

V. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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A. MAGNETIC FIELD HOMOGENEITY

A theoretical and experimental investigation of the homogeneity of magnetic fields produced by magnetized iron was undertaken. The results include specifications for cylindrical pole distributions (reported in the Quarterly Progress Report of January 15, 1956) to get rid of terms to the sixth order in the expansion about the midpoint in the pole gap. We have also found that micro-inhomogeneities caused by domain structure fall off exponentially with distance from the pole if the pole distribution is regular, as in a checkerboard arrangement, but proportionally to the inverse first power of the distance if the arrangement is random.

Micro-inhomogeneities were studied with a small coil mounted on an air-driven disc that can be made to scan a circular region approximately 1 inch in diameter. The coil axis is parallel to the magnet axis and to the disc axis, so that only field inhomogeneities will induce a voltage in the coil. Preliminary results indicate that the domain size on the soft iron pole that was studied changed in a rather complicated way for fields in the gap from 0-3000 gauss, and that the observed inhomogeneities decreased exponentially with distance from the surfaces.

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B. NUCLEAR MAGNETIC RESONANCE IN SOLIDS

1. Molecular Motion in Cobalt Complexes

The first phase of these studies was completed (1). The results can be summarized as follows. In all $\text{Co}(\text{NH}_3)_6^{+++}$ salts, the NH_3 groups reorient freely (more often than 10^4 sec^{-1}) at liquid nitrogen temperatures. The entire complex ion undergoes reorientation at a higher temperature. The onset of reorientation is "normal" only in the fluoborate, in the salts that were studied, and yields a barrier height in the vicinity of 12 kcal/mole. The onset of ionic motion in the chloride, bromide, iodide, and nitrate compounds is more complex than in the fluoborate and can probably be explained for all except the iodide salt by the existence of two structurally nonequivalent types of $\text{Co}(\text{NH}_3)_6^{+++}$ ions in the crystal lattice. X-ray diffraction studies are under way to determine whether or not this explanation is correct, and to elucidate certain puzzling features of the nuclear resonance behavior in the iodide salt. $\text{Co}(\text{NH}_3)_6(\text{PF}_6)_3$ also appears to exhibit an "anomalous" linewidth transition, although in this compound the transition is

(V. NUCLEAR MAGNETIC RESONANCE)

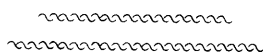
just beginning at the temperature at which the salt begins to decompose with the release of ammonia. In general, the barrier heights that were determined are reasonable for the salts investigated.

The work is being extended to include some substituted $\text{Co}(\text{NH}_3)_6^{+++}$ salts that, in qualitative experiments, were found to have high barriers, which would be expected from their lower ionic symmetry.

G. R. Murray, Jr., J. S. Waugh

References

1. This work is described in a Ph. D. Thesis submitted to the Department of Physics, M. I. T., by G. R. Murray, Jr., June 1956.



2. The Rotation of Methyl Groups in Solid Acetylenic Hydrocarbons

Methyl groups in dimethyl acetylene and dimethyl diacetylene are reorienting rapidly at the temperature of liquid nitrogen. When the temperature is raised above this point, there appears to be a slight broadening of the nuclear resonance line, the origin of which is now being investigated. Experiments at lower temperatures on the corresponding trifluoromethyl compounds will be made in order to find the region in which methyl reorientation begins.

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3. Chemical Shifts in Aromatic Compounds

Pople recently published (1) a theory for the qualitative prediction of positions of chemically shifted resonances of protons in condensed aromatic hydrocarbons, on the basis of a free-electron model. We recently recorded the spectra of 2,2-paracyclophane, dibenzyl, sodium cyclopentadienide, ferrocene, rhenium dicyclopentadienyl hydride and 10-paracyclane in order to investigate the validity of the theory. None of the results seem to support Pople's predictions. It may be significant that Pople's theory embodies the same assumptions as those of Pauling's theory of diamagnetic anisotropy and appears to fail in the same cases. Experiments continue in an attempt to establish the exact boundaries of the region of applicability of Pople's theory and the nature of the modifications that must be made to rescue it.

J. S. Waugh

References

1. J. A. Pople, J. Chem. Phys. 24, 1111 (May 1956).

(V. NUCLEAR MAGNETIC RESONANCE)

C. ISOTOPE SHIFT BETWEEN MERCURY¹⁹⁷ AND ^{197*}

The ultraviolet absorption spectroscope described in the Quarterly Progress Report of January 15, 1956, continues to operate reliably. A method was devised for displaying on an oscilloscope the hyperfine structure in absorption of a given sample of mercury. The accuracy, as can be seen from Fig. V-1, is poor and does not compare favorably with the quantitative point-by-point plot made with the dc bridge, but the device is very useful for quick analysis of the natural mercury content of preparations of Hg¹⁹⁷ that are made in the M. I. T. cyclotron. This rough analysis was performed often, for a considerable amount of difficulty was experienced in preparing samples of Hg¹⁹⁷ and ^{197*} which were free from contamination by natural mercury. There are five main absorption troughs of natural mercury (see Fig. V-1) which effectively hide the expected five absorption troughs of Hg¹⁹⁷ and ^{197*}. In other words, the radio-mercury must have very high specific activity; an acceptable sample would have to be at least 50 per cent Hg¹⁹⁷ and ^{197*}.

The targets from which the radio-isotopes are produced are pieces of gold foil. These are freed from mercury by prolonged heating in a vacuum furnace at a few degrees below the melting point of gold. The gold is left very pure but its surface is so clean that it will swiftly absorb mercury vapor from the air of the laboratory and from the helium atmosphere in the cyclotron target chamber. A great amount of effort was expended on the problem of preventing the gold from picking up stray natural mercury.

Exact expressions were worked out for the transmission of a Doppler-broadened incident line through a gas of absorbing atoms. This relative transmission is a function of:

- k_0 , the photon capture cross section;
- N , the number of absorbers per unit volume;
- L , the thickness of the absorbing gas;
- x , the wavelength, measured from the center of the absorption line in units related to the Doppler width;
- y , the difference in the mean wavelengths of the incident line and the absorption trough, in units related to the Doppler width; and
- β , the ratio of the temperatures of the emission lamp and the absorbing gas.

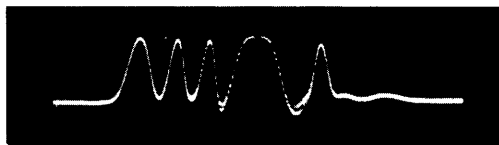


Fig. V-1. Rough absorption curve for natural mercury (from oscilloscope picture).

(V. NUCLEAR MAGNETIC RESONANCE)

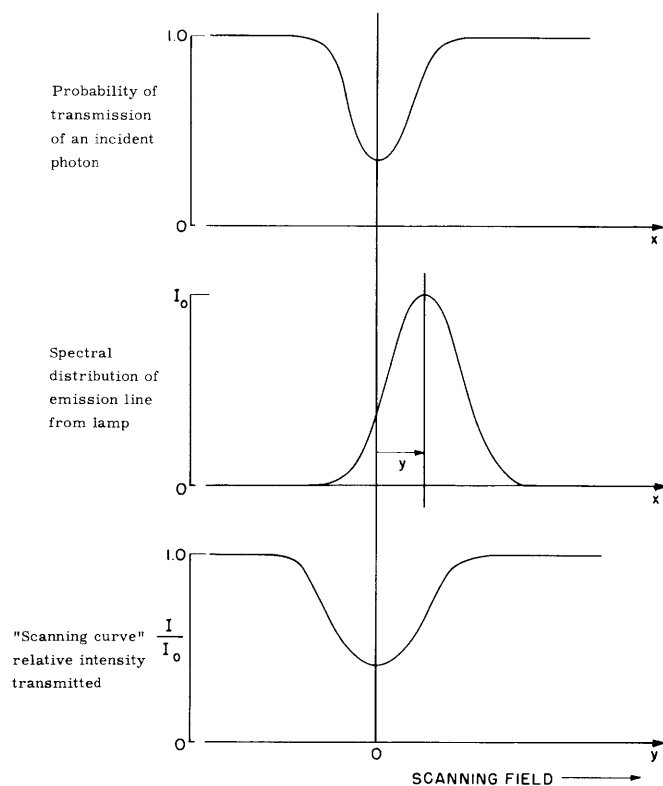
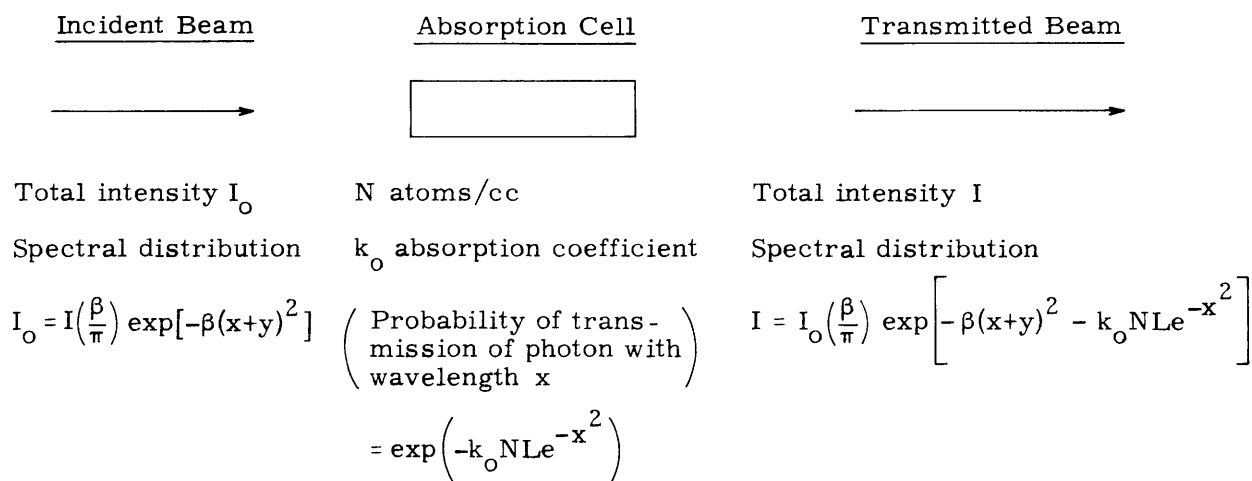


Fig. V-2. Derivation of theoretical scanning curve.

The theoretical derivation of the relative transmission is indicated below and in Fig. V-2.



The instrument measures $\frac{I}{I_0} = \frac{\int I_x dx}{\int I_{0x} dx}$

It can be shown that

$$\frac{I}{I_0} = (\beta)^{1/2} \sum_{n=0}^{\infty} \frac{(kNL)^n \exp\left(\frac{\beta^2}{n+\beta} - \beta\right) y^2}{n! (n+\beta)^{1/2}}$$

This expression which gives the form of the "scanning curve," shown in Fig. V-2, has a minimum at the bottom of the trough where $y = 0$. In this case

$$\left(\frac{I}{I_0}\right)_{\min} = \beta^{1/2} \sum_{n=0}^{\infty} \frac{(-k_0NL)^n}{n! (n+\beta)^{1/2}}$$

This function is plotted in Fig. V-3 for $\beta = 1$, that is, with emission lamp and absorption cell at the same temperature. These expressions were derived and tables of their

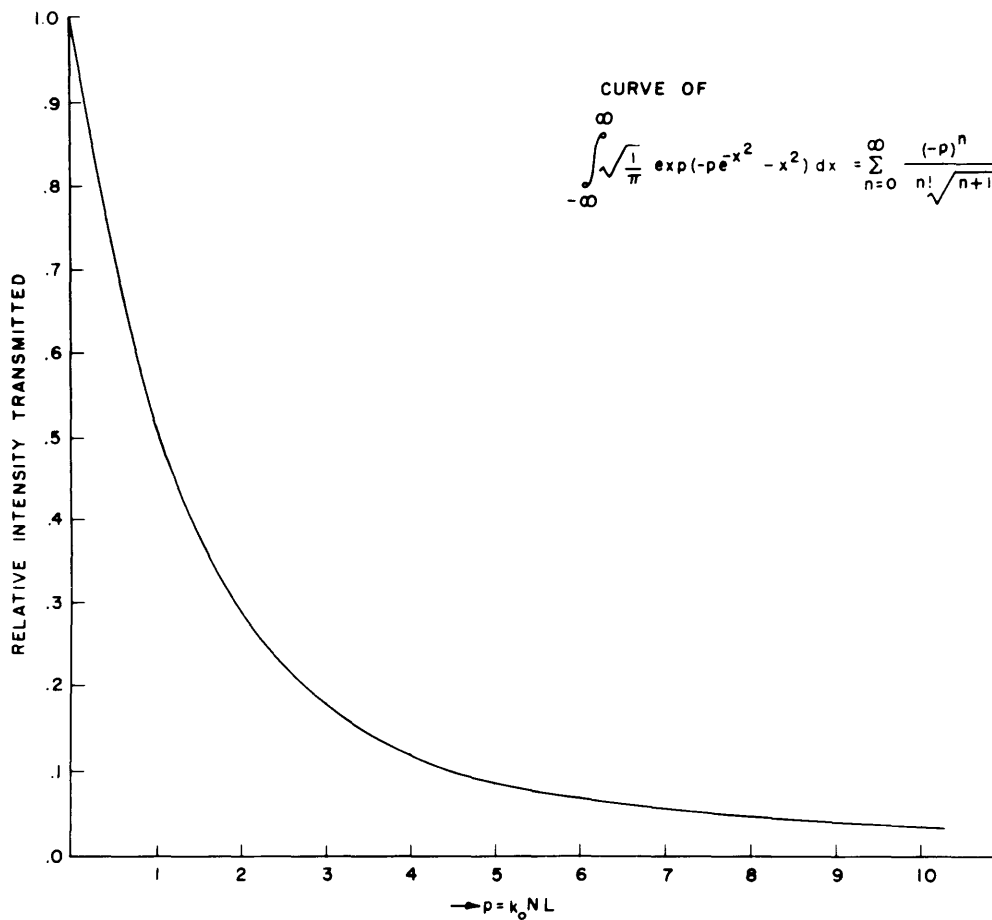


Fig. V-3. Calibration curve.

(V. NUCLEAR MAGNETIC RESONANCE)

values were prepared; these, together with further calculations concerning the form of a self-absorbed line, will be published later.

J. E. R. Young

D. HYPERFINE STRUCTURE OF THE 3P_1 STATE OF MERCURY BY DOUBLE-RESONANCE METHODS

1. In a Magnetic Field

The main object of our efforts was the improvement of the equipment for studying microwave transitions in the 3P_1 state of mercury to achieve greater accuracy. We have:

1. Completely stabilized the Hg¹⁹⁸ light source (microwave arc).
2. Used a self-balancing Leeds and Northrup strip-chart recorder.
3. Increased the microwave power so that "self-reversal" can be easily observed.
4. Obtained enriched samples of Hg¹⁹⁹ and Hg²⁰¹.
5. Replaced the sinusoidal sweep of the resonance magnet with a linear (triangular) one.

With the improved apparatus, a new exact "scanning curve" was obtained for the even isotopes, the signal-to-noise ratio of the resonance being of the order of 20. Resonance was also observed in the $F = 3/2$ level of Hg¹⁹⁹ with a signal-to-noise ratio of better than 5, and a preliminary "scanning curve" was made.

A. C. Melissinos, P. L. Sagalyn

2. In Zero Magnetic Field

A method for measuring the odd isotope hyperfine structure of the 3P_1 state of mercury with an error of less than one part in 10,000 was worked out in some detail for the $F = 3/2$ to $F = 1/2$ separation in Hg²⁰¹. (The $3/2$ to $1/2$ separation in Hg²⁰¹ is approximately 7.6 kmc; the $3/2$ to $5/2$ separation in Hg²⁰¹ is approximately 14.0 kmc; the single line of Hg¹⁹⁸ nearly coincides with the $3/2$ line of Hg²⁰¹.)

Excitation of Hg²⁰¹, $F = 3/2$, (and unavoidably of Hg¹⁹⁸) in natural mercury vapor is accomplished by radiation from an Hg¹⁹⁸ lamp. Transitions from the $F = 3/2$ state to the $F = 1/2$ state in Hg²⁰¹ are induced by the microwave fields of variable frequency in the waveguide (see Fig. V-4), if and only if the frequency corresponds to one of the approximate given separations. Discrimination is obtained by using a cell of Hg¹⁹⁸ vapor, which absorbs heavily the part of the scattered radiation that consists of Hg²⁰¹, $F = 3/2$ and Hg¹⁹⁸, and transmits the part that consists of Hg²⁰¹, $F = 1/2$.

Detection of this radiation is accomplished with photomultiplier I. Monitoring of the reradiated light intensity, which is subject to unpredictable variation both from lamp intensity changes and resonance cell density changes, is accomplished by a bridge-circuit

(V. NUCLEAR MAGNETIC RESONANCE)

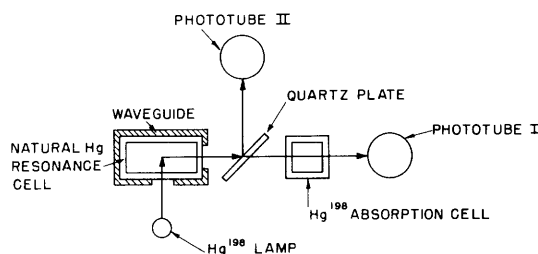


Fig. V-4. Diagram of apparatus.

measurement of the ratios of the outputs of photomultipliers I and II (see Fig. V-4).

In order to estimate signal and signal to noise, we need knowledge of the lamp intensity, and an approximate calculation of the following, for both off and on resonance conditions: excitation of Hg^{201} , $F = 3/2$ and Hg^{198} in the resonance cell for both off and on microwave resonance conditions; transition probability from the $F = 3/2$ to $F = 1/2$ state for the known microwave field strengths; discrimination percentage of the Hg^{198} cell against Hg^{201} , $3/2$, Hg^{198} and Hg^{201} , $1/2$; and detection efficiencies of the photomultipliers.

Lamp intensities were measured absolutely with a commercial radiation thermopile. The calculations mentioned above were made very roughly. The result is a signal-to-noise estimate of 10,000. Details of the calculations will be presented later.

The measurement described above can be applied directly to the $F = 3/2$ to $F = 5/2$ transition in Hg^{201} , and, with modification, to the $F = 1/2$ to $F = 5/2$ transition in Hg^{201} as well as the $F = 3/2$ to $F = 1/2$ transition in Hg^{199} .

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