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Nuclear Spin Relaxation and Nuclear Electric Dipole Moments

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Proposals that nuclear spin relaxation in an appropriate system could serve as a test for the existence of a nuclear electric dipole moment are examined with attention to the consequences of the fact that the electric field at the nucleus is proportional to the nuclear acceleration. It is found that low-frequency fluctuations of the local electric field are suppressed. In particular, the necessarily negative correlation of the momentum transferred in consecutive collisions of an atom in a gas alters the spectral density of the perturbation, from that of uncorrelated pulses, by the factor $\omega^2\tau_c^2/(1+\omega^2\tau_c^2)$, where τ_c is the mean time between collisions. It follows that fairly low gas density is preferable to high. At optimum density a light gas at room temperature carrying electric dipole moments of magnitude $e\times10^{-14}$ cm should have a spin relaxation time, in the absence of competing processes, of around 10 minutes. A formula is given for the electrically induced spin relaxation rate in a crystal. The process is hopelessly slow. In the electric coupling of the lattice vibrations to the spin the ordinarily dominant "two-phonon" or "Raman" process is absent, because of the linearity of the connection between local electric field and nuclear motion.

IT has been suggested that nuclear spin relaxation may afford a test for the existence of nuclear electric dipole moments. Most recently Franken and Boyne[1,2] have discussed the possible role of nuclear electric dipole coupling in nuclear relaxation in gases; also Bloom,[3] in an abstract, refers to nuclear relaxation by electric dipole coupling in crystals and to some other related effects. The general idea is that an electric field acting on the hypothetical nuclear electric dipole and modulated by thermal agitation of the environment would bring about spin relaxation, just as magnetic interactions do. Several years ago Ramsey and the author[4] in a search for experiments which might be sensitive to the presence of a nuclear electric dipole, canvassed a variety of processes, among them nuclear spin relaxation. This effect, attractive at first glance, was summarily dismissed when closer examination showed it to be hopelessly insignificant for dipoles of reasonable strength. The revival of the question may justify a short quantitative discussion with special attention to a peculiar feature of the interaction, a feature which is to blame for the extreme weakness of the process. Franken and Boyne, in reference 1, did not take this feature fully into account, and were led to overestimate by a large factor the relaxation rate to be expected with a nuclear dipole of given strength. This was corrected subsequently[2] and the source of the difficulty was qualitatively explained. The following discussion will not lead to different conclusions but it will provide a theoretical formula, accurate for a particular model, for the partial relaxation rate due to electric dipole coupling in a gas whose nuclei carry electric dipole moments. Also, stimulated by Bloom's proposals, we shall look into the question of relaxation in crystals. Here we shall find the theory surprisingly simple, and the result quite disappointing to anyone looking for an indicator of nuclear electric dipole moments.

The coupling of the assumed nuclear electric dipole of strength μ_e to the electric field at the nucleus is described by a term $\boldsymbol{\mu}\cdot\mathbf{E}$ in the Hamiltonian. The field $\mathbf{E}$ is in some sense a random function of the time; its fluctuations are a manifestation of the thermal agitation of the system. The probability of spin transitions leading to spin-lattice equilibrium can be determined if we know the spectral density, at the appropriate frequency, ω, of the "local field" $\mathbf{E}(t)$. In other words we proceed exactly as we do in the familiar "local field" approach to magnetic relaxation. Indeed, for the problem at hand the "local field" method is entirely appropriate (as it rarely is in the magnetic case) for the perturbation involves no coupling between spins of the system; we may properly consider the spins independent of one another.

The peculiar aspect of the electrical perturbation is the unique connection between the electric field at a nucleus and the nuclear velocity $\mathbf{v}$, namely

$$Ze\int_{t_1}^{t_2}\mathbf{E}dt=M(\mathbf{v}_2-\mathbf{v}_1),\tag{1}$$

where M is the nuclear mass. Owing to (1), the randomness of $\mathbf{E}(t)$ is severely restricted in any ordinary physical system. Consider a monatomic gas, for example. In a collision, the nucleus of one of the colliding atoms feels a "pulse" of electric field, exactly proportional to the momentum transfer. After a relatively long field-free interval the next collision applies another pulse, and so on. Now these pulses *cannot be* independent; an atom which receives an eastward impulse in one collision is more than likely to receive a westward impulse in the next. Were this not so, a typical atom would execute an unrestricted random walk in velocity-space and the expectation

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[1] P. A. Franken and H. S. Boyne, Phys. Rev. Letters 2, 422 (1959).

[2] P. A. Franken and H. S. Boyne, Phys. Rev. Letters 3, 67 (1959).

[3] Myer Bloom, Bull. Am. Phys. Soc. 4, 250 (1959).

[4] E. M. Purcell and N. F. Ramsey, Phys. Rev. 78, 807 (1950).

value of its kinetic energy would increase proportional to the time without limit! Actually $\mathbf{v}$ remains within the appropriate Maxwellian distribution. Remembering that, we can see from (1) that $\int \mathbf{E}dt$ is essentially bounded, which implies that the average of $\mathbf{E}$ over a long period T must vanish *more strongly* with increasing T, than would the corresponding average over a random sequence of uncorrelated pulses.

We therefore anticipate that the spectral density of the perturbation $\mathbf{E}(t)$ will approach zero at low frequencies, in contrast to the behavior of the spectrum of the usual random perturbation, which is constant in the neighborhood of $\omega=0$. The nucleus, in other words, is automatically safeguarded against the application of *low-frequency* electric fields. The safeguards are provided by nothing more mysterious than Newton's Second Law and the fact that the atom can't move with constant acceleration for a long time without bumping into something.

To make these ideas precise we shall examine the correlation function $G(\tau)$ of the perturbation $\mathbf{E}(t)$ experienced by a nucleus which moves as follows: the nucleus, of mass M and charge Ze, is carried within an atom which moves in a Maxwellian gas at temperature T. This atom suffers random collisions at the average rate $1/\tau_c$. The probability of collision, per unit time, is assumed independent of the atom's speed. That is, we shall ignore the actual correlation between v and the time between collisions. The duration of a collision τ_a, is short compared to the mean time between collisions, $\tau_a \ll \tau_c$. Immediately after each collision the velocity of the atom has its expectation distribution according to the Maxwell distribution, regardless of its velocity just before the collision. That is, the velocity *after* a collision is completely uncorrelated with the velocity before the collision. These assumptions specify our model completely.

We are interested in the impulse $\mathbf{p}$ acquired by the atom at each collision. As the three coordinates are independent, it will suffice to discuss a component of $\mathbf{p}$ only, say p_x, which we shall write simply p. Suppose we observe an atom making a collision and note the impulse it received, p_0. We then note the impulse p_1 received by the atom in its next collision. Let us measure p in units of $(Mk\mathrm{T})^{\frac{1}{2}}$, the rms x-momentum characteristic of the Maxwellian distribution. Then the distribution of p_0 is

$$\varphi_0(p_0)dp_0 = \tfrac{1}{2}\pi^{-\frac{1}{2}} \exp(-p_0^2/4)dp_0. \tag{2}$$

By the joint distribution of p_0 and p_1 we mean a function φ_{01} such that $\varphi_{01}dp_0dp_1$ is the probability that the initial collision involved momentum transfer p_0 in dp_0 and the next collision thereafter a momentum transfer p_1 in dp_1. To find φ_{01} we note that under the rules assumed an atom with x-velocity v is associated with a distribution of momentum transfer in its *next* collision of the form $(2\pi)^{-\frac{1}{2}} \exp[-\frac{1}{2}(v+p_1)^2]$ and with a distribution of momentum transfer in its last collision $(2\pi)^{-\frac{1}{2}} \exp[-\frac{1}{2}(v-p_0)^2]$. Here v is expressed in units of the rms x-velocity. Hence

$$\begin{aligned}\varphi_{01} = (2\pi)^{-\frac{3}{2}} \int_{-\infty}^{\infty} dv \exp[-\tfrac{1}{2}(v-p_0)^2] \\ \times \exp(-\tfrac{1}{2}v^2) \exp[-\tfrac{1}{2}(v+p_1)^2] \\ = (2\pi)^{-1} 3^{-\frac{1}{2}} \exp[\tfrac{1}{3}(p_0^2+p_1^2+p_0 p^1)].\end{aligned} \tag{3}$$

The correlation of successive momentum transfers is exhibited in the quantity $\langle p_0 p_1 \rangle$ which, computed from (3), is $-\frac{1}{2}$. For the model we have assumed, correlation cannot extend beyond the next collision. That is, $\langle p_0 p_\nu \rangle = 0$, $\nu > 1$, so there is no need to compute further joint probability distributions $\varphi_{0\nu}$.[5] In fact we do not need the exact value of $\langle p_0 p_1 \rangle$ in the following argument. It is enough to know that it is negative and of course we knew it had to be negative before we calculated it.

We now inquire about the correlation function of the x-component of electric field, $G(\tau) = \langle E_x(t) E_x(t+\tau) \rangle$. $G(\tau)$ will have a big positive spike at the origin, of width about τ_a, whose exact shape is not important. Outside this interval $G(\tau)$ is determined by the probability of occurrence of a collision at t and a collision at $t+\tau$ together with the correlation between the impulses in these collisions. Remembering that the probability of the next collision occurring in dt is, proportional to $\exp(-\tau/\tau_c)$ and that the correlation of successive momentum transfers is negative, we see that $G(\tau)$ must have the form, for $\tau > \tau_a$ and $\tau < -\tau_a$,

$$G(\tau) = -|\mathrm{constant} \times \exp(-|\tau|/\tau_c)|. \tag{4}$$

We do not need to compute the constant for the fact that $\int E_x dt$ is bounded guarantees that $\int_{-\infty}^{\infty} G(\tau)dt = 0$. The "negative tails" given by (4) just balance the area of the positive spike. In Fig. 1(a) this correlation function is compared with the familiar correlation function of a random sequence of uncorrelated pulses. Fig. 1(b) shows the corresponding spectral densities, these functions being as always the Fourier cosine transforms of the correlation functions. If $\tau_c \gg \tau_a$, as assumed, the addition of the negative tails to $G(\tau)$ simply multiplies the ordinary spectrum by the factor $[1-(1+\omega^2\tau_c^2)^{-1}]$. Thus for frequencies $\omega \gg \tau_c^{-1}$ the spectral density is simply that of an uncorrelated sequence reduced by the factor $\omega^2\tau_c^2$.

It is easy to compute the spin relaxation rate for *uncorrelated* collisions with given mean square momentum transfer in each coordinate. Consider a nucleus with spin $\frac{1}{2}$, initially in the state $m_z = +\frac{1}{2}$, and follow the motion of the vector which represents the expectation value of the angular momentum. A pulse of electric field E_x of duration τ_a tips the vector about the x axis by a small angle $\delta = 2\mu_e E_x \tau_a / \hbar$. In our model the mean

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[5] I am indebted to P. A. Franken and H. S. Boyne for straightening out this point, on which my original conclusion was wrong.

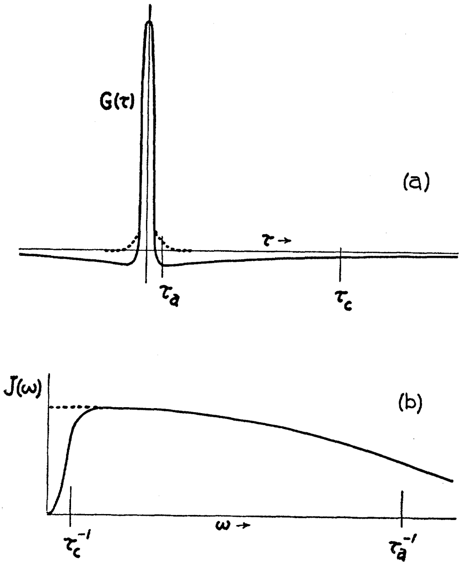

FIG. 1. (a) $G(\tau)$ for a random sequence of uncorrelated pulses (dotted curve) and for a sequence with negative correlation of consecutive pulses (solid curve); (b) the spectral densities corresponding to the two cases.

square x-momentum transfer in a collision is $2MkT$, so that $\delta^2 = 8\mu_e{}^2 Mk\,T/(\hbar^2 Z^2 e^2)$. Also each collision contributes a pulse $E_y\tau_a$ with the same mean square value. After a time $\Delta t \gg \tau_c$, when the large number $\Delta t/\tau_c$ collisions have occurred, the vector will have been carried in a random walk away from the pole by an angle θ (itself still small) such that $\langle\theta^2\rangle = 2\delta^2 \Delta t/\tau_c$. Projecting the vector on to the axis we find the probability to observe, at time Δt, the spin in the state $m_z = -\frac{1}{2}$. It is $\frac{1}{2}(1-\cos\theta)$ or, since $\theta \ll 1$, $\frac{1}{4}\theta^2$ approximately. The transition probability W is therefore $4Mk\,T\mu_e{}^2/(\hbar^2 Z^2 e^2)$. But this is simply related to the relaxation time T_1 for our two-level system by $1/T_1 = 2W$. Hence the partial relaxation rate which would arise from electrical perturbations if the momentum transfers were uncorrelated, would be (in agreement with reference 1)

$$\frac{1}{T_1} = \frac{8\mu_e{}^2 Mk\,T}{\hbar^2 Z^2 e^2 \tau_c}. \tag{5}$$

In view of the above, the actual rate is, instead,

$$\frac{1}{T_1} = \frac{8\mu_e{}^2 Mk\,T\omega^2\tau_c}{\hbar^2 Z^2 e^2 (1+\omega^2\tau_c{}^2)}, \tag{6}$$

where ω is the spin precession frequency determined, of course, by some other circumstance of the experiment, such as an applied magnetic field.

Now $\omega\tau_c$ is typically 10^{-2} to 10^{-4} in a gas under reasonable experimental conditions, so the reduction by correlation is severe. In fact a dipole moment as large as $e\times 10^{-14}$ cm would only allow relaxation in days, at one atmosphere. The shortest possible relaxation time is attained for $\omega\tau_c = 1$. Suppose, for instance, $\omega = 10^8$ sec^{-1}, $M/Z^2 =$ proton mass, $T = 300$°K and $\mu_e = e\times 10^{-14}$ cm. Then the shortest attainable spin relaxation time T_1 is 400 seconds.

This looks encouraging until one examines possible competing relaxation processes. Under the conditions assumed, any *intra*molecular magnetic coupling to a nuclear magnetic moment arising from other nuclei in the molecule or, more generally, from molecular rotation, would cause very rapid relaxation. Such processes too are most effective when $\omega\tau_c \approx 1$. Indeed they are described by a relation much like Eq. (6) except that the factor in front, which now involves the nuclear magnetic moment and the internal magnetic field, is typically 10^3 times larger than in our electric example above. So it is essential to use a monatomic gas. Of course, we must require further that the atom be electronically nonmagnetic, and in view of Eq. (6) a low atomic number is desirable. He^3 is perhaps as good a choice as any, *a priori*. Relaxation by magnetic spin-spin interaction occurring during collisions is relatively negligible if the electric dipole moment is as large as assumed above. Possibly more serious is the question of relaxation at the walls of the container. A collision rate of 10^8 sec^{-1} implies a mean free path so long that the time to diffuse several centimeters would be less than a second. On the other hand, increasing the gas density will not only reduce the electric relaxation, but will also increase the rate of relaxation by magnetic spin-spin interaction. Perhaps, as Franken and Boyne suggest,[2] a judicious compromise can still make accessible an interesting range of electric dipole strengths. It all depends on what range one considers interesting. A limit on dipole strength as low as has been established experimentally for the neutron[6] ($\mu_e < e\times 5\times 10^{-20}$ cm) is obviously far beyond reach.

We turn now to the question of electric relaxation in crystals. The fact that the relaxation rate is a gas decreases with increasing density is already an indication of what to expect. If we substitute into Eq. (6) a collision time τ_c appropriate to a fluid with its molecules nearly in contact, say 10^{-13} second, we obtain for our "nominal" dipole of strength $e\times 10^{-14}$ cm and the other quantities, M, Z, ω, and T assumed as before, a relaxation time in the neighborhood of one year. However, the correct figure for T_1, as we shall see, is even greater, and by a very large factor.

In the crystal, as in the gas, the motion of the nucleus uniquely determines the electric field acting on the nucleus. The acoustic spectrum of the lattice therefore provides all the information needed to determine the intensity at any frequency in the spectrum of $\mathbf{E}(t)$. Our problem is especially simple because we are concerned with frequencies very much lower than the Debye frequency, frequencies, that is, for which the

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[6] Smith, Purcell, and Ramsey, Phys. Rev. **108**, 120 (1957).

lattice may be treated as an elastic continuum. To find the intensity in the spectrum of E_x, say, in the neighborhood of ω, we have only to write down the density of elastic modes in the neighborhood of ω, assign energy kT per mode (since $\hbar\omega \ll k\mathrm{T}$) and calculate the corresponding nuclear acceleration. We are thus led directly to a transition probability and thence to a formula for the spin-lattice relaxation time:

$$\frac{1}{T_1}=\frac{2\mu_e^2M^2\omega^4k\,\mathrm{T}}{\pi^2\hbar^2Z^2e^2\rho c^3}. \tag{7}$$

In Eq. (7) ρ is the crystal density and c is the velocity of sound in the crystal, taken to the same for longitudinal and transverse waves. With $\rho=1\ \mathrm{g/cm^3}$, $c=10^5\ \mathrm{cm/sec}$, and the other quantities assigned their earlier values, Eq. (7) gives for T_1 about 10^{11} years.

The process we have considered bears some resemblance to magnetic spin relaxation in crystals, a problem first treated in a classic paper of Waller.[7] One is there concerned with the magnetic interaction between neighboring spins and its modulation by lattice vibrations which occurs because the dipole-dipole interaction depends on the distance between the spins. We recall that Waller identified two processes. In the first or "direct" process, lattice vibrations at the frequency corresponding to the nuclear spin transition frequency ω modulate the spin-spin coupling at this frequency, producing transitions with consequent relaxation. The second process involves lattice vibrations at two frequencies, ω' and ω'', much higher than ω but satisfying the relation $\omega'-\omega''=\omega$. Thanks to the nonlinear dependence of the dipole coupling on internuclear distance, the resulting modulation of the interaction has a component at the difference frequency ω which can cause the spin transition. Because the process can be described as the inelastic scattering of a lattice phonon by the spin system, it is often called the "Raman" process. Now this "indirect" or "Raman" process is under most circumstances vastly more effective than the "direct" process. It is the latter, obviously, whose electrical analog we have just been analyzing. One naturally wonders whether a two-phonon, or "Raman" process will dominate in the electrical problem.

The answer is very simple: there is *no* Raman process in electric dipole relaxation. It is rigorously excluded by the linearity of the connection between the nuclear coordinates and the nuclear acceleration, which apart from a constant factor is the same as the local electric field. To put it another way, the spectral intensity of lattice vibrations and the spectral intensity of the perturbation $\boldsymbol{\mu}_e\cdot\mathbf{E}$ are directly related, *frequency by frequency*. There is no such correspondence in the case of magnetic dipole-dipole interactions.

ACKNOWLEDGMENTS

I have enjoyed discussions of these questions with P. A. Franken and H. S. Boyne, and I thank also M. Bloom who sent me a detailed exposition of his unpublished considerations.

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[7] I. Waller, Z. Physik **79**, 370 (1932).