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Power-series analysis of light shifts in optical pumping experiments*

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By expanding the atomic density matrix in powers of the light intensity, it is possible to derive simple formulas for the light shifts and optical broadening of magnetic-resonance lines in optical pumping experiments. Thus, we have obtained for the first time approximate analytic formulas for the light shifts in Zeeman multiplets with spins greater than 1/2. The predicted light shifts for a high-spin atom are similar to those for a spin-1/2 atom, and shifts due to real and virtual transitions can be identified. However, in contrast to the situation with a spin-1/2 atom, the light shifts for a high-spin atom depend on the magnitude of the rf field, and the shifts for the longitudinal and transverse components of orientation and alignment are not necessarily the same.

I. INTRODUCTION

A number of optically pumped devices, for instance, magnetometers and gas-cell frequency standards, have become important practical instruments in recent years. The precision of these devices is limited by several factors, but one of the most characteristic and unavoidable sources of instability is the light-induced frequency shift and broadening of the magnetic resonance lines. Although these light shifts are understood in principle, their control and elimination as a source of error is difficult. One of the major problems is that so far it has only been possible to make detailed theoretical predictions of the light shifts for nondegenerate magnetic resonance transitions. For instance, Cohen-Tannoudji[1] derived simple formulas for the light shifts in Hg^{199}, which has only two ground-state sublevels. Similar formulas have been derived for the light shift of the "0-0 transition"[2] of an alkali-metal atom, and for the $\Delta m = 1$, $\Delta F = 0$ transitions of an alkali-metal atom[3] in magnetic fields large enough to resolve these transitions from each other. In all of these cases the agreement between experiment and theory was very good.

It has not yet been possible to derive simple formulas for the light shifts when several magnetic resonance transitions occur at the same frequency. In such a case the shifts can be obtained by the numerical solution of a set of coupled differential equations. The results are so cumbersome and untransparent that it is doubtful that they have been of much use to experimentalists. Unfortunately, one of the most important modern instruments, the optically pumped magnetometer, is a good example of a system whose light shifts can only be calculated by numerical methods in some important practical cases. Although very precise magnetometers have been constructed[4,5] by empirical control of the light shifts and other sources of instability, it might be hoped that even better instruments could be made if one had a clear theoretical understanding of the light shifts.

In this paper we show that it is possible to obtain simple approximate formulas for the light shifts of magnetic resonance lines for a Zeeman multiplet. The predictions of these simple formulas are in very good agreement with the results of exact numerical calculations when the pumping rate does not exceed the ground-state relaxation rate. This is the regime of most practical interest, since pumping rates in excess of the ground-state relaxation rate simply broaden the magnetic resonance lines without increasing the signal-to-noise ratio. Our formulas are exact in the limit of vanishing light intensity. These formulas show immediately how the light shift depends on the polarization of the pumping light, the asymmetry of the spectral profile of the exciting light, and the magnitude of the external field. The formulas can be used for arbitrary ground-state and excited-state angular momenta. The analytic formulas also predict other properties of the light shifts which do not seem to have been recognized before. For instance, the light shift may vary with the rf power.

In deriving our results we have made systematic use of a novel expansion of the atomic density matrix in powers of the light intensity. This allows us to analyze light shifts and optical broadening of the magnetic resonance lines in the spirit of perturbation theory, and it is possible to handle high-spin systems as easily as low-spin systems. In contrast, conventional "brute force" methods of analysis become rapidly more difficult as the atomic spin increases.

II. THEORY

The basic theory of optical pumping was developed in 1960 by Barrat and Cohen-Tannoudji.[6]

They showed that the evolution of the ground-state density matrix of an optically pumped system is governed by the equation

$$\frac{d}{dt}\rho = \frac{d^{(1)}}{dt}\rho + \frac{d^{(2)}}{dt}\rho + \frac{d^{(3)}}{dt}\rho + \frac{1}{i\hbar}[\mathcal{H}, \rho], \tag{1}$$

where the operator $(d^{(1)}/dt)\rho$ represents the transfer of atoms out of the ground state into the excited state (depopulation pumping), $(d^{(2)}/dt)\rho$ represents the replenishment of the ground state by spontaneous decay of excited atoms (repopulation pumping), and $(d^{(3)}/dt)\rho$ represents the relaxation of the polarized ground-state atoms. The interaction of the atoms with external magnetic fields and the hyperfine interactions in the atomic ground state are represented by the Hamiltonian operator $\mathcal{H}$. Detailed expressions for $(d^{(1)}/dt)\rho$ and $(d^{(2)}/dt)\rho$ are given by Barrat and Cohen-Tannoudji.[6] Although (1) is certainly correct for conventional optical pumping experiments, it is difficult to solve in closed form, and computer solutions are necessary for atoms with high-spin ground states. Such numerical solutions seldom provide as much insight into the behavior of the system as an analytic solution would.

A. Power-series expansion for ρ

The key to obtaining simple analytic formulas for light shifts in high-spin atoms is to express the density matrix as a power series in the intensity of the pumping light. Power-series solutions have been used by Ensberg,[7] but so far as we know, no one has previously recognized that the power series can be used to deduce simple formulas for the light shifts.

For computational convenience we shall think of the density matrix ρ as a "state vector," which we shall denote by

$$|\rho\rangle = |0\rangle + |P\rangle . \tag{2}$$

Here, $|0\rangle$ represents a completely unpolarized atomic ensemble and $|P\rangle$ represents the polarization of the ensemble.

We introduce a linear operator $\mathcal{S}$, which is defined by

$$\mathcal{S}|\rho\rangle = [\mathcal{H}, \rho] . \tag{3}$$

An explicit expression for $\mathcal{S}$ will be given in Sec. II C, Eq. (29).

We shall regard the expression $(d^{(1)}/dt)\rho$ for depopulation pumping as the product of a linear operator, $d^{(1)}/dt$, with the density matrix. Since depopulation pumping is proportional to the mean pumping rate R, we set

$$\frac{d^{(1)}}{dt} = R\mathfrak{L}_1 , \tag{4}$$

where $\mathfrak{L}_1$ is a dimensionless linear operator which is discussed in Appendix B.

In like manner we may regard the expression $(d^{(2)}/dt)\rho$ as the product of a linear operator $(d^{(2)}/dt)$ with the density matrix ρ. Since the repopulation pumping is also proportional to the mean pumping rate R we set

$$\frac{d^{(2)}}{dt} = R\mathfrak{L}_2 , \tag{5}$$

where $\mathfrak{L}_2$ is a dimensionless linear operator which is discussed in Appendix B.

Finally, we note that under many experimental conditions the relaxation rate $(d^{(3)}/dt)\rho$ may be regarded as the product of a linear operator $(d^{(3)}/dt)$ with the density matrix ρ. We introduce a mean relaxation rate γ and set

$$\frac{d^{(3)}}{dt} = -\gamma U , \tag{6}$$

where U is a linear operator which we shall discuss in Sec. II D, Eq. (38).

Physically, it is clear that neither the Hamiltonian operator $\mathcal{S}$ nor the relaxation operator U can generate polarization from an unpolarized ensemble of atoms. This implies that

$$\mathcal{S}|0\rangle = 0 \tag{7}$$

and

$$U|0\rangle = 0 . \tag{8}$$

The basic pumping equation (1) now assumes the form

$$\frac{d}{dt}|P\rangle = \left(R\mathfrak{L} - \gamma U + \frac{\mathcal{S}}{i\hbar}\right)|P\rangle + R\mathfrak{L}|0\rangle , \tag{9}$$

where the total pumping operator is

$$\mathfrak{L} = \mathfrak{L}_1 + \mathfrak{L}_2 . \tag{10}$$

In steady state the left-hand side of (9) is zero, and we obtain the steady-state equation

$$(R\mathfrak{L} - \gamma U + \mathcal{S}/i\hbar)|P\rangle = -R\mathfrak{L}|0\rangle . \tag{11}$$

Solving (11) for $|P\rangle$, we find

$$|P\rangle = (U + i\mathcal{S}/\gamma\hbar - x\mathfrak{L})^{-1} x\mathfrak{L}|0\rangle , \tag{12}$$

where we have introduced the dimensionless ratio of the mean pumping rate R to the mean relaxation rate γ,

$$x = R/\gamma . \tag{13}$$

The parameter x is less than unity in many experimental situations.

Equation (12) is exact but not very useful in practice. This is because the inverse of the complex operator $(U + i\mathcal{S}/\gamma\hbar - x\mathfrak{L})$ can seldom be obtained in a simple analytic form. For instance,

consider the $F=4$ ground-state Zeeman multiplet of cesium. The density matrix for this multiplet has 81 components, and the operator $(U+i\mathcal{S}/\gamma\hbar - x\mathcal{L})$ is therefore an 81×81 matrix. One row and column can be eliminated if the density matrix remains normalized, but an 80×80 matrix remains. Inversion of an 80×80 matrix is awkward and time consuming, and the inversion must be carried out for a large number of different experimental parameters in order to yield useful information about magnetic resonance line shapes and light shifts.

To avoid these difficulties we may develop a power-series expansion of (12). Call

$$A=(U+i\mathcal{S}/\gamma\hbar)^{-1}. \tag{14}$$

We shall assume that the matrix elements of A can be obtained without difficulty. We also note the operator identity

$$(a-b)^{-1}=a^{-1}+a^{-1}ba^{-1}+a^{-1}ba^{-1}ba^{-1}+\cdots. \tag{15}$$

If we identify a with $(U+i\mathcal{S}/\gamma\hbar)$ and b with $x\mathcal{L}$ in (15), then (12) becomes

$$\begin{aligned}|P\rangle&=(xA+x^2A\mathcal{L}A+x^3A\mathcal{L}A\mathcal{L}A+\cdots)\mathcal{L}|0\rangle\\&=\sum_{n=1}^{\infty}x^n|P^{(n)}\rangle.\end{aligned} \tag{16}$$

Equation (16) is the desired power series. The nth-order contribution to the polarization is simply

$$x^n|P^{(n)}\rangle=x^n(A\mathcal{L})^n|0\rangle. \tag{17}$$

B. Optical pumping of a Zeeman multiplet

We shall illustrate the use of the expansion (16) by deriving formulas for the light shifts of the Larmor frequency of a Zeeman multiplet. Suppose that the atomic ground state has angular momentum F_g and the atomic excited state has angular momentum F_e. The atom is situated in a static external magnetic field, and the ground-state and excited-state Larmor frequencies in this field are, respectively, ω_g and ω_e. We further suppose that the ground-state atoms are undergoing magnetic resonance transitions caused by a small rotating magnetic field, which causes the atoms to nutate at a frequency ω_1 on resonance. The rotation frequency is ω, and we assume that

$$\omega\simeq\omega_g. \tag{18}$$

The rf field is too weak to significantly affect the excited-state atoms. Thus, the effective ground-state Hamiltonian operator is

$$\mathcal{H}_g=\omega_gF_z+\omega_1(F_x\cos\omega t+F_y\sin\omega t). \tag{19}$$

The effective excited-state Hamiltonian operator is

$$\mathcal{H}_e=\omega_eF_z. \tag{20}$$

We shall expand ρ on the irreducible basis tensors[8]

$$\begin{aligned}|LM\rangle&=T_{LM}(F_gF_g),\\\langle LM|&=T^{\dagger}_{LM}(F_gF_g).\end{aligned} \tag{21}$$

The scalar product of two basis tensors is

$$\begin{aligned}\langle LM|L'M'\rangle&=\mathrm{Tr}[T^{\dagger}_{LM}(F_gF_g)T_{L'M'}(F_gF_g)]\\&=\delta_{LL'}\delta_{MM'}.\end{aligned} \tag{22}$$

The irreducible tensors form a complete set of basis states for $|\rho\rangle$ so

$$\begin{aligned}|\rho\rangle&=\sum_{LM}|LM\rangle\langle LM|\rho\rangle\\&=\sum_{L=1}^{2F_g}\sum_{M=-L}^{+L}|LM\rangle\langle LM|P\rangle+|00\rangle\langle00|0\rangle.\end{aligned} \tag{23}$$

Since we assume that the trace of ρ is unity, we get

$$\begin{aligned}1=\mathrm{Tr}[\rho]&=(2F_g+1)^{1/2}\,\mathrm{Tr}[T_{00}(F_gF_g)^{\dagger}\rho]\\&=(2F_g+1)^{1/2}\langle00|0\rangle,\end{aligned} \tag{24}$$

and the normalizing constant is

$$\langle00|0\rangle=(2F_g+1)^{-1/2}. \tag{25}$$

C. Transformation to a rotating coordinate system

Let us introduce an angular momentum operator $\vec{\mathrm{L}}$ which operates on the basis states $|LM\rangle$. We define $\vec{\mathrm{L}}$ by

$$\vec{\mathrm{L}}|LM\rangle=[\vec{\mathrm{F}},T_{LM}]. \tag{26}$$

From (26) it follows that $\vec{\mathrm{L}}$ has all of the commutation relations of an angular momentum operator.

The basis states $|LM\rangle$ are eigenfunctions of L^2 and L_z, i.e.,

$$L^2|LM\rangle=L(L+1)|LM\rangle, \tag{27}$$

$$L_z|LM\rangle=M|LM\rangle. \tag{28}$$

In view of (26) and (19), the operator $\mathcal{S}$ of (2) becomes

$$\mathcal{S}=\hbar\omega_gL_z+\hbar\omega_1(L_x\cos\omega t+L_y\sin\omega t). \tag{29}$$

We now define the polarization $|Q\rangle$ in the rotating coordinate system[9] by

$$|Q\rangle=e^{i\omega L_zt}|P\rangle. \tag{30}$$

Substituting (30) into (9), we obtain

$$\frac{d}{dt}|Q\rangle = (R\tilde{\mathfrak{L}} - \gamma\tilde{U} - i\Omega L_\zeta)|Q\rangle + R\tilde{\mathfrak{L}}|0\rangle, \tag{31}$$

where

$$\Omega^2 = (\omega_g - \omega)^2 + \omega_1^2 \tag{32}$$

and

$$\Omega L_\zeta = (\omega_g - \omega)L_z + \omega_1 L_x . \tag{33}$$

The frequency relationships (32) and (33) are summarized in Fig. 1. The transformed operators are denoted by a tilde, and we have

$$\tilde{\mathfrak{L}} = e^{i\omega L_z t}\mathfrak{L}e^{-i\omega L_z t}, \tag{34}$$

with an analogous definition of $\tilde{U}$.

Since we expect the polarizations to be constant in the rotating coordinate system, we shall drop the rapidly oscillating parts of $\tilde{\mathfrak{L}}$ and $\tilde{U}$. This is the secular approximation,[6] and it is well justified as long as the rotation frequency ω is much greater than the mean relaxation rate γ and the mean pumping rate R of the ground state. This is the usual experimental situation in a magnetometer. We denote the static parts of $\tilde{\mathfrak{L}}$ and $\tilde{U}$ by $\overline{L}$ and $\overline{U}$, respectively. Then (31) becomes

$$\frac{d}{dt}|Q\rangle = (R\overline{\mathfrak{L}} - \gamma\overline{U} - i\Omega L_\zeta)|Q\rangle + R\overline{\mathfrak{L}}|0\rangle . \tag{35}$$

D. Steady-state solution

Equation (35) is now in the form of Eq. (9), and the solution is therefore given by (16). The nth-order contribution to the polarization in the rotating coordinate system is

$$|Q^{(n)}\rangle = (A\overline{\mathfrak{L}})^n|0\rangle , \tag{36}$$

with

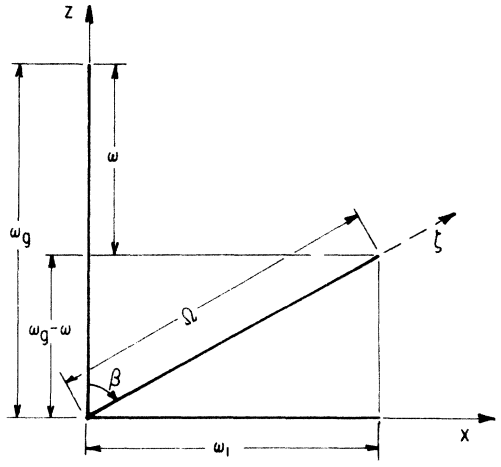

FIG. 1. Frequency relations in the rotating coordinate system.

$$A = \frac{1}{\overline{U} + i\Omega L_\zeta/\gamma} . \tag{37}$$

For simplicity let us assume that all components of the polarization relax at the same rate. It is not difficult to generalize the subsequent arguments to take multipole relaxation rates[10] into account. Then

$$\overline{U}|LM\rangle = (1 - \delta_{L0}\delta_{M0})|LM\rangle . \tag{38}$$

That is, we can regard $\overline{U}$ as the projection operator for the polarization. Since we shall always be taking matrix elements of A between states of nonzero angular momentum (polarized states), we may replace $\overline{U}$ by 1 in (37). Then the operator A is diagonal in L but not diagonal in M. We shall also show (see Appendix B) that the pumping operator $\overline{\mathfrak{L}}$ is diagonal in M but not diagonal in L. Keeping these properties of A and $\overline{\mathfrak{L}}$ in mind, we can use (36) to show that the first-order polarization is

$$x\langle LM|Q^{(1)}\rangle = x\langle LM|A|L0\rangle\langle L0|\overline{\mathfrak{L}}|0\rangle . \tag{39}$$

We shall return to discuss the physical significance of (39) after a brief review of the theory of transmission monitoring in optical pumping.

E. Transmission monitoring

The most direct way to detect the polarization of ground-state, optically pumped atoms is to measure the attenuation of a beam of resonant light which passes through the polarized atoms. For optically thin atomic vapors,[8] the attenuation of a beam of resonant light is proportional to the mean rate of absorption per atom, $\langle\delta\Gamma\rangle$, where

$$\langle\delta\Gamma\rangle = \mathrm{Tr}[\delta\Gamma\rho] = \langle\delta\Gamma|\rho\rangle = \sum_{LM}\langle\delta\Gamma|LM\rangle\langle LM|\rho\rangle , \tag{40}$$

and according to Appendix B [see (B7) and (B8)]

$$\langle\delta\Gamma|LM\rangle = \delta\Gamma(LF_gF_e)E_{LM} . \tag{41}$$

Combining (39)–(41), we see that the mean absorption rate is

$$\langle\delta\Gamma\rangle = R + \sum_{L=1}^{2}\sum_{M=-L}^{+L}\delta\Gamma(LF_gF_e)E_{LM}\langle LM|Q\rangle e^{-i\omega Mt} . \tag{42}$$

That is, the mean absorption rate is equal to the mean pumping rate R plus terms proportional to the orientation $\langle 1M|Q\rangle$ and alignment $\langle 2M|Q\rangle$ in the rotating coordinate system. The absorption associated with the transverse polarization $\langle LM|Q\rangle$ is modulated at the frequency ωM.

Consequently, (39) and (42) imply that to first

order in x, the transmission monitoring signal associated with $\langle LM|Q\rangle$ has a constant amplitude proportional to $x\langle L0|\bar{\mathfrak{L}}|0\rangle\delta\Gamma(LF_gF_e)E_{LM}$ and a resonance line-shape factor $\langle LM|A|L0\rangle$. The line-shape factor is independent of the atomic angular momenta F_g and F_e, and it describes how the signal depends on the rf power and on the detuning of the rf frequency ω from the resonance frequency ω_g. The line-shape factors are discussed in more detail in Appendix A. Some typical line-shape factors are illustrated in Fig. 2. The orientation line-shapes $\langle 1M|A|10\rangle$ are identical to the Bloch[11] resonance functions for longitudinal and transverse magnetization. The longitudinal-alignment line-shape factor $\langle 20|A|20\rangle$ was first derived by Brossel and Bitter,[12] and the function B of Eq. (5) in their paper[12] is

$$B=\tfrac{1}{8}I_0(1-\langle 20|A|20\rangle).$$

The transverse-alignment line-shape factors $\langle 2M|A|20\rangle$ $(M\neq 0)$ were first derived by Dodd, Series, and Taylor in their studies of modulated

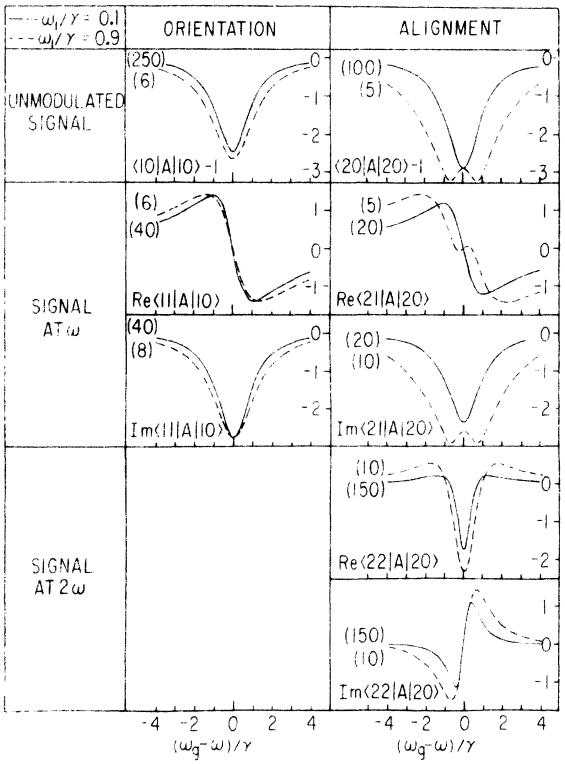

FIG. 2. First-order orientation and alignment resonance functions. The solid lines correspond to a low rf power, $\omega_1/\gamma=0.1$, and the dashed lines correspond to a higher rf power, $\omega_1/\gamma=0.9$. To the left of each curve a factor is given by which the curves should be divided to give the absolute value of the resonances. Unity has been subtracted from the longitudinal resonance curves for convenience in plotting.

fluorescent light in optical double-resonance experiments.[13] For instance, in terms of the series functions[13] D and E, we can write

$$\langle 22|A|20\rangle=\sqrt{\tfrac{3}{2}}(D-iE).$$

In summary, (42) and (39) imply that to first order in x the unmodulated transmission monitoring signal will be a linear combination of the line-shape factors $\langle 10|A|10\rangle$ and $\langle 20|A|20\rangle$, the transmission monitoring signal which is modulated at the rf frequency will be a linear combination of $\langle 11|A|10\rangle$ and $\langle 21|A|20\rangle$, and the transmission monitoring signal which is modulated at twice the rf frequency will be proportional to $\langle 22|A|20\rangle$.

F. Light shifts and line broadening

The first-order polarization of (39) is a good approximation to the real experimental situation only if the pumping rate is very small. The resonance curves $\langle LM|A|L0\rangle$ exhibit the proper rf power broadening (see Fig. 2), and the polarization is predicted to be proportional to the light intensity. A serious defect of the first-order solutions is that the predicted width and center frequency of the resonance curves is independent of the light intensity. It is well known that the pumping light broadens and shifts the magnetic resonance lines. Also, although we expect the polarization to be proportional to the light intensity for sufficiently weak pumping light, the polarization must eventually saturate and become independent of the light intensity for sufficiently intense light. We can account for the saturation of the polarization and for the optical broadening and the light shift by including higher-order terms in the series expansion (16).

Before proceeding to a more analytic treatment of the light shifts we shall illustrate our basic approach with a concrete example. In Fig. 3 we have shown exact and approximate magnetic resonance curves for the longitudinal orientation of Hg^{201}. The exact curve was calculated by numerically inverting the matrix equation (12) on an electronic computer. Note that the exact curve increases in amplitude, and broadens and shifts when the light intensity is increased by a factor of 3. The first-order contribution (39) to the power-series solution is also shown in Fig. 3. Note that the first-order solution increases in amplitude when the light intensity is increased, but there is no broadening or shift of the first-order curve with increasing light intensity. The second-order contribution to the power-series solution is also shown in Fig. 3. The second-order contribution increases as the square of the light intensity and it therefore becomes relatively more important as the

light intensity increases. The sum of the first- and second-order contributions to the signal exhibits all of the important features of the exact solution. The amplitude of the sum curve increases by a bit less than a factor of 3, as it should because of saturation effects, and there is a broadening and shift of the sum signal. The shift comes about because the first-order signal is symmetric, while the second-order signal has an antisymmetric component. We now proceed to a more analytic discussion of the light shifts.

According to (16) and (36) the polarization, correct to second order, is

$$\langle LM|Q\rangle \approx x\langle LM|Q^{(1)}\rangle + x^2\langle LM|Q^{(2)}\rangle$$
$$= x\langle 00|0\rangle\left\{\langle LM|A|L0\rangle\langle L0|\mathfrak{L}|00\rangle + x\sum_{L'M'}\langle LM|A|LM'\rangle\langle LM'|\mathfrak{L}|L'M'\rangle\langle L'M'|A|L'0\rangle\langle L'0|\mathfrak{L}|00\rangle\right\}. \quad (43)$$

We see that each component $\langle LM'|\mathfrak{L}|L'M'\rangle$ of the pumping operator can generate a correcting line-shape factor $\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle$ to the first-order line-shape factor $\langle LM|A|L0\rangle$ of the resonance. Since the second-order contribution to the polarization is a factor of x smaller than the first-order contribution, the correction will not cause a major change in the resonance line shape as long as x is much less than unity (cf. Fig. 3).

In Appendix A we shall show that the real and imaginary parts of $\langle LM|A|LM'\rangle$ always have a well-defined parity with respect to reversal of the sign of $(\omega_g - \omega)$. The parties of the real and imaginary parts are always opposite each other and are given by

$$\text{parity of } \mathrm{Re}\langle LM|A|LM'\rangle = (-1)^{M-M'},$$
$$\text{parity of } \mathrm{Im}\langle LM|A|LM'\rangle = (-1)^{M-M'-1}. \quad (44)$$

Now, let us examine the parities of the first-order and second-order contributions to the polarization of (43). We note that (43) can be separated into real and imaginary parts as follows:

$$\langle LM|Q\rangle = x\langle 00|0\rangle\left\{\mathrm{Re}\langle LM|A|L0\rangle\langle L0|\mathfrak{L}|00\rangle\right.$$
$$+x\sum_{L'M'}\langle L'0|\mathfrak{L}|00\rangle\,\mathrm{Re}\langle LM'|\mathfrak{L}|L'M'\rangle\,\mathrm{Re}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle)$$
$$\left.-x\sum_{L'M'}\langle L'0|\mathfrak{L}|00\rangle\,\mathrm{Im}\langle LM'|\mathfrak{L}|L'M'\rangle\,\mathrm{Im}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle)\right\}$$
$$+ix\langle 00|0\rangle\left\{\mathrm{Im}\langle LM|A|L0\rangle\langle L0|\mathfrak{L}|00\rangle\right.$$
$$+x\sum_{L'M'}\langle L'0|\mathfrak{L}|00\rangle\,\mathrm{Re}\langle LM'|\mathfrak{L}|L'M'\rangle\,\mathrm{Im}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle)$$
$$\left.+x\sum_{L'M'}\langle L'0|\mathfrak{L}|00\rangle\,\mathrm{Im}\langle LM'|\mathfrak{L}|L'M'\rangle\,\mathrm{Re}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle)\right\}. \quad (45)$$

In view of (44) we find that

$$\text{parity of } \mathrm{Re}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle) = (-1)^M,$$
$$\text{parity of } \mathrm{Im}(\langle LM|A|LM'\rangle\langle L'M'|A|L'0\rangle) = (-1)^{M+1}. \quad (46)$$

Thus, we see from (43) that the first-order resonance function $\mathrm{Re}\langle LM|A|L0\rangle$ of parity $(-1)^M$ is corrected by a function of like parity multiplied by $\mathrm{Re}\langle LM'|\mathfrak{L}|L'M'\rangle$, and it is corrected by a function of opposite parity multiplied by $\mathrm{Im}\langle LM'|\mathfrak{L}|L'M'\rangle$. Similarly, the first-order resonance function $\mathrm{Im}\langle LM|A|L0\rangle$ of parity $(-1)^{M+1}$ is corrected by a function of like parity multiplied by $\mathrm{Re}\langle LM'|\mathfrak{L}|L'M'\rangle$, and it is corrected by a function of opposite parity multiplied by $\mathrm{Im}\langle LM'|\mathfrak{L}|L'M'\rangle$. Since a small opposite-parity correction causes a shift in the magnetic resonance line (cf. Fig. 3) and a small like-parity correction causes a broadening, we conclude that

$\mathrm{Re}\langle LM|\mathfrak{L}|L'M\rangle$ causes a broadening of the line,

$\mathrm{Im}\langle LM|\mathfrak{L}|L'M\rangle$ causes a shift of the line.

Now let us calculate an approximate expression for the shift in the peak of an even function $f(\omega_g$

$-\omega)$ due to a small odd correction $g(\omega_g-\omega)$. That is, we wish to find the peak of the function

$$F(\omega_g-\omega)=f(\omega_g-\omega)+g(\omega_g-\omega)\,. \tag{47}$$

Making use of the parities f and g, we write

$$F(\omega_g-\omega)=f(0)+(\omega_g-\omega)\frac{\partial g}{\partial\omega_g}+\frac{(\omega_g-\omega)^2}{2}\frac{\partial^2 f}{\partial\omega_g{}^2}+\cdots\,, \tag{48}$$

where the derivatives are evaluated at $\omega_g=\omega$. If we retain only the first three terms of (48) and differentiate with respect to ω_g, we find an extremum when

$$\omega=\omega_g+\left(\frac{\partial^2 f}{\partial\omega_g{}^2}\right)^{-1}\frac{\partial g}{\partial\omega_g}=\omega_g+\Delta\omega_g\,. \tag{49}$$

Thus the shift in the peak resonance frequency is

$$\Delta\omega_g=+\left(\frac{\partial^2 f}{\partial\omega_g{}^2}\right)^{-1}\frac{\partial g}{\partial\omega_g}\,. \tag{50}$$

Consequently, if M is even, the shift of the even-parity resonance $\mathrm{Re}\langle LM\,|\,Q^{(1)}\rangle$, is

$$\Delta\omega_g=\left(x\,\mathrm{Re}\frac{\partial}{\partial\omega_g}\langle LM\,|\,Q^{(2)}\rangle\right)\Big/\left(\mathrm{Re}\frac{\partial^2}{\partial\omega_g{}^2}\langle LM\,|\,Q^{(1)}\rangle\right)\,. \tag{51}$$

Here, it is understood that both derivatives are evaluated at $\omega=\omega_g$. An analogous formula applies

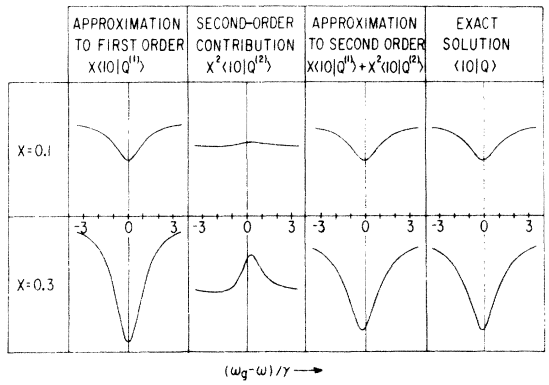

FIG. 3. Approximate and exact solutions for the longitudinal orientation of Hg^{201}. In these calculations the magnetic field was assumed to be 1 G, the asymmetry parameter κ was taken to be zero, the excited-state Landé factor was $g_J=1.4861$, the excited-state lifetime was 114 nsec, the light was assumed to pump from the ground-state Zeeman multiplet $F_g=\frac{3}{2}$ to the excited-state multiplet $F_e=\frac{5}{2}$, and the rf amplitude was $\omega_1/\gamma=0.5$. The vertical and horizontal scales are the same for all curves, although the curves have been displaced by an arbitrary amount vertically in some cases for convenience in plotting. The approximate curve, calculated from (45), is almost indistinguishable from the exact curve, calculated from (12).

to $\mathrm{Im}\langle LM\,|\,Q^{(1)}\rangle$ when M is odd. The formulas for $\langle LM\,|\,Q^{(1)}\rangle$ and $\langle LM\,|\,Q^{(2)}\rangle$ are given by (43) or (45).

One word of caution is necessary concerning (51). In the derivation of (51) it was assumed that the second derivative of the even function was nonzero. However, some even $L=2$ resonances can have vanishing second derivatives at the center of the resonance for certain rf power levels (see Fig. 2). Equation (51) is certainly not valid when $(\partial^2/\partial\omega_g{}^2)\,\langle LM\,|A\,|00\rangle$ is nearly zero. In such cases it is not difficult to analyze the situation graphically, as we illustrated in Fig. 3.

Let us now discuss the shift of an odd resonance function $j(\omega_g-\omega)$ due to the admixture of a small even correction function $k(\omega_g-\omega)$. That is, we seek the zero of the function

$$G(\omega_g-\omega)=j(\omega_g-\omega)+k(\omega_0-\omega)\,. \tag{52}$$

Making use of the parities of j and k, we write

$$G(\omega_g-\omega)=k+(\omega_g-\omega)\frac{\partial j}{\partial\omega_g}+\frac{(\omega_g-\omega)^2}{2\,!}\frac{\partial^2 k}{\partial\omega_g{}^2}+\cdots\,. \tag{53}$$

Retaining only the first two terms of (53), we see that G is zero when

$$\omega=\omega_g+k\left(\frac{\partial j}{\partial\omega_g}\right)^{-1}=\omega_g+\Delta\omega_g\,. \tag{54}$$

Applying (54) to (45), we conclude that for even M, the light shift of the odd resonance curve $\mathrm{Im}\langle LM\,|\,Q^{(1)}\rangle$ is

$$\Delta\omega_g=(+x\,\mathrm{Im}\langle LM\,|\,Q^{(2)}\rangle)\left(\mathrm{Im}\frac{\partial}{\partial\omega_g}\langle LM\,|\,Q^{(1)}\rangle\right) \tag{55}$$

An analogous formula holds for the light shift of the odd resonance $\mathrm{Re}\langle LM\,|\,Q^{(1)}\rangle$ when M is odd. Of course, (55) is not valid when the denominator is nearly zero, and a more careful analysis of the problem is required in such singular cases.

G. Light shifts of the orientation

For illustrative purposes we present a detailed discussion of the light shifts of the orientation resonances. The formulas (51) and (55) can be evaluated for three independent components of orientation. One finds that the longitudinal orientation $\langle 10\,|\,Q\rangle$ and the imaginary part of the transverse orientation $\mathrm{Im}\langle 11\,|\,Q\rangle$ have the same light shift,

$$\frac{1}{x}\left(\frac{\Delta\omega_g}{\gamma}\right)=a+bF\left(\frac{\omega_1}{\gamma}\right)\,. \tag{56}$$

Here, a and b are coefficients which can be expressed in terms of the matrix elements of the pumping operator (see Appendix B):

$$a=-\,\mathrm{Im}\langle 11\,|\,\bar{\mathfrak{L}}\,|\,00\rangle=\kappa a_v+\lambda a_r \tag{57}$$

$$b = -\sqrt{3}\,\mathrm{Im}\langle 11|\mathfrak{L}|21\rangle\frac{\langle 20|\mathfrak{L}|00\rangle}{\langle 10|\mathfrak{L}|00\rangle} = \kappa b_v + \lambda b_r . \quad (58)$$

The light-shift parameters a_v, a_r, b_v, and b_r are listed in Table I for $\sigma_\pm$ light and for low values of the atomic angular momenta F_e and F_g. The subscripts r and v refer to virtual and real transitions. The asymmetry parameter κ is discussed in Appendix B [Eq. (B4)], and the dephasing parameter λ is

$$\lambda = \frac{(\omega_e - \omega_g)\tau}{1+(\omega_e-\omega_g)^2\tau^2} , \quad (59)$$

where τ is the excited-state lifetime.

The power-dependence function $F(y)$ is

$$F(y) = \frac{1 - y^2/2}{1+4y^2} . \quad (60)$$

The light shift of the real part of the transverse orientation $\mathrm{Re}\langle 11|Q\rangle$ is

$$\frac{1}{x}\left(\frac{\Delta\omega_g}{\gamma}\right) = a + bG\left(\frac{\omega_1}{\gamma}\right) , \quad (61)$$

where a and b were already defined in (57) and (58), and the power-dependence function is

$$G(y) = \frac{1+y^2}{1+4y^2} . \quad (62)$$

TABLE I. Coefficients for the orientation ($L=1$) light shifts. For σ^+ pumping use upper signs; for σ^- pumping use lower signs.

$$\frac{\Delta\omega_g}{R} = \kappa a_v + \lambda a_r + (\kappa b_v + \lambda b_r)\frac{F(\omega_1/\gamma)}{G(\omega_1/\gamma)} .$$

F_g	F_e	a_v	a_r	b_v	b_r
0.5	0.5	±1.000 00	0.000 00	0.000 00	0.000 00
0.5	1.5	∓0.500 00	0.500 00	0.000 00	0.000 00
1.0	0.0	±0.750 00	0.000 00	±0.750 00	0.000 00
1.0	1.0	±0.375 00	0.375 00	±0.375 00	−0.375 00
1.0	2.0	∓0.375 00	0.675 00	∓0.075 00	0.225 00
1.5	0.5	±0.500 00	0.500 00	±0.450 00	0.750 00
1.5	1.5	±0.200 00	0.704 00	±0.221 54	−0.324 92
1.5	2.5	∓0.300 00	0.756 00	∓0.090 00	0.378 00
2.0	1.0	±0.375 00	0.675 00	±0.315 00	0.944 99
2.0	2.0	±0.125 00	0.874 99	±0.143 18	−0.238 64
2.0	3.0	∓0.250 00	0.800 00	∓0.090 00	0.480 00
2.5	1.5	±0.300 00	0.756 00	±0.240 00	1.007 99
2.5	2.5	±0.085 71	0.971 75	±0.099 74	−0.176 68
2.5	3.5	∓0.214 29	0.826 52	∓0.085 72	0.551 03
3.0	2.0	±0.250 00	0.800 00	±0.192 85	1.028 56
3.0	3.0	±0.062 50	1.031 24	±0.073 37	−0.134 51
3.0	4.0	∓0.187 50	0.843 74	∓0.080 36	0.602 68
3.5	2.5	±0.214 29	0.826 52	±0.160 71	1.033 15
3.5	3.5	±0.047 62	1.070 29	±0.056 21	−0.105 27
3.5	4.5	∓0.166 67	0.855 55	∓0.075 00	0.641 67
4.0	3.0	±0.187 50	0.843 74	±0.137 50	1.031 22
4.0	4.0	±0.037 50	1.097 24	±0.044 42	−0.084 40
4.0	5.0	∓0.150 00	0.864 00	∓0.070 00	0.672 00

The light shifts predicted by (56) and (61) bear many similarities to the light shifts of Hg^{199}, which were studied in detail by Cohen-Tannoudji, and our theoretical results are identical to his for the case of Hg^{199}. Irrespective of the ground-state angular momentum, we can identify light shifts due to real transitions (the terms proportional to λ) and light shifts due to virtual transitions (the terms proportional to κ). We recall that the shifts due to virtual transitions are mainly due to the off-resonance components of the pumping light, and they can be thought of as the Stark shifts caused by the rapidly oscillating electric field of the light wave. The shifts due to virtual transitions are positive or negative depending on whether the atomic resonance frequency is greater than ($\kappa>0$) or less than ($\kappa<0$) the frequency of the light. Consequently, the shifts due to virtual transitions are proportional to the parameter κ, which measures the preponderance of low-frequency light over high-frequency light [see (B4)]. The shifts due to real transitions are mainly due to the resonant components of the pumping light, and they arise because the atomic polarization rotates about the magnetic field at different frequencies in the ground state and in the excited state. Consequently, the shifts due to real transitions are proportional to the parameter λ [see (59)], which measures the degree to which the difference $(\omega_e - \omega_g)$ of the Larmor frequency in the ground state and in the excited state speeds up the effective ground-state precession frequency.

We predict some qualitatively new properties of the light shift for atoms with ground-state angular momenta greater than $\frac{1}{2}$. First, the light shifts depend on the rf power in a way described by the functions F and G. The power dependence is absent when the ground-state spin is $\frac{1}{2}$. Second, the light shift of the real part of the transverse orientation differs from the light shift of the longitudinal orientation. This difference is not present for a spin-$\frac{1}{2}$ atom, and the difference tends to zero in the limit of low rf power.

Analogous formulas can be derived for the broadening of the orientation resonances and for the shifts and broadening of the alignment resonances. We should point out that because of the complicated shapes of the alignment resonances at higher rf powers (see Fig. 2), the definition of a line center or width is not always unambiguous. For this reason we have limited our detailed discussion to the simpler light shifts of the orientation resonances, although our methods can be generalized in a straightforward way.

H. Limits of validity

The analytic formulas (51) and (55) certainly give the correct light shift in the limit of vanishing light intensity. However, optical pumping experiments are always done at finite light intensities, and values of x ranging from 0.01 to 1.0 are typical. Since our analytic formulas were obtained by assuming that x was much less than unity and by retaining only the terms of order x and x^2 in the series (16), one might expect the analytic formulas (51) and (55) to be rather poor approximations to the true light shift for $x \simeq 1$. However, we believe that the analytic formulas are much better approximations for $x \simeq 1$ than the nature of our derivation would indicate.

Rather than attempt a rigorous, analytic study of the limits of validity of our light-shift formulas, we have made extensive comparisons between the true light shifts obtained from exact numerical solutions to (12) and the light shifts predicted by (51) and (55). Some of these comparisons are shown in Figs. 4 and 5 for Hg^{201}. From the curves in these figures we see that there is excellent agreement between the exact light shift and the analytic light shift ($\lesssim 1\%$ discrepancy) for $x = 0.1$. The agreement is still reasonably good ($\lesssim 10\%$ discrepancy) for $x = 0.9$. Although Figs. 4 and 5 illustrate the situation when the asymmetry parameter κ is zero, equally good agreement is found between the exact and analytic shifts when κ is not zero. It is surprising that there is such good agreement between the analytic approximation and the exact results for $x \simeq 1$, where terms of higher order than x^2 should be retained in the series (16). Indeed, explicit numerical calculations show that the first two terms of (16) often give a very poor representation of the exact resonance curves for $x \simeq 1$. Thus, although the analytic formulas (51) and (55) appear to be very useful for $x \simeq 1$, their success for values of x close to unity remains puzzling.

APPENDIX A: PROPERTIES OF THE OPERATOR A

The matrix elements of the operator

$$A = \frac{1}{1 + i\Omega L_\zeta/\gamma} \tag{A1}$$

determine the shapes of the magnetic resonance

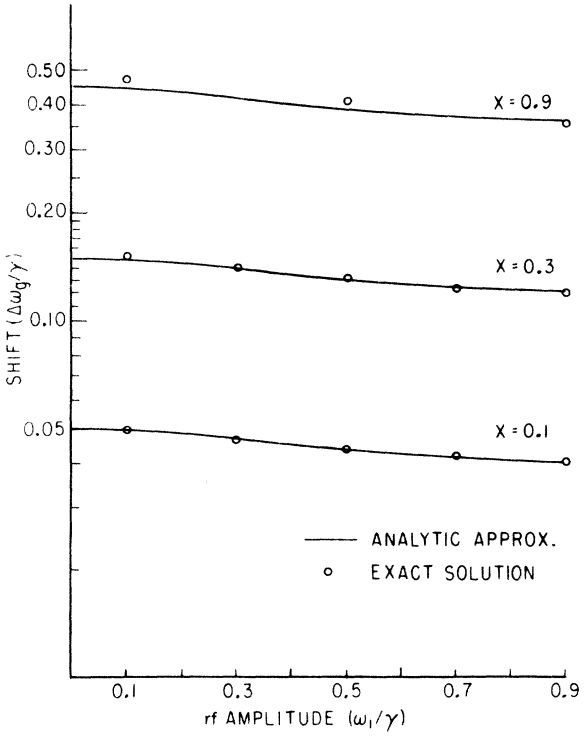

FIG. 4. Comparison of the light shifts in the zero of the transverse orientation $\mathrm{Re}\langle 11|Q\rangle$ as deduced from the analytic formula (56) and the true light shift determined by the numerical solution of (12). Atomic parameters were the same as listed in Fig. 3.

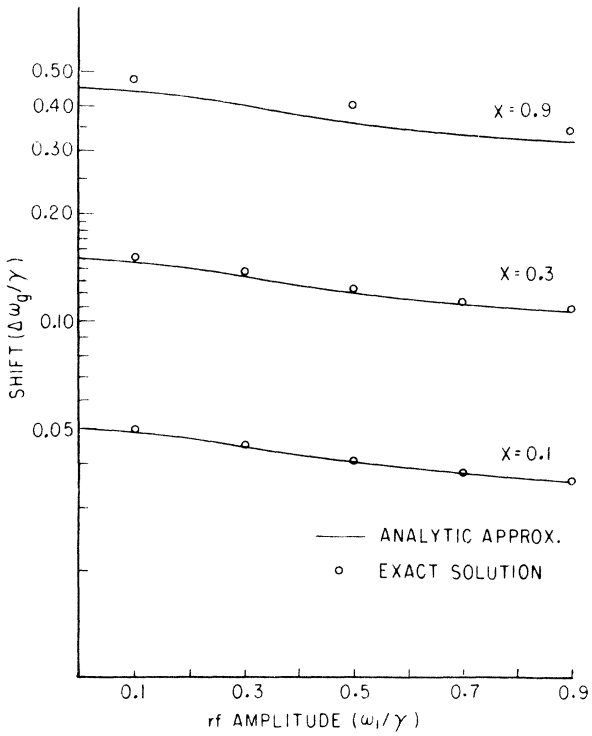

FIG. 5. Comparison of the light shift in the maximum of the transverse orientation $\mathrm{Im}\langle 11|Q\rangle$ as deduced from the analytic formula (56) and the true light shift determined by the numerical solution of (12). Atomic parameters were the same as listed in Fig. 3.

lines. To evaluate the matrix elements of A we note that

$$L_\zeta = \mathcal{R} L_z \mathcal{R}^{-1}, \tag{A2}$$

where the rotation operator $\mathcal{R}$ is (cf. Fig. 1)

$$\mathcal{R} = e^{-i\beta L_y}. \tag{A3}$$

Consequently, we can write

$$A = \mathcal{R} \frac{1}{1 + i(\Omega/\gamma) L_z} \mathcal{R}^{-1}. \tag{A4}$$

The matrix elements of A are therefore

$$\langle LM | A | LM' \rangle = \sum_{M''} \frac{D^L_{MM''} (D^L_{M''M'})^{-1}}{1 + i(\Omega/\gamma) M''}, \tag{A5}$$

where the Wigner D functions[14] are

$$D^L_{MM''}(0, \beta, 0) = \langle LM | \mathcal{R} | LM'' \rangle. \tag{A6}$$

We note that the D functions for the Euler angles (α, β, γ) are real and orthogonal as

$$(D^L_{MM'})^{-1} = D^L_{M'M}. \tag{A7}$$

Of course, (A7) is not true for arbitrary Euler angles, and we stress again that we shall only be considering the special Euler angles $(0, \beta, 0)$. From (A5) and (A7) it follows that the matrix elements of A are symmetric,

$$\langle LM | A | LM' \rangle = \langle LM' | A | LM \rangle. \tag{A8}$$

We also note[14] that for $\alpha = \gamma = 0$

$$D^L_{MM'} = (-1)^{M-M'} D^L_{-M,-M'}. \tag{A9}$$

From (A8) and (A5) we deduce that

$$\langle LM | A | LM' \rangle^* = (-1)^{M-M'} \langle L-M | A | L-M' \rangle. \tag{A10}$$

Let us now examine the parity of the matrix elements $\langle LM | A | LM' \rangle$ with respect to reversal of the sign of $(\omega_g - \omega)$. From Fig. 1 it is clear that the operation

$$(\omega_g - \omega) \to (\omega_g - \omega) \tag{A11}$$

is equivalent to the operation

$$\beta \to \pi - \beta. \tag{A12}$$

Both (A11) and (A12) are to be performed for a fixed value of the flipping frequency ω_1 and the relaxation rate γ. One can also show that

$$D^L_{MM'}(0, \pi - \beta, 0) = (-1)^{L-M} D^L_{M,-M'}(0, \beta, 0). \tag{A13}$$

Using (A13), (A8), and (A5) we deduce that

$$\langle LM | A(\omega - \omega_g, \omega_1, \gamma) | LM' \rangle = (-1)^{M-M'} \langle LM | A(\omega_g - \omega, \omega_1, \gamma) | LM' \rangle^*. \tag{A14}$$

Equation (A14) implies that the real and imaginary parts of $\langle LM | A | LM' \rangle$ have well-defined parities with respect to $(\omega_g - \omega)$ and that

$$\text{parity of } \mathrm{Re}\langle LM | A | LM' \rangle = (-1)^{M-M'},$$

$$\text{parity of } \mathrm{Im}\langle LM | A | LM' \rangle = (-1)^{M-M'+1}. \tag{A15}$$

The first-order resonances are listed in analytical form in Table II.

Finally, we prove three useful identities for the resonance functions. Note that

$$\frac{\partial}{\partial \omega_g} A = \lim_{\Delta\omega_g \to 0} \left[\frac{1}{1 + i\omega_g L_z/\gamma + i\omega_1 L_x/\gamma + i\Delta\omega_g L_z/\gamma} - \frac{1}{1 + i\omega_g L_z/\gamma + i\omega_1 L_x/\gamma} \right]. \tag{A16}$$

Using the expansion (15) for the first term in square brackets in (A16) we see that

$$\frac{\partial}{\partial \omega_g} A = \frac{A L_z A}{i\gamma} = -\frac{\partial A}{\partial \omega}. \tag{A17}$$

In like manner one can show that

$$\frac{\partial}{\partial \gamma} \left(\frac{A}{\gamma} \right) = -A^2 \tag{A18}$$

and also

$$\frac{\partial}{\partial \omega_1} A = \frac{A L_x A}{i\gamma}. \tag{A19}$$

Equation (17), which can be generalized to give higher-order derivatives of A with respect to ω_g, is very helpful in evaluating (51) and (55).

APPENDIX B: PROPERTIES OF THE PUMPING OPERATOR $\mathfrak{L}$

Barrat and Cohen-Tannoudji[6] have shown that the rate of depopulation pumping is given by

$$i\hbar \frac{d^{(1)}}{dt} \rho = \delta\mathcal{H}\rho - \rho\delta\mathcal{H}^+. \tag{B1}$$

The effective Hamiltonian operator[8] is composed of a Hermitian light-shift operator $\delta\mathcal{E}$, due mainly to the off-resonance components of the pumping light, and a Hermitian light-absorption operator $\delta\Gamma$, due mainly to the resonant components of the pumping light. We have

$$\delta\mathcal{H} = \delta\mathcal{E} - i\hbar\delta\Gamma/2. \tag{B2}$$

We shall be concerned with an atom with a single ground-state multiplet of angular momentum F_g which is pumped into a single excited-state multiplet F_e. We assume that the spectral profile $\Phi(\nu)$ of the light is narrow enough that no other hfs components of the absorption line are excited. Then one can show[8] that the light-shift operator and the light-absorption operator differ only by a constant

factor κ,

$$\delta\mathcal{E} = -\kappa(\hbar\delta\Gamma/2), \tag{B3}$$

where

$$\kappa = \frac{\int_0^\infty \Phi(\nu)\,\mathrm{Re}Z(\xi)\,d\nu}{\int_0^\infty \Phi(\nu)\,\mathrm{Im}Z(\xi)\,d\nu}. \tag{B4}$$

From (B4) one can see that κ is a measure of the asymmetry of the spectral profile of the pumping light with respect to the absorption profile $\mathrm{Im}Z(\xi)$ of the pumping light. The argument of the plasma dispersion function $Z(\xi)$ is[8,15]

$$\xi = \frac{1}{\omega_{eg}}\left(\frac{Mc^2}{2RT}\right)^{1/2}\{\omega - \omega_{eg} + i(\tfrac{1}{2}\Gamma + \gamma_c)\}, \tag{B5}$$

where

$$\omega_{eg} = [E(F_e) - E(F_g)]/\hbar. \tag{B6}$$

For an atom with a ground-state angular momentum F_g and an excited-state angular momentum F_e, one can show that[8]

$$\delta\Gamma = \sum \delta\Gamma(LF_gF_e)E_L T_L(F_gF_g), \tag{B7}$$

where

$$\delta\Gamma(LF_gF_e) = 3R(F_gF_e)(2F_g+1)W(1LF_eF_g;1F_g) \tag{B8}$$

and the mean pumping rate is

$$R(F_gF_e) = (\lambda r_0 c f u/2\hbar)(2J_g+1) \times(2F_e+1)W^2(J_eF_eJ_gF_g;I1), \tag{B9}$$

where f is the absorption oscillator strength of the *electronic* transition $J_g \to J_e$, and u is the mean energy density per unit frequency interval (cycles per second, not radians per second) of the pumping light in the neighborhood of the absorption line. Thus we see that

$$\frac{d^{(1)}}{dt}\rho = R\mathcal{L}_1\rho = \tfrac{1}{2}i\kappa[\delta\Gamma,\rho] - \tfrac{1}{2}(\delta\Gamma\rho + \rho\delta\Gamma). \tag{B10}$$

Now we note that the product of two irreducible basis tensors is

$$T_{LM}T_{L'M'} = \sum_{L''}(-1)^{L+L'+L''}[(2L+1)(2L'+1)]^{1/2} \times W(LL'FF;L''F)C(LL'L'';MM')T_{L'',M+M'}. \tag{B11}$$

Equations (B7)–(B11) imply that

$$\frac{\bar{d}^{(1)}}{dt} = R\bar{\mathcal{L}}_1 = R\sum_{L'}\mathcal{L}_1(L''L'L)E_{L'0}T_{L'0}(L''L) \times\{e(LL'L'') + i\kappa o(LL'L'')\}, \tag{B12}$$

where the even and odd functions are

$$e(LL'L'') = \tfrac{1}{2}[1 + (-1)^{L+L'L''}], \tag{B13}$$

$$o(LL'L'') = \tfrac{1}{2}[1 - (-1)^{L+L'+L''}]. \tag{B14}$$

We see that $e(LL'L'')$ is 1 if $L+L'+L''$ is even and zero if $L+L'+L''$ is odd; $o(LL'LL)$ is 1 if $L+L'+L''$ is odd and zero if $L+L'+L''$ is even. The function $\mathcal{L}_1(L''L'L)$ is

$$\mathcal{L}_1(L''L'L) = 3(-1)^{L+L'+L''+1}(2F_g+1)W(1L'F_eF_g;1F_g) \times[(2L+1)(2L''+1)]^{1/2}W(LL'F_gF_g;L''F_g). \tag{B15}$$

We note that the imaginary part of $d^{(1)}/dt$ is proportional to the asymmetry parameter κ. In Sec. II E we showed that the light shifts were proportional to the imaginary part of $\mathcal{L}$. Consequently, there will be a part of the light shift which is proportional to the asymmetry parameter κ, and we can identify this part of the shift as the "shift due to virtual transitions."

The quantities $T_{L'M'}(L''L)$ in (B12) are irreducible basis tensors in the space spanned by the basis vectors $|LM\rangle$ of (21). The nonzero matrix elements of the basis tensors are

$$\langle L''M''|T_{L'M'}(L''L)|LM\rangle = \left(\frac{2L'+1}{2L''+1}\right)^{1/2}C(LL'L'';MM'M''). \tag{B16}$$

In a similar way, one can show that the operator for repopulation pumping, $d^{(2)}/dt$, is

TABLE II. First-order resonance functions.

$$\langle 10|A|10\rangle = 1 - \frac{\omega_1^2}{C_1}$$

$$\langle 11|A|10\rangle = -\frac{\omega_1}{C_1\sqrt{2}}[(\omega_g-\omega)+i\gamma]$$

$$\langle 20|A|20\rangle = 1 - \frac{3\omega_1^2}{C_1C_2}[\gamma^2+\omega_1^2+4(\omega_g-\omega)^2]$$

$$\langle 21|A|20\rangle = -\frac{\omega_1}{C_1C_2}(\tfrac{3}{2})^{1/2}\{(\omega_g-\omega)[\gamma^2-2\omega_1^2+4(\omega_g-\omega)^2] + i\gamma[\gamma^2+\omega_1^2+4(\omega_g-\omega)^2]\}$$

$$\langle 22|A|20\rangle = \frac{\omega_1^2}{C_1C_2}(\tfrac{3}{2})^{1/2}\{[2(\omega_g-\omega)^2-\omega_1^2-\gamma^2] + 3i\gamma(\omega_g-\omega)\}$$

$$C_1 = \gamma^2+\omega_1^2+(\omega_g-\omega)^2$$

$$C_2 = \gamma^2+4\omega_1^2+4(\omega_g-\omega)^2$$

$$\langle L-M|A|L0\rangle = (-1)^M\langle LM|A|L0\rangle^*$$

$$\frac{\bar{d}^{(2)}}{dt} = R\bar{\mathfrak{L}}_2$$
$$= RB(F_e F_g) \sum_{LL'L''} \mathfrak{L}_2(L''L'L)$$
$$\times E_{L'0} T_{L'0}(L''L) \frac{1}{1+i(\omega_e-\omega_g)\tau L_z} . \quad \text{(B17)}$$

Here τ is the excited-state lifetime, and the coefficient $\mathfrak{L}_2(L''L'L)$ is

$$\mathfrak{L}_2(L''L'L)$$
$$= 3(-1)^{L'}(2F_e+1)(2F_g+1)[(2L''+1)(2L+1)]^{1/2}$$
$$\times W(1F_eF_g L''; F_g F_e) \begin{bmatrix} 1F_eF_g \\ 1F_eF_g \\ L'L''L \end{bmatrix} . \quad \text{(B18)}$$

Here $B(F_eF_g)$ is the branching ratio from the state F_e to the state F_g.

Now we would like to point out certain symmetries of the pumping operator $\bar{\mathfrak{L}}$. By inspection of (B12) and (B17) we see that

$$\langle LM|\bar{\mathfrak{L}}|L'M'\rangle = \delta_{MM'}\langle LM|\bar{\mathfrak{L}}|L'M\rangle . \quad \text{(B19)}$$

That is, $\bar{\mathfrak{L}}$ is diagonal in M. This is a consequence of the secular approximation, which amounts to ignoring the effects of the transverse components of the polarization tensors of the pumping light. Of course (B19) would not be valid if the Larmor frequency ω_g of the ground state were comparable to or less than the ground-state relaxation rate γ.

From (B12) and (B17) one can also verify that

$$\langle L''M|\bar{\mathfrak{L}}|LM\rangle^* = \langle L''-M|\bar{\mathfrak{L}}|L-M\rangle . \quad \text{(B20)}$$

The condition (B20) is necessary if the pumping process is to maintain the Hermiticity of the density matrix.

Finally, we note that

$$\langle 00|\bar{\mathfrak{L}}|LM\rangle = 3(-1)^{F_e-F_g+L} E_{L0}[(2F_g+1)]^{1/2}$$
$$\times W(11F_gF_g; LF_e)[B(F_eF_g)-1] . \quad \text{(B21)}$$

That is, $\langle 00|\bar{\mathfrak{L}}|LM\rangle$ would be identically zero if all excited atoms decayed to the same ground-state Zeeman multiplet from which they were pumped [i.e., if $B(F_eF_g)=1$]. The condition (B21) is an expression of the conservation of atoms.

In conclusion, we give the explicit form of the matrix elements of the pumping operator $\bar{\mathfrak{L}}$:

$$\langle L''M|\bar{\mathfrak{L}}|LM\rangle = \sum_{L'} E_{L'0}\left(\frac{2L'+1}{2L''+1}\right)^{1/2} C(LL'L'';M0) \left\{\mathfrak{L}_1(L''L'L)[e(LL'L'')+i\kappa o(LL'L'')]\right.$$
$$\left. + \mathfrak{L}_2(L''L'L)\left(\frac{1-i(\omega_e-\omega_g)M\tau}{1+(\omega_e-\omega_g)^2M^2\tau^2}\right) B(F_eF_g)\right\} . \quad \text{(B22)}$$

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