Magnetic optical activity in intense laser fields. I. Self-rotation and Verdet constant

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The Faraday rotation and circular dichroism of dilute gases in longitudinal magnetic fields and subject to strong radiation fields are studied. The use of irreducible tensorial sets as bare-atom states which are then dressed by the laser field allows a simple incorporation of the various multipole relaxation rates into the theory. The treatment considers magnetic fields which produce Zeeman shifts much smaller than inverse collision times but which may be greater or smaller than the multipole relaxation rates. Doppler broadening is also considered. Explicit expressions are given for dipole transitions in a two-level system with arbitrary angular momentum for strong and weak magnetic fields.

I. INTRODUCTION

Tunable lasers with improved power output and frequency stability and which cover larger frequency ranges than heretofore are now becoming available. This has stimulated experiments which use these sources to reinvestigate the classical magnetooptic effects with greater precision. An example is the experiment of Blum *et al.* on NO.[1] In addition, high-intensity sources have enabled the study of these same effects in the nonlinear regime where stimulated and multiphoton processes must be taken into account.[2] The optically induced analog of these magneto-optic effects which exists in the absence of a magnetic field has been discussed by Kaftandjian and Klein[3] and Kaftandijan, Klein, and Hanle.[4]

The present work presents a unified treatment of magnetooptic effects including the nonlinear contributions. In addition, effects due to dispersion near spectral resonances will be treated correctly using methods which have been developed in the theory of pressure broadening of spectral lines.[5] These nonlinear and dispersion contributions are important in the technology of Faraday rotators in high-power laser systems[6] and for the investigation of the molecular structure of gases in weak magnetic fields which are of astrophysical or geophysical interest.

For example, recently a study of the magnetic optical activity (MOA) of excimer molecules permitted a precise measurement of the coupling of the angular momentum of different electronic states.[7] Furthermore, studies of the effect of nonconservation of parity on atomic processes have been performed by Roberts *et al.*,[8] using the Faraday effect to examine the 647.6-nm transition in Bi (which is also a simple method of determining the proportion of atoms and molecules in the gas). A related method, forward scattering, which will be discussed in the following paper, has also be used by Gawlik *et al.*[9] to make precise measurements of the oscillator strengths of atomic transitions. Both types of measurements, magnetic rotation spectra and forward scattering, owe their precision to the fact that they are measurements of the intensity transmitted through crossed polarizers as a function of frequency or magnetic field. The fact that they are also magnetooptic effects permits the acquisition of supplementary information such as the Landé factors and, possibly, the individual broadening coefficients of the Zeeman components.

Magnetic optical activity results from the asymmetry in the indices of refraction for left and right circularly polarized light, induced in a medium by a longitudinal magnetic field. This activity has been traditionally divided into magnetic circular birefringence (MCB) and magnetic circular dichroism (MCD). The first, MCB, is known as the Faraday effect and is observed as the rotation of the plane of polarization of linearly polarized radiation propagating along a magnetic field. In general, the angle of rotation Θ is related to the left and right indices n_l, n_r and the distance traveled through the medium L by[10]

$$\Theta = (\omega L/2c)(n_r - n_l) , \tag{1}$$

where ω is the angular frequency of the radiation. For magnetic fields which are weak enough, the difference in indices is proportional to the magnetic intensity H_0, so that

$$\Theta/L = V(\omega)H_0 . \tag{2}$$

The constant of proportionality $V(\omega)$ is referred to as the Verdet constant and is characteristic of the medium being studied.

MCD is characterized by the difference in the absorption coefficients α_l, α_r for left and right circular polarizations. This results in elliptical polarization of the initially plane-polarized radiation after traversing the medium. The ellipticity is determined by

$$\Psi = (\omega L/4c)(\alpha_r - \alpha_l) . \tag{3}$$

The fraction of the intensity of radiation which is transmitted through crossed polarizers, I_t/I_0, depends on

both the MCB and MCD as

$$I_t/I_0=(\sin^2\Theta+\sinh^2\Psi)\exp[-(\alpha_r+\alpha_l)L/2]\ . \quad (4)$$

Thus, for this technique, a study of both MCB and MCD must be performed. Measuring the fraction transmitted as a function of ω is called magnetic rotation spectroscopy (MRS) and as a function of H_0, forward scattering (FS). Of course, in regions of strong spectral absorption, the MCF will dominate, and in regions far from resonance, MCB will be most important. Approximate expressions involving one or the other effect in the appropriate region can be found in the literature[11–13] as well as more general expressions using phenomenological profiles.[14,15]

In the following a comprehensive theory, valid through spectral resonances, will be presented. The formalism of this theory will be developed in Sec. II and a review of the linear theory of magneto-optic effects will be presented as a simple example. In this connection results for the line-shape parameters useful for MOA which were given in a previous publication[16] on the linear effect will also be reviewed.

In Sec. III a discussion of the nonlinear or stimulated MOA will be presented. The formalism will be applied to a two-level system quasiresonant with a laser of arbitrary polarization propagating along the magnetic-field direction. The two-level system will be considered to have arbitrary magnetic substate multiplicity. Although an analytic expression for the nonlinear MOA is not obtained to all orders in the laser field (except in the special case of a $j=1\rightarrow j=0$ or $j=\frac{3}{2}\rightarrow j=\frac{1}{2}$ transition) the necessary matrix elements for a numerical calculation of low-j transitions are given by Giraud-Cotton.[17] For arbitrary j, the analytic expression for the first nonlinear correction to the MOA (and to the Verdet constant near a transition) is calculated. This contribution is the third-order Faraday effect.

When the laser polarization is elliptical, terms independent of the applied magnetic field first appear in third order. The contribution of these terms describes the self-rotation which has been observed in gases by Tam and Happer,[18] in liquids by Maker *et al.*,[19] and in doped glasses.[20] Previous theoretical expressions for this effect which were found in the nonresonant[21] and resonant[22] approximations will be obtained as limiting cases. For dilute gases, the multipole relaxation rates which govern these processes will also be explicitly displayed.

Finally, we treat the case of dilute-gas spectra when the collisional relaxation processes are small with respect to the Doppler broadening of the transition. This produces a MRS dominated by the Doppler effect.

In the following paper,[23] based on the theoretical approach outlined here, the above considerations will be extended to include forward scattering, a technique in which the Doppler dominance of the MCD and MCB is reduced. Using this method a comparison with experiments on the sodium D lines will be presented.

II. THEORETICAL FORMULATION OF MRS

As described in the Introduction, the Faraday effect and MCD are proportional to the difference in the indices of refraction and absorption coefficients, respectively, for right and left circularly polarized radiation. We introduce the left (right) electric susceptibility χ_l (χ_r) of the gas, defined through $P^{(1)}_{+1}$ ($P^{(1)}_{-1}$), the circular components of the polarization vector, by

$$P^{(1)}_{+1\,(-1)}=\chi_{l\,(r)}E_{l\,(r)}\ , \quad (5)$$

where $E_{l\,(r)}$ is the left (right) circularly polarized laser field. Now the effects can be equally described by the real and imaginary parts of the difference in the susceptibilities:[14]

$$\Theta+i\Psi=(\pi\omega L/c)[\chi_r(\omega)-\chi_l(\omega)]\ . \quad (6)$$

Here, the magnetic susceptibility effects are neglected. Cases requiring the magnetic contribution, such as O_2 in the nonresonant region,[24] can be easily included using the same formalism.

The propagation direction of the incident laser radiation is, as noted above, along the magnetic field which also serves as the quantization axis for the atoms or molecules. Under this condition, the costandard components of the polarization vector defined above, $M=\pm1$, are given by the correlation function

$$P^{(1)}_M=\langle d^{(1)}_M(\mathbf{k})\rangle=(-1)^{1-M}\langle d^{[1]}_{-M}(\mathbf{k})\rangle$$
$$=\frac{N_A}{V}\mathrm{Tr}[d^{[1]}_{-M}(\mathbf{k})\rho(\omega)]\ , \quad (7)$$

where $d^{(1)}_M(\mathbf{k})=d^{(1)}_M e^{i\mathbf{k}\cdot\mathbf{R}}$ are the usual costandard components (with the definition of Fano and Racah[25]) of the Hermitian electric-dipole-moment operator for an atom at position $\mathbf{R}$ in an applied field of wave vector $\mathbf{k}$ and $d^{[1]}_M$ the contrastandard form of these components. The polarization-vector and laser-field components are always taken in a costandard form for convenience in the inner product. For simplicity, we have restricted the discussion here to electric-dipole transitions (otherwise, the notation must be generalized to allow Kth multipole transitions) of N_A atoms in a volume V. It has been assumed in Eq. (7) that the atoms or molecules interacting with the radiation field are independent, so that the trace is over the internal coordinates and the momenta of a single system of interest and a large thermal bath of perturbing particles. The quantity $\rho(\omega)$ is the Fourier transform at the laser radiation frequency ω of the time-dependent density operator for this situation.

The calculation of Eq. (7) will be performed using the Liouville space-operator methods introduced by Zwanzig[26] and Fano.[27] These methods have been adapted to nonlinear spectroscopy by the introduction of Floquet numbers by Ben-Reuven and Klein[28] and by use of a time-independent scattering theory.[29–31] The technique involves the calculation of elements of the reduced density matrix of the radiating or absorbing system. These elements are labeled both by the double atom dyadic vector states and by the Floquet numbers $\hat{\mathbf{n}}_l,\hat{\mathbf{n}}_r$ of left and right circularly polarized radiation. Using Liouville states derived from the Hilbert space of angular momentum operators, the components of the vector representing the density matrix in this extended space are written

$$\rho_{ab}^{\hat{\mathbf{n}}_l,\hat{\mathbf{n}}_r} = \langle\langle a j_a m_a, b j_b m_b; \hat{\mathbf{n}}_l, \hat{\mathbf{n}}_r \mid \rho \rangle\rangle \ , \tag{8}$$

where j_a, m_a are the angular momentum and magnetic quantum numbers of the state a. The extra index a, representing all other quantum numbers, will be ignored in the following. In the above, only $\rho_{ab}^{\hat{1}\hat{0}}$ and $\rho_{ab}^{\hat{0}\hat{1}}$ are required for the calculation of χ_l and χ_r, respectively.

Since the laser radiation will be taken to be plane polarized and hence a coherent superposition of left and right circularly polarized components, the interaction of the system with this field is best described using the standard base. In the dipole approximation, the time-independent operator for interaction with left (l) or right (r) circularly polarized radiation is

$$\mathscr{U}_{l\,(r)} = \sum_{M=\pm 1} \mathscr{U}_{l\,(r)}(M) \ , \tag{9a}$$

where

$$\mathscr{U}_l(M) = -D_M^{[1]} \mathscr{E}_{l_M}, \quad \mathscr{U}_r(M) = -D_M^{[1]} \mathscr{E}_{r_M} \ . \tag{9b}$$

The total interaction is therefore $\mathscr{U} = \mathscr{U}_l + \mathscr{U}_r$.

In the above, $D_M^{[1]}$ is a tetradic operator defined on the contrastandard components of the Hilbert space operator $d_M^{[1]}$. $D_M^{[1]}$ operates on a Liouville vector $|X\rangle\rangle$ following the definition

$$D_M^{[1]} |X\rangle\rangle = |[d_M^{[1]}, X]\rangle\rangle \ . \tag{9c}$$

The set of the three components $D_M^{[1]}$, $M = 0, \pm 1$, defines an irreducible tensor of rank 1 in the Liouville space. Their matrix elements satisfy the Wigner-Eckart theorem when the suitable set of Liouville states, the unitary irreducible tensor set of Hilbert space, is used.[32,17]

$\mathscr{E}_{lM}$ ($\mathscr{E}_{rM}$) is, for $M = \pm 1$, the amplitude $E_{l,+1}$ ($E_{r,+1}$) of the positive harmonic term in the external laser field times the raising operator for Floquet numbers of the left (right) circular polarization state, and for $M = -1$, the amplitude of the negative harmonic term $E_{l,-1}$ $(E_{r,-1}) = E_{l,+1}^*$ ($E_{r,+1}^*$) times the lowering operator for the Floquet numbers $\hat{\mathbf{n}}_l$ ($\hat{\mathbf{n}}_r$).

The evolution of the atomic density operator in the absence of the thermal bath, but in the presence of a longitudinal magnetic field H_z, is governed by the Liouville operator

$$L_A = L_0 - M_z H_z \ , \tag{10}$$

where M_z is the tetradic magnetic moment operator. For transitions $a \rightarrow b$ which are well separated from other electric-dipole transitions, the principle effect of the external magnetic field in Eq. (10) is to remove the degeneracy of the sublevels of a and b. In this approximation, L_A is diagonal in the dyads of the standard base of the Hilbert space of angular momentum vectors as well as in the Floquet numbers:

$$L_A \, | j_a m_a, j_b m_b; \hat{\mathbf{n}}_l, \hat{\mathbf{n}}_r \rangle\rangle = \Omega_{ab} \, | j_a m_a, j_b m_b; \hat{\mathbf{n}}_l, \hat{\mathbf{n}}_r \rangle\rangle \ , \tag{11}$$

where $\Omega_{ab} = \omega_{ab} + (\omega_L^a m_a - \omega_L^b m_b)$, $\omega_L^i = g_i \mu_B H_z$ is the Larmor frequency of the ith level, and $g_i \mu_B$ is the Landé g factor of the level i times the Bohr magneton.

As is customary, the density matrix will be assumed to have its equilibrium value ρ^{eq} at $t \rightarrow -\infty$, so that Eq. (8) can be expressed as

$$\rho_{ab}^{\hat{\mathbf{n}}_l\hat{\mathbf{n}}_r} = \sum_c \langle\langle j_a m_a, j_b m_b; \hat{\mathbf{n}}_l, \hat{\mathbf{n}}_r \mid \mathscr{G}(i\xi)\mathscr{U} \mid j_c m_c, j_c m_c; \hat{\mathbf{0}}, \hat{\mathbf{0}} \rangle\rangle \rho_{cc}^{\text{eq}}(j_c m_c) \tag{12}$$

(implying the limit $\epsilon \rightarrow +0$), where the explicit dependence on j and m due to the presence of the external magnetic field has been indicated in ρ_{cc}^{eq}, the equilibrium density matrix of state c. This dependence usually arises through the Larmor frequency as in Eq. (11).

The tetradic resolvent operator $\mathscr{G}(i\xi)$ in Eq. (12) contains $\mathscr{U} = \mathscr{U}_l + \mathscr{U}_r$, the radiation-system interaction,

$$\mathscr{G}(i\xi) = [\Omega - L_A - \langle \Pi(\omega) \rangle - \mathscr{U} + i\xi]^{-1} \ , \tag{13a}$$

and can be expressed in terms of $G(i\xi)$, which is free of this interaction, by the Dyson equation,

$$\mathscr{G}(i\xi) = \underline{G}(i\xi) + \underline{G}(i\xi)\mathscr{U}\mathscr{G}(i\xi) \ , \tag{13b}$$

where $\underline{G}(i\xi)$ is the resolvent operator

$$\underline{G}(i\xi) = [\Omega - L_A - \langle \Pi(\omega) \rangle + i\xi]^{-1} \ , \tag{13c}$$

which is also the familiar linear-response line-shape function. Here, $\langle \Pi(\omega) \rangle$ is the relaxation operator arising from the interaction between the radiating system and the thermal bath, averaged over all bath variables. The diagonal matrix Ω is the Doppler-shifted Floquet frequency matrix with elements $\hat{\mathbf{n}}_l(\omega_l - \mathbf{k}_l \cdot \mathbf{V}_a) + \hat{\mathbf{n}}_r(\omega_r - \mathbf{k}_r \cdot \mathbf{V}_a)$, which depend on the frequency and wave vector $\omega, \mathbf{k}$, of left and right circularly polarized states. Henceforth, these will be taken to be equal, corresponding to plane-polarized incident radiation. Also in the above, $\mathbf{V}_a$ is the atomic center-of-mass velocity of a radiator in a quantum state a. Note that this means that $\rho_{aa}^{\text{eq}}(j_a m_a)$ contains a velocity distribution function for the radiator and the states a contain the center-of-mass momentum. All velocity-changing collisions are ignored here. In addition, the speed dependence of $\langle \Pi(\omega) \rangle$ will be neglected. Both these corrections can be included[33] simply but would unnecessarily complicate the notation.

For convenience of notation and also to preserve the same algebraic form as in the strong-field theory developed in previous Floquet-number and dressed-atom theories,[27–30] we introduce the transformed Floquet base

$$\hat{\mathbf{n}}_1 = \hat{\mathbf{n}}_l + \hat{\mathbf{n}}_r, \quad \hat{\mathbf{n}}_2 = \hat{\mathbf{n}}_l - \hat{\mathbf{n}}_r \ . \tag{14}$$

Now, instead of harmonics of the left and right polari-

zation components, we have Floquet numbers which in the case of $\hat{\mathbf{n}}_1$ correspond to the total number of harmonics present irrespective of polarization and for $\hat{\mathbf{n}}_2$ represent the net angular momentum change carried by the field harmonics. In this new base, the field operator of Eq. (9), $\mathscr{E}_{l_M}$, raises (lowers) both $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$ by one unit, and $\mathscr{E}_{r_M}$ raises (lowers) $\hat{\mathbf{n}}_1$ and lowers (raises) $\hat{\mathbf{n}}_2$ by one unit each, for $M=+1$ (-1), so that

$$\mathscr{U}_{l\,(r)}(M)\,|\,j_a m_a,j_b m_b;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle$$
$$=\frac{1}{\hbar\sqrt{3}}\sum_{j_c,m_c}[\,(-1)^{j_a-m_a+1}\langle j_a||d||j_c\rangle\langle j_c j_a m_c-m_a\,|\,1\pm M\rangle\,|\,j_c m_c,j_b m_b;\hat{\mathbf{n}}_1+\hat{\mathbf{M}},\hat{\mathbf{n}}_2\pm\hat{\mathbf{M}}\rangle\rangle$$
$$+(-1)^{j_c-m_c}\langle j_b||d||j_c\rangle\langle j_b j_c m_b-m_c\,|\,1\pm M\rangle\,|\,j_a m_a,j_c m_c;\hat{\mathbf{n}}_1+\hat{\mathbf{M}},\hat{\mathbf{n}}_2\pm\hat{\mathbf{M}}\rangle\rangle\,]E_{lM\,(rM)}\,. \tag{15}$$

Here, the upper sign results from the action of $\mathscr{U}_l(M)$ and the lower sign from $\mathscr{U}_r(M)$ as defined in Eq. (9b), with the definition (9c) of $D_M^{[1]}$. The Wigner-Eckart theorem on Hilbert space has been used to write the dipole matrix elements as functions of the reduced matrix elements $\langle j||d||j'\rangle$ and of Clebsch-Gordan coefficients $\langle j,j',m-m'\,|\,1,\pm M\rangle$. Note also that the components of the vector representing the density operator in this basis are

$$\rho_{ab}^{\hat{\mathbf{n}}_1\hat{\mathbf{n}}_2}(\omega)=\langle\langle j_a m_a,j_b m_b;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\,|\,\rho(\omega)\rangle\rangle\,. \tag{16}$$

As can be seen from the definition in Eq. (7), the elements of $\rho_{ab}^{\hat{\mathbf{n}}_1\hat{\mathbf{n}}_2}$ required for the $M=\pm1$ circular components of the polarization are now $\rho_{ab}^{\hat{\mathbf{1}}\hat{\mathbf{M}}}(\omega)$ since Eq. (7) can be written in this base as

$$P_M^{(1)}=(N_A/V)\langle\langle d_M^{[1]};\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\rho(\omega)\rangle\rangle=(N_A/V)\sum_{a,b}(d_M^{[1]})_{ab}^{*}\rho_{ab}^{\hat{\mathbf{1}}\hat{\mathbf{M}}}(\omega)\,. \tag{17}$$

Using Eq. (12), we can write for an isolated $f\rightarrow i$ transition

$$P_M^{(1)}=(N_A/V)\sum_{c}(d_M^{[1]})_{fi}^{*}\langle j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\mathscr{U}\,|\,j_c m_c,j_c m_c;\hat{\mathbf{0}},\hat{\mathbf{0}}\rangle\rangle\rho_{cc}^{\mathrm{eq}}(j_c m_c)\,, \tag{18}$$

where $(d_M^{[1]})_{ab}$ represents the matrix element $\langle j_a m_a\,|\,d_M^{[1]}\,|\,j_b m_b\rangle$.

In the absence of a magnetic field (and later we shall see also in certain special cases), it is convenient to perform the trace operation of Eq. (7) using an irreducible representation with respect to rotations. The corresponding standard basis vectors $|\,j_a j_b;KQ\rangle\rangle$ are defined in terms of the $|\,j_a m_a,j_b m_b\rangle\rangle$ dyads according to the expansion

$$|\,j_a j_b;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle=\sum_{m_a,m_b}(-1)^{j_b-m_b}\langle j_a j_b m_a-m_b\,|\,KQ\rangle\,|\,j_a m_a,j_b m_b;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle\,. \tag{19}$$

The Qth component of a Kth-order multipole operator $\mathscr{O}_Q^K$ of the Hilbert space has, using that basis, the simple expansion in the Liouville space

$$|\,\mathscr{O}_Q^K\rangle\rangle=\sum_{j_a,j_b}\frac{\langle j_a||\mathscr{O}^K||j_b\rangle}{(2K+1)^{1/2}}\,|\,j_a j_b;KQ\rangle\rangle \tag{20}$$

so that, using the Wigner-Eckart theorem in Liouville space, the action of $\mathscr{U}_{l\,(r)}(M)$ in this basis corresponding to Eq. (15) is

$$\mathscr{U}_{l\,(r)}(M)\,|\,j_a j_b;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle$$
$$=\hbar^{-1}\sum_{K',Q'}\langle K,1,Q,\pm M\,|\,K'Q'\rangle(2K'+1)^{1/2}$$
$$\times\left[(-1)^{j_b+j_c+K}\begin{Bmatrix}1&K&K'\\ j_b&j_c&j_a\end{Bmatrix}\langle j_c||d||j_a\rangle\,|\,j_c j_b;K'Q';\hat{\mathbf{n}}_1+\hat{\mathbf{M}},\hat{\mathbf{n}}_2\pm\hat{\mathbf{M}}\rangle\rangle+(-1)^{j_a+j_c+K'}\begin{Bmatrix}1&K&K'\\ j_a&j_c&j_b\end{Bmatrix}\right.$$
$$\left.\times\langle j_b||d||j_c\rangle\,|\,j_a j_c;K'Q';\hat{\mathbf{n}}_1+\hat{\mathbf{M}},\hat{\mathbf{n}}_2\pm\hat{\mathbf{M}}\rangle\rangle\right]E_{lM\,(rM)}\,, \tag{21}$$

where the upper sign holds for left polarization and the lower sign for right polarization.

This basis is convenient[34,35] for problems in which the system under consideration is rotationally invariant, since then the corresponding Liouville operator is diagonal in the coupled states of Eq. (19). Thus, in the absence of magnetic fields, L_A and $\langle\Pi(\omega)\rangle$ of Eq. (13) conserve K and Q so that, using the definition of the components of the polarization, Eq. (7), we obtain for an isolated transition, in the absence of a magnetic field,

$$P_M^{(1)}=(N_A/V\sqrt{3})\sum_{c=i,f}\langle\langle j_f||d||j_i\rangle G^1_{fi}(\hat{\mathbf{1}},\hat{\mathbf{M}})\langle\langle j_fj_i;1M;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,(1+\mathscr{U}\mathscr{G})\mathscr{U}\,|\,j_cj_c;00;\hat{\mathbf{0}},\hat{\mathbf{0}}\rangle\rangle\rho^{\rm eq}_{cc}\rangle_{\mathbf{V}}\,, \tag{22}$$

which involves matrix elements of the linear response function, with $\omega_l=\omega_r=\omega$,

$$\begin{aligned}G^K_{fi}(\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)&=\langle\langle j_fj_i;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\,|\,G(i\xi)\,|\,j_fj_i;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle\\&=[\hat{\mathbf{n}}_1(\omega-\mathbf{k}\cdot\mathbf{V})-\omega_{fi}-\langle\Pi^K_{fi}\rangle+i\xi]^{-1}\,.\end{aligned} \tag{23}$$

In Eq. (22), $K=1$ for the dipole transition considered, $\hat{\mathbf{n}}_1=1$, $\hat{\mathbf{n}}_2=M$, and $M=+1$ or -1 corresponds to left and right susceptibilities, respectively. Finally, $\langle\cdots\rangle_{\mathbf{V}}$ means that an average over the center-of-mass speed $\mathbf{V}$ is to be performed in Eq. (22).

The line-shape parameter $\langle\Pi^K_{fi}\rangle$, having been assumed to be rotationally invariant and hence diagonal in K and Q, involves the assumption of a spherically symmetric perturber bath. In this case it is independent of Q (and hence of photon polarization) and contains no interference effects between different multipole moments:[34]

$$\begin{aligned}\langle\Pi^K_{fi}\rangle&=\langle\langle j_fj_i;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\,|\,\langle\Pi\rangle\,|\,j_jj_i;KQ;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle\\&=\sum_{\substack{m_f,m_i,\\m_f',m_i'}}(-1)^{m_i-m_i'}\langle j_fj_im_f-m_i\,|\,KQ\rangle\langle j_fj_im_f'-m_i'\,|\,KQ\rangle\\&\quad\times(2K+1)^{1/2}\langle\langle j_fm_f,j_im_i;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\,|\,\langle\Pi\rangle\,|\,j_fm_f',j_im_i';\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle\,.\end{aligned} \tag{24}$$

Note finally that, even though $\langle\Pi^K_{fi}\rangle$ has matrix elements connecting different Zeeman substates, the line-shape parameter is completely independent of the Zeeman substate involved in the transition. Thus, in the absence of magnetic fields, no Zeeman line-mixing effects occur.

Therefore, as is to be expected, in the absence of magnetic fields the linear susceptibility is independent of Q and, obviously, no magnetic optical activity is observed in the linear case. The case in which the incident radiation is elliptically polarized ($\mathscr{E}_l\neq\mathscr{E}_r$) which leads to self-rotation in the nonlinear regime will be discussed later. In addition, since $\mathscr{U}$ is not diagonal in K (in fact, in the dipole approximation it may raise or lower K by one unit—or leave K unchanged—each time it is applied), it mixes multipolar excitations and, therefore, the nonlinear response function is composed of products of $G(i\xi)$ functions, each of which can be a matrix in a different invariant subspace. This is true even in the absence of a magnetic field and is the reason for which the K index was retained on G in Eq. (22). The nonlinear response clearly remains diagonal in Q, however, so that it still leads to a vanishing MOA for linearly polarized radiation in the absence of magnetic fields.

In the presence of a magnetic field, the rotational invariance is broken and neither L_A nor $\langle\Pi(\omega)\rangle$ is diagonal in the states of Eq. (19). Nevertheless, if the magnetic field is not too large, so that the Larmor frequency of the a level, ω^a_L, is much smaller than the inverse of τ_c, the collision duration,

$$2j_a\omega^a_L\tau_c\ll 1\,, \tag{25}$$

then the relaxation matrix [in the impact approximation, at least, where $\langle\Pi(\omega)\rangle$ becomes independent of ω] will be unaffected by the field. This has been discussed by Omont.[34] It has been assumed also that the perturber bath remains spherically symmetric in the presence of the field. Since the duration of typical collisions in neutral gases is approximately 10^{-12}—10^{-14} sec, the collision matrix will be rotationally invariant for magnetic fields which are typically less than 50 kG.

However, as discussed in Eq. (11), the states which diagonalize the Liouvillian L_A and the equilibrium density matrix for an isolated transition in a magnetic field are those derived from the Hilbert space of angular momentum variables, $|j_am_a,j_bm_b;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle$. Using these states, Eq. (22) for an isolated transition becomes, in this basis,

$$\begin{aligned}P_M^{(1)}=(N_A/V\sqrt{3})\sum_{c=i,f}\sum_{\substack{m_i,m_f,\\m_i',m_f'}}&(-1)^{j_i-m_i}\langle j_f||d||j_i\rangle^*\langle j_fj_im_f-m_i\,|\,1M\rangle\\&\times\langle G_{fi}(\hat{\mathbf{1}},\hat{\mathbf{M}})\langle j_fm_f',j_im_i';\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,(1+\mathscr{U}\mathscr{G})\mathscr{U}\,|\,j_cm_c,j_cm_c;\hat{\mathbf{0}},\hat{\mathbf{0}}\rangle\rangle\rho^{\rm eq}_{cc}(j_cm_c)\rangle_{\mathbf{V}}\,,\end{aligned} \tag{26a}$$

where, with $\omega_l=\omega_r=\omega$,

$$\begin{aligned}G_{fi}(\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)&=\langle\langle j_fm_f,j_im_i;\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\,|\,G(i\xi)\,|\,j_fm_f',j_im_i';\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2\rangle\rangle\\&=[\hat{\mathbf{n}}_1(\omega-\mathbf{k}\cdot\mathbf{V})-\Omega_{fi}-\langle\Pi_{fi}\rangle+i\xi]^{-1}_{m_f,m_i;m_f',m_i'}\end{aligned} \tag{26b}$$

and where Ω_{fi} is the diagonal matrix of Zeeman transition frequencies defined in Eq. (11) and $\langle\Pi_{fi}\rangle$ is the impact-theory matrix of Zeeman off-diagonal cross relaxation and diagonal decay rates with elements in the magnetic subspace,

$$\begin{aligned}\langle\Pi_{fi}\rangle_{m_f,m_i;m_f',m_i'}&=\sum_{K,Q}\langle j_fj_im_f-m_i\,|\,KQ\rangle\langle j_fj_im_f'-m_i'\,|\,KQ\rangle\\&\quad\times(-1)^{m_i-m_i'}\langle\Pi^K_{fi}\rangle\,,\end{aligned} \tag{27}$$

where $\langle \Pi_{fi}^{K} \rangle$ is defined in Eq. (24). Again, as in Eq. (22), only $\hat{\mathbf{n}}_1 = 1$ and $\hat{\mathbf{n}}_2 = M$ are needed for the linear response.

Equation (26a) now contains the Zeeman line-mixing effects which were absent from Eq. (22). Thus, even assuming that condition (25) is fulfilled so that the impact-approximation line-relaxation matrix is essentially unmodified by the magnetic field, another problem now arises. The overlapping of different Zeeman transitions implies, as is well known, that the magnetic rotation spectra will not be the sum of the contributions of separate Zeeman lines. This means that the large matrices of Eq. (26) must be inverted.

There are, however, two cases in which these overlapping line effects become small. First, the weak-field case

$$\langle \Pi_{fi}^{1} \rangle \gg \omega_L^f, \omega_L^i \ , \tag{28}$$

where $\langle \Pi_{fi}^{1} \rangle$ is the dipole, $K=1$, zero-magnetic-field, impact-theory linewidth parameter from Eq. (24). In this case the off-diagonal terms and the $K \neq 1$ contributions from the sum in Eq. (27) are negligible in the impact approximation, the linear response function is now diagonal, and

$$G_{fi}(\hat{\mathbf{1}}, \hat{\mathbf{M}}) = (\omega - \mathbf{k}\cdot\mathbf{V} - \Omega_{fi} - \langle \Pi_{fi}^{1} \rangle + i\xi)^{-1}_{m_f m_i} \times \delta_{m_f, m_f'} \delta_{m_i, m_i'} \tag{29}$$

is to be used in Eq. (26).

The other case in which line mixing can be disregarded is whenever the Zeeman transitions are well separated in terms of their individual linewidths:

$$\omega_L^f, \omega_L^i \gg \langle \Pi_{fi}^{1} \rangle \ . \tag{30}$$

This is the case for fields which are strong, although not so strong that the relaxation matrix loses its spherical symmetry, i.e., the condition of Eq. (25) is still satisfied. Unlike the preceding case, however, all zero-field multipole moment broadening coefficients contribute to the relaxation matrix and we have

$$\langle \Pi_{fi} \rangle_{m_f m_i} = \sum_K \langle j_f j_i m_f - m_i \mid KQ \rangle^2 \langle \Pi_{fi}^{K} \rangle \ . \tag{31}$$

The breaking of the spherical symmetry of the system by the strong magnetic field reveals itself in the appearance of the different multipolar contributions to the relaxation. This results in a line-narrowing effect as the magnetic field is decreased and line overlapping becomes important. Recent experiments on the Stark components of the rotational spectrum of CH_3F by Brechignac[36] show clearly the analog of this effect as a function of the external electric field.

It can be seen that spectroscopic measurements of the shapes of the individual Zeeman components contain in principle more information on the intermolecular potential than zero-field measurements. Nevertheless, to observe these individual transitions it is necessary that the Doppler width not drown the components. For this, the condition, difficult to fulfill,

$$\omega_L^f, \omega_L^i > \omega_D \tag{32}$$

must be satisfied. Here ω_D is the Doppler width, $\omega_D = \omega(u/c)$ with u the most probable center-of-mass speed, and $u = (2kT/m)^{1/2}$. Elsewhere,[2] we have described a Doppler-free method of observing MOA using two counterpropagating laser beams.

In the following, we shall always assume that the magnetic field is not too strong so that collisions can still be described by the spherically symmetric theory [i.e., Eq. (25) is satisfied] and also that either Eq. (28) or (30) is satisfied, either of which leads to a relaxation matrix diagonal in the Zeeman states.

The linear MOA can now be obtained by neglecting $\mathscr{U}\mathscr{G}$ in Eq. (26a), performing the indicated velocity average, and calculating the difference between left and right susceptibilities as in Eq. (6). For this purpose, the case for which the Doppler effect is large and the laser frequency is near resonance will be considered. First, the weak-field case for which the condition of Eq. (28) is fulfilled, the linear Faraday complex rotation for the $f \rightarrow i$ transition at $\omega - \omega_{fi} \ll \omega_D$, is

$$(\Theta^{(1)} + i\Psi^{(1)})/L = (N_A/V)\rho_i^{\mathrm{eq}} \frac{\pi \mid d_{fi} \mid^2}{3\hbar c} \frac{\omega}{\omega_D^2} Z'(z_{fi}) \times \left[\omega_L^i + \omega_L^f + (\omega_L^i - \omega_L^f) \frac{j_i(j_i+1) - j_f(j_f+1)}{2} \right] , \tag{33a}$$

where Z' is the first derivative of the plasma dispersion function Z (Ref. 37) with the argument $z_{fi} = (\omega - \omega_{fi} - \langle \Pi_{fi}^{1} \rangle)/\omega_D$. Using $Z'(z_{fi}) = -2[1 + z_{fi} Z(z_{fi})]$ and $Z(0) = i\sqrt{\pi}$, Eq. (33a) becomes for very small detunings ($\Delta\omega \sim 0$)

$$\Theta^{(1)}/L \sim -(N_A/V)\rho_i^{\mathrm{eq}} \frac{2\pi \mid d_{fi} \mid^2}{3\hbar c} \frac{\omega}{\omega_D^2} \left[\omega_L^i + \omega_L^f + (\omega_L^i - \omega_L^f) \frac{j_i(j_i+1) - j_f(j_f+1)}{2} \right] . \tag{33b}$$

The linear circular dichroism is negligible in this limit.

For well-resolved Zeeman components, where the condition of Eq. (30) is fulfilled, we have for the linear effect of the transition $j_i m_i \rightarrow j_f m_i + q$

$$(\Theta^{(1)} + i\Psi^{(1)})/L = q(N_A/V)\rho_i^{\mathrm{eq}} \frac{\pi \mid d_{fi} \mid^2 \omega}{\hbar c \omega_D} \left[1 - \frac{\hbar\omega_L^i}{kT} m_i \right] \langle j_f j_i (m_i + q) - m_i \mid 1q \rangle^2 Z(z_q(m_i)) \ , \tag{34}$$

where the argument of the dispersion function Z is

$$z_q(m_i)=[\,\omega-\omega_{fi} -\omega_L^f(m_i+q)+\omega_L^i m_i-\langle \Pi_{fi}\rangle_{m_f m_i}]/\omega_D \ .$$

For large detunings, the expressions in Eqs. (33a) and (34) can be written in the form of Eq. (2), which is linear in the magnetic field. Approximate expressions for the Verdet constant $V(\omega)$ have been given for special cases in the literature.[11–15] There are three principle contributions, usually[14] denoted $A(\omega)$, $B(\omega)$, and $C(\omega)$, which arise from the magnetic-field dependence of the energy levels, the wave functions, and the level populations, respectively. The recent study of the MCD of the excimer molecule Cs-Ar is a good example of the usefulness of the method. A calculation of the expression corresponding to Eq. (2) for the MCD (which can be expressed in terms of A, B, and C through the dispersion relation for MCD and MCB), when compared to experimental measurement, permitted the determination of the Hund's-rule coupling scheme for the Cs-Ar ground state for the first time.[7] The usefulness of excimer molecules in short-wavelength-laser design indicates the importance of this method. General expressions for the nonlinear contributions to the Verdet constant will be given in Sec. III.

In addition, the linear Faraday effect has long been used in the identification of the electronic spectra of molecules. Since for P and R branches, the MOR is roughly inversely proportional to the rotational state j, band heads, which correspond to low-j values, are easily identified. Carrol,[38] in 1937, introduced the use of this effect for studies of the perturbation of certain vibrational-rotational levels of an electronic state by nearby states belonging to another electronic state. A systematic study of these effects can furnish complementary information on the potential of the perturbing states. It should also contribute to the determination of electronic states inaccessible to classical absorption spectroscopy once the molecular vibrational-rotational constant of the accessible electronic states is known. An example of this was the analysis of the laser-induced fluorescence spectrum of the $^1\Pi\rightarrow{}^1\Sigma$ transition of Na_2 and NaK which revealed the perturbation of the $^1\Pi$ state by a nearby $^3\Pi$ state.[39,40]

When the laser is very intense, stimulated or nonlinear effects must be taken into account, and these correlations will be treated in Sec. III. Heating or thermal lens effects which involve considerations of the thermal equilibrium of the interacting system will not be taken into account. This is the usual assumption of no back reaction in the system-bath interaction. The nonlinear MOA and the A and C contributions to the third-order nonlinear Verdet constant will be calculated for transitions in two-level systems with arbitrary angular momentum.

III. NONLINEAR MOA

To carry the calculation described in Sec. II to higher order in the radiation-matter interaction $\mathscr{U}$, of Eq. (9), we must calculate matrix elements of the $\mathscr{G}(i\xi)$ resolvent operator defined in the Dyson equation (13). To do this we restrict the states considered to those effectively coupled by the laser field, i.e., to those that are quasiresonant with the incident frequency. This is the rotating-wave approximation (RWA) which considers only denominators of G functions in the Dyson equation which contain near-resonance detunings.

Under this approximation, the matrix elements in the expression for the susceptibility, Eq. (26a), are calculated in a subspace restricted to vectors which have resonant G functions. This means that only eight matrix elements of $\mathscr{G}(i\xi)$ are required for an isolated $j_i\rightarrow j_f$ transition:

$$\begin{aligned}P_M^{(1)}=-(N_A/\hbar V)\sum_{m_f,m_i}\sum_{M'=\pm1}(d_M)^*_{fi}(\rho^{\rm eq}_{j_i m_i}-\rho^{\rm eq}_{j_f m_f})\\ \times\{(d^{[1]}_{M'})_{fi}[\langle\langle j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_f m_f,j_i m_i;\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{l_{M'}}\\ +\langle\langle j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_f m_f,j_i m_i;-\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{r_{-M'}}]\\ -(d^{[1]}_{M'})_{if}[\langle\langle j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_i m_i,j_f m_f,\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{l_{M'}}\\ +\langle\langle j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_i m_i,j_f m_f;-\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{r_{-M'}}]\}\ ,\end{aligned}\tag{35}$$

where $\beta\omega_L\ll1$ has been assumed ($\beta=\hbar/kT$).

In the calculation of these matrix elements in terms of the interaction-free response functions G through the Dyson equation (13), the Liouville vectors to be considered in the RWA are restricted to the subspace spanned by the vectors $|\,j_c m_c,j_c m_c;\hat{\mathbf{0}},\hat{\mathbf{n}}_2\rangle\rangle$ with $\hat{\mathbf{n}}_2=0,\pm2,\pm4,\ldots$ (an even integer), $j_c=j_i$ or j_f for the even-parity part and, as indicated in Eq. (35), $|\,j_f m_f,j_i m_i;\hat{\mathbf{1}},\hat{\mathbf{n}}_2\pm1\rangle\rangle$ or $|\,j_i m_i,j_f m_f;-\hat{\mathbf{1}},\hat{\mathbf{n}}_2\pm1\rangle\rangle$ for the odd-parity part.

As can be seen from Eq. (15), the required matrix elements of $\mathscr{G}(i\xi)$ are coupled to matrix elements between all these states (i.e., the intermediate states are dressed with all possible numbers of angular momentum harmonics), unlike the case of the first-order calculation in Sec. II which contained only a single odd subspace G function. Since there are an infinite number of coupled Dyson equations for these matrix elements, a solution of the Dyson equation (13) in terms of these diagonal G elements is not

possible. However, a solution in terms of continued fractions[41] can be obtained which yields the susceptibility to all orders in the external laser field. A closed-form solution can be obtained in certain special cases. For example, for isolated transitions involving two levels with the same Landé g factor (e.g., a normal Zeeman effect, or the Paschen-Back effect), matrix elements of L_A are diagonal in the irreducible representation of Eq. (19) and independent of K. This is the same as the case in the absence of magnetic fields. The $G_{fi}(\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)$ functions of Eq. (26) are also diagonal in this representation [assuming the condition of Eq. (25)]. The use of the irreducible representation simplifies the higher-order calculation since now, in the even subspace, $\hat{\mathbf{n}}_2$ can no longer be any even integer but is limited by the $|Q|$ (and, hence, K) of the irreducible vectors with which it is associated. This is because the dipole interaction $\mathscr{U}_{l(r)}(\pm 1)$ raises or lowers $\hat{\mathbf{n}}_2$ at the same time as it raises or lowers Q, so that in the even RWA subspace where $\hat{\mathbf{n}}_1=0$, $|\hat{\mathbf{n}}_2|$ can never be greater than $|Q|$. But Q is limited by the definition $|Q|\leq K\leq j_a+j_b$. Thus, the vectors which span the even subspace in this case are $|j_c j_c;KQ;\hat{\mathbf{0}},\hat{\mathbf{n}}_2\rangle\rangle$ with $|\hat{\mathbf{n}}_2|<2j_c$ (or $2j_c-1$ for half-integral angular momentum). Similar arguments apply to the odd RWA subspace where the vectors are $|j_f j_i;KQ;\hat{\mathbf{1}},\hat{\mathbf{n}}_2\pm 1\rangle\rangle$, $|j_i j_f;KQ;-\hat{\mathbf{1}},\hat{\mathbf{n}}_2\pm 1\rangle\rangle$ with $|\hat{\mathbf{n}}_2|$ limited as above to $|\hat{\mathbf{n}}_2|<j_i+j_f$.

The expression for the susceptibility in terms of these invariant vectors is, again in the RWA,

$$
\begin{aligned}
P_M^{(1)}=(N_A/3\hbar V)\langle j_f||d||j_i\rangle\rho_i^{\mathrm{eq}}
&\times\sum_{M'=\pm 1}\{\langle j_f||d||j_i\rangle[\langle\langle j_f j_i;1M;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_f j_i;1M';\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{l_{M'}}\\
&\quad+\langle\langle j_f j_i;1M;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_f j_i;1M';-\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{r_{M'}}]\\
&\quad+(-1)^{j_f-j_i}\langle j_f||d||j_i\rangle^*[\langle j_f j_i;1M;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_i j_f;1M';\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{l_{M'}}\\
&\quad+\langle\langle j_f j_i;1M;\hat{\mathbf{1}},\hat{\mathbf{M}}\,|\,\mathscr{G}(i\xi)\,|\,j_i j_f;1M';-\hat{\mathbf{M}}',\hat{\mathbf{M}}'\rangle\rangle E_{r_{-M'}}]\}\ ,
\end{aligned}
\tag{36}
$$

assuming only the initial state is populated and $\beta\omega_L\ll 1$.

For low-j transitions, the calculation is greatly simplified now, since, for example, in $1\rightarrow 0$ or $\frac{3}{2}\rightarrow\frac{1}{2}$ transitions, the coupled Dyson equations which determine the matrix elements in Eq. (36) are limited in number. In this case the only diagonal irreducible matrix elements of the RWA even functions $G_{cc}(\hat{\mathbf{0}},\hat{\mathbf{n}}_2)$ which occur have $\hat{\mathbf{n}}_2=0,\pm 2$. Also in this case, $K=0,1,2$. In the RWA odd subspace the diagonal functions $G_{ab}(\hat{\mathbf{1}},\hat{\mathbf{n}}_2)$ all have $\hat{\mathbf{n}}_2=\pm 1$. Thus, the solution of the coupled matrix elements of the Dyson equation now involves only low-rank-matrix inversion. The complete expression for this case has been developed by Giraud-Cotton.[17] We limit the following discussion to the third-order contribution to the susceptibilities and calculate the self-rotation and Verdet constant to this order of approximation.

A. Self-rotation

The simplest case in which the irreducible representation diagonalizes the interaction-free resolvent operators is the one for which the magnetic field is zero. Since, as was noted previously, the susceptibility is independent of Q in this case, the nonlinear susceptibilities χ_r and χ_l will be the same for linearly polarized light and no MOA can occur. However, for elliptically polarized light, there will be an effect proportional to the difference of intensities of the left and right circularly polarized components. The calculation of the matrix elements of Eq. (36) outlined above yields the following expression for the third-order complex rotation:

$$
\begin{aligned}
&(\bar{\Theta}^{(3)}+i\Psi^{(3)})/L\\
&\quad=[A(\beta_r^2-\beta_l^2)/\gamma_{fi}]\langle G_{fi}^1(\hat{\mathbf{1}},\hat{\mathbf{1}})\mathrm{Im}G_{fi}^1(\hat{\mathbf{1}},\hat{\mathbf{1}})\rangle_V\\
&\qquad\times(\rho_i^{\mathrm{eq}}-\rho_f^{\mathrm{eq}})F(i,f)\ ,\\
&A=(N_A/V)\frac{2\pi|d_{fi}|^2\omega}{\hbar c}\ ,\\
&F(i,f)=\sum_{K=1,2}(-1)^{K+1}\left[\Gamma_i^{-1}(K)\begin{Bmatrix}K&1&1\\ j_f&j_i&j_i\end{Bmatrix}\right.\\
&\qquad\left.+\Gamma_f^{-1}(K)\begin{Bmatrix}K&1&1\\ j_i&j_f&j_f\end{Bmatrix}\right]\ ,\\
&\Gamma_a(K)=\gamma_a(K)/\gamma_{fi}(1)\ ,
\end{aligned}
\tag{37}
$$

where $\beta_{l(r)}=|d_{fi}E_{l(r)}/\hbar|$ is the Rabi frequency of the left and right circularly polarized components, $\gamma_a(K)=\mathrm{Im}\langle\Pi_{aa}^K\rangle$ is the impact limit orientation ($K=1$) and alignment ($K=2$) relaxation rate of level a, and ρ_a^{eq} is the field-free population of level a.

For large detunings, only the rotation of the elliptically polarized radiation is important. The angle of rotation can be approximated by

$$
\Theta^{(3)}/L=-[A(\beta_r^2-\beta_l^2)/\gamma_{fi}\Delta\omega_{fi}^3](\rho_i^{\mathrm{eq}}-\rho_i^{\mathrm{eq}})F(i,f)\ ,
\tag{38}
$$

where $\Delta\omega_{fi}=\omega-\omega_{fi}$. In the opposite limit of near-resonance detunings with an important Doppler broadening, $\omega_D\gg\Delta\omega_{fi},\gamma_{fi}$, the circular dichroism dominates and we have

$$\Psi^{(3)}/L=[A(\beta_r^2-\beta_I^2)/\gamma_{fi}^2\omega_D](\rho_i^{eq}-\rho_f^{eq})F(i,f)\ . \quad (39)$$

Explicit expressions for $F(i,f)$ are given by Giraud-Cotton[17] for arbitrary values of j_i,j_f for dipole transitions $j_i-j_f=\Delta j=\pm1,0$. Here we note that for high-j values it has a particularly simple form that displays the dependence on $\Gamma(1)$ and $\Gamma(2)$, the orientation and alignment relaxation reduced rates:

$$\lim_{j\to\infty}F(i,f)=\begin{cases}-(1/15j)[\Gamma_i^{-1}(2)+\Gamma_f^{-1}(2)], & \Delta j=0\\ (1/12j)\{\Gamma_i^{-1}(1)+\Gamma_f^{-1}(1)-\frac{1}{5}[\Gamma_i^{-1}(2)+\Gamma_f^{-1}(2)]\}, & \Delta j=\pm1.\end{cases}$$

The alignment relaxation rate alone dominates the self-rotation for $\Delta j=0$ transitions, as is the case for nonlinear phenomena in the absence of magnetic fields (cylindrical symmetry with respect to the propagation direction). However, for $\Delta j=\pm1$ transitions, a combination of orientation and relaxation rates occurs.

Finally, we note that the self-rotation of the axis of polarization of the incident elliptical radiation when $\Delta\omega_{fi}\gg\gamma_{fi},\omega_D$ is of opposite sign for $\Delta j=0$ and $\Delta j=\pm1$ transitions without modification of its ellipticity. In the opposite quasiresonant limit $\Delta\omega_{fi},\gamma_{fi}\ll\omega_D$, only the ellipticity is affected, again with opposite sign for $\Delta j=0$ and $\Delta j=\pm1$ transitions. This last result, in the special case where the orientation and alignment rates are the same, has been discussed previously by Saikan.[22]

B. Verdet constant

The third-order contribution to the Verdet constant was studied for the first time by Yu and Osborn.[6] They calculated the influence of the intensity on both the diamagnetic and paramagnetic contributions, that is, on the terms independent of and dependent on the temperature. The calculation presented there considered only the normal Zeeman transition $j_i=1\to j_f=0$. Using the method presented above, we shall study the more general case of dipole transitions between levels of arbitrary angular momentum. We shall examine successively the case where the Zeeman effect is small with respect to the width of the levels involved and the case where it is large enough to lift completely the level degeneracy. The first case is of interest for the study of Faraday rotation in gases in the earth's magnetic field and subject to strong laser radiation. The second corresponds more nearly to the typical conditions for Faraday rotators in high-power glass-laser systems.

The expression defining the Verdet constant, Eq. (2), is valid for detunings from resonance which are much larger than the width and Zeeman shift of the transition being studied. This detuning must, however, be less than $\beta=\hbar/kT$ in order to preserve a product form for the system-bath density operator. Under these conditions, we can expand both $\rho_{aa}^{eq}(j_am_a)$ and $G_{ab}(\hat{\mathbf{n}}_1,\hat{\mathbf{n}}_2)$ in powers of the magnetic field H_z.

Recall that in the presence of a magnetic field the irreducible tensor basis does not diagonalize the resolvent operators. Nevertheless, as long as the detuning is much greater than the Larmor frequencies [which is the basic condition for the validity of Eq. (2) which defines the Verdet constant], we can write

$$G=G^0(1-M_zH_zG^0)\ , \quad (40)$$

where G^0 is the magnetic-field-free resolvent operator with matrix elements in the irreducible basis as given in Eq. (23). In Eq. (40) only M_z has off-diagonal elements and only in the odd-parity RWA subspace,[17] so we can write for those matrix elements

$$\begin{aligned}&\langle\langle j_aj_b;KQ;\pm\hat{\mathbf{1}},\hat{\mathbf{n}}_2\,|\,G\,|\,j_aj_b;K'Q;\pm\hat{\mathbf{1}},\hat{\mathbf{n}}_2\rangle\rangle\\ &\quad=G_{ab}^K(\pm\hat{\mathbf{1}},\hat{\mathbf{n}}_2)\delta_{K,K'}+(-1)^{j_a+j_b+K+Q}\omega_L\langle K1Q0\,|\,K'Q\rangle(2K+1)^{1/2}G_{ab}^K(\pm\hat{\mathbf{1}},\hat{\mathbf{n}}_2)G_{ab}^{K'}(\pm\hat{\mathbf{1}},\hat{\mathbf{n}}_2)\\ &\qquad\times\left[g_a[j_a(j_a+1)(2j_a+1)]^{1/2}\begin{Bmatrix}1&K&K'\\ j_b&j_a&j_a\end{Bmatrix}\right.\\ &\qquad\left.+(-1)^{K+K'}g_b[j_b(j_b+1)(2j_b+1)]^{1/2}\begin{Bmatrix}1&K&K'\\ j_a&j_b&j_b\end{Bmatrix}\right],\end{aligned} \quad (41a)$$

with the magnetic-field-free G_{ab}^K as defined in Eq. (23).

In the even-parity RWA subspace, M_z has only diagonal elements, but, since these matrix elements of the resolvent operators do not depend on the detuning, Eq. (40) is only valid in the weak-field limit; thus we write

$$\langle\langle j_aj_a;KQ;\hat{\mathbf{0}},\hat{\mathbf{n}}_2\,|\,G\,|\,j_aj_a;KQ;\hat{\mathbf{0}},\hat{\mathbf{n}}_2\rangle\rangle=\begin{cases}-(\omega_Lg_aQ)^{-1}\delta_{K,K'}, & \omega_Lg_a\gg\gamma_a(K)\\ G_{aa}^K(\hat{\mathbf{0}},\hat{\mathbf{n}}_2)[1+g_a\omega_LQG_{aa}^K(\hat{\mathbf{0}},\hat{\mathbf{n}}_2)]\delta_{K,K'}, & \omega_Lg_a\ll\gamma_a(K)\end{cases} \quad (41b)$$

where $\omega_L=\mu_BH_z$.

Note that a term independent of the magnetic field appears in Eqs. (41a) and (41b). This term is the self-rotation term discussed above. It contributes a term proportional to the difference of intensities of the left and right circularly polarized components as can be seen from Eq. (36). The remaining terms in the nonlinear effect, as we shall see, are always dependent on the sum of these intensities.

In order to investigate the T^{-2} dependence of the third-order Verdet constant, found by Yu and Osborn,[6] in the strong-field limit, we expand $\rho_{cc}^{eq}(j_c m_c)$ to second order in $\beta\omega_L g_c$:

$$\rho_{cc}^{eq}(j_c m_c)=\sum_{c=i,f}\rho_c^{eq}\left[\left[1+(\beta\omega_L g_c)^2\frac{j_c(j_c+1)}{3}\right](2j_c+1)^{1/2}\,|\,j_c j_c;00;\hat{0},\hat{0}\rangle\rangle\right.$$
$$-\beta\omega_L g_c[j_c(j_c+1)(2j_c+1)/3]^{1/2}\,|\,j_c j_c;10;\hat{0},\hat{0}\rangle\rangle$$
$$\left.+[(\beta\omega_L g_c)^2/3][j_c(j_c+1)(4j_c^2-1)(2j_c+3)/5]^{1/2}\,|\,j_c j_c;20;\hat{0},\hat{0}\rangle\rangle\right], \tag{42}$$

where $\rho_c^{eq}=Z^{-1}e^{-\beta\omega j_c}$ is the equilibrium population of sublevels c in the absence of a magnetic field. This expansion can be limited, in the weak-field case, to first order in $\beta\omega_L g_c$.

To simplify the notation in the strong- and weak-field limits of the Verdet constant, we distinguish a diamagnetic contribution V_d (from the magnetic-field dependence of the resolvent operators) and a paramagnetic contribution V_p (from the H_z dependence of the sublevel populations) as in Ref. 6:

$$V(\omega)=V_d(\omega+V_p(\omega)\ . \tag{43}$$

The expressions for those coefficients in the two limits discussed in the previous calculations of the linear effect can be written in the following forms.

(1) Weak field, Doppler broadened, $\omega_D\gg\Delta\omega_{fi}\gg\gamma_{fi}\gg\omega_L^i,\omega_L^f$:

$$V_d^{(3)}=\mu_B A(\beta_r^2+\beta_l^2)\pi^{1/2}(\rho_i^{eq}-\rho_f^{eq})F_1(j_i,j_f)\times e^{-\Delta\omega_{fi}^2/\omega_D^2}/\omega_D\gamma_{fi}^3(1)\ ,$$
$$V_p^{(3)}=\mu_B A(\beta_r^2+\beta_l^2)\pi^{1/2}\times[\rho_i^{eq}F_2(j_i,j_f)+\rho_f^{eq}F_3(j_i,j_f)]\times e^{-\Delta\omega_{fi}^2/\omega_D^2}\omega_D\gamma_{fi}^2(1)\ , \tag{44}$$

where A is defined in Eq. (37), and the $F_k(j_i,j_f)$ are real coefficients which depend on j_i,j_f and the relaxation rates only. They are tabulated in Ref. 17 for $\Delta j=0,\pm1$ transitions separately. Here we shall study only the case of large j. This case is appropriate for Faraday rotators in high-power laser systems which are usually composed of doped glasses and have ground states with large angular momentum eigenvalues or gases where the rotational number of populated states may be large.

For the large-j case, we assume also that the initial-state population and lifetime are much larger than those of the final state, $\rho_i^{eq}\gg\rho_f^{eq}$ and $\gamma_f\gg\gamma_i$. The linear effect, Eq. (33b), becomes in this case

$$V_d^{(1)}=-\mu_B A(\rho_i^{eq}/3\omega_D^2)\times[g_i+g_f+(g_i-g_f)(j_i^2-j_f^2)/2]\ ,$$
$$V_p^{(1)}=i\beta\mu_B A(\rho_i^{eq}/6\omega_D)g_i(j_i^2-j_f^2)/2\ . \tag{45}$$

Neglecting the difference between the $\gamma_a(K)$ values, the third-order contribution becomes

$$V_d^{(3)}=-\mu_B A\rho_i^{eq}\pi^{1/2}/(\omega_D\gamma_{fi}^3)e^{-\Delta\omega_{fi}^2/\omega_D^2}(\beta_r^2+\beta_l^2)(1/120\Gamma_i j)\times\{8(g_i+g_f+2g_i/\Gamma_i)(1-\Delta j^2)+[2(g_i+g_f)+4g_i/\Gamma_i+j\,|\,\Delta j\,|\,(1+\Delta j)(g_i-g_f)]\,|\,\Delta j\,|\,\}\ ,$$
$$V_p^{(3)}=\beta\mu_B A\rho_i^{eq}/(\omega_D\gamma_{fi}^2)e^{-\Delta\omega_{fi}^2/\omega_D^2}(\beta_r^2+\beta_l^2)g_i/\Gamma_i[(1-\Delta j^2)/30j-\Delta j/20]\ . \tag{46}$$

In these expressions, $\Delta j=0$ for Q transitions, $\Delta j=+1$ (-1) for R (P) transitions, respectively, and j is the highest of the two quantum numbers j_i,j_f.

We note that in this weak-field, large angular momentum, Doppler-broadened case, the diamagnetic contribution dominates and only the Faraday rotation is modified in third order. The ellipticity is unaffected.

(2) Large magnetic field, collision broadened, $\omega_L^f,\omega_L^i\gg\Delta\omega_{fi}\gg\gamma_{fi}\gg\omega_D$:

$$V_d^{(3)}=-\mu_B A(\rho_i^{eq}-\rho_f^{eq})(\beta_r^2+\beta_l^2)[F_4(j_i,j_f)+iF_5(j_i,j_f)]\ ,$$
$$V_p^{(3)}=-\beta\mu_B A(\beta_r^2+\beta_l^2)[\rho_i^{eq}F_6(j_i,j_f)+\rho_f^{eq}F_7(j_i,j_f)]-i\beta^2\mu_B A\gamma_{fi}(\beta_r^2+\beta_l^2)[\rho_i^{eq}F_8(j_i,j_f)+\rho_f^{eq}F_9(j_i,j_f)]\ , \tag{47}$$

where the $F_k(j_i,j_f)$ are real functions of $j_i j_f$, the relaxa-

tion rates, and the ratio $\Delta\omega_{fi}/\gamma_{fi}$. They are tabulated[17] as the F_k, $k=1,3$, for $\Delta j=0,\pm1$ transitions.

In the large-$j_i,\rho_i^{eq},\gamma_i^{-1}$ limit, the linear effect of Eq. (34) becomes

$$\begin{aligned} V_d^{(1)} &= \mu_B A(\rho_i^{eq}/6\Delta\omega_{fi}^2)(1-2i\gamma_{fi}/\Delta\omega_{fi}) \\ &\quad\times[g_i+g_f-j\Delta j(g_i-g_f)] , \\ V_p^{(1)} &= \beta\mu_B A(\rho_i^{eq}g_i/\Delta\omega_{fi})(1-i\gamma_{fi}/\Delta\omega_{fi}) \\ &\quad\times(1-j\Delta j-\Delta j^2) . \end{aligned} \tag{48}$$

The third-order contribution to the Verdet constant becomes in this case

$$\begin{aligned} V_d^{(3)} &= -\mu_B A\rho_i^{eq}(\beta_r^2+\beta_I^2) \\ &\quad\times(\Phi_1/\Delta\omega_{fi}^4+i\Phi_2/\gamma_i\Delta\omega_{fi}^3) , \\ V_p^{(3)} &= -\mu_B A\rho_i^{eq}(\beta_r^2+\beta_I^2) \\ &\quad\times[\beta(\Phi_3/\Delta\omega_{fi}^3+i\Phi_2/\gamma_i\Delta\omega_{fi}^2) \\ &\quad -i\beta^2\Phi_4\gamma_{fi}/\Delta\omega_{fi}^3] , \end{aligned} \tag{49}$$

where, for Q transitions,

$$\begin{aligned} \Phi_1 &= [2(g_i+g_f)+g_i-g_f]/15j\Gamma_i \\ &\quad +(g_i^2/g_f+g_f^2/g_i)/30j , \\ \Phi_2 &= g_i/15j , \\ \Phi_3 &= g_i/30j\Gamma_i+g_i^2/30jg_f , \\ \Phi_4 &= g_i(1+g_i/g_f)j/75 , \end{aligned}$$

and for R and P transitions,

$$\begin{aligned} \Phi_1 &= -\Delta j[g_i+g_f+2(j\Delta j+6)(g_i-g_f)] \\ &\quad\times(g_f/g_i-g_i/g_f)/240 \\ &\quad +[13(g_i+g_f)-14j\Delta j(g_i-g_f)]/40j\Gamma_i , \\ \Phi_2 &= g_i/60j , \\ \Phi_3 &= g_i/15\Gamma_i-\Delta j\{2(g_i+g_f)[1-j\Delta j(g_i/g_f-1)] \\ &\quad +6(g_i-g_f)\}/240 , \\ \Phi_4 &= g_i[2j(g_i+g_f)-5\Delta j(g_i-g_f)]/1200g_f . \end{aligned}$$

Note that when $g_i\sim0$ (or $g_f\sim0$) the quantities involving g_i (or g_f) may be simply omitted in Eq. (49), whenever the Landé factor appears in the numerator or denominator, provided that all products have been performed in the Φ's. Note that the ellipticity and not the rotation is primarily affected by the third-order contribution. However, since the radiation is nonresonant, the ellipticity is a small effect so that very little change in the MRS is to be expected when intense laser radiation is incident. This conclusion is at variance with that of Yu and Osborn,[6] who studied only spinless, noninteracting systems (i.e., a normal Zeeman effect). It is seen that, when relaxation is taken into account, terms proportional to Γ_i^{-1} appear which are at least as important in gases as those evaluated by Yu and Osborn. In addition, the term in T^{-2} in Eq. (42) appears here as a contribution to the ellipticity or imaginary part of the Verdet constant. This corrects what we believe is a misprint in the Yu and Osborn article,[6] where it appears in the real part. Except for this, our expressions reduce to theirs in the appropriate limit.

IV. CONCLUSION

Nonlinear response methods have been applied to calculate the components of the susceptibility which describe the MOA in intense laser fields. This formulation has been applied to generalize previous calculations of the effect. In particular, the third-order contribution for a two-level system with arbitrary angular momentum and an anomalous Zeeman effect has been presented. Extension of this calculation to an exact solution for this two-level system has been discussed for the case of a normal Zeeman effect or Paschen-Back effect.

Arbitrary polarization of the incident laser field has been included. When this polarization is elliptical, magnetic-field-independent terms arise. A self-rotation effect is shown to appear when the laser field has a large detuning. For near-resonance conditions, a modification of the ellipticity occurs. These results generalize those of Maker and Terhune[21] and Saikan.[22]

The calculation of the third-order term in the applied laser field which depends linearly on the longitudinal magnetic field strength leads to nonlinear corrections to the complex Verdet constant. Several cases of practical interest have been studied. First, the case of weak-magnetic-field energy (compared to the collisional linewidth) in Doppler-broadened transitions was investigated. These conditions are those which arise in problems of astrophysical interest. A second study was for the case of a laser detuned from resonance in a strong magnetic field, which is of interest for studies of Faraday rotators in high-power laser systems.

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