A New "Double Resonance" Method for Investigating Atomic Energy Levels. Application to Hg $^3P_1$*

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Excitation of atoms in a vapor by polarized light produces unequal population of the magnetic sublevels of the excited state. The emitted optical resonance radiation is therefore partly polarized. The application of radiofrequency or microwave fields at a magnetic resonance frequency will induce transitions between sublevels of the excited state. The degree of polarization of the emitted optical resonance radiation is altered when the magnetic resonance condition is fulfilled. As suggested by Brossel and Kastler, this effect may be used to reveal the structure of the energy level. A detailed theory applicable to, and experiments on the $^3P_1$ state of all the isotopes of mercury are reported. The results obtained indicate that double resonance phenomena constitute a valuable new tool for investigating the structure of atomic energy levels. The mean life of the $^3P_1$ state is shown by observations on the resonance line widths to be 1.55×10^{-7} sec for all the isotopes. The g-factor of the $^3P_1$ state for isotopes with zero spin, measured in terms of the proton g-factor, is 1.4838 ± 0.0004.

INTRODUCTION

THE only means available at present for investigating the internal structure of nuclei involves accurate determinations of nuclear moments and hyperfine structures.[1] These determinations have previously been made by magnetic resonance experiments on the ground state of atoms or molecules in a beam or on diamagnetic liquids. In such experiments magnetic dipole transitions are induced by an oscillating magnetic field. If, in the sample being investigated, there is an initial inequality in the population of the magnetic sublevels of any given state, the net effect of the transitions induced by the oscillating magnetic field is to change this inequality and therefore to modify any property depending on it. In an atomic or molecular beam experiment the number of particles having a given trajectory through the apparatus is altered. In a nuclear resonance experiment, the degree of magnetization of the core of a coil, and therefore its impedance, is altered. A further possibility, having the great advantage of extending observations to the excited states of atoms, is to detect magnetic resonance in an energy level by observing changes in the optical radiation involving transitions from or to that level.[2]

The present paper gives an analysis and a detailed description of effects first observed in 1950,[3] based on suggestions put forward by Brossel and Kastler.[4] Excitation of a level by optical resonance radiation with polarized light provides the initial inequality of population in the Zeeman pattern of the excited state. The degree of polarization of the light spontaneously reemitted depends on this initial inequality and changes when it is altered by magnetic resonance absorption. This is the physical basis of the observations reported below.

Changes in frequency of the optical resonance radiation caused by magnetic resonance among the sublevels of either the upper or lower of the energy levels involved in the radiation process have also been predicted.[2] Such changes have been observed by Autler and Townes[5] in a somewhat analogous case in molecular spectra but are much too small to be significant for the atomic spectra discussed in the following.

GENERAL DISCUSSION OF EFFECTS IN MERCURY VAPOR

Mercury was the element studied experimentally. Naturally occurring mercury was used for the investigation of isotopes with even mass number and zero nuclear spin. Samples enriched in Hg^{199} and Hg^{201} were supplied by the Atomic Energy Commission for the investigation of these isotopes. Isotopic abundances of the samples used are shown in Table I.

The level studied was the $^3P_1$ excited state reached by excitation with the intercombination line $^1S_0-^3P_1$, having a wavelength 2537A. A diagram of the transitions involved and of the hyperfine structure of the line is shown in Fig. 1. The ground state is a diamagnetic $^1S_0$ state. The optical transition probabilities have been computed using the formulas of Hill[6] and Inglis[7] and are shown in Fig. 2 for the weak field case of no decoupling of the nuclear and electronic angular momenta. In this diagram the vertical arrows correspond

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[1] A. Bohr, Phys. Rev. **73**, 1109 (1948); F. Bitter, Phys. Rev. **76**, 150 (1949); A. Bohr and F. Weisskopf, Phys. Rev. **77**, 94 (1950).
[2] F. Bitter, Phys. Rev. **76**, 833 (1949); M. L. Pryce, Phys. Rev. **77**, 136 (1950).
[3] Brossel, Sagalyn, and Bitter, Phys. Rev. **79**, 196, 225 (1950). Attention is also called to the pioneering work of E. Fermi and F. Rasetti [Nature **115**, 764 (1925); and Z. Physik **33**, 246 (1925)], who first observed the depolarization of the resonance radiation of mercury by radiofrequency magnetic fields.
[4] J. Brossel and A. Kastler, Compt. rend. **229**, 1213 (1949).
[5] S. H. Autler and C. H. Townes, Phys. Rev. **78**, 340 (1950).
[6] E. H. Hill, Proc. Nat. Acad. Sci. **15**, 779 (1929).
[7] D. Inglis, Z. Phys. **84**, 466 (1933).

to transitions with $\Delta m_F=0$, or plane polarized π-radiation in absorption or emission with the electric vector parallel to the applied field, and diagonal arrows correspond to transitions with $\Delta m_F=\pm 1$ or circularly polarized σ-radiation.

For isotopes with even mass number [shown in Fig. 2(a)] π-excitation leads to the middle upper state only, and in the absence of perturbations, the reemitted radiation contains this π-component only. The experiment then consists of the application of a radio-frequency field which transfers atoms to the states with $m=\pm 1$ when the magnetic resonance condition $\omega=\gamma H_z$ is fulfilled. Here ω is the frequency of the oscillating field, H_z is the constant magnetic field, and γ is the gyromagnetic ratio of the state in question, namely, the $^3P_1$ state. When the resonance condition is fulfilled, the intensity of the π-component diminishes, and that of the σ-component increases. These changes were observed and used to detect resonance.

Collisions involving excited atoms will modify the aforementioned simple description, since atoms can then be reoriented not only by the absorption of rf energy, but also as a result of inelastic collisions. According to previous work,[8] the vapor pressure of mercury at -15°C is low enough so that the effect of such collisions is negligible, but this is not true at 0°C, the temperature used in the experiments to be described. At this temperature a considerable fraction of the atoms excited to the level with $m=0$ are transferred by collisions to the levels with $m=\pm 1$, and the reemitted light is partly depolarized even in the absence of an oscillating field. This depolarization of resonance radiation as a result of inelastic collisions will reduce the magnitude of the signal to be expected when an oscillating field is applied, and will shorten the mean life of an atom in any given excited level. No experimental investigation of these effects was undertaken. It is simply assumed that magnetic relaxation phenomena may affect the two quantities just mentioned, but may otherwise be neglected.

The effects to be expected have been analyzed in considerable detail.[9] A summary of results will be given here. The problem concerns the reorientation of a magnetic dipole with fixed total angular momentum. This situation was analyzed in a very general way by Majorana[10] and by Rabi,[11] who derived the expressions for the required transition probabilities. An angular momentum F in one of its substates m_F is in a rotating field H_1 at right angles to a constant field H_z. Under these conditions the probability of transitions to another state m_F' is considered. For simplicity we shall write the magnetic quantum numbers without the subscript F. Modifications caused by use of linearly oscillating rather than rotating fields have been considered by Bloch and Siegert.[12] These modifications are negligible

TABLE I. Isotopic abundances of the samples of mercury used.

	Percent of isotopes with even mass number	Percent 199	Percent 201
Natural Hg	69.80	17.0	13.2
Enriched Hg^{199}	32.27	62.5	5.23
Enriched Hg^{201}	37.3	4.76	57.9

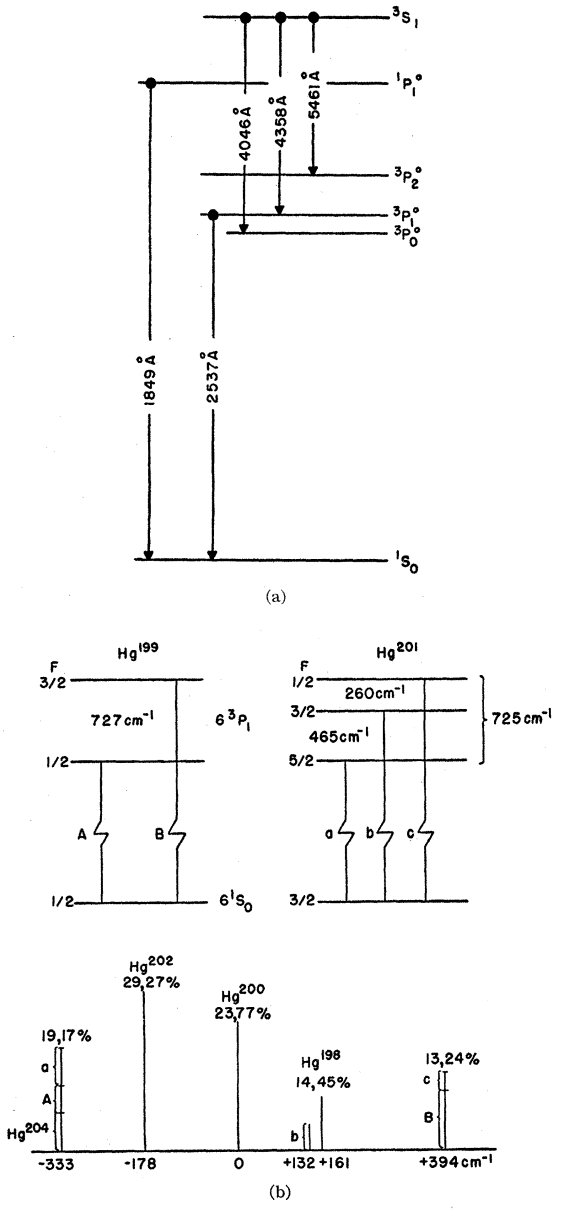


FIG. 1. (a) The low-lying energy levels of mercury; (b) the hyperfine structure of the resonance line.

[8] V. von Keussler, Ann. Physik **82**, 793 (1927).

[9] F. Bitter and J. Brossel, Technical Report No. 176, Research Laboratory of Electronics, M.I.T. (hereafter called simply Technical Report No. 176).

[10] E. Majorana, Nuovo cimento **9**, 43 (1932).

[11] I. I. Rabi, Phys. Rev. **51**, 652 (1932).

[12] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

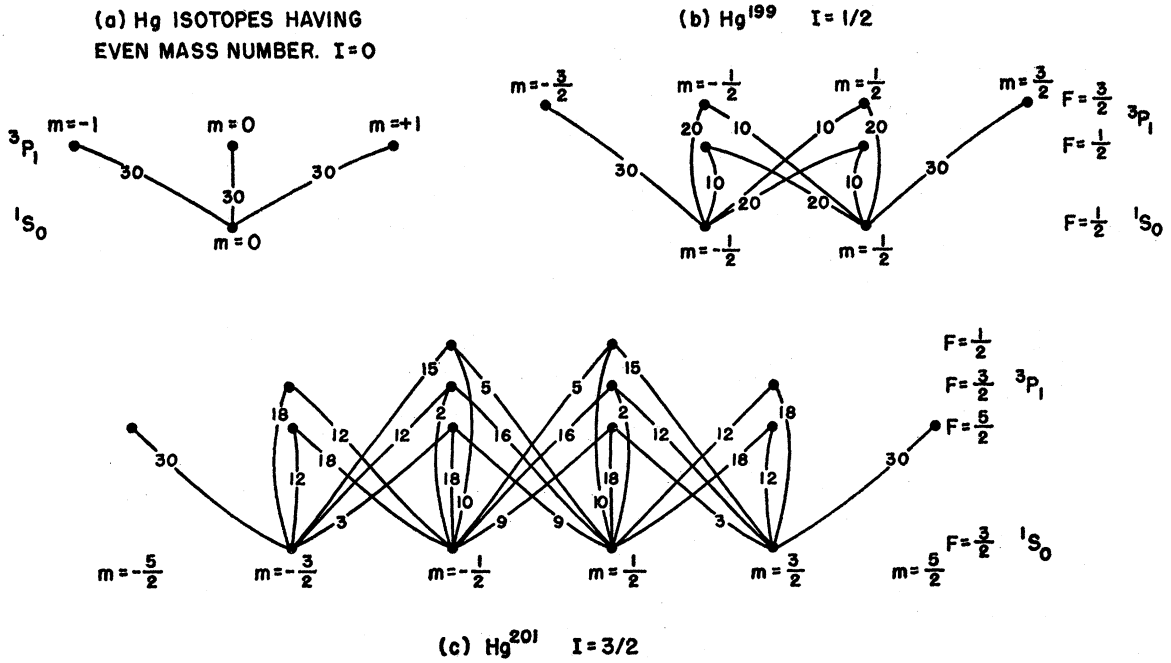


FIG. 2. Transition probabilities for the components of the resonance line of mercury (a) for isotopes and even mass number, (b) for Hg^{199} with $I=1/2$, and (c) for Hg^{201} with $I=3/2$.

for most purposes. We shall return to their discussion further on. For rotating fields Majorana and Rabi derive an expression for the probability that a system of total angular momentum F, known to be in a state m at time $t=0$, shall be in a state m' at some later time t. We designate this transition probability by $P(F, m, m', t)$. It is rigorously derived from the Schroedinger time dependent equation and is not arrived at by perturbation theory. It is therefore valid for large amplitudes of the rotating field and for large values of the time.

Let ω be the frequency, in radians per second, of the rotating field H_1. The gyromagnetic ratio is $\gamma=ge/2Mc$. The Larmor frequency ω_0 in the constant field H_z is given by $\omega_0=\gamma H_z$. The Landé g-factors for the various isotopes of mercury in the $^3P_1$ state in question are given in Table II. The values listed have only a limited validity, since g_J is computed on the assumption of L–S coupling which is surely not rigorously valid for the $^3P_1$ state of mercury. If it were, transitions to the ground state, which is a singlet state, would be forbidden, whereas in fact, the life of the metastable triplet state is of the order of 10^{-7} sec.

We now define an angle, α, by the relation

$$\sin^2\frac{\alpha}{2}=\frac{(\omega/\gamma H_1)^2}{1+[1+(H_z/H_1)]^2}\cdot\frac{(\gamma H_1)^2}{(\gamma H_1)^2+(\omega-\omega_0)^2}\cdot\sin^2\tfrac{1}{2}[(\gamma H_1)^2+(\omega-\omega_0)^2]^{\frac{1}{2}}t. \quad (1)$$

This is a periodic function of the time. The amplitude of this periodic function is shown in Fig. 3. From an inspection of this illustration it is clear that for $H_z/H_1 \gtrsim 10$ the function plotted has a maximum near $\omega=\omega_0$, and Eq. (1) may be written, to a good approximation,

$$\sin^2\frac{\alpha}{2}=\frac{(\gamma H_1)^2}{(\gamma H_1)^2+(\omega-\omega_0)^2}\times\sin^2\tfrac{1}{2}[(\gamma H_1)^2+(\omega-\omega_0)^2]^{\frac{1}{2}}t. \quad (2)$$

In terms of this angle α the required transition probabilities given by the Majorana formula are

$$P(F, m, m', t)=(\cos\tfrac{1}{2}\alpha)^{4F}(F+m)!(F+m')!(F-m)!(F-m')!\times\left[\sum_{n=0}^{2F}\frac{(-1)^n(\tan\frac{1}{2}\alpha)^{2n-m+m'}}{n!(n-m+m')!(F+m-n)!(F-m'-n)!}\right]^2. \quad (3)$$

The simplest case is for $F=1/2$. The aforementioned formula then reduces to

$$P(\tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}, t)=\sin^2\left(\frac{\alpha}{2}\right)=\frac{(\gamma H_1)^2}{(\gamma H_1)^2+(\omega-\omega_0)^2}\times\sin^2\tfrac{1}{2}[(\gamma H_1)^2+(\omega-\omega_0)^2]^{\frac{1}{2}}t.$$

Transitions induced by the oscillating field will take place with appreciable probability in a radiating vapor if the above transition probability has an appreciable value within the lifetime of the excited state. For example, for lifetimes of the order of 10^{-7} sec we must

have γH_1, of the order of 10^7 sec^{-1}, or since $\gamma \sim 10^7$, we must have rotating fields of the order of a gauss.

Effects caused by transitions induced by the rotating magnetic field must now be combined with effects caused by transitions involving optical resonance radiation. We shall describe here procedures to be followed in making the calculations and leave the discussion of specific formulas to later parts of this paper where they will be compared with experimental results.

Let n be the number of optical quanta absorbed per second involving transitions from some one particular magnetic sublevel of the ground state, designated by m_g, to one particular magnetic sublevel of the excited state, designated by the two quantum numbers F and m. The number of atoms excited in an interval of time dt at the time $t=0$ is then ndt. If T_e is the mean life of atoms in the excited state, the number of atoms remaining in the excited state after a time t has elapsed is $ndte^{-t/T_e}$. If the excited atoms were in a rotating magnetic field during the entire time interval t, the number in a sublevel m' of the excited state at the time t is $nP(F, m, m', t)e^{-t/T_e}dt$.

We wish to compute the total number of excited atoms in a vapor in the sublevel m'. We have just derived the number which had been in the excited state for a time between t and $t+dt$. Evidently, the total number may be arrived at by integrating

$$N_{m'}=\int_0^\infty nP(F, m, m', t)e^{-t/T_e}dt. \tag{4}$$

In this expression the excitation rate is obtained from the steady state condition $n=N_m/T_e$, where $N_m \sim A_{m,m_g}N_{m_g}I_0$. The coefficient A_{m,m_g} is the transition probability between an excited sublevel m and a ground state sublevel m_g shown in Fig. 2. N_{m_g} is the number of atoms in the ground state sublevel in question, and I_0 is the intensity of the light used to produce the excitation. The only one of these quantities requiring further discussion is N_{m_g}. For practically realizable intensities of illumination the fraction of the atoms in a vapor which are in an excited state at any instant is very small and may be neglected in comparison with the number in the ground state. Normally thermal relaxation processes insure that the various magnetic sublevels of the ground state are equally populated. The use of polarized resonance radiation may upset this thermal equilibrium, particularly when circularly polarized radiation is used. Such effects are not important in the experiments discussed here, and we shall therefore neglect them in this discussion. For isotopes with even mass number N_{m_g} is simply the total number of such atoms present. For Hg^{199} with a spin of $\frac{1}{2}$ there are two ground-state sublevels, and $N_{m_g}=N_{199}/2$. For Hg^{201} with a spin of $\frac{3}{2}$ there are four sublevels, and $N_{m_g}=N_{201}/4$.

The intensity of the light radiated by atoms which have been excited from m_g to m, transferred from m to m', and which finally decay from m' to m_g' is proportional to

$$N_{m'}A_{m',m_g'}.$$

$N_{m'}$ is given by Eq. (4), and the transition probability A is that shown in Fig. 2. The dependence of the state of polarization of the resonance radiation on the magnitude and frequency of the rotating magnetic field may then be obtained by summing over the various levels involved. In general, in a vapor containing a mixture of isotopes, several optical frequencies will be absorbed and some assumption must be made regarding the structure of the resonance line used [see Fig. 1(b)].

TABLE II. The Landé g-factors for the $^3P_1$ state of the isotopes of mercury computed from the relation

$$g_F=g_J\frac{F(F+1)+J(J+1)-I(I+1)}{2F(F+1)}-g_I\frac{F(F+1)+I(I+1)-J(J+1)}{2F(F+1)}$$

$$g_J=1+\frac{2J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}.$$

Isotopes with even mass number	F	g_F
	1	3/2
Hg^{199}	3/2	$1-1.81\times10^{-4}$
	1/2	$2+1.81\times10^{-4}$
Hg^{201}	5/2	$\frac{3}{5}+1.19\times10^{-4}$
	3/2	$\frac{2}{5}+1.46\times10^{-4}$
	1/2	$-1+3.31\times10^{-4}$

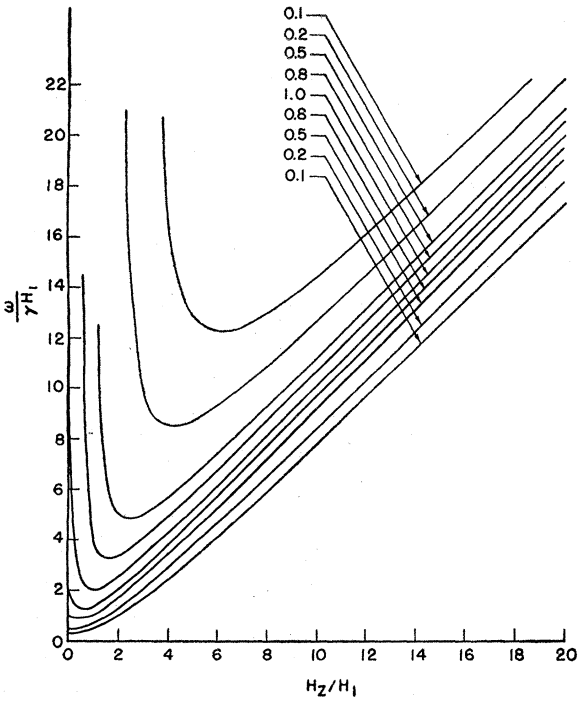


FIG. 3. A contour plot of $(\omega/\gamma H_1)^2/1+[1+(H_z/H_1)]^2\cdot(\gamma H_1)^2/[(\gamma H_1)^2+(\omega-\omega_0)^2]$.

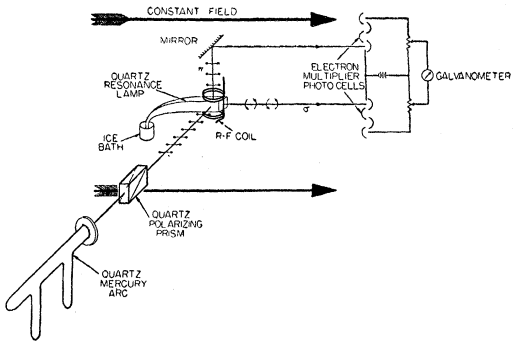


FIG. 4. Diagram of the apparatus.

The simplest assumption is that of "broad line" excitation, and this was used in the detailed calculations of Technical Report No. 176.

The aforementioned transitions refer exclusively to changes in the magnetic quantum number of a rigid rotator with a given total angular momentum F. Observations involving such transitions may be used to determine the gyromagnetic ratio of an atom in a particular state. High frequency magnetic fields may also be used to induce transitions resulting in the reorientation of the nucleus in the field of the electrons. Observations on such transitions give information on the hyperfine structure of a level and may be used to compute nuclear moments. Such transitions, however, are not reported in this paper.

EXPERIMENTAL ARRANGEMENTS

The apparatus used is illustrated in Fig. 4. Light from a low pressure mercury lamp made by Hanovia, operated at 150 ma and cooled with an air blast, is collimated by a quartz lens and polarized by a Glazebrook prism cemented with glycerine. This light is allowed to fall on one of the five mutually perpendicular faces of a fused quartz resonance lamp. The liquid mercury in the tail of the lamp was kept at a temperature of 0°C. The light incident on the lamp was polarized with its electric vector parallel to the constant field H_z. In other words, only the π-component was used for excitation in these experiments. A magnetic field of a few hundred gauss is produced by Helmholtz coils. The σ-component of the resonance radiation may be observed in the direction of this constant field, and both σ- and π-components may be observed at right angles to this field. Around the lamp are a few turns of water-cooled copper tubing forming part of a tuned radiofrequency circuit inductively coupled to a generator capable of supplying up to 100 watts. At maximum rf power the resonance lamp lights up if it is not very well evacuated or if traces of mercury have deposited on the windows of the lamp. The axis of the rf coils is at right angles to the constant field.

In the first experiments attempted, changes were observed in the intensity of the σ-component of the resonance radiation in the direction of the constant field. The intensity of the light emitted by the mercury arc lamp was found to be constant to only about 3 percent, so that small changes in intensity were difficult to measure against this fluctuating background. The sensitivity of the apparatus was greatly improved by the introduction of an optical bridge.[13] Two photomultiplier tubes are used. One of these receives the σ-component in the direction of the field, and the other receives the π-component or the π- and σ-components emitted at right angles to the field. The resistors shown in the illustration are so adjusted that under normal operation no current flows in the galvanometer. This was found to eliminate fluctuations in the galvanometer deflection resulting from fluctuations in the brightness of the light source. When magnetic resonance increases the intensity of the σ-component at the expense of the π-component, the balance of the bridge is upset, and the resulting galvanometer deflection measures directly the quantity desired. The response is linear. Galvanometers with sensitivities up to 10^{-11} amp/mm and periods from 10 to 40 seconds were used. The fluctuation in zero of the galvanometer was about that to be expected due to the IP28 phototubes, but some of this noise may have been caused by spontaneous fluctuations of the polarization of the resonance radiation. Without the optical bridge the random movements of the galvanometer were about 30 times as large.

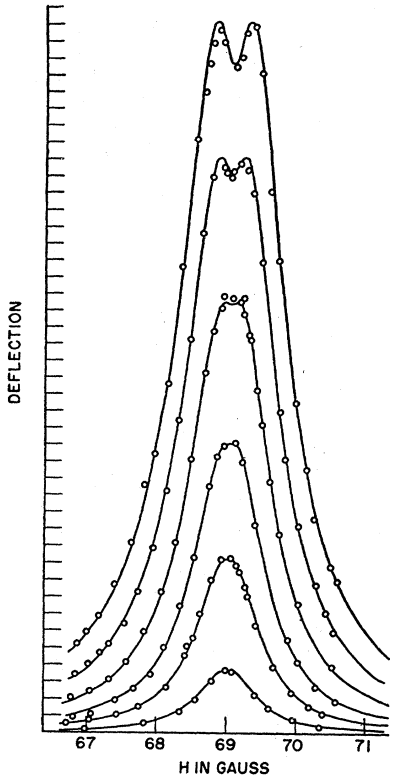


FIG. 5. Resonances observed in isotopes having even mass number and zero nuclear spin.

[13] O. Oldenberg and H. P. Broida, J. Opt. Soc. Am. **40**, 381 (1950).

No measurements were made of the absolute magnitude of the oscillating field. Relative measurements were made by means of a crest voltmeter in an auxiliary inductively coupled circuit and are considered reliable to about 1 percent.

Magnet currents were measured with a Leeds and Northrup Type K_2 potentiometer, with the auxiliary shunt kept at 0°C. Two magnets were used. The first, having a uniformity of only about one part in 10^3 over the volume of the resonance lamp, was used for the determination of line shape and of the mean life of the $^3P_1$ state. The second was uniform to better than one part in 10^4 over the region occupied by the lamp and was used in the determination of the gyromagnetic ratio. This magnet was calibrated by means of proton resonances at 1.6, 0.812, 0.530, and 0.350 Mc/sec. The local earth's field was evaluated by making resonance measurements with the magnet current flowing in both senses through the magnet.

OBSERVATIONS ON ISOTOPES WITH EVEN MASS NUMBER

With the aforementioned apparatus operated at frequencies from 50 to 150 Mc/sec, resonance curves such as are plotted in Fig. 5 are obtained. They show, at one given frequency, galvanometer deflections as a function of the applied constant field for various rf amplitudes. Increasing the rf amplitude produces a stronger and wider line and also produces characteristic changes in the line shape. All of these features, as we shall see, are accounted for by Eq. 4. In Technical Report No. 176 it is shown that for the case in question involving integrals containing $P(1, 0, 1, t)$, the galvanometer deflection should be proportional to a quantity which we call B:

$$B=\frac{I_0}{2}\frac{(\gamma H_1)^2}{(\gamma H_1)^2+(\omega-\omega_0)^2}\left[\frac{(\gamma H_1)^2}{(1/T_e)^2+4(\gamma H_1)^2+(\omega-\omega_0)^2}+\frac{(\omega-\omega_0)^2}{(1/T_e)^2+(\gamma H_1)^2+(\omega-\omega_0)^2}\right]. \quad (5)$$

This represents a bell-shaped curve for values of $\gamma H_1 \ll 1/T_e$, but for $\gamma H_1 \gg 1/T_e$ the curve has two maxima. The separation between these maxima is $\sqrt{2}H_1$, and the ratio of the intensity at maximum to that at resonance is, in the limit for large rf power, 4/3.

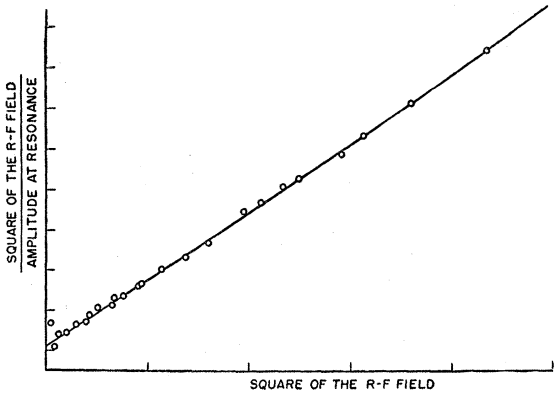
A detailed check of Eq. (5) was undertaken. One finds for the intensity at resonance

$$B_r=k\frac{(\gamma H_1)^2}{4(\gamma H_1)^2+(1/T_e)^2}, \quad (6)$$

where k is an arbitrary constant. In order to check this equation the quantity H_1^2/B_r was plotted as a function of H_1^2 in arbitrary units. The result is shown in Fig. 6(a). It is clear that this aspect of the theory is well borne out by the experiments. In the absence of an absolute determination of H_1, however, it is not possible to deduce T_e from this relation. Another procedure was adopted to determine this quantity. From Eq. (6) it is possible to compute the width of the resonance line $\Delta\omega$ when the amplitude is half its value at resonance, as a function of H_1. For our purposes the complete expression is not important. The first two terms in a power series expansion are

$$\Delta\omega^2=(4/T_e^2)[1+5.8(\gamma H_1 T_e)^2]. \quad (7)$$

The form of this expression is also experimentally verified for the range of rf amplitudes used, as is shown in Fig. 6(b) where the experimental data are plotted in arbitrary units. It is possible, however, to plot this data using the correct units. The half-width of the resonance curve in frequency units may be obtained from the observed half-width in gauss and the known



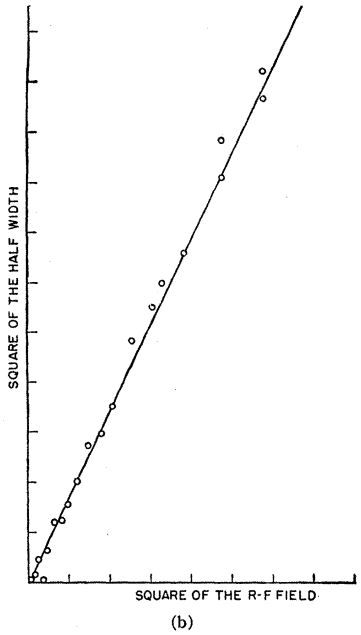


FIG. 6. (a) A plot of Eq. (6); (b) a plot of Eq. (7).

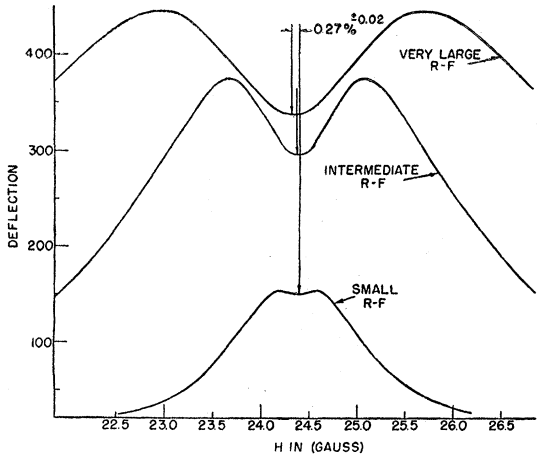


FIG. 7. Experimental verification of the expected shift of the resonant frequency with rf amplitude.

gyromagnetic ratio. The value of $(\gamma H_1 T_e)^2$ for any arbitrary setting of the rf amplitude may be obtained as follows. Calling the ordinate of Fig. 6(a) y, we may write

$$y=\frac{H_1^2}{B_r}=[4(\gamma H_1 T_e)^2+1]/k\gamma^2 T_e^2, \tag{8}$$

and for the value of y when $H_1=0$,

$$y_0=1/k\gamma^2 T_e^2. \tag{9}$$

Combining (8) and (9), we have the measurable dimensionless quantity

$$(y-y_0)/y_0=4(\gamma H_1 T_e)^2, \tag{10}$$

which may be used in plotting Eq. (7). By means of this procedure the value of the numerical coefficient 5.8 was verified, and the mean life of the excited state was obtained by extrapolation to zero amplitude of the rf field. This was done at frequencies of 50, 100, 120, and 144 Mc/sec. The same value was obtained from all these measurements with a total spread of 1 percent. The value obtained in this way for the mean life of the $^3P_1$ state of the even isotopes of Hg is 1.55×10^{-7} sec.[14] The true value may be somewhat longer because the broadening of the line as a result of collisions and field inhomogeneities was not explicitly taken into account. The above value is about 30 percent longer than the previously accepted value, obtained, not too consistently, by conventional optical methods. As we shall report further on, the same value was found for Hg^{199} and Hg^{201} within the experimental error.

The line shape itself, as given by Eq. (5), was then checked in the following way. T_e was given the above value. H_1 was obtained from experimental determinations of $\gamma H_1 T_e$ as aforementioned. The arbitrary constant determining the magnitude of the galvanometer deflection was chosen so that the greatest deflection at resonance coincided with the observed value. The parameters I_0, T_e, and H_1 being determined, a complete plot of Eq. (5) was made. This is shown in the solid curves of Fig. 5. In these curves the parameter $\gamma H_1 T_e$ assumes values up to 0.7. The experimental points corresponding to these curves are also plotted. The agreement seems to be entirely satisfactory and leaves little doubt as to the adequacy of the above theoretical discussion. Observations made at different frequencies proved that the resonant frequency is a linear function of the magnetic field to within one part in 5000.

At 50 Mc a slight shift in the resonance frequency with rf amplitude was observed at large rf amplitudes, as predicted by Bloch and Siegert,[12] when a linearly oscillating rather than a rotating field is used. As shown in Fig. 7, at high rf fields the resonant field for a given frequency is smaller than at low rf fields. The shift is predicted to be proportional to $(H_1/H_z)^2$. This dependence was roughly verified, but the magnitude of the observed shifts was 30 percent greater than the predicted shift. This discrepancy is not considered significant because the equivalent rotating field H_1 was arrived at only indirectly and because the oscillating field was certainly not completely linear, but somewhat elliptical.

The Landé g-factor for the $^3P_1$ state of the isotopes with zero spin was determined by measuring both the frequency and the field required to establish the resonance condition illustrated in Fig. 5. Frequency determinations were made with a Signal Corps BC 221 frequency meter and are considered reliable to one part in 10,000. The field was measured in terms of a proton resonance, so the computation takes the form

$$g=g_{\text{proton}}\times\frac{m}{M}\times\frac{\omega_{\text{Hg}}}{\omega_{\text{proton}}}. \tag{11}$$

Using 5.58501 for the gyromagnetic ratio of the proton[15] and 1836.12 for the ratio of the mass of the proton to

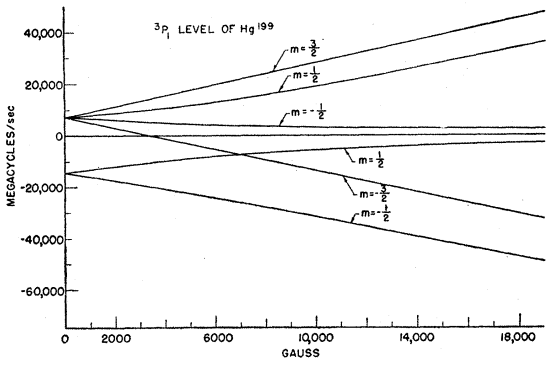


FIG. 8. Zeeman effect of the hyperfine structure of the $^3P_1$ level of Hg^{199}.

[14] J. Brossel, Phys. Rev. **83**, 210 (1951).

[15] Sommer, Thomas, and Hipple, Phys. Rev. **82**, 697 (1951).

that of the electron,[15] we find for the desired g-factor

$$g=1.4838+0.0004. \quad (12)$$

EXPERIMENTS ON Hg^{199} AND Hg^{201}

The 199 isotope with a nuclear spin of 1/2 has two hyperfine structure levels in the $^3P_1$ state with $F=1/2$ and $F=3/2$, as shown in Fig. 8. The use of π-excitation does not lead to any inequality of population of levels with $m=\pm 1/2$ [see Fig. 2(b)]. For this reason excitation to $F=1/2$ and magnetic resonance in this level produces no changes in polarization of the resonance radiation. Magnetic resonance in this level can therefore not be observed. However, magnetic resonance in the level with $F=3/2$ was observed and studied in some detail.

At 144 Mc the decoupling of I and J is sufficient to make the three frequencies $(-3/2\rightarrow -1/2)$, $(-1/2\rightarrow 1/2)$, and $(1/2\rightarrow 3/2)$ slightly different. The Zeeman effect of this case was computed following Inglis[7] and is shown in Fig. 8. The line corresponding to the transition $(-1/2\rightarrow 1/2)$ is not observable with π-excitation because the levels in question are equally populated. The other two transitions are displaced with respect to each other by an amount, in frequency units, equal to (Zeeman separation)^2/hfs separation, or $(150\times 10^6)^2/2\times 10^{10}$. This separation is only a small fraction of the line width, and therefore the two components were not resolved in the fields used.

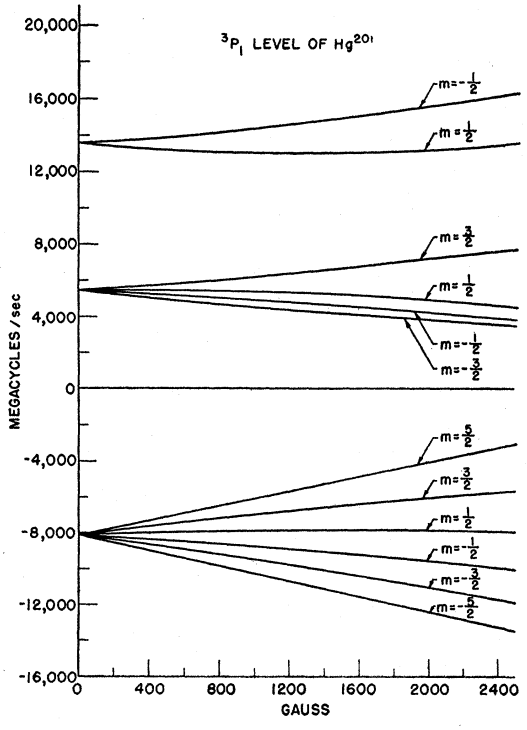


FIG. 9. The Zeeman effect of the hyperfine structure of the $^3P_1$ level of Hg^{201}.

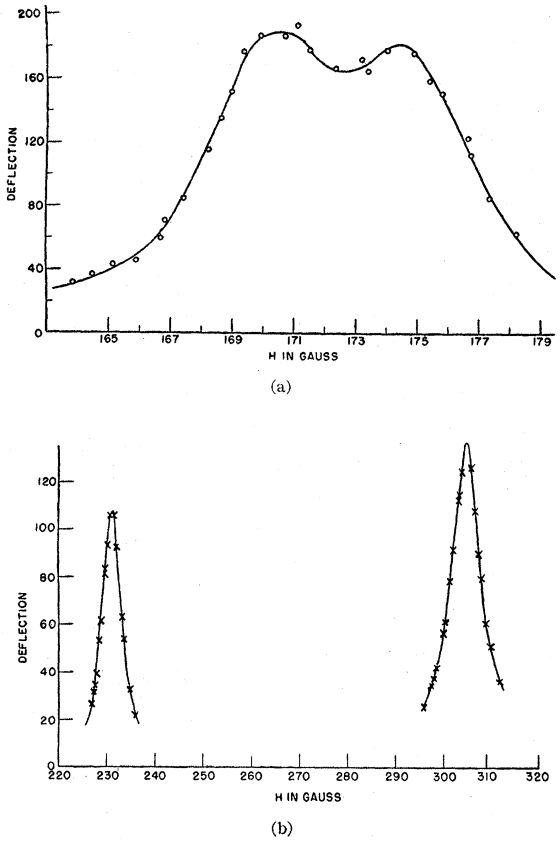


FIG. 10. Resonances observed at 144 Mc in the $^3P_1$ state of Hg^{20} (a) for the level $F=5/2$ and (b) for the level $F=3/2$.

Estimates of the mean life of the excited state of this isotope were made by computing $\gamma H_1 T_e$ for both the even and 199 isotopes [see Eq. (10)]. The ratio of the two values obtained for a fixed value of H_1 should give the ratio of the γ's if the mean life is the same for both isotopes. This was found to be the case at 50, 100, and 144 Mc to within 2 percent.

For the isotope Hg^{201} with a spin of 3/2, resonances were observed in the levels $F=5/2$ and $F=3/2$. Because of the small g-values, high rf field intensities are needed. These resonances are much less marked than those previously described, being only about 5 times the noise level. At frequencies above 50 Mc the decoupling of I and J is considerable, as may be seen from the inequality in spacing of the Zeeman levels in Fig. 9. At 50 Mc very broad resonances were observed for both the $F=3/2$ and $F=5/2$ levels. At 144 Mc the $F=5/2$ resonance shown in Fig. 10(a) was observed. This resonance consists of four unresolved components corresponding to the transitions $(5/2\rightarrow 3/2)$, $(3/2\rightarrow 1/2)$, $(-1/2\rightarrow -3/2)$, and $(-3/2\rightarrow -5/2)$. The resonances in the $F=3/2$ level consist of two well-resolved lines corresponding to the transitions $(3/2\rightarrow 1/2)$ and $(-1/2\rightarrow -3/2)$. The width of these lines agrees to

within 2 percent with that found for the isotopes of even mass number, again indicating that all isotopes have the same mean life in the excited state.

SUMMARY

1. An effective method has been demonstrated for extending rf absorption measurements to the excited states of atoms.

2. The g-factor and the level widths for the $^3P_1$ state of mercury have been studied. These levels could be examined in sufficient detail to establish their center to within 2 percent of the level widths.

3. The method can be extended to measurements of the hyperfine structure.

4. Other promising fields of observation include the Stark effect, the quenching and depolarization of resonance radiation, and in general, problems related to magnetic relaxation phenomena in vapors.

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Effect of the Atomic Core on the Magnetic Hyperfine Structure*

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Equations have been obtained for the magnetic field at the nucleus due to the current induced in the electron core by an external valence electron. The magnetic field is written as $-4\mu_0[\mathbf{j}/(j(j+1))]\langle r^{-3}\rangle_p(1+R_m)$, where $\langle r^{-3}\rangle_p$ is the average over the valence electron function, assumed in a p state, R_m is the correction due to the core, μ_0=Bohr magneton, j=angular momentum. R_m is of importance in obtaining the nuclear quadrupole moment Q from the value of the magnetic moment μ_I and the ratio b/a of the splittings due to Q and μ_I. The electric field gradient at the nucleus, $-\frac{2}{5}e\langle r^{-3}\rangle_p(1+R)$, which determines b, contains a similar term R for the distortion of the core by the valence electron. It is shown that R_m approximately cancels the exchange terms of R, so that the correction factor for Q is that predicted by the Thomas-Fermi model.

I. INTRODUCTION

IN the calculation of the effect of the quadrupole moment induced in the electron shells on the nuclear quadrupole coupling,[1] it was pointed out that the electron core may exert a similar effect on the coupling of the nuclear magnetic moment with the electrons. The closed shells are distorted by the electrostatic interaction with the valence electron. The exchange part of this interaction leads to additional terms in the core density for the electrons with spin parallel to the valence electron spin, which are not present for the electrons with antiparallel spin. Moreover, the density induced by the exchange depends on the magnetic quantum number of the core substate. Both terms in the core density give rise to a magnetic field at the nucleus, and hence to an interaction with the nuclear magnetic moment.

The purpose of this paper is to calculate the magnetic effect and to show that it approximately cancels the exchange terms in the quadrupole coupling correction. Therefore, the correction to nuclear quadrupole moments is essentially that predicted by the Thomas-Fermi model. Values of the correction are given for the nuclei whose Q has been determined.

II. THE MAGNETIC EFFECT

The magnetic splitting is determined by the component along $\mathbf{j}$ (angular momentum of atom) of the magnetic field at the nucleus $\mathbf{H}(0)$:

$$\mathbf{H}(0)\cdot\mathbf{j}=-2\mu_0\left\langle\sum_i\left(\frac{\mathbf{l}_i\cdot\mathbf{j}}{r_i^3}+\frac{3(\mathbf{s}_i\cdot\mathbf{r}_i)(\mathbf{r}_i\cdot\mathbf{j})}{r_i^5}-\frac{\mathbf{s}_i\cdot\mathbf{j}}{r_i^3}\right)\right\rangle, \quad (1)$$

where $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital angular momentum and the spin of the ith electron, whose radius vector is $\mathbf{r}_i$; μ_0=Bohr magneton. The excitation of s states will be considered first. To be specific, we consider the perturbation of $1s$ by the $3p$ electron in Al. The unperturbed wave function of the three electrons for the $^2P_{3/2}$ state with magnetic quantum number $m_j=3/2$ is

$$\Psi=3^{-\frac{1}{2}}[\psi(1,2,3)+\psi(2,3,1)+\psi(3,1,2)], \quad (2)$$

where

$$\psi(1,2,3)=\psi_{1s}(1)\psi_{1s}(2)\psi_{3p,1}(3)\times[2^{-\frac{1}{2}}\{a(1)b(2)-b(1)a(2)\}a(3)]. \quad (2a)$$

Here ψ_{1s} is the $1s$ function, $\psi_{3p,m}$ is the $3p$ function with magnetic quantum number m, $a(i)$ and $b(i)$ are spin functions for the z component of the spin of i, $s_{iz}=1/2$, and $-1/2$, respectively.

To obtain the perturbation of ψ due to exchange, we write the Schrödinger equation

$$\left[-\sum_i\left(\nabla_i^2+\frac{2Z}{r_i}\right)+\sum_{i>j}\frac{2}{r_{ij}}\right]\psi=E\psi, \quad (3)$$

where ∇_i is the gradient for the coordinates of i (in Bohr units a_H), $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$, E is the energy (in Ry units).

* Work done under the auspices of the AEC.
[1] R. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951). The latter paper will be referred to as I.