

Double-Quantum Transitions in Nuclear Magnetic Resonance Spectra of Liquids

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Observations of double-quantum transitions in the nuclear magnetic resonance spectra of liquids are reported. The presence of spin-spin interaction causes the double-quantum lines to form multiplets. A theoretical explanation of the multiplet structure is given.

MULTIPLE-QUANTUM transitions have previously been observed in atomic and molecular beams.^{1,2} We report here the observation of double-quantum transitions in the nuclear magnetic resonance spectra of liquids.†

In Fig. 1 typical proton resonance spectra of ethyl alcohol are given. The top trace was made at a low radio-frequency level, and shows the well-known alcohol spectrum.^{3,4} The triplet is due to the CH₃ protons, the quadruplet to the CH₂ protons, and the single line to the OH proton. The second trace in Fig. 1 was made at a much higher radio-frequency level ($H_1 = 3.4 \times 10^{-3}$ oersted), with all other conditions remaining the same. Double-quantum transitions now show up as a sharp quadruplet midway between the much broadened CH₃ and CH₂ lines. The spacing of the components of this quadruplet is half the spacing of the components of the low-field CH₃ and CH₂ multiplets. In interpreting the traces it should be borne in mind that at high power levels the amplitude of the absorption mode is much smaller than the amplitude of the dispersion mode.⁵ A small admixture of dispersion mode to the absorption mode could not be avoided experimentally, and seriously modified the shape of the observed resonance. The third trace in Fig. 1 was made in a field $H_1 = 6 \times 10^{-3}$ oersted, and shows broadening of the double-quantum quadruplet. Because of fast chemical exchange of the OH proton, no double-quantum lines appear between the CH₂ and OH resonances.

Double-quantum transitions have also been studied in the spectrum 1,1,2 trichloroethane, the low-power spectrum of which consists of a doublet and a triplet. In this case the double-quantum lines were found to form a doublet, the components of which have equal intensity and have a spacing half that of the low-level multiplets.

* Louis Lipsky Fellow 1956-1957.

¹ Brossel, Cagnac, and Kastler, *J. phys. radium* **15**, 6 (1954); P. Kusch, *Phys. Rev.* **93**, 1022 (1954).

² Multiple quantum transitions of a different kind have been reported by V. Hughes and L. Grabner, *Phys. Rev.* **79**, 314 (1950); **79**, 829 (1950); **82**, 561 (1951).

† *Note added in proof.*—The possibility of the occurrence of such transitions has been suggested by V. W. Hughes and J. S. Geiger, *Phys. Rev.* **99**, 1842 (1955). Their observation has recently been reported by W. Anderson, *Phys. Rev.* **104**, 850 (1956).

³ J. Arnold, *Phys. Rev.* **102**, 136 (1956).

⁴ The alcohol was made slightly basic by the addition of KOH, so that fast chemical exchange of the OH group averages the spin-spin interaction between the CH₂ and the OH protons to zero.

⁵ F. Bloch, *Phys. Rev.* **70**, 460 (1946).

The theory for multiple-quantum transitions applicable to atomic beams has been given by a number of authors.⁶ For the case treated here, where a steady-state solution is required, the theory is based on the averaged density matrix equation as developed by Bloch.⁷ To simplify the mathematical treatment the different relaxation quantities $\Gamma_{\sigma\sigma'}$ introduced by Bloch are assumed equal, and $\Gamma_{\sigma\sigma'}/\sum_p \Gamma_{\sigma\sigma'}$ is taken to be zero. This simplifies Eq. (2.44) of Bloch's paper⁷ to

$$\frac{d}{dt} (g|\chi|g') + i(g|[E, \chi]|g') - \frac{1}{\tau} (g|\chi|g') = i\zeta [\exp(-\hbar g/kT) - \exp(-\hbar g'/kT)] (g|E_1|g'), \quad (1)$$

where

$$1/\tau = \sum_p (\Gamma_{\sigma\sigma'} + \Gamma_{\sigma'\sigma'})$$

and the other notations are as given in Bloch's paper.⁷ This equation is only slightly different from one previously derived by Karplus and Schwinger.⁸

We shall treat the case of three energy levels with nearly equal spacing. We assume equal transition probabilities between adjacent levels, but no allowed direct transition between the extreme levels. The

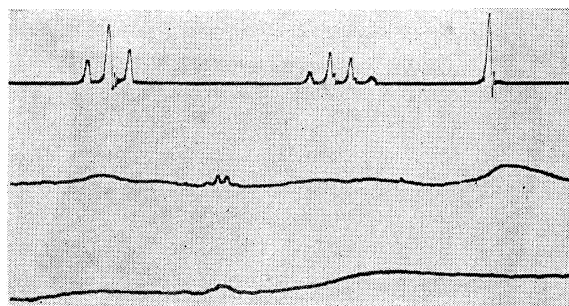


FIG. 1. Proton magnetic resonance spectra of ethyl alcohol at 31.6 Mc/sec. The top trace was obtained with a weak radio-frequency field (less than 10^{-4} oersted), and shows the well-known ethyl alcohol absorption spectrum. The second trace was made with a radio-frequency field of 3.4×10^{-3} oersted. The double quantum transitions show up as a sharp quadruplet, midway between the saturated one-quantum resonance lines. The third trace was made at a field of 6×10^{-3} oersted.

⁶ Besset, Horowitz, Messiah, and Winter, *J. phys. radium* **15**, 251 (1954); H. Salwen, *Phys. Rev.* **99**, 1274 (1955).

⁷ F. Bloch, *Phys. Rev.* **102**, 104 (1956).

⁸ R. Karplus and J. Schwinger, *Phys. Rev.* **73**, 1020 (1948).

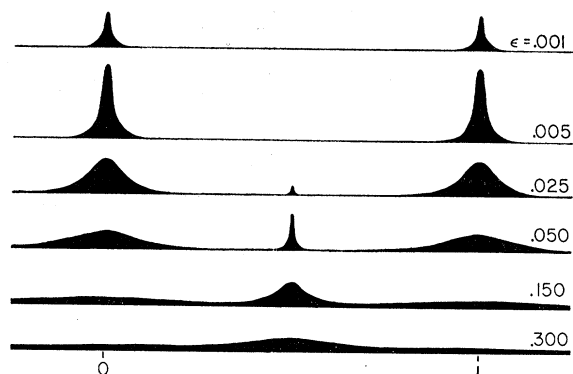


FIG. 2. Theoretical absorption spectra for a three-level system. The curves were computed from Eq. (2), taking $\gamma = 1/(\tau\delta\omega) = 0.01$. The strength of the radio-frequency field H_1 increases from top to bottom and is indicated by the parameter $\epsilon = (\gamma H_1)/(2\delta\omega)$. The abscissa is the quantity β defined in Eq. (5).

assumption of nearly equal spacing allows us to take the difference of the Boltzmann factors on the right side of Eq. (1) for adjacent levels as equal. It is then found that this term will only appear as a multiplying factor in the calculated magnetization. The result of the calculation is given in the Appendix, and can be expressed in terms of the dimensionless parameters $\gamma H_1/\delta\omega$ and $\tau\delta\omega$, where γ is the gyromagnetic ratio, H_1 the amplitude of the rf field, and $\delta\omega$ the frequency difference of the two lines corresponding to the allowed transitions. The numerical evaluation for a number of values of these parameters was carried out on the electronic computer of this Institute. Some of the results are plotted in Fig. 2, which gives the calculated absorption for different values of $\gamma H_1/\delta\omega$ and for $\tau\delta\omega = 100$.

In order to apply the theory to actual cases, in which the spin-spin interaction causes multiplet structure, we have assumed that there will always be a double-quantum transition associated with any three energy levels which are connected in the manner assumed for our theoretical calculation. The calculation of the number of lines and their relative intensities in alcohol is then made by assuming that the off-diagonal elements of the spin-spin interaction can be ignored.³ All allowed transitions will then have equal intensities. A simple counting of all possible three level combinations gives four double-quantum lines with relative intensities of 1:4:4:1. These lines will occur halfway between all combinations of a triplet and a quadruplet line except for the two combinations of an inside with an outside line.

The double-quantum doublet observed in 1,1,2 trichloroethane is explained in a similar way.

In the lower two traces of Fig. 1 can also be seen evidence of triple-quantum multiplets, at positions one third and two thirds the distance between the single-quantum multiplets. A simple theoretical interpretation of these multiplets, similar to the interpretation for the double-quantum transitions, gives for the left multiplet a ratio of intensities of 1:2:1 and for the right multiplet 1:1:1:1. The spacings of the left and right multiplets are $\frac{2}{3}$ and $\frac{1}{3}$, respectively, of the spacing of the single quantum multiplets. Although the amplitude of the multiplets was hardly above the noise level, comparison of a large number of traces seems to bear out this result.

It is thought that the interpretation of complex multiplet structure may be facilitated by finding the double-quantum transitions. The occurrence or non-occurrence of a particular double-quantum transition could possibly distinguish between two interpretations of a spectrum.

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APPENDIX

We assume three energy levels with nearly equally spaced adjacent levels. The matrix elements of the time dependent perturbation E_1 are defined by taking

$$(1|E_1|2) = (2|E_1|3) = \gamma H_1 \cos\omega t$$

and

$$(1|E_1|3) = 0.$$

A solution of Eq. (1) is assumed of the form

$$(i|\chi|j) = R_{ij} + P_{ij}^+ e^{-i\omega t} + P_{ij}^- e^{i\omega t} + S_{ij}^+ e^{-i2\omega t} + S_{ij}^- e^{i2\omega t},$$

where the Hermitian character of the Hamiltonian requires that

$$P_{ij}^+ = (P_{ji}^-)^* \quad \text{and} \quad S_{ij}^+ = (S_{ji}^-)^*.$$

The resonance frequencies are designated as ω_{12} and ω_{23} where $(\omega_{12}/\omega_{23}) > 1$. For this choice the contributing terms to our solution are R_{11} , R_{22} , R_{33} , P_{12}^+ , P_{23}^+ , S_{13}^+ , and their complex conjugates. The expectation value of the x -component of the magnetization, defined as

$$\bar{M}_x = \sum_i (i|M_x\chi|i)$$

is then given by

$$\bar{M}_x = [\text{Re}(P_{12}^+ + P_{23}^+)] \cos\omega t + [\text{Im}(P_{12}^+ + P_{23}^+)] \sin\omega t.$$

The absorption is proportional to the component of the signal out of phase with the radio-frequency field and is thus proportional to the imaginary part of

$$P_{12}^+ + P_{23}^+ \propto \frac{A_{12} + A_{23} + 6\alpha A_{23} \text{Im}A_{12} + 6\alpha A_{12} \text{Im}A_{23} - 4[1 + 3\alpha \text{Im}(A_{12} + A_{23})]B_{13}}{1 + 4\alpha \text{Im}(A_{12} + A_{23}) + 12\alpha^2 \text{Im}A_{12} \text{Im}A_{23} - 12\alpha^2 \text{Im}B_{13} \text{Im}(A_{12} + A_{23}) - 4\alpha \text{Im}B_{13}}, \quad (2)$$

where

$$A_{12} = \epsilon[(1-\beta) - i\gamma]D,$$

$$A_{23} = \epsilon[-\beta - i\gamma]D,$$

$$B_{13} = \epsilon^3[(1-2\beta) - i\gamma]^{-1}D, \quad (3)$$

$$D = \{[(1-\beta) - i\gamma][-\beta - i\gamma] - \epsilon^2[(1-2\beta) - 2i\gamma]/[(1-2\beta) - i\gamma]\}^{-1}, \quad (4)$$

$$\alpha = \epsilon/\gamma,$$

$$\beta = (\omega - \omega_{23})/\delta\omega,$$

$$\gamma = 1/(\tau\delta\omega),$$

$$\epsilon = (\gamma H_1)/(2\delta\omega),$$

$$\delta\omega = \omega_{12} - \omega_{23}. \quad (5)$$

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Precision Measurement of X-Ray Fine Structure; Effects of Nuclear Size and Quantum Electrodynamics*†

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Schawlow and Townes have made a theoretical calculation of the perturbing effect of the finite size of the nucleus on the L_{II} - L_{III} x-ray doublet splitting in heavy elements. Combined with approximate calculations by Christy and Keller of the unperturbed splitting for the case of a point nucleus, comparison of this theory with such experimental values of the splitting as were then available led to an anomalously large value of nuclear radius, $R = r_0 A^{1/3}$ with $r_0 = 2.1 \times 10^{-13}$ cm. Schawlow and Townes offered the suggestion to account for this that quantum electrodynamic effects probably modify the fine structure in much the same way as an oversize nucleus. The present investigation was undertaken to improve on the precision of the x-ray measurements yielding the L_{II} - L_{III} fine structure splitting and to incorporate into a new comparison between theory and experiment the recent vacuum polarization correction of Wichmann and Kroll. The measurements of the L_{II} - L_{III} splitting for W, Pt, Bi, Th, U, and Pu are based on two-crystal spectrometer determinations of the Bragg

angles of the $L\alpha_2$ and $L\beta_1$ x-ray lines of these elements. Techniques of measurement and corrections for vertical divergence and crystal diffraction pattern asymmetry leading to a relative precision (relative standard deviation) in the splitting of about 50 parts per million are described. A comparison is made with the data used by Schawlow and Townes, and a discrepancy is found in several earlier wavelength values which may account partly for the large value of r_0 obtained by them. A comparison of the theoretical to the present experimental values of the splitting, assuming no quantum electrodynamic effects, yields a value of $r_0 = 1.08 \times 10^{-13}$ cm. When corrections are made for vacuum polarization and a nuclear radius of $r_0 = 1.2 \times 10^{-13}$ cm, a comparison with experiment shows that a discrepancy remains which is then used to evaluate an empirical correction term. The sign, magnitude, and Z dependence of this term suggest that the remaining discrepancy might arise principally from the Lamb shift effect.

I. INTRODUCTION

THE recent experiments in high-energy electron scattering¹ and mesonic x-rays² have indicated that the nuclear charge distribution probably consists of a central region of uniform density with an extended "tail" at the periphery of the latter and with a root-mean-square radius of $R = r_0 A^{1/3}$, where A is the atomic mass number and $r_0 \cong 1.2 \times 10^{-13}$ cm.³ Cooper and Henley⁴ and Ford and Hill⁵ have compared these and other methods yielding information on the nuclear charge distribution and find, with one exception, that the results of the various experiments are consistent with this value of r_0 .

This exception is the value of r_0 obtained by Schawlow and Townes.⁶ Using the method of Broch,⁷ they have calculated the change in the electronic energy levels due to finite nuclear size. A correction term for the $2p_{3/2} - 2p_{1/2}$ (L_{II} - L_{III}) fine structure splitting was evaluated and added to the splitting formula of Christy and Keller⁸ which had been derived by assuming a point nucleus. A comparison of the theoretical fine structure splitting (without the nuclear size correction) with measured values obtained from the tables of Cauchois and Hulubei⁹ showed a systematic deviation for large atomic number which had a direction and order of magnitude predicted by the nuclear size effect theory. Under the assumption that the deviation was due entirely to the finite nuclear size, Schawlow and

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† Based on a Ph.D. thesis submitted by R. L. Shacklett, California Institute of Technology, 1956 (unpublished).

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⁵ K. W. Ford and D. L. Hill, Phys. Rev. **94**, 1630 (1954).

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⁷ E. K. Broch, Arch. Math. Naturvindenskab **48**, 25 (1945).

⁸ R. F. Christy and J. M. Keller, Phys. Rev. **61**, 147 (1942).

⁹ Y. Cauchois and H. Hulubei, *Longueurs d'Onde des Emissions X et des Discontinuités d'Absorption X* (Hermann et Cie, Paris, 1947).

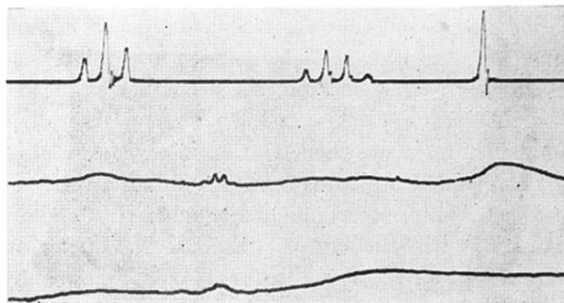


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