

Zeitschrift: Archives des sciences [1948-1980]
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 13 (1960)
Heft: 9: Colloque Ampère

Artikel: The measurement of indirect coupling and chemical shift using spin echoes
Autor: Powles, J.G. / Hartland, A.
DOI: <https://doi.org/10.5169/seals-738621>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 04.04.2026

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

The measurement of indirect coupling and chemical shift using spin echoes

by J. G. POWLES and A. HARTLAND

Physics Department, Queen Mary College (University of London),
Mile End Road, London, E.1

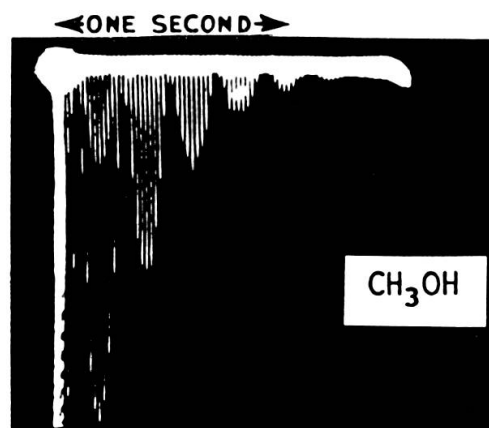
Résumé.

On présente une méthode de mesure de l'interaction indirecte (J) et du déplacement chimique (δ) par échos de spin qui est beaucoup plus précise que la méthode classique [1, 2]. Les effets de diffusion dans l'inhomogénéité du champ magnétique fixe sont diminués en utilisant une série spéciale de pulses [3, 5], ce qui permet l'observation de plusieurs périodes de modulation de l'amplitude des échos. De cette manière l'exactitude de détermination de J est beaucoup augmentée et il est possible que l'exactitude soit supérieure à celle atteinte par des spectrographes actuels.

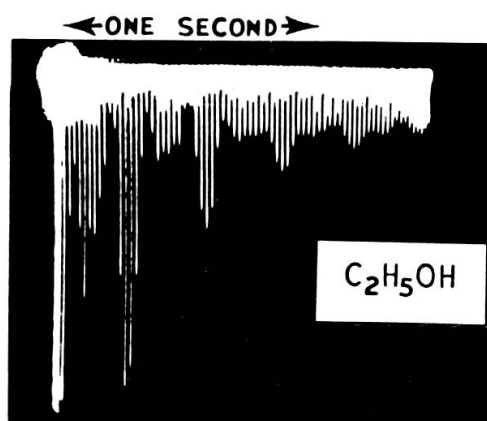
It has been known for some years [1, 2] that in the magnetic resonance spin echo experiment [3] the *amplitude* of the echo is modulated if neither the chemical shift (δ) nor the indirect coupling (J) between a pair of nuclei are zero. However the method has received very little attention since that time [4] because the accuracy of measurement, especially of J value is very low. This is because of the considerable attenuation of the signals due to self diffusion effects [3, 5]. In the $90^\circ, \tau, 90^\circ$ pulse sequence giving an echo at 2τ measured by multiple exposure for variable τ it turns out that for usual J values (say 5 c/s) only a small part of the J modulation can be observed. This is illustrated in figure 2 (*a*).

It occurred to us to reduce the self diffusion attenuation in the well known manner [5] by use of $90^\circ, \tau, 180^\circ, 2\tau, 180^\circ \dots$ pulse sequences. If there are n echoes in a given time the exponent of the exponential decay factor is reduced by the factor n^2 . Even using two echoes in a given time rather than one gives a very considerable reduction in attenuation as shown in figure 2 (*b*).

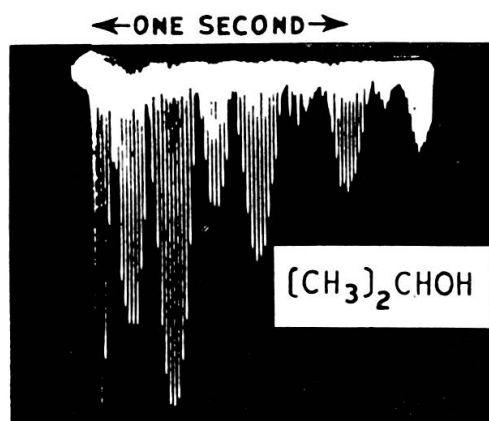
The expressions for the echo amplitude, $A(t)$, are simple when $J \ll \delta$. For a pair of single chemically shifted nuclei of spin $\frac{1}{2}$, both subject to the pulses for a $90^\circ, \tau, 90^\circ$ sequence [1, 2],



(a)



(b)



(c)

Fig. 1.

Captions to Figures.

1. Single exposure photographs of echo amplitude modulation for the 90° , τ , 180° , 2τ , 180° ... pulse sequence.
 - (a) Methyl alcohol at -71° C, $J = 4.95 \pm 0.05$ c/s.
 - (b) Ethyl alcohol at 25° C, $J = 6.93 \pm 0.10$ c/s.
 - (c) iso-Propyl alcohol at 23° C, $J = 6.15 \pm 0.15$ c/s.

$$A(t)/A(0) = |1 - \frac{1}{2}(1 - \cos \pi Jt)(1 - \cos \pi \delta t)| \quad (1)$$

where $t = 2\tau$.

For a $90^\circ, \tau, 180^\circ$ sequence [6],

$$A(t)/A(0) = |\cos \pi Jt| \quad (2)$$

In fact for *any* echo at time t in a $90^\circ, \tau, 180^\circ, 2\tau, 180^\circ \dots$ sequence equation (2) is valid [9]. Thus in the first case the amplitude depends on both δ and J and in the second on J only.

For more complex groupings it can be shown [9] that when $J \ll \delta$ the amplitude modulation is obtained by taking the high resolution spectrum, suppressing the chemical shift and taking the Fourier transform. Thus for methyl alcohol (with J coupling to the hydroxyl proton) we have

$$A(t)/A(0) = \frac{1}{16} |15 \cos \pi Jt + \cos 3\pi Jt| \simeq 0.94 |\cos \pi Jt| \quad (3)$$

For ethyl alcohol (with J coupling to the hydroxyl proton removed by exchange) we have

$$A(t)/A(0) = \frac{1}{12} |5 + 3 \cos \pi Jt + 3 \cos 2\pi Jt + \cos 3\pi Jt| \quad (4)$$

For iso-propyl alcohol (with J coupling to the hydroxyl proton removed by exchange) we have

$$A(t)/A(0) = \frac{1}{256} |42 + 192 \cos \pi Jt + 15 \cos 2\pi Jt + 6 \cos 4\pi Jt + \cos 6\pi Jt| \\ \simeq |0.16 + 0.75 \cos \pi Jt| \quad 5$$

These cases are shown in figure 1 [8] which are *single* exposure photographs and show the modulation of equations 3, 4 and 5 apart from an exponential decay due to T_2 with J values close to those found in the literature. We emphasise that these are not Fourier transforms of the high resolution signals which would be observed in a Bloch decay or a wiggles [7] experiment. We emphasise also that in the $90^\circ, \tau, 90^\circ$ experiment modulation barely to the first minimum in figure 1 is observed [1, 4]. The accuracy of determination of J is therefore enormously improved in our experiment.

We have found that the δ value can be obtained satisfactorily for the usual $90^\circ, \tau, 90^\circ$, variable τ experiment since usually $\delta \gg J$. More interest attaches to the accurate determination of J since it is often a small interaction which may not be well resolved in the usual steady state high resolution experiment.

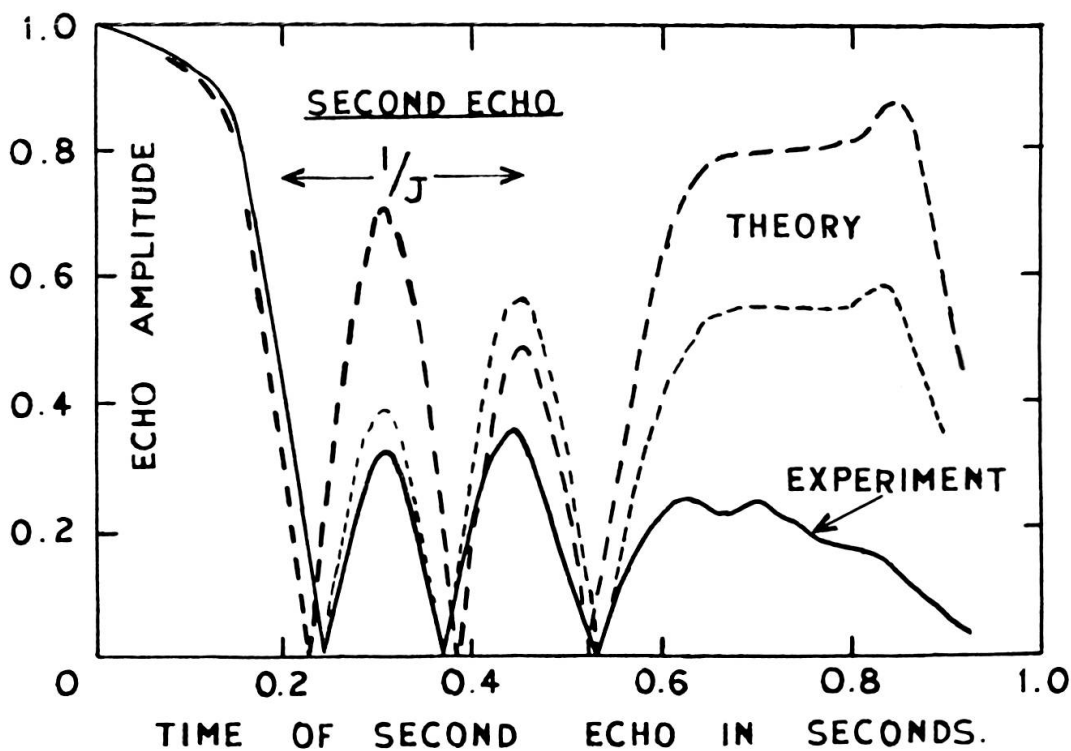
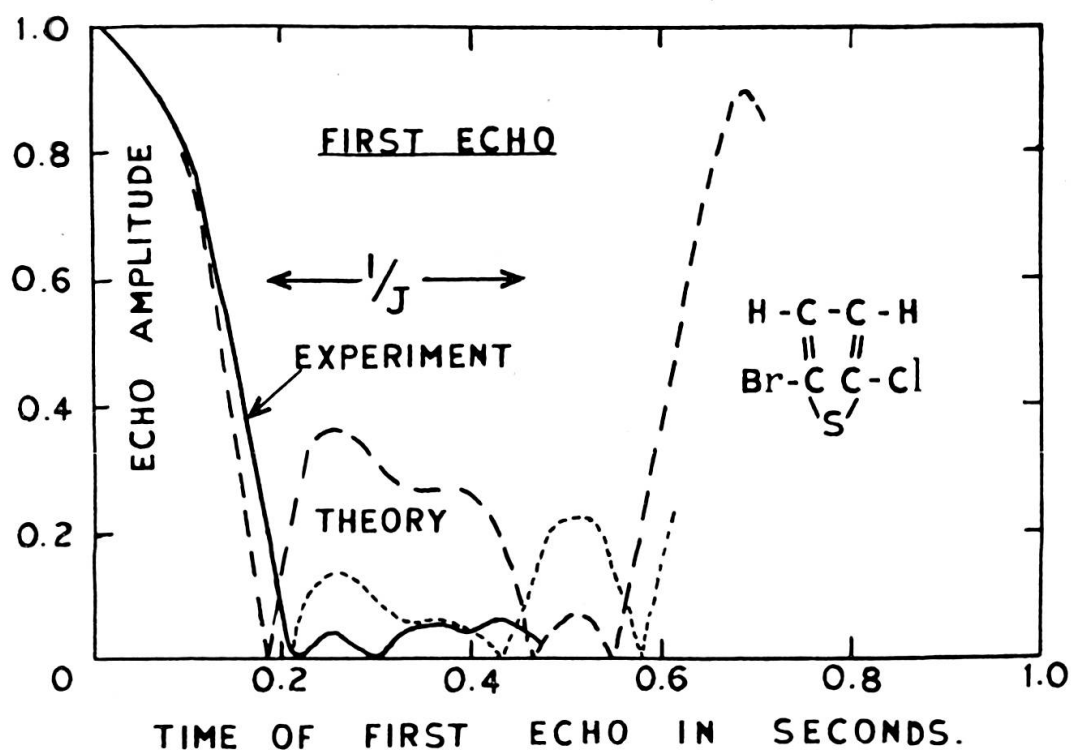


Fig. 2.

2. Echo amplitude modulation from multiple shot experiments in 2-bromo-5-chloro-thiophene at 25° C, (a) the first echo and (b) the second echo of a 90°, τ , 180°, τ , Echo₁, τ , 180°, τ , Echo₂ sequence. The theoretical curves are for $\delta = 3.97$ c/s and $J = 3.87$ c/s without attenuation.

When J is not much less than δ the situation is more complex and the 90° , τ , 180° , 2τ , 180° . . . echoes depend on both δ and J and of course on τ . However both J and δ may be determined. Figure 2 [8] shows our result for the classic case [1] of 2-bromo-5-chloro-thiophene for which we find $J/\delta = 0.98$ at 21.5 Mc/s. The modulation patterns for the first and second echoes are shown in figure 2 and are compared with theory [8]. Unfortunately the sample was found to contain a proportion of protons not in the thiophene which loads the signal. On allowing for this the excellent agreement shown in figure 2 (*b*) is obtained. We also find agreement for the third echo [9].

We have also observed echo amplitude modulation in n-propyl alcohol, n-butyl alcohol, 1,1,1,2-tetrachloropropane and 1,1,2-tribromoethane.

We have so far failed to find modulation in 1,1,2,3-tetrachloropropane, propargyl bromide, 2,3-dichloronitrobenzene, 2,5-dichloronitrobenzene, and 2,4,5,6-tetrachlorophenol. However only preliminary experiments have been made on possibly rather impure materials and we have noted that the appearance of modulation can be prevented by a number of factors. These and other substances are presently being investigated.

While this method will evidently not replace the usual high resolution experiment we feel it is of some interest because (*a*) only a moderately good magnet is required and (*b*) there is no arbitrary limit to the accuracy of measurement of J (and δ) values like the inhomogeneity in the high resolution experiment. The experimental limitation with the echo method remains to be seen but we believe that our present accuracy of about $\pm 2\%$ can be considerably improved upon.

A more detailed account of this work will be published elsewhere [8, 9].

REFERENCES

1. HAHN, E. L. and D. E. MAXWELL, *Phys. Rev.*, **84**, 1246, 1951; *ibid.*, **88**, 1070, 1952.
 2. McNEIL, E. R., C. P. SLICHTER and H. S. GUTOWSKY, *Phys. Rev.*, **84**, 1245, 1951.
 3. HAHN, E. L., *Phys. Rev.*, **80**, 580, 1950.
 4. CRAWFORD, G. J. B. and J. S. FOSTER, *Canad. J. Phys.*, **34**, 653, 1956.
 5. CARR, H. Y. and E. M. PURCELL, *Phys. Rev.*, **88**, 415, 1952; *ibid.*, **94**, 630, 1954.
 6. POWLES, J. G., *Reports on Progress in Physics*, **22**, 433, 1959.
 7. REILLY, C. A., *J. Chem. Phys.*, **25**, 604, 1956.
 8. POWLES, J. G. and A. HARTLAND, *Proc. Phys. Soc.*, accepted for publication.
 9. — and A. HARTLAND, *Proc. Phys. Soc.*, to be submitted for publication.
-