PHYSICAL REVIEW A VOLUME 29, NUMBER 6 JUNE 1984

Polarization of the nuclear spins of noble-gas atoms by spin exchange with optically pumped alkali-metal atoms

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(Received 16 December 1983)

The theory of spin exchange between optically pumped alkali-metal atoms and noble-gas nuclei is presented. Spin exchange with heavy noble gases is dominated by interactions in long-lived van der Waals molecules. The main spin interactions are assumed to be the spin-rotation interactions $\gamma\vec{N}\cdot\vec{S}$ between the rotational angular momentum $\vec{N}$ of the alkali-metal—noble-gas pair and the electron spin $\vec{S}$ of the alkali-metal atom, and the contact hyperfine interaction $\alpha\vec{K}\cdot\vec{S}$ between the nuclear spin $\vec{K}$ of the noble-gas atom and the electron spin $\vec{S}$. Arbitrary values for K and for the nuclear spin I of the alkali-metal atom are assumed. Precise formal expressions for spin transfer coefficients are given along with convenient approximations based on a perturbation expansion in powers of $(\alpha/\gamma N)^2$, a quantity which has been shown to be small by experiment.

I. INTRODUCTION

In this paper we discuss the theory of polarization transfer between the electron spins of alkali-metal atoms and the nuclear spins of noble-gas atoms in a gas. In 1960, Bouchiat, Carver, and Varnum[1] showed that the angular momentum could be transferred from the electron spins of optically pumped Rb atoms to the nuclear spins of ^{3}He in a gaseous mixture of the two elements. Unfortunately, the exchange times were extremely long, on the order of days, and the spin-exchange optical-pumping method was set aside in favor of the method of metastability exchange[2,3] where ^{3}He nuclei were polarized by hyperfine interactions with the electrons of the ^3S metastable state which have been polarized by optical pumping with 1.08-μm radiation. Leduc *et al.*[4,5] have shown that it is also possible to polarize the nuclei of ^{21}Ne by optically pumping the metastable states of neon and allowing metastability exchange collisions to carry the polarization to ground-state atoms. Presumably, similar polarization methods could work for other noble gases. A serious limitation to the method of metastability exchange is the need to operate at low gas pressures, a few Torr in the case of ^{3}He and a small fraction of a Torr for the heavier noble gases. Collisional decoupling of the fine structure in ^{3}He degrades the optical-pumping efficiency and collisional spin depolarization of the metastable states is a serious problem for the heavier noble gases. In contrast, the method of spin exchange with optically pumped alkali-metal atoms can be expected to work well at gas pressures of an atmosphere or more.

Renewed interest in spin-exchange optical pumping of noble-gas nuclei was generated when Grover[6] showed that the nuclei of ^{129}Xe could be polarized with remarkable efficiency by spin exchange with optically pumped Rb atoms. Subsequent work[7–9] has shown that spin-exchange rates between alkali-metal electron spins and the nuclei of heavy noble gases are completely dominated by interactions in van der Waals molecules. The basic process is illustrated in Fig. 1. A Rb atom and a Xe atom collide in the presence of a third body, a N_2 molecule in this example, and form a weakly bound van der Waals molecule. The molecule evolves freely for a time τ until it is broken up by a collision with a second N_2 molecule. During the relatively long molecular lifetime τ the weak coupling between the electron spin S of the alkali-metal atom, the rotational angular momentum N (not shown) of the molecule and the nuclear spin K of the noble-gas atom causes S to flip down and K to flip partway up. In contrast to electron spin exchange between $^2S_{1/2}$ atoms (alkali metals, H atoms, etc.), where the total electron spin of the colliding pair is very nearly conserved, only a small frac-

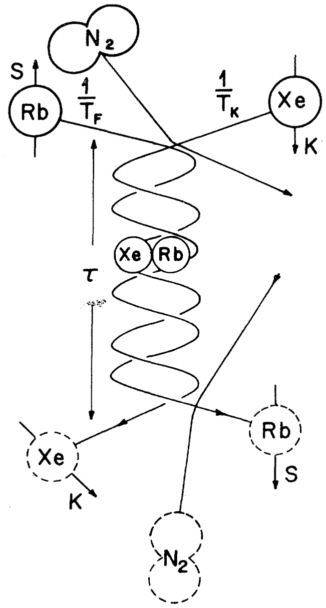

FIG. 1. Alkali-metal-atom—noble-gas molecules are formed in three-body collisions at a rate $(T_F)^{-1}$ per alkali-metal atom and $(T_K)^{-1}$ per noble-gas atom. They are broken up at a rate of $(\tau)^{-1}$ by collisions with other atoms or molecules.

tion ($<10\%$) of the spin lost by the alkali metal is transferred to the noble-gas nucleus. The rest is lost to N, the rotational motion of the alkali-metal atom and the noble-gas atom about each other.

It is noteworthy that the spin-exchange rates are extremely slow for noble gases in alkali-metal vapors because of the weakness of the spin interactions and the infrequency of three-body collisions. For example, the electron-electron spin-exchange rate constant for an alkali-metal atom in an alkali-metal-atom vapor is on the order of 10^{-9} cm^3 sec^{-1}. The nuclear-electron spin-exchange rate constant for a noble-gas atom in an alkali-metal-atom vapor is at most 10^{-14} cm^3 sec^{-1} (for ^{129}XeRb at about 15 Torr N_2 pressure) and the rate constant depends strongly on the third-body pressure.

Since the principal experimental facts about spin-exchange optical pumping of noble-gas nuclei are not widely known, we thought it would be useful to briefly review some of them here. A sketch of a typical apparatus used in our laboratory[10] is shown in Fig. 2. A source of pumping light which in Fig. 2 is a resonance lamp, but which can also be a tunable laser, is circularly polarized and is used to pump the D_1 transition of an alkali-metal atom. The time required to polarize the noble-gas nuclei depends on the cell temperature and on the gas pressure and composition in the cell. A few minutes of pumping are usually necessary. After the noble-gas nuclei are polarized, the subsequent evolution of the polarization can be monitored by removing the circular polarizer from the lamp and observing the circular dichroism of the vapor for D_1 resonance light. As indicated in Fig. 2, it is useful to adiabatically invert the nuclear spins of the noble-gas nuclei from time to time during the decay to eliminate problems due to slow drifts in the response of the detection system. A representative decay curve is shown in Fig. 3. By analyzing the data of Fig. 3 we find that the ^{129}Xe nuclei decay at a rate of 5.5×10^{-3} sec^{-1} after a loss of about 1% of the nuclear polarization per spin inversion has been taken into account. In Fig. 4 we show the measured dependence of the intrinsic decay rate of the noble-gas nuclear polarization on the alkali-metal atomic density, as deduced from the cell temperature and saturated vapor pressure formulas. Note that the noble-gas spin-polarization rate depends linearly on the alkali-metal number density. We may thus interpret the intercept of the curve in Fig. 4 as the relaxation rate due to collision with the walls. In Fig. 5 we show how the alkali-metal-induced relaxation depends on the third-body gas pressure, measured in units of a characteristic pressure p_0 which is discussed in more detail in connection with Eq. (156). The relaxation rate is a maximum at a pressure of about 15 Torr of N_2 and the rate diminishes for higher or

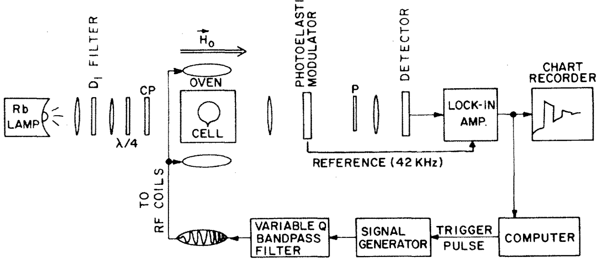

FIG. 2. Main parts of an apparatus to study spin-exchange optical pumping of noble gases. Detailed description of the apparatus is contained in the text and in Ref. 10.

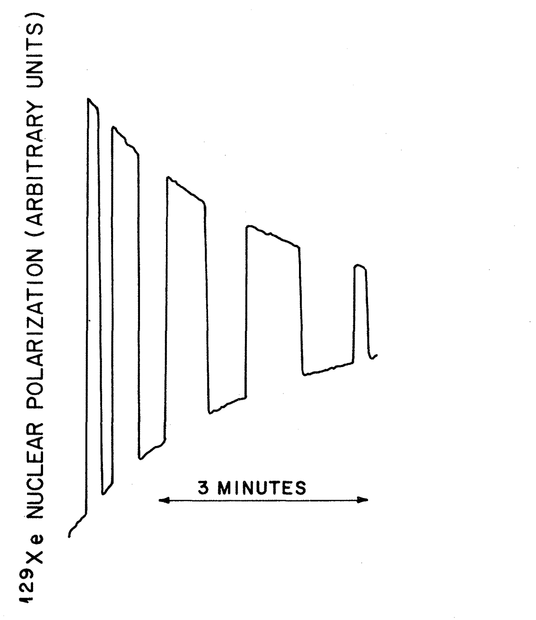

FIG. 3. A representative relaxation curve of ^{129}Xe nuclear spins in a cell containing 1 Torr ^{129}Xe, 35 Torr N_2, and a few droplets of ^{85}Rb metal. Cell temperature was 70.2 °C; the decay time of 181 sec is due to collisions with Rb atoms and with the cell walls. Each spin inversion destroys about 1% of the spin polarization.

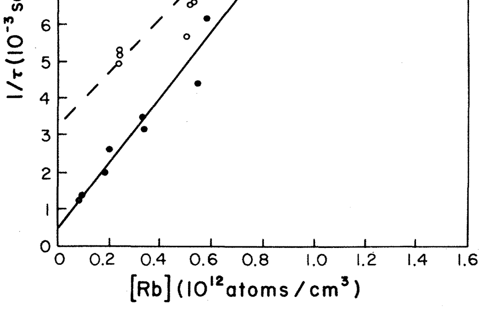

FIG. 4. Dependence of the ^{129}Xe spin-relaxation rate on the ^{87}Rb number density in an uncoated Pyrex cell containing 21 Torr of N_2 and in a silicone-coated Pyrex cell containing 14.9 Torr of N_2. Wall-induced relaxation rate is the intercept at [Rb]=0. Silicone-coated cells have much longer wall relaxation times for ^{129}Xe than uncoated cells (Ref. 10).

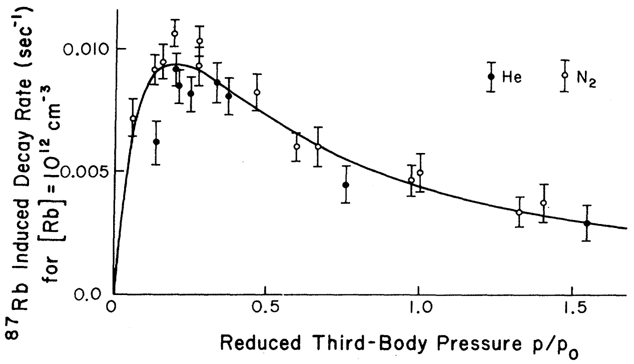

FIG. 5. Dependence of the ^{87}Rb-induced relaxation rate of ^{129}Xe spins on third-body pressures for cells containing $\frac{1}{2}$ Torr ^{129}Xe and operated at a temperature of 75 °C where [Rb] = 10^{12} cm^{-3}. Solid line is calculated from formula (82) (Ref. 11).

lower third-body pressures. Essentially the same relaxation rates are observed with He or N_2 as third bodies provided that the helium pressure is 1.6 times greater than the N_2 pressure.[11] Finally, in Fig. 6 we show the dependence of the alkali-metal-induced relaxation rate on the external field.[9] The relaxation rate is slowed down to values close to the wall-induced rate when a magnetic field of a few hundred gauss is applied to the sample. The width of the magnetic slowing-down curve increases with the third-body pressure. Data such as those of Fig. 6 show unequivocally that the relaxation of the noble-gas nuclear spins is completely dominated by long-lived van der Waals molecules. If the relaxation were caused by binary collisions, with correlation times on the order of 10^{-12} sec, magnetic fields on the order of 10^6 G would be needed to slow down the relaxation rate. Figure 6 shows that the correlation times of the interaction responsible for spin relaxation are on the order of 10^{-7} sec, the Larmor period of an electron spin in a field of 100 G. This long correlation time is almost certainly the collisionally limited lifetime of a van der Waals molecule.

Spin interactions between alkali-metal and noble-gas atoms also lead to significant polarization-dependent shifts in the magnetic resonance frequencies of the spins. Grover[6] has developed a widely used method to detect the spin polarization of noble gases at very small magnetic fields by observing the shifts which they produce in the magnetic resonance frequencies of alkali-metal atoms. A related method which works at large magnetic fields has been developed by McClelland.[12] A major advantage to the frequency-shift methods is their sensitivity to spin interactions of such short duration that negligible transfer of longitudinal spin occurs. Thus the frequency-shift method is especially useful for observing the effects of binary collisions. A disadvantage of frequency-shift methods is their great sensitivity to magnetic field fluctuations. A substantial investment in magnetic shielding is necessary for the successful application of frequency-shift methods.

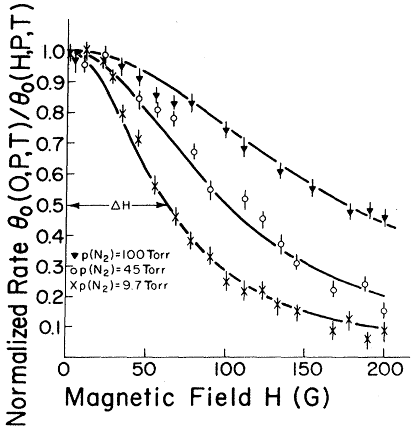

FIG. 6. Dependence of the ^{87}Rb-induced relaxation rate of ^{129}Xe spins on the magnitude of an external magnetic field H. Relaxation rate slows down substantially for fields of a few hundred gauss. Higher magnetic fields are needed to slow down the relaxation rates in cells with higher gas pressure (Ref. 9).

In this paper we present the basic theory of spin exchange between alkali-metal atoms and noble-gas nuclei. We have made extensive experimental studies of spin-exchange optical pumping of noble-gas nuclei during the past several years and the development of the theory has been guided and constrained by experimental facts. A particularly important experimental result is that the spin-rotation interaction is usually much larger than the spin-exchange interaction. We have carried out experiments on the alkali-metal atoms ^{133}Cs, ^{85}Rb, ^{87}Rb, and ^{39}K with nuclear spins $I=\frac{7}{2}$, $\frac{5}{2}$, $\frac{3}{2}$ and $\frac{3}{2}$, respectively. We have also investigated ^{129}Xe and ^{131}Xe with nuclear spins $K=\frac{1}{2}$ and $\frac{3}{2}$. Consequently the theory has been cast in a form for which I and K are free parameters. We have also adhered as closely as possible to the notation of Bouchiat *et al.*[13,14] who first recognized the importance of van der Waals molecules for the spin relaxation of alkali-metal atoms in heavy noble gases but who did not address the question of spin-exchange polarization and relaxation of noble-gas nuclei. The theory presented here reduces to that of Bouchiat *et al.*[13] when the noble-gas nuclear spin K is zero.

Since our own experiments have been mostly concerned with isotopes of xenon where the spin relaxation is com-

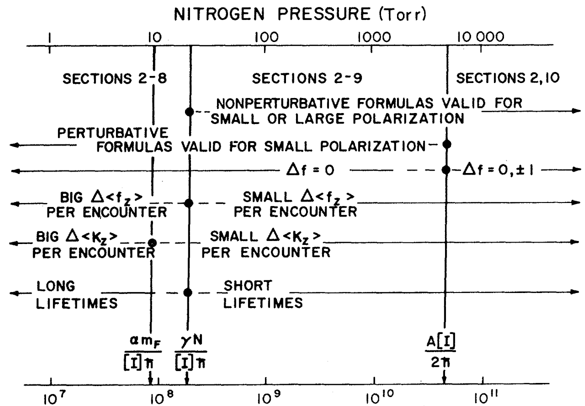

FIG. 7. An overview of the phenomena considered in this paper and of the ranges of validity of various approximations. Parameters A, γN, and am_F are to be interpreted as root-mean-square values.

pletely dominated by van der Waals molecules, we have stressed the relaxation due to molecules in this paper. However, we do discuss the simpler situation of relaxation due to binary collisions in Sec. X.

We derive formal expressions for spin-transfer and spin-relaxation rates of general validity but of such complexity that solutions by electronic computers are needed to compare with experiment. One goal of this paper has been to present simpler, easily evaluated formulas which are in good agreement with exact numerical results in clearly defined regimes of applicability. These regimes are delimited by the molecular breakup rates τ^{-1} which are equal (when multiplied by $\hbar$) to certain terms in the spin Hamiltonian. An overview of the main physical properties of these regimes and of the sections of the paper devoted to each regime is contained in Fig. 7.

II. BASIC THEORY

The simplest spin Hamiltonian which is consistent with currently known data on spin relaxation and spin transfer in mixtures of alkali-metal vapors and noble gases is

$$H=A\vec{I}\cdot\vec{S}+\gamma\vec{N}\cdot\vec{S}+\alpha\vec{K}\cdot\vec{S}+g_S\mu_B\vec{B}\cdot\vec{S}$$
$$+g_I\mu_B\vec{B}\cdot\vec{I}+g_K\mu_B\vec{B}\cdot\vec{K}+\cdots\ . \tag{1}$$

The physical significance of the various angular momentum vectors of (1) is illustrated in Fig. 8. The electronic spin $\vec{S}$ of the alkali-metal atom in the molecule is coupled to the nuclear spin $\vec{I}$ of the alkali-metal atom by the magnetic dipole interaction $A\vec{I}\cdot\vec{S}$. The electron spin of the alkali-metal is also coupled to the rotational angular momentum $\vec{N}$ of the molecule by the spin-rotation interaction $\gamma\vec{N}\cdot\vec{S}$. The nuclear spin of $\vec{K}$ of the noble-gas atom is coupled to the electron spin of the alkali metal by the magnetic dipole interaction $\alpha\vec{K}\cdot\vec{S}$. An external magnetic field $\vec{B}$ couples to the magnetic moments of $\vec{S}$, $\vec{I}$, and $\vec{K}$ as shown in (1). The g factors g_I and g_K will be some 3 orders of magnitude smaller than g_S. All of the coupling coefficients $A,\gamma,\alpha,\ldots$ will depend somewhat on the vibrational and rotational state of the van der Waals molecule or on the intermolecular separation and velocity of an unbound colliding pair. We shall understand that subsequent formulas are to be averaged over appropriate molecular quantum states or collisional parameters.

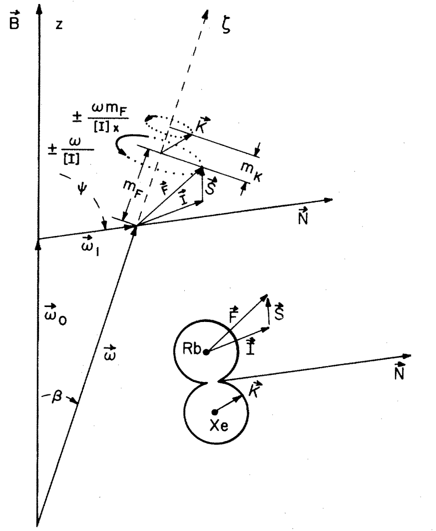

FIG. 8. Interacting spins of an alkali-metal—noble-gas van der Waals molecule. Nuclear spins of the alkali-metal and noble-gas atoms are denoted by I and K, respectively. Electron spin of the alkali-metal atom is S and the rotational angular momentum of the molecule is N. An external field B adds vectorially to the internal spin-rotation field to produce a net rotation velocity ω for the electron spin S of an alkali-metal atom without hyperfine structure. For alkali-metal atoms with a nuclear spin I the total angular momentum F rotates at a velocity $\pm\omega/(2I+1)$ about $\vec{\omega}$ for $F=I\pm\frac{1}{2}$. Finally, the nuclear spin K of the noble gas rotates at a velocity $\pm\omega m_f/[x(2I\pm1)]$ about $\vec{\omega}$ where m_f is the azimuthal quantum number of $\vec{F}$ and $x=\gamma N/\alpha$ is the Breit-Rabi field parameter defined in Eq. (55). Experiments show that $x^2\gg1$ for many alkali-metal—noble-gas pairs.

In the conventional notation introduced by Frosch and Foley[15] the magnetic dipole hyperfine coupling is written in the form

$$H_{\text{dipole}}=b\vec{K}\cdot\vec{S}+cK_RS_R\ , \tag{2}$$

where K_R and S_R are projections of the angular momentum operators $\vec{K}$ and $\vec{S}$ along the internuclear axis R. In subsequent calculations of spin-relaxation and spin-transfer processes it will be more convenient to write the interaction (2) as the sum of purely scalar and purely tensor parts

$$H_{\text{dipole}}=\alpha\vec{K}\cdot\vec{S}+c\left[K_RS_R-\frac{\vec{K}\cdot\vec{S}}{3}\right]\ , \tag{3}$$

where the relationship between α and the conventional Frosch-Foley parameters is

$$\alpha=b+\frac{c}{3}\ . \tag{4}$$

We expect the purely scalar interaction $\alpha\vec{K}\cdot\vec{S}$ to be relatively large in a van der Waals molecule because of the substantial overlap of the alkali-metal valence electron wave function with the noble-gas nucleus, as discussed by Herman.[16]

The purely tensor interaction is less effective in causing spin transfer and spin relaxation than the scalar interaction. For example, one can show that for binary collisions or for short-lived molecules the relaxation rates of $\langle K_z\rangle$ due to the two interactions are in the ratio

$$\frac{\mathscr{R}_{\text{tensor}}}{\mathscr{R}_{\text{scalar}}}=\frac{c^2}{18\alpha^2}\ . \tag{5}$$

Although no direct information about the tensor interaction is available for alkali-metal—noble-gas van der Waals molecules, Herman[16] states, without giving numbers, that the tensor interaction is small relative to the scalar interaction for alkali-metal—noble-gas pairs. In this connection it is interesting to note that Childs, Cok, and Goodman[17] have made very precise spectroscopic studies of molecules like CaCl which are well described by the ionic structure Ca^+Cl^-. This ionic molecule is isoelectronic to the van der Waals molecule KAr and it has the same $^2\Sigma_{1/2}$ ground-state symmetry. If the scalar and tensor coupling coefficients have similar relative sizes in alkali-metal—noble-gas molecules as in the alkaline-earth—halogen molecules studied by Childs *et al.*[17] there will be negligible contribution to the relaxation and spin-transfer processes from the tensor interaction. For example, in CaCl, Childs *et al.*[17] measure $b=19.2$ MHz and $c=12.5$ MHz, and therefore (5) implies that less than 2% of the relaxation of $\langle K_z\rangle$ would be caused by the tensor interaction. We have therefore omitted the tensor interaction from the Hamiltonian (1), and we shall ignore the contribution of the tensor interaction to the various spin-transfer rates in the subsequent discussions.

The rotational angular momentum $\vec{N}$ of (1) is typically on the order of 100 and it is so large compared to the other spins in the problem that we may regard N to be a fixed classical vector during the molecular lifetime which is limited by collisions to about 10^{-7} sec at 1 Torr of gas pressure. For convenience we introduce a rotation frequency

$$\vec{\omega}_1=\frac{\gamma\vec{N}}{\hbar} \tag{6}$$

to represent the effect of $\vec{N}$ on $\vec{S}$. In a like manner we introduce the rotational frequency due to the external field $\vec{B}$:

$$\vec{\omega}_0=\frac{g_S\mu_B\vec{B}}{\hbar}\ . \tag{7}$$

These frequencies are sketched in Fig. 8 along with their vector sum

$$\vec{\omega}=\vec{\omega}_0+\vec{\omega}_1=\omega\hat{\zeta}\ , \tag{8}$$

where $\hat{\zeta}$ is a unit vector along the direction of $\hat{\omega}$. Note that we may now write (1) as

$$H=A\vec{I}\cdot\vec{S}+\hbar\omega S_\zeta+\alpha\vec{K}\cdot\vec{S}+g_I\mu_B\vec{I}\cdot\vec{B}+g_B\mu_B\vec{K}\cdot\vec{B}+\cdots\ . \tag{9}$$

We shall find it convenient to introduce a laboratory coordinate system (x,y,z) whose z axis lies along the direction of the external magnetic field $\vec{B}$. The laboratory system will be used to describe the results of experimental measurements. We shall also find it convenient to introduce an orthonormal coordinate system (ξ,η,ζ) with the ζ axis defined by (8). As is shown in Fig. 8, the ζ axis is tilted by an angle β from the z axis. We see that the molecular Hamiltonian (9) is axially symmetric about ζ if we ignore the very small terms involving g_I and g_K, and it will therefore be expedient to calculate wave functions of (9) in the (ξ,η,ζ) coordinate system.

It will be convenient to calculate the spin-transfer and spin-relaxation rates in the interaction picture,[18,19] i.e., in a system for which the density matrices of the spins would be time independent if there were no interactions between the alkali-metal and noble-gas atoms. If an alkali-metal atom and a noble-gas atom are so far apart that they do not interact with each other the Hamiltonian H_n for the noninteracting pair would be

$$H_n=A\vec{I}\cdot\vec{S}+g_S\mu_BBS_z+g_I\mu_BBI_z+g_K\mu_BBK_z\ . \tag{10}$$

The interaction-picture density matrix σ is related to the Schrödinger picture density matrix ρ by

$$\rho=U_n\sigma U_n^{-1}\ , \tag{11}$$

where the evolution operator U_n is related to the noninteracting Hamiltonian (10) by

$$U_n=\exp(-iH_nt/\hbar)\ . \tag{12}$$

Since the alkali-metal atom and the noble-gas atom form molecules very infrequently, typically once every hundred seconds for a noble-gas atom, and since the more frequent binary collisions are of very short duration, typically 10^{-12} sec, it is an excellent approximation to write the density matrix of an alkali-metal—noble-gas pair at the instant of molecular formation, or just before a binary collision, as

$$\sigma_0=\sigma_{\text{Rb}}\sigma_{\text{Xe}}\ . \tag{13}$$

The initial density matrix (13) will evolve, after a time t, to

$$\sigma_{\text{ev}}=U_n^{-1}U\sigma_0U^{-1}U_n\ , \tag{14}$$

where U_n was defined in (12) and the evolution operator for an interacting pair as

$$U=\exp(-iHt/\hbar)\ . \tag{15}$$

Then the rate of change of some observable quantity M, for example, the spin K_z of a noble-gas nucleus, is

$$\begin{aligned}\frac{d}{dt}\langle M\rangle&=\frac{1}{T(M)}\text{Tr}[(\sigma_{\text{ev}}-\sigma_0)M]\\&=\frac{1}{T(M)}\text{Tr}[(M_{\text{ev}}-M)\sigma_0]\ ,\end{aligned} \tag{16}$$

where the time-evolved operator is

$$M_{\text{ev}}=U^{-1}U_nMU_n^{-1}U \tag{17}$$

and the symbol Tr denotes a trace over all spin basis states of the alkali-metal—noble-gas pair. The rate of formation of van der Waals molecules per atom of the type associated with the observable M is denoted by $T^{-1}(M)$. For convenience we will set

$$T^{-1}(M)=T_F^{-1} \tag{18}$$

for any observable associated with an alkali-metal atom and

$$T^{-1}(M)=T_K^{-1} \tag{19}$$

for any observable associated with a noble-gas atom. We will normally find that $T_K\gg T_F$ because the number density of the noble-gas atoms greatly exceeds that of the alkali-metal atoms.

The density matrix of the noble-gas atoms can be written as

$$\sigma_{\text{Xe}}=[K]^{-1}+\frac{3\langle\vec{K}\rangle\cdot\vec{K}}{K(K+1)[K]}+\cdots\ . \tag{20}$$

We shall henceforth denote the statistical weight of any angular momentum quantum number, e.g., K, by

$$[K]=2K+1 \; . \tag{21}$$

The contribution from higher multipole moments,[19,20] which we have denoted by ellipses, is small when the noble-gas nuclei are weakly polarized, the situation which prevailed for most of the experiments described in this paper. Similarly, the density matrix of the alkali-metal atoms is

$$\sigma_{\mathrm{Rb}}=\frac{1}{2[I]}+\sum_f \frac{3\langle \vec{\mathrm{f}}\rangle\cdot\vec{\mathrm{f}}}{f(f+1)[f]}+\cdots \; . \tag{22}$$

Here the sum is over the two possible values of the total angular momentum quantum number of the alkali-metal atom, $f=I\pm\frac{1}{2}$. The projection of the total angular momentum

$$\vec{\mathrm{F}}=\vec{\mathrm{I}}+\vec{\mathrm{S}} \tag{23}$$

within each hyperfine multiplet is denoted by

$$\vec{\mathrm{f}}=p(f)\vec{\mathrm{F}}p(f) \; , \tag{24}$$

where the projection operators are

$$p(f=I\pm\tfrac{1}{2})=\frac{[f]\pm4\vec{\mathrm{I}}\cdot\vec{\mathrm{S}}}{2[I]}=\frac{\hat{f}^2}{f(f+1)} \; . \tag{25}$$

In the future we shall call $f=a$ if $f=I+\frac{1}{2}$ and $f=b$ if $f=I-\frac{1}{2}$. The corresponding operators from (24) will be denoted by $\vec{\mathrm{a}}$ and $\vec{\mathrm{b}}$. We shall henceforth use the notation $\hat{f}^2$ to denote the square of the angular momentum operator. By substituting (13), (20), (22), and (17) into (16) we find

$$\frac{d}{dt}\langle\vec{\mathrm{J}}\rangle=\frac{1}{T(J)}\sum_L[q(J,L)\langle\vec{\mathrm{L}}\rangle-\vec{\mathrm{S}}(J,L)] \; , \tag{26}$$

where the symbols J and L can be a, b, or K, the labels of the three angular momenta which characterize the polarization of the alkali-metal and noble-gas atoms.

The spin-transfer coefficient is

$$q(J,L)=-\delta_{JL}+\frac{3}{2[I][K]L(L+1)W(L)} \times\mathrm{Tr}(U_n\vec{\mathrm{J}}U_n^{-1}U\vec{\mathrm{L}}U^{-1}) \; . \tag{27}$$

The terms $\vec{\mathrm{S}}(J,L)$ describe the spin-polarization-dependent shifts of the magnetic resonance frequencies of the alkali-metal and noble-gas atoms and they are given by

$$\vec{\mathrm{S}}(J,L)=\frac{9\,\mathrm{Tr}(\vec{\mathrm{J}}U_n^{-1}U\langle\vec{\mathrm{J}}\rangle\cdot\vec{\mathrm{J}}\vec{\mathrm{L}}\cdot\langle\vec{\mathrm{L}}\rangle U^{-1}U_n)}{J(J+1)[J]L(L+1)[L]} \; . \tag{28}$$

The argument of the time-evolution operators U and U_n is t, the lifetime of the van der Waals molecule before collisional breakup. The weights $W(L)$ are defined by

$$W(a)=\frac{[a]}{2[I]} \; ,$$
$$W(b)=\frac{[b]}{2[I]} \; , \tag{29}$$
$$W(K)=1 \; .$$

They may be thought of as the probabilities $W(L)$ for finding an unpolarized atom in the angular momentum state L. We have neglected in (26) terms $\vec{\mathrm{S}}(J',L')$ with $J'\neq J$ and $L'\neq J$. The coefficients of these terms are negligibly small under conditions of interest for this work. Finally, we note the special case $\vec{\mathrm{S}}(a,b)=\vec{\mathrm{S}}(b,a)=0$ which occurs because there are no terms with products of $\langle\vec{\mathrm{a}}\rangle$ and $\langle\vec{\mathrm{b}}\rangle$ in σ_0 of (13).

The lifetime of a van der Waals molecule may depend weakly on the rotational and vibrational state of the molecule. However, we shall make the simplifying assumption that, independent of the state of the molecule, the probability to find the lifetime between t and $t+dt$ is

$$P(t)dt=\tau^{-1}e^{-t/\tau}dt \; , \tag{30}$$

where τ is the mean lifetime of the molecule. When (27) and (28) are averaged over (30) the oscillatory time factors of the operators U and U_n are converted into resonance denominators appropriate to the matrix elements of the numerators, as we shall show in the next few sections.

III. FORMAL AVERAGE OVER THE DIRECTION OF N FOR NEGLIGIBLY SMALL MAGNETIC FIELD $B \ll \gamma N/\mu_B$

We consider the situation where (see Fig. 8)

$$\omega_0\ll\omega_1 \; . \tag{31}$$

For RbXe molecules this corresponds to fields of a few gauss or less. Then neither the eigenvalues nor eigenvectors [expressed in the (ξ,η,ζ) system of coordinates] of (1) will depend appreciably on the direction of $\vec{\mathrm{N}}$, and the average over all directions of $\vec{\mathrm{N}}$ reduces the tensor $q(J,L)$ to the scalar

$$q(J,L)=\frac{1}{2[I][K]}\sum_{i,j}\frac{-(\omega_{ij}\tau)^2}{1+(\omega_{ij}\tau)^2}\frac{\langle i\,|\,\vec{\mathrm{J}}\,|\,j\rangle\cdot\langle j\,|\,\vec{\mathrm{L}}\,|\,i\rangle}{L(L+1)W(L)} \tag{32}$$

and the frequency-shift terms reduce to the vector cross products

$$\vec{\mathrm{S}}(J,L)=s(J,L)\langle\vec{\mathrm{J}}\rangle\times\langle\vec{\mathrm{L}}\rangle \; , \tag{33}$$

where the scalar coefficients are

$$s(J,L)=\frac{3}{4[I][K]}\sum_{i,j}\frac{i\omega_{ij}\tau}{1+(\omega_{ij}\tau)^2} \times\frac{\langle j\,|\,\vec{\mathrm{J}}\,|\,i\rangle\cdot\langle i\,|\,(\vec{\mathrm{J}}\times\vec{\mathrm{L}})\,|\,j\rangle}{J(J+1)L(L+1)W(J)W(L)} \; . \tag{34}$$

The basis states $|\,i\rangle$ and $|\,j\rangle$ are eigenstates of the Hamiltonian (1), and the circular frequencies ω_{ij} are related to the energy eigenvalues E_i and E_j of (1) by the Bohr condition

$$\hbar\omega_{ij}=E_i-E_j \ . \qquad (35)$$

IV. FORMAL AVERAGE OVER THE DIRECTION OF $\vec{\rm N}$ FOR MAGNETIC FIELDS $B \gtrsim N/\mu_B$

We now consider the situation where the Larmor frequency ω_0 of (7) is comparable to the internal Larmor frequency ω_1 of (6); i.e.,

$$\omega_0 \gtrsim \omega_1 \ . \qquad (36)$$

For RbXe this regime occurs for fields greater than a few gauss. The average over the azimuthal direction of $\vec{\rm N}$ (see Fig. 8) reduces the spin-transfer coefficients to a form which is diagonal in the spherical laboratory basis system,[21] i.e.,

$$q(J,L)=\sum_{\mu=-1}^{+1} q_{\mu\mu}(J,L)\hat{x}_\mu\hat{x}_\mu^* \ , \qquad (37)$$

where

$$\hat{x}_{\pm 1}=\frac{\hat{x}\pm i\hat{y}}{\mp\sqrt{2}} \ , \qquad \hat{x}_0=\hat{z} \ . \qquad (38)$$

The longitudinal component of $q(J,L)$ is

$$q_{00}(J,L)=\frac{3}{2[I][K]L(L+1)W(L)}\int_0^\pi \sin\psi\, d\psi \sum_{i,j,\rho} \frac{-(\omega_{ij}\tau)^2\langle j\,|\,J_\rho\,|\,i\,\rangle\langle i\,|\,L_{-\rho}\,|\,j\,\rangle(-1)^\rho\,|\,d^1_{\rho 0}\,|^2}{1+(\omega_{ij}\tau)^2} \ , \qquad (39)$$

where the Wigner functions are

$$d^1_{\pm 1,0}=\mp\frac{\sin\beta}{\sqrt{2}} \ , \qquad d^1_{00}=\cos\beta \ . \qquad (40)$$

We note that the basis states $|\,i\,\rangle$ and $|\,j\,\rangle$ of (39) are eigenstates of the Hamiltonian (9). They are axially symmetric about the axis ζ and they depend on the colatitude angle ψ of Fig. 8.

The subscript ρ in (39) refers to one of the spherical unit vectors $\hat{\xi}_\rho$ in the (ζ,η,ξ) coordinate system:

$$\hat{\xi}_{\pm 1}=\frac{\hat{\xi}\pm i\hat{\eta}}{\mp\sqrt{2}} \ , \qquad \hat{\xi}_0=\hat{\zeta} \ , \qquad (41)$$

we have

$$J_\rho=\hat{\xi}_\rho\cdot\vec{\rm J} \ . \qquad (42)$$

The transverse spin-transfer coefficients $q_{11}(J,L)$ and $q_{-1-1}(J,L)$ are given by formulas analogous to (39). They have imaginary as well as real parts and they account for field-dependent frequency shifts of the magnetic resonance spectrum. Since the transverse spin-transfer coefficients at high fields have not yet been needed for the interpretation of experimental data we shall not discuss them further here.

V. THE SPIN-TEMPERATURE LIMIT

Under many experimental conditions, including most of those considered here, the alkali-metal atoms are well described by a spin temperature,[22,23] i.e., the density matrix of the alkali-metal atom can be written as

$$\rho_{\rm Rb}=Z^{-1}e^{\vec{\beta}\cdot\vec{\rm F}} \ , \qquad (43)$$

where the sum on states is

$$Z={\rm Tr}\,e^{\vec{\beta}\cdot\vec{\rm F}} \ . \qquad (44)$$

We may think of β^{-1} as a spin temperature.

Under the conditions of interest for the work described here, the parameter β is small compared to unity and we may therefore write (23) as

$$\rho_{\rm Rb}=\frac{1}{2[I]}(1+\vec{\beta}\cdot\vec{\rm F}+\cdots) \ , \qquad (45)$$

where we have neglected higher-order terms in β. When (45) is valid we may write

$$\langle\vec{\rm f}\,\rangle=\frac{[f]f(f+1)}{2[I]\{I(I+1)+\frac{3}{4}\}}\langle\vec{\rm F}\rangle+\cdots \ . \qquad (46)$$

The spin polarization of the alkali-metal atoms is described by the single vector $\langle\vec{\rm F}\rangle$ rather than by $\langle\vec{\rm a}\rangle$, $\langle\vec{\rm b}\rangle$, and the higher multipole moments which characterize an arbitrary state of polarization when spin-temperature equilibrium does not prevail. It will therefore be convenient to use (46) to reduce the spin-transfer equation (26) to the coupled pair

$$\frac{d}{dt}\langle\vec{\rm K}\rangle=\frac{1}{T_K}\{q(K,K)\langle\vec{\rm K}\rangle+q(K,F)\langle\vec{\rm F}\rangle\} \ , \qquad (47)$$

$$\frac{d}{dt}\langle\vec{\rm F}\rangle=\frac{1}{T_F}\{q(F,K)\langle\vec{\rm K}\rangle+q(F,F)\langle\vec{\rm F}\rangle\} \ . \qquad (48)$$

We have ignored the frequency-shift terms for simplicity. The transfer coefficients $q(K,K)$, $q(F,F)$, and

$$q(F,K)=\frac{I(I+1)+\frac{3}{4}}{K(K+1)}q(K,F) \qquad (49)$$

are given by (32) or (39) where the labels J and L can each take on the two possible symbols F and K, and the weight factors $W(F)$ which occur are to be defined by

$$F(F+1)W(F)=I(I+1)+\tfrac{3}{4} \ . \qquad (50)$$

VI. PERTURBATION SOLUTION

It is possible to evaluate the spin-transfer coefficients directly by numerical diagonalization of the Hamiltonian (1) to obtain eigenvalues and eigenvectors for evaluation of the energy denominators and matrix elements. In Sec. XIII we shall discuss the results of numerical calculations. However, extensive experimental studies of van der Waals molecules of alkali-metal atoms (K, Rb, and Cs) with ^{129}Xe and ^{131}Xe have shown that at least for these systems there is a convenient hierarchy of magnitudes

$$A^2 \gg (\gamma N)^2 \gg \alpha^2 \tag{51}$$

in the Hamiltonian (1). For example, for ^{87}Rb^{129}Xe, $A/h \simeq 3400$ MHz, $\gamma N/h \simeq 116$ MHz, and $\alpha/h \simeq 37$ MHz. We shall develop the perturbation theory of this section with the assumption that (51) is valid. The Hamiltonians (1) or (9) will be written as

$$H = H_0 + V_0 + V_1 \ . \tag{52}$$

The unperturbed Hamiltonian is

$$H_0 = A\vec{I}\cdot\vec{S} + \frac{\hbar\omega}{[I]}(a_\xi - b_\xi) \ . \tag{53}$$

The eigenstates of (53) will form the basis states for our perturbation expansion.

The most important perturbation is

$$V_0 = \frac{\hbar\omega}{x[I]}(\vec{a} - \vec{b})\cdot\vec{K} \ . \tag{54}$$

This is the projection of $\alpha\vec{S}\cdot\vec{K}$ within the multiplets $f = I + \frac{1}{2} = a$ and $f = I - \frac{1}{2} = b$. The parameter x is the Breit-Rabi field parameter

$$x = \frac{\hbar\omega}{\alpha} \ . \tag{55}$$

In view of (51) we see that

$$x^{-2} \ll 1 \ , \tag{56}$$

so x^{-1} is an appropriate expansion parameter for perturbation calculations. The perturbation V_1 is

$$V_1 = \hbar \sum_{\substack{f,f' \\ f \neq f'}} p(f)\{\omega S_\xi + (\omega/x)\vec{S}\cdot\vec{K}\} p(f') \ . \tag{57}$$

This perturbation causes transitions between the two hyperfine multiplets a and b. Such transitions can occur only if the molecular lifetime τ is comparable to or less than the hyperfine period divided by 2π. Experiments show that the molecular lifetime is on the order of 10^{-7} sec at 1 Torr of gas pressure. Consequently we can neglect V_1 for pressures below an atmosphere, with the possible exception of systems containing isotopes like ^{41}K which have unusually small hyperfine structure. With this caveat we shall ignore V_1 for all perturbation calculations.

The energy eigenvalues of $H_0 + V_0$, correct to order x^{-2}, are

$$E(f, m_f m_K) = E_f \pm \frac{\hbar\omega}{[I]}\left[m_f + \frac{1}{x} m_f m_K + \frac{1}{2x^2} m_f \{K(K+1) - m_K^2\} - \frac{1}{2x^2} m_K \{f(f+1) - m_f^2\} \right] , \tag{58}$$

where the "center of mass" of the multiplet f is

$$E_f = \tfrac{1}{2} A \{f(f+1) - I(I+1) - \tfrac{3}{4}\} \ . \tag{59}$$

The energies are sketched in Fig. 9.

The perturbed states $|f, m_f, m_K\rangle$, i.e., the approximate eigenstates of $H_0 + V_0$, can be labeled by the same quantum numbers as the eigenstates $|f, m_f, m_K)$ of H_0. The two sets of states are related to each other by the unitary transformation

$$|f, m_f, m_K\rangle = R\, |f, m_f, m_K) \ , \tag{60}$$

where the unitary operator R, correct to order x^{-2}, is

$$R = 1 + u + \tfrac{1}{2} u^2 + v \ . \tag{61}$$

The anti-Hermitian operators u and v are

$$u = \frac{1}{2x}(F_- K_+ - F_+ K_-) \tag{62}$$

and

$$v = \frac{1}{2x^2}[F_\xi K_\xi, (F_+ K_- + F_- K_+)] \tag{63}$$

and as usual the subscripts $\pm$ denote

$$K_\pm = K_\xi \pm i K_\eta \ . \tag{64}$$

Then we may evaluate the matrix elements of (32), (34), or

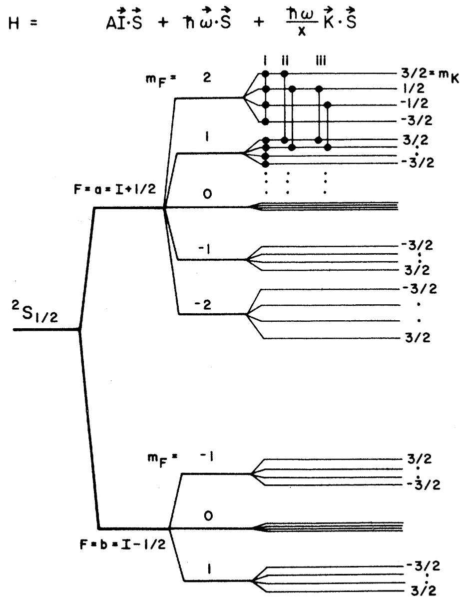

FIG. 9. Energy levels of the Hamiltonian $H_0 + V_0$ of Eq. (52).

(39) by replacing the true operators, e.g., K_ζ, by perturbed operators $\widetilde{K}_\zeta$ which give the correct matrix elements when inserted between the pure states, i.e.,

$$\langle i\,|K_\zeta|\,j\rangle = (i\,|\widetilde{K}_\zeta|\,j)\ , \tag{65}$$

where, to order x^{-2},

$$\widetilde{K}_\zeta = R^{-1}K_\zeta R = K_\zeta - [u,\, K_\zeta] + \tfrac{1}{2}[u,\, [u,\, K_\zeta]] - [v,\, K_\zeta] + \cdots\ . \tag{66}$$

We note that the spin-transfer coefficients, e.g., (32), contain squares of matrix elements of $\vec{\mathrm{K}}$ or $\vec{\mathrm{F}}$ or they may contain the product of a matrix element of $\vec{\mathrm{K}}$ with a matrix element of $\vec{\mathrm{F}}$. We may therefore ignore any components of $\widetilde{K}_\zeta$, etc., which upon squaring, or being paired as a matrix element with a corresponding matrix element of $\widetilde{F}_\zeta$, will give a term of order higher than $1/x^2$. Because each term in (32) and in analogous expressions contains one or more factors of ω_{ij} in the numerator we may ignore all components of $\widetilde{K}_\zeta$ or $\widetilde{F}_\zeta$ which contribute to diagonal matrix elements. Thus the components of the perturbed operators needed for our calculations are

$$\widetilde{K}_\zeta = \frac{1}{2x}(K_+F_- + K_-F_+) + \cdots\ , \tag{67}$$

$$\widetilde{F}_\zeta = \frac{-1}{2x}(K_+F_- + K_-F_+) + \cdots\ . \tag{68}$$

These operators cause transitions of the type denoted by iii in Fig. 9. The raising and lowering operators $\widetilde{K}_\pm$ and $\widetilde{F}_\pm$ [cf. (64)] each have two classes of terms which we denote by the subscripts 1 and 2:

$$\widetilde{K}_+ = (\widetilde{K}_+)_1 + (\widetilde{K}_+)_2\ . \tag{69}$$

The terms with the selection rules $\Delta m_f = 0$, $\Delta m_K = 1$ are

$$(\widetilde{K}_+)_1 = K_+ - \frac{1}{8x^2}(\{F_+,\, F_-\}K_+ + 2\{K_+,\, K_\zeta\}F_\zeta)\ . \tag{70}$$

They cause transitions of the type denoted by i in Fig. 9. The terms with the selection rules $\Delta m_f = 1$, $\Delta m_K = 0$ are

$$(\widetilde{K}_+)_2 = -\frac{1}{x}K_\zeta F_+ - \frac{1}{2x^2}(\{F_+,\, F_\zeta\}K_\zeta - [3K_\zeta^2 - \hat{K}^2]F_+)\ . \tag{71}$$

They cause transitions of the type denoted by ii in Fig. 9. The curly brackets denote an anticommutator, i.e.,

$$\{K_+,\, K_-\} = K_+K_- + K_-K_+ \tag{72}$$

and the notation $\hat{K}^2$ indicates the squared angular momentum *operator* with eigenvalue $K(K+1)$. The corresponding terms for F_+ are

$$\widetilde{F}_+ = (\widetilde{F}_+)_1 + (\widetilde{F}_+)_2\ , \tag{73}$$

where

$$(\widetilde{F}_+)_1 = \frac{K_+F_\zeta}{x} + \frac{K_+}{2x^2}[3F_\zeta^2 - \hat{F}^2] - \frac{F_\zeta}{2x^2}\{K_+,\, K_\zeta\} \tag{74}$$

and

$$(\widetilde{F}_+)_2 = F_+\left[1 - \frac{1}{8x^2}\{K_-,\, K_+\}\right] - \frac{K_\zeta}{4x^2}\{F_\zeta,\, F_+\}\ . \tag{75}$$

We shall only evaluate the frequency-shift coefficients (34) to order $1/x$. The components of the cross product

$$\vec{\mathrm{F}} \times \vec{\mathrm{K}} = \vec{\mathrm{G}} \tag{76}$$

needed for calculation of the shift coefficients are then

$$\widetilde{G}_\zeta = \frac{i}{2}(F_+K_- - F_-K_+) + \cdots\ , \tag{77}$$

$$\widetilde{G}_+ = (\widetilde{G}_+)_1 + (\widetilde{G}_+)_2\ , \tag{78}$$

$$(\widetilde{G}_+)_1 = iK_+F_\zeta - \frac{i}{4x}K_+\{F_+,F_-\} - \frac{i}{2x}\{K_+,K_\zeta\}F_\zeta + \cdots\ , \tag{79}$$

$$(G_+)_2 = -iF_+K_\zeta - \frac{i}{4x}F_+\{K_+,K_-\} - \frac{i}{2x}\{F_+,F_\zeta\}K_\zeta + \cdots\ . \tag{80}$$

VII. PERTURBATION FORMULAS FOR SPIN-TRANSFER COEFFICIENTS WHEN $B \ll \gamma N/\mu_B$

We may now evaluate the spin-transfer coefficients (32) and the frequency-shift coefficients (34) with the perturbed energies and perturbed operators discussed in Sec. VI. Since we are considering the situation of a magnetic field which satisfies the smallness criterion (31) we may set

$$x \simeq x_1 = \frac{\gamma N}{\alpha} \tag{81}$$

and we may neglect the dependence of the eigenvalues and eigenvectors on the orientation of $\vec{\mathrm{N}}$. Then the coefficient $q(K,K)$ is found to be

$$-q(K,K)=\frac{1}{9x^2}[4I^2+4I+3]\frac{\left[\dfrac{\phi}{[I]}\right]^2}{1+\left[\dfrac{\phi}{[I]}\right]^2}$$

$$+\frac{1}{3[I]}\sum_{f,m_f}\left\{1-\frac{1}{2x^2}[f(f+1)-m_f^2]\right\}\left\{\frac{\left[\dfrac{\phi m_f}{[I]x}\right]^2}{1+\left[\dfrac{\phi m_f}{[I]x}\right]^2}+\delta_{m_f0}\frac{\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}{1+\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}\right\}. \tag{82}$$

Here the phase is

$$\phi=\omega\tau\simeq\frac{\gamma N\tau}{\hbar}. \tag{83}$$

In (82) the terms involving m_F come from matrix elements between states $|i\rangle$ and $|j\rangle$ with $\Delta m_K \pm 1$, $\Delta m_f=0$. The first term in (82) came from matrix elements with $\Delta m_f=\pm 1$, $\Delta m_K=0$ and $\Delta m_f=\pm 1$, $\Delta m_K=\mp 1$.

In a like manner we find the self-transfer coefficient $q(F,F)$ to be

$$-q(F,F)=\frac{2}{3}\frac{\left[\dfrac{\phi}{[I]}\right]^2}{1+\left[\dfrac{\phi}{[I]}\right]^2}+\frac{2K(K+1)}{9x^2}\frac{\left[3-\left[\dfrac{\phi}{[I]}\right]^2\right]}{\left[1+\left[\dfrac{\phi}{[I]}\right]^2\right]^3}\left[\frac{\phi}{[I]}\right]^2+\frac{2K(K+1)}{3x^2 2[I]\{I(I+1)+\frac{3}{4}\}}\sum_{f,m_f}\frac{m_f^2\left[\dfrac{\phi m_f}{x[I]}\right]^2}{1+\left[\dfrac{\phi m_f}{x[I]}\right]^2}. \tag{84}$$

In (84) the first term, which is independent of x, comes from matrix elements with $\Delta m_f=1$, $\Delta m_K=0$. The second term which is proportional to $[1+(\phi/[I])^2]^{-3}$ arises from the same class of matrix elements, but it is due to the dependence of the energy factor $(\omega_{ij}\tau)^2[1+(\omega_{ij}\tau)^2]^{-1}$ on x. The last term comes from matrix elements with $\Delta m_K=1$, $\Delta m_f=0$.

The transfer coefficient between F and K is

$$q(K,F)=\frac{2K(K+1)}{9x^2}\left[\frac{\phi}{[I]}\right]^2\frac{\left[3+\left[\dfrac{\phi}{[I]}\right]^2\right]}{\left[1+\left[\dfrac{\phi}{[I]}\right]^2\right]^2}$$

$$-\frac{K(K+1)}{6x^2[I]\{I(I+1)+\frac{3}{4}\}}\sum_{f,m_f}[3m_f^2-f(f+1)]\left\{\frac{\left[\dfrac{\phi m_f}{x[I]}\right]^2}{1+\left[\dfrac{\phi m_f}{x[I]}\right]^2}+\delta_{m_f0}\frac{\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}{1+\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}\right\}. \tag{85}$$

We may use (49) to obtain $q(F,K)$ from (85).

Finally, the scalar frequency-shift coefficients (34) are, to order x^{-1},

$$s(f,K)=\pm\frac{1}{3x}\frac{\phi}{[I]}\frac{3+\left[\dfrac{\phi}{[I]}\right]^2}{\left[1+\left[\dfrac{\phi}{[I]}\right]^2\right]^2}, \tag{86}$$

$$s(K,f)=\pm\frac{\phi}{x[I]}\left[\frac{2}{3}\frac{1}{1+\left[\dfrac{\phi}{[I]}\right]^2}+\frac{1}{f(f+1)[f]}\sum_{m_f}\frac{(m_f)^2}{1+\left[\dfrac{\phi m_f}{x[I]}\right]^2}\right], \tag{87}$$

where the ± signs are associated with $f=I\pm\frac{1}{2}$.

VIII. PERTURBATION FORMULAS FOR SPIN-TRANSFER COEFFICIENTS WHEN $B \gtrsim \gamma N/\mu_B$

All magnetic decoupling experiments done so far have been concerned with the slowing down of the relaxation of the longitudinal noble-gas spin $\langle K_z \rangle$ or the longitudinal alkali-metal spin $\langle F_z \rangle$ in a large magnetic field B which defines the z axis of the laboratory coordinate system. The transverse spin polarization is negligible in such experiments. The relaxation processes of the alkali-metal and the noble-gas spins are therefore described by the longitudinal components of the spin coupling coefficients $q(F,F)$ and $q(K,K)$, and we shall therefore limit our discussion to them.

By substituting the perturbed energies and operators of Sec. VI into (39) we find

$$-q(K,K)=\tfrac{1}{2}\int \sin\psi\, d\psi \left\{ \frac{1}{6x^2}(4I^2+4I+3)\frac{\left[\dfrac{\phi}{[I]}\right]^2}{1+\left[\dfrac{\phi}{[I]}\right]^2}(1-\tfrac{1}{2}\sin^2\beta)+\frac{\sin^2\beta}{2[I]}\sum_{f,m_f}\left[1-\frac{1}{2x^2}[f(f+1)-m_f^2]\right] \times \left[\frac{\left[\dfrac{\phi m_f}{[I]x}\right]^2}{1+\left[\dfrac{\phi m_f}{[I]x}\right]^2}+\delta_{m_f 0}\frac{\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}{1+\left[\dfrac{\phi f(f+1)}{2[I]x^2}\right]^2}\right]\right\} . \tag{88}$$

Here both ϕ and x depend on the angle ψ since they are defined as

$$\phi=\omega\tau , \tag{89}$$

$$x=\frac{\hbar\omega}{\alpha} , \tag{90}$$

and ω depends on ψ as shown in Fig. 8.

Although the integrals over ψ in (88) can be evaluated in closed form, the general result is so cumbersome that we shall only present two limiting cases here, the situations with very long and very short molecular lifetimes τ. For very short molecular lifetimes such that

$$\left|\frac{\gamma N\tau}{\hbar}\right| \ll 1 , \tag{91}$$

$$\left|\frac{\alpha\tau}{\hbar}\right| \ll 1 , \tag{92}$$

but also for lifetimes sufficiently long that I and S can couple to F during a molecular lifetime, i.e.,

$$\left|\frac{[I]A\tau}{2\hbar}\right| \gg 1 , \tag{93}$$

the limiting value of (88) can be verified to be

$$-q(K,K)=\tfrac{2}{3}[I(I+1)+\tfrac{3}{4}]\frac{\left[\dfrac{\alpha\tau}{[I]\hbar}\right]^2}{1+\left[\dfrac{\omega_0\tau}{[I]}\right]^2} . \tag{94}$$

In a similar way we may show that the short-lifetime limit for $q(F,F)$ is

$$-q(F,F)=\frac{2}{3}\left[\left[\frac{\gamma N\tau}{[I]\hbar}\right]^2+K(K+1)\left[\frac{\alpha\tau}{[I]\hbar}\right]^2\right] \times\frac{1}{1+\left[\dfrac{\omega_0\tau}{[I]}\right]^2} . \tag{95}$$

For ${}^{87}\mathrm{Rb}{}^{129}\mathrm{Xe}$ the range of validity of the criteria (91)–(93) is indicated in Fig. 7.

For the limit of very long molecular lifetimes where

$$\left|\frac{\alpha\tau}{[I]\hbar}\right| \gg 1 . \tag{96}$$

The limiting value of (88) can be shown to be

$$-q(K,K)=\frac{\mathscr{h}^2+1+\dfrac{4}{3x_1^2}[I(I+1)+\tfrac{3}{4}]}{4\mathscr{h}^2} + \frac{\dfrac{4}{3x_1^2}[I(I+1)+\tfrac{3}{4}]-\mathscr{h}^2+1}{16\mathscr{h}^3} \times(\mathscr{h}^2-1)\ln\left[\frac{\mathscr{h}+1}{\mathscr{h}-1}\right]^2 , \tag{97}$$

where the dimensionless field parameter is

$$\mathscr{h}=\frac{\omega_0}{\omega_1}=\frac{g_S\mu_B B}{\gamma N} \tag{98}$$

and in a like manner we can show that

$$-q(F,F)=\frac{\mathscr{h}^2+1+\frac{4}{3x_1^2}K(K+1)}{4\mathscr{h}^2}+\frac{\frac{4}{3x_1^2}K(K+1)-\mathscr{h}^2+1}{16\mathscr{h}^3}\times(\mathscr{h}^2-1)\ln\left[\frac{\mathscr{h}+1}{\mathscr{h}-1}\right]^2 . \tag{99}$$

IX. SHORT MOLECULAR LIFETIMES: RELAXATION AND SPIN TRANSFER WITH $\Delta f=0$

All of the spin coupling equations (26), (47), and (48) become much simpler when the criteria (91)—(93) are satisfied. We note that the compound unitary operator of (14) and (17) satisfies the Schrödinger equation

$$i\hbar\frac{d}{dt}U_n^{-1}U=\Delta\tilde{H}\,U_n^{-1}U , \tag{100}$$

where

$$\Delta H=H-H_n \tag{101}$$

and

$$\Delta\tilde{H}=U_n^{-1}\Delta H\,U_n . \tag{102}$$

If we write out the matrix elements of $\Delta\tilde{H}$ in terms of the eigenstates of H_n we notice that the terms which are off diagonal in f oscillate many times during the molecular lifetime because of the criterion (93). The matrix elements which are diagonal in f are time independent if the external magnetic field B is zero, or they oscillate a small fraction of a cycle if

$$B\ll\frac{\hbar}{\mu_B\tau} \tag{103}$$

we shall assume that the smallness criterion (103) for B is satisfied along with (91)—(93). Then the rapidly oscillating parts of $\Delta\tilde{H}$ will have negligible effect on the Schrödinger equation (100) and we may therefore drop the rapidly oscillating terms from $\Delta\tilde{H}$, ignore, because of (103), the slow oscillations due to B, and replace $\Delta\tilde{H}$ by its secular part

$$\Delta\bar{H}=\sum_f\Delta H(f) , \tag{104}$$

where the projections within the multiplets f are

$$\Delta H(f)=p(f)\,\Delta H\,p(f) . \tag{105}$$

The evolution operator is therefore

$$U_n^{-1}U=\exp\left[-\frac{i\,\Delta\bar{H}\,t}{\hbar}\right]=\sum_f\left[1-\frac{i\,\Delta H(f)t}{\hbar}-\frac{1}{2}\left[\frac{\Delta H(f)t}{\hbar}\right]^2+\cdots\right]p(f) \tag{106}$$

and the evolved operator (17) becomes

$$M_{\text{ev}}=M+\frac{it}{\hbar}\sum_f[\Delta H(f),M]-\frac{1}{2}\left[\frac{t}{\hbar}\right]^2\sum_f[\Delta H(f),[\Delta H(f),M]]+\cdots . \tag{107}$$

The commutators in (107) can be readily evaluated. If we assume that purely longitudinal polarization exists we find from (16), after averaging according to (30) over t and over all directions of $\vec{N}$,

$$\frac{d}{dt}\langle f_z\rangle=-\frac{1}{T_F}\frac{2}{3}\left[\frac{\gamma N\tau}{[I]\hbar}\right]^2\langle f_z\rangle+\frac{1}{T_F}\left[\frac{\alpha\tau}{[I]\hbar}\right]^2\times[\langle\hat{f}^2-f_z^2\rangle\langle K_z\rangle-\langle\hat{K}^2-K_z^2\rangle\langle f_z\rangle] , \tag{108}$$

$$\frac{d}{dt}\langle K_z\rangle=\frac{1}{T_K}\left[\frac{\alpha\tau}{[I]\hbar}\right]^2[\langle\hat{K}^2-K_z^2\rangle\langle F_z\rangle-\langle\hat{F}^2-F_z^2\rangle\langle K_z\rangle] . \tag{109}$$

The significance of the factors $\langle\hat{K}^2-K_z^2\rangle$ and $\langle\hat{F}^2-F_z^2\rangle$ is discussed in Sec. XII.

In the event that transverse polarization exists, e.g., during a magnetic resonance experiment or after a $\frac{1}{2}\pi$ pulse, the terms linear in τ from (107) lead to frequency-shift terms of the form

$$\frac{d}{dt}\langle f_x\pm if_y\rangle=\pm i\frac{s(f,K)\langle K_z\rangle}{T_F}\langle f_x\pm if_y\rangle+\cdots , \tag{110}$$

$$\frac{d}{dt}\langle K_x\pm iK_y\rangle=\pm i\frac{s(K,S)\langle S_z\rangle}{T_K}\langle K_x\pm iK_y\rangle+\cdots , \tag{111}$$

where the frequency-shift coefficients are

$$s(a,K)=-s(b,K)=\frac{s(K,S)}{[I]}=\frac{\alpha\tau}{\hbar[I]} \tag{112}$$

and where the electron spin (in the absence of coherence between the multiplets a and b) is

$$\vec{S}=\frac{1}{[I]}(\vec{a}-\vec{b}) . \tag{113}$$

We note that the restriction to low spin polarization which was implicit in the use of the multipole expansions (20) and (22) does not apply to (108) and (109), which remain valid for arbitrarily large spin polarization. We also note that the expressions (108) and (109) are valid for arbitrary values of the ratio $x=\gamma N/\alpha$ and one can therefore analyze experiments at high buffer gas pressures, where (108) and (109) are valid, to determine the internal field parameter x, which plays a key role in the perturbation theory of Secs. VI—VIII. One can verify that the perturbation formulas of Sec. VII reduce to the formulas of this section when the criteria (91)—(93) are satisfied and when the factors $\langle \hat{f}^2 - f_z^2 \rangle$ and $\langle \hat{K}^2 - K_z^2 \rangle$ are replaced by their low-polarization limits $f(f+1)[f]/3[I]$ and $\frac{2}{3}K(K+1)$, respectively.

X. VERY SHORT MOLECULAR LIFETIMES, BINARY COLLISIONS, AND RELAXATION AND SPIN TRANSFER WITH $\Delta f = 0, \pm 1$

We consider finally the limit of very short molecular lifetimes where in addition to the criteria (91) and (92) we have

$$\left| \frac{[I]A\tau}{2\hbar} \right| \ll 1 \ . \tag{114}$$

The criterion (114) will always obtain for binary collisions between alkali-metal atoms and noble-gas atoms where the encounter duration is on the order of 10^{-12} sec. It will also hold for van der Waals molecules in the case of third-body pressures of a few atmospheres or greater as is indicated in Fig. 7. In view of (114) we may to good approximation write (102) as

$$\Delta \tilde{H} \simeq \Delta H \tag{115}$$

during the encounter between an alkali-metal atom and a noble-gas atom. Then the evolution operator is

$$\begin{aligned} U_n^{-1} U &\simeq \exp\left[\frac{-i\,\Delta H\, t}{\hbar} \right] \\ &= 1 - \frac{i\,\Delta H\, t}{\hbar} - \frac{1}{2}\left[\frac{\Delta H\, t}{\hbar} \right]^2 + \cdots \end{aligned} \tag{116}$$

and the evolved operator (17) becomes

$$M_{\text{ev}} = M + \frac{it}{\hbar}[\Delta H, M] - \frac{1}{2}\left[\frac{t}{\hbar} \right]^2 [\Delta H, [\Delta H, M]] + \cdots \ . \tag{117}$$

The commutators in (117) can be evaluated in a straightforward way. If we assume purely longitudinal polarization and average according to (30) over all times t and over all directions of $\vec{\mathrm{N}}$ we find from (16)

$$\begin{aligned} \frac{d}{dt}\langle a_z \rangle = &-\frac{1}{T_F}\left\{ \frac{2}{3}\left[\frac{\gamma N \tau}{\hbar} \right]^2 + \left[\frac{\alpha\tau}{\hbar} \right]^2 \langle \hat{K}^2 - K_z^2 \rangle \right\} \{ (1 - B_{aa})\langle a_z \rangle - B_{ab}\langle b_z \rangle \} \\ &- \frac{1}{T_F}\left[\frac{\alpha\tau}{\hbar} \right]^2 \left\langle K_z^2 - \frac{\hat{K}^2}{3} \right\rangle \left\{ \frac{3[I]}{4}\langle S_z \rangle - \frac{3}{[I]^2}(\langle a_z^3 \rangle - \langle b_z^3 \rangle) \right\} \\ &+ \frac{1}{T_F}\left[\frac{\alpha\tau}{\hbar} \right]^2 \frac{\langle K_z \rangle}{[I]^2} \left\{ ([I]-2)\langle a_z^2 \rangle + \langle \hat{a}^2 \rangle + \frac{[I]+2}{[I]-2}\langle \hat{b}^2 \rangle + ([I]+2)\langle b_z^2 \rangle \right\} , \end{aligned} \tag{118}$$

$$\begin{aligned} \frac{d}{dt}\langle b_z \rangle = &-\frac{1}{T_F}\left\{ \frac{2}{3}\left[\frac{\gamma N \tau}{\hbar} \right]^2 + \left[\frac{\alpha\tau}{\hbar} \right]^2 \langle \hat{K}^2 - K_z^2 \rangle \right\} \{ -B_{ba}\langle a_z \rangle + (1 - B_{bb})\langle b_z \rangle \} \\ &+ \frac{1}{T_F}\left[\frac{\alpha\tau}{\hbar} \right]^2 \left\langle K_z^2 - \frac{\hat{K}^2}{3} \right\rangle \left\{ \frac{3[I]}{4}\langle S_z \rangle - \frac{3}{[I]^2}(\langle a_z^3 \rangle - \langle b_z^3 \rangle) \right\} \\ &+ \frac{1}{T_F}\left[\frac{\alpha\tau}{\hbar} \right]^2 \frac{\langle K_z \rangle}{[I]^2} \left\{ -([I]+2)\langle b_z^2 \rangle + \langle \hat{b}^2 \rangle + \frac{[I]-2}{[I]+2}\langle \hat{a}^2 \rangle - ([I]-2)\langle a_z^2 \rangle \right\} , \end{aligned} \tag{119}$$

where the coupling matrix is

$$B_{ff'} = \frac{1}{2[I]^2}\{ [I] + 2(-1)^{a-f} \}\{ [I] - (-1)^{a-f'} \} \ . \tag{120}$$

Physically, B'_{ff} is the fraction of the angular momentum $\langle f'_z \rangle$ originally in the multiplet f' which is transferred to the multiplet f after a collision which destroys the electron spin S of the alkali-metal atom but which does not affect the nuclear spin I. This is often called an electron randomizing collision, and it occurs for collisions of very short duration because the Hamiltonian ΔH of (101) does not contain $\vec{I}$ explicitly (except possibly in a term of the form $\Delta A\, \vec{\mathrm{I}} \cdot \vec{\mathrm{S}}$ which could contribute to the coupling of $\langle I_z \rangle$ and $\langle S_z \rangle$ at very large magnetic fields).[24] As was first pointed out by Bouchiat,[26] the eigensolutions of (118) and (119) in the absence of noble-gas polarization correspond to two different time constants

$$\frac{1}{T_e} = \frac{1}{T_F}\left\{ \frac{2}{3}\left[\frac{\gamma N \tau}{\hbar} \right]^2 + \frac{1}{2}\left[\frac{\alpha\tau}{\hbar} \right]^2 \right\} \tag{121}$$

and

$$\frac{1}{T_n} = \frac{2}{[I]^2}\frac{1}{T_e} \ . \tag{122}$$

These time constants correspond to an observable which Bouchiat denotes by Q_e which is similar but not identical to the electron spin and to a slowly relaxing observable $\langle I_z \rangle$ which is identical to the longitudinal nuclear spin. We refer the reader to the literature[19,25] for a more detailed discussion of relaxation by electron randomization. The relaxation equation for $\langle K_z \rangle$ is much simpler and is

$$\frac{d}{dt}\langle K_z\rangle=\frac{1}{T_K}\left[\frac{\alpha\tau}{\hbar}\right]^2[\langle\hat{K}^2-K_z^2\rangle\langle S_z\rangle-\tfrac{1}{2}\langle K_z\rangle]\ . \quad (123)$$

In the practically important case of spin-exchange equilibrium (see Sec. V) one can ignore the complicated coupled equations (118) and (119) and consider their sum which is simply

$$\frac{d}{dt}\langle F_z\rangle=-\frac{1}{T_F}\left\{\frac{2}{3}\left[\frac{\gamma N\tau}{\hbar}\right]^2+\left[\frac{\alpha\tau}{\hbar}\right]^2\langle\hat{K}^2-K_z^2\rangle\right\}\langle S_z\rangle+\frac{1}{2T_F}\left[\frac{\alpha\tau}{\hbar}\right]^2\langle K_z\rangle\ . \quad (124)$$

The frequency-shift formulas (110)—(112) remain valid for the conditions of this section as well as those of Sec. IX.

XI. OPTICAL PUMPING

For completeness we briefly discuss the primary source of angular momentum for the system considered here; of course this is the beam of circularly polarized light which is absorbed by the alkali-metal atoms. One of the simplest situations to analyze and also a situation which frequently is closely approximated in practice is broad-line pumping with circularly polarized D_1 light in the presence of an appropriate buffer gas.[26] As discussed in Ref. 26 broad-line pumping refers to a situation where the spectral profile of the exciting light is such that equal light intensities are available to drive transitions from any of the two ground-state multiplets $f_g=I\pm\frac{1}{2}$ to any of the excited-state multiplets $f_e=I\pm\frac{1}{2}$. As the name "broad-line" implies, this will usually be true if a pressure-broadened resonance lamp or a multimode laser is used as the pumping source. It will also be true for a single-mode laser if the Doppler and collisional broadening of the absorption line are much bigger than the hyperfine splitting.

It is well known that the details of optical pumping depend on the fate of the excited $P_{1/2}$ atoms which are produced when a photon is absorbed. Here we consider an especially simple situation which is nearly realized in many of the experiments on spin-exchange optical pumping of noble-gas nuclei.[8] We shall assume that the electronic angular momentum J of the excited $P_{1/2}$ atom is completely randomized before the excited atom decays either by spontaneous emission or, more likely, by a quenching collision with a N_2 molecule. We shall also assume that the hyperfine coupling in the excited state is so weak and the J-randomization time is so short that there is negligible depolarization of the nuclear spin I in the excited state. Under these conditions one can show that optical pumping is completely equivalent to spin exchange with a pseudo spin-$\frac{1}{2}$ particle.

The equivalence of optical pumping to spin exchange for the optical-pumping conditions mentioned above can be proved with the methods outlined in Ref. 27. However, we will give a physical plausibility argument here. In a binary spin-exchange collision the collision duration is so short compared to the hyperfine period of the alkali-metal atom that the nucleus has no time to evolve during the collision and the nuclear polarization is conserved. For broad-line optical pumping the duration of a "collision" between an alkali-metal atom and a photon can be thought of as the inverse of the optical frequency linewidth of the light source or the inverse of the optical absorption linewidth of the alkali-metal atoms, whichever is shorter. We are considering a situation where the photon collision duration is very short compared to the hyperfine period so the nucleus is unable to evolve during the time of a photon-atom collision. If the atoms are rapidly deexcited before the nuclear polarization can evolve under the influence of hyperfine interactions in the excited state, the collision with a photon will have no effect on the nuclear polarization. With respect to the electron spin, we know that an alkali-metal atom with a spin-down electron can undergo a binary spin-exchange collision with a spin-up collision partner. There will be no interaction if the electron spin of the alkali-metal atom is parallel to that of its collision partner. Similarly, an alkali-metal atom with a spin-down electron can absorb a σ_+ photon of D_1 light but no light will be absorbed if σ_- photons impinge on alkali-metal atoms with spin-down electrons or σ_+ photons impinge on alkali-metal atoms with spin-up electrons. After a spin-exchange collision between an alkali-metal atom with a spin-down electron and a spin-up collision partner the mean electron spin of the alkali-metal atom will be zero, so $\frac{1}{2}$ a unit of angular momentum will have been added to the alkali-metal atom. In a like manner, after a collision between a spin-down alkali-metal atom and a σ_+ photon the mean electron spin of the alkali-metal atom will be zero and $\frac{1}{2}$ a unit of angular momentum will have been added to the alkali-metal atom. The nuclear polarization of the alkali-metal atom is changed by ground-state hyperfine interactions in the relatively long intervals between spin-exchange or photon collisions.

Because of the equivalence of broad-line optical pumping with conservation of the nuclear spin polarization to spin-exchange collisions, the evolution of the observables $\langle a_z\rangle$ and $\langle b_z\rangle$ is given by Eqs. (118), (119), and (124) of Sec. X, with the following replacements:

$$\langle K_z\rangle\to\frac{s_z}{2}\ , \quad (125)$$

where s_z is the mean spin of the pumping photons,

$$\langle\hat{K}^2-K_z^2\rangle\to\tfrac{1}{2}\ , \quad (126)$$

$$\langle K_z^2-\tfrac{1}{3}\hat{K}^2\rangle\to 0\ . \quad (127)$$

Equations (126), (127), and (128) are all consequences of the fact that the photons behave like spin-$\frac{1}{2}$ particles as far as angular momentum transfer is concerned. To make use of (118), (119), and (124) we must also set

$$\gamma N=0\ , \quad (128)$$

and

$$\frac{1}{2T_F}\left[\frac{\alpha\tau}{\hbar}\right]^2\to R\ , \quad (129)$$

where R is the mean photon absorption rate for unpolarized alkali-metal atoms. For example, (124) becomes

$$\frac{d}{dt}\langle F_z\rangle = R\left[\frac{s_z}{2} - \langle S_z\rangle\right] . \tag{130}$$

Since the details of optical pumping are not a central part of this paper we refer the reader to Ref. 27 for additional discussions of broad-line optical pumping with conservation of the nuclear spin in the optical-pumping cycle.

XII. *RC* NETWORK MODEL

Some insight into the behavior of the systems under consideration here can be gained by representing the system with the electrical circuit model shown in Fig. 10 and discussed in detail below. For simplicity we have limited our discussion to the high-pressure regime of Sec. IX. The collection of alkali-metal atoms in the sample cell is represented by the capacitor C_{Rb} and the noble-gas atoms are represented by the capacitor C_{Xe}. The total spin angular momentum of the alkali-metal atoms is equivalent to the charge stored on the capacitor:

$$Q_{\mathrm{Rb}} = \Omega[\mathrm{Rb}]\langle F_z\rangle , \tag{131}$$

where Ω is the volume of the cell and $\langle F_z\rangle$ is the volume averaged angular momentum per alkali-metal atom. In a like manner the total spin angular momentum of the noble-gas atoms is

$$Q_{\mathrm{Xe}} = \Omega[\mathrm{Xe}]\langle K_z\rangle . \tag{132}$$

If we sum (108) over the two possible values of f to obtain a formula for $(d/dt)\langle F_z\rangle$ and multiply the resulting equation by $\Omega[\mathrm{Rb}]$ we obtain

$$\frac{d}{dt}Q_{\mathrm{Rb}} = -\frac{V_{\mathrm{Rb}}}{R_{\mathrm{sr}}} + \frac{1}{R_{\mathrm{ex}}}(V_{\mathrm{Xe}} - V_{\mathrm{Rb}}) , \tag{133}$$

where the "voltages" V_{Rb} and V_{Xe} are

$$V_{\mathrm{Rb}} = \frac{\langle F_z\rangle}{\langle \hat{F}^2 - F_z^2\rangle} , \tag{134}$$

$$V_{\mathrm{Xe}} = \frac{\langle K_z\rangle}{\langle \hat{K}^2 - K_z^2\rangle} . \tag{135}$$

In the following discussion we shall assume that the spin systems are described by the spin-temperature distribution (43). Then one can show that

$$V_{\mathrm{Rb}} = \frac{\langle F_z\rangle}{\langle \hat{F}^2 - F_z^2\rangle} = \frac{\langle I_z\rangle}{\langle \hat{I}^2 - I_z^2\rangle} = 2\langle S_z\rangle = \tanh\frac{\beta(\mathrm{Rb})}{2} , \tag{136}$$

where $\beta(\mathrm{Rb})$ is the spin-temperature parameter of the alkali-metal atoms. Similarly, we assume that

$$V_{\mathrm{Xe}} = \frac{\langle K_z\rangle}{\langle \hat{K}^2 - K_z^2\rangle} = \tanh\left[\frac{\beta(\mathrm{Xe})}{2}\right] , \tag{137}$$

where we expect, in general, that $\beta(\mathrm{Xe}) \neq \beta(\mathrm{Rb})$. The magnitudes of the voltage are always less than one and angular momentum will flow from a "high-voltage" spin system to a "low-voltage" spin system just as ordinary charge flows under the influence of ordinary voltage.

The spin-rotation admittance is given by

$$\frac{1}{R_{\mathrm{sr}}} = \frac{1}{T_0}\frac{2}{3}\left[\frac{\gamma N \tau}{[I]\hbar}\right]^2 \langle \hat{F}^2 - F_z^2\rangle , \tag{138}$$

where

$$\frac{1}{T_0} = \frac{\Omega[\mathrm{Rb}]}{T_F} = \frac{\Omega[\mathrm{Xe}]}{T_K} \tag{139}$$

is the total rate of formation of molecules in the sample cell.

The spin-exchange admittance is given by

$$\frac{1}{R_{\mathrm{ex}}} = \frac{1}{T_0}\left[\frac{\alpha\tau}{[I]\hbar}\right]^2 \langle \hat{F}^2 - F_z^2\rangle\langle \hat{K}^2 - K_z^2\rangle , \tag{140}$$

In a like manner, if we multiply (109) by $\Omega[\mathrm{Xe}]$ we see that it can be written as

$$\frac{d}{dt}Q_{\mathrm{Xe}} = \frac{1}{R_{\mathrm{ex}}}(V_{\mathrm{Rb}} - V_{\mathrm{Xe}}) - \frac{1}{R_w}V_{\mathrm{Xe}} , \tag{141}$$

where the wall admittance is given by

$$\frac{1}{R_w} = \frac{C_{\mathrm{Xe}}}{T_w} . \tag{142}$$

The capacitors are defined as the ratios of charge to voltage for the two types of atoms, i.e.,

$$C_{\mathrm{Rb}} = \frac{Q_{\mathrm{Rb}}}{V_{\mathrm{Rb}}} = \Omega[\mathrm{Rb}]\langle \hat{F}^2 - F_z^2\rangle , \tag{143}$$

$$C_{\mathrm{Xe}} = \frac{Q_{\mathrm{Xe}}}{V_{\mathrm{Xe}}} = \Omega[\mathrm{Xe}]\langle \hat{K}^2 - K_z^2\rangle . \tag{144}$$

If we multiply (131) by $\Omega[\mathrm{Rb}]$ we find

$$\frac{d}{dt}Q_{\mathrm{Rb}} = \frac{1}{R_{\mathrm{opt}}}(V_{\mathrm{opt}} - V_{\mathrm{Rb}}) , \tag{145}$$

where the optical emf is equal to the mean photon spin

$$V_{\mathrm{opt}} = s_z \tag{146}$$

and the optical admittance is given by

$$\frac{1}{R_{\mathrm{opt}}} = \frac{\Omega[\mathrm{Rb}]R}{2} . \tag{147}$$

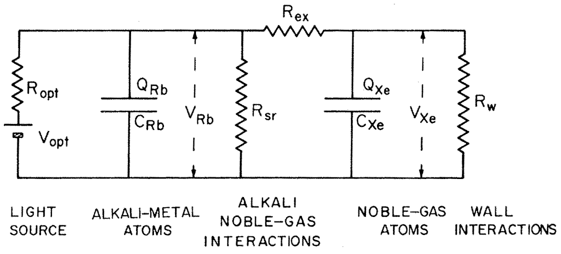

FIG. 10. Process of spin-exchange optical pumping is well described by an *RC* network model. Angular momentum is analogous to electrical charge which is stored on capacitors which represent the alkali-metal and noble-gas atoms. Spin polarization, $\tanh(\beta/2)$, is analogous to voltage. The resistors are related to various terms in the Hamiltonian (1).

That is, the optical admittance is just half the number of photons absorbed per second by the alkali-metal atoms in the sample cell.

We note that the capacitances $C_{\rm Rb}$ and $C_{\rm Xe}$ are proportional to factors $\langle \hat{F}^2 - F_z^2 \rangle$ and $\langle \hat{K}^2 - K_z^2 \rangle$ which depend on the spin polarization, except for the special case of spin $\frac{1}{2}$. For $S=\frac{1}{2}$ we have, independent of polarization,

$$\langle \hat{S}^2 - S_z^2 \rangle = \tfrac{1}{2} \ .$$

For spins greater than $\frac{1}{2}$, factors like $\langle \hat{K}^2 - K_z^2 \rangle$ are always larger than $\frac{1}{2}$ and they reflect the fact that more angular momentum can be stored in a large-spin atom than in an atom with the minimum spin $\frac{1}{2}$. Thus we may think of a minimum-spin atom (i.e., a spin-$\frac{1}{2}$ atom) as the equivalent of an "air-gap" capacitor for angular momentum, while an atom with spin greater than $\frac{1}{2}$ is like a capacitor with dielectric material between its plates. This suggests that we define a "paramagnetic constant" for a spin-K atom by

$$\epsilon(K,\beta) = 2\langle \hat{K}^2 - K_z^2 \rangle = 2\left\{ K(K+1) - \frac{1}{Z}\frac{d^2 Z}{d\beta^2} \right\} , \tag{148}$$

where

$$Z = \sum_{m_K=-K}^{+K} \exp(\beta m_K) \tag{149}$$

then the capacitance (144) can be written as

$$C_{\rm Xe} = \Omega[{\rm Xe}]\tfrac{1}{2}\epsilon(K,\beta) , \tag{150}$$

where $\frac{1}{2}$ is the capacitance per atom for a spin-$\frac{1}{2}$ atom, the ideal air-gap capacitance, and $\epsilon(K,\beta)$ is the paramagnetic constant which corrects for the fact that the spin K may be larger than $\frac{1}{2}$.

For $K > \frac{1}{2}$ the paramagnetic constant will depend on the degree of polarization and the capacitance (150) will therefore be voltage dependent in somewhat the same way as the capacitance of a back-biased *pn* junction. We note that the paramagnetic constant decreases with increasing polarization and saturates at a minimum value

$$\epsilon(K,\infty) = 2K \tag{151}$$

for a fully polarized nucleus with $V_{\rm Xe}=1$ and all atoms in the state with maximum azimuthal angular momentum K. This ensures that the charge of a fully polarized nucleus of spin K is K. We also note that for very weak polarization the paramagnetic constant reaches its maximum value which is

$$\epsilon(K,0) = \tfrac{4}{3}K(K+1) \ . \tag{152}$$

Paramagnetic constants for a few selected examples are shown in Fig. 11 as a function of the voltage, $\tanh(\beta/2)$, of (137).

For an alkali-metal atom in spin-temperature equilibrium the paramagnetic constant is

$$\epsilon(F,\beta) = 2\langle \hat{F}^2 - F_z^2 \rangle = 2\langle \hat{S}^2 - S_z^2 \rangle + 2\langle \hat{I}^2 - I_z^2 \rangle$$
$$= 1 + \epsilon(I,\beta) , \tag{153}$$

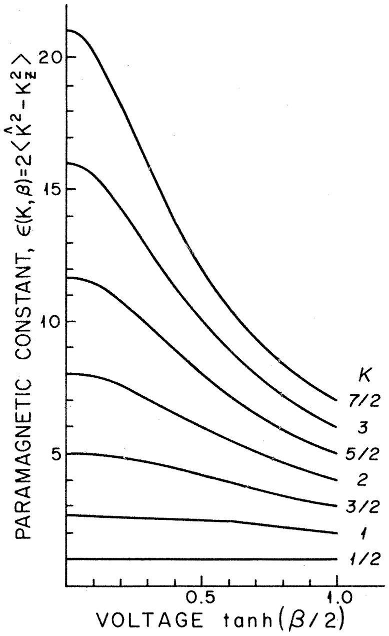

FIG. 11. Paramagnetic constants of a spin system are a measure of the amount of angular momentum which can be stored in a spin system.

where $\epsilon(I,\beta)$ is defined by (148). One may therefore obtain the paramagnetic constant for an alkali-metal atom of nuclear spin $I=K$ by adding one unit to the appropriate curves of Fig. 11. We note that the paramagnetic constants (148) are related as follows to the Brillouin functions $B_K(x)$ defined by Smart:[28]

$$\epsilon(K,\beta) = \frac{2KB_K(K\beta)}{B_{1/2}(\beta/2)} \ . \tag{154}$$

We note that in a typical experiment with stable heavy noble gases where the relaxation of both the alkali-metal and noble-gas spins is dominated by molecular formation, the number density (and therefore the capacitance $C_{\rm Xe}$) of the noble-gas atoms is orders of magnitude larger than the number density (and therefore the capacitance $C_{\rm Rb}$) of the alkali-metal atoms. Consequently, the *RC* time constant for charging or discharging the noble-gas capacitor with angular momentum will be orders of magnitude longer than the *RC* time constant for the alkali-metal capacitor. Representative time constants for the alkali-metal capacitor are a few milliseconds while representative time constants for the noble-gas capacitor are minutes to nearly one hour in our own work. We note that the effects on the alkali-metal atoms of other spin-destroying mechanisms like diffusion have been omitted from Fig. 10. These additional spin-relaxation mechanisms can be represented by resistor in parallel with $R_{\rm sr}$.

XIII. COMPARISON OF PERTURBATION FORMULAS WITH EXACT NUMERICAL SOLUTIONS

We conclude this paper with a comparison between the relatively simple perturbation formulas of Secs. VII and

VIII and exact numerical evaluations of (32), (34), and (39) with a computer. To carry out the numerical evaluation, the matrix elements of the Hamiltonian (9) were evaluated in terms of the basis states $|f,m_f,m_K)$ discussed in connection with Eq. (60). By dropping the very small terms proportional to g_I and g_K we obtained a matrix which was block diagonal, with each block corresponding to a total azimuthal quantum number m_f+m_K about the ζ axis of Fig. 8. The blocks were diagonalized and the eigenvectors were used to calculate the matrix elements in the numerators of (32), (34), and (39), while the eigenvalues were used to calculate the resonant denominators. We used the following parameters, which are representative of the ^{87}Rb^{129}Xe molecule:

$$I=\tfrac{3}{2},\quad K=\tfrac{1}{2},\quad \gamma N=4,\quad \alpha=1,\quad A=118\,. \tag{155}$$

The molecular lifetime τ of (30) was expressed in terms of the ratio p/p_0 of the third-body pressure to a characteristic pressure p_0

$$\tau=\frac{\hbar}{\gamma N}\frac{p_0}{p}\,. \tag{156}$$

That is, p_0 is that third-body pressure for which the molecular lifetime τ is equal to the spin rotational period $\hbar(\gamma N)^{-1}$. Ramsey *et al.*[11] have shown that the characteristic pressures p_0 for N_2 and He are 81 and 133 Torr, respectively.

We note that the spin-transfer rates are the product of a molecular formation rate $T^{-1}(J)$ and a spin-transfer coefficient $q(J,L)$ as shown in (26). We have therefore plotted as a function of p/p_0 the quantities $(p/p_0)q(J,L)$ which are proportional to $\{1/T(J)\}q(J,L)$, as one can see from the following arguments.

In chemical equilibrium the breakup rate of molecules per unit volume must equal the formation rate per unit volume and we must therefore have

$$[\mathrm{RbXe}]\tau^{-1}=\frac{[\mathrm{Xe}]}{T_K}=\frac{[\mathrm{Rb}]}{T_F}\,. \tag{157}$$

Thus, we may rewrite (157) as

$$\frac{1}{T_F}=[\mathrm{Xe}]\kappa\tau^{-1}=\frac{\gamma N}{\hbar}\kappa[\mathrm{Xe}]\frac{p}{p_0} \tag{158}$$

or

$$\frac{1}{T_K}=[\mathrm{Rb}]\kappa\tau^{-1}=\frac{\gamma N}{\hbar}\kappa[\mathrm{Rb}]\frac{p}{p_0}\,, \tag{159}$$

where the chemical equilibrium constant is

$$\kappa=\frac{[\mathrm{RbXe}]}{[\mathrm{Rb}][\mathrm{Xe}]} \tag{160}$$

thus

$$\frac{1}{T_F}q(f,K)=\frac{\gamma N}{\hbar}\kappa[\mathrm{Xe}]\frac{p}{p_0}q(f,K) \tag{161}$$

and

$$\frac{1}{T_K}q(K,f)=\frac{\gamma N}{\hbar}\kappa[\mathrm{Rb}]\frac{p}{p_0}q(K,f)\,. \tag{162}$$

We note that the parameters γN and α will depend on the vibrational and rotational state of the van der Waals molecule. If γ/α is approximately independent of the quantum state the important ratio $x=\gamma N/\alpha$ will depend on the distribution of the rotational quantum number N. All of the formulas of the preceding sections have implicitly assumed a fixed value of N. For the short-lifetime regimes described in Secs. IX and X, we are only concerned with the mean-squared value of N and the form of the probability distribution is unimportant. However, for the longer molecular lifetimes discussed in Secs. VII and VIII the rms value of N is not sufficient to determine the average-coupling constants. Bouchiat *et al.*[13] suggested that the following simple distribution of N is a reasonable approximation for heavy van der Waals molecules:

$$P(N)=\frac{9N}{10N_r^2}\left[2-\left[\frac{6}{5}\right]^{1/2}\frac{N}{N_r}\right] \tag{163}$$

for

$$0\le N\le 2\left[\frac{5}{6}\right]^{1/2}N_r \tag{164}$$

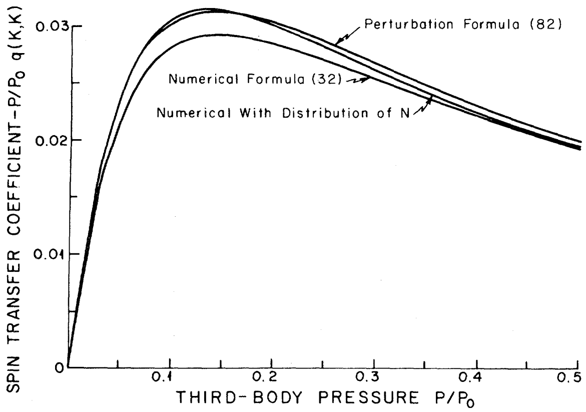

FIG. 12. Comparison between exact numerical evaluations and perturbative approximations of the spin-transfer coefficient $q(K,K)$. Effect of assuming a distribution in the rotational quantum number N is also shown.

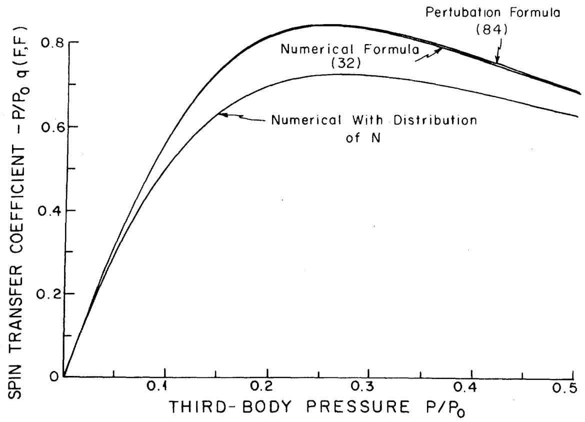

FIG. 13. Comparison between exact numerical evaluations and perturbative approximations of the spin-transfer coefficient $q(F,F)$. Effect of assuming a distribution in the rotational quantum number N is also shown.

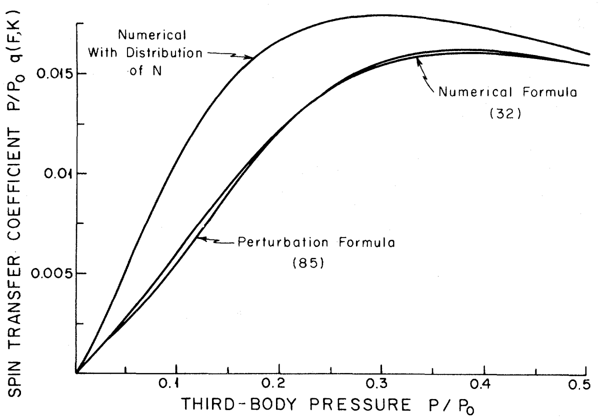

FIG. 14. Comparison between exact numerical evaluations and perturbative approximations of the spin-transfer coefficient $q(F,K)$. Effect of assuming a distribution in N is also shown.

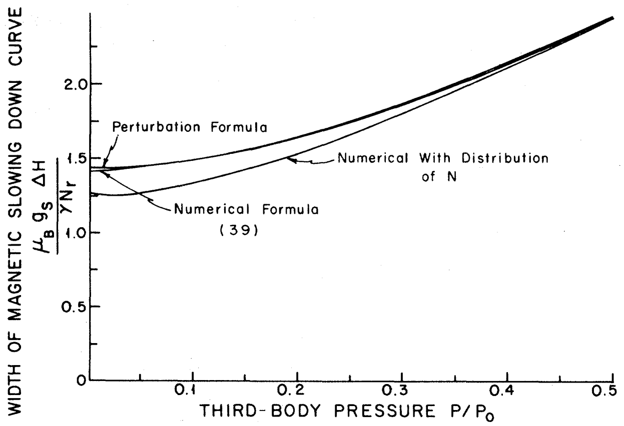

FIG. 16. Comparison between exact numerical evaluations and perturbative approximations to the width ΔH of the magnetic slowing-down curves. Effect of assuming a distribution of N is also shown.

and $P(N)=0$ for all other values of N. Here the constant N_r is the rms value of N defined by

$$N_r^2=\int_0^{\infty} N^2P(N)dN \,. \tag{165}$$

Since the perturbation formulas of Secs. VII and VIII are obtained as power-series expansions in N^{-1} we can expect difficulties if we naively average the formulas over the distribution (163), which has substantial contributions from small values of N where the expansion parameter $x^{-1}=\alpha/\gamma N$ exceeds unity. However, it is straightforward to average the numerical evaluations of (32), (34), and (39) over the distribution (163).

A comparison of the perturbation formula (82) with the numerical evaluations of (32) is shown in Fig. 12. There is good agreement over the whole range of relative pressures p/p_0 and the distribution of N makes little difference. A similar comparison of the perturbation formula (84) with the numerical evaluation of (32) is shown in Fig. 13. The distribution of N lowers the relaxation rate by about 10% near the peak of the curve. In Fig. 14 we compare the perturbation formula (85) to the numerical evaluation of (32). The distribution of N causes $q(F,K)$ to increase by nearly a factor of 2 for low third-body pressures. In Fig. 15 we compare the perturbation formula (86) for the frequency-shift coefficient $s(a,K)$ to the numerical evaluation of (34). There is good agreement even when the distribution of N is taken into account. From Figs. 12—15 we see that there is good agreement between perturbation formulas and the numerical evaluation of the coefficients in most cases, but the distribution of N can have a very large effect on the spin-transfer coefficient $q(F,K)$ for small third-body pressures. The overall agreement is best for the coefficient $q(K,K)$.

Studies of the slowing down of the spin-relaxation rates in a large external magnetic field, as illustrated in Fig. 6, have played an important role in determining the magnitudes of the coupling constants in the Hamiltonian (1). We will define the width of a magnetic slowing-down curve like one of those in Fig. 6 as the magnetic field ΔH at which the relaxation rate has decreased to half of its peak value. The width ΔH_0 at very low third-body pressures is a fairly direct gauge of the spin-rotation interaction constant γN. In Fig. 16 we show a comparison of the width determined from numerical evaluation of (39)

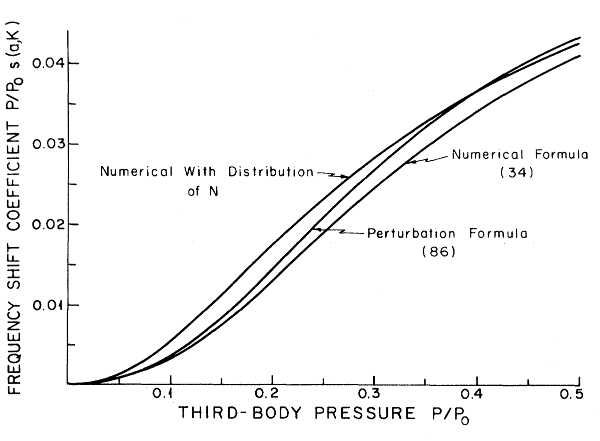

FIG. 15. Comparison between exact numerical evaluations and perturbative approximations of the frequency-shift coefficient $s(a,K)$. Effect of assuming a distribution in N is also shown.

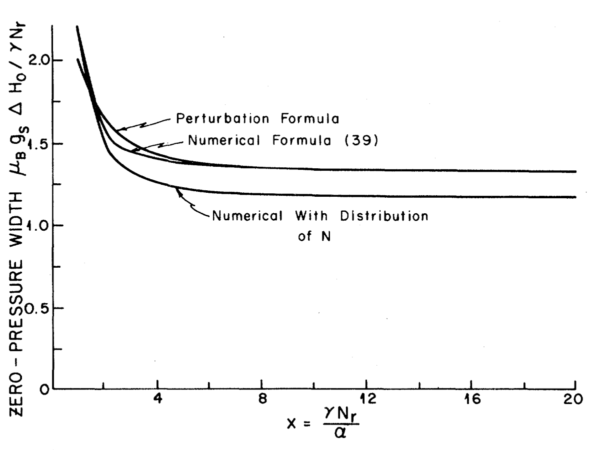

FIG. 17. Comparison between exact numerical evaluations and perturbative approximations to the zero-pressure width ΔH_0 of the magnetic slowing-down curves. Effect of assuming a distribution of N is also shown.

with the width obtained from the perturbation formulas (94) and (97). The zero-pressure width ΔH_0 is obtained by numerical evaluation of (97). The high-pressure width obtained from (94) is

$$\Delta H = \frac{\gamma N[I]}{g_S \mu_B} \frac{p}{p_0} . \tag{166}$$

We have used the simple hyperbolic formula

$$\Delta H = \left[(\Delta H_0)^2 + \left[\frac{\gamma N[I]}{g_S \mu_B} \frac{p}{p_0} \right]^2 \right]^{1/2} \tag{167}$$

to interpolate between the low- and high-pressure expressions for ΔH. The agreement between the perturbation formula and the numerical formula is excellent. The effect of a distribution of N is to decrease the predicted width by some 15%.

In Fig. 17 we show how the low-pressure width ΔH_0 depends on the coupling constant γN for fixed values of the other parameters of (155). Over a large range of the ratio $x = \gamma N/\alpha$ the width is proportional to the spin-rotation coupling constant. The effect of a distribution of N is to lower the predicted ratio of ΔH to γN by about 15%.

ACKNOWLEDGMENTS

This work was supported by the U.S. Air Force Office of Scientific Research under Grant No. AFOSR-81-0104-C.

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