Solid-effect rate equations for a spin-1 nucleus

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We derive and solve the rate equations for the solid-effect dynamic nuclear polarization of an electron and spin-1 nuclear system in the limit where the electron-spin-resonance linewidth is small compared with the nuclear-resonance frequency. Although the equations are considerably more complicated than in the case of spin-$\frac{1}{2}$ nuclei, the nuclear polarization and time to polarization are comparable with the results for the spin-$\frac{1}{2}$ system with similar intrinsic rates.

I. INTRODUCTION

The solid effect was the first mechanism discovered for dynamic nuclear polarization (DNP). In this effect the electrons are polarized by brute force in a large dc magnetic field and/or low temperatures. The system is irradiated by microwaves at the frequency to induce simultaneous electron-spin-resonance (ESR) and nuclear-magnetic-resonance (NMR) transitions, which occur because of the weak dipolar interaction between the electron and nuclear spins. If the nuclear magnetic relaxation is long enough and the electron spin relaxation is short enough, then one nuclear state will be filled up preferentially. For the best results, it is necessary that the ESR linewidth be less than the NMR frequency. This mechanism[1,2] has been described in detail for nuclear spin $I=\frac{1}{2}$ and it is commonly inferred that the equations for the case of nuclear spin $I>\frac{1}{2}$ are similar. However, we know of no publication where the equations for the case of $I>\frac{1}{2}$ are derived and/or solved. In this paper we derive and solve the equations for the solid effect in the case where $I=1$.

This work has been motivated by the program to spin-polarize both nuclei in deuterium-tritium systems in order to enhance the fusion cross section for laser-driven fusion. The tritium's radioactive decay heat poses a formidable problem in cooling to the low temperatures required for nuclear polarization. For this reason, DNP for spin-1 and spin-$\frac{1}{2}$ systems is of technological as well as intrinsic interest. DNP has been tried on externally irradiated solid hydrogen deuteride and the observed deuteron polarization was about 0.1 of the observed proton polarization.[3,4] The reason for this difference is unknown and it could have been caused by many factors. However, it does lead to one of the questions to be considered here: is there an inherent difference in polarization efficiency between $I=\frac{1}{2}$ and $I=1$ nuclear-spin systems?

There are several general articles on the dynamic polarization of $I=1$ nuclei,[5-7] but we know of no derivation of the solid effect for the case. One reason is that actual ESR lines are generally broad compared to the NMR frequency of the deuteron. Also, there exists another mechanism, dynamic cooling, which requires a broad inhomogeneous ESR line to work well.[8,9] This mechanism may be the dominant one in almost all actual deuteron polarization experiments. However, available dc magnetic fields get larger and the electron spins in the deuterium-tritium system are in orbital S states which should have a relatively small amount of inhomogeneous broadening. Thus, a $I=1$ solid effect may soon be seen.

II. RATE EQUATIONS

In what follows we shall let S and I denote the electron and nuclear spins, respectively.

A. Case of $I=\frac{1}{2}$

The polarization equations for $S=\frac{1}{2}, I=\frac{1}{2}$ have been described by Jeffries,[1] by Abragam and Goldman,[2] and by many others. However, we shall briefly summarize this case for the purpose of comparing it to the case of $I=1$. We shall use Jeffries's terminology in which all rates are expressed in units of ω_1, the rate for the $\Delta m_S=\pm 1, \Delta m_I=0$ transition, or

$$\omega_1 = 1/(2T_{1e}) \tag{1}$$

where T_{1e} is the longitudinal relaxation rate for the electrons. The transition rates involving the pump (or electronic-spin) system are shown schematically in Fig. 1. In particular $\beta\omega_1$ is the externally induced rf pumping rate, $\theta\omega_1$ is the nuclear relaxation rate for $\Delta m_I=\pm 1$ that is induced by the electrons, and $\sigma\omega_1$ is the rate for the $\Delta m_I=\pm 1$ and $\Delta m_S=\pm 1$ transitions. It is easily shown that both θ and σ must be much less than one. Further, there is the usual NMR relaxation rate of the nuclear spins in the absence of the electron spins,

$$1/T_{1n} = 2\phi\omega_1 \, . \tag{2}$$

The nuclear polarization P_n is defined as

$$P_n = (n_+ - n_-)/n \, , \tag{3}$$

where $n_\pm$ is the number of nuclear spins with $m_I=\pm\frac{1}{2}$

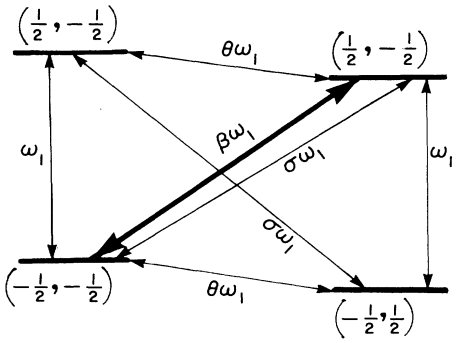

FIG. 1. Energy levels (m_S,m_I) for the electronic and nuclear spins for the case of $I=S=\frac{1}{2}$. The rates shown in the diagram are explained further in the text. The pumping shown will produce an abundance of nuclei in the state $m_I=\frac{1}{2}$ and a positive nuclear polarization.

and n is the total number of nuclear spins. The electronic polarization P_e is defined similarly. Note that the equilibrium electronic polarization P_0 is negative and

$$P_0=-\tanh(\mu_e H_0/kT)\ , \tag{4}$$

where H_0 is the magnitude of the applied external field and μ_e is the electron's magnetic moment. We shall assume that the nuclear moment is small enough so that the equilibrium nuclear polarization is zero.

The calculation of the rate equations is essentially the same as Jeffries except we allow for a finite P_0. That is, it is assumed that the ESR line is narrow compared to the nuclear-resonance frequency so that only the one transition shown in Fig. 1 is pumped and it is also assumed that the nuclear spins stay in equilibrium with each other. The relative rates θ and σ are appropriate averages as discussed by Abragam and Goldman and c is the number of electrons divided by the number of nuclei. Using the fact that θ and σ are much less than one, the results can be expressed in the convenient form

$$\begin{aligned} T_{1e}\frac{dP_e}{dt}&=-P_e(1+\tfrac{1}{2}\beta)-P_0-\tfrac{1}{2}\beta P_n\ ,\\ T_{1n}^*\frac{dP_n}{dt}&=-P_n[1+\tfrac{1}{2}(\beta/2f)]-(\beta/2f)P_e\ , \end{aligned} \tag{5}$$

where

$$\begin{aligned} (1/T_{1n}^*)&=2\omega_1[\phi+c\theta+c\sigma(1-P_eP_0)]\ ,\\ f&=T_{1e}/T_{1n}^*c\ . \end{aligned} \tag{6}$$

These equations are slightly different than those of Jeffries because of the finite value of P_0. Further, we note that T_{1n}^*, the effective nuclear-spin relaxation rate, depends upon P_e.

In order to facilitate a comparison with the $I=1$ case, we shall solve for the equilibrium values of the nuclear and electronic polarizations and the relevant time scales. Equations (6) can be solved in the steady state to yield (for $\sigma\ll 1$)

$$\begin{aligned} P_n(\infty)&=-\beta P_0/[\beta+f(\beta+2)+2\sigma(1-P_0^2)]\ ,\\ P_e(\infty)&=P_0(\beta+2f+\sigma)/[\beta+f(\beta+2)+2\sigma(1-P_0^2)]\ . \end{aligned} \tag{7}$$

Further, if one assumes that the electronic spins respond much faster than the nuclear spins, one can derive equation for the individual time scales. The assumption can then be easily verified. Thus, one can show that the electronic spins respond at a rate λ_e where

$$\lambda_e=(2+\beta)/2T_{1e}\ , \tag{8}$$

and that the electronic polarization responds by relaxing to a value $P_e(n)$ that depends on P_n:

$$P_e(n)=(2P_0-\beta P_n)/(2+\beta)\ . \tag{9}$$

Further, if we neglect the term $\sigma(1-P_eP_0)$ in Eq. (5), then the nuclear-spin relaxation rate is λ_n where

$$\lambda_n=[\beta+f(2+\beta)]/T_{1n}f(2+\beta)\ . \tag{10}$$

B. Case of $I=1$

The description of the case of $I=1$ is similar to the case of $I=\frac{1}{2}$ but with some significant differences. The transition rates involving the pump (electronic-spin) system are shown schematically in Fig. 2 and β, σ, and θ are the same as in the $I=\frac{1}{2}$ case. In addition to these rates there are two additional rates from other sources (such as phonons). The rate $\phi_1\omega_1$ is due to $\Delta m_I=\pm 1$ transitions and the rate $\phi_2\omega_1$ is due to $\Delta m_I=\pm 2$ transitions.

For the case of $I=\frac{1}{2}$ there are two nuclear states and the sum of the populations of the states is a constant. Thus, the populations of the individual levels can be described by one variable, the nuclear polarization P_n. Since there are three nuclear states in the case of $I=1$, one more variable is needed to describe the level populations. For this extra variable it is convenient to choose the quadrupole polarization

$$Q_n=(n_++n_--2n_0)/n\ . \tag{11}$$

For complete nuclear polarization we are interested in filling the $m_I=+1$ state. Thus we define Z_n as a measure of this where

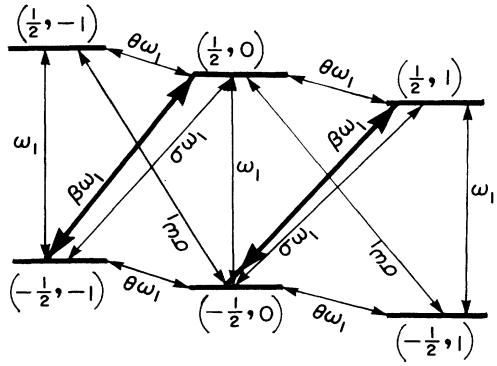

FIG. 2. Energy levels (m_S,m_I) for the electronic and nuclear spins for the case of $S=\frac{1}{2}, I=1$. The rates shown in the diagram are explained further in the text. The pumping shown will produce an abundance of nuclei with $m_I=1$.

$$Z_n = \tfrac{3}{4}P_n + \tfrac{1}{4}Q_n = (3n_+ - n)/2n \ . \tag{12}$$

Note that $Z_n = 1$, $P_n = 1$, and $Q_n = \frac{1}{2}$ when all of the nuclear spins are in the $m_I = +1$ state and $Z_n = P_n = Q_n = 0$ in a sample with $n_+ = n_- = n_0$.

The method for constructing equations of motion for P_e, P_n, and Q_n is similar to the case of $I = \frac{1}{2}$. That is, equations for n_+, n_-, n_0, N_+, and N_- are constructed by taking into account all of the possible spin-flipping processes. These equations are then converted into equations for P_e, P_n, and Q_n yielding

$$\begin{aligned}
\frac{dP_e}{dt} &= -\beta\omega_1[P_e(\tfrac{4}{3} - \tfrac{1}{3}Q_n) + P_n] - 2(1+\sigma)\omega_1(P_e - P_0) \ , \\
\frac{dP_n}{dt} &= -\tfrac{1}{2}c\beta\omega_1[P_n + P_e(\tfrac{4}{3} - \tfrac{1}{3}Q_n)] - \phi_1\omega_1 P_n \\
&\quad - c(\sigma+\theta)\omega_1(P_e - P_0)P_n \ , \\
\frac{dQ_n}{dt} &= -\tfrac{3}{2}c\beta\omega_1(Q_n + P_e P_n) - \phi_2\omega_1 Q_n \\
&\quad - 3c(\sigma+\theta)\omega_1(P_e - P_0)Q_n \ .
\end{aligned} \tag{13}$$

If we neglect the relaxation rates σ and θ, we obtain the rather simple set of equations

$$\begin{aligned}
T_{1e}\frac{dP_e}{dt} &= -\tfrac{1}{2}\beta[P_e(\tfrac{4}{3} - \tfrac{1}{3}Q_n) + P_n] - (P_e - P_0) \ , \\
T_{1n}\frac{dP_n}{dt} &= -(\beta/4f_1)[P_n + P_e(\tfrac{4}{3} - \tfrac{1}{3}Q_n)] - P_n \ , \\
T_{1q}\frac{dQ_n}{dt} &= -(3\beta/4f_2)(Q_n + P_e P_n) - Q_n \ , \\
T_{1n} &= 1/\phi_1\omega_1 \ , \\
T_{1q} &= 1/\phi_1\omega_1 \ , \\
f_1 &= T_{1e}/cT_{1n} \ , \\
f_2 &= T_{1e}/cT_{1q} \ .
\end{aligned} \tag{14}$$

The ratio T_{1n}/T_{1q} can vary from 0.6 to 3. However, for the anharmonic Raman process, the most common nuclear-spin—phonon decay scheme, we expect[10]

$$T_{1q} = \tfrac{5}{3}T_{1n} \ , \tag{15}$$

so that

$$\frac{f_2}{f_1} = 0.6 \ . \tag{16}$$

These equations have been solved numerically for the steady-state values in order to obtain actual nuclear polarizations. We have found that the solutions are very insensitive to the ratio of f_2/f_1 and thus we use a ratio of 0.6 in the remainder of this paper. The results are summarized in Fig. 3 where, for purposes of comparison, we have included the spin-$\frac{1}{2}$ case with $f = f_1$. Further, we implicitly assume that the values of β are the same in the two systems. For $f_1 = 0.01$ and 0.1, where good polariza-

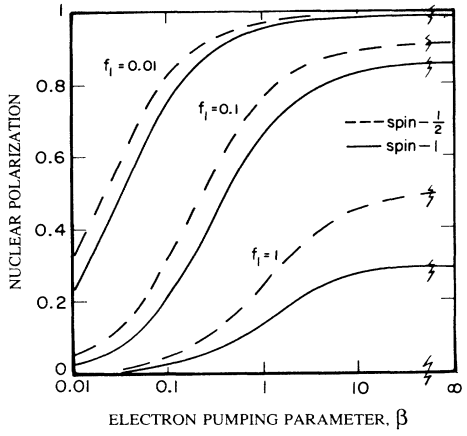

FIG. 3. Calculated steady-state polarization for dynamic nuclear polarization of the spin-$\frac{1}{2}$ (P_n) and spin-1 (Z_n) systems.

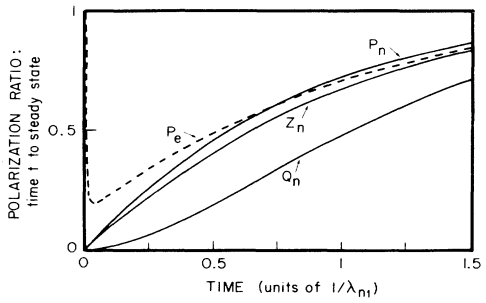

FIG. 4. Typical time-dependent behavior for the polarization of a spin-1 nuclear. In this example $\beta = 10$, $f_1 = 0.1$, $f_2/f_1 = 0.6$, and $P_e(0) = 1$.

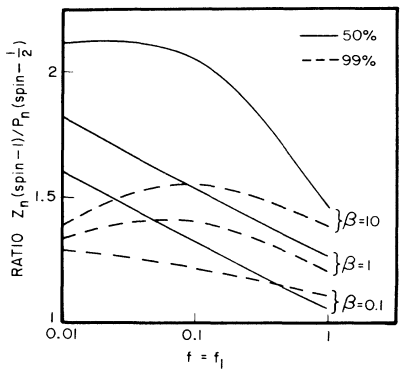

FIG. 5. Comparison of times of various percents polarization for a spin-1 and a spin-$\frac{1}{2}$ system.

tion values are achievable, we find the spin-1 system to be just slightly less efficient than the spin-$\frac{1}{2}$ system in achieving polarization. For $f_1=1.0$, where polarization values are low, the spin-$\frac{1}{2}$ system is about twice as efficient as the spin-1 system.

We now analyze the time dependence of the polarization of the spin-1 system in a manner similar to the spin-$\frac{1}{2}$ case. We assume that $c \ll 1$ and that $T_{1e} \ll T_{1n} \sim T_{1q}$ so that there are again two time scales. The electronic spins respond quickly at a rate

$$\lambda_e=(2\beta+3)/3T_{1e} . \tag{17}$$

The nuclear spins approach steady state at the slower of the two rates

$$\begin{aligned} \lambda_{n1}&=[1+(\beta/4f_1)/(1+\tfrac{2}{3}\beta)]/T_{1n} , \\ \lambda_{n2}&=[1+(3\beta/4f_2)]/T_{1q} . \end{aligned} \tag{18}$$

An example of the approach to equilibrium is given in Fig. 4. Further, we have solved both the spin-$\frac{1}{2}$ and spin-1 equations to find 50% and 99% polarization. The results are given in Fig. 5.

In summary, we find that the spin-1 system is only slightly slower than the spin-$\frac{1}{2}$ system for similar parameters. Thus, differences in the amount of polarization presumably depends on the fact that deuterium has a much smaller magnetic moment than tritium or hydrogen. Further, since deuterium has a small quadrupole moment, the deuterium nucleus could undergo substantial quadrupole broadening which could inhibit spin diffusion.

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