

the experimental ones. One of the reasons for this difference may be the fact that the relation connecting impact parameter, scattering angle, and incident energy is unsatisfactory, inasmuch as it fails to take account of the influence of the particular electronic state on the trajectory.

In Table III we present our results for the cross sections of capture in the ground state and the excited states of the He^+ ion, in the energy range 1.6–32.4 keV. In Fig. 3 we compare our results of total cross section with the experimental findings of Fite, Smith, and Stebbings.² Here we have found a very good agreement. The general tendency of our theoretical results approaching zero in the zero-velocity limit of the α

particle is a characteristic feature of accidentally resonant reactions, as has been remarked by Bates *et al.*³ It seems clear that the predominantly large cross section for the capture into the $2s$ or $2p$ states compared with that in the ground state is due to the accidental resonance of the two states with the ground state of the hydrogen atom.

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Effective Operator Formalism in Optical Pumping*

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Real and virtual absorption of weak monochromatic light is analyzed with semiclassical radiation theory. The influence of the light on the atoms is described by an effective ground-state Hamiltonian operator, and the effect of the atoms on the light is described by a dielectric susceptibility operator. These operators are expressed explicitly in terms of familiar ground-state observables, angular factors, oscillator strengths, and plasma dispersion functions. The theory gives a comprehensive description of optical pumping, light shifts, and light modulation due to real and virtual absorption of light, and several new effects are predicted. Repopulation of the atomic ground state from a polarized excited state is not considered in this paper.

I. INTRODUCTION

A FORMAL theory of optical pumping was first developed by Barrat and Cohen-Tannoudji.¹ They show that for normal light intensities the pumping of the atomic ground state is due to two distinct processes: absorption by the ground-state atoms of light which is not completely isotropic or whose spectral intensity varies strongly in the region of the atomic absorption lines, and repopulation of the ground state by spontaneous emission from a polarized excited state. In their work the atoms are treated with the density matrix formalism while the light is represented by a many-photon state of the radiation field. Although this approach yields a detailed description of the evolution of the atoms, the corresponding influence of the polarized atoms on the light is treated only superficially.

In this paper we consider the effects due to the real and virtual absorption of light by atoms. We shall not be concerned with the repopulation of the atomic

ground state by spontaneous emission from a polarized excited state. The interaction of the atoms with the light is treated semiclassically. The electric field of the incident light is represented by a quasimonochromatic wave²

$$\mathbf{E}(\mathbf{r}, t) = (\mathbf{E}_0/2)e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + \text{c.c.}, \quad (\text{I.1})$$

where the amplitude \mathbf{E}_0 is a slowly varying function of space and time and c.c. denotes complex conjugate. We shall assume that the incident light intensity is weak enough so that spontaneous emission from the excited state is much more probable than stimulated emission. We shall also assume that any external magnetic field which may be present is small enough that the Zeeman splittings of the atom are much less than the Doppler widths of the optical absorption lines or than the hfs splittings of the atomic states. Under these loose restrictions we show that the effect of real and virtual absorption of light by the atoms can be represented by an effective ground-state Hamiltonian operator $\delta\mathcal{H}$; i.e., as if the evolution of the atomic ground state were determined by a Schrödinger equation of the form

$$i\hbar(\partial\psi/\partial t) = (\mathcal{H}_0 + \delta\mathcal{H})\psi. \quad (\text{I.2})$$

² This formalism has been extended to the case where several monochromatic light waves are present simultaneously.

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† Alfred P. Sloan Research Fellow.

¹ J. P. Barrat and C. Cohen-Tannoudji, *J. Phys. Radium* 22, 329 (1961); 22, 443 (1961).

The ground-state Hamiltonian of the atoms in the absence of light is represented by \mathcal{H}_0 . The effective Hamiltonian $\delta\mathcal{H}$ is in general not Hermitian, but it can be expressed as a linear combination of a Hermitian *light-shift operator* $\delta\mathcal{E}$ and a Hermitian *light-absorption operator* $\delta\Gamma$, i.e.,

$$\delta\mathcal{H} = \delta\mathcal{E} - i(\hbar/2)\delta\Gamma. \quad (\text{I.3})$$

The light shift operator $\delta\mathcal{E}$ has exactly the same effect on the atoms as a small Hermitian perturbation of the zeroth-order Hamiltonian \mathcal{H}_0 . The diagonal matrix elements of $\delta\mathcal{E}$ represent a shift of the energy levels of the atom.¹ If the light is modulated³ at some ground-state transition frequency, then the off-diagonal matrix elements of $\delta\mathcal{E}$ can induce real transitions between ground-state sublevels.⁴

The light-absorption operator $\delta\Gamma$ gives rise to a dissipative term in the effective Hamiltonian, and it is responsible for the relaxation and optical pumping of atomic vapors due to absorption of light. If the ground state of the atoms is described with the density matrix ρ , then the rate of disappearance of atoms due to absorption of light is

$$-(d/dt) \text{Tr}[\rho] = \text{Tr}[\rho\delta\Gamma] = \langle\delta\Gamma\rangle. \quad (\text{I.4})$$

The diagonal matrix elements of $\delta\Gamma$ cause a longitudinal pumping of the atomic sublevels, and the off-diagonal matrix elements of $\delta\Gamma$ can produce ground-state coherence⁵ if the light is modulated near some ground-state transition frequency.⁶

The macroscopic dielectric polarization vector \mathbf{P} of the vapor is related to the electric field \mathbf{E} of the light by a susceptibility dyadic $\langle\chi\rangle$

$$\mathbf{P} = \langle\chi\rangle(\mathbf{E}_0/2)e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{c.c.} \quad (\text{I.5})$$

The susceptibility dyadic $\langle\chi\rangle$ is the expectation value of a susceptibility dyadic operator χ which depends only on the observables of the atomic ground state. The absorptive components of $\langle\chi\rangle$ describe the attenuation of a beam of light by a polarized vapor, while the dispersive components describe the anisotropic index of refraction. The susceptibility dyadic is, of course, closely related to the light-shift operator and to the light-absorption operator.⁷

³ When the light is modulated at frequencies which are large compared to the Doppler widths of the optical absorption lines (hfs frequencies), it is necessary to consider the sideband structure of the light in detail.

⁴ W. Happer and B. S. Mathur, Phys. Rev. Letters 18, 727 (1967).

⁵ In problems associated with optical pumping and optical double resonance, the term "coherence" is used to describe the off-diagonal, oscillating components of the density matrix, which can be induced, for instance, by a small periodic perturbation on an atomic system in which population differences exist.

⁶ W. E. Bell and A. L. Bloom, Phys. Rev. Letters 6, 280 (1961).

⁷ The light absorption operator and the light-shift operator were first derived in Ref. 1 for light with a broad spectral profile. Naturally, the dielectric susceptibility dyadic was not considered since it has significance only for monochromatic light. The results of the present paper can be applied to light with a broad spectral profile in the usual way by representing the light with many monochromatic waves of random phase.

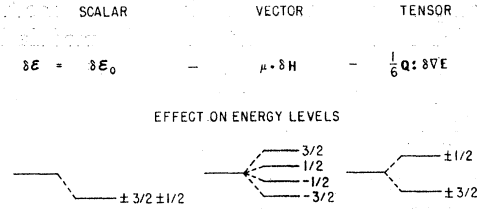


FIG. 1. Different types of light shifts.

The basic form of (I.1) through (I.5) is valid for any atom. However, the effective ground-state operators take on a particularly simple form for atoms with a single Zeeman multiplet in the ground state, i.e., atoms with the nuclear spin equal to zero or with the ground-state electronic spin equal to zero. Then the light-shift operator is

$$\delta\mathcal{H} = \delta\mathcal{E}_0 - \mathbf{u} \cdot \delta\mathbf{H} - \frac{1}{6} \mathbf{Q} : \delta\nabla\mathbf{E}. \quad (\text{I.6})$$

Here $\delta\mathcal{E}_0$ is a common shift of all the sublevels of the ground-state multiplet (a shift of the center of gravity), $\delta\mathbf{H}$ is an effective magnetic field which interacts with the magnetic dipole moment \mathbf{u} of the atom, and $\delta\nabla\mathbf{E}$ is an effective electric-field gradient which interacts with the electric quadrupole moment \mathbf{Q} of the atom. The type of light shift which is caused by each term in (I.6) is illustrated in Fig. 1.

The light absorption operator for atoms with a single Zeeman multiplet in the ground state has the form

$$\delta\Gamma = \delta\Gamma_0 + \mathbf{u} \cdot \delta\Gamma_1 + \mathbf{Q} : \delta\Gamma_2, \quad (\text{I.7})$$

so that the rate of absorption is (I.4)

$$\langle\delta\Gamma\rangle = \delta\Gamma_0 + \langle\mathbf{u}\rangle \cdot \delta\Gamma_1 + \langle\mathbf{Q}\rangle : \delta\Gamma_2. \quad (\text{I.8})$$

Thus, the absorption rate depends on the expectation value of the magnetic dipole moment and on the expectation value of the electric quadrupole moment of the atom. Explicit expressions for the scalar damping constant $\delta\Gamma_0$, for the vector damping constant $\delta\Gamma_1$, and for the tensor damping constant $\delta\Gamma_2$ are derived in Sec. IV.

Finally, for atoms with only one Zeeman multiplet in the ground state, the dielectric susceptibility dyadic is⁸

$$\langle\chi\rangle = X_0 + X_1\langle\mathbf{u}\rangle + X_2\langle\mathbf{Q}\rangle. \quad (\text{I.9})$$

The scalar part X_0 is responsible for the absorptive and dispersive components of the scalar index of refraction. The vector part $X_1\langle\mathbf{u}\rangle$ is responsible for the orientation-dependent absorption of light and for the paramagnetic Faraday effect. The tensor part, $X_2\langle\mathbf{Q}\rangle$, is responsible for the alignment-dependent absorption of light by the vapor and for refractive effects similar to those in an optically active crystal. If coherence exists in the atomic vapor, both $\langle\mathbf{u}\rangle$ and $\langle\mathbf{Q}\rangle$ will contain

⁸ The dyadic $\langle\chi\rangle$ is expressed as the sum of a scalar, vector, and tensor part so that the product of $\langle\chi\rangle$ with a vector \mathbf{E} is another vector $\langle\chi\rangle\mathbf{E}$ whose Cartesian components are $(\langle\chi\rangle\mathbf{E})_i = X_0E_i + X_1(\langle\mathbf{u}\rangle \times \mathbf{E})_i + X_2 \sum_j Q_{ij}E_j$.

oscillating terms which give rise to the modulated absorption of resonant light⁹ and to the modulation of the polarization of transmitted off-resonant light.¹⁰ A detailed discussion of atoms with a single Zeeman multiplet in the ground state can be found in Sec. IV.

The alkali atoms present a special problem because of the presence of hyperfine structure in both the ground state and in the excited state. Neglecting the excited-state hfs separations,¹¹ one finds that the light-shift operator has the form

$$\delta\mathcal{E} = \delta\mathcal{E}_0 + h\delta\mathbf{A}\cdot\mathbf{J} - \mathbf{u}\cdot\delta\mathbf{H}. \quad (\text{I.10})$$

A common shift of all of the sublevels of the ground state is described by $\delta\mathcal{E}_0$. This shift of the center of gravity of the ground state cannot, of course, be detected as a shift in some ground-state transition frequency. The term $h\delta\mathbf{A}\cdot\mathbf{J}$ in (I.10) represents an effective shift of the magnetic dipole coupling constant of the atom. This term will not affect the Zeeman frequencies of the atom, but it will shift the resonant frequencies of the hfs transitions. The term $-\mathbf{u}\cdot\delta\mathbf{H}$ in (I.10) represents the interaction of the magnetic dipole moment of the atom with an effective magnetic field $\delta\mathbf{H}$. This term will shift the Zeeman frequencies of the alkali atom. The effective field $\delta\mathbf{H}$ is present only if the light is circularly polarized, and in this case $\delta\mathbf{H}$ is directed parallel or antiparallel to the direction of the light beam.

Because of the large hfs separations in the ground states of alkali atoms, it is convenient to write a ground-state operator, O , as the sum of two Zeeman components O_f and a hfs component O_{hfs} , i.e.,

$$O = \sum_{f=-I-1/2}^{I+1/2} O_f + O_{\text{hfs}}, \quad (\text{I.11})$$

where

$$O_f = \sum_{\mu\mu'} |f\mu\rangle\langle f\mu| O |f\mu'\rangle\langle f\mu'|, \quad (\text{I.12})$$

and

$$O_{\text{hfs}} = \sum_{\substack{f \neq f' \\ \mu\mu'}} |f\mu\rangle\langle f\mu| O |f'\mu'\rangle\langle f'\mu'|. \quad (\text{I.13})$$

The expectation value $\langle O_f \rangle$ will contain static terms, and, if Zeeman coherence exists, terms which oscillate near the Zeeman frequencies of the atom. The expectation value $\langle O_{\text{hfs}} \rangle$ will be zero unless hfs coherence exists and then it will oscillate near the hfs frequencies of the atom.

Neglecting the excited-state hfs separations one finds that the Zeeman susceptibilities of an alkali vapor have the form

$$\langle \chi_f \rangle = X_0 + X_1 \langle \mathbf{u}_f \rangle \times. \quad (\text{I.14})$$

⁹ H. G. Dehmelt, Phys. Rev. **105**, 1924 (1957); W. E. Bell and A. L. Bloom, *ibid.* **107**, 1559 (1957).

¹⁰ J. Manuel and C. Cohen-Tannoudji, Compt. Rend. **257**, 413 (1963); W. Happer and B. S. Mathur, Phys. Rev. Letters **18**, 577 (1967).

¹¹ When the hfs separations of the excited state are taken into account, it is necessary to add a small term which transforms like a quadrupole moment to the effective operators for the alkali atoms (see Sec. III).

If a microwave field of frequency ω_m has induced hfs coherence in the atomic vapor, the hfs component of the magnetic dipole moment can be expressed as

$$\langle \mathbf{u}_{\text{hfs}} \rangle = \mathbf{u}_1 e^{-i\omega_m t} + \mathbf{u}_1^* e^{i\omega_m t}. \quad (\text{I.15})$$

One finds that the hfs susceptibility of the vapor can be written in the form

$$\langle \chi_{\text{hfs}} \rangle = \frac{1}{2} [X_1(a) \mathbf{u}_1 e^{-i\omega_m t} + X_1(b) \mathbf{u}_1^* e^{i\omega_m t}] \times. \quad (\text{I.16})$$

The functions $X_1(a)$ and $X_1(b)$ depend on the frequency of the incident light wave and in general $X_1(a) \neq X_1(b)$ so that the hfs susceptibility will generate asymmetric sidebands from a monochromatic light wave. Several interesting experimental consequences of the hfs susceptibility are discussed in Sec. III. The amplitude and phase of the hfs modulation of the pumping light are closely related to the magnitude and sign of the hfs light shift, so that observation of the light modulation signals from optically pumped frequency standards could provide a means for monitoring and eliminating the light shifts.

The algebra of spherical tensors is used to carry out the computations in this paper. All optical reduced matrix elements are expressed in terms of oscillator strengths for the transition, and whenever possible the effective operators are written in terms of familiar ground-state operators such as \mathbf{J} , $\mathbf{I}\cdot\mathbf{J}$, etc. The optical absorption and dispersion profiles are expressed in terms of plasma dispersion functions.¹²

II. SEMICLASSICAL THEORY OF THE ABSORPTION OF LIGHT BY ATOMIC VAPORS

Let the electric field of a monochromatic light wave be represented by

$$\mathbf{E}(\mathbf{r}, t) = (E_0/2) [\mathbf{e} e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + \text{c.c.}]. \quad (\text{II.1})$$

Here \mathbf{e} , the complex polarization vector of the light, is normalized so that

$$\mathbf{e} \cdot \mathbf{e}^* = \mathbf{e}^* \cdot \mathbf{e} = 1, \quad (\text{II.2})$$

and E_0 is a slowly varying function of space and time. The Hamiltonian operator of the atom can be written in the form

$$\mathcal{H} = \mathcal{H}_{\text{opt}} + \mathcal{H}_{\text{hfs}} + \mathcal{H}_z - \mathbf{p} \cdot \mathbf{E} + \mathcal{H}_c. \quad (\text{II.3})$$

These terms have the following significance :

(a) \mathcal{H}_{opt} describes the optical energy levels of the atom, excluding the hyperfine structure. \mathcal{H}_{opt} is a multiple of the unit operator within the subspace characterized by the electronic angular momentum J and by any other quantum numbers necessary to distinguish multiplets with the same J .

(b) \mathcal{H}_{hfs} describes the hyperfine structure of the optical energy levels.

(c) \mathcal{H}_z describes the interaction of the atom with any static external magnetic field which may be present.

(d) $-\mathbf{p} \cdot \mathbf{E}$ describes the interaction of the electric dipole moment \mathbf{p} of the atom with the electric field \mathbf{E} of the light.

(e) \mathcal{H}_c describes collisions of the atom with other atoms or molecules or with the walls of the container. It also describes the effects of radiation trapping.

We shall only be interested in the \mathcal{H}_c insofar as it modifies the absorption of light by the atoms. Extensive work on collisional relaxation effects in the ground state¹³ and in the excited state¹⁴ of the atom can be found in the literature.

The quantum numbers used to designate the eigenstates of the atom are indicated in Fig. 2. The nuclear spin I is coupled to the ground-state atomic spin J_g to form the ground-state hfs levels F_g, F'_g , etc. A similar situation holds in the excited state.

Let us represent the state of the atom by the wave function

$$\psi(t) = \sum_m a_m e^{-i(E_m t/\hbar)} |m\rangle + \sum_\mu a_\mu e^{-i(E_\mu t/\hbar)} |\mu\rangle. \quad (\text{II.4})$$

The basis functions $|m\rangle$ and $|\mu\rangle$ represent the excited states and ground states of the atom. They are eigenfunctions of the basic Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_{\text{opt}} + \mathcal{H}_{\text{hs}} + \mathcal{H}_z. \quad (\text{II.5})$$

In this interaction picture the amplitudes a_m and a_μ change continuously under the influence of the light and in discontinuous jumps as a result of collisions. During the time between collisions, the excited-state amplitude a_m obeys the Schrödinger equation

$$i\dot{a}_m = -i\frac{\Gamma}{2}a_m - \sum_\mu \langle m | \frac{\mathbf{E} \cdot \mathbf{p}}{\hbar} | \mu \rangle a_\mu e^{i\omega_{m\mu}t}, \quad (\text{II.6})$$

where

$$\hbar\omega_{m\mu} = E_m - E_\mu. \quad (\text{II.7})$$

The damping of the excited-state amplitude due to spontaneous radiation has been accounted for¹⁵ by adding the term $-i(\Gamma/2)a_m$ to (II.6). The radiative lifetime of the excited state is $\tau = 1/\Gamma$. If the center of mass of the atom is located at the position $\mathbf{R}(t) = \mathbf{R}_0 + \mathbf{v}t$, then one can use (II.1) to write (II.6) in the form

$$i\frac{d}{dt} a_m e^{(\Gamma/2)t} = -\frac{E_0 e^{i\mathbf{k} \cdot \mathbf{R}_0}}{2\hbar} \sum_\mu \{ \mathbf{e} \cdot \mathbf{p}_{m\mu} e^{i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)]t} a_\mu + \text{rapidly oscillating terms} \}. \quad (\text{II.8})$$

For ordinary light intensities the coefficients a_μ will be

¹² B. D. Fried and S. D. Conte, *The Plasma Dispersion Function* (Academic Press Inc., New York, 1961).

¹³ F. A. Franz, *Phys. Rev.* **139**, A603 (1965); H. M. Gibbs and R. J. Hull, *ibid.* **153**, 132 (1967); M. A. Bouchiat and J. Brosselet, *ibid.* **147**, 41 (1966).

¹⁴ J. P. Barrat, *J. Phys. Radium* **20**, 541 (1959); **20**, 633 (1959); F. W. Byron, M. N. McDermott, and R. Novick, *Phys. Rev.* **134**, A615 (1964); A. Omont, *J. Phys. (Paris)* **26**, 26 (1965); J. P. Barrat, D. Casalta, J. L. Cojan, and J. Hamel, *J. Phys. (Paris)* **27**, 608 (1966).

¹⁵ A more rigorous justification for the introduction of the damping constant can be found in Ref. 1.

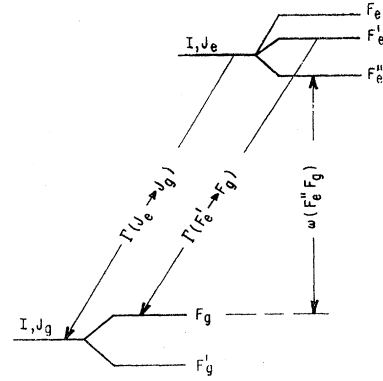


FIG. 2. Sketch of quantum states.

slowly varying¹⁶ with respect to the excited-state decay rate Γ , so that (II.8) may be integrated to give

$$i a_m(t) = i a_m(t') e^{-(\Gamma/2)(t-t')} - \frac{E_0}{2\hbar} e^{i(\mathbf{k} \cdot \mathbf{R} - \omega t)} \sum_\mu e^{i\omega_{m\mu} t} \mathbf{e} \cdot \mathbf{p}_{m\mu} a_\mu \times \left\{ \frac{1 - e^{-i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)](t-t')}}{i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)]} \right\}. \quad (\text{II.9})$$

The physical meaning of (II.9) is that the last collision occurred at the time t' leaving an excited-state amplitude $a_m(t')$. At a later time t , the original amplitude has decayed by the factor $e^{-(\Gamma/2)(t-t')}$ and an additional amplitude, coherent with the monochromatic light, has built up. Equation (II.9) may now be used to compute two important physical parameters: the dielectric susceptibility of the vapor, which describes the influence of the atoms on the light, and the effective ground-state Hamiltonian, which describes the effect of the light on the atoms.

A. The Dielectric Susceptibility

The dielectric susceptibility $\langle \chi \rangle$ is a dyadic (tensor) which relates the macroscopic polarization vector \mathbf{P} of the vapor to the electric field of the exciting light;

$$\mathbf{P} = \langle \chi \rangle \frac{E_0 \mathbf{e}}{2} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{c.c.} = N \langle \mathbf{p} \rangle. \quad (\text{II.10})$$

In anticipation of a result which we will obtain presently, the susceptibility has been written in the form of an expectation value of a certain operator χ . The macroscopic polarization \mathbf{P} must be equal to the atomic density N times the ensemble averaged electric dipole moment operator $\langle \mathbf{p} \rangle$ of an individual atom. The en-

¹⁶ If weak rf magnetic fields have coupled the ground-state sublevels there will be additional slow variations of the amplitudes a_μ . However, the flipping frequencies involved are normally much smaller than the excited-state decay rate Γ , and the evolution of the atomic ground state caused by the rf magnetic field can be considered separately from the evolution caused by the absorption of light.

semble average should include all possible collisional histories of the atoms and a Maxwellian velocity distribution.

The expectation value of \mathbf{p} for a single atom is [see (II.4)]

$$\langle \psi | \mathbf{p} | \psi \rangle = \sum_{\nu m} a_{\nu}^* e^{i\omega_{\nu m} t} \mathbf{p}_{\nu m} a_m + \text{c.c.} \quad (\text{II.11})$$

Substituting a_m from (II.9), we obtain

$$\begin{aligned} \langle \psi | \mathbf{p} | \psi \rangle &= \sum_{\nu m} a_{\nu}^* e^{i\omega_{\nu m} t} \mathbf{p}_{\nu m} a_m(t') e^{-(\Gamma/2)(t-t')} \\ &= \frac{E_0}{2\hbar i} e^{i(\mathbf{k} \cdot \mathbf{R} - \omega t)} \sum_{\mu \nu m} e^{i\omega_{\nu m} t} a_{\mu} a_{\nu}^* \mathbf{p}_{\nu m} \mathbf{p}_{m \mu} \cdot \mathbf{e} \\ &\quad \times \left\{ \frac{1 - e^{i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)](t-t')}}{i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)]} \right\} + \text{c.c.} \quad (\text{II.12}) \end{aligned}$$

We may now perform an ensemble average of $\langle \psi | \mathbf{p} | \psi \rangle$ over the collisional histories and over the velocity distribution of the atoms. Suppose that the probability $P(\tau) d\tau$ that the last collision occurred at a time between $t-\tau$ and $t-\tau+d\tau$ is given by

$$P(\tau) d\tau = e^{-\gamma_c \tau} \gamma_c d\tau. \quad (\text{II.13})$$

Let us further assume that the atoms have a Maxwellian velocity distribution so that the probability of finding an atom with the velocity \mathbf{v} is

$$N(\mathbf{v}) d^3v = \left(\frac{M}{2\pi RT} \right)^{3/2} \exp\left(-\frac{Mv^2}{2RT} \right) d^3v. \quad (\text{II.14})$$

Here M is the gram molecular weight of the atoms, T is the absolute temperature, and R is the gas constant. Thus, neglecting any correlations between the velocity of the atoms and the collisional histories, one can write the statistical average of $\langle \psi | \mathbf{p} | \psi \rangle$ as

$$\langle \mathbf{p} \rangle = \int_{-\infty}^t P(t-t') dt' \int N(\mathbf{v}) d^3v \langle \psi | \mathbf{p} | \psi \rangle. \quad (\text{II.15})$$

The first term of (II.12) will average to zero when substituted into (II.15) because the amplitudes $a_m(t')$ will be randomized by hard, velocity changing collisions. The collisional history average over the second term of (II.12) gives

$$\begin{aligned} \langle \mathbf{p} \rangle &= \frac{1}{\hbar} \sum_{\nu m \mu} \mathbf{p}_{\nu m} \mathbf{p}_{m \mu} \int \frac{N(\mathbf{v}) d^3v}{\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i[(\Gamma/2) + \gamma_c]} \\ &\quad \times \langle a_{\mu} a_{\nu}^* \rangle_{\text{av}} e^{i\omega_{\nu m} t} \mathbf{e} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + \text{c.c.} \quad (\text{II.16}) \end{aligned}$$

Note that the denominator of the line-shape term now contains the damping factor $\Gamma/2 + \gamma_c$, where $1/\Gamma$ is the natural radiative lifetime of the excited state, and γ_c is

the frequency of optical dephasing collisions [see (II.13)]. The result of the average over velocities can be expressed in terms of a plasma-dispersion function.¹²

$$Z(\zeta) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{du e^{-u^2}}{u - \zeta}. \quad (\text{II.17})$$

One obtains

$$\begin{aligned} \int \frac{N(\mathbf{v}) d^3v}{\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i[(\Gamma/2) + \gamma_c]} \\ = \frac{1}{k} \left(\frac{M}{2RT} \right)^{1/2} Z[x(F_{em}; F_{g\mu}) + iy], \quad (\text{II.18}) \end{aligned}$$

where the arguments of the plasma-dispersion function (profile factor) are

$$x(F_{em}; F_{g\mu}) = \frac{1}{k} \left(\frac{M}{2RT} \right)^{1/2} [\omega - \omega(F_{em}; F_{g\mu})], \quad (\text{II.19a})$$

$$y = \frac{1}{k} \left(\frac{M}{2RT} \right)^{1/2} \left(\frac{\Gamma}{2} + \gamma_c \right). \quad (\text{II.19b})$$

Since we shall only be concerned with situations where the Zeeman splittings of the hfs states are small with respect to the Doppler widths of the optical absorption lines, it will always be true that

$$x(F_{em}; F_{g\mu}) - x(F_{em'}; F_{g\mu'}) \ll 1, \quad (\text{II.20})$$

so that we can neglect the dependence of Z on the magnetic quantum numbers. It is convenient to express the profile factors as the matrix elements of a diagonal ground-state operator $z(F_e)$.

$$Z[x(F_{em}; F_{g\mu}) + iy] \equiv Z(F_e F_g) = \langle F_g | z(F_e) | F_g \rangle, \quad (\text{II.21})$$

where

$$z(F_e) = \sum_{F_g} \hat{p}(F_g) Z(F_e F_g). \quad (\text{II.22})$$

Here $\hat{p}(F_g)$ is the projection operator for the ground-state hfs multiplet F_g .

$$\hat{p}(F_g) = \sum_{\mu} |F_{g\mu}\rangle \langle F_{g\mu}|. \quad (\text{II.23})$$

It is also convenient to define the effective ground-state operator $\kappa(F_e)$.

$$\kappa(F_e) = \sum_m \mathbf{p} |F_{em}\rangle \langle F_{em} | \mathbf{p}. \quad (\text{II.24})$$

If we now introduce the polarizability operator α

$$\alpha = \sum_{F_e} \alpha(F_e) = \frac{\lambda}{\hbar} \left(\frac{M}{2RT} \right)^{1/2} \kappa(F_e) z(F_e), \quad (\text{II.25})$$

and the ground-state density matrix

$$\rho = \sum_{\mu \nu} |\mu\rangle \langle \nu | \langle a_{\mu} a_{\nu}^* \rangle_{\text{av}} e^{i\omega_{\nu \mu} t}, \quad (\text{II.26})$$

we find that (II.16) may be written in the compact form

$$\langle \mathbf{p} \rangle = \langle \alpha \rangle \cdot \frac{E_0 \mathbf{e}}{2} e^{i(\mathbf{k} \cdot \mathbf{R} - \omega t)} + \text{c.c.} \quad (\text{II.27})$$

Here $\langle \alpha \rangle$ is the expectation value of the polarizability operator

$$\langle \alpha \rangle = \text{Tr}[\alpha \rho]. \quad (\text{II.28})$$

Then from (II.27) and (II.10), we find that the susceptibility dyadic operator is

$$\chi = N \alpha. \quad (\text{II.29})$$

The dielectric tensor operator is then

$$\epsilon = 1 + 4\pi \chi = 1 + 4\pi N \alpha. \quad (\text{II.30})$$

B. The Effective Ground-State Hamiltonian

The effect of the light on the evolution of the atomic ground state can be represented by adding a small effective Hamiltonian $\delta \mathcal{H}$ to the zeroth-order Hamiltonian \mathcal{H}_0 (II.5) of the system. To show this we note that the ground-state amplitudes a_ν obey the Schrödinger equation¹⁶;

$$i \dot{a}_\nu = - \sum_m \langle \nu | \frac{\mathbf{E} \cdot \mathbf{p}}{\hbar} | m \rangle a_m e^{i\omega_\nu m t}. \quad (\text{II.31})$$

Substituting \mathbf{E} from (II.1) and a_m from (II.9), we obtain

$$i \dot{a}_\nu = - \sum_m \langle \nu | \frac{\mathbf{E} \cdot \mathbf{p}}{\hbar} | m \rangle a_m(t') e^{-i(\Gamma/2)(t-t')} e^{i\omega_\nu m t} \\ - \frac{|E_0|^2}{4\hbar^2} \sum \mathbf{e}^* \cdot \mathbf{p}_{\nu m} \mathbf{p}_{m\mu} \cdot \mathbf{e} a_\mu e^{i\omega_\nu \mu t} \\ \times \left\{ \frac{1 - e^{-i[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)](t-t')}}{[\omega_{m\mu} + \mathbf{k} \cdot \mathbf{v} - \omega - i(\Gamma/2)]} \right\}. \quad (\text{II.32})$$

Now from (II.26)

$$\frac{d}{dt} \langle e^{i\omega_{\mu\nu} t} \rho_{\mu\nu} \rangle = \langle \dot{a}_\mu a_\nu^* \rangle_{\text{av}} + \langle a_\mu \dot{a}_\nu^* \rangle_{\text{av}}. \quad (\text{II.33})$$

Thus, in order to compute the rate of change of the density matrix, we must perform the same sort of statistical average over the ground-state amplitudes in (II.33) as was performed in obtaining (II.16) from (II.12). Substituting (II.32) into (II.33) and carrying out the average, we find

$$\frac{d}{dt} \langle e^{i\omega_{\mu\nu} t} \rho_{\mu\nu} \rangle = - \frac{|E_0|^2}{4\hbar} \sum_m \langle \mu | \mathbf{e}^* \cdot \alpha \cdot \mathbf{e} | \sigma \rangle e^{i\omega_{\mu\nu} t} \rho_{\sigma\nu} \\ + \frac{|E_0|^2}{4\hbar} \sum_m \rho_{\mu\sigma} \langle \sigma | (\mathbf{e}^* \cdot \alpha \cdot \mathbf{e})^\dagger | \nu \rangle e^{i\omega_{\mu\nu} t}. \quad (\text{II.34})$$

Equation (II.34) may be rewritten in operator form to

give the Liouville equation

$$i\hbar(d/dt)\rho = [\mathcal{H}_0, \rho] + (\delta \mathcal{H} \rho - \rho \delta \mathcal{H}^\dagger). \quad (\text{II.35})$$

The evolution of the density matrix in the absence of light is determined by \mathcal{H}_0 (II.5), and the additional evolution due to the light can be described by the effective Hamiltonian $\delta \mathcal{H}$;

$$\delta \mathcal{H} = -(|E_0|^2/4) \mathbf{e}^* \cdot \alpha \cdot \mathbf{e}. \quad (\text{II.36})$$

In general, $\delta \mathcal{H}$ will not be Hermitian since it must describe the disappearance of ground-state atoms due to the absorption of light. However, we may write $\delta \mathcal{H}$ as a linear combination of the Hermitian operators $\delta \mathcal{E}$ and $\delta \Gamma$,

$$\delta \mathcal{H} = \delta \mathcal{E} - i\hbar(\delta \Gamma/2), \quad (\text{II.37})$$

where the *light-shift operator* $\delta \mathcal{E}$ is defined as

$$\delta \mathcal{E} = \frac{\delta \mathcal{H} + \delta \mathcal{H}^\dagger}{2} = - \frac{|E_0|^2}{8} (\mathbf{e}^* \cdot \alpha \cdot \mathbf{e} + \mathbf{e} \cdot \alpha^\dagger \cdot \mathbf{e}^*), \quad (\text{II.38})$$

and the *light absorption operator* $\delta \Gamma$ is defined as

$$\delta \Gamma = \frac{i}{\hbar} (\delta \mathcal{H} - \delta \mathcal{H}^\dagger) = - \frac{i|E_0|^2}{4\hbar} (\mathbf{e}^* \cdot \alpha \cdot \mathbf{e} - \mathbf{e} \cdot \alpha^\dagger \cdot \mathbf{e}^*). \quad (\text{II.39})$$

Using these definitions, we may rewrite (II.35) as

$$\frac{d\rho}{dt} = [(\mathcal{H}_0 + \delta \mathcal{E}), \rho] - \frac{i\hbar}{2} (\delta \Gamma \rho + \rho \delta \Gamma). \quad (\text{II.40})$$

From (II.40) we see that $\delta \mathcal{E}$ may be regarded as a small perturbation of the zeroth-order Hamiltonian \mathcal{H}_0 (II.5). Thus the diagonal matrix elements of $\delta \mathcal{E}$ will cause small shifts in the energy levels of the atomic ground state, while the off-diagonal matrix elements of $\delta \mathcal{E}$ may cause transitions between the different sublevels of the atomic ground state.

The rate of disappearance of atoms from the ground state due to the absorption of light is just $-\text{Tr}[\dot{\rho}]$. From (II.40), one obtains

$$-\text{Tr}[\dot{\rho}] = \text{Tr}[\delta \Gamma \rho] \equiv \langle \delta \Gamma \rangle. \quad (\text{II.41})$$

Thus, the light-absorption rate is just equal to the expectation value of the light-absorption operator $\langle \delta \Gamma \rangle$.

Finally, we should point out that a simple relationship exists between $\langle \delta \Gamma \rangle$ and the energy dissipated by the light wave as it drives the macroscopic polarization of the vapor. Using (II.1), (II.10), (II.29), and (II.39), one can verify that

$$\langle \mathbf{E} \cdot (d\mathbf{P}/dt) \rangle_{\text{av}} = \omega \hbar N \text{Tr}[\rho \delta \Gamma], \quad (\text{II.42})$$

where the average in (II.42) is taken over many optical cycles. The left-hand side of (II.42) is the average macroscopic energy dissipation of the medium per unit volume, and the right-hand side of (II.42) is the rate of disappearance of atoms per unit volume times the energy of an optical photon.

III. THE ALKALI ATOMS

The hyperfine structure of the ${}^2S_{1/2}$ ground state of the alkali atoms is always much larger than the hyperfine structure of any of the 2P_J excited states. Consequently, the optical absorption frequencies of the alkali atoms fall into two groups: frequencies involving absorption from the upper ground-state hfs level $a=I+\frac{1}{2}$ and a corresponding set of frequencies involving absorption from the lower ground-state hfs level $b=I-\frac{1}{2}$. The excited-state hfs splittings of most of the alkali atoms are small compared to the Doppler widths of the atomic absorption lines. The only exceptions are the first excited states of rubidium and cesium (see Table I).

All of the effective operators are expressed in terms of the polarizability operator α (II.25), which may be written as [see (A25)]

$$\alpha = \sum_L \alpha^L = \sum_{\substack{ff' \\ F_e LM}} \xi^L(ff'; F_e) (-1)^M \mathbf{Q}_{-M}^L T_M^L(ff') z. \quad (\text{III.1})$$

The multipole components α^L may be written in the more convenient form

$$\alpha^L = \sum_{ff'M} A^L(ff') (-1)^M \mathbf{Q}_{-M}^L T_M^L(ff'). \quad (\text{III.2})$$

The coefficients $A^L(ff')$ are

$$A^L(ff') = \sum_{F_e} \xi^L(ff'; F_e) Z(F_e f'), \quad (\text{III.3})$$

and the profile factors $Z(F_e f')$ are defined in (II.21).

A. Alkali Atoms with Negligible Excited-State Hyperfine Structure

We shall first consider the more common case where the hfs separations of the excited state are small compared to the Doppler widths of the optical-absorption lines. Then we may neglect the dependence of $Z(F_e f')$ on F_e and write

$$Z(F_e f) = Z(F_e' f) = Z_f. \quad (\text{III.4})$$

Thus the profile factors can be removed from the summation (III.3) and we can use (A28) to write

$$A^L(ff') = \xi^L(ff') Z_{f'}. \quad (\text{III.5})$$

The triangle condition for the arguments ($\frac{1}{2} \frac{1}{2} L$) of the second Racah coefficient in (A28) implies that only the multipolarities $L=0$ and $L=1$ are allowed. A quadrupole component ($L=2$) which is present in the general case is identically zero as long as the hfs separations of the excited state are neglected (see Sec. IIIB). Substituting the appropriate angular momenta into (A28) and using (III.5) and (III.2), one finds that the

scalar polarizability operator α^0 becomes

$$\alpha^0 = G \sum_f \hat{p}(f) Z_f, \quad (\text{III.6})$$

where the factor G is defined in (A27) and the $\hat{p}(f)$ are the ground-state projection operators defined in (II.23). It will also prove useful to express α^0 in terms of the ground-state operator $\mathbf{I} \cdot \mathbf{J}$. Using (A35) and (A36), we obtain

$$\alpha^0 = G \left(Z^+ + \frac{Z^-}{2I+1} \right) + \frac{4GZ^-}{2I+1} \mathbf{I} \cdot \mathbf{J}, \quad (\text{III.7})$$

where

$$Z^+ = \frac{Z_a + Z_b}{2}, \quad (\text{III.8a})$$

and

$$Z^- = \frac{Z_a - Z_b}{2}. \quad (\text{III.8b})$$

The dipole polarizability can be evaluated in like manner. From (III.5) and (III.2), we obtain

$$\alpha^1 = -\frac{G}{4} [11 - 4J_e(J_e + 1)] \sum_{ff'} [(2f+1)(2f'+1)]^{1/2} \times W(1 \frac{1}{2} f I; \frac{1}{2} f') \sum (-1)^M \mathbf{Q}_{-M}^1 T_{-M}^1(ff') Z_{f'}. \quad (\text{III.9})$$

We may use (A34) to express α^1 in terms of the familiar magnetic dipole moment operator, $\mathbf{u} = -g_J \mu_0 \mathbf{J}$, of the alkali atom ground state. One obtains

$$\alpha^1 = \frac{G\sqrt{2}}{4g_J\mu_0} [11 - 4J_e(J_e + 1)] \sum_M (-1)^M \mathbf{Q}_{-M}^1 \times \left\{ \sum_f \hat{p}(f)_{\mu M} \hat{p}(f) Z_f + \sum_{f \neq f'} \hat{p}(f)_{\mu M} \hat{p}(f') Z_{f'} \right\}. \quad (\text{III.10})$$

Thus, the scalar polarizability α^0 contains only Zeeman components, but the dipole polarizability α^1 contains both Zeeman and hfs components [see (I.12) and (I.13)].

1. The Light-Shift Operator $\delta\mathcal{E}$

The scalar part of the light-shift operator $\delta\mathcal{E}_0$ is [see Eq. (II.38)]

$$\delta\mathcal{E}_0 = -\frac{|E_0|^2}{8} (\mathbf{e}^* \cdot \alpha^0 \cdot \mathbf{e} + \mathbf{e} \cdot \alpha^{0\dagger} \cdot \mathbf{e}^*). \quad (\text{III.11})$$

Using (III.7) for α^0 , one obtains

$$\delta\mathcal{E}_0 = \delta\mathcal{E}_{0g} + \hbar \delta A \mathbf{I} \cdot \mathbf{J}, \quad (\text{III.12})$$

where a shift in the center of gravity of the ground state is given by

$$\delta\mathcal{E}_{0g} = -\frac{|E_0|^2}{4} G \operatorname{Re} \left(Z^+ + \frac{Z^-}{2I+1} \right), \quad (\text{III.13})$$

and an effective shift in the magnetic dipole hfs constant is given by

$$\delta A = -\frac{|E_0|^2 G}{2I+1 \hbar} \text{Re} Z^-. \quad (\text{III.14})$$

The vector part of the light-shift operator $\delta \mathcal{E}_1$ is [see Eq. (II.38)]

$$\delta \mathcal{E}_1 = -\frac{|E_0|^2}{8} (\mathbf{e}^* \cdot \alpha^1 \cdot \mathbf{e} + \mathbf{e} \cdot \alpha^{1\dagger} \cdot \mathbf{e}^*). \quad (\text{III.15})$$

Substituting (III.10) into (III.15), we obtain

$$\begin{aligned} \delta \mathcal{E}_1 = & \frac{i|E_0|^2 G}{16g_J \mu_0} [11 - 4J_e(J_e + 1)] \\ & \times \left\{ \sum_f p(f) \mathbf{y} p(f) \text{Re} Z_f + \frac{1}{2} \sum_{f \neq f'} p(f) [\mathbf{y} z + z^\dagger \mathbf{y}] p(f') \right\} \\ & \times (\mathbf{e}^* \times \mathbf{e}). \quad (\text{III.16}) \end{aligned}$$

The diagonal matrix elements of $\delta \mathcal{E}_1$ give the vector light shift for alkali atoms. The off-diagonal matrix elements of $\delta \mathcal{E}_1$ cause transitions between the ground-state sublevels. For a steady monochromatic light wave these will be virtual transitions which result in negligibly small second-order light shifts. However, this analysis remains valid if the light is amplitude modulated at frequencies which are small compared to the Doppler width of the optical absorption lines, so that modulated off-diagonal components of $\delta \mathcal{E}_1$ can cause real Zeeman transitions. For higher modulation frequencies of the light a more detailed analysis of the problem is required, so that we shall only consider the off-diagonal matrix elements of $\delta \mathcal{E}_1$ within a given Zeeman sublevel. Then the hfs components of $\delta \mathcal{E}_1$ can be neglected and the dipole light-shift operator may be written in the form

$$\delta \mathcal{E}_1 = -\delta \mathbf{H} \cdot \mathbf{y}, \quad (\text{III.17})$$

where we have introduced an effective magnetic field operator defined by

$$\begin{aligned} \delta \mathbf{H} = & \frac{|E_0|^2 G}{16g_J \mu_0} [11 - 4J_e(J_e + 1)] \sum_f p(f) \\ & \times \text{Re} Z_f \frac{(\mathbf{e}^* \times \mathbf{e})}{i}. \quad (\text{III.18}) \end{aligned}$$

Note that since the effective magnetic field is an operator, it may have different values within the two different Zeeman multiplets of the alkali ground state.

In summary, the light-shift operator can be expressed in the simple physical form

$$\delta \mathcal{E} = \delta \mathcal{E}_0 + \hbar \delta A \mathbf{I} \cdot \mathbf{J} - \delta \mathbf{H} \cdot \mathbf{y}. \quad (\text{III.19})$$

2. Evaluation of the Light-Absorption Operator

The scalar part of the light-absorption operator is [see Eq. (II.39)]

$$\delta \Gamma_0 = -\frac{i|E_0|^2}{4\hbar} (\mathbf{e}^* \cdot \alpha^0 \cdot \mathbf{e} - \mathbf{e} \cdot \alpha^{0\dagger} \cdot \mathbf{e}^*). \quad (\text{III.20})$$

Using (III.6) for α^0 , one obtains

$$\delta \Gamma_0 = \frac{|E_0|^2 G}{2\hbar} \sum_f p(f) \text{Im} Z_f. \quad (\text{III.21})$$

The vector part of the light-absorption operator is

$$\delta \Gamma_1 = -\frac{i|E_0|^2}{4\hbar} \{ \mathbf{e}^* \cdot \alpha^1 \cdot \mathbf{e} - \mathbf{e} \cdot \alpha^{1\dagger} \cdot \mathbf{e}^* \}. \quad (\text{III.22})$$

Substituting (III.10) into (III.22) and collecting terms, we find

$$\begin{aligned} \delta \Gamma_1 = & \frac{|E_0|^2 G [11 - 4J_e(J_e + 1)]}{8\hbar g_J \mu_0} \left\{ \sum_f p(f) \mathbf{y} p(f) \text{Im} Z_f \right. \\ & \left. + \frac{1}{2} i \sum_{f \neq f'} p(f) [\mathbf{y} z - z^\dagger \mathbf{y}] p(f') \right\} \cdot \left(\frac{\mathbf{e}^* \times \mathbf{e}}{i} \right). \quad (\text{III.23}) \end{aligned}$$

Note that in contrast to $\delta \mathcal{E}_1$ both the Zeeman and hfs components of $\delta \Gamma_1$ are of potential physical significance since there is the experimental possibility of detecting light which is modulated near the hfs frequencies of the atom.¹⁷

3. Evaluation of the Susceptibility Dyadic

The scalar susceptibility is [see (II.29) and (III.6)]

$$\langle \chi_0 \rangle = N \langle \alpha^0 \rangle = NG \sum_f n(f) Z_f, \quad (\text{III.24})$$

where $n(f)$ is the probability that an atom is in the ground-state hfs level f .

$$n(f) = \text{Tr} [p(f) \rho]. \quad (\text{III.25})$$

The Zeeman components of the dipole susceptibility are [see (II.29) and (III.10)]

$$\begin{aligned} \langle \chi_{1f} \rangle = & N \langle \alpha_f^1 \rangle \\ = & \frac{iGN [11 - 4J_e(J_e + 1)]}{4g_J \mu_0} Z_f \langle \mathbf{y}_f \rangle \times. \quad (\text{III.26}) \end{aligned}$$

The Zeeman susceptibilities are responsible for the paramagnetic Faraday effect and for the orientation-dependent attenuation of light by a polarized alkali vapor.

The hfs component of the dipole susceptibility is [see (II.29) and (III.10)]

$$\begin{aligned} \langle \chi_{1 \text{ hfs}} \rangle = & N \langle \alpha_{\text{hfs}}^1 \rangle \\ = & \frac{iGN [11 - 4J_e(J_e + 1)]}{4g_J \mu_0} \sum_{\mu \mu'} \{ \langle a_\mu | \mathbf{y} | b_{\mu'} \rangle \\ & \times \langle b_{\mu'} | \rho | a_\mu \rangle Z_0 + \langle b_{\mu'} | \mathbf{y} | a_\mu \rangle \\ & \times \langle a_\mu | \rho | b_{\mu'} \rangle Z_0 \} \times. \quad (\text{III.27}) \end{aligned}$$

¹⁷ A. H. Firester and T. R. Carver, Phys. Rev. Letters 17, 947 (1966).

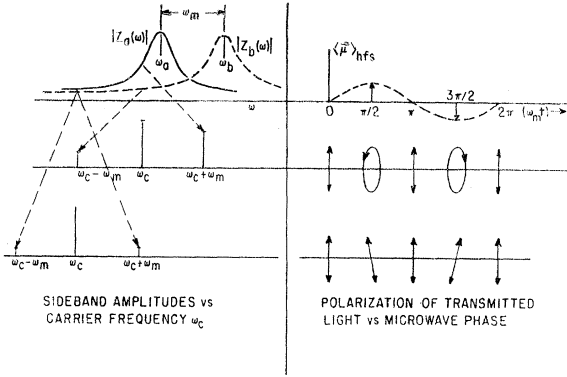


FIG. 3. Hfs paramagnetic Faraday effect.

If microwave coherence has been produced by a microwave field of frequency ω_m , then the hfs component of the magnetic dipole moment will have the form

$$\langle \mathbf{u} \rangle = \frac{1}{2} \mathbf{u}_1 e^{-i\omega_m t} + \frac{1}{2} \mathbf{u}_1^* e^{i\omega_m t}, \quad (\text{III.28})$$

where

$$\frac{1}{2} \mathbf{u}_1 e^{-i\omega_m t} = \sum_{\mu\mu'} \langle b\mu' | \mathbf{u} | a\mu \rangle \langle a\mu | \rho | b\mu' \rangle, \quad (\text{III.29a})$$

and

$$\frac{1}{2} \mathbf{u}_1^* e^{i\omega_m t} = \sum_{\mu\mu'} \langle a\mu | \mathbf{u} | b\mu' \rangle \langle b\mu' | \rho | a\mu \rangle. \quad (\text{III.29b})$$

Substituting (III.29a) and (III.29b) into (III.27), we obtain

$$\langle \chi_{1 \text{ hfs}} \rangle = \frac{iGN}{8gJ\mu_0} [11 - 4J_e(J_e + 1)] \times (Z_a \mathbf{u}_1 e^{-i\omega_m t} + Z_b \mathbf{u}_1^* e^{i\omega_m t}) \times. \quad (\text{III.30})$$

When (III.30) is substituted into (II.10), one finds that components of the polarization proportional to $Z_a \mathbf{u}_1 \times \mathbf{E}_0 \exp[-i(\omega + \omega_m)t]$ and $Z_b \mathbf{u}_1^* \times \mathbf{E}_0 \exp[-i(\omega - \omega_m)t]$ are generated. Thus, to lowest order, two coherent sidebands will be generated from a monochromatic wave propagating along the direction of \mathbf{u}_1 . The sidebands will not, in general, have equal amplitudes since the

TABLE I. Doppler widths and excited-state hyperfine structure of the first resonance lines of the alkali atoms.

Atom	Atomic weight	Nuclear spin I	First resonance line in Å	Hyperfine constant of first excited state, A ($n^2 P_{1/2}$), in MHz	Hyperfine separation of first excited state, $\Delta\nu_{\text{hfs}}$, in mK	Doppler width of first resonance line, $\Delta\nu_D$, in mK
Li ⁶	6.017	1	6708	17.48 ± 0.15 ^a	0.874	70.793
Li ⁷	7.018	$\frac{3}{2}$		46.17 ± 0.35 ^a	3.078	
Na ²³	22.989	$\frac{3}{2}$	5895	94.45 ± 0.5 ^b	6.297	43.784
K ³⁹	39.102	$\frac{3}{2}$	7699	28.85 ± 0.3 ^c	1.923	25.642
Rb ⁸⁵	84.939	$\frac{5}{2}$	7948	120.7 ± 1 ^d	12.070	16.811
Rb ⁸⁷	86.937	$\frac{3}{2}$		409.0 ± 4 ^d	27.267	
Cs ¹³³	132.905	7/2	8944	279.75 ± 7 ^e	37.3	11.997

^a G. J. Ritter, Can. J. Phys. 43, 770 (1965).

^b M. L. Perl, I. I. Rabi, and B. Senitzky, Phys. Rev. 98, 611 (1955).

^c P. Buck and I. I. Rabi, Phys. Rev. 107, 1291 (1957).

^d B. Senitzky and I. I. Rabi, Phys. Rev. 103, 315 (1956).

^e Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1952), Vol. 1, Part 5, p. 37.

polarization component oscillating at the frequency $(\omega + \omega_m)$ is proportional to the profile factor Z_a , while the polarization component oscillating at the frequency $(\omega - \omega_m)$ is proportional to the profile factor Z_b . Furthermore, if the carrier light is linearly polarized, the sideband will be linearly polarized perpendicular to the carrier polarization.

The main qualitative features of the hfs paramagnetic Faraday effect are illustrated in Fig. 3. When a linearly polarized optical carrier frequency is significantly closer to one atomic absorption frequency than to the other [Fig. 3(a)], the sidebands have markedly different amplitudes and the light is alternately left elliptically polarized and right elliptically polarized. When the optical carrier frequency is well removed from both atomic absorption lines [Fig. 3(b)], the sidebands have approximately equal amplitudes and the plane of polarization rocks back and forth as in the normal paramagnetic Faraday effect.¹⁰ Straightforward solutions for the propagation of light through an alkali vapor with hfs coherence may be obtained by using (III.30) for the susceptibility and applying the methods used to analyze parametric transmission lines.¹⁸

B. Alkali Atoms with Large Excited-State Hyperfine Structure

When the excited-state hfs separations are appreciable compared to the Doppler widths of the atomic absorption lines, (III.5) is no longer valid and we must use the more general expression (III.3) for the coefficients $A^L(ff')$. However, for the multipolarities $L=0$ and $L=1$, $\xi^L(ff') \neq 0$ [see (A28)], and we can write

$$A^L(ff') = \xi^L(ff') \zeta^L(ff'), \quad (\text{III.31})$$

which is of the same form as (III.5) except that the simple profile factor $Z_{f'}$ has been replaced by the linear combination

$$\zeta^L(ff') = \frac{\sum_{F_e} \xi^L(ff'; F_e) Z(F_e f')}{\xi^L(ff')}. \quad (\text{III.32})$$

Then all of the expressions derived earlier in this section remain valid if the simple profile factors $Z_{f'}$ are replaced by appropriate linear combinations $\zeta^L(ff')$. In particular, the scalar polarizability (III.6) becomes

$$\alpha^0 = G \sum_f p(f) \zeta^0(ff), \quad (\text{III.33})$$

and the dipole polarizability becomes

$$\alpha^1 = \frac{G\sqrt{2}}{4gJ\mu_0} [11 - 4J_e(J_e + 1)] \sum_M (-1)^M \mathbf{Q}_{-M}^{-1} \times \left\{ \sum_f p(f) \mu_M p(f) \zeta^1(ff) + \sum_{f \neq f'} p(f) \mu_M p(f') \zeta^1(ff') \right\}. \quad (\text{III.34})$$

¹⁸ B. A. Auld and R. L. Comstock, Proc. IEEE 55, 532 (1967).

Consequently, the general form of the scalar and dipole effective operators is unchanged for large excited-state hfs separations, but the dependence of these operators on the frequency of the exciting light is somewhat more complicated, reflecting the detailed structure of the optically resolved hfs of the excited state.

One significant qualitative feature is different when the excited-state hyperfine structure is resolved. A quadrupole-like contribution ($L=2$) is present in the effective operators since α^2 is no longer identically zero. However, since the coefficients $A^2(ff')$ change sign rapidly as a function of frequency in the vicinity of an optical absorption line, the quadrupole-like terms will not be important for light with a broad spectral profile.

As an illustrative example we list the coefficients $A^L(ff')$ for an alkali atom with nuclear spin $I=\frac{3}{2}$, illuminated by light whose frequency is close to the optical transition frequency between the ground state and one of the $^2P_{1/2}$ excited states:

$$\begin{aligned}
 A^0(11) &= \frac{G}{2} [5Z(21) + Z(11)]; \\
 A^0(22) &= \frac{G(\sqrt{15})}{2} [Z(22) + Z(12)]; \\
 A^1(11) &= \frac{G}{4} [5Z(21) - Z(11)]; \\
 A^1(22) &= -\frac{(\sqrt{5})G}{4} [3Z(12) + Z(22)]; \\
 A^1(21) &= \frac{(\sqrt{5})G}{4} [Z(11) + 3Z(21)]; \\
 A^1(12) &= -\frac{(\sqrt{5})G}{4} [Z(12) + 3Z(22)]; \\
 A^2(11) &= \frac{G}{4} [Z(21) - Z(11)]; \\
 A^2(22) &= \frac{(\sqrt{21})G}{4} [Z(12) - Z(22)]; \\
 A^2(21) &= \frac{3G}{4} [Z(21) - Z(11)]; \\
 A^2(12) &= \frac{3G}{4} [Z(12) - Z(22)].
 \end{aligned} \tag{III.35}$$

Note that the coefficients $A^2(ff')$ are zero when $Z(F_e f) = Z(F_e' f)$, i.e., when the excited-state hfs is negligible.

IV. ATOMS WITH ONE ZEEMAN MULTIPLET IN THE GROUND STATE

In this section we present explicit formulas for the effective Hamiltonian operators and for the dielectric

susceptibility operators for atoms with only one Zeeman multiplet in the ground state. Such atoms fall into two classes: atoms with no nuclear spin such as the metastable 3S_1 state of He⁴,¹⁹ and atoms with no electronic angular momentum such as the 1S_0 ground states of the odd mercury,²⁰ cadmium,²¹ and zinc²² isotopes. The derivation of these results will be omitted since it involves the same sort of tensor algebra as was used in Sec. III, and the ensuing formulas can be verified easily using the material of Appendix A.

A. Atoms with No Nuclear Spin

The scalar light shift is

$$\delta\mathcal{E}_0 = -\frac{|E_0|^2}{4} G \operatorname{Re} Z, \tag{IV.1}$$

where G is defined in (A27) and the profile factor $Z \equiv Z(J_e J_g)$ is defined by (II.21) and (II.19).

The dipole light-shift operator is

$$\delta\mathcal{E}_1 = -\delta\mathbf{H} \cdot \mathbf{u}, \tag{IV.2}$$

where $\mathbf{u} = -g_J \mu_0 \mathbf{J}$ is the magnetic dipole operator of the atomic ground state and the effective magnetic field is given by

$$\begin{aligned}
 \delta\mathbf{H} = & \frac{3|E_0|^2 G \operatorname{Re} Z}{g_J \mu_0 16 J_g (J_g + 1)} [J_e (J_e + 1) - J_g (J_g + 1) - 2] \\
 & \times \left[\frac{\mathbf{e} \times \mathbf{e}^*}{i} \right]. \tag{IV.3}
 \end{aligned}$$

The quadrupole light-shift operator is

$$\delta\mathcal{E}_2 = -\frac{1}{6} \mathbf{Q} : \delta \nabla \mathbf{E}, \tag{IV.4}$$

where the quadrupole moment operator is defined in (A33) and the effective electric-field gradient is

$$\begin{aligned}
 \delta \nabla \mathbf{E} = & \sum_{\mathbf{t}} (-1)^M E_{-M}^2 \mathbf{Q}_M^2 \frac{3|E_0|^2 G \operatorname{Re} Z}{2 e Q} \\
 & \times \left[\frac{30 J_g (2J_g - 1)(2J_g + 1)}{(J_g + 1)(2J_g + 3)} \right]^{1/2} W(12 J_e J_g; 1 J_g). \tag{IV.5}
 \end{aligned}$$

The scalar light-absorption operator is

$$\delta\Gamma_0 = \frac{|E_0|^2 G \operatorname{Im} Z}{2\hbar}. \tag{IV.6}$$

The dipole light-absorption operator is

$$\delta\Gamma_1 = \mathbf{u} \cdot \delta\Gamma_1, \tag{IV.7}$$

¹⁹ F. D. Colegrove and P. A. Franken, Phys. Rev. **119**, 680 (1960).

²⁰ B. Cagnac, Ann. Phys. (N. Y.), **6**, 467 (1961).

²¹ J. Lehmann and J. Brüssel, Compt. Rend. **258**, 869 (1964).

²² P. W. Spence and M. N. McDermott, Phys. Letters **24A**, 430 (1967).

where the vector damping constant is

$$\delta\Gamma_1 = \frac{3|E_0|^2 G \text{Im}Z}{8g_{J\mu_0}\hbar J_\sigma(J_\sigma+1)} [J_e(J_e+1) - J_\sigma(J_\sigma+1) - 2] \times \left[\frac{\mathbf{e} \times \mathbf{e}^*}{i} \right]. \quad (\text{IV.8})$$

The quadrupole light-absorption operator is

$$\delta\Gamma_2 = \mathbf{Q} : \delta\Gamma_2, \quad (\text{IV.9})$$

where the tensor damping constant is

$$\delta\Gamma_2 = \sum (-1)^M E_{-M}{}^2 \mathbf{Q}_M{}^2 \frac{|E_0|^2 G \text{Im}Z}{2\hbar e Q} \times \left[\frac{30J_\sigma(2J_\sigma-1)(2J_\sigma+1)}{(J_\sigma+1)(2J_\sigma+3)} \right]^{1/2} W(12J_e J_\sigma; 1J_\sigma). \quad (\text{IV.10})$$

The scalar susceptibility operator is

$$\chi_0 = X_0 = NGZ, \quad (\text{IV.11})$$

where N is the atomic density. The dipole susceptibility operator is

$$\chi_1 = X_1 \mathbf{u} \times = -\frac{i3NGZ}{4g_{J\mu_0} J_\sigma(J_\sigma+1)} \times [J_e(J_e+1) - J_\sigma(J_\sigma+1) - 2] \mathbf{u} \times. \quad (\text{IV.12})$$

The quadrupole susceptibility operator is

$$\chi_2 = X_2 \mathbf{Q} \cdot = \frac{NGZ}{eQ} \left[\frac{30J_\sigma(2J_\sigma-1)(2J_\sigma+1)}{(J_\sigma+1)(2J_\sigma+3)} \right]^{1/2} \times W(12J_e J_\sigma; 1J_\sigma) \mathbf{Q} \cdot. \quad (\text{IV.13})$$

B. Atoms with No Ground-State Electronic Spin

The effective operators will be sums of terms due to real and virtual absorption to different hfs levels F_e of the excited state. For instance, the light-shift operator may be represented in the form

$$\delta\mathcal{E} = \sum_L \sum_{F_e} \delta\mathcal{E}_L(F_e). \quad (\text{IV.14})$$

The light-absorption operator and the dielectric susceptibility operator are composed of analogous terms. The scalar light-shift operators are

$$\delta\mathcal{E}_0(F_e) = -\frac{|E_0|^2 G (2F_e+1)}{12 (2I+1)} \text{Re}Z. \quad (\text{IV.15})$$

The dipole light-shift operators are

$$\delta\mathcal{E}_1(F_e) = -\delta\mathbf{H} \cdot \mathbf{u}, \quad (\text{IV.16})$$

where $\mathbf{u} = \gamma \mathbf{I}$ is the nuclear dipole moment operator and the effective magnetic field is

$$\delta\mathbf{H}(F_e) = \frac{|E_0|^2 G \text{Re}Z (2F_e+1)}{16\gamma I(I+1)(2I+1)} \times [2+I(I+1) - F_e(F_e+1)] \left[\frac{\mathbf{e} \times \mathbf{e}^*}{i} \right]. \quad (\text{IV.17})$$

The quadrupole light-shift operator is

$$\delta\mathcal{E}_2(F_e) = -\frac{1}{6} \mathbf{Q} : \delta\nabla \mathbf{E}(F_e), \quad (\text{IV.18})$$

where the nuclear quadrupole dyadic \mathbf{Q} is defined according to (A33) and the effective electric-field gradient is

$$\delta\nabla \mathbf{E}(F_e) = \sum_M (-1)^M E_{-M}{}^2 \mathbf{Q}_M{}^2 \frac{3|E_0|^2 G \text{Re}Z}{2Q_e} \times (2F_e+1) W(12F_e J; 1I) \times \left[\frac{10I(2I-1)}{3(2I+1)(I+1)(2I+3)} \right]^{1/2}. \quad (\text{IV.19})$$

The scalar light-absorption operators are

$$\delta\Gamma_0(F_e) = \frac{|E_0|^2 G \text{Im}Z (2F_e+1)}{6\hbar (2I+1)}. \quad (\text{IV.20})$$

The dipole light-absorption operators are

$$\delta\Gamma_1(F_e) = \mathbf{u} \cdot \delta\Gamma_1, \quad (\text{IV.21})$$

where the vector damping constants are

$$\delta\Gamma(F_e) = \frac{|E_0|^2 G \text{Im}Z (2F_e+1)}{8\hbar\gamma I(I+1)(2I+1)} \times [2+I(I+1) - F_e(F_e+1)] \left[\frac{\mathbf{e} \times \mathbf{e}^*}{i} \right]. \quad (\text{IV.22})$$

The quadrupole light-absorption operators are

$$\delta\Gamma_2(F_e) = \mathbf{Q} : \delta\Gamma_2(F_e), \quad (\text{IV.23})$$

where the tensor damping constants are

$$\delta\Gamma_2(F_e) = \sum (-1)^M E_{-M}{}^2 \mathbf{Q}_M{}^2 \frac{|E_0|^2 G \text{Im}Z (2F_e+1)}{2\hbar Q_e} \times \left[\frac{10I(2I-1)}{3(2I+1)(I+1)(2I+3)} \right]^{1/2} W(12F_e J; 1I). \quad (\text{IV.24})$$

The scalar susceptibility operators are

$$\chi_0(F_e) = X_0(F_e) = \frac{NGZ(2F_e+1)}{3(2I+1)}. \quad (\text{IV.25})$$

The dipole susceptibility operators are

$$\chi_1(F_e) = X_1(F_e) \mathbf{u} \times = -\frac{iNGZ(2F_e+1)}{4\gamma I(I+1)(2I+1)} \\ \times [2+I(I+1)-F_e(F_e+1)] \mathbf{u} \times. \quad (\text{IV.26})$$

The quadrupole susceptibility operators are

$$\chi_2(F_e) = X_2(F_e) \mathbf{Q}. \\ = \frac{NGZ(2F_e+1)}{eQ} \left[\frac{10I(2I-1)}{3(2I+1)(I+1)(2I+3)} \right]^{1/2} \\ \times W(12F_e I; 1I) \mathbf{Q}. \quad (\text{IV.27})$$

The arguments of the profile factor $Z \equiv Z(F_e I)$ [see (II.21)] have been suppressed in (IV.15) through (IV.27).

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APPENDIX A

The numerical computations in this work were carried out with the aid of spherical tensor algebra. Since we are interested in situations where the Zeeman splitting of the hfs levels of the atom is small compared to the Doppler widths of the optical absorption lines, it is convenient to express all wave functions of the atom in terms of the coupled basis states $|JF\mu\rangle \equiv |F\mu\rangle$. The corresponding hfs basis operators (spherical tensors) will be defined as²³

$$T_M^L(F, F') = \sum_{\mu} |F\mu\rangle \langle F'\mu-M| (-1)^{\mu-M-F'} \\ \times C(FF'L; \mu, M-\mu). \quad (\text{A1})$$

The inverse relationship is

$$|F\mu\rangle \langle F'\nu| = \sum_L T_{\mu-\nu}^L(F, F') (-1)^{\nu-F'} \\ \times C(FF'L; \mu, -\nu). \quad (\text{A2})$$

The Hermitian conjugate of a hfs tensor operator is

$$[T_M^L(FF')]^\dagger = (-1)^{F-F'-M} T_{-M}^L(F', F). \quad (\text{A3})$$

The hfs tensors form an orthonormal basis set of operators since

$$\text{Tr}\{T_M^L(FF')[T_{m'}^L(ff')]^\dagger\} = \delta_{Ll} \delta_{Mm} \delta_{Ff} \delta_{F'f'}. \quad (\text{A4})$$

Consequently any ground-state operator O can be ex-

²³ The notation used in this paper is that of M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

panded in terms of the hfs basis tensors

$$O = \sum_{\substack{LM \\ FF'}} O_M^L(FF') T_M^L(FF'), \quad (\text{A5})$$

where

$$O_M^L(FF') = \text{Tr}[O T_M^L(FF')]. \quad (\text{A6})$$

Spatial vectors will be expanded in terms of the unit vectors in spherical coordinates

$$\mathbf{i}_1 = \frac{\mathbf{i}_x + i\mathbf{i}_y}{-\sqrt{2}}, \quad (\text{A7a})$$

$$\mathbf{i}_0 = \mathbf{i}_z, \quad (\text{A7b})$$

$$\mathbf{i}_{-1} = \frac{\mathbf{i}_x - i\mathbf{i}_y}{\sqrt{2}}. \quad (\text{A7c})$$

The orthogonality relations for the basis vectors are

$$(\mathbf{i}_\mu)^* \cdot \mathbf{i}_\nu = \delta_{\mu\nu}. \quad (\text{A8})$$

Note that

$$(\mathbf{i}_\mu)^* = (-1)^\mu \mathbf{i}_{-\mu}.$$

Any vector \mathbf{A} may be expanded as

$$\mathbf{A} = \sum_{\mu} (-1)^\mu A_{\mu} \mathbf{i}_{-\mu} = \sum_{\mu} (-1)^\mu (\mathbf{A} \cdot \mathbf{i}_\mu) \mathbf{i}_{-\mu}. \quad (\text{A9})$$

Since we shall have occasion to deal with spatial tensors such as the dielectric susceptibility of the vapor, we shall introduce a set of basis dyadics \mathbf{Q}_M^L .

$$\mathbf{Q}_M^L = \sum_{\mu} \mathbf{i}_\mu (\mathbf{i}_{\mu-M})^* (-1)^{\mu-M-1} C(11L; \mu, M-\mu). \quad (\text{A10})$$

The inverse relationship is

$$\mathbf{i}_\nu \mathbf{i}_\mu = -\sum_L \mathbf{Q}_{\mu+\nu}^L C(11L; \nu\mu). \quad (\text{A11})$$

The basis dyadics are orthogonal since

$$\mathbf{Q}_M^L : \mathbf{Q}_{M'}^{L'} = \sum_{\mu\nu} \mathbf{i}_\nu^* \cdot \mathbf{Q}_M^L \cdot \mathbf{i}_\mu (\mathbf{i}_\mu)^* \cdot \mathbf{Q}_{M'}^{L'} \cdot \mathbf{i}_\nu \\ = (-1)^M \delta_{LL'} \delta_{M, -M'}. \quad (\text{A12})$$

The complex conjugate of a basis dyadic is

$$[\mathbf{Q}_M^L]^* = (-1)^{L+M} \mathbf{Q}_{-M}^L. \quad (\text{A13})$$

The commutation relation for the product of \mathbf{Q}_M^L with any vector \mathbf{A} is

$$\mathbf{A} \cdot \mathbf{Q}_M^L = (-1)^L \mathbf{Q}_M^L \cdot \mathbf{A}. \quad (\text{A14})$$

Several special relationships involving the basis dyadics are noteworthy. The unit dyadic is just

$$\sqrt{3} \mathbf{Q}_0^0 = \sum_{\mu} \mathbf{i}_\mu (\mathbf{i}_\mu)^* = \mathbf{i}_x \mathbf{i}_x + \mathbf{i}_y \mathbf{i}_y + \mathbf{i}_z \mathbf{i}_z. \quad (\text{A15})$$

The cross product of any pair of vectors \mathbf{A} and \mathbf{B} may be expressed as

$$\mathbf{A} \times \mathbf{B} = -i\sqrt{2} \sum_M (-1)^M A_{-M} \mathbf{Q}_M^1 \cdot \mathbf{B}. \quad (\text{A16})$$

The polarization of the incident light is described by the complex polarization vectors \mathbf{e} and \mathbf{e}^* [see (II.1) and (II.2)]. Since the expressions for the light-shift operator and for the light-absorption operator always involve quadratic forms of the polarization vectors [see (II.38) and (II.39)], it is convenient to introduce bilinear spherical tensor products E_M^L of the components of \mathbf{e} .

$$E_M^L = \sum e_\mu (e_{\mu-M})^* (-1)^{\mu-M-1} C(11L; \mu, M-\mu). \quad (\text{A17})$$

We shall call the quantities E_M^L the polarization tensors. Note that

$$(E_M^L)^* = (-1)^M E_{-M}^L. \quad (\text{A18})$$

All electric dipole matrix elements between different optical levels can be expressed in terms of oscillator strengths and angular factors. To do this we note that the total transition rate from the excited electronic state J_e to the ground state J_g is (see Fig. 2 and 7⁴³ of Ref. 24)

$$\Gamma(J_e \rightarrow J_g) = \frac{1}{2J_e+1} \frac{64\pi^4}{h\lambda^3} \sum_m |\langle J_e m | \hat{p}_z | J_g \mu \rangle|^2. \quad (\text{A19})$$

From the Wigner-Eckart theorem and from the sum rule for Clebsch-Gordan coefficients, this becomes

$$\Gamma(J_e \rightarrow J_g) = \frac{64\pi^4}{3h\lambda^3} \left[\frac{2J_g+1}{2J_e+1} \right]^{1/2} (-1)^{J_e-J_g} \times \langle J_e || \mathbf{p} || J_g \rangle \langle J_g || \mathbf{p} || J_e \rangle. \quad (\text{A20})$$

The spontaneous transition probability is related to the oscillator strength for the transition by the expression²⁵

$$\Gamma(J_e \rightarrow J_g) = \frac{2e^2\omega^2}{mc^3} \frac{(2J_g+1)}{(2J_e+1)} f_{ge}. \quad (\text{A21})$$

One can now use (A20) and (A21) together with (6.25) of Ref. 23 to obtain

$$\begin{aligned} & \langle IJ_g F_g || \mathbf{p} || IJ_e F_e \rangle \langle IJ_e F_e || \mathbf{p} || IJ_g F_g' \rangle \\ &= \frac{3he^2 f_{ge}}{2\omega m} (-1)^{F_e-F_g'} [(2F_e+1)(2F_g'+1)]^{1/2} (2J_g+1) \\ & \quad \times W(J_e F_e J_g F_g; I1) W(J_e F_e J_g F_g'; I1). \quad (\text{A22}) \end{aligned}$$

The important dyadic operator κ (II.25) can be expressed in terms of the basis dyadics (A11) and the basis tensors (A1). From (II.25) and (A10), we obtain

$$\begin{aligned} \kappa(F_e) &= \sum_m \mathbf{p} | F_e m \rangle \langle F_e m | \mathbf{p} \\ &= \sum_{\substack{\rho\sigma \\ \mu\mu' \\ m \\ F_e F_g'}} (-1)^{\rho+\sigma} \mathbf{i}_\rho \mathbf{i}_\sigma | F_g \mu \rangle \langle F_g \mu | \hat{p}_{-\rho} | F_e m \rangle \\ & \quad \times \langle F_e m | \hat{p}_{-\sigma} | F_g' \mu' \rangle \langle F_g' \mu' |. \quad (\text{A23}) \end{aligned}$$

²⁴ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1957).

²⁵ E. W. Foster, Rept. Progr. Phys. 27, 469 (1964).

The inverse relations (A2) and (A11) and the Wigner-Eckart theorem can be used to express the right-hand side of (A23) as

$$\begin{aligned} & \sum (-1)^{\rho+\sigma+\mu'-F_g'+1} \mathbf{Q}_{\rho+\sigma}^L T_{\mu-\mu'}^L(F_g F_g') \langle F_g || \mathbf{p} || F_e \rangle \\ & \quad \times \langle F_e || \mathbf{p} || F_g' \rangle C(11L; \rho, \sigma) C(F_g F_g' \Lambda; \mu, -\mu') \\ & \quad \times C(F_e 1 F_g; m, -\rho, \mu) C(F_g' 1 F_e; \mu', -\sigma, m). \end{aligned}$$

The sum over the four Clebsch-Gordan coefficients can be expressed as a standard Racah relationship [see Ref. 23, Eq. (6.6b)] and we obtain

$$\begin{aligned} \kappa(F_e) &= \sum_{\substack{LM \\ F_g F_g'}} (-1)^{L+M} \mathbf{Q}_{-M}^L T_M^L(F_g F_g') \\ & \quad \times [(2F_g+1)(2F_e+1)]^{1/2} W(11F_g F_g'; LF_e) \\ & \quad \times \langle F_g || \mathbf{p} || F_e \rangle \langle F_e || \mathbf{p} || F_g' \rangle. \quad (\text{A24}) \end{aligned}$$

Substituting (A22) for the reduced matrix elements of \mathbf{p} into (A24), we obtain

$$\begin{aligned} \kappa(F_e) &= \frac{h}{\lambda} \left(\frac{2RT}{M} \right)^{1/2} \sum_{\substack{ML \\ F_g F_g'}} \xi^L(F_g F_g'; F_e) (-1)^M \\ & \quad \times \mathbf{Q}_{-M}^L T_M^L(F_g F_g'), \quad (\text{A25}) \end{aligned}$$

where the coefficient ξ is

$$\begin{aligned} \xi^L(F_g F_g'; F_e) &= 3G (-1)^{F_e-F_g'-1} [(2F_g+1)(2F_g'+1)]^{1/2} \\ & \quad \times (2J_g+1)(2F_e+1) W(11F_g F_g'; LF_e) \\ & \quad \times W(J_e F_e J_g F_g; I1) W(J_e F_e J_g F_g'; I1), \quad (\text{A26}) \end{aligned}$$

and the factor G is

$$G = \frac{\lambda^2 e^2 f_{ge}}{8\pi^2 mc^2} \left[\frac{Mc^2}{2RT} \right]^{1/2}. \quad (\text{A27})$$

A sum rule for the Racah coefficients [see (6.15) of Ref. 23] can be used to sum ξ (A26) over all of the hfs levels F_e of the excited state. One obtains

$$\begin{aligned} \xi^L(F_g F_g') &= \sum_{F_e} \xi^L(F_g F_g'; F_e) \\ &= (-1)^L 3G (2J_g+1) [(2F_g+1)(2F_g'+1)]^{1/2} \\ & \quad \times W(F_g L I J_g; F_g' J_g) W(1L J_e J_g; 1J_g). \quad (\text{A28}) \end{aligned}$$

An important special case is when the atom has no hfs ($I=0$). Then (A28) reduces to

$$\xi^L = (-1)^L 3G (2J_g+1) W(1L J_e J_g; 1J_g). \quad (\text{A29})$$

Another important special case is when the ground state of the atom has no electronic angular momentum ($J_g=0$). Then one must have $J_e=1$, and (A26) becomes

$$\xi^L(F_e) = (-1)^L G (2F_e+1) W(1L F_e J; 1I). \quad (\text{A30})$$

In order to give a more physical appearance to our final equations, we shall make use of (A5) to express the spherical tensor operators in terms of more familiar ground-state operators such as the magnetic moment operator \mathbf{u} , the electric quadrupole moment operator

\mathbf{Q} , etc. The total angular-momentum operator $\mathbf{F} = \mathbf{I} + \mathbf{J}$ is

$$\mathbf{F} = \sum_{M, F_g} (-1)^M \mathbf{i}_{-M} T_M^1(F_g F_g) \times \left[\frac{F_g(F_g+1)(2F_g+1)}{3} \right]^{1/2}. \quad (\text{A31})$$

The electronic angular momentum operator can be expressed as

$$\mathbf{J} = \sum_{\substack{M \\ F_g F_g'}} (-1)^M \mathbf{i}_{-M} T_M^1(F_g F_g') W(1 J_g F_g I; J_g F_g') \times \left[\frac{J_g(J_g+1)(2J_g+1)(2F_g+1)(2F_g'+1)}{3} \right]^{1/2}. \quad (\text{A32})$$

For atoms with only a single Zeeman multiplet in the ground state ($J_g=0$ or $I=0$), the nuclear (or atomic) quadrupole moment operator is²⁶

$$\mathbf{Q} = \frac{eQ}{I(2I-1)} \left[\frac{3}{2} \{ \mathbf{I} + (\mathbf{I})^\dagger \} - \mathbf{I} \cdot \mathbf{I} \right] = eQ \left[\frac{3(2I+3)(I+1)(2I+1)}{10I(2I-1)} \right]^{1/2} \sum_M (-1)^M \times T_M^2(II) \mathbf{Q}_{-M^2}. \quad (\text{A33})$$

²⁶ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

The alkali atoms are of special concern in this paper and we will write down several operator identities which apply to an atom with a ground-state electronic spin $J_g = \frac{1}{2}$ and with ground-state hfs levels $a = I + \frac{1}{2}$ and $b = I - \frac{1}{2}$. From (A32) the electronic angular-momentum operator is

$$\mathbf{J} = \sum_{\substack{M \\ F_g F_g'}} (-1)^M \mathbf{i}_{-M} T_M^1(F_g F_g') W(1 \frac{1}{2} F_g I; \frac{1}{2} F_g') \times \left[\frac{(2F_g+1)(2F_g'+1)}{2} \right]^{1/2}. \quad (\text{A34})$$

The projection operator for the hfs level a is

$$p(a) = (2a+1)^{1/2} T_0^0(aa) = \frac{I+1+2\mathbf{I} \cdot \mathbf{J}}{2I+1}, \quad (\text{A35})$$

and the corresponding projection operator for the level b is

$$p(b) = (2b+1)^{1/2} T_0^0(bb) = \frac{I-2\mathbf{I} \cdot \mathbf{J}}{2I+1}. \quad (\text{A36})$$

The operator $\mathbf{I} \cdot \mathbf{J}$ is then

$$\mathbf{I} \cdot \mathbf{J} = \frac{I}{2} (2a+1)^{1/2} T_0^0(aa) - \frac{(I+1)}{2} \times (2b+1)^{1/2} T_0^0(bb). \quad (\text{A37})$$