

## Theory of spin-exchange optical pumping of $^3\text{He}$ and $^{129}\text{Xe}$

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We present a comprehensive theory of nuclear spin polarization of  $^3\text{He}$  and  $^{129}\text{Xe}$  gases by spin-exchange collisions with optically pumped alkali-metal vapors. The most important physical processes considered are (1) spin-conserving spin-exchange collisions between like or unlike alkali-metal atoms; (2) spin-destroying collisions of the alkali-metal atoms with each other and with buffer-gas atoms; (3) electron-nuclear spin-exchange collisions between alkali-metal atoms and  $^3\text{He}$  or  $^{129}\text{Xe}$  atoms; (4) spin interactions in van der Waals molecules consisting of a Xe atom bound to an alkali-metal atom; (5) optical pumping by laser photons; (6) spatial diffusion. The static magnetic field is assumed to be small enough that the nuclear spin of the alkali-metal atom is well coupled to the electron spin and the total spin is very nearly a good quantum number. Conditions appropriate for the production of large quantities of spin-polarized  $^3\text{He}$  or  $^{129}\text{Xe}$  gas are assumed, namely, atmospheres of gas pressure and nearly complete quenching of the optically excited alkali-metal atoms by collisions with  $\text{N}_2$  or  $\text{H}_2$  gas. Some of the more important results of this work are as follows: (1) Most of the pumping and relaxation processes are sudden with respect to the nuclear polarization. Consequently, the steady-state population distribution of alkali-metal atoms is well described by a spin temperature, whether the rate of spin-exchange collisions between alkali-metal atoms is large or small compared to the optical pumping rate or the collisional spin-relaxation rates. (2) The population distributions that characterize the response to sudden changes in the intensity of the pumping light are not described by a spin temperature, except in the limit of very rapid spin exchange. (3) Expressions given for the radio-frequency (rf) resonance linewidths and areas can be used to make reliable estimates of the local spin polarization of the alkali-metal atoms. (4) Diffusion effects for these high-pressure conditions are mainly limited to thin layers at the cell surface and at internal resonant surfaces generated by radio-frequency magnetic fields when the static magnetic field has substantial spatial inhomogeneities. The highly localized effects of diffusion at these surfaces are described with closed-form analytic functions instead of the spatial eigenmode expansions that are appropriate for lower-pressure cells. [S1050-2947(98)07408-3]

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### I. INTRODUCTION

Spin-exchange optically pumped systems are of growing importance for producing large amounts of hyperpolarized  $^3\text{He}$  and  $^{129}\text{Xe}$  for medical imaging and other applications [1]. Such systems need to be optimized, but we have found it impossible to make realistic computer models of their performance because of uncertainties in the basic physics of the optical pumping, spin-exchange, and spin-relaxation processes. Although there is an extensive experimental and theoretical literature on optical pumping and related physics, going back many years, the reported values of important rate coefficients often differ by factors of two or even much more, and some key aspects of the physics are not discussed at all or are discussed in a misleading way. We have therefore carried out a series of experimental and theoretical studies of the key physical processes in spin-exchange optically pumped systems to determine the parameters with sufficient accuracy to support reliable modeling. This paper summarizes the essential theoretical framework of spin-exchange optical pumping. It is followed by papers summarizing our experimental studies. The theory describes the main gas-phase phenomena: (1) spin-conserving spin-exchange collisions between like or unlike alkali-metal atoms; (2) spin-destroying collisions of the alkali-metal atoms with each other and with buffer-gas atoms; (3) electron-nuclear spin-exchange collisions between alkali-metal atoms and  $^3\text{He}$  or

$^{129}\text{Xe}$  atoms; (4) spin exchange with the angular momentum of molecular rotation and with the nuclear spin of a  $^{129}\text{Xe}$  atom bound to an alkali-metal atom in a van der Waals molecule; (5) optical pumping by laser photons; (6) spatial diffusion. For the high-pressure conditions of spin-exchange optical pumping, the main effects of spatial diffusion are confined to a thin layer near the cell surface. Also, diffusion of transverse polarization in such systems limits the spatial resolution that can be obtained from the internal resonant surfaces of gradient imaging [2]. To describe those highly localized effects would require hundreds of diffusion eigenmodes [3], so localized solutions are used instead. The experimental papers that form part of this study include thorough measurements of all the fundamental rate coefficients needed to describe these gas-phase processes.

The theory summarized here is based on our previous work and that of others, especially the following: Anderson, Pipkin, and Baird [4], who introduced the important spin-temperature distribution for alkali-metal atoms in the limiting case of very rapid spin exchange; Barrat and Cohen-Tannoudji [5], who first made systematic use of the density matrix to describe optical pumping; Bouchiat [6], who first demonstrated the importance of nuclear slowing-down factors for spin relaxation in alkali-metal vapors; Grosstête [7], who made the first detailed studies of spin-exchange between like and unlike alkali-metal atoms; and Bouchiat, Brossel, and Pottier [8], who demonstrated the key role played by van

der Waals molecules for the spin relaxation of alkali-metal atoms in heavy noble gases.

Systems to spin polarize the nuclei of  $^3\text{He}$  and  $^{129}\text{Xe}$  by spin-exchange optical pumping are almost always designed to operate at quite high gas pressures, typically one to ten atmospheres, and also with such high number densities of alkali-metal atoms that the vapor is optically thick at the center of the  $D_1$  optical pumping lines. To avoid radiation trapping, enough nitrogen or hydrogen buffer gas is added to nonradiatively deexcite (quench) the excited atoms before they can reradiate a photon. The high gas pressure causes the hyperfine structure of the  $D_1$  absorption line to be completely unresolved. As a consequence, the act of absorbing a photon may change the electron polarization but not the nuclear polarization. The optically excited atoms have their electron polarization nearly completely destroyed by collisions in the high-pressure gas before they are deexcited by a collision with a nitrogen or hydrogen molecule. Even though the electron polarization is destroyed before the atom is deexcited, the nuclear polarization of the excited atom is hardly affected. Sudden binary collisions of ground-state alkali-metal atoms are of such short duration that they modify the electron polarization with negligible effects on the nuclear polarization. So almost all of the important pumping and collisional relaxation mechanisms for spin-exchange optical pumping are "sudden" with respect to the nuclear polarization. The nuclear polarization changes only because of its hyperfine coupling to the electron polarization in the time intervals between photon absorptions or spin-flip collisions.

Because the pumping and relaxation processes are sudden with respect to the nuclear polarization, the steady-state probability of finding an alkali-metal atom in a ground-state sublevel of azimuthal quantum number  $m$  is very nearly  $e^{\beta m}/Z$ , where  $\beta$  is the spin-temperature parameter and  $Z = \sum e^{\beta m}$  is the partition function (*Zustandssumme*). The simple spin-temperature distribution prevails *whether the rate of spin-exchange collisions between alkali-metal atoms is large or small compared to optical pumping rates or spin-relaxation rates*. Without the high gas pressures characteristic of spin-exchange optical pumping, Anderson and Ramsey [9] have shown that the spin-temperature distribution occurs only if the rate of spin-exchange collisions greatly exceeds the optical pumping rate and other relaxation rates in the system. The existence of a spin temperature for the steady-state population distribution greatly simplifies the analysis of these systems.

A collision between a Xe atom and an alkali-metal atom in the presence of a third body can lead to the formation of a van der Waals molecule, which lives until it is broken up by a subsequent collision. A very few van der Waals molecules escape collisional breakup for so long that the electron and nuclear spins are depolarized by comparable amounts. This is the main relaxation mechanism that is not sudden with respect to nuclear polarization. However, because of rapid collisional breakup of the molecules in the high gas pressures used for spin-exchange optical pumping, most of the molecules break up before there is time for much depolarization of the nucleus. So most of the molecular-induced relaxation is also sudden with respect to the nuclear polarization.

Sections II (free atoms) and III (colliding atoms) review

the fundamental spin interactions known to be important for spin-exchange optical pumping. Section IV reviews the density matrix and its representation in Liouville space. Sections V–VII review the relaxation produced by the fundamental collisional interactions. Section VIII reviews optical pumping for high-pressure, heavily quenched conditions. The pumping and relaxation processes are discussed together in Sec. IX, where we show that they normally lead to a spin-temperature distribution for steady-state conditions with negligible spatial diffusion. Section IX also contains a discussion of the thin diffusion layers of low spin polarization that form near walls of the optical pumping cell. Section X includes a discussion of the radio-frequency resonances of alkali-metal atoms. Section XI contains an analysis of relaxation in the dark, an important experimental method for deducing key parameters that determine the performance of spin-exchange optically pumped systems. Section XII contains a discussion of the consequences of spatial diffusion on gradient imaging. Two appendices contain important details on the relaxation due to van der Waals molecules (Appendix A) and optical pumping (Appendix B).

## II. COLLISION-FREE SPIN HAMILTONIANS

During the intervals between collisions with other atoms or photons, the spin wave function  $|\psi\rangle$  of an atom evolves according to the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi\rangle = H |\psi\rangle. \quad (1)$$

For an alkali-metal atom the ground-state Hamiltonian operator is [10]

$$H_g = A_g \mathbf{I} \cdot \mathbf{S} + g_S \mu_B S_z B_z - \frac{\mu_I}{I} I_z B_z, \quad (2)$$

where  $A_g \mathbf{I} \cdot \mathbf{S}$  describes the coupling of the nuclear spin  $\mathbf{I}$  to the electron spin  $\mathbf{S}$ . The isotropic magnetic-dipole coupling coefficient is  $A_g$ . The magnetic-dipole coupling of the electron spin to the static magnetic field  $B_z$ , which defines the  $z$  axis of the coordinate system, is described by the term  $g_S \mu_B S_z B_z$ , where  $g_S = 2.00232$  is the  $g$  value of the electron, and  $\mu_B = 9.2741 \times 10^{-21}$  erg G $^{-1}$  is the Bohr magneton. The magnetic-dipole coupling of the nuclear spin to the static field is given by the term  $-\mu_I I_z B_z / I$ , where  $\mu_I$  is the nuclear moment (often tabulated in units of the nuclear magneton  $\mu_n = \mu_B / 1836$ ). The nuclear-spin quantum number is  $I$ .

The eigenstates  $|fm\rangle$  of Eq. (2) will be labeled by  $f$ , the total angular momentum quantum number of the state in the limit  $B_z \rightarrow 0$  and by  $m$ , the rigorously good azimuthal quantum number and eigenvalue of  $F_z = I_z + S_z$ , the longitudinal component of the total angular momentum operator. Then

$$H_g |fm\rangle = E(fm) |fm\rangle. \quad (3)$$

The possible values of  $f$  are  $f = I + 1/2 = a$  or  $f = I - 1/2 = b$ . For transitions with  $\Delta m = 1$  and  $\Delta f = 0$ , the resonance frequencies are given by

$$\hbar \omega_{f\bar{m}} = E(fm) - E(f, m-1), \quad (4)$$

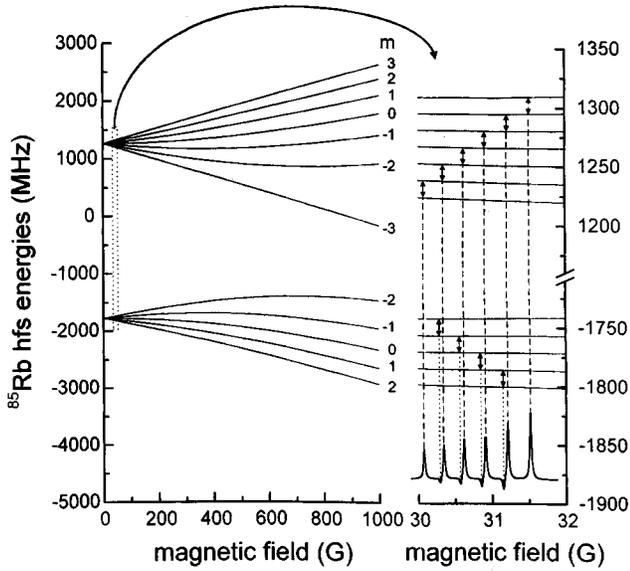


FIG. 1. Energy levels of the  $^2S_{1/2}$  ground state of an alkali-metal atom ( $^{85}\text{Rb}$  with  $I=5/2$ ). Resonances (discussed in Sec. XI) for radio-frequency transitions between ground-state sublevels are sketched.

where  $\bar{m} = m - 1/2$  is the mean azimuthal quantum number of the transition. Solving Eq. (3) by perturbation theory to second order in  $B_z$  we find that the resonance frequencies are

$$\omega_{a\bar{m}} = \frac{B_z(g_S\mu_B - 2\mu_I)}{\hbar[I]} - \frac{B_z^2\bar{m}^4(g_S\mu_B + \mu_I/I)^2}{[I]^3\hbar A_g}, \quad (5)$$

$$\omega_{b\bar{m}} = -\frac{B_z(g_S\mu_B + \{2 + 2/I\}\mu_I)}{\hbar[I]} + \frac{B_z^2\bar{m}^4(g_S\mu_B + \mu_I/I)^2}{[I]^3\hbar A_g}. \quad (6)$$

Here and in the future we will denote the statistical weight of a spin quantum number by  $[I] = 2I + 1$ .

An alkali-metal atom in the first excited  $^2P_{1/2}$  state evolves under the influence of an analogous Hamiltonian

$$H_e = A_e \mathbf{I} \cdot \mathbf{J} + g_J \mu_B J_z B_z - \frac{\mu_I}{I} I_z B_z. \quad (7)$$

The well-known Zeeman splitting of the energy levels of the  $^2S_{1/2}$  ground state of a typical alkali-metal atom is shown in Fig. 1.

In the time intervals between collisions, the spins of the noble gases  $^3\text{He}$  and  $^{129}\text{Xe}$  evolve by simple precession about the applied field  $B_z$ , as described by spin Hamiltonians of the form

$$H_{\text{NG}} = -\frac{\mu_K}{K} K_z B_z. \quad (8)$$

Here  $\mu_K$  is the magnetic moment of the noble-gas nucleus, and  $K$  is the nuclear spin quantum number. In this paper we are only interested in the noble gases  $^3\text{He}$  and  $^{129}\text{Xe}$ , for both of which  $K=1/2$ . The precession frequencies per unit magnetic field are  $-\mu_K/(hK) = \omega_K/(2\pi B_z) = 3243$  and  $1178$  Hz/G, respectively. The eigenstates of Eq. (8) are

simple Zeeman sublevels  $|q\rangle$  with  $q = \pm 1/2$  being the eigenvalue of  $K_z$ , the projection of the nuclear spin operator along the  $z$  axis:

$$H_{\text{NG}}|q\rangle = \hbar\omega_K q|q\rangle. \quad (9)$$

### III. COLLISIONAL HAMILTONIANS

During a binary collision of a ground-state alkali-metal atom with a buffer-gas atom or during the lifetime of a van der Waals molecule formed from a ground-state alkali-metal atom and a xenon atom, there will be two interactions in addition to the free-atom interactions (2) and (7). The spin-rotation interaction [11–14]

$$V_{\text{NS}} = \gamma \mathbf{N} \cdot \mathbf{S} \quad (10)$$

ouples the electron spin  $\mathbf{S}$  to the relative angular momentum  $\mathbf{N}$  of the colliding pair of atoms. The nuclear-electron spin-exchange interaction [15]

$$V_{\text{KS}} = \alpha \mathbf{K} \cdot \mathbf{S} \quad (11)$$

ouples the nuclear spin  $\mathbf{K}$  of a  $^3\text{He}$  or  $^{129}\text{Xe}$  atom to the electron spin  $\mathbf{S}$  of the alkali-metal atom. The coupling coefficients  $\gamma = \gamma(R)$  and  $\alpha = \alpha(R)$  depend on the internuclear separation  $R$  between the alkali-metal atom and the buffer-gas atom. Both coefficients approach zero very rapidly with increasing  $R$ .

The spin relaxation caused by collisions between pairs of alkali-metal atoms with electron spins  $\mathbf{S}_i$  and  $\mathbf{S}_j$  is dominated by the exchange interaction [16]

$$V_{\text{ex}} = J \mathbf{S}_i \cdot \mathbf{S}_j, \quad (12)$$

where the coupling coefficient  $J = J(R)$  is of electrostatic origin. The exchange interaction conserves the internal spin of the colliding atoms.

Also acting during a collision between alkali-metal atoms is an interaction that couples the electron spins to the orbital angular momentum  $\mathbf{N}$  of the atoms about each other. This interaction is hypothesized to be of the form [17–19]

$$V_{\text{SS}} = \frac{2}{3} \lambda (3S_\zeta S_\zeta - 2), \quad (13)$$

where  $\lambda = \lambda(R)$  is the coupling coefficient, and  $S_\zeta = (\mathbf{S}_i + \mathbf{S}_j) \cdot \mathbf{R}/R$  is the projection of the total electronic spin along the internuclear axis. There is experimental evidence that the interaction (13) or some similar interaction that couples the internal spin to the orbital angular momentum  $\mathbf{N}$  of the colliding atoms, causes significant losses of spin angular momentum at high densities of the alkali-metal vapor. Initial theoretical estimates of the magnitude of  $\lambda$  [20] are much too small to account for the observed losses.

The hyperfine coupling coefficient  $A_g$  of Eq. (2) also changes during a collision, and the resulting collisional interaction can be described in terms of a potential  $\Delta A_g \mathbf{I} \cdot \mathbf{S}$ , where  $\Delta A_g = \Delta A_g(R)$  is a rapidly decreasing function of the internuclear separation  $R$ . This collisional modification of  $A_g$  is the source of the pressure shifts of the frequencies of gas-cell atomic clocks [21], and the interaction can also cause  $\Delta m = 0$  transitions between the states  $|am\rangle$  and  $|bm\rangle$  at large applied magnetic fields  $B_z$ , where  $f$  is not a good quantum

number [22]. However,  $\Delta A_g \mathbf{I} \cdot \mathbf{S}$  will have a negligible effect on a spin state characterized by a spin temperature, which normally prevails for spin-exchange optical pumping. The buffer gas atom will also induce small, higher-order hyperfine interactions, for example, anisotropic magnetic-dipole hyperfine interactions or electric-quadrupole interactions. Walter [23] has estimated the effects of these higher-order interactions and has shown that they are of negligible importance for spin-exchange optical pumping. The magnetic-dipole interactions that occur for  $^3\text{He}$ - $^3\text{He}$  collisions, and the nuclear spin-rotation interactions that occur for gas-phase collisions of  $^{129}\text{Xe}$  cause very slow nuclear spin relaxation. We will ignore this gas-phase collisional relaxation since it is so slow compared to the relaxation caused by collisions with alkali-metal atoms.

The collisional spin relaxation is critically dependent on the spin-independent potential  $V_0$ , which determines the internuclear force  $-dV_0/dR$  that acts during a collision. For collisions between alkali-metal atoms and noble-gas atoms, the spin-dependent potentials (10) and (11) are so small compared to  $V_0$ , that  $V_0$  completely determines the classical trajectories needed for a semiclassical calculation of spin relaxation. In like manner, for a partial-wave calculation of spin relaxation with the distorted-wave Born approximation,  $V_0$  determines the distorted partial waves. Because the interactions (10) and (11) decrease so rapidly with increasing internuclear separation, small uncertainties in  $V_0(R)$  cause as much uncertainty in the calculated spin-relaxation rates as do uncertainties in the coupling coefficients  $\alpha$  and  $\gamma$ . For collisions between alkali-metal atoms, the exchange coupling coefficient  $J$  of Eq. (12) is comparable in size to  $V_0$  so the starting point for calculations of spin relaxation due to the spin-destroying potential  $V_{SS}$  of Eq. (13) is the triplet potential  $V_0 + J/4$ .

#### IV. THE DENSITY MATRIX

The average value of some spin observable  $M$  for an ensemble of  $N$  identical atoms, each described by a wave function  $|\psi_n\rangle$ ,  $n = 1, 2, \dots, N$ , is

$$\langle M \rangle = \frac{1}{N} \sum_n \langle \psi_n | M | \psi_n \rangle = \sum_{ij} \langle i | M | j \rangle \langle j | \rho | i \rangle = \text{Tr } M \rho. \quad (14)$$

The first sum extends over the labels  $n$  of the  $N$  atoms and the second sum extends over the possible values of the quantum numbers  $i$  ( $i, j = fm, f'm'$  for an alkali-metal atom or  $i, j = q, q'$  for a noble-gas atom). From Eq. (14), one can readily see that the density matrix [24] is

$$\langle j | \rho | i \rangle = \frac{1}{N} \sum_n \langle j | \psi_n \rangle \langle \psi_n | i \rangle. \quad (15)$$

The diagonal element  $\langle i | \rho | i \rangle$  is the occupation probability of the state  $|i\rangle$ , and the off-diagonal element  $\langle j | \rho | i \rangle$  is the coherence between the states  $|j\rangle$  and  $|i\rangle$ . From Eq. (15) we see that the density matrix may be thought of as the matrix elements of the density operator

$$\rho = \frac{1}{N} \sum_n |\psi_n\rangle \langle \psi_n|. \quad (16)$$

According to the Schrödinger equation (1), the collision-free evolution of the density operator is given by the Liouville equation

$$\frac{d}{dt} \rho = \frac{1}{i\hbar} [H, \rho], \quad (17)$$

where the square brackets and comma denote the commutator  $[H, \rho] = H\rho - \rho H$ .

*Liouville space.* The analysis of optical pumping and spin relaxation is notationally simpler when described in ‘‘Liouville space’’ rather than the more customary Schrödinger space discussed above. In Schrödinger space the density matrix  $\rho_{ij} = \langle i | \rho | j \rangle$  of an alkali-metal atom is a square, Hermitian matrix with  $2[I]$  rows and  $2[I]$  columns. In Liouville space we write the density matrix as a ‘‘state vector’’

$$|\rho\rangle = \sum_{ij} |ij\rangle \langle ij | \rho \rangle, \quad (18)$$

where the  $4[I]^2$  basis vectors are

$$|ij\rangle = |i\rangle \langle j|, \quad (19)$$

and the amplitudes are

$$\langle ij | \rho \rangle = \text{Tr}[(|i\rangle \langle j|)^\dagger \rho] = \rho_{ij}. \quad (20)$$

For describing the detailed buildup of spin polarization or its relaxation, it is convenient to work with the special basis vectors of Liouville space,

$$|ff' \bar{m} \Delta m\rangle = |fm\rangle \langle f'm'|, \quad (21)$$

with  $|fm\rangle$  defined by Eq. (3). The mean azimuthal quantum number  $\bar{m}$  and the azimuthal increment are

$$\bar{m} = (m + m')/2 \quad \text{and} \quad \Delta m = m - m'. \quad (22)$$

The basis vectors (21) have total azimuthal spin  $\Delta m$ . They are particularly appropriate for the commonly encountered situation of axial symmetry about an externally applied magnetic field.

Any pair of matrices  $M$  and  $N$  of Schrödinger space can be represented by a corresponding pair of Liouville-space vectors  $|M\rangle$  and  $|N\rangle$ , defined in analogy to Eqs. (18)–(20). We define a scalar product between these vectors, in analogy to Eq. (20), by

$$\langle M | N \rangle = \text{Tr } M^\dagger N = (N | M)^*. \quad (23)$$

The squared length  $\langle \rho | \rho \rangle$  is a measure of the spin polarization. For completely unpolarized alkali-metal atoms the state vector is

$$|\rho_0\rangle = \frac{1}{2[I]} \sum_i |ii\rangle, \quad (24)$$

with the squared length  $\langle \rho_0 | \rho_0 \rangle = (2[I])^{-2}$ . For completely polarized atoms, all in some Schrödinger spin state  $|i\rangle$ ,

$$|\rho\rangle = |ii\rangle. \quad (25)$$

The squared length of Eq. (25) is  $\langle\rho|\rho\rangle = 1$ .

The commutator  $[H, \rho]$  of the Liouville equation (17) can be described in Liouville space by an operator  $[H]$  acting on  $|\rho\rangle$  from the left, that is,

$$[H]|\rho\rangle = |[H, \rho]\rangle. \quad (26)$$

We will use the square-bracket notation defined in Eq. (26) to denote a Liouville-space operator, which is equivalent to an operator used in a Schrödinger-space commutator. For example, the Liouville equation (17) becomes

$$i\hbar \frac{d}{dt}|\rho\rangle = [H]|\rho\rangle, \quad (27)$$

formally equivalent to the Schrödinger equation (1).

From Eqs. (23) and (26) we deduce the simple identity

$$(M|[H])M = ([M, M^\dagger]H). \quad (28)$$

For a Hermitian Schrödinger operator, say  $M = \rho = \rho^\dagger$ , Eq. (28) implies that  $\langle\rho|[H]|\rho\rangle = 0$ . Thus, the evolution governed by the Schrödinger equation (27) does not change the length of  $|\rho\rangle$ ,

$$\frac{d}{dt}\langle\rho|\rho\rangle = \left\langle\rho\left|\frac{d}{dt}\rho\right.\right\rangle + \text{c.c.} = \frac{1}{i\hbar}\langle\rho|[H]|\rho\rangle + \text{c.c.} = 0. \quad (29)$$

Here c.c. denotes the complex conjugate of the preceding number.

The simple Liouville equation (27) with the commutator operator  $[H]$  is inadequate to describe changes in spin polarization, since it cannot cause the length of  $|\rho\rangle$  to change. However, an excellent description of the spin polarization and relaxation of atoms can often be obtained with a simple generalization of Eq. (27), the relaxation equation

$$\frac{d}{dt}|\rho\rangle = -\Lambda|\rho\rangle. \quad (30)$$

The relaxation operator  $\Lambda$  can be defined by its matrix elements in Liouville space,

$$\Lambda = \sum_{ij:rs} |ij\rangle\langle ij|\Lambda|rs\rangle\langle rs|. \quad (31)$$

$\Lambda$  will include terms due to optical pumping that make  $\langle\rho|\rho\rangle$  increase with time, and it will contain terms due to various relaxation mechanisms that make  $\langle\rho|\rho\rangle$  decrease with time. Despite its formal simplicity, Eq. (30) contains nonlinear terms. The parts of  $\Lambda$  describing spin-exchange collisions between like alkali-metal atoms include terms proportional to the electron spin polarization. So  $\Lambda$  depends linearly on  $|\rho\rangle$ .

The relaxation operator  $\Lambda$  will have left,  $\{\lambda|\$ , and right,  $|\lambda\rangle$ , eigenvectors with the common eigenvalue  $\lambda$ , defined by

$$\{\lambda|\Lambda = \{\lambda|\lambda \quad \text{and} \quad \Lambda|\lambda\rangle = \lambda|\lambda\rangle. \quad (32)$$

The  $|\lambda\rangle$  are analogous to oblique lattice vectors of a crystal. As long as the  $|\lambda\rangle$  form a complete set, the left eigenvectors  $\{\lambda|$ , which are analogous to reciprocal lattice vectors, can be normalized such that

$$\{\lambda|\lambda'\rangle = \delta_{\lambda,\lambda'}. \quad (33)$$

Because the  $|\lambda\rangle$  may not be orthogonal to each other, it is normally not true that  $\langle\lambda|\lambda'\rangle = \delta_{\lambda,\lambda'}$ , where  $\langle\lambda| = |\lambda\rangle^\dagger$ .

We will be concerned with spin-relaxation processes that conserve the number of atoms, that is, processes for which

$$\text{Tr } d\rho/dt = -\sum_{fm} (ffm0|\Lambda|\rho) = 0, \quad (34)$$

where  $(ffm0|$  is the Hermitian conjugate of  $|ffm0\rangle$ , defined by Eq. (21). This means that the columns of the matrix  $(ffm0|\Lambda|ffm'0\rangle$  sum to zero, or equivalently that

$$\{0|\Lambda = 0, \quad \text{where} \quad \{0| = \sum_{fm} (ffm0|. \quad (35)$$

One eigenvalue of  $\Lambda$  is always  $\lambda = 0$ , and it corresponds to the simple left eigenvector  $\{0|$ , defined by Eq. (35). A consequence of Eq. (33) with special physical significance is

$$\{0|\lambda\rangle = \sum_{fm} (ffm0|\lambda\rangle) = 0, \quad \text{if } \lambda \neq 0. \quad (36)$$

The populations  $(ffm0|\lambda\rangle$  of relaxing ( $\lambda \neq 0$ ) right eigenvectors must sum to zero. In Sec. XI we discuss some simple, explicit examples of the relaxation matrix  $\Lambda$ , the eigenvalues  $\lambda$ , and the left  $\{\lambda|$  and right  $|\lambda\rangle$  eigenvectors.

*Parts of  $\rho$  with and without electron polarization.* As discussed in the Introduction, the dominant optical pumping and collisional processes are ‘‘sudden’’ with respect to the nuclear polarization. Such processes are most conveniently described if the density operator of the alkali-metal atoms is written as the sum of a part without electron polarization, which is unaffected by these sudden processes,

$$\varphi = \frac{1}{4}\rho + \mathbf{S} \cdot \rho \mathbf{S}, \quad (37)$$

and an electron-polarized part,

$$\Theta \cdot \mathbf{S} = \frac{3}{4}\rho - \mathbf{S} \cdot \rho \mathbf{S}, \quad (38)$$

which is destroyed. In Eq. (37)  $\varphi$  is a purely nuclear operator with no electronic polarization. Similarly, in Eq. (38) the Cartesian vector  $\Theta$  has three purely nuclear operators as components:  $\Theta_x$ ,  $\Theta_y$ , and  $\Theta_z$ . From Eqs. (37) and (38) we find the simple identity

$$\rho = \varphi + \Theta \cdot \mathbf{S}. \quad (39)$$

The density operator of a  $^3\text{He}$  or  $^{129}\text{Xe}$  atom, both of which have  $K = 1/2$ , is simply

$$\rho = \frac{1}{2} + 2\langle\mathbf{K}\rangle \cdot \mathbf{K}, \quad (40)$$

which is analogous to Eq. (39) with  $\varphi \rightarrow 1/2$  and  $\Theta \rightarrow 2\langle\mathbf{K}\rangle$  and  $\mathbf{S} \rightarrow \mathbf{K}$ .

It is convenient to describe relaxation and pumping processes that are sudden with respect to the nuclear polarization in terms of the uncoupled multipole tensors [25,26]

$$|\lambda\mu lm\rangle = T_{\lambda\mu}(II)T_{lm}(SS), \quad (41)$$

which are linear combinations of the basis vectors (21) with  $\Delta m = \mu + m$ . The basis vectors (41) are an orthonormal set so

$$|\rho\rangle = \sum |\lambda\mu lm\rangle (\lambda\mu lm|\rho\rangle), \quad (42)$$

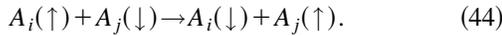
where the sum extends over all possible values of the multipole indices  $\lambda = 0, 1, \dots, 2I$ ;  $\mu = -\lambda, -\lambda + 1, \dots, \lambda$ ;  $l = 0, 1$  and  $m = -l, -l + 1, \dots, l$ . The parts of the density matrix without and with electron polarization are simply

$$|\varphi\rangle = \sum_{\lambda\mu} |\lambda\mu 00\rangle (\lambda\mu 00|\rho\rangle),$$

$$|\Theta \cdot \mathbf{S}\rangle = \sum_{\lambda\mu m} |\lambda\mu 1m\rangle (\lambda\mu 1m|\rho\rangle). \quad (43)$$

## V. BINARY COLLISIONS BETWEEN ALKALI-METAL ATOMS

The interaction (12) leads to very efficient spin exchange for collisions between a pair of alkali-metal atoms,  $A_i$  and  $A_j$ , as indicated symbolically by



The atoms  $A_i$  and  $A_j$  could be the same isotope, e.g.,  $A_i = A_j = {}^{85}\text{Rb}$ , they could be different isotopes of the same chemical species, e.g.,  $A_i = {}^{85}\text{Rb}$ ,  $A_j = {}^{87}\text{Rb}$ , or they could be isotopes of different chemical species, e.g.,  $A_i = {}^{85}\text{Rb}$ ,  $A_j = {}^{133}\text{Cs}$ . The arrows in Eq. (44) denote the direction of the *electron* spins. The binary spin-exchange collision (44) is sudden with respect to the nuclear polarization. For a monoisotopic vapor of alkali-metal atoms like Na or Cs, Grossetête [7] has shown that the exchange process (44) causes the density matrix to evolve as

$$\frac{d}{dt}\rho = \frac{1}{T_{\text{ex}}}\{\varphi(1 + 4\langle \mathbf{S} \rangle \cdot \mathbf{S}) - \rho\} + \frac{1}{i\hbar}[\delta\mathcal{E}_{\text{ex}}, \rho]. \quad (45)$$

The spin-exchange rate is proportional to the number density of the alkali-metal atoms

$$\frac{1}{T_{\text{ex}}} = [A]\langle v\sigma_{\text{ex}} \rangle. \quad (46)$$

Balling *et al.* [27,28] have shown that the frequency-shift operator of Eq. (45) is

$$\delta\mathcal{E}_{\text{ex}} = \frac{2\hbar\kappa}{T_{\text{ex}}}\langle \mathbf{S} \rangle \cdot \mathbf{S}, \quad (47)$$

where the dimensionless parameter  $\kappa$  is quite small, typically only a few percent. The rate coefficient  $\langle v\sigma_{\text{ex}} \rangle$  and  $\kappa$  are expected to have some temperature dependence.

For Li, K, or Rb vapors, which contain several stable isotopes (e.g.,  ${}^{85}\text{Rb}$  and  ${}^{87}\text{Rb}$ ), or for vapors containing alkali-metal atoms of several different chemical species, (e.g., Cs and Rb), Eq. (45) can be generalized to

$$\frac{d}{dt}\rho_i = \sum_j \frac{1}{T_{\text{ex},ij}}(\varphi_i\{1 + 4\langle \mathbf{S}_j \rangle \cdot \mathbf{S}_i\} - \rho_i) + \frac{1}{i\hbar}[\delta\mathcal{E}_{\text{ex},ij}, \rho], \quad (48)$$

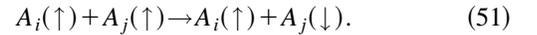
where the exchange rate of an alkali-metal atom of species  $i$  with atoms of species  $j$  and number density  $[A_j]$  is

$$\frac{1}{T_{\text{ex},ij}} = [A_j]\langle v\sigma_{\text{ex}} \rangle_{ij} \quad (49)$$

and the frequency-shift operator is

$$\delta\mathcal{E}_{\text{ex},ij} = \frac{2\hbar\kappa_{ij}}{T_{\text{ex},ij}}\langle \mathbf{S}_j \rangle \cdot \mathbf{S}_i. \quad (50)$$

There is strong experimental evidence that some interaction, presently believed to have the form (13), causes spin angular momentum to be lost to the rotational angular momentum  $\mathbf{N}$  of a colliding pair of alkali-metal atoms, for example, in a process like



The detailed physics of the process described by Eq. (51) is still uncertain. Experiments at the University of Wisconsin [29] have shown that the relaxation described by Eq. (51) can be slowed down by tens of percent by magnetic fields of a few thousand Gauss or less, so not all of the relaxation can be due to binary collisions, for which much larger magnetic fields would be needed to have an appreciable effect on the spin relaxation rate.

For an electron-electron interaction like Eq. (13) the spin evolution due to sudden binary collisions will be sudden with respect to the nuclear polarization, and the density operator will evolve at the rate

$$\frac{d}{dt}\rho = \frac{1}{T_{SS}}[\varphi - \rho], \quad (52)$$

with

$$\frac{1}{T_{SS}} = [A]\langle v\sigma_{SS} \rangle. \quad (53)$$

Experiments show that the rate coefficient  $\langle v\sigma_{SS} \rangle$  is several orders of magnitude smaller than the rate coefficient  $\langle v\sigma_{\text{ex}} \rangle$  of the spin-conserving exchange process (44).

We shall refer to a relaxation process like that of Eq. (52) where  $d\rho/dt \propto \varphi - \rho$  as an ‘‘S-damping’’ process, that is, a process that destroys the part (38) of  $\rho$  with electron polarization but does not affect the part (37) with purely nuclear polarization. S damping occurs when the spin-interaction potential couples  $\mathbf{S}$  and  $\mathbf{N}$  but does not contain the nuclear spin  $\mathbf{I}$  explicitly. To be in the S-damping limit, the correlation time of the collisional interaction must be very short compared to the hyperfine precession period of the atomic ground state.

## VI. BINARY COLLISIONS BETWEEN ALKALI-METAL ATOMS AND NOBLE-GAS ATOMS

Binary collisions between an alkali-metal atom and a buffer-gas atom are sudden with respect to the nuclear polarization. During such collisions, the spin-rotation interaction (10) will cause the density operator of the alkali-metal atom to evolve at a rate

$$\frac{d}{dt}\rho = \frac{1}{T_{NS}}(\varphi - \rho). \quad (54)$$

The rate is proportional to the density  $[X]$  of the buffer-gas atoms

$$\frac{1}{T_{NS}} = [X]\langle v\sigma_{NS} \rangle. \quad (55)$$

The rate coefficient  $\langle v\sigma_{NS} \rangle$  depends strongly on temperature [30].

For collisions of an alkali-metal atom with the noble-gas atoms  $^3\text{He}$  or  $^{129}\text{Xe}$ , the nuclear-electron exchange interaction (11) will cause the density operator of the alkali-metal atoms to evolve as

$$\frac{d}{dt}\rho = \frac{\eta_K}{T_{KS,a}}\{\varphi(1 + 4\langle \mathbf{K} \rangle \cdot \mathbf{S}) - \rho\} + \frac{1}{i\hbar}[\delta\mathcal{E}_{KS,a}, \rho]. \quad (56)$$

The binary rate per alkali-metal atom is

$$\frac{1}{T_{KS,a}} = [X]\langle v\sigma_{KS} \rangle \quad (57)$$

and the atomic fraction of the noble gas, which is  $^3\text{He}$  or  $^{129}\text{Xe}$ , is

$$\eta_K = [^3\text{He}]/[\text{He}] \quad \text{or} \quad \eta_K = [^{129}\text{Xe}]/[\text{Xe}]. \quad (58)$$

The frequency-shift operator for collisions with  $^3\text{He}$  or  $^{129}\text{Xe}$  atoms is

$$\delta\mathcal{E}_{KS,a} = \frac{8\pi g_S \mu_B \mu_K}{3K}(\kappa_0 - \kappa_1)\eta_K[X]\langle \mathbf{K} \rangle \cdot \mathbf{S}. \quad (59)$$

The dimensionless coefficients  $\kappa_0$  and  $\kappa_1$  depend weakly on temperature, and are a measure of the ensemble average of the interaction (11) for binary collisions [31].

Conversely, the nuclear-electron exchange interaction (11) will cause the nuclear spin polarization of the noble-gas atom to evolve as

$$\frac{d}{dt}\langle \mathbf{K} \rangle = \frac{1}{T_{KS,x}}(\langle \mathbf{S} \rangle - \langle \mathbf{K} \rangle) - \frac{\mu_K}{\hbar K}\delta\mathbf{B}_{KS,x} \times \langle \mathbf{K} \rangle. \quad (60)$$

The rate for collisions with alkali-metal atoms of number density  $[A]$  is

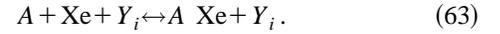
$$\frac{1}{T_{KS,x}} = [A]\langle v\sigma_{KS} \rangle. \quad (61)$$

The effective magnetic field produced by the spin-polarized alkali-metal atoms is

$$\delta\mathbf{B}_{KS,x} = -\frac{8\pi g_S \mu_B}{3}(\kappa_0 - \kappa_1)[A]\langle \mathbf{S} \rangle. \quad (62)$$

## VII. RELAXATION DUE TO van DER WAALS MOLECULES

In the case of spin-exchange optical pumping of  $^{129}\text{Xe}$ , a significant fraction of the spin relaxation of alkali-metal atoms  $A$  occurs because of the formation of  $A\text{Xe}$  van der Waals molecules. These molecules are created and destroyed by the collisional process



Scanned from left to right, Eq. (63) represents the formation of a van der Waals molecule with the binding energy carried off by the third body  $Y_i$ . Scanned from right to left (time-reversed), (63) represents the collisional breakup of the van der Waals molecule, with breakup energy supplied by the third-body  $Y_i$ . The van der Waals molecules are so weakly bound that nearly every collision breaks them apart into atoms again.

The three-body formation rates  $1/T_{vW,A}$  per  $A$  atom and  $1/T_{vW,Xe}$  per  $\text{Xe}$  atom are

$$\frac{1}{T_{vW,A}} = \sum_i Z_i[Y_i][\text{Xe}] \quad \text{and} \quad \frac{1}{T_{vW,Xe}} = \sum_i Z_i[Y_i][A]. \quad (64)$$

The number density of the the xenon atoms is  $[\text{Xe}]$  and the number density of the third body needed to form or break up the molecule is  $[Y_i]$ . For example, we might have  $[Y_1] = [\text{He}]$ ,  $[Y_2] = [N_2]$ , and  $[Y_3] = [\text{Xe}]$  in a typical gas mixture for spin-exchange optical pumping of  $^{129}\text{Xe}$ . The rate coefficients for the three-body processes (63) are  $Z_i$ .

Assume that

$$p(t)dt = e^{-t/\tau}dt/\tau \quad (65)$$

is the probability that a van der Waals molecule is broken up by a collision with a third-body in the time interval  $dt$  at a time  $t$  after formation. The mean lifetime  $\tau$  is given by

$$\frac{1}{\tau} = \sum_i \langle v\sigma_{vW} \rangle_i [Y_i]. \quad (66)$$

In chemical equilibrium at a temperature  $T$ , the chemical equilibrium coefficient  $\mathcal{K}$  of the van der Waals molecules is related to the three-body formation rate coefficients  $Z_i$ , the breakup rate coefficients  $\langle v\sigma_{vW} \rangle_i$ , the formation rates  $1/T_{vW,A}$  per alkali-metal atom, and  $1/T_{vW,Xe}$  per xenon atom, and to the mean molecular lifetime  $\tau$  by

$$\mathcal{K} = \frac{[A\text{Xe}]}{[A][\text{Xe}]} = \frac{Z_i}{\langle v\sigma_{vW} \rangle_i} = \frac{\tau}{T_{vW,A}[\text{Xe}]} = \frac{\tau}{T_{vW,Xe}[A]}. \quad (67)$$

During the lifetime of a van der Waals molecule, the interaction (10) couples the electron spin  $\mathbf{S}$  to the rotational angular momentum  $\mathbf{N}$  of the molecule, and the interaction

(11) couples the nuclear spin  $\mathbf{K}$  of the noble-gas atom to the electron spin  $\mathbf{S}$ . The molecular breakup rate  $1/\tau$  will normally be so fast that

$$\frac{\gamma N \tau}{\hbar} \ll 1 \quad \text{and} \quad \frac{\alpha \tau}{\hbar} \ll 1, \quad (68)$$

so the spins  $\mathbf{S}$  and  $\mathbf{K}$  rotate by only a very small angle due to the interactions (10) and (11), even in the relatively long-lived van der Waals molecule.

For the heavier alkali-metal atoms, the ground-state hyperfine frequency

$$\omega_{\text{hf}} = \frac{[I]A_g}{2\hbar} \quad (69)$$

is large enough (e.g.,  $\omega_{\text{hf}} = 5.78 \times 10^{10} \text{ sec}^{-1}$  for  $^{133}\text{Cs}$ ) that  $\omega_{\text{hf}}\tau \sim 1$ , even for very high buffer gas pressures and correspondingly short molecular lifetimes. The power spectrum of the interactions (10) and (11) will therefore be more intense at the low frequencies that cause  $\Delta f = 0$  transitions than at frequencies on the order of  $\omega_{\text{hf}}$ , which cause  $\Delta f = 1$  transitions between the sublevels  $|fm\rangle$ . In Appendix A, we show that a fraction,

$$f_S = \frac{1}{1 + (\omega_{\text{hf}}\tau_c)^2}, \quad (70)$$

of the van der Waals molecules have such a short correlation time  $\tau_c$  that the formation and breakup of the van der Waals molecule is sudden with respect to the nuclear polarization. The remaining fraction

$$f_F = \frac{(\omega_{\text{hf}}\tau_c)^2}{1 + (\omega_{\text{hf}}\tau_c)^2} \quad (71)$$

of molecules has correlation times  $\tau_c$ , which are so long that only  $\Delta f = 0$  transitions can be induced, and the process is not sudden with respect to the nuclear polarization. The correlation time  $\tau_c$  of the spin-rotation interaction (10) in a van der Waals molecule cannot be longer than the molecular lifetime  $\tau$ . Because most collisions violent enough to cause an appreciable change in the direction of  $\mathbf{N}$  have enough energy to break up the molecule, we will henceforth assume that  $\tau = \tau_c$ . We may think of  $f_F$  as the fraction of molecules with ‘‘short’’ lifetimes and  $f_S$  as the fraction of molecules with ‘‘very short’’ lifetimes, as discussed in [32].

As shown in Eq. (A30), the relaxation due to the spin-rotation interaction (10) is given by

$$\frac{d}{dt}\rho = \frac{2\phi_\gamma^2}{3T_{\text{vw},A}} \left( f_S [\varphi - \rho] + \frac{f_F}{[I]^2} [\mathbf{F} \cdot \rho \mathbf{F} - \mathbf{F} \cdot \mathbf{F} \rho] \right). \quad (72)$$

The relaxation due to the nuclear-electron spin-exchange interaction (11) is given by Eq. (A31) as

$$\begin{aligned} \frac{d}{dt}\rho = & \frac{\phi_\alpha^2 \eta_K}{2T_{\text{vw},A}} \left( f_S [\varphi(1 + 4\langle \mathbf{K} \rangle \cdot \mathbf{S}) - \rho] + \frac{f_F}{[I]^2} [\mathbf{F} \cdot \rho \mathbf{F} - \mathbf{F} \cdot \mathbf{F} \rho] \right. \\ & \left. + (\{\mathbf{F}, \rho\} - 2i\mathbf{F} \times \rho \mathbf{F}) \cdot \langle \mathbf{K} \rangle \right) + \frac{1}{i\hbar} [\delta \mathcal{E}_{\text{vw},A}, \rho], \quad (73) \end{aligned}$$

where  $\{\mathbf{F}, \rho\} = \mathbf{F}\rho + \rho\mathbf{F}$  is an anticommutator. The mean squared phase evolution angles for the van der Waals molecules are

$$\phi_\alpha^2 = \left( \frac{\alpha \tau}{\hbar} \right)^2 \quad \text{and} \quad \phi_\gamma^2 = \left( \frac{\gamma N \tau}{\hbar} \right)^2. \quad (74)$$

In this paper the phase angles  $\phi_\gamma$  and  $\phi_\alpha$  are the same as  $\phi$  and  $\phi/x$  in Zeng *et al.* [33]. The gas pressure is assumed to be sufficiently high that  $\phi_\gamma^2 \ll 1$  and  $\phi_\alpha^2 \ll 1$ . The frequency-shift operator is

$$\delta \mathcal{E}_{\text{vw},A} = \frac{8\pi g_S \mu_B \mu_K}{3K} \kappa_1 \eta_K [X] \langle \mathbf{K} \rangle \cdot \mathbf{S}. \quad (75)$$

## VIII. OPTICAL PUMPING

For spin-exchange optical pumping of  $^3\text{He}$  or  $^{129}\text{Xe}$ , the buffer gas pressure is always very high, for example, several atmospheres of a  $^3\text{He-N}_2$  mixture, or several atmospheres of a  $^{129}\text{Xe-}^4\text{He-N}_2$  mixture. The number density of alkali-metal atoms is also high enough that the vapor is quite optically thick. Therefore, nitrogen, hydrogen, or some other quenching gas must be present to ensure that an excited atom has little chance of reradiating a photon, which could be multiply scattered before escaping from the pumping cell, thereby causing significant spin depolarization. A collision with a  $\text{N}_2$  or  $\text{H}_2$  molecule allows the excited atom to transfer its energy to vibrational and rotational degrees of freedom in the diatomic molecule. The energy eventually equilibrates with the translational degrees of freedom to heat the gas.

We describe the pumping or probing light as a superposition of monochromatic plane waves, for which the electric field is

$$\mathbf{E} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + \text{c.c.} \quad (76)$$

The transverse, complex field amplitude  $\mathbf{E} = \mathbf{E}(\zeta)$  is a function of the distance  $\zeta = \mathbf{r} \cdot \hat{\zeta}$  of propagation through the vapor in the direction  $\hat{\zeta} = \mathbf{k}/k$  of the photon wave vector  $\mathbf{k}$ . Neglecting the small phase retardation due to the buffer gas, we find  $\mathbf{E}$  will obey an evolution equation analogous to the Schrödinger equation (1)

$$\frac{\partial}{\partial \zeta} \mathbf{E} = 2\pi i k [A] \langle \boldsymbol{\alpha} \rangle \mathbf{E}. \quad (77)$$

The dielectric polarizability tensor  $\boldsymbol{\alpha}$ , which plays the role of the Hamiltonian (2), depends on the mean electron spin polarization  $\langle \mathbf{S} \rangle$  of the alkali-metal atoms and is given by

$$\boldsymbol{\alpha} = \alpha(1 - 2i\mathbf{S} \times). \quad (78)$$

It is to be understood that components on the right of Eq. (77) that are parallel to  $\hat{\zeta}$  (longitudinal) are to be omitted (since electric dipoles do not radiate along their axis of os-

cillation). The real and imaginary parts of the complex polarizability coefficient  $\alpha = \alpha' + i\alpha''$  are Kramers-Kronig transforms of each other:

$$\alpha'(\nu) = \frac{\wp}{\pi} \int_{-\infty}^{\infty} \frac{\alpha''(\nu') d\nu'}{\nu' - \nu},$$

$$\alpha''(\nu) = -\frac{\wp}{\pi} \int_{-\infty}^{\infty} \frac{\alpha'(\nu') d\nu'}{\nu' - \nu}. \quad (79)$$

Here  $\wp$  denotes the principal part of the integral. The pressure broadening eliminates complicated contributions to  $\alpha$  from the hyperfine observable  $\mathbf{I} \cdot \mathbf{S}$  and the quadrupole observables that are important at low pressures for the heavier alkali-metal atoms, especially Rb and Cs [34]. The oscillating electric field of Eq. (76) will induce an oscillating electric dipole moment

$$\langle \mathbf{p} \rangle = \langle \boldsymbol{\alpha} \rangle \mathbf{E} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + \text{c.c.} \quad (80)$$

The mean optical power absorbed by the oscillating electric dipole moment is

$$-i\omega \mathbf{E}^* \cdot \langle \boldsymbol{\alpha} \rangle \mathbf{E} + \text{c.c.} = \langle \sigma \rangle h\nu \Phi d\nu. \quad (81)$$

Inserting the expression (78) for  $\boldsymbol{\alpha}$  into Eq. (81) we find that the absorption cross section of  $D_1$  light is

$$\langle \sigma \rangle = \sigma_{\text{op}}(1 - 2\mathbf{s} \cdot \langle \mathbf{S} \rangle), \quad (82)$$

where the cross section for unpolarized atoms is

$$\sigma_{\text{op}} = 4\pi k \alpha''. \quad (83)$$

The photon flux  $\Phi = \Phi(\nu)$  of the light wave (76) is

$$\Phi d\nu = \frac{cE^2}{2\pi h\nu}, \quad (84)$$

where  $\nu = \omega/2\pi$  is the optical frequency in Hz, and the units of  $\Phi$  are photons  $\text{cm}^{-2} \text{sec}^{-1} \text{Hz}^{-1}$ . The mean photon spin is

$$\mathbf{s} = \frac{1}{iE^2} \mathbf{E}^* \times \mathbf{E}. \quad (85)$$

We will assume that the oscillator strength  $f$ , defined by

$$\int \sigma_{\text{op}} d\nu = \pi r_e c f, \quad (86)$$

is unaffected by the properties of the gas. Here  $r_e = 2.82 \times 10^{-13} \text{ cm}$  is the classical electron radius,  $c = 3.00 \times 10^{10} \text{ cm sec}^{-1}$  is the speed of light, and to good approximation for  $D_1$  light,  $f = 1/3$ . For  $D_2$  light, the oscillator strength is very nearly  $f = 2/3$ , and in Eqs. (78) and (82) we should make the replacement  $\langle \mathbf{S} \rangle \rightarrow -\langle \mathbf{S} \rangle/2$ .

The effects of the absorbed light on the alkali-metal atom can be described by an effective Hamiltonian

$$\delta H = \delta \mathcal{E}_v - \frac{i\hbar}{2} \delta \Gamma = -\mathbf{E}^* \cdot \boldsymbol{\alpha} \mathbf{E}. \quad (87)$$

Inserting Eq. (78) into Eq. (87) and using Eqs. (83) and (85) we find that the light absorption operator is

$$\delta \Gamma = R(1 - 2\mathbf{s} \cdot \mathbf{S}), \quad (88)$$

where the mean pumping rate per unpolarized alkali-metal atom is

$$R = \int_0^{\infty} \Phi \sigma_{\text{op}} d\nu. \quad (89)$$

Using Eq. (87) and the Kramers-Kronig transforms (79) we find that the light-shift operator is

$$\delta \mathcal{E}_v = \hbar \delta \Omega_v \left(-\frac{1}{2} + \mathbf{s} \cdot \mathbf{S}\right), \quad (90)$$

where frequency shift parameter is

$$\delta \Omega_v = \frac{\wp}{\pi} \int \frac{\Phi(\nu) \sigma_{\text{op}}(\nu')}{\nu - \nu'} d\nu d\nu'. \quad (91)$$

The depopulation pumping rate of the ground-state is described by

$$\frac{d}{dt} \rho = \frac{1}{i\hbar} (\delta H \rho - \rho \delta H^\dagger) = -R \varphi (1 - 2\mathbf{s} \cdot \mathbf{S}) + R \left( \frac{\mathbf{s}}{2} - \mathbf{S} \right) \cdot \boldsymbol{\Theta} + \frac{1}{i\hbar} [\delta \mathcal{E}_v, \rho]. \quad (92)$$

It is often assumed that before the excited atoms produced by optical pumping are transformed back into ground-state atoms, typically by a quenching collision with a  $\text{N}_2$  molecule, their spin is completely depolarized because of collisions in the high-pressure buffer gas. While this is certainly a good approximation for the electron polarization, it is not a good approximation for the nuclear polarization, where most of the spin angular momentum is stored. The excited-state electronic angular momentum  $\mathbf{J}$  changes directions so frequently due to collisions that the relatively weak hyperfine interactions have insufficient time to depolarize the nuclear spin before the atom is quenched. The passage through the excited state is very nearly sudden with respect to the nuclear polarization [35]. As described in more detail in Appendix B, the repopulation pumping rate, given by Eq. (B24), is

$$\frac{d}{dt} \rho = R \left( \varphi - \frac{\mathbf{s} \cdot \boldsymbol{\Theta}}{2} \right) + \frac{1}{i\hbar} [\delta \mathcal{E}_r, \rho], \quad (93)$$

which represents the return of pure nuclear polarization to the ground state. Shifts due to the real transitions are described by the term proportional to  $[\delta \mathcal{E}_r, \rho]$ . Summing Eqs. (92) and (93) we find the net evolution due to optical pumping

$$\frac{d}{dt} \rho = R [\varphi (1 + 2\mathbf{s} \cdot \mathbf{S}) - \rho] + \frac{1}{i\hbar} [\delta \mathcal{E}_{\text{op}}, \rho], \quad (94)$$

where

$$\delta \mathcal{E}_{\text{op}} = \delta \mathcal{E}_v + \delta \mathcal{E}_r. \quad (95)$$

Comparing Eq. (94) with Eq. (45) we see that optical pumping causes the density matrix to evolve in exactly the same way as spin exchange at a rate  $R$  with fictitious alkali-metal atoms of electronic spin  $s/2$ . More details of the pumping and light shifts are contained in Appendix B.

### IX. LONGITUDINAL OPTICAL PUMPING AND SPIN TEMPERATURE

For spin-exchange optical pumping, the evolution of the spin polarization of the alkali-metal atoms is determined by six dominant processes: (1) the hyperfine interactions and interactions with external static or radio-frequency (rf) magnetic fields, for which  $\partial\rho/\partial t$  is given by Eq. (17); (2) binary collisions between pairs of alkali-metal atoms (for example,  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ ) for which  $\partial\rho/\partial t$  is given by the sum of Eqs. (48) and (52); (3) binary collisions between alkali-metal atoms and buffer gas atoms, for which  $\partial\rho/\partial t$  is given by the sum of Eqs. (54) and (56); (4) relaxation due to van der Waals molecules, for which  $\partial\rho/\partial t$  is given by the sum of Eqs. (72) and (73); (5) optical pumping, for which  $\partial\rho/\partial t$  is given by Eq. (94); and (6) spatial diffusion of the polarized atoms for which  $\partial\rho/\partial t = D\nabla^2\rho$ , with appropriate boundary conditions. The diffusion coefficient for the alkali-metal atoms is  $D$ . We assume that experimental conditions are such that evolution due to other processes—for example, radiation trapping—can be neglected. Adding the evolution rates of these six processes, we find

$$\begin{aligned} \frac{\partial\rho}{\partial t} = & D\nabla^2\rho + \frac{1}{i\hbar}[H'_g, \rho] + \sum_j \frac{1}{T_{\text{ex},ij}}[\varphi(1+4\langle\mathbf{S}_j\rangle\cdot\mathbf{S}) - \rho] \\ & + \frac{1}{T_{\text{SD}}}[\varphi - \rho] + R[\varphi(1+2\mathbf{s}\cdot\mathbf{S}) - \rho] + \frac{4}{T_{\text{SE}}}\langle\mathbf{K}\rangle\cdot\mathbf{S}\varphi \\ & + \frac{1}{[I]^2 T_{\text{FD}}}[\mathbf{F}\cdot\rho\mathbf{F} - \mathbf{F}\cdot\mathbf{F}\rho] + \frac{1}{[I]^2 T_{\text{FE}}} \\ & \times \langle\mathbf{K}\rangle\cdot(\{\mathbf{F}, \rho\} - 2i\mathbf{F}\times\rho\mathbf{F}). \end{aligned} \quad (96)$$

In Eq. (96)  $H'_g$  denotes the free-atom Hamiltonian (2) to which we have added the small, frequency-shift Hamiltonians  $\delta\mathcal{E}$  associated with the collisional and pumping processes, for example, the  $\delta\mathcal{E}_{\text{ex},ij}$  of Eq. (48). These cause relatively small shifts of the center frequencies (5) and (6) of the Zeeman resonances. Also included in  $H'_g$  are interactions with a resonant radio-frequency field, which we will discuss in more detail in Sec. X. The sum on  $j$  extends over all isotopes of the alkali-metal atoms including the isotope  $i$  whose evolution is described by Eq. (96). To avoid index clutter in Eq. (96) we have suppressed the isotope label  $i$  on  $\rho = \rho_i$ ,  $H'_g = H'_{ig}$ ,  $\varphi = \varphi_i$ ,  $S_z = S_{iz}$ , etc.

In Eq. (96) the rate  $1/T_{\text{ex},ij}$  of spin exchange of the alkali-metal isotope  $i$  with the isotope  $j$  was given by Eq. (49). The S-damping rate is

$$\begin{aligned} \frac{1}{T_{\text{SD}}} = & [A]\langle v\sigma_{SS}\rangle + [X](\langle v\sigma_{NS}\rangle + \eta_K\langle v\sigma_{KS}\rangle) + \sum_i [Y_i] \\ & \times \langle v\sigma_{NS}\rangle_i + \frac{f_S}{T_{\text{vW,A}}}\left(\frac{\eta_K\phi_\alpha^2}{2} + \frac{2\phi_\gamma^2}{3}\right). \end{aligned} \quad (97)$$

Contributions from spin-depolarizing binary collisions between alkali-metal atoms occur at the rate  $1/T_{SS} = [A]\langle v\sigma_{SS}\rangle$ , discussed in connection with Eq. (53). For spin-exchange pumping of  $^3\text{He}$  or  $^{129}\text{Xe}$ , binary collisions with He or Xe atoms makes the contribution  $(\langle v\sigma_{NS}\rangle + [X]\eta_K\langle v\sigma_{KS}\rangle)[X]$  to the S damping rate, as discussed in connection with Eqs. (54) and (56). The coefficient  $\eta_K$  is the atomic fraction of  $^3\text{He}$  or  $^{129}\text{Xe}$  in the He or Xe gas.  $^3\text{He}$  is normally isotopically pure, which would correspond to  $\eta_K = 1$ . For pumping  $^{129}\text{Xe}$  in a gas of natural isotopic abundance, we would have  $\eta_K = 0.264$ . Contributions from the much smaller nuclear moment of  $^{131}\text{Xe}$  to the S-damping or S-exchange rates have been ignored. Relaxation due to binary collisions with buffer gases of number density  $[Y_i]$  not directly involved in spin-exchange optical pumping, for example, the quenching gas  $\text{N}_2$  or the optical pressure-broadening gas  $^4\text{He}$  for a xenon accumulator system [36], occurs at the rate  $[Y_i]\langle v\sigma_{NS}\rangle_i$ , in close analogy to Eq. (55). The contribution of van der Waals molecules to S damping is described by the last term in (97), where the formation rate  $1/T_{\text{vW,A}}$  is given by Eq. (64), the phase angles by Eq. (74), and the fraction  $f_S$  of van der Waals molecules that break up quickly enough to cause  $\Delta f = \pm 1$  transitions is given by Eq. (70).

The S-exchange rate for the transfer of spin  $\langle K_z \rangle$  from  $^3\text{He}$  or  $^{129}\text{Xe}$  of atomic number density  $\eta_K[X]$  to the spin of the alkali-metal atom has contributions from binary collisions and short-lived van der Waals molecules,

$$\frac{1}{T_{\text{SE}}} = \eta_K\left(\langle v\sigma_{KS}\rangle[X] + \frac{f_S\phi_\alpha^2}{2T_{\text{vW,A}}}\right). \quad (98)$$

The last two terms of Eq. (96) represent relaxation due to long-lived van der Waals molecules. The F-damping rate is

$$\frac{1}{T_{\text{FD}}} = \frac{f_F}{T_{\text{vW,A}}}\left(\frac{\eta_K\phi_\alpha^2}{2} + \frac{2\phi_\gamma^2}{3}\right), \quad (99)$$

and the F-exchange rate is

$$\frac{1}{T_{\text{FE}}} = \frac{f_F\phi_\alpha^2\eta_K}{2T_{\text{vW,A}}}. \quad (100)$$

The distribution of the alkali-metal atoms between the sublevels  $|fm\rangle$  and also their response to resonant radio-frequency magnetic fields, can be found by writing Eq. (96) more explicitly as

$$\begin{aligned}
\frac{\partial \rho}{\partial t} = & D\nabla^2 \rho + \frac{1}{i\hbar} [H'_g, \rho] + R'(S_z \rho S_z - \frac{3}{4} \rho + \frac{1}{2} [S_+ \rho S_- \\
& + S_- \rho S_+]) + R' s'_z (\frac{1}{2} \{S_z, \rho\} + \frac{1}{2} [S_+ \rho S_- - S_- \rho S_+]) \\
& + \frac{1}{T_{\text{ex},ii}} [\langle S_+ \rangle (\frac{1}{2} \{S_-, \rho\} + S_- \rho S_z - S_z \rho S_-) + \langle S_- \rangle \\
& \times (\frac{1}{2} \{S_+, \rho\} - S_+ \rho S_z + S_z \rho S_+)] \\
& + \frac{1}{[I]^2 T_{\text{FD}}} (F_z \rho F_z - \mathbf{F} \cdot \mathbf{F} \rho + \frac{1}{2} [F_+ \rho F_- + F_- \rho F_+]) \\
& + \frac{2 \langle K_z \rangle}{[I]^2 T_{\text{FE}}} (\frac{1}{2} \{F_z, \rho\} + \frac{1}{2} [F_+ \rho F_- - F_- \rho F_+]). \quad (101)
\end{aligned}$$

In passing from Eq. (96) to Eq. (101), we have eliminated  $\varphi$  of Eq. (37) with the identity

$$\varphi \mathbf{S} = \{\rho, \mathbf{S}\} / 4 - i \mathbf{S} \times \rho \mathbf{S} / 2, \quad (102)$$

and we have written the vector cross product explicitly as

$$\begin{aligned}
-2i(\mathbf{S} \times \rho \mathbf{S}) = & (S_+ \rho S_- - S_- \rho S_+) \mathbf{z} \\
& - (S_+ \rho S_z - S_z \rho S_+) (\mathbf{x} - i\mathbf{y}) \\
& + (S_- \rho S_z - S_z \rho S_-) (\mathbf{x} + i\mathbf{y}). \quad (103)
\end{aligned}$$

We have also assumed a longitudinal mean photon spin,  $\mathbf{s} = s_z \mathbf{z}$ . The effective pumping rate of Eq. (101) is

$$R' = \frac{1}{T_{\text{ex}}} + \frac{1}{T_{\text{SD}}} + R, \quad (104)$$

and the effective photon spin  $s'_z$  is given by

$$R' s'_z = \sum_j \frac{2 \langle S_{jz} \rangle}{T_{\text{ex},ij}} + \frac{2 \langle K_z \rangle}{T_{\text{SE}}} + R s_z. \quad (105)$$

The electron-electron spin exchange rate with all species of alkali-metal atoms (e.g., both  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ ) is

$$\frac{1}{T_{\text{ex}}} = \sum_j \frac{1}{T_{\text{ex},ij}}. \quad (106)$$

Equation (101) describes the evolution of the density matrix  $\rho = \rho_i$  of the alkali-metal isotope  $i$ , which is undergoing spin-exchange with other alkali-metal isotopes with  $j \neq i$ , and with identical isotopes with  $j = i$ . We assume the other isotopes are out of resonance with the applied rf field, so the electron spins are longitudinal, that is,  $\langle \mathbf{S}_j \rangle = \langle S_{jz} \rangle \mathbf{z}$  if  $j \neq i$ . A resonant rf field, if present, can excite transverse components of the electron spin of the isotope  $i$ . These transverse spin components  $\langle S_{\pm} \rangle$  contribute to the spin-exchange relaxation due to collisions with like isotopes, as we shall discuss in more detail in Sec. X.

*Longitudinal pumping.* In the absence of any radio-frequency magnetic fields, the density matrix will have no coherences ( $\langle S_{\pm} \rangle = 0$ ), and the polarization of the alkali-metal atoms is determined by the occupation probabilities of

each Zeeman sublevel  $|fm\rangle$ . The density matrix for such longitudinally polarized atoms can be described by the Liouville-space vector

$$|\rho\rangle = \sum_{fm} |fm\rangle \langle fm|\rho\rangle, \quad (107)$$

where the notation for the Liouville basis vectors (21) with  $f' = f$  and  $\Delta m = 0$  has been simplified to  $|ff\bar{m}0\rangle = |fm\rangle$ .

Then Eq. (101) can be written, in accordance with Eq. (30), as

$$\frac{\partial}{\partial t} |\rho\rangle = \{D\nabla^2 - \Lambda\} |\rho\rangle. \quad (108)$$

The nonzero matrix elements  $\langle fm|\Lambda|f'm'\rangle$  can be found by inspection of Eq. (101) to be

$$\begin{aligned}
\langle fm|\Lambda|fm\rangle = & R' \frac{3a^2 - 2ams'_z(-1)^{a-f-m^2}}{4a^2} \\
& + \frac{f(f+1) - m^2}{4a^2 T_{\text{FD}}} - \frac{\langle K_z \rangle m}{2a^2 T_{\text{FE}}}, \\
\langle fm|\Lambda|f'm\rangle = & -R' \frac{a^2 - m^2}{4a^2}, \quad (109)
\end{aligned}$$

$$\begin{aligned}
\langle fm|\Lambda|f'm'\rangle = & -\frac{1}{8a^2} \left\{ R'(1 + \Delta m s'_z) + \frac{1}{T_{\text{FD}}} + \frac{2\Delta m \langle K_z \rangle}{T_{\text{FE}}} \right\} \\
& \times (f - m_{<})(f + m_{>}),
\end{aligned}$$

$$\begin{aligned}
\langle fm|\Lambda|f'm'\rangle = & -\frac{R'}{8a^2} (1 + \Delta m s'_z) (a + m\Delta f\Delta m) \\
& \times (a + m'\Delta m\Delta f),
\end{aligned}$$

where

$$\Delta f = f - f' = \pm 1, \quad \text{and} \quad \Delta m = m - m' = \pm 1, \quad (110)$$

and where  $m_{<}$  is the algebraically smaller of the pair  $(m, m')$  and  $m_{>}$  is the larger. One can verify that Eq. (35) is satisfied by Eq. (109).

We will describe the parts of Eq. (109) proportional to  $R'$  as the relaxation due to *sudden processes*, and the parts of Eq. (109) proportional to  $1/T_{\text{FD}}$  and  $1/T_{\text{FE}}$  as the relaxation due to *slow processes*. The sudden processes have such a short correlation time that they can cause transitions between different hyperfine multiplets  $f = a$  and  $f = b$ , while the slow process have such long correlation times that they only cause transitions within a given hyperfine multiplet  $f$ . van der Waals molecules and possibly some fraction of the spin relaxation (51) due to collisions between alkali-metal atoms contribute to the slow processes.

*Spin temperature.* Let us first consider the steady-state solution of Eq. (108) for a location far enough from the depolarizing walls that the effects of diffusion can be neglected ( $D\nabla^2 \rho = 0$ ). Then we seek the solution of

$$\Lambda|\rho\rangle=0. \quad (111)$$

Evidently the steady-state solution  $|\rho\rangle$  of Eq. (111) is the right eigenvector of  $\Lambda$  with the eigenvalue  $\lambda=0$ . Consider first the practically important situation of negligible slow processes, where we can neglect all but the terms proportional to  $R'$  in Eq. (109). Then the solution to Eq. (111) turns out to be the spin-temperature distribution

$$\rho = \frac{e^{\beta F_z}}{Z} = \frac{e^{\beta I_z} e^{\beta S_z}}{Z_I Z_S}. \quad (112)$$

The *Zustandssumme*  $Z = Z_I Z_S$  is the product of a nuclear part  $Z_I$  and an electronic part  $Z_S$ . For a spin of integer or half-integer quantum number  $J$ ,

$$Z_J = \sum_{m=-J}^J e^{\beta m} = \frac{\sinh \beta[J/2]}{\sinh \beta/2} = \frac{(1+P)^{[J]} - (1-P)^{[J]}}{2P(1-P^2)^J}. \quad (113)$$

We have characterized the spin-temperature distribution with an overall spin polarization  $P$ , defined in terms of the mean electron spin and the spin-temperature parameter  $\beta$  by

$$P = 2\langle S_z \rangle = \tanh \frac{\beta}{2}, \quad \text{or conversely} \quad \beta = \ln \frac{1+P}{1-P}. \quad (114)$$

To show that the sudden processes lead to a spin-temperature distribution, we substitute Eq. (112) into Eq. (111). Since  $\Lambda|\rho\rangle = \sum_{f'm} \Lambda|f'm\rangle e^{\beta m}/Z$ , Eq. (111) implies that

$$e^{\beta} \sum_{f'} (f'm|\Lambda|f'm+1) + \sum_{f'} (f'm|\Lambda|f'm) + e^{-\beta} \sum_{f'} (f'm|\Lambda|f'm-1) = 0. \quad (115)$$

The sums of Eq. (115) can be evaluated with Eq. (109) to give

$$\sum_{f'} (f'm|\Lambda|f'm\pm 1) = -\frac{R'}{4} (1 \mp s'_z) \left[ 1 \mp \frac{m(-1)^{a-f}}{a} \right],$$

$$\sum_{f'} (f'm|\Lambda|f'm) = \frac{R'}{2} \left[ 1 - \frac{ms'_z(-1)^{a-f}}{a} \right]. \quad (116)$$

Using Eqs. (116) and (114) we find that Eq. (115) is satisfied provided that  $s'_z = \tanh \beta/2 = P$ .

Thus, we have shown that when spatial diffusion is negligible, sudden optical pumping processes generate the spin-temperature distribution (112) first introduced by Anderson *et al.* The spin temperature is inversely proportional to the spin-temperature parameter  $\beta$ . One can readily show that Eq. (112) can be written as a special case of Eq. (39),

$$\rho = \varphi(1 + 4\langle S_z \rangle S_z) \quad \text{where} \quad \varphi = \frac{e^{\beta I_z}}{2Z_I}. \quad (117)$$

TABLE I. Expressions for  $\epsilon(I, P)$ , defined by the formula  $1 + \epsilon(I, P) = \langle F_z \rangle / \langle S_z \rangle$  for atoms described by a spin temperature distribution, as a function of nuclear spin quantum number  $I$  and the overall spin polarization  $P$ .

$I$	$\epsilon(I, P)$
0	0
1/2	1
1	$8/(3+P^2)$
3/2	$(5+P^2)/(1+P^2)$
2	$(40+24P^2)/(5+10P^2+P^4)$
5/2	$(35+42P^2+3P^4)/(3+10P^2+3P^4)$
3	$(112+224P^2+48P^4)/(7+35P^2+21P^4+P^6)$
7/2	$(21+63P^2+27P^4+P^6)/(1+7P^2+7P^4+P^6)$

For atoms described by the spin-temperature distribution (112) we shall find it convenient to introduce a paramagnetic coefficient, defined by

$$1 + \epsilon(I, P) = \frac{\langle F_z \rangle}{\langle S_z \rangle} = 2\langle \mathbf{F} \cdot \mathbf{F} - F_z^2 \rangle = 1 + 2\langle \mathbf{I} \cdot \mathbf{I} - I_z^2 \rangle. \quad (118)$$

The functions  $\epsilon(I, P)$  depend on the nuclear spin quantum number  $I$  of the alkali-metal atom and are listed for the low values of  $I$  in Table I. They are related to the Brillouin functions  $B_I(x)$  by  $\epsilon(I, P) = 2IB_I(I\beta)/B_{1/2}(\beta/2)$  [37]. We note that  $\epsilon(I, 0) = 4I(I+1)/3$  and  $\epsilon(I, 1) = 2I$ .

We may use Eq. (96) directly to deduce the rate of change of the total angular momentum  $\langle F_z \rangle$  per alkali-metal atom. The rates (97)–(100) are the same for all alkali-metal isotopes of the same chemical species. For a chemically pure alkali-metal vapor, the isotopically averaged longitudinal spin polarizations are

$$\langle F_z \rangle = \sum_i \eta_i \langle F_{iz} \rangle \quad \text{and} \quad \langle S_z \rangle = \sum_i \eta_i \langle S_{iz} \rangle. \quad (119)$$

The isotopic fractions are  $\eta_i = [A_i]/[A]$ , where  $[A_i]$  is the atomic number density of the isotope of species  $i$ , and  $[A] = \sum_i [A_i]$  is the total number density of alkali-metal atoms.

The expectation values of the photon, atomic, and nuclear spins are all longitudinal, so  $s_z$ ,  $\langle S_z \rangle$ ,  $\langle F_z \rangle$ , and  $\langle K_z \rangle$  are the only nonzero components of the respective vectors. Adding an isotope label subscript  $i$  to  $\rho$ ,  $H'_g$ ,  $\varphi$ ,  $S_z$ ,  $I$ , and  $\mathbf{F}$  in Eq. (96), multiplying Eq. (96) by  $\eta_i F_{iz}$ , taking the trace for each isotope, and summing the result for all alkali-metal isotopes  $i$  we find

$$\frac{d}{dt} \langle F_z \rangle = -\frac{1}{T_{SD}} \langle S_z \rangle + R \left( \frac{s_z}{2} - \langle S_z \rangle \right) - \frac{1}{T_{FD}} \sum_i \frac{\eta_i}{[I_i]^2} \langle F_{iz} \rangle + \langle K_z \rangle \left( \frac{1}{T_{SE}} + \frac{1}{T_{FE}} \sum_i \frac{\eta_i}{[I_i]^2} 2\langle \mathbf{F}_i \cdot \mathbf{F}_i - F_{iz}^2 \rangle \right). \quad (120)$$

The hyperfine Hamiltonian  $H'_g$  is axially symmetric so  $[H'_g, F_z] = 0$  and  $H'_g$  makes no contribution to Eq. (120).

Spin-exchange collisions make no contribution because the exchange term from Eq. (96) can be written as

$$\begin{aligned} & \frac{1}{[A]} \sum_{ij} \langle v \sigma_{\text{ex}} \rangle_{ij} [A_i][A_j] \text{Tr} F_{i_z} [\varphi_i (1 + 4 \langle S_{j_z} \rangle S_{i_z}) - \rho_i] \\ &= \frac{1}{[A]} \sum_{ij} \langle v \sigma_{\text{ex}} \rangle_{ij} [A_i][A_j] [\langle S_{j_z} \rangle - \langle S_{i_z} \rangle] = 0, \end{aligned} \quad (121)$$

since  $\langle v \sigma_{\text{ex}} \rangle_{ij} = \langle v \sigma_{\text{ex}} \rangle_{ji}$  by detailed balance.

We can also show directly that the spin temperature distribution (112) is the steady-state solution of Eq. (96) for longitudinal pumping in the absence of diffusion, rf fields, and slow processes. Let us assume that the spin state of each isotope  $j$  of the alkali-metal atoms is described by a spin-temperature distribution (112) with the same value of  $\beta$  for each isotope. The axially symmetric Hamiltonian  $H'_g$  will commute with the axially symmetric  $\rho$  of Eq. (112). In view of Eqs. (114) and (117), the exchange term on the right of Eq. (96) vanishes since for all isotopes  $j$  we have  $\langle S_{j_z} \rangle = (1/2) \tanh(\beta/2)$ . In steady state  $\partial \rho / \partial t = 0$ , and Eq. (96) becomes

$$0 = \left[ - \left( \frac{1}{T_{\text{SD}}} + R \right) 2 \langle S_z \rangle + R s_z + \frac{2}{T_{\text{SE}}} \langle K_z \rangle \right] 2 \varphi S_z, \quad (122)$$

which has the solution

$$P = 2 \langle S_z \rangle = \frac{s_z R T_{\text{SD}} + 2 \langle K_z \rangle T_{\text{SD}} / T_{\text{SE}}}{1 + R T_{\text{SD}}}. \quad (123)$$

Now let us consider the equilibrium polarization in the absence of diffusion when some of the relaxation is due to slow processes, as will be the case for  $^{129}\text{Xe}$ , where van der Waals molecules are important. As the buffer-gas pressure increases, Eqs. (70) and (71) imply that  $f_S \rightarrow 1$  and  $f_F \rightarrow 0$  and the slow processes—proportional to  $f_F$ —would vanish. The steady-state solution in this limit is the spin temperature distribution (112), as we have outlined above. Since spin-exchange optical pumping of  $^{129}\text{Xe}$  is most conveniently done at high buffer gas pressures, the relaxation due to long-lived van der Waals molecules, that is the slow processes, will be very small compared to the sudden processes, and the spin-temperature distribution (112) will remain a good description of the polarization. Then we can write Eq. (120) as

$$\begin{aligned} \frac{d}{dt} [1 + \bar{\epsilon}(P)] \langle S_z \rangle &= - \left( \frac{1}{T_{\text{SD}}} + R + \frac{\nu(P)}{T_{\text{FD}}} \right) \langle S_z \rangle \\ &+ \frac{R s_z}{2} + \left( \frac{1}{T_{\text{SE}}} + \frac{\nu(P)}{T_{\text{FE}}} \right) \langle K_z \rangle. \end{aligned} \quad (124)$$

The isotopically averaged paramagnetic coefficient is

$$\bar{\epsilon}(P) = \sum_i \eta_i \epsilon(I_i, P). \quad (125)$$

The coefficient  $\nu(P)$ , which accounts for relaxation in long-lived van der Waals molecules is

$$\nu(P) = \sum_i \frac{\eta_i}{[I_i]^2} [1 + \epsilon(I_i, P)]. \quad (126)$$

The steady-state solution of Eq. (124) is

$$P = 2 \langle S_z \rangle = \frac{s_z R T_{\text{SD}} + 2 \langle K_z \rangle [T_{\text{SD}} / T_{\text{SE}} + \nu(P) T_{\text{SD}} / T_{\text{FE}}]}{1 + R T_{\text{SD}} + \nu(P) T_{\text{SD}} / T_{\text{FD}}}, \quad (127)$$

which can be solved for  $P$  with the aid of Eq. (126). For spin-exchange optical pumping of  $^{129}\text{Xe}$  at high pressures, the slow processes make a very small contribution to the relaxation ( $T_{\text{FD}} \gg T_{\text{SD}}$ ), and the value of  $P$  given by Eq. (127) is very nearly the same as that given by Eq. (123).

*Diffusion layer.* At the high gas pressures used for spin-exchange optical pumping the spatial diffusion coefficient  $D$  for the alkali-metal atoms is normally very small. For example, in high-density ( $\sim 10$  amagat) He gas  $D \approx 0.04 \text{ cm}^2 \text{ sec}^{-1}$  [38]. Near the input wall of the cell representative optical pumping rates are  $R \gg 10^4 \text{ sec}^{-1}$ . To a good approximation, the cell walls are nearly completely depolarizing for the alkali-metal atoms. The walls are often coated with a thin film of the metal, so that an atom impinging on the wall from the gas is replaced by a completely unpolarized atom evaporating from the metal film. Therefore, the spin polarization of the alkali-metal atoms can be expected to grow from zero at the wall to the equilibrium value (123) or (127) in a distance of order  $\sqrt{D/R} \sim 2 \times 10^{-3} \text{ cm}$  [19]. For very optically thick vapors, a sizable fraction of the spin from the optical pumping photons can be lost to the cell walls in the diffusion layer.

The polarization will vary with distance  $z$  from the cell wall in accordance with the steady-state solution of Eq. (108):

$$\left\{ D \frac{d^2}{dz^2} - \Lambda \right\} |\rho\rangle = 0. \quad (128)$$

In spite of its formal simplicity, Eq. (128) is a nonlinear equation, since the relaxation operator  $\Lambda$  depends on the atomic spin polarization  $\langle S_{j_z} \rangle$  through the term  $R' s'_z$  of Eq. (105). The solution of Eq. (128) can be obtained by an iterative method, analogous to the use of Hartree self-consistent fields for finding electron wave functions of many-electron atoms. A first approximation, adequate for most purposes, can be obtained by (1) neglecting the slow processes proportional to  $1/T_{\text{FD}}$  and  $1/T_{\text{FE}}$ ; (2) neglecting the spin-exchange terms in Eqs. (104) and (105), proportional to  $1/T_{\text{ex}}$ ,  $1/T_{\text{ex},ij}$ , and  $1/T_{\text{SE}}$ ; (3) neglecting any change in  $R$  due to attenuation of the pumping light in the diffusion layer. Then the relaxation matrix  $\Lambda$  will be independent of position in the diffusion layer, and the solution of Eq. (128) can be conveniently found with the aid of the eigenvectors (32) of  $\Lambda$ . For the longitudinal polarization under consideration here, the eigenvalues  $\lambda$  are real and non-negative.

We multiply Eq. (128) on the left by  $\{\lambda\}$  to find the differential equation for the  $z$ -dependent amplitude  $\{\lambda|\rho\rangle$ ,

$$\left\{ D \frac{d^2}{dz^2} - \lambda \right\} \{\lambda|\rho\rangle = 0. \quad (129)$$

The solution of Eq. (129) that does not diverge for large  $z$  is

$$\{\lambda|\rho\} = \{\lambda|\rho_0\}e^{-z\sqrt{\lambda D}}, \quad (130)$$

where  $\rho_0$  is the unpolarized state of Eq. (24) ( $fm|\rho_0\rangle = 1/(2[I])$ ). Using the completeness of  $|fm\rangle$  and  $|\lambda_n\rangle$  we find that the  $z$ -dependent spin-polarization near the walls is

$$\begin{aligned} \langle J_z \rangle &= \langle J_z|\rho \rangle = \frac{1}{2[I]} \sum_{\lambda, fm, f'm'} (J_z|fm\rangle)(fm|\lambda\rangle) \\ &\quad \times \{\lambda|f'm'\rangle e^{-z\sqrt{\lambda D}}, \end{aligned} \quad (131)$$

where  $J_z = S_z$  or  $J_z = I_z$ . From the projection theorem,

$$\langle S_z|fm\rangle = \frac{m(-1)^{a-f}}{[I]}, \quad \langle I_z|fm\rangle = m - \frac{m(-1)^{a-f}}{[I]}. \quad (132)$$

As a simple example, consider a hypothetical alkali-metal atom with  $I = 1/2$ . There will be four population basis states  $|fm\rangle$ , so

$$(fm|\rho\rangle = \begin{bmatrix} (11|\rho\rangle \\ (10|\rho\rangle \\ (00|\rho\rangle \\ (1, -1|\rho\rangle \end{bmatrix}. \quad (133)$$

For simplicity, neglect all relaxation processes and assume perfect circular polarization for the pumping light. Then  $1/T_{FD} = 0$ ,  $1/T_{FE} = 0$ ,  $R' = R$ ,  $s'_z = 1$ , and the relaxation matrix of Eq. (109) becomes

$$\Lambda = \frac{R}{4} \begin{pmatrix} 0 & -2 & -2 & 0 \\ 0 & 3 & -1 & -2 \\ 0 & -1 & 3 & -2 \\ 0 & 0 & 0 & 4 \end{pmatrix}. \quad (134)$$

The rows and columns of Eq. (134) are labeled in the same order as the column matrix (133). The eigenvalues of Eq. (134) are readily found to be

$$(\lambda_1, \lambda_2, \lambda_3, \lambda_4) = (0, R/2, R, R). \quad (135)$$

(See Fig. 2.) The corresponding right eigenvectors  $|\lambda_n\rangle$  are

$$(fm|\lambda_n\rangle = \begin{pmatrix} 1 & 2 & 1 & 1 \\ 0 & -1 & 1 & -1 \\ 0 & -1 & -3 & -1 \\ 0 & 0 & 1 & 1 \end{pmatrix}, \quad (136)$$

where the  $n$ th column is the right eigenvector corresponding to  $\lambda_n$ . The left eigenvectors are

$$\{\lambda_n|fm\rangle = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & -1/2 & -1/2 & -1 \\ 0 & 1/4 & -1/4 & 0 \\ 0 & -1/4 & 1/4 & 1 \end{pmatrix}, \quad (137)$$

where the  $n$ th row is the left eigenvector corresponding to  $\lambda_n$ . Substituting Eqs. (132)–(137) into Eq. (131) we find

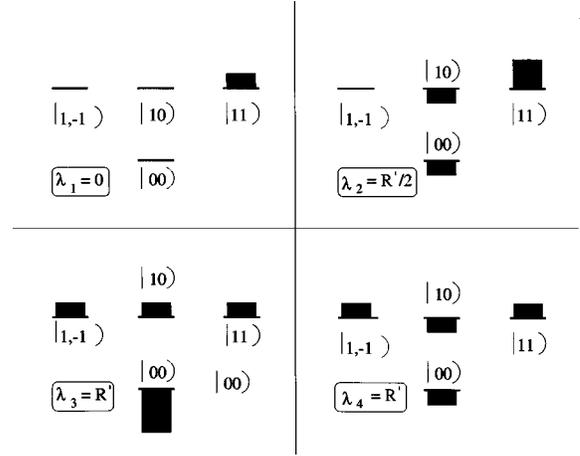


FIG. 2. Eigenvalues  $\lambda_n$  from Eq. (135) and eigenvectors  $|\lambda_n\rangle$  from Eq. (136) for populations of a hypothetical alkali-metal atom with nuclear spin quantum number  $I = 1/2$ . The effective pumping rate (104) is  $R' = R$  and the effective photon spin of Eq. (105) is  $s'_z = 1$ . Collisional relaxation processes have been neglected. In the absence of spatial diffusion, the population distributions  $(fm|\lambda_n\rangle$  decay exponentially at the rate  $\lambda_n$ .

$$\langle S_z \rangle = \langle I_z \rangle = \frac{1}{2}(1 - e^{-z\sqrt{R/2D}}). \quad (138)$$

The extension to nonzero collisional relaxation rates and to  $I > 1/2$  is straightforward.

## X. RADIO-FREQUENCY RESONANCES

Suppose that the atoms are subject to a weak magnetic field  $2B_1 \cos \omega t$ , oscillating along the  $x$  axis of the coordinate system with a radio frequency  $\omega$ . The low-field Larmor frequency is given by

$$\omega_L/2\pi = 2.8B_z/[I] \text{ MHz/G}. \quad (139)$$

We assume that  $B_z > 0$ , so for resonant rf we will also have  $\omega \approx \omega_L > 0$ . The interaction of an alkali-metal atom with the rf field is

$$H_{\text{rf}} = 2g_S\mu_B S_x B_1 \cos \omega t, \quad (140)$$

where we have ignored the thousandfold smaller interaction with the nuclear moment.

In the steady state, the density matrix can be written as a sum of harmonics of the rf frequency  $\omega$ ,

$$\rho = \sum_n \rho^{(n)} e^{in\omega t}. \quad (141)$$

To lowest order in  $B_1$ ,  $\rho^{(n)} \sim B_1^{|n|}$ . We substitute Eq. (141) into Eq. (101) and neglect the effects of spatial diffusion, which we will discuss in more detail in Sec. XII. Taking matrix elements between the resonantly coupled states  $|fm\rangle$  and  $|f, m-1\rangle$ , and retaining only the terms linear in  $\rho^{(n)}$  ( $n = \pm 1$ ) or  $B_1$  we find

$$\begin{aligned}
\sum_{n=\pm 1} in\omega e^{in\omega t} \langle fm|\rho^{(n)}|f,m-1\rangle &= \frac{1}{i\hbar} g_S \mu_B B_1 \langle fm|[S_x, \rho^{(0)}]|f,m-1\rangle 2 \cos \omega t \\
&+ \sum_{n=\pm 1} e^{in\omega t} \langle fm| \left\{ \frac{1}{i\hbar} [H_g, \rho^{(n)}] + R' \left( \frac{1}{[I]^2} F_z \rho^{(n)} F_z - \frac{3}{4} \rho^{(n)} + \frac{s'_z (-1)^{a-f}}{2[I]} \{F_z, \rho^{(n)}\} \right) \right. \\
&+ \frac{1}{[I]^2 T_{FD}} \left( F_z \rho^{(n)} F_z - f(f+1) \rho^{(n)} + \frac{T_{FD}}{T_{FE}} \langle K_z \rangle \{F_z, \rho^{(n)}\} \right) \\
&+ \frac{R'}{2[I]^2} ([1+s'_z] F_+ \rho^{(n)} F_- + [1-s'_z] F_- \rho^{(n)} F_+) + \frac{1}{2[I]^2} \left( \frac{1}{T_{FD}} + \frac{2\langle K_z \rangle}{T_{FE}} \right) F_+ \rho^{(n)} F_- \\
&+ \left. \left[ \frac{1}{T_{FD}} - \frac{2\langle K_z \rangle}{T_{FE}} \right] F_- \rho^{(n)} F_+ \right\} |f,m-1\rangle + \frac{\eta}{T_{ex}} \langle S_- \rangle \langle fm|\frac{1}{2}\{S_+, \rho^{(0)}\} - S_+ \rho^{(0)} S_z \\
&+ S_z \rho^{(0)} S_+ |f,m-1\rangle. \tag{142}
\end{aligned}$$

Passing from Eq. (101) to Eq. (142) we have neglected the couplings of Zeeman coherences of different multiplets,  $a$  and  $b$ , since the evolution frequencies  $\omega_{a\bar{m}}$  and  $\omega_{b\bar{m}}$  are nearly equal and opposite.

We will assume that the zeroth-order density matrix is the spin temperature distribution  $\rho^{(0)} = e^{\beta F_z}/Z$  of Eq. (112). Then the matrix element of the term proportional to the rf field in Eq. (142) is

$$\langle fm|[S_x, \rho^{(0)}]|f,m-1\rangle = -\langle fm|S_+|f,m-1\rangle \frac{P Q_{\bar{m}}}{2}, \tag{143}$$

where  $\bar{m} = m - 1/2$  is the mean azimuthal quantum number of the coupled states,  $P$  is the polarization of Eq. (114), and

$$Q_{\bar{m}} = \frac{e^{\beta \bar{m}}}{Z_I} = \frac{2P(1+P)^{I+\bar{m}}(1-P)^{I-\bar{m}}}{(1+P)^{[I]} - (1-P)^{[I]}}. \tag{144}$$

Physically,  $Q_{\bar{m}}$  is the probability that the nuclear spin has the azimuthal quantum number  $\bar{m}$  for the spin-temperature distribution (112). One can readily show that  $Q_{\bar{m}} \rightarrow 1/[I]$  as  $P \rightarrow 0$ , and  $Q_{\bar{m}} \rightarrow \delta_{\bar{m}, I}$  as  $P \rightarrow 1$ . Since  $S_z S_+ = -S_+ S_z = S_+$  and  $[S_z, e^{\beta S_z}] = 0$  we can write the matrix element in the last term of Eq. (142) as

$$\begin{aligned}
\langle fm|\frac{1}{2}\{S_+, \rho^{(0)}\} - S_+ \rho^{(0)} S_z + S_z \rho^{(0)} S_+ |f,m-1\rangle &= \langle fm|\frac{e^{\beta I_z}}{Z} \{S_+, e^{\beta S_z}\} |f,m-1\rangle \\
&= \langle fm|S_+|f,m-1\rangle \frac{e^{\beta m} + e^{\beta(m-1)}}{Z_I Z_S} = \langle fm|S_+|f,m-1\rangle Q_{\bar{m}}. \tag{145}
\end{aligned}$$

For further analysis, it is convenient to use the Liouville basis vectors (21), for the special case  $f' = f$  and  $\Delta m = 1$ . To simplify subsequent notation we write  $|ff\bar{m}1\rangle = |f\bar{m}\rangle$ . Setting  $\langle fm|\rho^{(n)}|f,m-1\rangle = (f\bar{m}|\rho^{(n)})$  in Eq. (142) and equating coefficients of  $e^{in\omega t}$ , we find

$$(\Lambda + in\omega)|\rho^{(n)}\rangle = |\sigma\rangle. \tag{146}$$

The components of the source vector are

$$(f\bar{m}|\sigma\rangle = \frac{ig_S \mu_B B_1 P Q_{\bar{m}} (f\bar{m}|S_+)}{2\hbar}, \tag{147}$$

with the matrix element

$$(f\bar{m}|S_+) = \frac{(-1)^{a-f}}{2[I]} \sqrt{([f]^2 - 4\bar{m}^2)}. \tag{148}$$

The Liouville vectors  $|\rho^{(n)}\rangle$  and  $|\sigma\rangle$  of Eq. (146) and subsequent discussion are understood to include only the projections with azimuthal quantum number  $\Delta m = 1$ .

The matrix elements of the relaxation operator  $\Lambda$  have real parts

$$\begin{aligned} \text{Re}(f\bar{m}|\Lambda|f'\bar{m}') &= \delta_{ff'} \left\{ \delta_{\bar{m}\bar{m}'} \left( R' \frac{3[I]^2 + 1 - 4\bar{m}^2}{4[I]^2} - R' s'_z \frac{\bar{m}}{[I]} (-1)^{a-f} + \frac{(f\bar{m}|S_+)^2}{T_{\text{FD}}} - \frac{2\langle K_z \rangle \bar{m}}{T_{\text{FE}}[I]^2} \right) \right. \\ &\quad \left. - \sum_{p=\pm 1} \frac{\delta_{\bar{m},\bar{m}'+p}}{2} \left( R' + pR' s'_z + \frac{1}{T_{\text{FD}}} + \frac{2p\langle K_z \rangle}{T_{\text{FE}}} \right) (f\bar{m}|S_+)(S_+|f\bar{m}') - \frac{\eta Q_{\bar{m}}(f\bar{m}|S_+)(S_+|f\bar{m}')}{T_{\text{ex}}} \right\}, \end{aligned} \quad (149)$$

and imaginary parts

$$i \text{Im}(f\bar{m}|\Lambda|f'\bar{m}') = i\omega_{f\bar{m}} \delta_{ff'} \delta_{\bar{m}\bar{m}'}. \quad (150)$$

It is convenient to discuss  $\Lambda$ , as defined by Eqs. (149) and (150), in terms of its left and right eigenvectors  $\{\lambda|\}$  and  $|\lambda\rangle$  and their common eigenvalues  $\lambda$  defined by Eq. (32). The eigenvalues for the transverse coherence will be complex numbers with positive real parts  $\text{Re } \lambda$  describing the damping of the free coherence. Under the conditions of interest here, the imaginary parts  $\text{Im } \lambda$ , representing the precession frequencies of the coherence, will be several orders of magnitude larger than the real parts. We can partition the eigenvalues  $\lambda$  and their associated eigenvectors into a group of  $2a$  eigenvalues  $\lambda_a, \lambda'_a, \dots$ , associated with the Zeeman multiplet  $a$ , for which  $\text{Im } \lambda_a \approx \omega_L$ , with  $\omega_L$  given by Eq. (139), and a second group of  $2b$  eigenvalues  $\lambda_b, \lambda'_b, \dots$ , associated with the Zeeman multiplet  $b$ , for which  $\text{Im } \lambda_b \approx -\omega_L$ . We multiply Eq. (146) on the left by  $\{\lambda|$  to find

$$\{\lambda|\rho^{(n)}\rangle = \{\lambda|\sigma\rangle(\lambda + in\omega)^{-1}. \quad (151)$$

Imaging signals, observed as the rf modulation of a transverse probe beam, are linear combinations of the electron spin projections

$$\begin{aligned} \langle S_- \rangle^{(n)} &= \text{Tr}[(S_+)^{\dagger} \rho^{(n)}] = \sum_{\lambda} (S_+|\lambda)\{\lambda|\rho^{(n)}\} \\ &= \sum_{\lambda} \frac{(S_+|\lambda)\{\lambda|\sigma\rangle}{\lambda + in\omega}. \end{aligned} \quad (152)$$

For magnetic fields large enough that the Zeeman resonance frequencies are well resolved, that is,

$$|\omega_{f\bar{m}} - \omega_{f\bar{m}'}| \gg |\text{Re}(f\bar{m}|\Lambda|f\bar{m}')|, \quad (153)$$

with  $\bar{m}' = \bar{m} \pm 1$ , we may think of Eq. (150) as a nondegenerate, zeroth-order part of  $\Lambda$  with Eq. (149) as a small perturbation. The zeroth-order (orthogonal) eigenvectors are

$$\{\lambda_f| = (f\bar{m}|, \quad \text{and} \quad |\lambda_f\rangle = |f\bar{m}\rangle. \quad (154)$$

The eigenvalues, correct to first order in Eq. (149), are

$$\lambda_f = i\omega_{f\bar{m}} + \gamma_{f\bar{m}}, \quad \text{with} \quad \gamma_{f\bar{m}} = \text{Re}(f\bar{m}|\Lambda|f\bar{m}\rangle. \quad (155)$$

Substituting Eqs. (154) and (155) into Eq. (152), we find the transverse spin for a well-resolved Zeeman resonance  $f\bar{m}$

$$\langle S_- \rangle_{f\bar{m}}^{(n)} = \frac{(S_+|f\bar{m}\rangle)(f\bar{m}|\sigma\rangle)}{\gamma_{f\bar{m}} + i(\omega'_{f\bar{m}} + n\omega)}. \quad (156)$$

When the magnetic field is small enough that Eq. (153) is no longer valid, the eigenvectors will become superpositions of the zeroth-order eigenvectors of Eq. (154), that is,  $|\lambda_f\rangle \rightarrow \sum_{\bar{m}} |f\bar{m}\rangle (f\bar{m}|\lambda_f\rangle)$ . The damping rates  $\text{Re } \lambda_f$  will undergo substantial relative changes, but there will be little change of the precession frequencies, which will remain  $\text{Im } \lambda_f \approx (-1)^{a-f} \omega_L$ . Thus, whether or not the Zeeman resonances are well resolved, Eq. (152) gives two resonantly enhanced parts,

$$\begin{aligned} \langle S_- \rangle_a^{(-1)} &= \sum_{\lambda_a} \frac{(S_+|\lambda_a)\{\lambda_a|\sigma\rangle}{\lambda_a - i\omega}, \\ \langle S_- \rangle_b^{(1)} &= \sum_{\lambda_b} \frac{(S_+|\lambda_b)\{\lambda_b|\sigma\rangle}{\lambda_b + i\omega}. \end{aligned} \quad (157)$$

The resonant, transverse electron spin polarizations are therefore the sum of a positively rotating part from the multiplet  $a$ ,

$$\begin{aligned} \langle \mathbf{S}_{\perp} \rangle_a &= \frac{1}{2} \langle S_- \rangle_a^{(-1)} (\mathbf{x} + i\mathbf{y}) e^{-i\omega t} + \text{c.c.} \\ &= \text{Re} \langle S_- \rangle_a^{(-1)} (\mathbf{x} \cos \omega t + \mathbf{y} \sin \omega t) \\ &\quad + \text{Im} \langle S_- \rangle_a^{(-1)} (\mathbf{x} \sin \omega t - \mathbf{y} \cos \omega t), \end{aligned} \quad (158)$$

and a negatively rotating part from the multiplet  $b$ ,

$$\begin{aligned} \langle \mathbf{S}_{\perp} \rangle_b &= \frac{1}{2} \langle S_- \rangle_b^{(1)} (\mathbf{x} + i\mathbf{y}) e^{i\omega t} + \text{c.c.} \\ &= \text{Re} \langle S_- \rangle_b^{(1)} (\mathbf{x} \cos \omega t - \mathbf{y} \sin \omega t) \\ &\quad - \text{Im} \langle S_- \rangle_b^{(1)} (\mathbf{x} \sin \omega t + \mathbf{y} \cos \omega t). \end{aligned} \quad (159)$$

For the special case of well-resolved Zeeman resonances, the sum of Eqs. (158) and (159) can be evaluated explicitly from Eqs. (156), (147), and (148) to give

$$\begin{aligned}
\langle \mathbf{S}_\perp \rangle &= P \sum_{\bar{m}} \frac{g_S \mu_B B_1 ([a]^2 - 4\bar{m}^2) Q_{\bar{m}}}{8[I]^2 \hbar [(\omega_{a\bar{m}} - \omega)^2 + \gamma_{a\bar{m}}^2]} [(\omega_{a\bar{m}} - \omega) \\
&\quad \times (\mathbf{x} \cos \omega t + \mathbf{y} \sin \omega t) + \gamma_{a\bar{m}} (\mathbf{x} \sin \omega t - \mathbf{y} \cos \omega t)] \\
&\quad + P \sum_{\bar{m}} \frac{g_S \mu_B B_1 ([b]^2 - 4\bar{m}^2) Q_{\bar{m}}}{8[I]^2 \hbar [(\omega_{b\bar{m}} + \omega)^2 + \gamma_{b\bar{m}}^2]} [(\omega_{b\bar{m}} + \omega) \\
&\quad \times (\mathbf{x} \cos \omega t - \mathbf{y} \sin \omega t) - \gamma_{b\bar{m}} (\mathbf{x} \sin \omega t + \mathbf{y} \cos \omega t)]. \quad (160)
\end{aligned}$$

The experimental signals are obtained with a lock-in (phase-sensitive) amplifier with an offset  $\theta$  between the phase of the rf-drive field and the light-modulation signal, and with an integration time constant  $\tau$ , such that  $\omega\tau \gg 1$ . The signals from the the lock-in amplifier are proportional to  $\mathbf{n} \cdot \overline{\langle \mathbf{S}_\perp \rangle}$  where  $\mathbf{n}$  is the direction of propagation of the probe beam and

$$\overline{\langle \mathbf{S}_\perp \rangle} = \frac{2}{\tau} \int_0^\infty dt' e^{-t'/\tau} \langle \mathbf{S}_\perp(t-t') \rangle \cos\{\omega(t-t') - \theta\}. \quad (161)$$

Substituting Eqs. (158) and (159) into Eq. (161) we find  $\overline{\langle \mathbf{S}_\perp \rangle} = \overline{\langle \mathbf{S}_\perp \rangle}_a + \overline{\langle \mathbf{S}_\perp \rangle}_b$  where

$$\begin{aligned}
\overline{\langle \mathbf{S}_\perp \rangle}_a &= \text{Re}\langle S_- \rangle_a^{(-1)} (\mathbf{x} \cos \theta + \mathbf{y} \sin \theta) + \text{Im}\langle S_- \rangle_a^{(-1)} \\
&\quad \times (\mathbf{x} \sin \theta - \mathbf{y} \cos \theta), \\
\overline{\langle \mathbf{S}_\perp \rangle}_b &= \text{Re}\langle S_- \rangle_b^{(1)} (\mathbf{x} \cos \theta - \mathbf{y} \sin \theta) - \text{Im}\langle S_- \rangle_b^{(1)} \\
&\quad \times (\mathbf{x} \sin \theta + \mathbf{y} \cos \theta). \quad (162)
\end{aligned}$$

The amplitudes  $\langle S_- \rangle_f^{(n)}$  may vary on a time scale much longer than the time constant  $\tau$  of the lock-in amplifier, for example, during a relatively slow scan of  $\omega$  or  $B_0$  across a spectrum of Zeeman resonance lines.

For poorly resolved Zeeman resonances, the frequency dependence of  $\overline{\langle \mathbf{S}_\perp \rangle}_f$  is complicated, but the resonance ‘‘area’’ is relatively simple to interpret. The resonance areas are proportional to

$$\begin{aligned}
\int_0^\infty d\omega \langle S_- \rangle_f^{(n)} &= \pi \sum_{\lambda_f} (S_+ | \lambda_f \rangle \{ \lambda_f | \sigma \rangle \\
&= \pi \sum_{\bar{m}} (S_+ | f\bar{m} \rangle (f\bar{m} | \sigma \rangle). \quad (163)
\end{aligned}$$

Carrying out the integral over  $\omega$  of terms from Eq. (157), a sum of  $2a$  poles in the complex  $\omega$  plane just below the real axis, and a sum of  $2b$  poles just above the real axis, both sets of poles at  $\text{Re } \omega \approx \omega_L$ , amounts to replacing the factors  $\int d\omega (\lambda_f \pm i\omega)^{-1}$  by  $\pi$ . Substituting Eqs. (147) and (148) into the last term of Eq. (163), we find, aside from a multiplicative factor, the sum

$$\sum_{\bar{m}} Q_{\bar{m}} ([f]^2 - 4\bar{m}^2) = [f]^2 - [I]^2 + 1 + 2\epsilon(I, P), \quad (164)$$

which we have evaluated using the definition (118) of the paramagnetic coefficient  $\epsilon(I, P)$ . Then Eq. (163) becomes the purely imaginary expression

$$\int_0^\infty d\omega \langle S_- \rangle_f^{(n)} = \frac{i\pi g_S \mu_B B_1 P}{8[I]^2 \hbar} \{ [f]^2 - [I]^2 + 1 + 2\epsilon(I, P) \}, \quad (165)$$

which when substituted into Eq. (162) yields the total resonance area of the transverse spin

$$\begin{aligned}
\int_0^\infty (\overline{\langle \mathbf{S}_\perp \rangle}_a + \overline{\langle \mathbf{S}_\perp \rangle}_b) d\omega &= \frac{\pi g_S \mu_B B_1 P}{2[I]^2 \hbar} (\mathbf{x}[I] \sin \theta \\
&\quad - \mathbf{y}\{1 + \epsilon(I, P)\} \cos \theta). \quad (166)
\end{aligned}$$

Thus, for either resolved, partially resolved, or unresolved Zeeman resonances, the total resonance area, when probed along the direction  $\mathbf{x}$  of the rf field, is strictly proportional to the longitudinal electron polarization  $P$ . Since the part of the transverse spin  $\langle S_x \rangle$  that contributes to the resonance area is  $90^\circ$  out of phase with the rf field, the lock-in phase must be  $\theta = \pm 90^\circ$  for maximum response amplitude. The ‘‘area theorem’’ (166) for Zeeman resonances is an analog of various oscillator-strength sum rules from atomic and nuclear physics.

We will often be interested in the limit of intense, circularly polarized pumping light when  $P \rightarrow 1$ ,  $s'_z \rightarrow 1$ ,  $Q_{\bar{m}} \rightarrow \delta_{\bar{m},1}$ , and when all relaxation rates are negligible except for the optical pumping rate  $R$  and the spin-exchange rate  $1/T_{\text{ex}}$ . Then one can verify by inspection of Eq. (149) that the elements of the matrix  $(f\bar{m} | \Lambda | f\bar{m}')$  with  $\bar{m} < \bar{m}'$  will be negligible compared to nonzero matrix elements  $(f\bar{m} | \Lambda | f\bar{m}')$  with  $\bar{m} \geq \bar{m}'$ . That is, for high polarization  $P$ ,  $(f\bar{m} | \Lambda | f\bar{m}')$  will be very nearly upper triangular (with the rows and columns labeled in order of decreasing values of  $\bar{m}$  and  $\bar{m}'$ ). The eigenvalues will be very nearly the diagonal elements  $(f\bar{m} | \Lambda | f\bar{m})$  of the triangular matrix. These high-polarization eigenvalues are valid whether the resonances are well resolved, poorly resolved, or completely overlapping. They are formally the same as the eigenvalues (155) for well resolved resonances. One can also verify that as  $P \rightarrow 1$ , all components of the source vector (147) will be negligibly small except for the ‘‘top’’ component  $(aI | \sigma)$ . With such a source vector and with  $\Lambda$  given by an upper triangular matrix, the solution of Eq. (146) is simply

$$|\rho\rangle = \frac{|aI\rangle (aI | \sigma\rangle)}{\gamma_{aI} + i(\omega'_{aI} - \omega)}. \quad (167)$$

For  $P \rightarrow 1$  we may neglect all but the optical-pumping and spin-exchange contributions to the width, and we find from Eqs. (155) and (149)

$$\gamma_{aI} = \frac{R}{[I]} + (1 - \eta) \frac{1}{[I]T_{\text{ex}}}. \quad (168)$$

The spin-exchange contribution to the resonance width is diminished by the fraction  $\eta$  of like isotope. For a monoisotopic alkali metal, there will be no spin-exchange broadening at all.

In summary, for resolved, partially resolved, or completely overlapping Zeeman resonances, the time-dependent transverse spin for the limit  $P \rightarrow 1$  is given by the first term of (9.21):

$$\langle \mathbf{S}_\perp \rangle = \frac{g_S \mu_B B_1 [(\omega_{aI} - \omega)(\mathbf{x} \cos \omega t + \mathbf{y} \sin \omega t) + \gamma_{aI}(\mathbf{x} \sin \omega t - \mathbf{y} \cos \omega t)]}{2[I] \hbar [(\omega_{aI} - \omega)^2 + \gamma_{aI}^2]}. \quad (169)$$

The lock-in signal (162) can be obtained by letting  $\omega t \rightarrow \theta$  in the right side of Eq. (169).

### XI. RELAXATION IN THE DARK

Important information about the relaxation mechanisms of alkali-metal atoms can be obtained by measurements of the relaxation of the spin polarization in the dark, an experimental method introduced by Franzen [39]. In such experiments, the pumping light is suddenly removed and the polarization of the vapor is monitored by such a weak optical probe beam that optical pumping effects on the relaxation can be ignored or extrapolated to zero. According to Eq. (82) the photon absorption cross section depends on the isotopically averaged, longitudinal spin polarization,

$$\langle S_z \rangle = \sum_i \eta_i \langle S_{iz} \rangle = \sum_i \frac{\eta_i}{[I_i]} (\langle a_{iz} \rangle - \langle b_{iz} \rangle), \quad (170)$$

so analyzing relaxation in the dark amounts to analyzing the relaxation of the spin-projections  $\langle a_{iz} \rangle = \sum_m \langle am | \rho_i | am \rangle$ , and  $\langle b_{iz} \rangle$ , defined in like manner, where  $i$  labels one of the  $N$  different isotopic species in the vapor of alkali-metal atoms. Because of spin-exchange collisions between the alkali-metal atoms, the relaxation equation (96) is a non-linear (Riccati) equation. Therefore, the general decay cannot be described by a finite sum of exponentials.

However, experiments show that in the final stages of relaxation in the dark, all of the  $\langle f_{iz} \rangle$  decay with the same time constant  $T_1$ . This is to be expected since the nonlinear terms from Eq. (96) become negligibly small compared to the linear terms in the low-polarization limit. The single exponential decay that is observed experimentally corresponds to the slowest or *fundamental* relaxation mode of the linearized form of Eq. (96).

The symmetry of Eq. (96) ensures that the density matrix, if not already longitudinal, will become longitudinal and remain that way as the polarization decays to zero in the dark. We will also assume that the pumping light is never kept on long enough for appreciable nuclear polarization to build up in  $^3\text{He}$  or  $^{129}\text{Xe}$ , so we will neglect the terms proportional to  $\langle \mathbf{K} \rangle$  in Eq. (96). Because the density matrix is longitudinal, the Hamiltonian  $H'_g$  has no direct influence on the relaxation, and we account for its presence by ignoring the hyperfine coherences that are generated by the spin-exchange and S-damping terms of Eq. (96) but that oscillate rapidly because of  $H'_g$  and therefore average to zero.

The relaxation equations are obtained by evaluating  $\text{Tr} f_z d\rho/dt$ , with  $d\rho/dt$  given by Eq. (96), and  $f_z = \sum_m m |fm\rangle \langle fm|$  to find

$$\frac{d}{dt} \langle f_{iz} \rangle = - \sum_{f'i'} \langle f_i | \Gamma | f'_i \rangle \langle f'_{i'} \rangle. \quad (171)$$

The relaxation matrix  $\Gamma$  is the sum of contributions from spin-exchange collisions between alkali-metal atoms, from S-damping collisions, and from F-damping collisions.

$$\Gamma = \Gamma_{\text{ex}} + \Gamma_{\text{SD}} + \Gamma_{\text{FD}}. \quad (172)$$

Because we are interested in relaxation in the dark, the terms from Eq. (96) proportional to the optical pumping rate  $R$  have been neglected in Eq. (172).

The F-damping contributions come from the terms of Eq. (96) proportional to  $1/T_{\text{FD}}$

$$T_{\text{FD}} \frac{d}{dt} \langle f_z \rangle = \frac{1}{[I]^2} \langle \mathbf{F} \cdot f_z \mathbf{F} - \mathbf{F} \cdot \mathbf{F} f_z \rangle = - \frac{1}{[I]^2} \langle f_z \rangle. \quad (173)$$

The well-known commutation relations for angular momentum operators were used in simplifying Eq. (173). Comparing Eq. (173) with Eq. (171) we find the diagonal matrix

$$\langle f_i | \Gamma_{\text{FD}} | f'_i \rangle = \delta_{ff'} \delta_{ii'} \frac{1}{[I_i]^2 T_{\text{FD}}}, \quad (174)$$

where the F-damping rate  $1/T_{\text{FD}}$  is given by Eq. (99).

The S-damping contributions come from the terms of Eq. (96) proportional to  $1/T_{\text{SD}}$ , which give, with the aid of Eq. (39),

$$T_{\text{SD}} \frac{d}{dt} \langle f_z \rangle = \langle \mathbf{S} \cdot f_z \mathbf{S} - \frac{3}{4} f_z \rangle. \quad (175)$$

From rotational symmetry  $\mathbf{S} \cdot f_z \mathbf{S}$  must be a superposition of  $a_z$ ,  $b_z$ , and hyperfine coherences between the multiplets  $a$  and  $b$ , which can be neglected. Thus, we may use the projection theorem,  $S_z \rightarrow (-1)^{a-f} f_z / [I]$  etc., to write Eq. (175) as

$$T_{\text{SD}} \frac{d}{dt} \langle a_z \rangle = \left[ \frac{a(a+1) - 1}{[I]^2} - \frac{3}{4} \right] \langle a_z \rangle + B \langle b_z \rangle, \quad (176)$$

$$T_{\text{SD}} \frac{d}{dt} \langle b_z \rangle = A \langle a_z \rangle + \left[ \frac{b(b+1)-1}{[I]^2} - \frac{3}{4} \right] \langle b_z \rangle. \quad (177)$$

The coefficients  $A$  and  $B$  can be determined with the substitution  $f_z \rightarrow F_z = a_z + b_z$  in Eq. (175), which gives

$$T_{\text{SD}} \frac{d}{dt} (\langle a_z \rangle + \langle b_z \rangle) = -\langle S_z \rangle = -\frac{1}{[I]} (\langle a_z \rangle - \langle b_z \rangle). \quad (178)$$

Substituting Eqs. (176) and (177) into the left of Eq. (178) and equating coefficients of  $\langle a_z \rangle$  and  $\langle b_z \rangle$ , we find

$$A = \frac{3}{4} - \frac{a(a+1)-1}{[I]^2} - \frac{1}{[I]},$$

$$B = \frac{3}{4} - \frac{b(b+1)-1}{[I]^2} + \frac{1}{[I]}. \quad (179)$$

Comparing Eqs. (176) and (177) with Eq. (171) and making the substitutions  $a = [I]/2$ ,  $b = [I]/2 - 1$ , and  $I \rightarrow I_i$  we find

$$\begin{pmatrix} \langle a_i | \Gamma_{\text{SD}} | a_i \rangle & \langle a_i | \Gamma_{\text{SD}} | b_i \rangle \\ \langle b_i | \Gamma_{\text{SD}} | a_i \rangle & \langle b_i | \Gamma_{\text{SD}} | b_i \rangle \end{pmatrix} = \frac{1}{2[I_i]^2 T_{\text{SD}}} \begin{pmatrix} [I_i]^2 - [I_i] + 2 & -[I_i]^2 - 3[I_i] - 2 \\ -[I_i]^2 + 3[I_i] - 2 & [I_i]^2 + [I_i] + 2 \end{pmatrix}. \quad (180)$$

The S-damping rate  $1/T_{\text{SD}}$  is given by Eq. (97). S damping couples the angular momentum components  $\langle a_{iz} \rangle$  and  $\langle b_{iz} \rangle$  of a given isotope  $i$  to each other, but it does not couple components of different isotopes.

The spin-exchange contributions come from the terms of Eq. (96) proportional to  $1/T_{\text{ex},ij}$ . With the aid of Eq. (39) we find

$$T_{\text{ex}} \frac{d}{dt} \langle f_z \rangle = \langle \mathbf{S} \cdot f_z \mathbf{S} - \frac{3}{4} f_z \rangle + 4 \sum_j \eta_j \langle S_{jz} \rangle \text{Tr} \varphi f_z S_z. \quad (181)$$

The second term on the right of Eq. (181) is nonlinear, but it can be linearized by setting  $\varphi \rightarrow (2[I])^{-1}$ , the uniform population distribution for unpolarized atoms. Then we have

$$4 \sum_j \eta_j \langle S_{jz} \rangle \text{Tr} \varphi f_z S_z = (-1)^{a-f} \frac{2}{[I]^2} \text{Tr} f_z^2 \sum_j \eta_j \langle S_{jz} \rangle = (-1)^{a-f} \frac{2f(f+1)(2f+1)}{3[I]^2} \sum_j \frac{\eta_j}{[I_j]} (\langle a_{jz} \rangle - \langle b_{jz} \rangle). \quad (182)$$

The first term on the right of Eq. (181) is of the same form as the right side of Eq. (175), and will make a contribution analogous to Eq. (180). Thus, the linearized contribution to the relaxation matrix from spin exchange is

$$\begin{pmatrix} \langle a_i | \Gamma_{\text{ex}} | a_j \rangle & \langle a_i | \Gamma_{\text{ex}} | b_j \rangle \\ \langle b_i | \Gamma_{\text{ex}} | a_j \rangle & \langle b_i | \Gamma_{\text{ex}} | b_j \rangle \end{pmatrix} = \frac{\delta_{ij}}{2[I_i]^2 T_{\text{ex}}} \begin{pmatrix} [I_i]^2 - [I_i] + 2 & -[I_i]^2 - 3[I_i] - 2 \\ -[I_i]^2 + 3[I_i] - 2 & [I_i]^2 + [I_i] + 2 \end{pmatrix} + \frac{\eta_j}{6[I_i][I_j] T_{\text{ex}}} \begin{pmatrix} -[I_i]^2 - 3[I_i] - 2 & [I_i]^2 + 3[I_i] + 2 \\ [I_i]^2 - 3[I_i] + 2 & -[I_i]^2 + 3[I_i] - 2 \end{pmatrix}. \quad (183)$$

The spin-exchange rate  $1/T_{\text{ex}}$  is given by Eq. (106). Spin-exchange collisions couple the angular momenta of different isotopes to each other.

*Fundamental rate for relaxation in the dark.* To find the fundamental relaxation rate we assume exponentially damping solutions of the form

$$\langle f_{iz} \rangle = \langle f_i | n \rangle e^{-\gamma_n t}. \quad (184)$$

Substituting Eq. (184) into Eq. (171) we find the eigenvalue equation

$$\sum_{f'_i} \langle f_i | \Gamma | f'_i \rangle \langle f'_i | n \rangle = \gamma_n \langle f_i | n \rangle, \quad (185)$$

which can be solved numerically for the eigenvalues  $\gamma_1 \leq \gamma_2 \leq \dots \leq \gamma_{2N}$ . The fundamental time constant is  $T_1$

$= 1/\gamma_1$ . Here  $N$  is the number of different species of alkali-metal atoms, coupled by spin exchange in the vapor. For example,  $N=2$  for the natural isotopic mixture of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ .

For a monoisotopic alkali-metal vapor like Na or Cs, the matrix equation (185) is only two dimensional, and it can be solved to yield an explicit formula for the fundamental relaxation rate,

$$\begin{aligned} \gamma = & \frac{1}{[I]^2 T_{\text{FD}}} + \left( \frac{1}{2T_{\text{SD}}} + \frac{1}{3T_{\text{ex}}} \right) \left( 1 + \frac{2}{[I]^2} \right) \\ & - \left[ \left( \frac{1}{2T_{\text{SD}}} + \frac{1}{3T_{\text{ex}}} \right)^2 \left( 1 + \frac{2}{[I]^2} \right)^2 \right. \\ & \left. - \frac{2}{[I]^2 T_{\text{SD}}} \left( \frac{1}{T_{\text{SD}}} + \frac{1}{T_{\text{ex}}} \right) \right]^{1/2}. \quad (186) \end{aligned}$$

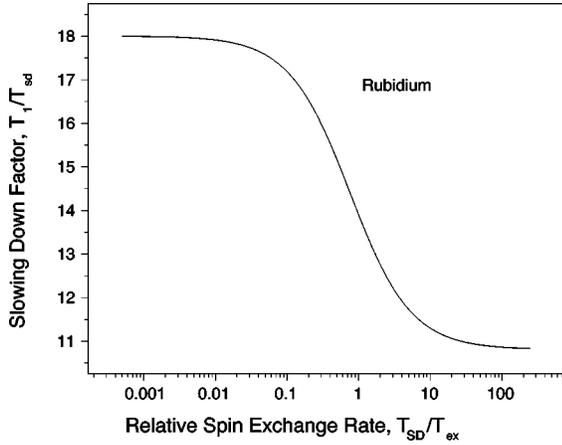


FIG. 3. The slowing-down factors  $T_1/T_{SD}$  for Rb vapor of natural isotopic abundance 72.15%  $^{85}\text{Rb}$  and 27.85%  $^{87}\text{Rb}$ , plotted as a function of the ratio  $T_{SD}/T_{ex}$  of the spin exchange rate  $1/T_{ex}$  to the S-damping rate  $1/T_{SD}$ . The F-damping rate  $1/T_{FD}$  was assumed to be negligibly small.

Under the conditions of spin-exchange optical pumping, van der Waals molecules are negligible for  $^3\text{He}$ , and for  $^{129}\text{Xe}$ , the gas pressures are sufficiently high that the F-damping rates are relatively small. So for  $^3\text{He}$ —and to a good approximation for  $^{129}\text{Xe}$ —the fundamental time constant  $T_1$  is determined by the S-damping rate  $1/T_{SD}$  and by the spin-exchange rate  $1/T_{ex}$ . We define the “slowing-down factor” as the ratio  $T_1/T_{SD}$  of the fundamental time constant  $T_1$  to the S-damping rate  $T_{SD}$ . For example, in Fig. 3 we have plotted the slowing-down factor for Rb vapor of natural isotopic abundance, as obtained from the smallest eigenvalue  $\gamma_1 = 1/T_1$  of Eq. (185) with  $1/T_{FD} = 0$ . The horizontal scale is the relative spin-exchange rate,  $T_{SD}/T_{ex}$  the ratio of the spin-exchange rate to the S-damping rate.

For fast relative spin-exchange rates  $T_{SD}/T_{ex} \gg 1$  the limiting value of the slowing-down factors of Fig. 2 can be obtained from the following simple arguments. When the spin-exchange rates (49) are large enough compared to other relaxation rates of the system, the alkali-metal atoms will continue to be described by the spin-temperature distribution (112) as the spin angular momentum is removed by the S-damping and F-damping collisions. We can find the limiting relaxation rate by taking the limit of Eq. (124) as  $P \rightarrow 0$ ,  $R \rightarrow 0$ , and  $\langle K_z \rangle \rightarrow 0$ . The limiting longitudinal relaxation rate  $1/T_1$  is then

$$\frac{1}{T_1} = \frac{1}{1 + \bar{\epsilon}(0)} \left( \frac{1}{T_{SD}} + \frac{\nu(0)}{T_{FD}} \right), \quad (187)$$

so the high-temperature slowing-down factor for negligible F damping is simply  $T_1/T_{SD} = 1 + \bar{\epsilon}(0)$ . For rubidium of natural isotopic composition ( $\eta_{85} = 0.7215$  and  $\eta_{87} = 0.2785$ ), we can use Table I together with Eqs. (125) and (126) to find the high-temperature slowing-down factor  $1 + \bar{\epsilon}(0) = 10.81$  and the F-damping coefficient  $\nu(0) = 0.3583$ .

## XII. SPATIAL DIFFUSION AND GRADIENT IMAGING

One of the most convenient ways to measure the polarization of an optically pumped alkali-metal vapor is to apply

a magnetic field gradient that causes the Larmor frequency of the atoms to vary across the pumping cell. As first shown by Tam [40], when resonant rf fields are applied to high-pressure, optically pumped vapors, “resonant surfaces” of precessing atoms are produced. The resonant surfaces are the loci of points where the applied rf frequency  $\omega$  is equal to a Zeeman resonance frequency  $\omega_f$  of the alkali-metal atoms. For high field gradients, the precessing atoms can be so localized that they diffuse away from the resonant surface before they relax due to optical pumping or spin-flip collisions.

To account for effects of spatial diffusion on the rf resonances, we reinsert the diffusion term into Eq. (146), which becomes

$$(\Lambda + in\omega - D\nabla^2)|\rho^{(n)}\rangle = |\sigma\rangle. \quad (188)$$

Here  $D$  is the spatial diffusion coefficient of the alkali-metal atoms in the gas, and we now think of the relaxation operator  $\Lambda = \Lambda(\mathbf{r})$ , the density vector  $|\rho^{(n)}\rangle = |\rho^{(n)}(\mathbf{r})\rangle$  and the source vector  $|\sigma\rangle = |\sigma(\mathbf{r})\rangle$  as functions of the position  $\mathbf{r}$  of the alkali-metal atoms in the cell.

The thickness  $b$  (half width at half maximum) of the layer of atoms precessing near a resonant surface decreases as the magnetic-field gradient  $\nabla B_z$  increases. The gradient is normally chosen to ensure that  $b \ll L$ , where  $L$  is a characteristic linear dimension of the cell. Define a unit vector, normal to the resonance surface, by

$$\mathbf{u} = \nabla B_z / |\nabla B_z|, \quad (189)$$

with the gradient evaluated at a point  $\mathbf{r}_s$  on the resonant surface. The displacement  $u$ , normal to the surface, of a point  $\mathbf{r}$  near  $\mathbf{r}_s$  is

$$u = (\mathbf{r} - \mathbf{r}_s) \cdot \mathbf{u}. \quad (190)$$

We assume that the transverse density matrix  $|\rho^{(\pm 1)}\rangle$  depends strongly on  $u$  but that its variation for displacements parallel to the resonant surface is negligible.

In accordance with Eq. (150),  $\Lambda$  has diagonal imaginary parts  $\text{Im}(f\bar{m}|\Lambda|f\bar{m}) = \omega_{f\bar{m}}$ . These are very nearly equal and opposite for the two Zeeman multiplets,  $\omega_{a\bar{m}} \approx -\omega_{b\bar{m}}$ . For most situations of interest in spin-exchange optical pumping we can neglect the dependence on the mean azimuthal quantum number  $\bar{m}$  and write

$$\partial\omega_{f\bar{m}}/\partial u = kn_f, \quad \text{where} \quad k = \frac{g_S\mu_B}{\hbar[T]} |\nabla B_z|. \quad (191)$$

In Eq. (191) we have assigned a precession-direction number  $n_f = (-1)^{a-f}$  to each multiplet. Thus, we can approximate the spatial dependence of the relaxation operator near a resonant surface as

$$\Lambda(\mathbf{r}) = \Lambda(\mathbf{r}_s) + iukN, \quad (192)$$

where the operator  $N$  is defined by  $N|f\bar{m}\rangle = n_f|f\bar{m}\rangle$ . As indicated in Eq. (192), it is possible to ignore the  $u$  dependence of all but the imaginary, diagonal matrix elements of  $\Lambda$ , which determine the magnetic resonance frequencies of the atoms. Then Eq. (188) becomes

$$\left[ \Lambda + i(n\omega + ukN) - D \frac{d^2}{du^2} \right] |\rho^{(n)}\rangle = |\sigma\rangle, \quad (193)$$

where the relaxation operator  $\Lambda$  and the source vector  $|\sigma\rangle$  are taken to be independent of  $u$  and equal to their values at  $\mathbf{r}_s$ . Multiplying Eq. (193) by the left eigenvector  $\{\lambda_f|\}$ , we obtain a set of scalar equations, one for each eigenvalue  $\lambda_f$  of  $\Lambda$ ,

$$\left[ \lambda_f + i(n\omega + ukn_f) - D \frac{d^2}{du^2} \right] \{\lambda_f|\rho^{(-n_f)}\rangle = \{\lambda_f|\sigma\rangle. \quad (194)$$

As discussed in connection with Eq. (157), there are resonant enhancements of the density matrix  $\rho^{(n)}$  in the multiplet  $f$  when  $n = -n_f$ . Each eigenvalue  $\lambda_f$  defines a resonant surface such that

$$\text{Im } \lambda_f(\mathbf{r}_s) = \omega n_f \quad (195)$$

for each point  $\mathbf{r}_s$  on the surface.

We introduce a dimensionless complex variable  $\zeta$  defined by

$$\zeta \Delta u = -iun_f - \gamma_f/k, \quad \text{where } \gamma_f = \text{Re } \lambda_f(\mathbf{r}_s). \quad (196)$$

The characteristic length is the positive cube root

$$\Delta u = (D/k)^{1/3}, \quad (197)$$

where the diffusion coefficient  $D$  and the Larmor-frequency gradient  $k$  of Eq. (191) are both positive. Then the solution of Eq. (194) subject to the boundary condition  $\{\lambda_f|\rho^{(-n_f)}\rangle \rightarrow 0$  as  $|u| \rightarrow \infty$  is

$$\{\lambda_f|\rho^{(-n_f)}\rangle = \frac{\pi}{k\Delta u} \{\lambda_f|\sigma\rangle \text{Hi}(\zeta), \quad (198)$$

where  $\text{Hi}$  is the solution of the inhomogeneous Airy equation [41,42]

$$\left( \frac{d^2}{d\zeta^2} - \zeta \right) \text{Hi} = \frac{1}{\pi}, \quad (199)$$

defined for all finite  $\zeta$  by

$$\text{Hi}(\zeta) = \frac{1}{\pi} \int_0^\infty e^{\zeta t - t^3/3} dt. \quad (200)$$

The integral extends along the real axis of the complex  $t$  plane.

One can substitute into Eq. (198) the identity

$$\int_V \text{Hi}(\zeta) d\zeta = i, \quad (201)$$

where the path of integration is any ‘‘vertical’’ line  $V$  parallel to the imaginary axis of the complex  $\zeta$  plane, to find

$$k \int_{-\infty}^\infty \{\lambda_f|\rho^{(-n_f)}\rangle du = \pi \{\lambda_f|\sigma\rangle. \quad (202)$$

Comparing Eq. (202) with the discussion of Eq. (163), we see that the area theorem remains rigorously valid when diffusion is taken into account and the simple poles of Eq. (151) are replaced by  $\text{Hi}$  in Eq. (198).

As the displacement  $u$  of Eq. (190) varies, the complex variable  $\zeta$  of Eq. (196) always lies to the left of the imaginary axis in the complex  $\zeta$  plane, and the minimum value of  $|\zeta|$  is  $\gamma_f/(k\Delta u)$ . If  $\gamma_f/(k\Delta u) \gg 1$ , we can substitute into Eq. (198) the asymptotic expansion

$$\text{Hi}(\zeta) \sim -\frac{1}{\pi\zeta} - \dots, \quad \text{for } \arg \zeta > \frac{\pi}{3} \quad \text{and} \quad |\zeta| \gg 1, \quad (203)$$

to find

$$\{\lambda_f|\rho^{(-n_f)}\rangle \sim \frac{\{\lambda_f|\sigma\rangle}{\lambda_f + ikun_f - i\omega n_f}, \quad (204)$$

which is the same as Eq. (151).

For a given damping rate  $\gamma_f$  and diffusion coefficient  $D$  we may define a crossover gradient  $k_c$  and a crossover width  $b_c$  by

$$k_c = \sqrt{\frac{\gamma_f^3}{D}} \quad \text{and} \quad b_c = \sqrt{\frac{D}{\gamma_f}}. \quad (205)$$

Then the relative gradient  $\kappa$  and the relative width  $\beta$  are

$$\kappa = k/k_c \quad \text{and} \quad \beta = b/b_c. \quad (206)$$

In view of Eq. (198) the relative width  $\beta$  of the resonating atoms, for a given relative gradient  $\kappa$ , can be defined as the solution of

$$2 \text{Re } \text{Hi}(i\beta\kappa^{1/3} - \kappa^{-2/3}) = \text{Hi}(-\kappa^{-2/3}). \quad (207)$$

The context will make clear whether  $\beta$  is the relative width of Eq. (206) or the unrelated spin-temperature parameter of Eq. (115). From inspection of Eq. (203) and from the fact that  $2 \text{Re } \text{Hi}(1.29i) = \text{Hi}(0)$  we find the limiting solutions

$$\beta \rightarrow \begin{cases} \kappa^{-1} & \text{for } \kappa \ll 1 \\ 1.29\kappa^{-1/3} & \text{for } \kappa \gg 1. \end{cases} \quad (208)$$

The function  $\beta(\kappa)$  defined by Eq. (207) is plotted in Fig. 4. For spin-exchange optical pumping, a representative diffusion coefficient would be  $D \approx 0.04 \text{ cm}^2 \text{ sec}^{-1}$  and a representative damping rate would be  $\gamma_f = 3 \times 10^4 \text{ sec}^{-1}$ . Then the crossover Larmor-frequency gradient would be  $k_c = 2.6 \times 10^7 \text{ sec}^{-1} \text{ cm}^{-1}$ . In view of Eq. (191), for  $^{85}\text{Rb}$  with  $I = 5/2$ , the crossover magnetic-field gradient would be  $\nabla B_z = 8.9 \text{ G cm}^{-1}$ . Such large field gradients are seldom used in practice. The crossover width would be  $b_c = 1.2 \times 10^{-3} \text{ cm}$  or  $12 \text{ } \mu\text{m}$ .

#### APPENDIX A: VAN DER WAALS MOLECULES

We will be interested in a  $^{129}\text{Xe}$  bound to an alkali-metal atom. The rate of change of the density vector of the pair is given by

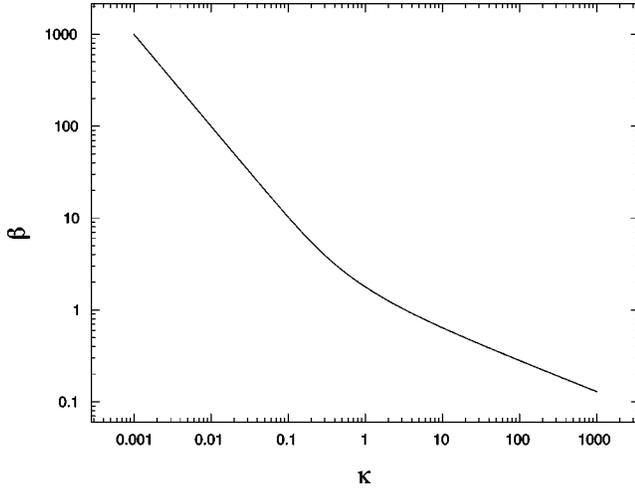


FIG. 4. The relative width (half width at half maximum)  $\beta = b/b_c$  of the layer of resonating atoms for gradient imaging, plotted as a function of the relative spatial gradient  $\kappa = k/k_c$  of the Larmor frequency. For small gradients,  $k \ll k_c$ , diffusion effects are negligible and  $\beta$  decreases as  $\kappa^{-1}$ . For large gradients,  $k \gg k_c$ ,  $\beta$  is limited by diffusion and decreases only as  $1.29\kappa^{-1/3}$ .

$$i\hbar \frac{d}{dt} |\rho\rangle = ([H] + [V]) |\rho\rangle. \quad (\text{A1})$$

Here the Hamiltonian  $H$  is the sum of Eqs. (2) and (8):

$$H = H_g + H_{\text{NG}}, \quad (\text{A2})$$

and the perturbation is the sum of (10) and (11)

$$V = \gamma \mathbf{N} \cdot \mathbf{S} + \alpha \mathbf{K} \cdot \mathbf{S}. \quad (\text{A3})$$

The Liouville-space operators  $[H]$  and  $[V]$  of Eq. (A1) are defined in terms of corresponding Schrödinger-space operators by Eq. (26).

We transform from the Schrödinger-picture density vector  $|\rho\rangle$  to the interaction-picture density vector

$$|\tilde{\rho}\rangle = e^{i[H]t/\hbar} |\rho\rangle. \quad (\text{A4})$$

When Eq. (A4) is substituted into Eq. (A1) we find

$$i\hbar \frac{d}{dt} |\tilde{\rho}\rangle = [\tilde{V}] |\tilde{\rho}\rangle, \quad (\text{A5})$$

where

$$[\tilde{V}] = e^{i[H]t/\hbar} [V] e^{-i[H]t/\hbar}. \quad (\text{A6})$$

For an ensemble of molecules formed at time  $t$ , the mean change in  $\tilde{\rho}$  after the molecule has been broken up by a collision at time  $t_m$ , can be found from the perturbation-series solution of Eq. (A5),

$$\begin{aligned} \tilde{\Delta} |\tilde{\rho}\rangle &= \int_t^\infty \frac{dt_m}{\tau} e^{-(t_m-t)/\tau} [\tilde{\rho}(t_m)] - |\tilde{\rho}\rangle \\ &= (\tilde{\Delta}^{(1)} + \tilde{\Delta}^{(2)} + \dots) |\tilde{\rho}\rangle. \end{aligned} \quad (\text{A7})$$

The increment has been averaged over the distribution (65) of molecular breakup times. In Eq. (A7) the density operator  $\tilde{\rho} = \tilde{\rho}(t)$  at the time  $t$  of formation of the molecule is a simple product of the density operator  $\tilde{\rho}_A = \tilde{\rho}_A(t)$  of the alkali-metal atoms and the density operator  $\tilde{\rho}_{\text{Xe}} = \tilde{\rho}_{\text{Xe}}(t)$  of the  $^{129}\text{Xe}$  atoms

$$\tilde{\rho} = \tilde{\rho}_A \tilde{\rho}_{\text{Xe}}. \quad (\text{A8})$$

The lowest-order terms of the increment operator are

$$\tilde{\Delta}^{(1)} = \int_t^\infty \frac{dt_m}{\tau} e^{-(t_m-t)/\tau} \frac{1}{i\hbar} \int_t^{t_m} dt' [\tilde{V}'] \quad (\text{A9})$$

and

$$\tilde{\Delta}^{(2)} = \int_t^\infty \frac{dt_m}{\tau} e^{-(t_m-t)/\tau} \frac{1}{(i\hbar)^2} \int_t^{t_m} dt'' [\tilde{V}''] \int_t^{t''} dt' [\tilde{V}']. \quad (\text{A10})$$

Here  $[V'] = [V(t')]$  and  $[V''] = [V(t'')]$ .

To find the evolution of alkali-metal atoms we multiply  $\Delta |\rho\rangle$  by the formation rate  $1/T_{\text{vWA}}$  per alkali-metal atom, trace over the spin states of the  $^{129}\text{Xe}$  nucleus, and take an ensemble average over the vibrational and rotational states of the van der Waals molecules to find (in matrix space)

$$\frac{d\rho_A}{dt} = \frac{1}{T_{\text{vWA}}} \langle \text{Tr}_x \Delta \rho_A \rho_{\text{Xe}} \rangle_n. \quad (\text{A11})$$

We have reverted to the Schrödinger picture in Eq. (A11), as signified by dropping the “tilde” symbol over the operators. The corresponding rate of change of the density matrix for the  $^{129}\text{Xe}$  atoms is obtained from Eq. (A11) by interchanging the atom indices  $x$  and  $a$ . The averages over the directions of  $\mathbf{N}$ , denoted by  $\langle \dots \rangle_n$  are

$$\langle N_i \rangle_n = 0, \quad \text{and} \quad \langle N_i N_j \rangle_n = \frac{N^2}{3} \delta_{ij}, \quad (\text{A12})$$

where  $i$  and  $j$  denote projections on the Cartesian axes  $i$  and  $j$  of a laboratory-fixed coordinate system.

In view of Eq. (A12) the ensemble average of the first-order increment Eq. (A9) is simply

$$\Delta^{(1)} = \frac{\tau}{i\hbar} \alpha [\mathbf{K} \cdot \mathbf{S}]. \quad (\text{A13})$$

We label the  $16[I]^2$  independent basis operators  $|i\rangle = |f_i m_i q_i\rangle \langle f'_i m'_i q'_i|$  by a single index  $i$  and we label the eigenfrequencies by the same index,  $\hbar \Omega_i = E(f_i m_i) - E(f'_i m'_i) + \hbar \omega_K (q_i - q'_i)$ , where  $q_i$  and  $q'_i$  are azimuthal quantum numbers of the nucleus, as defined by Eq. (9). Then

$$[H] |i\rangle = \hbar \Omega_i |i\rangle. \quad (\text{A14})$$

Using the completeness property  $\sum_i |i\rangle \langle i| = 1$ , we may evaluate the expression (A10) for  $\tilde{\Delta}^{(2)}$  by steps:

$$\int_t^{t''} dt' [\tilde{V}'] = |j\rangle [V]_{ji} \langle i| \frac{e^{i\Omega_{ji}t''} - e^{i\Omega_{ji}t}}{i\Omega_{ji}}, \quad (\text{A15})$$

where

$$\Omega_{ji} = \Omega_j - \Omega_i, \quad (\text{A16})$$

with the characteristic frequencies  $\Omega_j$  and  $\Omega_i$  defined by Eq. (A14).

In like manner

$$\begin{aligned} & \int_t^{t_m} dt'' [\tilde{V}''] \int_t^{t''} dt' [\tilde{V}'] \\ &= |k\rangle [V]_{kj} [V]_{ji} \\ & \times \langle i | \frac{e^{i\Omega_{ki}t}}{\Omega_{ji}} \left\{ \frac{e^{i\Omega_{ki}(t_m-t)} - 1}{i\Omega_{ki}} - \frac{e^{i\Omega_{kj}(t_m-t)} - 1}{i\Omega_{kj}} \right\}. \end{aligned} \quad (\text{A17})$$

Carrying out the final integral of Eq. (A10) over the distribution of molecular breakup times  $t_m$  we find

$$\tilde{\Delta}_{ki}^{(2)} = -\frac{\tau^2}{\hbar^2} \sum_j \frac{[V]_{kj} [V]_{ji} e^{i\Omega_{ki}t}}{(1 - i\Omega_{ki}\tau)(1 - i\Omega_{kj}\tau)}. \quad (\text{A18})$$

Define a hyperfine coherence operator  $[\hat{n}]$  and coherence number  $n_k = 0, \pm 1$  for the polarization state  $|k\rangle$  by

$$[\hat{n}]|k\rangle = n_k|k\rangle \quad \text{where} \quad n_k = f_k - f'_k. \quad (\text{A19})$$

In the limit of low magnetic fields, one can readily verify that  $\hat{n} = \mathbf{F} \cdot \mathbf{F} / [I]$ . Since it is used in a commutator,  $\hat{n}$  is defined only to within an arbitrary, additive constant term.

We will be interested in spin-polarized alkali-metal vapors with no hyperfine coherence, that is, vapors for which  $\langle i|\rho\rangle = 0$  when  $n_i = \pm 1$ . Then we may limit the sum in Eq. (A18) to those indices  $k$  and  $i$  for which  $n_k = 0$  and  $n_i = 0$ . The sum over intermediate states  $j$  in Eq. (A18) is unrestricted since there can be important contributions from virtually excited states with  $n_j = \pm 1$  as well as from states with  $n_j = 0$ . Under the conditions of spin-exchange optical pumping (i.e., a few tens of Gauss or less for  $B_z$  and several atmospheres of buffer gas) the molecular lifetimes  $\tau \sim 10^{-10}$  sec, and the Zeeman spin precession frequencies  $\omega_K \sim 10^5 \text{ sec}^{-1}$  and  $g_S \mu_B B_z / ([I]\hbar) \sim 10^8 \text{ sec}^{-1}$  are small enough that it is a good approximation to set  $\Omega_{ij}\tau \approx (n_i - n_j)\omega_{\text{hf}}\tau$ . Consequently, Eq. (A18) can be written to good approximation as

$$\Delta^{(2)} = -\frac{\tau^2}{\hbar^2} \sum_{nm} [V^{(n)}] \frac{1}{1 + im\omega_{\text{hf}}\tau} [V^{(m)}]. \quad (\text{A20})$$

We have written the perturbation as the sum of three terms

$$V = \sum_{n=-1}^1 V^{(n)}, \quad (\text{A21})$$

where  $n$  is the hyperfine coherence number and

$$V^{(n)} = \sum_{fmm'} |f+n, m\rangle \langle f+n, m| V |f, m'\rangle \langle f, m'|. \quad (\text{A22})$$

The bras and kets in Eq. (A22) are defined by Eq. (3). Terms in the sum are omitted unless the indices are within their permissible range, for example,  $f+n = I \pm 1/2$ ,  $|m| \leq f+n$ , and  $m' \leq f = I \pm 1/2$ , etc.

We may write Eq. (A20) as the sum of four terms

$$\Delta^{(2)} = \Delta_S^{(2)} + \Delta_F^{(2)} + \Delta_X^{(2)} + \Delta_Y^{(2)}, \quad (\text{A23})$$

where

$$\Delta_S^{(2)} = -\frac{\tau^2 f_S}{\hbar^2} [V][V], \quad (\text{A24})$$

$$\Delta_F^{(2)} = -\frac{\tau^2 f_F}{\hbar^2} [V^{(0)}][V^{(0)}], \quad (\text{A25})$$

$$\Delta_X^{(2)} = \frac{i\omega_{\text{hf}}\tau^3/\hbar^2}{1 + (\omega_{\text{hf}}\tau)^2} ([V^{(1)}][V^{(-1)}] - [V^{(-1)}][V^{(1)}]), \quad (\text{A26})$$

$$\Delta_Y^{(2)} = \frac{\tau^2}{\hbar^2} \sum_{n+m \neq 0} [V^{(n)}][V^{(m)}] \left( \frac{1}{1 + (\omega_{\text{hf}}\tau)^2} - \frac{1}{1 + im\omega_{\text{hf}}\tau} \right). \quad (\text{A27})$$

The molecular fractions  $f_S$  and  $f_F$  were defined in Eqs. (70) and (71). The term  $\Delta_Y^{(2)}$  of Eq. (A27) can be ignored, since it adds hyperfine coherence that averages to zero because of the rapid, incoherent oscillations at the frequency  $\omega_{\text{hf}}$ .

We shall presently show that  $\Delta_X^{(2)}$  is negligible, so we set  $\Delta \rightarrow \Delta^{(1)} + \Delta_S^{(2)} + \Delta_F^{(2)}$  in Eq. (A7) to find

$$\begin{aligned} \Delta|\rho\rangle &= \frac{\tau}{i\hbar} \alpha [\mathbf{K} \cdot \mathbf{S}] |\rho\rangle \\ & - \frac{\tau^2}{\hbar^2} \langle f_S [V][V] + f_F [V^{(0)}][V^{(0)}] \rangle |\rho\rangle. \end{aligned} \quad (\text{A28})$$

Equivalently, in matrix space

$$\begin{aligned} \Delta\rho &= \frac{\tau}{i\hbar} \alpha [\mathbf{K} \cdot \mathbf{S}, \rho] - \frac{\tau^2}{T_{\text{vw}}\hbar^2} (f_S [V, [V, \rho]] \\ & + f_F [V^{(0)}, [V^{(0)}, \rho]]). \end{aligned} \quad (\text{A29})$$

Because  $\langle N_i \rangle_n = 0$ , cross terms between  $\gamma \mathbf{N} \cdot \mathbf{S}$  and  $\alpha \mathbf{K} \cdot \mathbf{S}$  from Eq. (A28) or Eq. (A29) will average to zero. The spin-rotation interaction (10) and nuclear-electron spin exchange interaction (11) will contribute independently to the relaxation. Substituting Eq. (A29) into Eq. (A11) we find that the contribution of the spin-rotation interaction (10) is

$$\frac{d\rho}{dt} = \frac{2\phi_\gamma^2 f_S}{3T_{\text{vw},A}} (\mathbf{S} \cdot \rho \mathbf{S} - \mathbf{S} \cdot \mathbf{S} \rho) + \frac{2\phi_\gamma^2 f_F}{3[I]^2 T_{\text{vw},A}} (\mathbf{F} \cdot \rho \mathbf{F} - \mathbf{F} \cdot \mathbf{F} \rho), \quad (\text{A30})$$

which is Eq. (72), with the mean squared phase angle  $\phi_\gamma^2$  defined by Eq. (74). The density matrix in Eq. (A30) is that of the alkali-metal atoms,  $\rho = \rho_a$ . In simplifying Eq. (A30)

we made use of the angular momentum projection theorem  $\mathbf{S} = \pm \mathbf{F}/[I]$ ; the  $\pm$  signs are taken for matrix elements between states with  $F = I \pm 1/2$ .

Similarly, the nuclear-electron spin exchange interaction (11) causes the evolution

$$\begin{aligned} \frac{d\rho}{dt} = & \frac{f_S \phi_\alpha^2 \eta_x}{2T_{\text{vw},A}} (\mathbf{S} \cdot \rho \mathbf{S} - \mathbf{S} \cdot \mathbf{S} \rho + [\{\mathbf{S}, \rho\} - 2i\mathbf{S} \times \rho \mathbf{S}] \cdot \langle \mathbf{K} \rangle) \\ & + \frac{f_F \phi_\alpha^2}{2[I]^2 T_{\text{vw},A}} (\mathbf{F} \cdot \rho \mathbf{F} - \mathbf{F} \cdot \mathbf{F} \rho + [\{\mathbf{F}, \rho\} - 2i\mathbf{F} \\ & \times \rho \mathbf{F}] \cdot \langle \mathbf{K} \rangle) + \frac{\eta_x \tau \langle \alpha \rangle}{i\hbar T_{\text{vw},A}} [\langle \mathbf{K} \rangle \cdot \mathbf{S}, \rho], \end{aligned} \quad (\text{A31})$$

which is Eq. (73), with the mean squared phase angle  $\phi_\alpha^2$  defined by Eq. (74). The effective magnetic field of Eq. (73) is given by

$$g_S \mu_B \delta \mathbf{B}_{\text{vw},A} = \frac{\eta_x \tau \langle \alpha \rangle}{T_{\text{vw},A}} \langle \mathbf{K} \rangle. \quad (\text{A32})$$

In like manner, the evolution of the nuclear spin of the  $^{129}\text{Xe}$  atoms is found to be

$$\begin{aligned} \frac{d}{dt} \langle \mathbf{K} \rangle = & \frac{f_F \phi_\alpha^2}{2[I]^2 T_{\text{vw},\text{Xe}}} (\langle \mathbf{F} \rangle - \langle 2\mathbf{F} \cdot \mathbf{F} - \mathbf{F}\mathbf{F} - (\mathbf{F}\mathbf{F})^\dagger \cdot \rangle \langle \mathbf{K} \rangle) \\ & + \frac{f_S \phi_\alpha^2}{2T_{\text{vw},\text{Xe}}} (\langle \mathbf{S} \rangle - \langle \mathbf{K} \rangle) + \frac{\tau \langle \alpha \rangle}{\hbar T_{\text{vw},\text{Xe}}} \langle \mathbf{S} \rangle \times \mathbf{K}. \end{aligned} \quad (\text{A33})$$

For spin exchange with alkali-metal atoms of several isotopic species, like  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ , Eq. (A33) is replaced by an isotopic average; an isotopic index  $i$  is added to the quantities representing the alkali-metal atoms, ( $I \rightarrow I_i$ ,  $\mathbf{F} \rightarrow \mathbf{F}_i$ ,  $\mathbf{S} \rightarrow \mathbf{S}_i$ ), and both sides of Eq. (A33) are multiplied by  $\sum_i \eta_i$ . If the polarizations are longitudinal and the alkali-metal atoms have the spin-temperature distribution (112), Eq. (A33) reduces to

$$\frac{d}{dt} \langle K_z \rangle = \frac{\phi_\alpha^2}{2T_{\text{vw},\text{Xe}}} (f_S + \nu(P) f_F) (\langle S_z \rangle - \langle K_z \rangle), \quad (\text{A34})$$

where the coefficient  $\nu(P)$  was defined by Eq. (126).

It remains to show that  $\Delta_X^{(2)}$  of Eq. (A26) represents a negligible frequency shift. Multiplying Eq. (A26) on the right by  $|\rho\rangle$ , we find

$$\Delta_X^{(2)} |\rho\rangle = \frac{i \omega_{\text{hf}} \tau^3 / \hbar^2}{1 + (\omega_{\text{hf}} \tau)^2} [(V^{(1)} V^{(-1)} - V^{(-1)} V^{(1)}) \rho], \quad (\text{A35})$$

From Eq. (A22) we find that

$$\begin{aligned} V^{(1)} V^{(-1)} = & \sum_{mm'm''} |am\rangle \langle am| V |bm'\rangle \langle bm'| V |am''\rangle \langle am''| \\ = & \sum_{mm''} |am\rangle \langle am| V V - V^{(0)} V^{(0)} |am''\rangle \langle am''|. \end{aligned} \quad (\text{A36})$$

Taking an ensemble average of Eq. (A36) over the directions of  $\mathbf{N}$  we find

$$\begin{aligned} \langle V^{(1)} V^{(-1)} \rangle_n = & \left( \frac{(\gamma N)^2}{3} + \frac{\alpha^2}{4} \right) \left( \frac{3}{4} - \frac{a(a+1)}{[I]^2} \right) \\ & \times \sum_m |am\rangle \langle am| - \frac{\alpha^2 I}{[I]^2} K_z a_z. \end{aligned} \quad (\text{A37})$$

In like manner

$$\begin{aligned} \langle V^{(-1)} V^{(1)} \rangle_n = & \left( \frac{(\gamma N)^2}{3} + \frac{\alpha^2}{4} \right) \left( \frac{3}{4} - \frac{b(b+1)}{[I]^2} \right) \\ & \times \sum_m |bm\rangle \langle bm| + \frac{\alpha^2 (I+1)}{[I]^2} K_z b_z. \end{aligned} \quad (\text{A38})$$

Here we denote the projection of  $F_z$  in the multiplet  $f = a$  by  $a_z = \sum |am\rangle \langle am| m$ , with an analogous definition of  $b_z$ . Substituting Eqs. (A35), (A37), and (A38) into Eq. (A11) we find for the alkali-metal atoms

$$\frac{d\rho}{dt} = \frac{(\omega_{\text{hf}} \tau) \phi_\alpha^2 \langle K_z \rangle}{i[1 + (\omega_{\text{hf}} \tau)^2][I]^2 T_{\text{vw},A}} [I a_z - (I+1) b_z] \rho. \quad (\text{A39})$$

The corresponding evolution of the density matrix of the noble-gas atoms is

$$\frac{d\rho}{dt} = \frac{(\omega_{\text{hf}} \tau) \phi_\alpha^2 [I a_z - (I+1) b_z]}{i[1 + (\omega_{\text{hf}} \tau)^2][I]^2 T_{\text{vw},\text{Xe}}} [K_z, \rho]. \quad (\text{A40})$$

These second-order frequency shifts can be ignored since they are smaller than the first-order shifts from Eq. (A13) by a factor of order  $(\phi_\alpha^2)^{1/2} \ll 1$ .

## APPENDIX B: OPTICAL PUMPING AND LIGHT SHIFTS

We may think of the  $D_1$  pumping light as an incoherent superposition of  $\sigma_\pm$  circularly polarized photons. Let the mean photon spin be  $\mathbf{s} = s \boldsymbol{\zeta}$ . Then a fraction  $(1 \pm s)/2$  of the photons has circular polarization  $\sigma_\pm$  with respect to the unit vector  $\boldsymbol{\zeta}$  along the direction of the mean photon spin (normally the direction of propagation of the pumping light). The high buffer-gas density will broaden the optical absorption line so much that the hyperfine structure is completely unresolved. This means that the correlation time for the absorption of a photon is very short compared to the hyperfine coupling periods. The excitation is very nearly sudden with respect to the nuclear polarization.

Denote by  $|m\rangle$  and  $|m\rangle$  electronic sublevels with azimuthal quantum number  $m = \pm 1/2$  (with respect to  $\boldsymbol{\zeta}$ ) of the  $^2S_{1/2}$  ground state and of the  $^2P_{1/2}$  excited state, respectively. The  $\sigma_\pm$  photons will not excite the ground-state sublevels  $|\pm 1/2\rangle$  because of angular-momentum selection rules, but the  $|\mp 1/2\rangle$  sublevels will be excited to the sublevels  $|\pm 1/2\rangle$ . Therefore, the evolution rate of the excited-state density matrix is given by

$$\frac{d}{dt}\rho_e = R \sum_m (1+2ms)|m\rangle\langle -m|\rho_g| -m\rangle\langle m|. \quad (\text{B1})$$

Using the expression (39) for  $\rho_g$ , and noting that  $\sum|m\rangle\langle m|=1$  and  $\sum m|m\rangle\langle m|=J_\zeta$ , we can rewrite Eq. (B1), the source term for excited atoms, as

$$\begin{aligned} \frac{d}{dt}|\rho_e\rangle = |Q_e\rangle = \sum_{\lambda\mu} |\lambda\mu 00\rangle\langle \lambda\mu 00|Q_e\rangle \\ + \sum_{\lambda\mu} |\lambda\mu 10\rangle\langle \lambda\mu 10|Q_e\rangle, \end{aligned} \quad (\text{B2})$$

where the nuclear part of the source term is

$$\sum_{\lambda\mu} |\lambda\mu 00\rangle\langle \lambda\mu 00|Q_e\rangle = R|\varphi - s\Theta_\zeta/2\rangle, \quad (\text{B3})$$

and the electronic part is

$$\sum_{\lambda\mu} |\lambda\mu 10\rangle\langle \lambda\mu 10|Q_e\rangle = R[2s\varphi - \Theta_\zeta]J_\zeta. \quad (\text{B4})$$

The Liouville-space bra and ket vectors of Eqs. (B2)–(B4) are quantized with respect to the azimuthal axis  $\zeta$ , and the multipole basis states  $|\lambda\mu lm\rangle$  were defined by Eq. (41).

Once created by optical pumping, the spin state of the excited atom will evolve because of three main influences:  $J$ -damping collisions of excited atoms with buffer gas atoms, quenching collisions of excited atoms with  $\text{N}_2$  or  $\text{H}_2$  molecules, and hyperfine coupling between the nucleus and the electrons of the excited atoms.

$J$ -damping collisions with buffer gas atoms or molecules will randomize the direction of  $\mathbf{J}$  at a rate  $1/T_J$ . As an example, consider a cell with a He density of 10 amagats and a temperature of 100 C. Taking a  $J$ -damping cross section for collisions of  $\text{Rb}(5^2P_{1/2})$  atoms with He atoms to be  $23 \times 10^{-16} \text{ cm}^2$  [43] and a mean relative RbHe velocity of  $v = 1.40 \times 10^5 \text{ cm sec}^{-1}$ , we would have

$$\frac{1}{T_J} = 8.7 \times 10^{10} \text{ sec}^{-1}, \quad (\text{B5})$$

or about 11.5 psec between  $J$ -damping collisions. As a result of  $J$ -damping collisions, the excited-state density matrix will evolve as

$$\frac{d}{dt}|\rho_e\rangle = -\frac{1}{T_J} \sum_{\lambda\mu m} |\lambda\mu 1m\rangle\langle \lambda\mu 1m|\rho_e\rangle. \quad (\text{B6})$$

The  $J$ -damping process described by Eq. (B6) is completely analogous to the  $S$ -damping process (54), which can be written in a form analogous to Eq. (B6) with the aid of Eqs. (39) and (43). The relaxation due to  $J$  damping of Eq. (B6) is sudden with respect to nuclear polarization.

Quenching collisions with molecular buffer gases like  $\text{N}_2$  or  $\text{H}_2$  will deexcite the atoms at a rate  $1/T_Q$ , which is independent of the excited-state spin polarization, so the evolution rate is simply

$$\frac{d}{dt}|\rho_e\rangle = -\frac{1}{T_Q}|\rho_e\rangle. \quad (\text{B7})$$

To avoid spin depolarization due to radiative trapping, enough quenching gas is added to ensure that excited atoms, decaying with the natural radiative lifetime  $\tau \approx 25 \text{ nsec}$ , are much more likely to be quenched than to radiate a photon. A representative quenching rate is

$$\frac{1}{T_Q} = 10^9 \text{ sec}^{-1}, \quad (\text{B8})$$

which would correspond to a fluorescent branching rate of about 2.5%.

Hyperfine coupling of  $\mathbf{I}$  and  $\mathbf{J}$  in the excited state and magnetic-dipole coupling of  $\mathbf{J}$  to the longitudinal field  $B_z$  will cause some coupling of the nuclear and electronic spin polarization. The corresponding evolution of the density matrix is given in analogy to Eq. (27) by

$$i\hbar \frac{d}{dt}|\rho_e\rangle = [H_e]|\rho_e\rangle, \quad (\text{B9})$$

where the Hamiltonian (7) for the excited state can be approximated adequately by

$$H_e \approx A_e \mathbf{I} \cdot \mathbf{J}. \quad (\text{B10})$$

In most spin-exchange optical pumping experiments, the static field  $B_z$  will be small enough to be neglected, as indicated in Eq. (B10). The hyperfine coupling in the first excited  $^2P_{1/2}$  state is relatively large. For example, for the  $5^2P_{1/2}$  of  $^{85}\text{Rb}$

$$\frac{A_e}{\hbar} = 7.6 \times 10^8 \text{ sec}^{-1} \sim \frac{1}{T_Q} \ll \frac{1}{T_J}. \quad (\text{B11})$$

The net rate of change of the density matrix  $|\rho_e\rangle$  is obtained by summing the right-hand sides of Eqs. (B2), (B6), (B7), and (B9) to find

$$\frac{d}{dt}|\rho_e\rangle = \left( -\Gamma + \frac{1}{i\hbar}[H_e] \right) |\rho_e\rangle + |Q_e\rangle. \quad (\text{B12})$$

The relaxation operator is

$$\Gamma = \sum_{\lambda\mu lm} \gamma_l |\lambda\mu lm\rangle\langle \lambda\mu lm|, \quad (\text{B13})$$

and the decay rates  $\gamma_0$  for purely nuclear polarization and  $\gamma_1$  for electronic polarization are

$$\begin{aligned} \gamma_0 &= \frac{1}{T_Q} \sim 10^9 \text{ sec}^{-1}, \\ \gamma_1 &= \frac{1}{T_Q} + \frac{1}{T_J} \sim 10^{11} \text{ sec}^{-1}. \end{aligned} \quad (\text{B14})$$

Denote a Laplace transform—for example, of  $\rho_e$ —by

$$\tilde{\rho}_e = \int_0^\infty \rho_e e^{-\sigma t} dt. \quad (\text{B15})$$

The well-known inverse transformation is

$$\rho_e = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \tilde{\rho}_e e^{\sigma t} d\sigma, \quad (\text{B16})$$

Here  $\rho_e$  and  $\tilde{\rho}_e$  are functions of  $t$  and  $\sigma$ , respectively, and in Eq. (B16)  $a$  is a constant such that all singularities of  $\tilde{\rho}_e$  lie to the left of the vertical path of integration in the complex  $\sigma$  plane. Then the Laplace transform of Eq. (B12) has the formal solution

$$|\tilde{\rho}_e\rangle = \left( \Gamma + \sigma - \frac{1}{i\hbar} [H_e] \right)^{-1} |\tilde{Q}_e\rangle + |\rho_{e0}\rangle. \quad (\text{B17})$$

Henceforth, we shall neglect  $\rho_{e0}$ , the value of the excited-state density matrix at time  $t=0$ . This is because we will be interested in values of the density matrix at times  $t \gg T_Q$ , when initial transients have decayed away to negligible values. Since  $|\Gamma + \sigma| \gg |[H_e]/i\hbar|$ , we may expand the inverse operator of Eq. (B17) in a power series to find

$$|\tilde{\rho}_e\rangle = \sum_{n=0}^{\infty} \left( \frac{(\Gamma + \sigma)^{-1} [H_e]}{i\hbar} \right)^n (\Gamma + \sigma)^{-1} |\tilde{Q}_e\rangle = \sum_{n=0}^{\infty} |\tilde{\rho}_e^{(n)}\rangle. \quad (\text{B18})$$

Combining Eqs. (B13) and (B18) we see that to zeroth order

$$|\tilde{\rho}_e^{(0)}\rangle = (\Gamma + \sigma)^{-1} |\tilde{Q}_e\rangle = \sum_{\lambda\mu l} (\gamma_l + \sigma)^{-1} |\lambda\mu l 0\rangle \langle \lambda\mu l 0 | \tilde{Q}_e\rangle. \quad (\text{B19})$$

Using Eq. (B16) we may invert Eq. (B19), which has simple poles at  $\sigma = -\gamma_l$ , to find

$$|\rho_e^{(0)}\rangle = \sum_{\lambda\mu l} |\lambda\mu l 0\rangle \int_{-\infty}^t \langle \lambda\mu l 0 | \tilde{Q}_e'\rangle e^{-\gamma_l(t-t')} dt', \quad (\text{B20})$$

where  $Q_e' = Q_e(t')$  is the source term at time  $t'$ .

In view of Eq. (B14), for comparable nuclear and electronic source terms the purely nuclear part of  $|\rho_e^{(0)}\rangle$  with  $l=0$  is about 100 times larger than the electronic part with  $l=1$ , so a good approximation of Eq. (B20) is

$$\begin{aligned} |\rho_e^{(0)}\rangle &\approx \sum_{\lambda\mu} |\lambda\mu 00\rangle \int_{-\infty}^t \langle \lambda\mu 00 | \tilde{Q}_e'\rangle e^{-(t-t')/T_Q} dt' \\ &= RT_Q |\varphi - s\Theta_\zeta/2\rangle + \frac{1}{i\hbar} [\delta\mathcal{E}_r] T_Q |\rho\rangle. \end{aligned} \quad (\text{B21})$$

To correct for writing the excited state at time  $t$  in terms of the source term  $\varphi - s\Theta_\zeta/2$  at exactly the same time  $t$ , we have added the ‘‘retardation correction’’

$$\begin{aligned} \frac{1}{i\hbar} [\delta\mathcal{E}_r] T_Q |\rho\rangle &= R \int_{-\infty}^t (\varphi' - \varphi - s[\Theta_\zeta' - \Theta_\zeta]/2) \\ &\quad \times e^{-(t-t')/T_Q} dt'. \end{aligned} \quad (\text{B22})$$

From Eq. (B18) we see that the first-order contribution is

$$|\rho_e^{(1)}\rangle = \frac{(\Gamma + \sigma)^{-1} [H_e]}{i\hbar} |\rho_e^{(0)}\rangle. \quad (\text{B23})$$

If we approximate  $\rho_e^{(0)}$  with the purely nuclear operator of Eq. (B21), the first-order correction will be purely electronic and of order  $A_e T_Q / \hbar \sim 1$  compared to the zeroth-order, purely nuclear contribution (B21). However, the time  $T_Q \sim 10^{-12}$  sec of a quenching collision is long enough for the spin-orbit and anisotropic Coulomb interactions to destroy most of the electronic polarization of the atoms during the deexcitation collisions, so we will neglect the electronic first-order correction (B23) and all higher-order corrections from Eq. (B18).

The hyperfine interactions, which have characteristic evolution times  $\leq 10^{-10}$  sec, cannot appreciably change the nuclear polarization during the time of a quenching collision, so the nuclear polarization Eq. (B21) is transferred with negligible change to the ground state at a rate  $1/T_Q$ . The repopulated ground state is produced with no electronic polarization, and the repopulation pumping makes the ground-state density matrix  $\rho$  evolve at the rate

$$\begin{aligned} \frac{d}{dt} |\rho\rangle &= \frac{1}{T_Q} \sum_{\lambda\mu} |g, \lambda\mu 00\rangle \langle e, \lambda\mu 00 | \rho_e^{(0)}\rangle \\ &= R |\varphi - s\Theta/2\rangle + \frac{1}{i\hbar} [\delta\mathcal{E}_r] |\rho\rangle, \end{aligned} \quad (\text{B24})$$

which is equivalent to Eq. (93). In Eq. (B24) we have added the labels  $g$  and  $e$  to distinguish ground-state and excited-state basis vectors of the form (41).

*Light shifts due to real transitions.* For steady-state pumping with no rf coherence, the retardation correction of Eq. (B22) vanishes, since  $\varphi' = \varphi$  and  $\Theta_\zeta' = \Theta_\zeta$ . When an rf field is generating coherence in the ground state, the nuclear part of the coherence very nearly ceases to evolve after the atom has been optically excited. This is because of the collisional decoupling of the excited-state hyperfine interactions discussed above. When the nuclear coherence returns to the ground state after a quenching collision it will partially regenerate rf coherence, and the regenerated coherence will be retarded in phase with respect to the coherence of atoms that have not been excited. The resulting small shift of the resonant frequency of the ground-state atoms was first recognized and studied by Cohen-Tannoudji [44] who called it the ‘‘light shift due to real transitions.’’

One can use the identity

$$S_i S_j = \frac{1}{4} \delta_{ij} + \frac{i}{2} \sum_k \epsilon_{ijk} S_k \quad (\text{B25})$$

(where  $\epsilon_{ijk}$  is the antisymmetric unit tensor) to show that  $2\{\mathbf{s}\cdot\mathbf{S}, \Theta\cdot\mathbf{S}\} = \mathbf{s}\cdot\Theta$ . Using Eqs. (37), (38) and additional applications of Eq. (B25) we find that the purely nuclear part of the sources term of Eqs. (B3) and (B21) is

$$\varphi - \frac{1}{2} \mathbf{s}\cdot\Theta = \frac{1}{4} \rho + \mathbf{S}\cdot\rho\mathbf{S} - \frac{1}{2} \{\mathbf{s}\cdot\mathbf{S}, \rho\} - i\mathbf{s}\cdot\mathbf{S}\times\rho\mathbf{S}. \quad (\text{B26})$$

As discussed further in Sec. X, we assume that a resonant rf field has excited coherence between the ground-state sublev-

els  $|fm\rangle$  and  $|f,m-1\rangle$  (now quantized along  $\mathbf{z}$ ) so that the coherent part  $\rho'_{f\bar{m}}$  of the ground-state density matrix at time  $t'$  is

$$\rho'_{f\bar{m}} = |fm\rangle\langle fm|\rho|f,m-1\rangle\langle f,m-1|e^{-i\omega_{f\bar{m}}(t'-t)}. \quad (\text{B27})$$

The amplitude  $\langle fm|\rho|f,m-1\rangle$  is the value at time  $t$ . The mean azimuthal quantum number is  $\bar{m}=m-1/2$ . For the evolution with time  $t'$  over time intervals  $|t-t'|\sim T_Q$ , it is an excellent approximation to replace the rf drive frequency  $\omega$  with the rf resonant frequency  $\omega_{f\bar{m}}$ , since the amplitude (B27) will be negligibly small unless  $\omega\approx\omega_{f\bar{m}}$ . Substituting Eq. (B27) into Eq. (B26) and assuming a longitudinal mean photon spin  $\mathbf{s}=s_z\mathbf{z}$ , we find

$$\varphi' - \frac{1}{2}\mathbf{s}\cdot\mathbf{\Theta}' = \frac{[I]^2 + 4\bar{m}^2 - 1 - 4(-1)^{a-f}[I]s_z\bar{m}}{4[I]^2}\rho'_{f\bar{m}} + \dots \quad (\text{B28})$$

Other coherences in addition to the self-coupling term written out explicitly in Eq. (B28) are represented by  $+\dots$ . The additional terms are needed to ensure that the right-hand side of Eq. (B28) is a purely nuclear operator, like the left-hand side, but they do not contribute to the light shift.

Substituting Eq. (B28) into Eq. (B22) and evaluating the integral, we find to a good approximation

$$\frac{1}{i\hbar}[\delta\mathcal{E}_r]|\rho\rangle = -i\delta\Omega_{r,f\bar{m}}|\rho_{f\bar{m}}\rangle, \quad (\text{B29})$$

where the light shift due to real transitions is

$$\delta\Omega_{r,f\bar{m}} = -\omega_{f\bar{m}}RT_Q \frac{[I]^2 + 4\bar{m}^2 - 1 - 4(-1)^{a-f}[I]s_z\bar{m}}{4[I]^2}. \quad (\text{B30})$$

For the conditions of spin-exchange optical pumping, the light shift due to real transitions is always a small fraction, of order  $\omega_{f\bar{m}}T_Q$  of the optical pumping rate  $R$ .

The Liouville-space operator  $[\delta\mathcal{E}_r]$  is uniquely defined by Eqs. (B29) and (B30), and to simplify the notation of Sec. VIII we have used square brackets as though a matrix-space operator  $\delta\mathcal{E}_r$  existed, in accordance with Eqs. (26). Although this is permissible for our applications, it is not generally true. It is simple to construct an operator  $\delta\mathcal{E}_r$  that gives the correct light shifts for  $\Delta m=1$ , single-quantum Zeeman transitions, for example, by spacing the diagonal matrix elements such that  $\langle fm|\delta\mathcal{E}_r|fm\rangle - \langle f,m-1|\delta\mathcal{E}_r|f,m-1\rangle = \hbar\delta\Omega_{r,f\bar{m}}$ . However, an operator constructed in this way will fail to give the correct light shifts for multiple-quantum Zeeman transitions. An example is an atom with  $I=1/2$ , for which the double-quantum transition from  $|1,1\rangle$  to  $|1,-1\rangle$  has no light shift due to real transitions. This is because the nuclear coherence (B26) associated with a double-quantum transition is quadrupolar and cannot exist for  $I=1/2$ . The light shifts (B30) for the two single-quantum transitions, from  $|1,1\rangle$  to  $|1,0\rangle$  and from  $|1,0\rangle$  to  $|1,-1\rangle$  sum to  $-RT_Q\omega_2/4$ , where  $\omega_2$  is the unperturbed resonance frequency of the double-quantum transition. So the light shifts of the two single-quantum Zeeman transitions do not add up to the light shift

for the double-quantum transition, as required if a  $\delta\mathcal{E}_r$  corresponding to  $[\delta\mathcal{E}_r]$  existed. This failing is irrelevant as long as we limit our attention to single-quantum Zeeman transitions. Then  $\delta\mathcal{E}_r$ , constructed as outlined above, correctly describes the light shifts due to real transitions. No such limitations exist for the matrix-space operator  $\delta\mathcal{E}_v$  of Eqs. (87) and (90), which represents the light shift due to virtual transitions to the excited state.

*Light shifts due to virtual transitions.* Experiments show that in high-pressure helium gas the optical absorption cross section  $\sigma_{\text{op}}$  of D<sub>1</sub> light is well described by a simple Lorentzian line profile

$$\sigma_{\text{op}} = \frac{r_e c f (\delta\nu_a/2)}{(\nu - \nu_a)^2 + (\delta\nu_a/2)^2}, \quad (\text{B31})$$

where the full width at half maximum  $\delta\nu_a$  of the line profile is proportional to the helium pressure [45]. For an absorption profile like Eq. (B31), one can readily show that the mean pumping rate  $R$  of Eq. (89) and the frequency shift parameter  $\delta\Omega_v$  of Eq. (91) can be considered as real and imaginary parts of a single complex rate, given by

$$R + i\delta\Omega_v = r_e c f \int \frac{\Phi(\nu)}{\delta\nu_a/2 + i(\nu - \nu_a)} d\nu. \quad (\text{B32})$$

A serviceable approximation for the spectral profile  $\Phi$  of the laser light is a Gaussian function with a central frequency  $\nu_l = c/\lambda_l$  and a full width at half maximum  $\delta\nu_l = c\delta\lambda_l/\lambda_l^2$

$$\Phi(\nu) = \Phi(\nu_l) e^{-4(\nu - \nu_l)^2 \ln 2 / (\delta\nu_l)^2}. \quad (\text{B33})$$

For a laser beam of intensity  $I_l$  (units: W cm<sup>-2</sup>) we would have

$$\Phi(\nu_l) = \frac{2I_l \sqrt{\pi \ln 2}}{\pi h \nu_l \delta\nu_l}. \quad (\text{B34})$$

Substituting Eq. (B33) into Eq. (B32), we find

$$R + i\delta\Omega_v = \frac{2\sqrt{\pi \ln 2} r_e f \lambda_l^3 I_l w}{hc \delta\lambda_l}, \quad (\text{B35})$$

where the complex function  $w$  is

$$\begin{aligned} w([ir-s]\sqrt{\ln 2}) &= \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{e^{-[rx-s]^2 \ln 2} dx}{x-i} \\ &= e^{[r+is]^2 \ln 2} \text{erfc}([r+is]\sqrt{\ln 2}). \end{aligned} \quad (\text{B36})$$

The last equality can be proved by expressing the simple pole,  $(x-i)^{-1}$ , in terms of its spatial Fourier transform. The relative atomic linewidth is

$$r = \frac{\delta\nu_a}{\delta\nu_l}, \quad (\text{B37})$$

and the relative detuning is

$$s = \frac{\nu_l - \nu_a}{\delta\nu_l/2}. \quad (\text{B38})$$

Tables of the complex function  $w$  of Eqs. (B35) and (B36) have been compiled by Abramowitz and Stegun [42]. Alternately, the complimentary error function of Eq. (B36)

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = 1 - \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt \quad (\text{B39})$$

can be readily evaluated by carrying out the numerical integration on the right of Eq. (B39) for the relatively small values of  $z = (r + is)\sqrt{\ln 2}$  of interest for spin-exchange optical pumping.

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