The Research Laboratory of Electronics is an interdepartmental Laboratory in which faculty members and graduate students from numerous academic departments conduct research.

The research reported in this document was made possible in part by support extended the Massachusetts Institute of Technology, Research Laboratory of Electronics, jointly by the U.S. Army (Signal Corps), the U.S. Navy (Office of Naval Research), and the U.S. Air Force (Office of Scientific Research) under Signal Corps Contract DA-36-039-sc-78108, Department of the Army Task 3-99-20-001 and Project 3-99-00-000.

Reproduction in whole or in part is permitted for any purpose of the United States Government.
Magnetic Resonance in Radiating or Absorbing Atoms

F. Bitter

In the last ten years a great deal of work has been done on the experimental investigation of atomic energy levels using magnetic resonance techniques. This paper concerns itself primarily with a review of some of the studies of atomic vapors in connection with level structures, on the one hand, and the mutual interactions of light oscillating magnetic fields and the effects of collisions, on the other.

1. Introduction

This subject, now just over ten years old, appears to merit attention and review for three main reasons: (1) It makes possible the precise investigation of the detailed structure of atomic energy levels, and requires only very few atoms ($\sim 10^{12}$). This is of particular importance in the investigation of the hyperfine structure of radioactive isotopes. (2) It makes possible detailed investigation of the processes of radiation and absorption of light, by providing observable effects that are due to a known controllable perturbation that is operative during optical transitions. In effect, this amounts to saying that the detailed shape of energy levels is becoming more readily accessible for experimental investigation, and so a new facet is being added to our knowledge of atomic structure. (3) Just as magnetic-resonance investigations in solids and liquids have added enormously to our knowledge of how matter is constituted, so it appears most likely that similar investigations in gases, and particularly in plasmas, will prove to be illuminating. Much has already been done by radio-frequency and microwave spectroscopy, on the one hand, and by optical spectroscopy, on the other. It is not clear just how these two techniques can best be combined to study plasmas, but surely the pioneering double-resonance investigation of the imprisonment of resonance radiation will point the way.

II. Magnetic-Resonance Techniques

Magnetic resonance involves the reorientation of a magnetic dipole, as a whole, in an external field, or the reorientation of one of the magnetic dipoles constituting an atom with respect to the others. In the former case, transitions are produced between the Zeeman components of an energy level; in the latter, between the fine-structure or hyperfine-structure components. This requires an oscillating magnetic field that will induce transitions from the lower to the upper state involved (absorption of energy from the field by the atom), or from the upper to the lower state (forced emission). Spontaneous emission of magnetic-dipole radiation at these microwave or radio frequencies may be neglected.

During the decade of 1930, Majorana and Rabi discussed magnetic-resonance absorption theoretically, and Rabi and his collaborators detected nuclear magnetic resonance experimentally in atomic beams. In their experiments no differences in populations of these various levels involved in the resonance were required. The trajectory of any atom in the beam is changed by a “flip” from one state to another, and it is this change in the number of atoms following one particular path to a detector which is used to monitor the resonance.

The next step was the detection of magnetic resonance in solids and liquids, and also in gases. In thermal equilibrium even closely-spaced nondegenerate energy levels, as, for instance, the Zeeman components of an atom in its ground state, are not equally occupied, and magnetic resonance between such levels will involve the absorption of energy as the slightly more densely populated lower levels are transformed into excited levels. This can be detected directly as a removal of power from the exciting circuit. The resonance effect can also be detected by means other than absorption. An atom in a steady state is accompanied by or surrounded by its own stationary fields, but not...
by oscillating fields. This is, in fact, what is meant by a stationary state, namely, that its charge distributions and currents are time-independent. In an electric-dipole transition, however, there is an oscillating dipole, oscillating at the radiating frequency. Similarly, in a magnetic transition there is a precessing magnetic dipole, precessing at the Larmor frequency. Normally, the magnetic dipoles in a sample of matter in thermal equilibrium in a magnetic field will precess around the field direction, but with random phases. The Larmor frequency can therefore be detected only as noise. An applied oscillating or rotating magnetic field at the Larmor frequency can induce a certain amount of coherence between the precessing dipoles, and will result in a precessing magnetization of the order of that produced by the constant field. This precession can be detected by means of a suitably tuned circuit that includes a coil surrounding the sample. The precessing magnetization produces a periodic change in flux linkage, and therefore an emf in the coil. All these magnetic-resonance effects depend on the Boltzmann factor, which determines the slight difference of population of adjacent levels in thermal equilibrium.

Next, Lamb,9 Retherford, and others investigated the fine structure of various states, including the $n = 2$ level of hydrogen shown in Fig. 1, by using a novel magnetic-resonance technique. This level consists of two $P$-levels which decay readily to the ground state, and an $S$-level involving a forbidden transition to the ground state. In an atomic-beam experiment involving excited atoms, only those in the $S$-state will populate the beam, as the others will have decayed at the outset. By introducing an oscillating magnetic field of the proper frequency at some point along the path of the beam, transitions to the $P$-states can be induced. These immediately decay to the ground state, and the number of atoms arriving at a detector while still in the excited state is reduced. In this way, the now well-known “Lamb shift” was established.

Finally, the optical methods of detecting magnetic resonance were developed after 1950. A discussion of this work follows a review of certain purely optical aspects of the problem.

### III. Selective Excitation by Optical Pumping and by Collisions

A prerequisite to the magnetic-resonance investigation of an atomic state is to put a sufficient number of atoms into that state. For most experiments it is desired to excite an atom not only to some one state, but selectively into one of the Zeeman components, or into one of the fine-structure or hyperfine-structure components. No generally applicable techniques for doing this perfectly are at present available, but some of the methods used in the case of mercury resonance radiation may serve to illustrate the possibilities.

The hyperfine structure of the 2536 A resonance line of natural mercury consists of five components of roughly equal intensity separated by approximately two Doppler widths. Some of these components, however, consist of overlapping lines which originate in several isotopes. The details of this structure will be discussed at length below. The first attempts to produce a 2536 A resonance line consisting of one of these components only were made by Mrozowski who used a mercury-vapor filter in a magnetic field, which transmitted one component but absorbed all of the others. At the present time, because of the availability of separated isotopes, lamps radiating single components can readily be constructed. Of the isotopes having even mass numbers (and no nuclear spin), $\text{Hg}^{198}$ is the cheapest and commonest, but satisfactory lamps operated by high-frequency electrodeless discharge have been constructed from most of the stable, and some of the radioactive, isotopes. The $\text{Hg}^{198}$ lamps are particularly convenient because they radiate, in a magnetic field, just the classical Zeeman triplet (see Fig. 2), of which two components can be eliminated, if desired, by polarization filters. The remaining transmitted line may be “tuned” by varying the field intensity to any desired value for the selective excitation of some one isotope. This technique was first demonstrated10 in 1953. By noting the absorption in a cell containing mercury vapor as a function of the frequency of the excited light, hyperfine-structure patterns like that shown in Fig. 3 have been obtained11 for a variety of isotopic mixtures. The resolving power is limited here by the Doppler width of the emission and absorption lines. Work is now in progress in an attempt to increase the resolving power by using atomic beams, both in the emitting and absorbing units.

The magnets used in these magneto-optic scanning experiments were the powerful air-core solenoids of the M.I.T. Magnet Laboratory. These are capable of delivering 60 kgauss in a central tube, 10 cm diam, but at a cost of 1.5 megawatts, or more. An $\text{Hg}^{198}$ lamp
Fig. 2. The Zeeman effect of the $^3P_1$ state of mercury in an isotope having no nuclear spin. The splitting is approximately 2 Me/ gauss. For spectroscopic considerations, this may be put into the more convenient form, approximately $630 \times 10^{-3}$ cm$^{-1}$ for 10,000 gauss.

Fig. 3. The hyperfine structure of $\lambda = 2536$ A of natural mercury as plotted by magneto-optic scanning.

placed in such a solenoid will radiate only the two circularly polarized $\sigma$ components in the direction of field, and one of these can be suppressed by using a quarter-wave plate and a polarizing filter. The demands on the laboratory are now such that some other way of producing the required 10 kgauss must be found. Magnets for this purpose are being constructed. It might be mentioned, at this point, that the field of an air-core solenoid of internal radius $a_1$ in cm, operated at a power level of $W$ watts, is of the order of

$$H = 100\sqrt{\frac{W}{a_1}} \text{ gauss.}$$

Thus, to produce 10 kgauss in a tube that is 4 cm in diameter would require only 20 kw. By the use of auxiliary iron, this figure can be further reduced. Quite small magnets, weighing only forty-five kg or so, can be designed for such work. If it is not necessary to extinguish all but one of the Zeeman components, as for example in the selective excitation of an atom at the frequency of one component while the other components are not absorbed, the light may be taken at right angles to the field of an ordinary small iron-core electromagnet.

A most important adjunct in optical selective excitation is the polarization of the exciting light. If it is desired to excite one of the Zeeman sublevels of the $^3P_1$ state of Hg$^{199}$, shown in Fig. 2, in a field that is so small that the splitting is much less than the Doppler width of the exciting light, this may be done by arranging that the exciting light be plane-polarized, with the electric vector, for instance, parallel to the applied field. This is, in fact, the method used in the first double-resonance experiments.

The term "optical pumping" may well be taken to mean the selective population of any state by optical means. It was first proposed, however, by Kastler$^{12}$ in a particularly elegant form in which it was possible not only to equalize the populations of two states by resonance absorption between them, but to force a selective population of a state which can, under certain circumstances, approach completeness. This involves absorption from state 1 to the excited state 2, from which radiation can take place either back to state 1 or to some intermediate state 3, as shown in Fig. 4. If this state is metastable or long-lived, and exciting radiation is sufficiently intense, essentially all of the atoms in state 1 can be transferred to state 3. This condition can be detected by noting the decrease in the absorption of the incident light as the population of state 1 decreases. Population inversions achieved in this way form the basis of the recently invented optical masers.$^{18}$ Our interest in this type of optical pumping centers around the production of nuclear orientation or nuclear alignment. In this case the two levels, 1 and 3, correspond to two different orientations of a nucleus in a magnetic field. The levels are almost degenerate, and it is necessary to avoid exciting atoms in state 3 with the same light that excites them in state 1, by making use of polarization conditions. This is illustrated in Fig. 5 for Hg$^{199}$ with a nuclear spin of $\frac{1}{2}$. Circularly polarized light of one sign of rotation can be absorbed only by atoms with their spins in one orientation, and the optical pumping transfers these to the other orientation. The incident light continues to

Fig. 4. Optical pumping to an intermediate level.
Fig. 5. Optical pumping in Hg having a nuclear spin of \(1/2\) by the absorption of circularly polarized light and excitation to the \(F = 1/2\) hyperfine level of the \(2P_{1/2}\) state. In the subsequent decay some of the atoms are transferred, or "pumped," into a different \(m\)-level.

"pump" until thermal relaxation processes of one kind or another just balance the pumping rate. Distributions with 80-90% of the nuclei pointing in one direction have been achieved in this way.

Selective excitation of the sublevels of higher excited states has been most successfully accomplished by using directed beams of electrons of controlled energy. This is accomplished at low pressures by accelerating electrons from a plane cathode with a nearby plane grid. As the electrons move through the gas or vapor toward the plate, they excite the atoms, and the radiated lines are, in general, polarized; this indicates that the sublevels are not equally populated.

**Optical Effects Involving Magnetic Resonance**

The first attempts to detect magnetic resonance optically were undertaken by Brossel, at the author's suggestion, more than ten years ago, while he was at M.I.T. These attempts were abandoned, as they were shown by Pryce to be based on a miscalculation. The effects that were sought, which involved a splitting of the radiated lines by the oscillating magnetic field, were too small to detect, being of the order of the Zeeman effect in a constant field of the magnitude of the rf amplitude. Kastler then suggested that effects resulting from induced transitions between sublevels be sought. Soon afterward, the effect was found by Brossel in the \(2P_{3/2}\) level of the even isotopes of mercury. By exciting the \(m = 0\) level with \(\pi\) resonance radiation (see Fig. 2), the appearance of the \(\sigma\) components in the scattered light could be used as an indication of magnetic resonance. The resonance curves shown in Fig. 6 were obtained. The author was then able to show that the distinctive shape of these resonance curves was due to the multiple degeneracy of the magnetic-resonance transitions in this level with \(J = 1\), and could be accounted for by a straightforward application of the Majorana formula for the magnetic-resonance transition probabilities.

This method of using changes in the polarization of the emitted resonance radiation to detect magnetic resonance has been used extensively since that time.

Recently, however, two new techniques have been used. One of these, which is due to Kohler, is particularly useful for measuring the distance between levels separated by more than the Doppler line width. One of the two levels whose spacing is to be measured is illuminated by a suitably tuned lamp, and the re-radiated light is passed through a filter that absorbs this same frequency. Magnetic-resonance transitions to the second level will alter the frequency of the re-radiated light, which can now pass through the filter and be detected by a photocell. This method makes use of a frequency change, rather than a polarization change as in the earlier experiments.

The final method, which is due to Series, makes use of the fact that the light emitted by a precessing atom is modulated at the precessional frequency. In the absence of an externally applied field oscillating at the resonance frequency, there is no phase relationship between the various precessing atoms, but just as in the case of nuclear magnetic resonance in solids and liquids discussed above, the applied rf field produces a certain degree of coherence in the precession of the radiating atoms, and the emitted light is therefore modulated. As is apparent from the form of the Majorana expression for the transition probabilities, when more than two equally spaced levels are involved in a resonance.
various multiples and submultiples of the normal Larmor frequency may be expected. The modulation of the resonance radiation emitted by a precessing atom is formally equivalent to a "beat" phenomenon between two coherent radiations whose frequencies differ by the amount of the precessional frequency. For this reason, the above-described method has been termed the method of "light beats."

Magnetic resonance in a state may be monitored by absorption, as well as by emission involving that state. This is particularly important for the measurement of nuclear moments or hyperfine structures in ground states whose sublevels are selectively populated by optical pumping.

IV. Level Structures

The detailed measurement of fine structures and hyperfine structures and other resonant frequencies by the methods of radio-frequency spectroscopy has been of great importance in physics. Outstanding in this connection is the Lamb shift, the anomalous magnetic moment of the electron, the shell structure of atomic nuclei, based in large measure on precise measurements of nuclear moments, and atomic hyperfine structures. We shall focus our attention primarily here on some recent results with mercury, which, so far, have been published only separately, as they illustrate typical examples of double-resonance and related optical experiments.

Results obtained, thus far, are summarized in Fig. 7, which shows the best values for the resonant frequencies of all isotopes measured, plotted with respect to the resonant frequency of Hg\(^{199}\). The shift in frequencies from the 198 isotope is determined primarily by spectroscopic means and is given in units of \(10^{-3}\) cm\(^{-1}\) while the separation of the hyperfine structure components is measured directly by magnetic-resonance methods, and is measured and given in Mc/sec. First, let us consider the isotopes of even mass number, and zero spin. Since the lines for Hg\(^{194}\) and Hg\(^{198}\), as shown in Fig. 3, are coincident with other lines that are due to Hg\(^{199}\) and Hg\(^{201}\), their centers are not necessarily the centers of the desired lines. A double-resonance method has been developed to eliminate this effect by measuring only the change in intensity of re-radiated light when magnetic resonance in the isotopes of even mass number was induced. This, in effect, selects that part of two or more overlapping lines which is radiated by atoms having selected g-factors. This does not, however, eliminate the Doppler width of the lines, and the results are therefore not as accurate as recent interferometric measurements by Schweitzer, who used atomic beams. His values are given for the position of all of the lines that are due to stable isotopes except Hg\(^{198}\), which is normally present at a concentration of only 0.16%, but was prominently present in residues from some of our radioactive samples, and is also available in small quantities in enriched mixtures. These results on isotope shift are considered to be particularly important, especially if the accuracy of the measurements can be improved still further, since they give promise of our being able to investigate the charge distribution within a nucleus with the same detail that the hyperfine-structure anomalies (Bohr-Weisskopf effect) provide for the analysis of the current distribution, or the nonuniform distribution of nuclear magnetization.

### Table

<table>
<thead>
<tr>
<th>Isotope</th>
<th>(\mu_{\text{Hg}})</th>
<th>(\text{MHz})</th>
<th>(\text{Mc/sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>-500.77 ± 43</td>
<td></td>
<td>221.40 ± 0.2</td>
</tr>
<tr>
<td>202</td>
<td>-336.96 ± 15</td>
<td></td>
<td>191.4</td>
</tr>
<tr>
<td>201</td>
<td>13,986.57 ± 0.08</td>
<td>7,556.133 ± 0.13</td>
<td>22,128.56 ± 0.02</td>
</tr>
<tr>
<td>200</td>
<td>-160.296 ± 15</td>
<td></td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>201</td>
<td>-5.926 ± 0.45</td>
<td>-21.734 ± 0.21</td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>199</td>
<td>0.178 ± 0.03</td>
<td></td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>198</td>
<td>18,249.3 ± 0.10</td>
<td>14,234.86 ± 0.09</td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>197</td>
<td>0.369 ± 0.05</td>
<td></td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>197</td>
<td>-437.1 ± 4</td>
<td>75.15 ± 0.4</td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>196</td>
<td>-23,086.37 ± 0.2</td>
<td>171.6 ± 0.4</td>
<td>224.40 ± 0.23</td>
</tr>
<tr>
<td>195</td>
<td>0.185 ± 0.07</td>
<td>-91.4 ± 0.2</td>
<td>224.40 ± 0.23</td>
</tr>
</tbody>
</table>

Fig. 7. Summary of available data on the structure of the 2536 A resonance line emitted by various isotopes of mercury. The separations of the various frequencies from the Hg\(^{199}\) frequency are given in units of \(10^{-3}\) cm\(^{-1}\). The frequency differences between the radiations from a single atom are given in megacycles per second. The ratios of the nuclear moments to the proton moment are frequency ratios, and are not corrected for the diamagnetic shielding caused by the outer electrons. The data for Hg\(^{197}\) are calculated from the hyperfine structure in the \(P_1\) state. All other moments are obtained by optical pumping in the ground state.
The hyperfine-structure intervals of the stable nuclei Hg\(^{201}\) and Hg\(^{199}\) were obtained by Kohler\(^{29}\) and Stager,\(^{27}\) with the use of a double-resonance technique involving the change in frequency of the re-radiated light. For Hg\(^{201}\), light from an Hg\(^{198}\) lamp was used to excite atoms in the cell to the \(F = \frac{3}{2}\) level, which happens to fall within the line width radiated by the lamp. The re-radiated light was passed through an Hg\(^{198}\) filter, and was absorbed until magnetic resonance changed its frequency. For the Hg\(^{199}\), an Hg\(^{201}\) emission and absorption lamp was used.

Obtaining the results for the radioactive isotopes, Hg\(^{197}\), and its isomer, Hg\(^{197*}\), was a lengthy process. The first experiments with the use of simple magneto-optic scanning\(^{11}\) gave a preliminary indication of the structure of Hg\(^{197}\), but it was impossible to identify the lines that were due to Hg\(^{197*}\). The many overlapping lines provided us with too complicated a situation to sort out reliably. It was found that usable electrodeless-discharge lamps could be made, even with the very small quantities of the radioactive isotopes available, and, by using standard spectroscopic techniques involving several spectral lines, Melissinos and Davis\(^{26}\) were able to make preliminary estimates of the splitting and shift of the 2536 A radiation of Hg\(^{197*}\). With these preliminary values for the hyperfine separations, Melissinos\(^{27}\) and Hirsch\(^{29}\) conducted the first successful double-resonance experiments in Hg\(^{197}\) and Hg\(^{197*}\). These investigations were made with already existing apparatus, and the resonances were observed in relatively large magnetic fields. To obtain the desired hyperfine splitting, the observed resonances had to be extrapolated back to zero field. Kohler's methods, however, are better suited to precise measurements of the desired quantities directly, or in very weak fields which can be corrected for linearity. These final measurements by Kohler's method are listed in Fig. 7; they were obtained by Stager\(^{29}\) for Hg\(^{197}\), and for the \(11/2 \rightarrow 13/2\) transition of Hg\(^{197*}\) by Brot.\(^{30}\) The less accurate value for the \(15/2 \rightarrow 15/2\) transition is an extrapolation from high-field resonances observed by Hirsch.\(^{29}\) These included both conventional double-resonance effects, and effects caused by "level crossing" recently reported by Colgrove \textit{et al.},\(^{31}\) for the crossing of helium fine-structure lines in a magnetic field, and used here most effectively for the first time for hyperfine-structure determinations.

The hyperfine-structure splittings of the mercury resonance line described above occur in the excited \(\textit{P}1\) state. The ground state, \(8S_0\), with no angular momentum, is diamagnetic, and has no permanent moment except for the very small nuclear moment of the odd-A isotopes. The nuclear moments can best be determined by measuring the Larmor precession frequency in a known externally applied field.

The optical-pumping technique, first successfully applied to alkali atoms,\(^{32}\) was finally developed in 1958 to the point at which it led to positive results in mercury vapor. This work is summarized in the doctoral thesis of Cagnac\(^{24}\) and has led to several important results, some of which are described in this section, and some, relating to depolarizing collisions, in the next section.

The difficulties encountered in earlier attempts to produce nuclear alignment, or orientation, in mercury vapor were due to a variety of causes that took time to track down. First of all, even if wall collisions are not disorienting, the atoms that are being oriented must be isolated from the parent substance to which they will surely adhere and so lose their orientation. Second, the total light flux through the vapor must be as great as possible. In the apparatus used to orient Hg\(^{199}\) and Hg\(^{201}\) nuclei, a disc-shaped quartz lamp is used, 25 mm diam and 2 mm thick, containing 1 mg of either Hg\(^{199}\) or Hg\(^{204}\), with 8-mm pressure of argon. It is excited with a magnetron unit delivering 100 watts at 2400 Mc. The Hg\(^{204}\) lamp will excite Hg\(^{199}\) to the \(F = \frac{1}{2}\) level, or Hg\(^{201}\) to the \(F = \frac{1}{2}\) level. On the other hand, the Hg\(^{198}\) lamp will excite Hg\(^{201}\) to the \(F = \frac{3}{2}\) level. The light from these lamps falls on the cell in which the optical pumping is to take place in the direction of the magnetic field, and is therefore classed as \(\sigma\)-light, and may be polarized either as \(\sigma^+\) or \(\sigma^-\). The orientation produced by the optical pumping in this way can be destroyed by magnetic resonance, and can be detected optically by the change in absorption or scattering of light by the cell. The field, which must be extremely uniform to produce accurate results, can be monitored by a nuclear-resonance probe. The results obtained by Cagnac are:

\[
\mu_{199} = (0.1782796 \pm 3 \times 10^{-4})\mu_0
\]
\[
\mu_{201} = -(0.1974197 \pm 12 \times 10^{-4})\mu_0.
\]

At the M.I.T. Magnet Laboratory an effort has been made to provide a variable-frequency light source of sufficient intensity for use in optical-pumping experiments. A disc-shaped lamp of large diameter, approximately 8 cm, in the throat of an air-core solenoid, has recently led to positive results. This is of particular importance in the case of Hg\(^{197}\) and Hg\(^{197*}\) whose lines do not coincide with those of stable isotopes. A preliminary result obtained by Walter\(^{34}\) on Hg\(^{199}\) is

\[
\mu_{199} = (0.18585 \pm 7 \times 10^{-4})\mu_0.
\]

This result is less accurate because of the width of the lines obtained in the first version of the apparatus. The resonance in the isomeric state has not, thus far, been detected.

A word of comment may be justified about the effort required to produce the results shown in Fig. 7. They
involve, first of all, the development of optical scanning
and atomic-beam techniques, combined with high-
resolution spectroscopy. They required the develop-
ment of very bright and large lamps, of variable fre-
quency in some cases, and of specially designed magnets.
They required the development of methods for pro-
ducing and handling the radioactive samples, of build-
ing resonance lamps, and also of electrodeless-discharge
lamps containing only very few atoms. Finally, they
required the application of microwave techniques with
quartz cells within high-Q microwave cavities. The
chances of failure in an experiment involving several
new and difficult techniques rise very quickly as the
number of steps increases, especially if all of the opera-
tions involved must take place without failure during
the limited lifetime of radioactive isotopes. The suc-
cessful methods of procedure have, in the main, been
described in detail in the theses and publications of the
various authors cited. Further work is in progress on
(1) other isotopes, (2) the factors governing the useful
life of electrodeless lamps and hollow-cathode lamps
containing very few atoms, (3) the development of
magnets especially suited to this work, and (4) the
development of atomic-beam techniques, especially
for magneto-optic scanning. A special word of appreci-
ation is due to Henry H. Stroke, whose name has not
appeared in this discussion, but who, in fact, has con-
tributed more than anyone else to the success of the
experimental part of the work carried out in the M.I.T.
Magnet Laboratory, to an understanding of its signifi-
cance for nuclear-structure theory, and to the main-
tenance of a spirit of eager interest among the M.I.T.
students and staff over a long period of discouraging
failures and partial successes. The friendly coopera-
tion and extensive exchange of information with other
laboratories, especially the Laboratoire de Physique of
the École Normale Supérieure, is also gratefully
acknowledged.

Optical pumping in the alkalis promises to be of
considerable practical importance, in addition to the
theoretical importance of the results of hyperfine-
structure measurements of various isotopes in several
states by atomic-beam, as well as double-resonance,
techniques.² Dehmelt’s investigations,²³ starting with
investigations of relaxation times and the orientation
of free electrons by collisions with oriented sodium
atoms, led to proposals by Bell and Bloom²⁶ for the use
of magnetic resonances in optically pumped vapors as
frequency standards, and as indicators in weak-field
magnetometers. Magnetic resonances can be mon-
tored in optically pumped alkali vapors by the absorp-
tion of the pumping beam, or by an independent sepa-
rate beam traversing the pumped vapor. In transi-
tions of the type \( m_1 = 0 \rightarrow m_2 = 0 \), \( \Delta F = 1 \) the resonant
frequency is practically field-independent in weak fields,
and can be used as frequency standards under some
conditions, for instance, with not too strong light²⁷ and
not too strong radio frequency,²⁸ to avoid the various
shifts that have been discovered. Other transitions
are field-dependent, and may be used in weak-field
magnetometers.

V. Transitions

In addition to the results already cited, several in-
teresting effects involving optical transitions have been
investigated in detail, particularly at the Laboratoire
de Physique of the École Normale Supérieure, in Paris,
during the last decade. It is not possible to do this
work justice here, but at least some illustrative ex-
amples will be presented and an effort will be made to
indicate some particularly intriguing aspects of the
results obtained.

The first deals with the imprisonment of resonance
radiation. Instead of involving the emission and ab-
sorption of a quantum in a series of independent events,
it has been found that phase coherence among several
participating atoms may be maintained by the elec-
tromagnetic field in which they are resonating, and
that this can be studied by double-resonance techniques.

It has been found²⁹ that double-resonance curves,
such as those shown in Fig. 6, are materially modified as
the mercury vapor pressure is changed, and this in a
range of pressures so low that atomic collisions are surely
not responsible. At very low pressures, below 0.1 \( \mu \),
or so, they have the form shown in Fig. 6, but at higher
pressures they become narrower, and their shape is
modified. This can be accounted for by considering
the interaction of the atoms with the electromagnetic
field. The many papers dealing with this subject are
summarized by Barrat³⁰ who succeeds in developing a
theory in spite of the inherent complexity of the
problem. It is not surprising that such effects exist,
or that imprisonment produces a narrowing of the
resonance levels, but it is both surprising and gratifying
to find that explicit theoretically-based formulations
are possible. The limiting half-width of the resonance
curves, \( \Delta \omega/2 \), at low rf power specifies a time \( T = 2/\Delta \omega \)
which Barrat calls the coherence time. At low vapor
pressures, at which the probability of a quantum being
absorbed more than once before escaping from the
cell is negligibly small, \( T \) approaches \( \tau \), the natural
lifetime of the excited state. When the vapor pressure
is increased, that quanta will, on the average, be ab-
sorbed more than once before escaping; \( T \) is greater
than \( \tau \) and the line shape is altered. Figure 8 shows
results obtained in a series of measurements of \( T \) on
cells in which resonances in Hg²⁵ and Hg³³ were ob-
served as a function of vapor pressure with varying
atomic concentrations of isotopes in the cell. As is to be
expected, if this is indeed an effect caused by imprison-
ment, the concentration of resonating atoms alone
determines the coherence time. The calculation for
Fig. 8. "Coherence time" of imprisoned mercury resonance radiation in a 2.5-cm$^3$ cell as a function of $N$, the number of atoms/cm$^3$ of the isotope in which resonance occurs. The points are experimentally measured inverse line widths, and the curve is based on Barrat's theoretical predictions. ○—Hg$^{199}$ resonance radiation in a cell containing natural Hg; X—Hg$^{200}$ resonance radiation in a cell containing natural Hg; +—Hg$^{202}$ resonance radiation in a cell containing Hg$^{202}$ only.

odd-A isotopes is more involved, but equally in accord with experiment. The depolarization of imprisoned resonance radiation$^{40,41}$ can also be taken into account.

We have an important new experimental technique for studying radiating atoms, and likewise an important theoretical method of analysis to help us understand the results. The technique used does not lend itself to the study of imprisonment at higher vapor pressures and in larger cells, since the resonance radiation is largely depolarized, and the small changes resulting from magnetic resonance will then be difficult to detect. Other means of observing the magnetic-resonance curves should be sought, so that the interaction between radiating atoms may be studied more in detail as a function of their number, the distance between them, and, as we shall discuss below, with the effect of collisions on this interaction included.

Another class of experiments deals with excitation by multiple quanta. This is a subject that has been studied theoretically for many years,$^{42}$ and has been found experimentally in atomic-beam experiments,$^{43}$ as well as in double-resonance experiments.$^{44}$

The conditions of conservation of energy and angular momentum are illustrated in Fig. 9, taken from a note by Margerie and Brossel.$^{45}$ These transitions were found experimentally between adjacent Zeeman levels in the ground state of sodium, as shown in Fig. 2. The curves are for three different intensities of the 1206 Mc/s field. At low intensity, the resonances are sharp and only the single and double quantum resonances occur. At the higher fields, the resonances broaden, are shifted in frequency because of the Bloch-Siegert effect,$^{38}$ and resonances involving three and four quantum transitions appear. An intermediate level that does not coincide with the intermediate double-quantum jump, as shown in Fig. 11, modifies the resonance curves. Blamont and Winter$^{46}$ investigated this case theoretically and experimentally. The three Zeeman levels of the $^3P_1$ state of mercury for isotopes of even-A, shown in Fig. 2, are equally spaced. But if an electric field is applied, the central level, $m = 0$, is shifted by a variable amount $\epsilon$ with respect to the other two. The experimental results obtained throughout these investigations bear out the theory, and constitute a most elegant means for a detailed investigation of the interaction of matter with the electromagnetic radiation field.

Fig. 9. Possible multiple quantum transitions between adjacent levels.

Fig. 10. Multiple quantum transitions found between the Zeeman levels of the ground state of sodium.

A final aspect of transitions between atomic-energy levels, which we discuss here, is the role of collisions. These we divide into two classes. First, those that produce or destroy atomic orientation, and second, those that excite or de-excite electronic levels.

Fig. 11. Intermediate levels in multiple quantum transitions.
The question of selective excitation of Zeeman or hyperfine components by oriented beams of electrons having closely controlled energies has already been discussed as an important modification of the double-resonance technique, which is enormously important for the investigation of levels other than resonance levels. The subject appears to be of interest primarily because of its practical usefulness in this connection.

1. The disorienting effect of collisions with solid-container walls or with atoms is a quite different matter. On the one hand, extensive investigations have been carried out on optically oriented alkali vapors in their paramagnetic ground state.47-48 Collisions between alkali atoms and glass walls appear to produce reorientation more or less on every collision, but various coatings appear to be effective in preventing this. Thus, for example, Robinson et al.49 and Franzen50 report organic coatings that greatly reduce this effect.

The most severe source of disorientation under certain circumstances, however, is the occurrence of electron exchange between like atoms during collisions. The cross section for this has been estimated50 as approaching 1000 times the kinetic theory cross section. Collisions with diamagnetic rare gas atoms, on the other hand, have little effect on the orientation, the cross sections in oriented Rb vapor being estimated in the range $10^{-7}$-$10^{-4}$ of the kinetic theory cross section in the series Ne, A, Kr, Xe.

During the last few years, extensive work has been done on diamagnetic Hg atoms with odd-A nuclei. This work has recently been reviewed by Cagnac.51 There are distinctively different results for the two stable isotopes, Hg$^{201}$ with a nuclear spin of $\frac{3}{2}$, and Hg$^{200}$ with a nuclear spin of $\frac{1}{2}$. The former has a nuclear quadrupole moment. In a collision, the nucleus may be exposed to an electric-field gradient, for example, because of the deformation of the atom, and this exerts a torque that is instrumental in producing reorientation. There is no such nuclear quadrupole moment in Hg$^{200}$ and its nuclear orientation is consequently much more stable. The nuclear orientation in a vapor containing this isotope can have a much longer lifetime, and the nuclear magnetic-resonance curves can be much narrower. The actual mechanism (or mechanisms) responsible for producing thermal equilibrium is not clear, at present, and the observed relaxation effects and line widths require further experimental investigation. One of the very interesting results of this work is that it is apparently possible to study not only the various collision processes involved, but the actual duration of contact of a mercury atom with a wall. In the investigations reported with fused quartz cells used, this was estimated to be at least 1000 times the duration of an elastic collision at room temperature, but was markedly decreased by heating the cell.

Of great interest in another context are collisions leading to excited states. The great interest in plasmas indicates their practical and theoretical importance, and it is clear that in order to use them effectively and understand their properties thoroughly we shall have to investigate them in the same detail, for example, to which solid-state semiconductors have been examined on a world-wide scale during the past decade. In addition to studies of the electron-energy distribution and concentration, the ambipolar diffusion to the walls, and the extent of volume recombination of ions and electrons, we must also know something of the transitions between the various excited states and the radiations leaving the plasma. Figure 12, taken from an article by Kenty,52 illustrates the complexities, even in a simplified energy-level diagram. Direct experimental evidence for the correctness of the calculations is greatly to be desired and could be supplied by accurate measurement of the various level widths, as has been done, for example, for the $3P_1$ level in a resonance lamp. Such measurements have not yet been attempted, but would be most valuable to the student of plasma physics. A technique that may prove of importance in this connection is to measure the magnetic-resonance line width in a small-resonance lamp adjacent to the discharge that is to be investigated. The resonance lamp will, after all, be coupled to the discharge in just the same way as atoms in the same resonance cell, as studied by Barrat and others, are coupled to each other. The effects going on in the discharge can then be monitored externally more conveniently.

![Fig. 12. A diagram after Kenty,52 showing the principal processes occurring in a fluorescent lamp plasma-mercury vapor plus a few mm of rare gas, usually argon. Straight arrows are calculated collisions of the first and second kinds. Wavy arrows are measured radiation output (except for the heavy arrows). One full arrow, either straight or wavy, represents $3 \times 10^{16}$ transitions per second per centimeter of length. Decimals are fractions of full arrows.](image-url)
This is, perhaps, a good note on which to end this review. There is much fascinating work to be done in many fields with these new experimental techniques. There is still ample room for originality.

References

1. E. Majorana, Nuovo cimento 9, 43 (1932).
3. I. I. Rabi, S. S. Millman, P. Kusch, and J. R. Zacharias, Phys. Rev. 53, 318, 495 (1938); ibid. 55, 826 (1939); J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. 56, 728 (1939); see also many subsequent papers by these authors.
