

cient), we obtain  $\sigma_{\text{coh}} = 3 \times 10^4$  b, and  $\sigma_T = 10^6$  b at resonance.

As a second example we consider the 77-kev level in  $\text{Au}^{197}$  [ $\Gamma/2 = 1.1 \times 10^{-7}$  ev,  $(\Gamma_i/\Gamma) = 0.22$ ]. At zero temperature we have  $k_0^2 \langle x^2 \rangle = 1.6$ , at room temperature it is some eight times larger, so appreciable scattering will occur only for  $T \ll 164^\circ$ . At these low temperatures the corrections to Eq. (39) are still only of the order of  $10^{-5} \approx 10^{-4}$  of the resonant value of Eq. (39), and thus may be neglected, near resonance, at low temperatures. Assuming that the  $(\frac{3}{2}+) \rightarrow (\frac{1}{2}+)$  transition is predominantly  $M1$ , Eqs. (41) and (42) will also apply to this case. Inserting numbers into Eqs. (42) and (43) we obtain  $\sigma_{\text{coh}} = 200$  b, and  $\sigma_T = 3 \times 10^4$  b, at resonance.

Turning now to neutron resonances it is only necessary to multiply  $f_{R,T}$  by  $[(2j_1+1)/2(2j_0+1)]$  to obtain the coherent scattering amplitude (unpolarized neutrons, unpolarized nuclei).

As a first example we consider the 4.9-ev neutron resonance in  $\text{Au}^{197}$ . These neutrons have a little shorter  $(3/4)$  wavelength than the 77-kev  $\gamma$  ray. We have<sup>29</sup>  $\Gamma/2 = 0.07$  ev,  $\Gamma_n/2 = 0.008$  ev,  $j_0 = \frac{3}{2}$ ,  $j_1 = 2$ , and, from the table,  $k_0^2 \langle x^2 \rangle = 2.9$ , at low temperatures. Now,  $\hbar\omega_m \approx \kappa\Theta \approx 0.014$  ev, and so the conditions (short collision time) leading to the validity of Eq. (24) are met. We have  $\Re = 4.9/197 = 0.025$  ev and  $\langle \epsilon \rangle \approx \frac{1}{2}\hbar\omega_m$  at low temperatures (in the Debye approximation  $\langle \epsilon \rangle$

$= \frac{3}{8}\hbar\omega_m = 0.005$  ev). Approximating Eq. (27) by Eq. (32), we have

$$f_{\text{coh}} \approx \frac{510^{-3}}{k_0} e^{-2.9(1-\cos\theta)} \left[ \frac{0.665}{\Delta - 0.025 \cos\theta + 0.07i} + \frac{0.167}{\Delta - 0.025 \cos\theta + 0.07i + 0.027(\cos\theta)^{\frac{1}{2}}} + \frac{0.167}{\Delta - 0.025 \cos\theta + 0.07i - 0.027(\cos\theta)^{\frac{1}{2}}} \right]. \quad (44)$$

The corrections to the resonance denominator of the simple fixed-nucleus Breit-Wigner formula are small, but not completely negligible. Equation (44) when squared yields a maximum,  $d\sigma_{\text{coh}}/d\Omega \approx 200e^{-2.9\theta^2}$  b/sr, for small  $\theta$ .

As our last example we consider the 1-ev resonance in  $\text{Pu}^{240}$ . This resonance is given as having the remarkably small width,  $\Gamma/2 = 0.017$  ev,  $\Gamma_n/2 = 0.001$  ev.<sup>29</sup> According to our estimate of  $\Theta$  for Pu,  $\hbar\omega_m \approx 0.02$  ev. Consequently, the coherent scattering amplitude, and therefore the total cross section, will be rather sensitive to the details of the phonon spectrum (during the scattering process the nucleus will execute a vibration or so). According to the table the Debye-Waller factor is not small even at room temperature. The scattering amplitude will, then, not be very small in the region for which Eq. (25) is valid, and an experimental study of the coherent scattering could give detailed information concerning the crystal vibrational spectrum.

<sup>29</sup> *Neutron Cross Sections*, completed by D. J. Hughes and R. Schwartz, Brookhaven Natural Laboratory Report BNL-325 (Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 1958), 2nd ed.

## Nuclear Magnetic Relaxation of a Three-Spin Asymmetric Molecule in a Liquid\*

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The semiclassical density-matrix theory of relaxation is employed to calculate the relaxation of the  $z$  component of nuclear magnetization of molecules in a liquid for the case in which three identical nuclei of spin  $\frac{1}{2}$  are arranged at the vertices of an isosceles triangle whose angles are  $30^\circ$ ,  $30^\circ$ , and  $120^\circ$ . It is found that, if the initial state of the spin systems is characterized by a spin temperature, the relaxation consists of the sum of seven terms which decay exponentially with different time constants. It is also found that even though the  $z$  component of the magnetization is a function of seven distinct time constants, a plot of  $\ln(M_z - M_{eq})$  can be approximated by a single straight line for regions of experimental interest. The time constant for this straight line differs less than 1% from the average relaxation time calculated from the formulas of Gutowsky and Woessner.

### I. INTRODUCTION

THE semiclassical density-matrix theory of relaxation was employed by P. S. Hubbard<sup>1</sup> to calculate the relaxation of the  $z$  component of nuclear magnetization for a system of identical nuclei of spin  $\frac{1}{2}$  arranged, respectively, at the corners of an equilateral triangle or

a regular tetrahedron. Hubbard showed, for the former case, that, although the  $z$  component of the magnetization relaxed with two distinct relaxation times, the relaxation was dominated by a single relaxation time. This relaxation time differed less than 1% from the one calculated using the method of Gutowsky and Woessner<sup>2</sup>

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<sup>1</sup> P. S. Hubbard, Phys. Rev. **109**, 4 (1958).

<sup>2</sup> H. S. Gutowsky and D. E. Woessner, Phys. Rev. **104**, 843 (1956).

which assumes that each pair of nuclei relaxes independently of the others.

The question immediately arises as to whether the high degree of symmetry influenced the results of this calculation. To examine this point we calculated the  $z$  component of the magnetization for a less symmetric system but still one of physical significance.

In this paper, we employed the general method developed by Hubbard to calculate the  $z$  component of the magnetization for a system of identical spin  $\frac{1}{2}$  nuclei at the corners of an isosceles triangle whose angles are  $30^\circ$ ,  $30^\circ$ , and  $120^\circ$ . This configuration can be realized in triply substituted ring compounds. The symbols and definitions of quantities appearing in the sequel are the same as those used by Hubbard.

## II. CALCULATIONS

For a system of  $N$  molecules per unit volume, the  $z$  component of the magnetization can be expressed as

$$M_z - M_{eq} = N\gamma\hbar \sum_{\alpha=1}^{2^n} [\sigma - \sigma^T]_{\alpha\alpha} (I_z)_{\alpha\alpha}, \quad (1)$$

where

$$\sigma^T = \exp\left(-\frac{\hbar E}{kT}\right) / \sum_{\alpha} \exp\left(-\frac{\hbar E_{\alpha}}{kT}\right). \quad (2)$$

We therefore need to determine the time dependence of the elements  $\sigma$  of the density matrix. Redfield<sup>3</sup> has shown that the matrix elements of the density operator formed with the eigenfunctions of  $E$  are determined by the equation

$$\frac{d\sigma_{\alpha\alpha'}}{dt} + i\omega_{\alpha\alpha'}\sigma_{\alpha\alpha'} = \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} (\sigma_{\beta\beta'} - \sigma_{\beta\beta'}^T), \quad (3)$$

where

$$R_{\alpha\alpha'\beta\beta'} = \int_0^\infty d\tau [2P_{\alpha\beta\alpha'\beta'}(\tau) - \delta_{\alpha'\beta'} \sum_{\gamma} P_{\gamma\beta\gamma\alpha}(\tau) - \delta_{\alpha\beta} \sum_{\gamma} P_{\gamma\alpha'\gamma\beta'}(\tau)] \quad (4)$$

and

$$P_{\alpha\beta\alpha'\beta'} = \langle G_{\alpha\beta}(t) G_{\alpha'\beta'}^*(t+\tau) \rangle. \quad (5)$$

The matrix elements  $G_{\alpha\beta}$  are calculated by using the perturbation Hamiltonian

$$\hbar G = \gamma^2 \hbar^2 \sum_{i < j} [\mathbf{I}^i \cdot \mathbf{I}^j - 3(\mathbf{I}^i \cdot \hat{r}_{ij})(\mathbf{I}^j \cdot \hat{r}_{ij})] r_{ij}^{-3}. \quad (6)$$

Since all the  $r_{ij}$ 's are not the same and due to the particular configuration we are considering, irrational

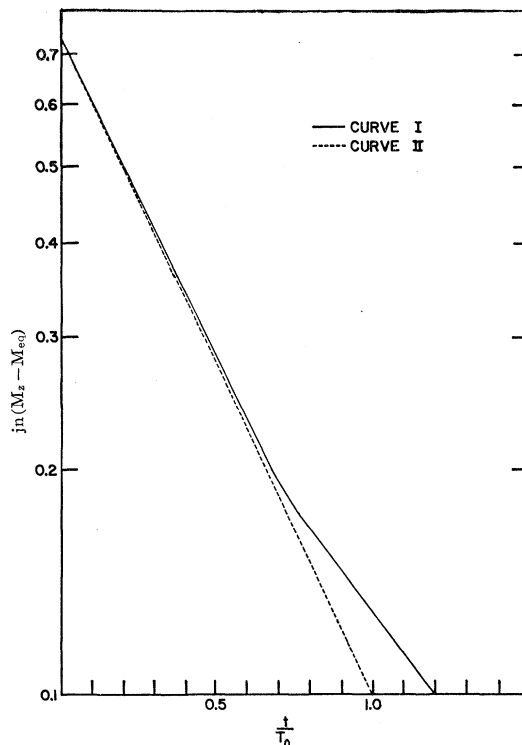


FIG. 1. Comparison of relaxation times for a three-spin asymmetric molecule in a liquid, showing the small variation of the exact calculations (curve I) from that of the Gutowsky and Woesner approximation (curve II).

numbers appear in certain elements of our perturbation matrix which do not appear in those of Hubbard's.

In the sum on the right-hand side of Eq. (4), the only terms which are included are those for which  $E_{\alpha} - E_{\beta} = E_{\alpha'} - E_{\beta'}$  since the nonsecular terms produce no appreciable change in the density operator  $\sigma$  over a time greater than  $\tau_c$ .

A convenient check on the computation is afforded by the invariance of the matrices under inversion of the magnetic field. Under inversion  $|1\rangle$  becomes  $|8\rangle$ ,  $|2\rangle$  becomes  $|5\rangle$ , etc. This implies, for example, that  $G_{12} = G_{85}$ .

In the case considered by Hubbard, the fourteen simultaneous differential equations determined by (3) were reduced to a system of three simultaneous, first order, linear, homogeneous differential equations due to the fact that all fourteen equations were not linearly independent. One of the roots of the cubic equation appeared in factored form, and an analytic solution was obtained without any numerical approximations. For the system we considered, no such reduction was possible. The system of fourteen simultaneous differential equations was solved using the I.B.M. 650 digital computer. The program used provided both the eigenvalues and eigenvectors of the matrix of coefficients of the differential equations. A solution satisfying the initial conditions for the magnetization was constructed

<sup>3</sup> A. G. Redfield, IBM J. Research Develop. **1**, 19 (1957).

from the eigenvectors and eigenvalues. The result is

$$M_z - M_{eq} = \frac{N\gamma^2\hbar^2 H_0 (T - T_s)}{kTT_s} \frac{1}{32} [0.024e^{-1.04t/T_0} + 18.18e^{-2.41t/T_0} + 0.006e^{-0.998t/T_0} + 0.33e^{-1.62t/T_0} + 1.7e^{-0.844t/T_0} + 0.75e^{-2.02t/T_0} + 3.15e^{-0.556t/T_0}], \quad (7)$$

where

$$T_0 = r_0^6 / \gamma^4 \hbar^2 \tau_c$$

and  $r_0$  is the distance between the two closest nuclei in the molecule.

### III. DISCUSSION OF RESULTS

Although in our case there are seven different exponents in the relaxation equation, only three are sufficiently large to warrant consideration. The time rate of change of the magnetization considering only these three leading terms is plotted in Fig. 1 as curve I. It can be seen that for times up to the order of  $1\frac{1}{2}$  relaxation times curve I could be approximated by a straight line and for times somewhat greater than this the curve could be approximated by another straight line with a slope about 20% smaller than that of the first. Curve I is given by the following equation

$$M_z - M_{eq} = \frac{K}{32} [18.18e^{-2.41t/T_0} + 3.15e^{-0.556t/T_0} + 1.7e^{-0.844t/T_0}], \quad (8)$$

where

$$K = N\gamma^2\hbar^2 H_0 (T - T_s) / kTT_s.$$

This result can be compared with that obtained from a simpler approximation in which the relaxation of each nuclear pair is considered independently. In this case, one finds according to Gutowsky and Woessner

$$\frac{1}{T_{1i}} = \frac{3r_0^6}{2T_0} \sum_{i < j} r_{ij}^{-6}. \quad (9)$$

This equation gives two distinct relaxation times,

$$\frac{1}{T_{11}} = \frac{3}{T_0} \quad \text{and} \quad \frac{1}{T_{12}} = \frac{1.554}{T_0}. \quad (10)$$

However, if there is appreciable cross relaxation, the system will show a single relaxation time. Taking the weighted average of the two relaxation times, the  $z$  component of the magnetization becomes

$$M_z - M_{eq} = 0.75K(e^{-2.04t/T_0}). \quad (11)$$

The important result is that curve I differed less than 1% from curve II up to the order of  $1\frac{1}{2}$  relaxation times. This result is in agreement with what has been observed experimentally.<sup>4</sup> It was shown that for liquids possessing the benzene ring structure, a single relaxation time could be used to describe the relaxation and this relaxation time was in close agreement with the average relaxation time calculated from the Gutowsky and Woessner formula. There was also some evidence that, for times greater than  $1\frac{1}{2}$  relaxation times, the magnetization no longer followed a single straight line but appeared to deviate from it. This result is very difficult to establish experimentally since in this region the change in magnetization is quite small.

In the solution obtained by Hubbard, a single relaxation time dominated the relaxation for regions of experimental interest. This single relaxation time differed less than 1% from the one calculated using the Gutowsky and Woessner formula. In the case we considered, the  $z$  component of the magnetization was a function of seven exponentials each containing a different time constant; however, the combined effect showed that the system relaxed with effectively a single relaxation time which was the one calculated using the Gutowsky and Woessner formula. The method we have used in the solution to this particular problem can be applied to a completely asymmetric molecule, and it is anticipated that the  $z$  component of the magnetization will be a function of eight exponentials each having a different time constant.

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<sup>4</sup> R. W. Mitchell and M. Eisner, J. Chem. Phys. 24, 86 (1960).