2}(r_+)_{an}(r_+)_{nb}-2(e^2\hbar^{-1})\mathcal{E}_L{}^*\mathcal{E}_R\sum_n\frac{\omega_{nb}}{\omega_{nb}{}^2-\omega^2}(r_-)_{an}(r_-)_{nb}. \quad (4.2)$$

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[7] J. Fiutak, Can. J. Phys. **41**, 12 (1963).

Assume that J is a good quantum number for the ground-state manifold. Note that this does not say that the ground state is isotropic but rather that the strength of the "crystal-field" perturbation is weaker than the electron-electron interactions. The particular crystal-field ground state is a linear combination of different M values $|0J\Gamma\mu\rangle=\sum_M|0JM\rangle\langle M|\Gamma\mu\rangle$. A valid procedure is to calculate all the matrix elements $\langle 0JM''|\mathcal{H}_{\text{eff}}|0JM\rangle$ and from knowledge of the $\langle M|\Gamma\mu\rangle$ one can calculate pertinent matrix elements between the states of real interest (i.e., $|0J\Gamma\mu\rangle$).

This same procedure can be followed even if J is not a good quantum number so long as L is. For example, with a ground state $|0LS\Gamma\mu\rangle=\sum_M|0LM_LSM_s\rangle\langle M_LM_s|\Gamma\mu\rangle$ one replaces every J in the equations that follow with L; all matrix elements of $\mathcal{H}_{\text{eff}}$ between states $|0LM_LSM_S\rangle$ and $|0LM_L'SM_S'\rangle$ will be diagonal in M_s.

Relying on the theory of tensor operators[8] one can replace the matrix elements of r_+ and r_- by

$$(\alpha J'M'|r_\pm|0JM)=(-1)^{J'-M'}\begin{pmatrix} J' & 1 & J \\ -M' & \pm1 & M\end{pmatrix}(\alpha J'\|r\|0J)\,, \quad (4.3)$$

where $(\alpha J'\|r\|0J)$ is independent of M and M'. Assume also that the dc magnetic field is zero and that one can neglect the dependence of $\omega_{\alpha J'M':0JM}$ on M' and M (i.e., $\omega_{\alpha J'M':0JM}=\omega_{\alpha J':0J}$).[9] This is equivalent to neglecting the crystal-field splitting of the various J' multiplets. If one uses states $|0LS\Gamma\mu\rangle$ one must neglect the energy's dependence on $\Gamma\mu$. On substitution of (4.3) into (4.2), one obtains $\langle 0JM''|\mathcal{H}_{\text{eff}}|0JM\rangle$, the result depending only on J, M, and M'' and being summed over different configuration quantum numbers α. Further simplification results from the observation that the dependence on M and M'' can be simulated by replacing the actual functions of M and M'' by matrix elements of the type $\langle M''|J_z|M\rangle$, $\langle M''|J_z^2|M\rangle$, and $\langle M''|J_\pm^2|M\rangle$. For our purposes we will neglect terms independent of M. One thus obtains

$$\begin{aligned}\mathcal{H}_{\text{eff}}=&(\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*)J_zA\\ &+\{(\mathcal{E}_R\mathcal{E}_R^*+\mathcal{E}_L\mathcal{E}_L^*)[J_z^2-\tfrac{1}{3}J(J+1)]\\ &-\mathcal{E}_{\rm L}\mathcal{E}_R^*J_-^2-\mathcal{E}_L^*\mathcal{E}_RJ_+^2\}C\,, \quad (4.4)\end{aligned}$$

where

$$\begin{aligned}A=(2e^2/\hbar)\sum_\alpha\bigg[&\frac{\omega\langle 0J\|r\|\alpha J-1\rangle\langle\alpha J-1\|r\|0J\rangle}{(2J+1)(2J)[(\omega_{\alpha J-1,0J})^2-\omega^2]}\\ &-\frac{2\omega\langle 0J\|r\|\alpha J\rangle\langle\alpha J\|r\|0J\rangle}{(2J+2)(2J+1)(2J)[(\omega_{\alpha J,0J})^2-\omega^2]}\\ &-\frac{\omega\langle 0J\|r\|\alpha J+1\rangle\langle\alpha J+1\|r\|0J\rangle}{(2J+2)(2J+1)[(\omega_{\alpha J+1,0J})^2-\omega^2]}\bigg] \quad (4.5)\end{aligned}$$

and

$$\begin{aligned}C=\frac{2e^2}{\hbar}\sum_\alpha\bigg[&\frac{\omega_{\alpha J-1,0J}\langle 0J\|r\|\alpha J-1\rangle\langle\alpha J-1\|r\|0J\rangle}{(2J+1)(2J)(2J-1)[(\omega_{\alpha J-1,0J})^2-\omega^2]}\\ &+\frac{2\omega_{\alpha J,0J}\langle 0J\|r\|\alpha J\rangle\langle\alpha J\|r\|0J\rangle}{(2J+2)(2J+1)(2J)[(\omega_{\alpha J,0J})^2-\omega^2]}\\ &+\frac{\omega_{\alpha J+1,0J}\langle 0J\|r\|\alpha J+1\rangle\langle\alpha J+1\|r\|0J\rangle}{(2J+3)(2J+2)(2J+1)[(\omega_{\alpha J+1,0J})^2-\omega^2]}\bigg]. \quad (4.6)\end{aligned}$$

The relationship between this effective Hamiltonian and the IFE is clear. In the presence of circularly polarized light, $\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*$, the crystal is no longer invariant under time reversal and symmetry no longer requires that spins parallel and antiparallel to the direction of light propagation have the same energy. Thus $\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*$ acts as an effective magnetic field ($\mathcal{H}_{\text{eff}}=+g\beta H_{\text{eff}}J_z$)

$$H_{\text{eff}}=+(\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*)A(g_J\beta)^{-1}\,, \quad (4.7)$$

which polarizes the spins. At thermal equilibrium, for kT much greater than the splitting of the different crystal-field states of the ground multiplet,

$$\langle J_z\rangle_{\text{thermal}}=-[J(J+1)/3kT](\mathcal{E}_R\mathcal{E}_R^*-\mathcal{E}_L\mathcal{E}_L^*)A \quad (4.8)$$

and the inverse Faraday effect is thus described by

$$M=-g_J\beta\langle J_z\rangle_{\text{thermal}}N\,, \quad (4.9)$$

where N is the number of atoms per unit volume.

Comparison with Eq. (2.7) shows

$$\chi=[-g_J\beta J(J+1)/3kT]NA\,. \quad (4.10)$$

These expressions and the effective Hamiltonian, from which they were obtained, describe the paramagnetic IFE. The diamagnetic effects arise from terms in $\mathcal{H}_{\text{eff}}$ which depend on H_{dc} and which were excluded from this calculation. This will be discussed later. The terms in J_z^2 and $J_\pm^2$ will cause further splittings but in the absence of a dc magnetic field they cannot produce a magnetization.

The ion Eu^{++} with which the original IFE measurement were carried out,[5] has ground state $^8S_{7/2}$ and the operator J_z is equivalent to the spin operator S_z. For this case, and similarly for all other S-state ions, A is nonvanishing because the spin-orbit coupling, $\lambda\mathbf{L}\cdot\mathbf{S}$, lifts the degeneracy of the $^{2S+1}P_{S-1}$, $^{2S+1}P_S$, $^{2S+1}P_{S+1}$ states. Terms quadratic in $\mathbf{S}$, however, only appear when spin-orbit interactions are taken twice. Thus for S-state ions, if the only effect of spin-orbit interactions is to lift the ^{2S+1}P degeneracy, $C=0$. For non-S-state ions however, spin-orbit interaction is automatically employed in choosing a ground state $^{2S+1}L_J$, and its use once more to lift the degeneracy of the excited states is sufficient to ensure $C\neq0$.

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[8] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 75.

[9] This assumption has been discussed in relation to the Faraday effect by J. H. Van Vleck and M. H. Hebb, Phys. Rev. **46**, 17 (1934).

5. EVALUATION OF $\mathcal{H}_{\text{eff}}$ FOR A DIAMAGNETIC EXAMPLE, $H_{\text{dc}}\neq 0$

The general expressions (3.8) or (4.2) could be evaluated using states $|a\rangle$ and $|b\rangle$ which are eigenfunctions of a Hamiltonian $\mathcal{H}_0$ that contains the effects of a dc magnetic field. This would result in rather cumbersome expressions which could not be numerically evaluated and the equivalent of Eq. (4.5) and (4.6) for the case of $H_{\text{dc}}\neq 0$ will not be presented here. It will however be possible from purely symmetry considerations, to write down the general form of $\mathcal{H}_{\text{eff}}$ in terms of phenomenological constants like A and C. Before proceeding to that however it will be informative to treat one special example to illustrate the quantum-mechanical origin of the "diamagnetic" IFE.

Consider a diamagnetic molecule[10] with a singlet, isotropic ground state $|0\rangle$. Let there be two excited states $|+\rangle=\alpha|x\rangle+i\gamma|y\rangle$ and $|-\rangle=\alpha|y\rangle+i\gamma|x\rangle$ with energies $E_{\pm}=\hbar\omega_{\pm}=\hbar\bar{\omega}\pm[(\hbar\Delta\omega)^2+(g\beta H)^2]^{1/2}$ and $(\gamma/\alpha)=g\beta H\{\hbar\Delta\omega+[(\hbar\Delta\omega)^2(g\beta H)^2]^{1/2}\}^{-1}$; take $\hbar\bar{\omega}\gg h\Delta\omega\gg g\beta H$ where g is an effective g value for the excited state. This is illustrated in Fig. 3. The states $|x\rangle$ and $|y\rangle$ have the properties $\langle x|X|0\rangle=\langle 0|X|x\rangle=\langle y|Y|0\rangle=\langle 0|Y|y\rangle$ and all other matrix elements of $\mathbf{r}$ are zero. This calculation will be done only for the z axis of the molecule parallel to the direction of light propagation. The result of averaging over all molecular orientations would simply be to reduce A' by a factor $\frac{1}{3}$. Substitution into the leading term in Eq. (4.2) obtains

$$\mathcal{H}_{\text{eff}}=A'H(\mathcal{E}_R\mathcal{E}_R{}^*-\mathcal{E}_L\mathcal{E}_L{}^*), \tag{5.1}$$

where $A'=-(e/\hbar)^2 g\beta|\langle 0|X|x\rangle|^2 4\omega\bar{\omega}(\omega^2-\omega^2)^{-2}$.

Equation (5.1) describes the fact that circularly polarized light mixes a fraction of the excited-state wave function into the ground state and causes the perturbed ground state to have a net magnetic moment,

$$\mu=-A'(\mathcal{E}_R\mathcal{E}_R{}^*-\mathcal{E}_L\mathcal{E}_L{}^*). \tag{5.2}$$

With N molecules per unit volume circularly polarized light induces a magnetization as per Eq. (2.7) but with a temperature-independent

$$\chi=+NA'. \tag{5.3}$$

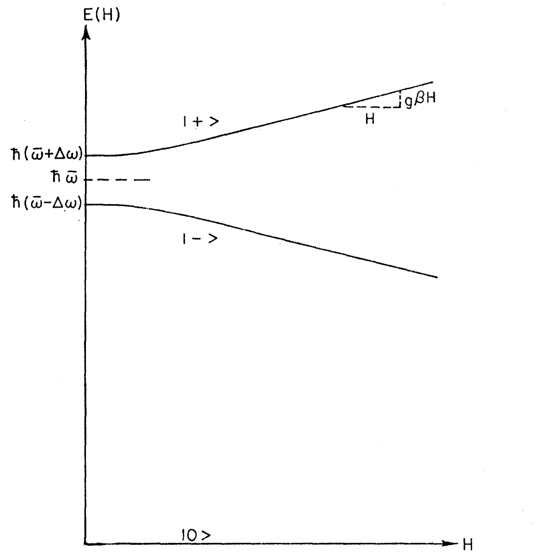

FIG. 3. Typical energy levels for a diamagnetic system. In zero magnetic field $|+\rangle$ and $|-\rangle$ are $|x\rangle$ and $|y\rangle$ states, respectively, and the splitting is due to an asymmetric crystal field.

A similar term must also appear for paramagnetic ground states and Van Vleck and Hebb[9] write the general form of the Verdet constant as $V=a+b/T$. The temperature-independent term is related to the effects discussed here. The b/T factor arises from the paramagnetic terms discussed in Sec. 4.

6. GENERAL FORM FOR $\mathcal{H}_{\text{eff}}$ WHEN $H_{\text{dc}}\neq 0$

Consider a material of cubic symmetry; then $\mathcal{H}_{\text{eff}}$ must be invariant under all those operations that leave the crystal invariant. It is thus possible to demonstrate that if the ground state has an "effective spin" S

$$\begin{aligned}\mathcal{H}_{\text{eff}}=&+i(\boldsymbol{\varepsilon}\times\boldsymbol{\varepsilon}^*)\cdot[A\mathbf{S}+A'\mathbf{H}]-(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}^*)[BS(S+1)+B'H^2+B''(\mathbf{S}\cdot\mathbf{H})]\\&-\textstyle\sum_\alpha \mathcal{E}_\alpha\mathcal{E}_\alpha{}^*[C(S_\alpha{}^2-\frac{1}{3}S(S+1))+C'(H_\alpha{}^2-\frac{1}{3}H^2)+C''(S_\alpha H_\alpha-\frac{1}{3}\mathbf{S}\cdot\mathbf{H})]-\displaystyle\sum_{\alpha>\beta}(\mathcal{E}_\alpha\mathcal{E}_\beta{}^*+\mathcal{E}_\beta\mathcal{E}_\alpha{}^*)\\&\times[D(S_\alpha S_\beta+S_\beta S_\alpha)+D'(2H_\alpha H_\beta)+D''(S_\alpha H_\beta+S_\beta H_\alpha)]+\text{terms of higher order in } S,\ H, \text{ etc.,}\end{aligned} \tag{6.1}$$

where the directions α, β, etc., are the $\langle 1,0,0\rangle$ directions of the cubic crystal. The coefficients A, A', B, B', etc., appear here as phenomenological constants whose values must be inferred from either experiments or quantum-mechanical calculation. As mentioned in Sec. 4, the coefficients of terms linear in $\mathbf{S}$ are linearly dependent, and terms quadratic in $\mathbf{S}$ are quadratically dependent, on the spin-orbit interaction. In the approximation for which Eq. (4.4) was derived, taking $\mathbf{S}=\mathbf{J}$, Eqs. (4.5) and (4.6) are expressions for A and $C=2D$. In the case of a crystal field, however, one may express the ground states as a linear combination of $|JM\rangle$ states, i.e., $|S'M'\rangle=\sum_M|JM\rangle\langle JM|S'M'\rangle$ where S' is the effective spin. Matrix elements of $\mathcal{H}_{\text{eff}}$, given by Eq. (4.4), between $|S'M'\rangle$ states can be generated by Eq. (6.1) if

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[10] This model is a good approximation to the derivatives of the porphyrin molecules on which Faraday rotation measurements have been made, and should also approximate the qualitative features of many other diamagnetic molecules. The theory of Faraday rotation in these and other diamagnetic molecules will be presented elsewhere: P. S. Pershan, M. Gouterman, and R. L. Fulton, Mol. Phys. (to be published).

A, C, and $D(C\neq 2D)$ are taken as proper linear combinations of Eqs. (4.5) and (4.6).

Quantum-mechanical expressions for the other coefficients in Eq. (6.1) could also be obtained from Eq. (4.2) if one started with correct states $|a\rangle$ and $|b\rangle$ and carried out the calculation to sufficient order in H. From a practical point of view, this does not seem likely to yield new information. As mentioned above, numerical evaluation of any of these terms is similar to calculation of a dielectric constant and one almost never knows the excited states sufficiently well to obtain a meaningful number.

Experimentally one can determine A and A' from Eqs. (6.1) or Eq. (4.10) by measuring the Verdet constant. For example, in the case of Eu^{2+} in CaF_2,[5] assuming a concentration of Eu^{2+} ions equivalent to the mole fraction of EuF_3 added to the mixture from which the crystal was grown, leads to a value of $A=-3.5\times 10^{-26}$ ergs $(\text{dyne/esu})^{-2}$ or in other units 4.8×10^{-5} cps $(\text{V/cm})^{-2}$. Since the concentration of Eu^{2+} ions is likely to be smaller than this, the above value is probably a lower limit. Theoretically one can also obtain an estimate of A for Eu^{2+}: CaF_2 by assuming it arises mainly from the lowest lying $(f^6d\ {}^8P)$ states and that the degeneracy of these states is lifted by a spin-orbit interaction $\zeta L\cdot S$. Equation (4.5) can be reduced to

$$A=-(\tfrac{4}{3})|(d\|r\|f)|^2e^2\omega_{\alpha,7/2;0,7/2}\omega\zeta\hbar^{-1}\times[(\omega_{\alpha,7/2;0,7/2})^2-\omega^2]^{-2}.$$

Reasonable numerical values $\zeta=500\ \text{cm}^{-1}$, $\omega_{\alpha,7/2,0,7/2}=2\pi c(30\,000\ \text{cm}^{-1})$, and $\langle f\|r\|d\rangle\approx 10^{-8}$ cm yields, for ruby wavelengths, $A\approx -1.3\times 10^{-25}$ ergs $(\text{dyn/esu})^{-2}$ which is about four times larger than our experimental lower limit. In view of the approximations employed in both the experimental and theoretical determination of A these values are in satisfactory agreement.

Measurement of the Cotton-Mouton effect could determine C', C'', D', and D'' and possibly C and D. For example if H is in the z direction

$$(\epsilon_{zz}-\epsilon_{xx})/4\pi=-[g\beta H^2(S)(S+1)/3kT]NC''+H^2NC'+(g^2\beta^2H^2/10k^2T^2)[\tfrac{2}{3}S(S+1)-\tfrac{1}{2}]NC;\quad(6.2)$$

the last term comes from the thermal average of $(S_z^2-S_x^2)$. The term $B''(\mathbf{S}\cdot\mathbf{H})$ predicts an intensity-dependent isotropic shift in the g factor and the C'' and D'' terms contribute anisotropic g-factor shifts. The C and D terms induce intensity-dependent contributions to the zero-field splittings. In the presence of a dc magnetic field laser radiation can induce a magnetization through the B' and B'' terms but not through the B term which has no effect.[5] Magnetizations induced through the B' and B'' terms would not be an inverse Cotton-Mouton effect and could possibly be larger than that effect.

Numerical estimates of some of these terms for paramagnetic crystals (in which Cotton-Mouton or Faraday effects have not been measured) may be obtained by comparing $\mathcal{H}_{\text{eff}}$ as given by Eq. (6.1) with the phenomenological Hamiltonian used to interpret the experiments on linear electric-field shifts of electron-spin-resonance lines.[11] If the ion in question is not at a site of inversion symmetry, the phenomenological Hamiltonian is of the form $\mathcal{H}_s=\sum_{ij}\varphi_{ijk}H_iS_jE_k+\sum_{ij}r_{ijk}S_iS_jE_k$. Assuming an internal local field E_{int} of 10^7 V/cm resulting from this lack of inversion symmetry one may compare $\boldsymbol{\varphi}$ and $\mathbf{r}$ to the quantities C'' and C, respectively. Typical values of $\mathbf{r}/E_{\text{int}}$ are of the order 10^{-4} cps/$(\text{V cm}^{-1})^2$ or in cgs units $\sim 6\times 10^{-26}$ ergs$(\text{dyn/esu})^{-2}$ which is comparable to our measured value of $A\simeq -3.5\times 10^{-26}$ ergs $(\text{dyn/esu})^{-2}$ for Eu^{++} in CaF_2. The quantity φ/E_{int} is two or three orders of magnitude smaller.

Suits and Argyle[12] measured both the Faraday rotation and Cotton-Mouton effects in ferromagnetic EuSe and found them to be of the same order of magnitude at fields of about 5000 G. These effects are related primarily to the expectation values of S_z and S_z^2, respectively, and the field dependence enters only as it changes these expectation values.[13] Thus in EuSe A and either C or C'' are of the same order of magnitude. From Suits and Argyle's measurements on paramagnetic EuSe[14] the Verdet constant varies as $(1/T)$ and is 57 times larger than the paramagnetic Verdet constant in Eu^{2+}: CaF_2.[5] However, since EuSe is about 30 times more concentrated, in terms of spins per unit volume, the A's of these two crystals are approximately equal and thus the C or (C'') of EuSe must also be $\sim 3.5\times 10^{-26}$ ergs $(\text{dyn/esu})^{-2}$ which is the A value of Eu^{+2}: CaF_2. This is consistent with our previous estimates based on the linear electric field effects.

7. RAMAN EFFECTS

The effective Hamiltonian, Eq. (5.3) can be separated into

$$\mathcal{H}_{\text{eff}}=\mathcal{H}'_{\text{eff}}+\mathcal{H}''_{\text{eff}},\tag{7.1}$$

where $\mathcal{H}'_{\text{eff}}$ is diagonal in the eigenstates of the unperturbed Hamiltonian and $\mathcal{H}''_{\text{eff}}$ has only off-diagonal matrix elements. For perfectly monochromatic radiation, to lowest order in the perturbation, $\mathcal{H}''_{\text{eff}}$ would induce no physical effects. In general laser radiation is not perfectly monochromatic and $\mathcal{E}_R$ and $\mathcal{E}_L$ are functions of time. The effective Hamiltonian was derived on the assumption that $\mathcal{E}_R(t)$ and $\mathcal{E}_L(t)$ could be time-dependent [see Eqs. (3.1) to (3.8)] and in fact all of the equations obtained so far are still correct providing $\mathcal{E}_\alpha(t)\mathcal{E}_\beta{}^*(t)$ is a slowly varying function of time. In this

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[11] N. Bloembergen, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1962), p. 39.

[12] J. C. Suits and B. E. Argyle, Phys. Rev. Letters **14**, 687 (1965).

[13] N. Bloembergen, P. S. Pershan, and L. R. Wilcox, Phys. Rev. **120**, 2014 (1960).

[14] J. C. Suits and B. E. Argyle, J. Appl. Phys. **36**, 1251 (1965).

case slowly varying simply means slow compared to $|\omega \pm \omega_{na}|$. Thus if

$$\mathcal{H}''_{\text{eff}}(\omega_n) = T^{-1} \int_{-T/2}^{+T/2} \mathcal{H}''(t) \exp(-i\omega_n t) dt, \quad (7.2)$$

where $\omega_n = 2\pi n T^{-1}$,

$$\mathcal{H}''_{\text{eff}}(t) = \sum_n \mathcal{H}''(\omega_n) \exp i\omega_n t \quad (7.3)$$

and

$$\mathcal{H}''_{\text{eff}}(\omega_n) = -\sum_{i,j} \chi_{a,b}{}^{i,j} \sum_m \mathcal{E}_i{}^*(\omega_m) \mathcal{E}_j(\omega_m + \omega_n). \quad (7.4)$$

Unless rather extreme precautions are taken almost all lasers oscillate simultaneously at a number of discrete frequencies near the mean laser frequency.[15] Assume a laser with a sufficiently broad spectral output that the envelope of the beat frequency Fourier intensities, $\mathcal{H}''_{\text{eff}}(\omega_n)$, has a width $\Delta\omega_{\text{laser}}$ greater than some crystal field, or Zeeman, splittings of the atomic system. In weak dc fields, for example, typical splittings are of 0.01 $\text{cm}^{-1} \sim 0.1$ cm^{-1}. If the spacing between adjacent beat frequencies is small compared to the atomic linewidths, the effective Hamiltonian, Eq. (7.4), will always have resonant terms that can induce transitions between states $|a\rangle$ and $|b\rangle$. The transition probability per unit time is

$$W_{a\to b} = 2\pi\hbar^{-2} \sum_n g(\omega_n - \omega_{ba}) |\mathcal{H}''_{\text{eff}}(\omega_n)_{ab}|^2, \quad (7.5)$$

where $g(\omega_n - \omega_{ba})$ is the atomic-line-shape function. For convenience assume only one polarization component. For example, one sense of circular polarization would be suitable if $\mathcal{H}_{\text{eff}}$ consists of only the A term in Eq. (6.1). Further simplification results if the Fourier components $\mathcal{E}(\omega_n)$, $\mathcal{E}(-\omega_n)$, $\mathcal{E}^*(\omega_n)$, etc., are taken to be independent random variables. It follows from this that the average of $W_{a\to b}$ is proportional to the statistical average $\langle |(\mathcal{E}\mathcal{E}^*)_{\omega_\nu}|^2 \rangle$, where $(\mathcal{E}\mathcal{E}^*)_{\omega_\nu} = \sum_m \mathcal{E}^*(\omega_m)\mathcal{E}(\omega_m + \omega_\nu)$. Taking

$$\langle |(\mathcal{E}\mathcal{E}^*)_{\omega_\nu}|^2 \rangle = (2\pi)^{1/2} (T\Delta\omega_{\text{laser}})^{-1} \langle |\mathcal{E}(t)\mathcal{E}^*(t)|^2 \rangle \times \exp\{-\omega_\nu{}^2 [2(\Delta\omega_{\text{laser}})^2]^{-1}\}$$

as a simple distribution function satisfying

$$\sum_\nu \langle |(\mathcal{E}\mathcal{E}^*)_{\omega_\nu}|^2 \rangle = \langle |\mathcal{E}(t)\mathcal{E}^*(t)|^2 \rangle,$$

one can show that for a Gaussian random process $\langle |\mathcal{E}(t)\mathcal{E}^*(t)|^2 \rangle = 2\langle \mathcal{E}(t)\mathcal{E}^*(t) \rangle^2$, so that for $\omega_{ab} \ll (\Delta\omega)_{\text{laser}}$

$$W_{ab} \approx 4\pi\hbar^{-2} |\langle \mathcal{H}_{\text{eff}} \rangle|^2 (\Delta\omega_{\text{laser}})^{-1}. \quad (7.6)$$

Note that since $\mathcal{E}(t)$ is complex $\langle \mathcal{E}(t)^2 \rangle = 0$.

The IFE measurements on Eu^{++}: CaF_2 yielded a value of $\mathcal{H}_{\text{eff}}$ corresponding to $H_{\text{eff}} = 0.01$ G[5] [see Eq. (4.7)] using an unfocused Q-switched ruby laser. Taking a conservative value of $(\Delta\omega)_{\text{laser}} = 2\pi \times 10^{10}$ cps obtains $W_{ab} = 16\pi^3 (2.8 \times 10^4)^2 (2\pi \times 10^{10})^{-1}$ $\text{sec}^{-1} \approx 6.2$ sec^{-1}. With 10^{21} spins per cm^3 this rate implies approximately 6×10^{21} photons/sec are inelastically scattered by 1 cm^3 of material. Since the incident flux of 6940-Å photons required to induce this transition rate was approximately 3.5×10^{25} photon sec^{-1} cm^{-2} approximately 0.04% of the incident photons are scattered per centimeter of path length. Unfortunately since they are all scattered parallel to the incident beam, similarly polarized, and frequency shifted by only a fraction of the laser bandwidth, this mechanism produces a negligible change in the incident light beam. Spin-lattice relaxation rates are also considerably shorter than 6 sec^{-1} so that, although this mechanism induces transitions tending to saturate the spin system, relaxation processes do not allow a change in the dc magnetic moment.

Focused lasers are capable of producing optical power density 100 times larger. These could induce transition rates of 6×10^4 sec^{-1} which may be short compared to a spin-lattice relaxation time and would partially saturate the spin system. This effect might be detected as a change of an electron spin resonance intensity. Note however that these power densities can only be maintained over a much smaller volume so that the fraction of scattered photons only increases by a factor of 100 to 4% of the incident photons. With this scattering factor the stimulated Raman mechanism may induce detectable changes in the fine structure of the laser frequency distribution. If the laser linewidth is not appreciably larger than the Zeeman or crystal field splitting, this mechanism might possibly be detected as a change in the optical linewidth.

In Sec. 8 we discuss a particular example in which the the spectrum consists of only two frequency components separated by an atomic resonance frequency. In that case this effect may be more readily detected.

This entire calculation was done on the assumption of classical fields. The vectors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}^*$ could of course be replaced by creation and annihilation operators and the cross section for spontaneous Raman transitions obtained. The atomic cross section for scattering an incident photon with complex polarization unit vector $\tilde{e}(0)$ and frequency ω_0 into one with polarization $\tilde{e}(k)$ and frequency $\omega_k < \omega_0$ propagating into a solid angle $d\Omega_k$ is

$$\frac{d\sigma_{0\to\mathbf{k}}}{d\Omega} = \omega_0 \omega_k{}^3 c^{-4} \times \sum_{a,b} \{ |\sum_{i,j}{}' \chi_{ba}{}^{ij} [e(k)_i]^* [e(0)_j]|^2 \rho_{aa} \}, \quad (7.7)$$

where the primed summation is only over states $|b\rangle$ such that $\omega_0 - \omega_k \approx \omega_{b,a} > 0$. For anti-Stokes scattering

$$\omega_k - \omega_0 \approx \omega_{b,a} > 0.$$

Using the measured value of $A \approx -3.5 \times 10^{-26}$ ergs $(\text{dyn/esu})^{-2}$ from Eq. (4.4), or (6.1), and Eq. (3.10) the cross section of Eq. (7.8) can be estimated numerically. Consider an effective spin $\frac{1}{2}$ with this value of A. Then for $\rho_{aa} = \frac{1}{2}$ and light propagating perpendicular to

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[15] R. C. Miller and A. Savage, Phys. Rev. **128**, 2175 (1962); J. Ducuing and N. Bloembergen, *ibid.* **133**, A1493 (1964); Phys. Letters **12**, 290 (1964).

the dc magnetic field the cross section for the forward scattering of right circularly polarized photon at ω_0 ($\lambda = 6940$ Å) into a right circularly polarized photon at $\omega_0 - g\beta H$ is $(d\sigma/d\Omega) \sim 4\times 10^{-32}$ cm². The same cross section is obtained for an incident X-polarized photon at ω_0 scattered into a Y photon at $\omega_0 - g\beta H$ if the dc magnetic field is in either the X or Y directions. If the number of atoms per cm³ is $\sim 10^{21}$, the total cross section per cm³$\sim 4\times 10^{-11}$ cm².

This is considerably smaller than the scattering rate for the stimulated Raman scattering discussed previously. However, here the scattering is in all directions and can be shifted by more than the optical linewidth. Other terms in $\mathcal{H}_{\text{eff}}$ can also induce Raman transitions. From the numerical estimates of the previous section they should yield similar cross sections.

8. KRAMERS-KRONIG RELATIONS AND THEIR APPLICATIONS

The IFE, the inverse Cotton-Mouton effect, and the stimulated Raman scattering phenomena are examples of effects resulting from the response of the material system to the low-frequency components of $[E(t)]^2$. The effective Hamiltonian formulation provides a simple means for linearizing these effects in terms of normal forces, quadratic in the Fourier components of $E(t)$, and the conjugate normal coordinates of the system.

Consider the form of $\mathcal{H}_{\text{eff}}$ given by Eq. (3.10), and expand χ^{ij} in terms of the irreducible tensor operators $Q_\mu{}^{\alpha\Gamma}$, where α is a configuration index, Γ indicates the particular irreducible representation, and μ is a component of that representation.

$$\mathcal{H}_{\text{eff}} = -\sum_{ij} (Q_\mu{}^{\alpha\Gamma})_{ab} \chi_{\alpha\Gamma\mu}{}^{ij} \mathcal{E}_i(t)\mathcal{E}_j{}^*(t)\,, \tag{8.1}$$

where $\chi_{\alpha\Gamma\mu}{}^{ij} = \partial\chi^{ij}/(\partial Q_\mu{}^{\alpha\Gamma})$. For the example of an ion in a site of cubic symmetry [Eq. (4.4)] α is unnecessary and

$$Q_\mu{}^{T_1} = S_\mu\,,\quad Q_\theta{}^E = \{S_z{}^2 - [S(S+1)/3]\}\,,\quad Q_\epsilon{}^E = S_x{}^2 - S_y{}^2\,,$$

and $Q_z{}^{T_2} = (1/\sqrt{2})(S_xS_y + S_yS_x)$, etc. For a more general system Q could represent normal vibrational modes, spin-wave modes or any other physical observable. Defining a normal force in the usual manner obtains

$$F_\mu{}^{\alpha\Gamma}(t) = +\sum_{i,j} \chi_{\alpha\Gamma\mu}{}^{ij} \mathcal{E}_i(t)\mathcal{E}_j{}^*(t)\,, \tag{8.2}$$

so that

$$\mathcal{H}_{\text{eff}} = -\sum_{\alpha,\Gamma,\mu} Q_\mu{}^{\alpha\Gamma} F_\mu{}^{\alpha\Gamma}(t)\,. \tag{8.3}$$

Assuming the existence of a linear response function obtains

$$\langle Q_\mu{}^{\alpha\Gamma}(\omega)\rangle = \sum_{\alpha',\mu'} \Lambda_{\alpha\mu,\alpha'\mu'}{}^\Gamma(\omega) F_{\mu'}{}^{\alpha'\Gamma}(\omega)\,, \tag{8.4}$$

where $\langle Q_\mu{}^{\alpha\Gamma}(\omega)\rangle$ is the Fourier transform [see Eq. (7.2)] of the change in the expectation value of $Q_\mu{}^{\alpha\Gamma}(t)$ caused by the normal force $F_\mu{}^{\alpha\Gamma}(t)$; $F_\mu{}^{\alpha\Gamma}(\omega)$ is the Fourier transform of this normal force. The tensor $\mathbf{\Lambda}$ will have both real and imaginary parts $\mathbf{\Lambda} = \mathbf{\Lambda}'(\omega) - i\mathbf{\Lambda}''(\omega)$ and it follows from the fact that this is now a linear, stationary system which obeys causality that $\mathbf{\Lambda}'$ and $\mathbf{\Lambda}''$ are connected by Kramers-Kronig relations[16]

$$\mathbf{\Lambda}'(\omega) = \frac{2}{\pi} P\int_0^\infty \mathbf{\Lambda}''(\omega')\omega'[(\omega')^2 - (\omega)^2]^{-1} d\omega'\,,$$

$$\mathbf{\Lambda}''(\omega) = -\frac{2\omega}{\pi} P\int_0^\infty \mathbf{\Lambda}'(\omega')[(\omega')^2 - \omega^2]^{-1} d\omega'\,. \tag{8.5}$$

Dispersion relations for nonlinear problems have been discussed by Caspers[17] and Price[18] with results analogous to Eq. (8.5). Bloembergen has also obtained similar relations between the nonlinear polarizabilities involved in stimulated Raman effects. The assumption he makes, equivalent to assumptions made here, is that only one of the energy denominators in his expressions is near resonance.[1]

The utility of this relation can best be illustrated through a particular example. Consider only the first term in the effective Hamiltonian Eq. (6.1) for a spin-$\frac{1}{2}$ system

$$\mathcal{H}_{\text{eff}} = +iA\mathbf{S}\cdot\boldsymbol{\mathcal{E}}\times\boldsymbol{\mathcal{E}}^*\,. \tag{8.6}$$

The other intensity-dependent terms are assumed negligible and the system is taken to be in a strong magnetic field along the z direction. Consider a light wave

$$E(t) = 2\,\text{Re}[\{\tilde{x}\mathcal{E}_x \exp[-(i\omega'/2)(t - y/c')] + \tilde{z}\mathcal{E}_z \exp[+i(\omega'/2)(t - y/c')]\} \exp i\omega(t - y/c')]\,, \tag{8.7}$$

where $\omega' \ll \omega$ and c' is the speed of light at frequency ω in the media. Then at a point $\omega' y c^{-1} \ll 1$

$$\mathcal{H}_{\text{eff}} = +iAS_y[\mathcal{E}_z\mathcal{E}_x{}^* \exp(i\omega' t) - \mathcal{E}_x\mathcal{E}_z{}^* \exp(-i\omega' t)]\,, \tag{8.8}$$

the normal force [Eq. (8.2)] is

$$\begin{aligned} F_y &= -iA[\mathcal{E}_z\mathcal{E}_x{}^* \exp(i\omega' t) - \mathcal{E}_x\mathcal{E}_z{}^* \exp(-i\omega' t)] \\ &= -2\,\text{Re}[iA\,\mathcal{E}_z\mathcal{E}_x{}^* \exp(i\omega' t)] \end{aligned} \tag{8.9}$$

and the response function is

$$\langle S_\nu(\omega')\rangle = \Lambda(\omega')_{\nu,y} F_y(\omega') = -i\Lambda(\omega')_{\nu y} A\,\mathcal{E}_z\mathcal{E}_x{}^*\,. \tag{8.10}$$

If ω' is small compared to the reciprocal spin-lattice relaxation time $S_y(\omega)$ is simply the Fourier transform of the thermal equilibrium value of $S_y(t)$,

$$\langle S_y(t)\rangle = -(iA/4kT)[\mathcal{E}_z\mathcal{E}_x{}^* \exp(i\omega' t) - \mathcal{E}_x\mathcal{E}_z{}^* \exp(-i\omega' t)] \tag{8.11}$$

and

$$\Lambda_{yy}'(\omega') = +\Lambda_{yy}'(-\omega') = +(1/4kT)\,. \tag{8.12}$$

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[16] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, England, 1961).

[17] Wilem J. Caspers, Phys. Rev. **133**, A1249 (1964).

[18] P. J. Price, Phys. Rev. **130**, 1972 (1963).

In the limit $\omega' \to 0$, $\langle S_y(t) \rangle \to 0$ unless the light is circularly polarized ($\mathcal{E}_z = \pm i\mathcal{E}_x$), however

$$\Lambda_{yy}'(0) = \lim_{\omega' \to 0} \Lambda_{yy}'(\omega') = +1/4kT.$$

Consider the case when ω' is not small but rather let ω' be near $g\beta H$ which is now assumed much greater than the spin lattice relaxation times ($\omega' \gg T_1^{-1}$). Then it follows from Eq. (8.10) that the average power absorbed by a single spin is given by

$$P = \langle \dot{S}_y F_y \rangle = +\{2\omega' \Lambda_{yy}''(\omega') A^2 |\mathcal{E}_z|^2 |\mathcal{E}_x|^2\}. \quad (8.13)$$

The imaginary part of $\mathbf{\Lambda}$, i.e., $\Lambda_{yy}''(\omega')$, thus describes the average of stimulated Raman scattering processes in which photons at $\omega + \omega'/2$ polarized along H are scattered into photons at $\omega - \omega'/2$ polarized along x and the reverse process. Equivalently Λ_{yy}'' describes the average power absorbed from the optical waves by stimulated Raman scattering. From the Kramers-Kronig relation

$$\Lambda_{yy}'(0) = (4kT)^{-1} = 2\hbar(\pi g\beta H)^{-1} \int_0^\infty \Lambda_{yy}''(\omega') d\omega', \quad (8.14)$$

since $\Lambda_{yy}''(\omega')$ is sharply peaked about $g\beta H$.[16]

Taking

$$\int_0^\infty \Lambda_{yy}''(\omega') d\omega' = \left(\frac{\pi}{2} \Delta\omega_{ba}\right) \Lambda_{yy}''(\omega_{ba}),$$

where ω_{ba} and $\Delta\omega_{ba}$ are the atomic resonance frequency and half-widths, respectively, the total absorbed power per spin would be

$$P_{\text{spin}} = 2(g\beta H/\hbar)^2 \Lambda_{yy}'(0) \Delta\omega_{ba}^{-1} \times [\Lambda_{yy}''(\omega') / \Lambda_{yy}''(\omega_{ba})] A^2 |\mathcal{E}_z|^2 |\mathcal{E}_x|^2, \quad (8.15)$$

where ω', the beat frequency between the two laser modes, is near the atomic resonance.

From Eqs. (4.9), (4.10), and (2.6)

$$\Lambda_{yy}'(0) = n_0 \lambda_0 V (4\pi^2 g\beta N A)^{-1}, \quad (8.16)$$

where N is the number of spins per unit volume and V is the Verdet constant. Exactly at resonance the total power absorbed by all spins in a unit volume is

$$P_{\text{total}} = (g\beta / 2\pi^2 \hbar^2) H^2 n_0 \lambda_0 V A |\mathcal{E}_x|^2 \times |\mathcal{E}_z|^2 (\Delta\omega_{ba})^{-1}. \quad (8.17)$$

For $H = 10^4$G, $A = -3.5 \times 10^{-26}$ ergs (dyn/esu^{-1})^2, $V = (-1.7 \times 10^{-3}/T)$ rad cm^{-1} G^{-1}, $g = 2$, $\lambda = 6940$ Å and 10^7 W/cm^2 in both beams of light, and for the very conservative half-width $\Delta\omega_{ba} = 2\pi \times 10^9$ cps this corresponds to approximately 0.4 W/cm^3 at 4.2°K. If this is equated to $g\beta H(d/dt)\ \frac{1}{2}(N_{+1/2} - N_{-1/2})$, $\frac{1}{2}(d/dt) \times (N_{+1/2} - N_{-1/2}) = 2.2 \times 10^{22}$ sec^{-1} cm^{-3}. If we assume the above value of A, which was taken from a Eu^{2+}: CaF$_2$[5] crystal that had approximately 3×10^{20} spins/cm^3, is approximately valid for a spin-$\frac{1}{2}$ ground-state ion of the same concentration, this mechanism can partially saturate a paramagnetic species with $T_1 \sim 0.001 \sim 0.01$ sec.

The Manley-Rowe relations[19] can be applied here to show that if 2.2×10^{22} spins sec^{-1} cm^{-3} make transitions from the $-\frac{1}{2}$ to $+\frac{1}{2}$ states an equal number of photons must be scattered into the Stokes wave. Initially the Stokes wave had 3.5×10^{25} photons sec^{-1} cm^{-2} so that if $T_1 \lesssim 0.001$ sec at 4.2°K the spins will not saturate and the Stokes wave has approximately 0.06% gain per centimeter of path. This percentage gain is linearly proportional to the incident power density at the upper frequency ($\omega + \omega'/2$) but is independent of the incident power density at the Stokes frequency, ($\omega - \omega'/2$).[1] Note also that linewidths 10^{-2} smaller than the $\Delta\omega_{ba}$ assumed above are common. It is thus possible to increase the gain to 6% per centimeter of path by choice of a suitable EPR line.

9. CONCLUSION

We have demonstrated the quantum-mechanical origin of the IFE and shown how it can be related to an effective Hamiltonian. The general form for this effective Hamiltonian has been presented in terms of phenomenological constants. On the basis of the existence of this effective Hamiltonian it has been possible to establish certain relationships between the constants of seemingly different phenomena. In some cases these relationships take the form of nonlinear analogs of the Kramers-Kronig relations for linear materials. Numerical estimates for spontaneous and stimulated Raman coefficients are obtained from measurements of the Verdet constant for paramagnetic Eu^{++}: CaF$_2$. The approximation of an effective Hamiltonian is a generally useful technique for linearizing many nonlinear problems and this should find application in the study of many diverse phenomena.

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[19] H. A. Haus, IRE Trans. Microwave Theory Tech. **6**, 317 (1958).