Nuclear Magnetic Resonances at Low Temperatures*

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We have recently completed a preliminary set of experiments on nuclear magnetic resonances at temperatures down to 4°K, using the $9\frac{1}{2}$-inch gap of the M.I.T. cyclotron magnet which was recently made available to us for a period of several days. Following is a summary of the results of these experiments and of a series of room temperature experiments done with a small electromagnet.

Proton or fluorine resonances have been observed in all substances investigated. Among these have been: benzene, ether, paraffin, lithium hydroxide, lithium fluoride, and hydrofluoric acid at room temperature; glycerine down to 195°K (solid CO_2); ammonium chloride, water and ice both as pure H_2O and in the form of a mixture containing 95 percent D_2O+5 percent H_2O down to 77°K (liquid nitrogen); liquid hydrogen at its boiling point; and solid methane down to liquid helium temperature.

In general, broad resonance lines, many gauss wide, were found in solids, with the exception of CH_4, while lines of the order of one gauss and less in width were observed in liquids. In reference to the distilled water and heavy water solutions, the D_2O was found to have no appreciable effect on the width of the resonance line in both the liquid and frozen states. The glycerine resonance line broadened from a width of the order of one gauss to a width of about 16 gauss as the temperature was reduced to 195°K. The LiF gave the broadest resonance observed, greater than 25 gauss wide at room temperature. The resonance line in liquid hydrogen was slightly broader than for protons in water at room temperature. In most cases, narrow lines were observed on an oscilloscope. Because of the lower amplitude of broad resonances, these were investigated on the output meter of a narrow-band 30-cycle amplifier in order to obtain a better signal to noise ratio.

Our observations of narrow lines in liquids and broad lines in solids are in agreement with the theory of line widths outlined by Bloembergen, Pound, and Purcell.[1] In this theory the rotational states in liquids are the key to narrow lines. In solids the internuclear fields serve to broaden the observed resonance line. However, when rotations occur with frequencies greater than the Larmor frequency involved (about 30 Mc for these experiments), the internuclear fields practically average out to zero during one Larmor cycle, thus resulting in a narrow line.

Since rotational states generally lead to narrow lines, it was decided to study the possibility of rotational states above the λ-points of ammonium chloride and solid methane, which have specific heat anomalies at -30°C and 20°K, respectively. Although some slight broadening of the proton line occurred in cooling ammonium chloride from room temperature to 77°K, it was a consistently broad line, such as is characteristic of normal solids. This indicates that the transition across the λ-point is due to an order-disorder phenomenon, in agreement with conclusions drawn by Lawson[2] from an analysis of thermodynamic data. In contrast to this are the observations of proton resonances in solid methane. In a liquid helium bath a broad line, about 12 gauss wide, was found. When the sample was allowed to warm up through the λ-point, the broad line changed to a narrow line, presumably in the vicinity of the λ-point. At liquid hydrogen and nitrogen temperatures, narrow lines, somewhat less than 1 gauss wide, were observed in solid methane.

It should be noted that those molecules with H atoms showing λ-point transitions are among the easiest to study by this method but present considerable difficulty in studies by means of x-rays. More detailed investigations of rotational states in solids are now being undertaken.

Larger signals were observed at low temperatures, approximately following the inverse temperature variation in Curie's formula for the equilibrium magnetization. This is in agreement with results obtained at hydrogen temperatures by Rollin and Hatton[3] and indicates that, in the substances examined, relaxation times do not undergo drastic variations at low temperatures. In the case of resonances in liquid hydrogen, signal-to-noise ratios of from 300 to over 1000 were obtained on an oscilloscope without the use of a narrow-band amplifier. These results indicate that low temperatures may be useful in the study of small samples or of substances with low concentrations of the nucleus under observation, particularly if narrow lines can be retained as in methane. However, in most substances, broad resonance lines are to be expected, and this will tend to reduce the gain caused by the low temperatures. If the structure of resonance lines is to be studied, or if the natural width of narrow lines is to be measured, stringent requirements must be placed on the uniformity of the magnetic field over the sample. Otherwise the line width and shape will be determined by the magnet and not by the sample.

We are indebted to Professor E. M. Purcell of Harvard for his suggestions in reference to the r.f. circuit which we are using. We also wish to thank many members of the M.I.T. staff, particularly Professor C. F. Squire for his assistance in the low temperature experiments, and Dr. E. T. Clarke, through whose cooperation we were able to use the cyclotron magnet.

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[1] N. Bloembergen, R. V. Pound, and E. M. Purcell, Phys. Rev. **71**, 466(A) (1947).

[2] Rollin and Hatton, Nature **156**, 201 (1947).

[3] Andrew W. Lawson, Phys. Rev. **57**, 417 (1940).

The Unboundedness of Quantum-Mechanical Matrices

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Hilbert's definition of a *bounded* infinite matrix A is equivalent to the requirement that the linear substitution $y=Ax$ should define a vector $y=(y_1, y_2, \cdots)$ of finite length whenever $x=(x_1, x_2, \cdots)$ is a vector of finite length (i.e., a point of Hilbert's space). Direct inspections show that all those quantum-mechanical matrices Q, P which have been calculated explicitly (linear oscillator, hydrogen atom, etc.) fail to be bounded in Hilbert's sense.

It is natural to expect that this failure is independent of the explicit choice of the particular Hamiltonians H in question. In fact, the unboundedness of Q, P is indicated by heuristic considerations concerning the location of possible energy levels. However, the literature consulted does not contain a general proof. The purpose of this note is the construction of such a proof.

If Planck's constant is expressed in appropriate units, Heisenberg's relation can be written in the form

$$QP-PQ=\tfrac{1}{2}iE, \qquad (1)$$

where E denotes the unit matrix and Q, P are supposed to be Hermitian. Without any reference to a Hamiltonian H, it will be shown that these assumptions prevent the boundedness of Q *and* P.

Let A^* denote the transposed matrix of the complex-conjugate of an arbitrary matrix A. Thus A is Hermitian if and only if $A^*=A$. Since Q and P are Hermitian, it follows that A^* is $Q-iP$, if A denotes $Q+iP$. Hence, Eq. (1) can be written in the form

$$A^*A-AA^*=E. \qquad (2)$$

Furthermore, if P and Q are bounded, then A is bounded. It will be shown that these assumptions lead to a contradiction.

By the spectrum of a bounded matrix A is meant the set of those real or complex values λ for which the bounded matrix $\lambda E-A$ fails to have a (unique) bounded reciprocal $(\lambda E-A)^{-1}$. It is known that the spectrum of every bounded matrix is contained in a sufficiently large circle about the origin of the λ-plane, and that every bounded matrix *has* a spectrum[1] (i.e., that the spectrum contains at least one λ-value). Because of the first of these two properties, $A-\lambda E$ must have a bounded reciprocal matrix if the absolute value of λ is large enough. On the other hand, it is clear that the expression to the left side of Eq. (2) remains unaltered if A is replaced by $A-\lambda E$, where λ is any real value. Hence, if $A-\lambda E$, where λ is real and large enough, is denoted by A, there results a bounded matrix A satisfying Eq. (2) and possessing a bounded reciprocal A^{-1}. But Eq. (2) can then be written in the form

$$B-ABA^{-1}=E, \qquad (3)$$

where $B=A^*A$. In fact, the product of bounded matrices is bounded, and their multiplication is associative. In particular, B is bounded.

It is clear from the above definition of a spectrum that if A, A^{-1} and B are bounded, then B and its transform ABA^{-1} have the same spectrum. Since Eq. (3) means that ABA^{-1} is identical with $B-E$, it follows that B and $B-E$ have the same spectrum. Finally, the definition of a spectrum also shows that the spectrum of $B-E$ results from that of B by a rigid motion, representing a translation (of unit span) of the λ-plan into itself.

Accordingly, the spectrum of B remains invariant under a certain translation. Consequently, either the spectrum of B contains every point of a line in the λ-plane or the spectrum of B has no point at all. However, as mentioned above,[1] both of these possibilities are ruled out by the boundedness of B. This contradiction proves the unboundedness of $B=A^*A$, and therefore that of $A=Q+iP$.

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[1] A. Wintner, *Spektraltheorie der Unendlichen Matrizen* (Hirzel, Leipzig, 1929) pp. 143–44.

On the Dependence of Nuclear Radius on the Mass Number

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In an earlier paper[1] we reported some measurements on nuclear radius for 19 elements with Z between 4 and 83, and sought a linear representation of our results by an expression of the form

$$R=b+r_0A^{\frac{1}{3}}. \qquad (1)$$

By graphical interpolation, in which we intentionally enhanced the importance of results corresponding to elements with high atomic number, we obtained for b and r_0 the following values:

$$b=1.5 \text{ to } 2.0\times10^{-13}\text{ cm}, \quad r_0=1.3 \text{ to } 1.0\times10^{-13}\text{ cm}. \qquad (2)$$

The quantity b represents the surface effect of the nucleus, that is, the contribution of nuclear force range of superficial particles to the value of R; in fact our measurements refer to a nuclear radius R defined as the distance from the center of a nucleus at which a fast neutron interacts with the nucleus. Other definitions may be given; for instance,[2] when the binding energies of contiguous and specular isobar pairs are compared, the nuclear radius can be defined as the radius of the proton-distribution sphere. In all cases in which a comparison was possible, the values obtained using this second definition were found to be smaller than ours by about 1×10^{-13} cm.

In our former paper[1] it was mentioned that, notwithstanding the accuracy of the values which we found for R, it is not possible to determine the values of b and r_0 with great precision, owing to the appreciable deviations of the individual points from the linear representation of Eq. (1).

Therefore we thought it worth while to treat the question again by statistical methods in order to test the correctness of fit of a theoretical curve to a set of experimental values, although such procedures are generally open to some criticism.

The second column of Table I gives the values of $R_i+\delta R_i$ for 17 elements. The results obtained for C and Au have been omitted; the geometrical conditions for the C measurements were not quite the same as for the other elements, and the results obtained with Au were much less accurate than for other elements.

The third column gives the ratio of the statistical error to the standard deviation; the values δR_i of the second column are in all cases the greater of the two errors. A detailed account of the calculation of these two errors was given in reference 1; we shall only stress the fact that in