Optical Pumping Theory and Experiments*

Reuben Benumof

Staten Island Community College, Staten Island, New York

(Received 15 November 1963)

The theory of several experiments involving optical pumping is presented in a simplified form. Vector methods are employed to discuss the hyperfine energy levels of an atom in a weak magnetic field, and, for the purposes of considering relaxation time, the system is assumed to have only two effective levels. The Breit–Rabi equation for the ground-state hyperfine Zeeman energy levels of an alkali atom is derived from the Schrödinger equation to facilitate the interpretation of the quadratic Zeeman effect. A number of suggestions for practical optical pumping experiments are made.

I. INTRODUCTION

THE atoms of a material at a specified temperature are normally distributed among a number of different energy levels. Under ordinary conditions, the higher the energy level, the smaller is the number of atoms in that particular state. Thus, the lowest energy level is populated to the greatest extent. Such a distribution is called thermal. It is possible, of course, to cause the atoms to be distributed differently. When a nonthermal distribution is achieved by using a source of light, the process is called optical pumping.

Experiments in optical pumping are highly instructive. Usually, when working with photon interactions, only energy relations are involved. In the case of optical pumping, however, both the energy and the angular momentum of the photons are of importance. The experiments afford one an opportunity to integrate knowledge of optics, simple electronics, and atomic physics.

There are several objectives of this paper. The first is to describe quantitatively the main features of optical pumping without making full use of quantum mechanics. Vector methods are employed to discuss the hyperfine energy levels of an atom in a weak magnetic field, and a simplified treatment of relaxation time is given. In this way, students who have not yet gained competence in the handling of the Schrödinger equation are nevertheless able to do much of the work with understanding. A second objective of this paper is to discuss both single and multiple quantum induced transitions. This is of interest in connection with comprehending absorption or emission of radiation from a system with a nonthermal population. A third objective is to present a quantum mechanical treatment of the ground state of a one electron atom in a form suitable for senior students. This becomes important when effects caused by magnetic fields that are not extremely weak are studied. First approximations, such as the vector model, are then no longer adequate. A fourth and final objective is to give detailed suggestions for experiments involving the techniques of optical pumping.

II. VECTOR MODEL OF THE HYPERFINE ENERGY LEVELS OF AN ATOM

The resultant angular momentum $\mathbf{F}$ of an atom may be viewed as being the vector sum of the total angular momentum $\mathbf{J}$ of the electrons and the angular momentum $\mathbf{I}$ of the nucleus. The total angular momentum $\mathbf{J}$ of the electrons is the vector sum of the spin angular momentum $\mathbf{S}$ of the electrons and the orbital angular momentum $\mathbf{L}$ of the electrons. These vectors are shown in Fig. 1. The vector $\mathbf{B}$ denotes the magnetic flux density of an impressed magnetic field.

Since the electrons and the nucleus are electrically charged, a magnetic moment is associated with each angular momentum. We have

$$\mathbf{\mu}_S = -g_S(e/2m)\mathbf{S}, \tag{1}$$

$$\mathbf{\mu}_L = -g_L(e/2m)\mathbf{L}, \tag{2}$$

$$\mathbf{\mu}_J = -g_J(e/2m)\mathbf{J}, \tag{3}$$

$$\mathbf{\mu}_I = g_I(e/2m)\mathbf{I}, \tag{4}$$

$$\mathbf{\mu}_F = -g_F(e/2m)\mathbf{F}, \tag{5}$$

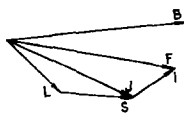where the $\mathbf{\mu}$'s are the magnetic moments, the g's

151

FIG. 1. The angular momentum vectors of an atom.

are the Landé factors, and e/m is the ratio of charge to mass for an electron. The reader may observe that, since the charge of an electron is negative, all of the μ's are negative except μ_I which pertains to the nucleus. The magnetic moment μ_I may be either positive or negative. The value of g_I is of the order of 1/1836, the ratio of the mass of an electron to that of a proton. By experiment, it has been found that

$$g_S = 2.00232, \qquad (6)$$

and that

$$g_L = 1.0. \qquad (7)$$

Clearly, the values of g_J and g_F need to be derived.

By use of the vector model diagrammed in Fig. 1, it may be easily shown[1] that

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \qquad (8)$$

If the vectors, **J**, **I**, and **F**, are treated in a manner similar to the vectors, **S**, **L**, and **J**, the result is[2]

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}, \qquad (9)$$

where the term involving g_I has been neglected.

In a weak magnetic field **B**, the potential energy E of an atom having a magnetic moment μ_F is

$$E = -\mu_F \cdot \mathbf{B}. \qquad (10)$$

In moderately strong fields, the last equation must be modified. The magnetic field, under such circumstances, interacts individually with the moments μ_J and μ_I and not with the resultant moment μ_F. This is discussed in Sec. VII. Returning to the consideration of the energy in a weak field, if the value of μ_F given in Eq. 5

[1] G. P. Harnwell and W. E. Stephens, *Atomic Physics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 164.

[2] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 374.

is substituted, we have

$$E = g_F(e/2m)\mathbf{F} \cdot \mathbf{B}.$$

The z axis is taken parallel to **B**, and, hence, the z component of **F** is $\hbar m_F$, where m_F is the quantum number corresponding to the projection of **F** on the z axis. Thus,

$$E = g_F(e\hbar/2m)Bm_F. \qquad (11)$$

The quantity $e\hbar/2m$ is known as the Bohr magneton, and its value is $0.9273(10^{-23})$J·m²/Wb. Equation 11 specifies the Zeeman splitting of the hyperfine levels.

The energy levels of a one electron atom with $I = \frac{3}{2}$, for example, ^{87}Rb, may be depicted as shown in Fig. 2. The notation $^2S_{\frac{1}{2}}$ for the ground state implies that the electron spin quantum number S is $\frac{1}{2}$, the orbital angular momentum quantum number is zero, and the total electron angular momentum quantum number J is $\frac{1}{2}$. The values of F in this state are, therefore, $\frac{3}{2} + \frac{1}{2} = 2$ and $\frac{3}{2} - \frac{1}{2} = 1$. For $F = 2$, $g_F = \frac{1}{2}$, and, for $F = 1$, $g_F = -\frac{1}{2}$. From Eq. 11, we can see that, for $g_F = \frac{1}{2}$, increasing values of m_F yields higher energy levels whereas for $g_F = -\frac{1}{2}$, decreasing values of m_F yields higher energy levels.

A similar situation holds for the $^2P_{\frac{1}{2}}$ state, the first-excited state. In this case, $S = \frac{1}{2}$, $L = 1$, $J = 1 - \frac{1}{2} = \frac{1}{2}$, and $F = \frac{3}{2} \pm \frac{1}{2}$. Here, $g_J = \frac{2}{3}$ and $g_F = \pm \frac{1}{6}$. As can be seen from Eq. 11, the energy differences between adjacent hyperfine Zeeman levels are smaller for the $^2P_{\frac{1}{2}}$ state than for the $^2S_{\frac{1}{2}}$ state.
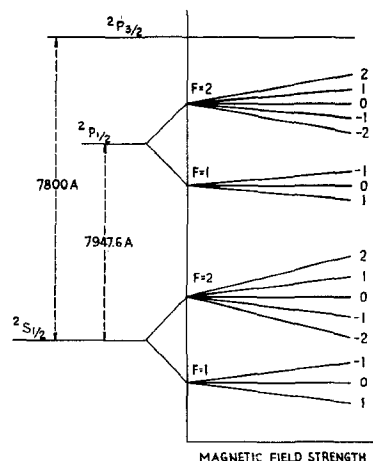

FIG. 2. A diagram of the energy levels of Rubidium 87 ($I = \frac{3}{2}$).

For ^{85}Rb, $I=\frac{5}{2}$. Therefore, for the $^2S_{\frac{1}{2}}$ and $^2P_{\frac{1}{2}}$ states, the values of F are 3 and 2. In the ground state, $g_F=\pm\frac{1}{3}$. By referring to Eq. 11, we can see that the energy differences arising from a transition $\Delta m_F=1$ would be only $\frac{2}{3}$ as great for ^{85}Rb as for ^{87}Rb.

III. OPTICAL PUMPING

When light of wavelength 7947.6 Å obtained from a Varian rubidium vapor lamp is incident on a rubidium 87 vapor cell, some atoms are raised to the $^2P_{\frac{1}{2}}$ state (see Fig. 2). If the light is circularly polarized, the photons have an angular momentum of one unit (expressed in terms of h). The circularly polarized light is denoted as σ^+ if the photons convey positive angular momentum relative to the direction of the magnetic field **B**, and the light is denoted as σ^- if the photons convey negative angular momentum. Thus, right circularly polarized light parallel to **B** is σ^+ and right circularly polarized light antiparallel to **B** is σ^-. Linearly polarized light conveys no angular momentum and is called π light. The point of this discussion is that, if a σ^+ photon is absorbed, the quantum number m_F must increase by 1. Evidently, atoms in all the ground-state sublevels can absorb σ^+ photons except the atoms in the $+2$ state since there is no $+3$ state in the $^2P_{\frac{1}{2}}$ energy level. No change in the quantum number m_F occurs when a π photon is absorbed, and the quantum number m_F decreases by 1 when a σ^- photon is absorbed.

An atom in an excited state emits radiation spontaneously. The emitted photon may be σ^+, σ^-, or π. Thus, atoms tend to return to all the ground state sublevels from the various excited sublevels. This is particularly true in view of the fact that the $^2P_{\frac{1}{2}}$ sublevels tend to be more or less equally populated as a result of collisions.

If σ^+ pumping light is used, then, eventually, because of continual absorption and subsequent reemission of photons, atoms will collect in the $m_F=+2$ ground state, where they are "trapped." In time, the population of the $+2$ ground state sublevel becomes greater than that of the others. Thus, a nonthermal distribution may be a-chieved. The entire process is called optical pumping.

When the pumping with σ^+ light begins, the intensity of the light transmitted through the
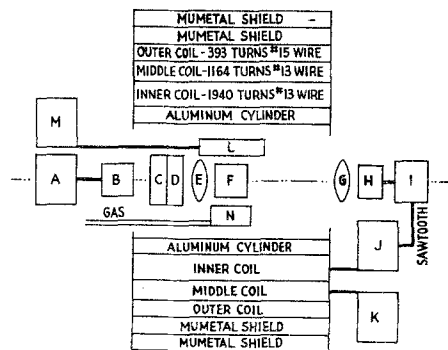

Fig. 3. A diagram of an optical pumping arrangement. A—300 V dc source, B—Varian Associates rubidium vapor lamp, C—interference filter, D—circular polarizer, E—convex lens, F—rubidium vapor cell, G—convex lens, H—917 photocell connected to battery and 1-MΩ resistor, I—Tektronix 531 oscilloscope with type E plug-in pre-amplifier, J—3000-Ω resistor, K—regulated dc power supply, L—two 20-turn coils, M—signal generator, N—gas flame.

rubidium vapor cell is low. Even though photons are emitted after being absorbed, the emission is not necessarily in the forward direction. Linearly polarized (π) light is certainly emitted at right angles to the initial direction of propagation. Also, atoms may return to the ground state by making nonradiative transitions as a result of collisions with buffer gas atoms, other rubidium atoms, and cell-wall atoms. To sum up, the absorption is not compensated by equal forward emission.

When the population of the $m_F=+2$ ground state is a maximum, the transparency of the rubidium vapor cell is much higher than initially. Nevertheless, some absorption of the 7947.6 Å incident light still occurs. As a result of collisions with other atoms, some atoms in the $m_F=+2$ ground state are continually dropping into lower energy states. Clearly, some energy must be abstracted from the incident light to maintain the pumped state. A similar explanation may be given if σ^- light is used.

IV. THE EXPERIMENTAL ARRANGEMENT

The experimental arrangement of apparatus is diagrammed in Fig. 3. A highly uniform magnetic field can be provided by means of solenoidal windings on an aluminum cylinder having an inner diameter of 9 in. and a length of 30 in. As shown in Fig. 3, all transverse magnetic fields may be excluded by surrounding
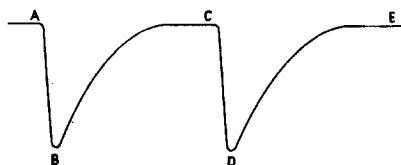
FIG. 4. The oscilloscope trace for two
passages through zero field.

the cylinder with two mumetal shields. Another
method of canceling transverse fields is to use two
pairs of Helmholtz coils.

The innermost coil (1940 turns) on the
aluminum cylinder is a five-layer winding, the
1164-turn coil is a three-layer winding, and the
outer coil is a single-layer winding. In use, a
sawtooth voltage from a model 531 Tektronix
oscilloscope is impressed on the 1940-turn coil
through a 3000-Ω resistor, and a steady current
from a regulated 30-V power supply is passed
through the 1164-turn coil. The larger coil is
used for the sawtooth because the current
obtained from the oscilloscope is comparatively
small. The single layer coil is not used in the
present experiment.

A convenient source lamp (labeled B in Fig. 3)
is the Varian Associates rubidium vapor lamp.
This lamp is easily energized by a 300-V dc
power supply (A). The emitted light which
consists of essentially parallel rays passes through
an interference filter (labeled C) capable of
transmitting light of wavelength 7950 Å. The
light is then circularly polarized by means of a
polaroid sheet and a quarter wave plate (D).
The convex lens (E) focuses the light on the
rubidium vapor cell (F). The convex lens (G),
in turn, focuses the light on a shielded 917
photocell (H) which is connected to a battery
and a 1-MΩ resistor. A Tektronix type E plug-in
preamplifier (I) is connected across the 1-MΩ
resistor.

The rubidium vapor cell contains a little bit
of rubidium metal and an inert gas (neon or
krypton) having a pressure of approximately 3
cm of mercury. The purpose of the inert gas is
to prevent diffusion of the pumped rubidium
atoms out of the path of the light beam. Since
the melting point of rubidium is 38.5°C, the cell
must be heated (preferably by a gas or candle
flame to avoid distorting the magnetic field).

The optimum working temperature for rubidium
87 is approximately 55°C whereas the optimum
temperature for rubidium 85 is approximately
42°C.

A transverse radio-frequency magnetic field
may be provided by surrounding the cell with a
pair of 20-turn Helmholtz coils (L) having a
vertical axis. These coils are connected to a
signal generator (M) capable of operating in the
range 300 k/sec to 30 Mc/sec. If desired, an
axial radio-frequency field may be provided in a
similar manner.

V. RELAXATION TIME

The oriented atoms in a pumped rubidium
vapor cell tend to become disoriented mainly
because of collisions with the glass wall. A
measure of the importance of disorienting
collisions is the time required for a fully pumped
isolated cell to become completely disoriented.
This interval is called the relaxation time. It
may be approximated very well by observing
the oscilloscope trace formed as the cell proceeds
from the completely disoriented state to the
fully pumped state using a minimum light
intensity. In the following explanation, for
simplicity the cell will be assumed to contain
only rubidium 87 vapor.

Experimentally, a sawtooth voltage (sweep
rate 50 msec/cm) from the oscilloscope is im-
pressed on the 1940-turn coil and an *opposing*
steady field is provided by a small current in the
proper direction in the 1164-turn coil. The saw-
tooth field and the steady field exactly cancel
each other twice during each cycle, once during
the steady rise of the sawtooth and once during
the flyback of the sawtooth. An oscilloscope
trace of the form shown in Fig. 4 is obtained.

It is very interesting to analyze the form of this
trace. The section AB represents the sharp drop
in the intensity of the transmitted light resulting
from the disorientation of the atoms in the fully
pumped cell during the flyback of the oscilloscope
sweep (which is in phase with the sawtooth
voltage connected to the 1940-turn winding).
If the magnetic field were perfectly uniform, the
curve AB would be a vertical line. At some time
during the interval AB, the field caused by the
sawtooth exactly cancels the field due to the

1164-turn winding, and, then, as shown in Fig. 2, the various m_F sublevels coalesce into two hyperfine levels. If the field is not perfectly uniform, different parts of the cell become disoriented at different times. As soon as a field is established, the pumping process begins. The curve BC represents the rise in light intensity as the cell approaches the fully pumped state. The curve CD is similar to AB except that it occurs during the steady rise of the sawtooth. The position of CD may be controlled by adjusting the current in the 1164–turn coil. It is best to have CD near the center of the screen, which means that zero field occurs at the center of the sawtooth. Since the sawtooth may not be perfectly sharp, distortions may arise if the disorientation period is too near the beginning or the end of the sawtooth. The curve DE is similar to BC. It represents the rise in intensity as the cell approaches the fully pumped state.

The problem that remains is to explain the form of the curve BC or DE. We consider the change in the population of the $m_F = +2$ ground state of ^{87}Rb relative to the other sublevels. In effect, we assume that the pumping process consists essentially of raising atoms indiscriminately from all the other ground states to the $m_F = +2$ ground state. The following equations may therefore be written

$$dn/dt = -nW_d + NW_u, \quad dN/dt = -NW_u + nW_d,$$

where n is the population of the $+2$ ground state, N the total population of the other ground states, $W_d dt$ the probability of a downward transition from the $m_F = +2$ state due to disorienting collisions, and $W_u dt$ the probability of an upward transition to the $m_F = +2$ ground state (of ^{87}Rb). At $t = 0$, $n = n_0$ and $N = N_0$. Therefore,

$$n = n_0 + C_1[1 - e^{-(W_u + W_d)t}],$$

$$N = N_0 + C_2[1 - e^{-(W_u + W_d)t}].$$

Since

$$dn/dt = -nW_d + NW_u,$$

we must have

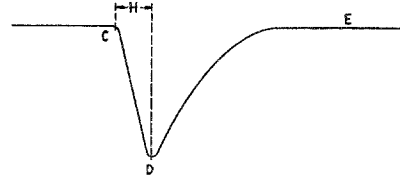$$C_1 = \frac{N_0 W_u - n_0 W_d}{W_u + W_d} = -C_2.$$

FIG. 5. A typical resonance resulting from the application of an rf field having a frequency given by Eq. (13).

Therefore

$$n = n_0 + \frac{N_0 W_u - n_0 W_d}{W_u + W_d}[1 - e^{-(W_u + W_d)t}],$$

$$N = N_0 - \frac{N_0 W_u - n_0 W_d}{W_u + W_d}[1 - e^{-(W_u + W_d)t}].$$

The intensity I of the transmitted light is a function of the number of excess atoms in the $+2$ ground state. As a first approximation, we may write

$$I = I_0 + \alpha(n - n_0),$$

where α is a constant and I_0 is the intensity at $t = 0$. Therefore,

$$I = I_0 + \alpha \frac{N_0 W_u - n_0 W_d}{W_u + W_d}[1 - e^{-(W_u + W_d)t}],$$

$$I = I_\infty - \alpha \frac{N_0 W_u - n_0 W_d}{W_u + W_d} e^{-(W_u + W_d)t}, \quad (12)$$

where I_∞ is the intensity when the cell is fully pumped.

Equation 12 is in qualitative agreement with the observed results. At $t = 0$, when the atoms are completely disoriented, I is a minimum. Thereafter, as the pumping proceeds, I increases exponentially. If the intensity of the light is reduced, I_0 becomes more and more nearly equal to I_∞. This means that $N_0 W_\mu$ approaches $n_0 W_d$. For ^{87}Rb, n_0/N_0 is of the order of 1/7. By measuring successive oscilloscope traces, it is possible to find an upper limit for $(n_0/N_0 + 1)W_d$. The time $\tau = 1/W_d$ is a measure of the rate at which the fully pumped cell would become disoriented when completely isolated.

It is interesting to note that, if the passage through zero magnetic field is too rapid, the atoms will not have time to become disoriented. As a result of the rapid reversal of the field, an

atom originally in a -2 state is found in a $+2$ state. The component of angular momentum parallel to the magnetic field simply changes sign. Also, in a sense, the pumping light is reversed. Right circularly polarized light which was originally σ^- light becomes σ^+ light after the field is reversed. Thus, if the cell was fully pumped with the atoms in the -2 state, the cell remains fully pumped with the atoms in the $+2$ state since the pumping light "reverses" and maintains the orientation of the atoms. This conclusion is easily verified by observing the oscilloscope trace when the sweep rate is increased.

VI. INDUCED TRANSITIONS

If the current in the 1164-turn winding is increased, the portion CDE of the oscilloscope trace shown in Fig. 4 may be moved further and further to the right. Eventually, the magnitude of the sawtooth field is too small in comparison to the steady field to produce zero total field. It is still possible, however, to disorient the atoms. If an alternating magnetic field of the proper (resonant) frequency *normal to the axial field* is applied by means of a signal generator connected to L in Fig. 3, an oscilloscope trace of the form shown in Fig. 5 is observed. To obtain this trace, *it is essential to have the sawtooth field superposed* on the constant axial field. As the total axial field passes through the proper value to produce resonance, the trace shown in Fig. 5 is seen.

It is very interesting to study the curve CDE. The section CD clearly represents the disorientation resulting from the alternating field. If the axial field were perfectly uniform throughout the cell and if the frequency of the alternating field were absolutely constant, the line CD would be vertical. A measure of the nonuniformities is the half width H. This is usually specified by stating the change in frequency required to shift the oscilloscope trace a distance equal to H in Fig. 5. The shape of the remainder of the curve, the portion DE, is explained on the same basis as the portion DE in Fig. 4. It represents the rise in intensity as the cell returns to the fully pumped state.

An important question is why an alternating field can disorient the atoms. The answer involves the fact that the alternating magnetic field constitutes a time dependent perturbation. The difference in energy between two adjacent hyperfine Zeeman levels is

$$\Delta E = g_F (eh/2m) B.$$

In terms of frequency,

$$\Delta E = h\nu,$$

and

$$\nu = g_F (e/4\pi m) B. \tag{13}$$

If the frequency of the oscillating magnetic field is equal to that given in Eq. 13, there will either be absorption or stimulated emission of photons. If the $m_F = +2$ ground state is overpopulated, for example, stimulated emission will predominate and the levels will become equally populated. A good discussion of the problem as it arises in magnetic resonance experiments is given by G. E. Pake.[3] The oscillating field should be at right angles to the axial field so that a maximum torque is exerted on the atoms.

In the situation just described, the conditions for conservation of energy and momentum are met by the emission or absorption of a single photon. Through the use of higher (than first) order time-dependent perturbation theory,[4] it is possible to show that when the perturbation is of the form

$$-\mathbf{\mu} \cdot \mathbf{B}_1 \cos 2\pi \nu_1 t - \mathbf{\mu} \cdot \mathbf{B} \cos 2\pi \nu_2 t,$$

the resonance condition is

$$p\nu_1 \pm q\nu_2 = g_F (e/4\pi m) B = \nu, \tag{14}$$

where p and q are integers.

Equation 14 indicates that it is possible to have two or more photons participate in a transition from one sublevel to another. Physically, this means that the energy of all the photons must be taken into account when conservation of energy is considered but only an odd number of photons can possibly be effective in transferring the resultant single unit of momentum to an electron. To realize these conditions experimentally, an axial oscillating field is used as well as a transverse oscillating

[3] G. E. Pake, *Paramagnetic Resonance* (W. A. Benjamin, Inc., New York, 1962), pp. 30–33.
[4] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., pp. 201–205.

field. Much work has been done on this aspect of optical pumping by A. Kastler.[5]

VII. QUANTUM MECHANICAL SOLUTION FOR THE GROUND STATE OF ALKALI ATOMS

In Sec. II, where the vector model of an atom was discussed, mention was made of the fact that, in moderately strong fields, the moments $\mathbf{u}_J$ and $\mathbf{u}_I$ interact individually with the magnetic field **B**. In other words, the moments $\mathbf{u}_J$ and $\mathbf{u}_I$ become uncoupled, and the vectors **J** and **I** process around **B** rather than around **F**. Under such circumstances, the magnetic energy of an atom is given by

$$E = -\mathbf{u}_J \cdot \mathbf{B} - \mathbf{u}_I \cdot \mathbf{B} + \eta \mathbf{I} \cdot \mathbf{J}, \qquad (15)$$

where η is a constant. The last term represents the magnetic interaction between the nucleus and the electrons. Since the z axis is parallel to **B**, we have, on the basis of the vector model

$$E = g_J \left(\frac{e\hbar}{2m}\right) B m_J - g_I \left(\frac{e\hbar}{2m}\right) B m_I$$
$$+ \eta(m_J m_I \hbar^2 + \cdots), \qquad (16)$$

where $m_J m_I \hbar^2$ corresponds to $J_z I_z$ and the terms corresponding to $J_x I_x$ and $J_y I_y$ have been neglected on the presumption that, when the magnetic field is strong enough, only the term $J_z I_z$ is important. Unfortunately, magnetic field strengths are usually not sufficiently high to permit neglecting $J_x I_x$ and $J_y I_y$, and a quantum mechanical solution must be sought.

The Hamiltonian operator H_0 for a single electron having a charge $-e$ is

$$H_0 = -(\hbar^2/2m)\nabla^2 - Ze^2/4\pi\epsilon_0 r,$$

where Ze is the charge fixed at the origin of the coordinates, r, θ, ϕ. The energy eigenfunctions are defined by the equation

$$H_0\psi = E\psi. \qquad (17)$$

When Eq. 17 is solved, the result is

$$\psi_{nlm_l} = N_{nlm_l} R_{nl}(r) P_l^{m_l}(\cos\theta) e^{\pm im_l\phi}, \qquad (18)$$

where N_{nlm_l} is a normalizing factor. If the electron has spin and it is desired to include this fact in the description of the energy eigenstates, then Eq. (18) must be modified as follows:

$$\psi_{nlm_l m_s} = N_{nlm_l m_s} R_{nl}(r) P_l^{m_l}(\cos\theta)$$
$$\times e^{\pm im_l\phi} S_{\pm\frac{1}{2}}(\sigma_z), \qquad (19)$$

where $S_{\pm\frac{1}{2}}$ are the two spin eigenfunctions of the spin variable σ_z. Equation 19 is valid only if there is no interaction involving the coordinate σ_z and the other coordinates, r, θ, ϕ. Since $S_{\pm\frac{1}{2}}(\sigma_z)$ is independent of r, θ, ϕ, the function $\psi_{nlm_l m_s}$ satisfies Eq. 17 and the inclusion of the function $S_{\pm\frac{1}{2}}(\sigma_z)$ does not affect the eigenvalues.

The energy eigenstates of an alkali atom may be described by functions similar to those given by Eq. (19) except that, here, the function $R_{nl}(r)$ may be more complicated than in the case of a simple central force field. If nuclear spin is, for the moment, disregarded, the atom may be in either one of the two *ground* states specified by

$$\psi_{100\pm\frac{1}{2}} = N_{100\pm\frac{1}{2}} R_{10}(r) S_{\pm\frac{1}{2}}(\sigma_z).$$

To include the nuclear spin I in the description of the ground states, we may write

$$\psi_{100\pm\frac{1}{2}Im_I} = NR_{10} S_{\pm\frac{1}{2}} Y_I^{m_I}, \qquad (20)$$

where $Y_I^{m_I}$ is an angular-momentum eigenfunction of the nuclear spin coordinates only. The function $Y_I^{m_I}$ is unspecified except that it obeys the commutation rules for angular momentum.[6] Solely as an outcome of these rules, the following relations must hold:

$$I_z Y_I^{m_I} = m_I \hbar Y_I^{m_I}, \qquad (21)$$

$$(I_x \pm iI_y) Y_I^{m_I} = \hbar(I \pm m_I + 1)^{\frac{1}{2}}(I \mp m_I) Y_I^{m_I \pm 1}, \qquad (22)$$

where I_x, I_y, and I_z are the operators corresponding to the three components of nuclear angular momentum. The electron spin functions also obey the angular-momentum commutation rules and, consequently, relations that are special cases of Eqs. 21 and 22 are valid, namely,

$$J_z S_{\pm\frac{1}{2}} = \pm\frac{1}{2}\hbar S_{\pm\frac{1}{2}}, \qquad (21a)$$

$$(J_x \pm iJ_y) S_{\mp\frac{1}{2}} = \hbar S_{\pm\frac{1}{2}}, \qquad (22a)$$

where J_x, J_y, and J_z are the operators correspond-

[5] A. Kastler, "Different Types of Multiple Quantum Transitions," The Ann Arbor Conference on Optical Pumping (June, 1959).

[6] E. Feenberg and G. E. Pake, *Notes on the Quantum Theory of Angular Momentum* (Stanford University Press, Stanford, California, 1953), pp. 10–28.
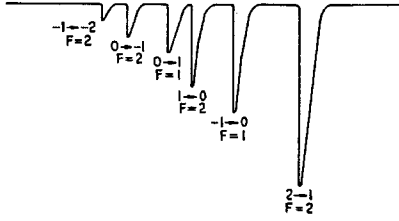
FIG. 6. At sufficiently high-magnetic field strengths, there are six separate resonances resulting from six different transitions.

ing to the three components of electron angular momentum (spin).

The eigenfunctions specified by Eq. 20 satisfy

$$H_0\psi = E_{1I}\psi, \tag{23}$$

where E_{1I} is the ground-state energy of an atom having nuclear spin I. The Hamiltonian H_0 does not take into account the interaction between the electron spin and the nuclear angular momentum and does not include the interaction between an external magnetic field $\mathbf{B}$ and the moments $\mathbf{\mu}_J$ and $\mathbf{\mu}_I$. To do so, we must add the operator H' to H_0 and write the eigenvalue equation as follows:

$$(H_0 + H')\psi = E\psi, \tag{24}$$

where

$$H' = \eta \mathbf{I} \cdot \mathbf{J} - \mathbf{\mu}_J \cdot \mathbf{B} - \mathbf{\mu}_I \cdot \mathbf{B}$$
$$= \eta[I_z J_z + \tfrac{1}{2}(I_x + iI_y)(J_x - iJ_y)$$
$$+ \tfrac{1}{2}(I_x - iI_y)(J_x + iJ_y)] + g_J(e/2m)J_z B$$
$$- g_I(e/2m)I_z B.$$

The quantity η is a proportionality constant. To satisfy Eq. 24, a linear combination of the functions given by Eq. 20 is used. Thus,

$$\psi = \sum_{m_I} R_{10} Y_I{}^{m_I}(a_{m_I} S_{\frac{1}{2}} + b_{m_I} S_{-\frac{1}{2}}). \tag{25}$$

Equation 25 is an approximation in that only ground-state electronic functions have been utilized. The summation may conceivably contain other electronic state functions.

The basic problem is to determine the various eigenvalues denoted by E in Eq. 24. The first step is to combine Eqs. 23 and 24. We obtain

$$H'\psi = (E - E_{1I})\psi. \tag{26}$$

Next, ψ as given in Eq. 25 is substituted in Eq. 26. The coefficients of like functions on both

sides of Eq. 26 are now equated. The result is a number of pairs of equations such as the following:

$$\left[E_{1I} - E - \frac{\eta(m_I + 1)\hbar^2}{2} - \frac{g_J\epsilon}{2} - g_I\epsilon(m_I + 1) \right] b_{m_I+1}$$
$$+ \eta\frac{\hbar^2}{2}(I + m_I + 1)^{\frac{1}{2}}(I - m_I)a_{m_I} = 0,$$

$$\eta\frac{\hbar^2}{2}(I - m_I)^{\frac{1}{2}}(I + m_I + 1)^{\frac{1}{2}}b_{m_I+1}$$

$$- \left[E_{1I} - E + \eta\frac{\hbar^2}{2}m_I + \frac{g_J\epsilon}{2} - g_I\epsilon m_I \right]a_{m_I} = 0,$$

where $\epsilon = (e\hbar/2m)B = 0.9273(10^{-23})B$. In order for these equations to be compatible, the value of E must be

$$E = E_{1I} - \frac{\Delta}{2(2I+1)} - \epsilon g_I m_F$$

$$\pm \frac{\Delta}{2}\left(1 + \frac{4m_F w}{2I+1} + w^2 \right)^{\frac{1}{2}}, \tag{27}$$

where

$$\Delta = \eta\hbar^2(I + \tfrac{1}{2}), \ w = (g_J + g_I)\epsilon/\Delta, \text{ and } m_F = m_I \pm \tfrac{1}{2}.$$

The physical meaning of Δ can be ascertained by setting B equal to zero. In this case

$$E = E_{1I} - \Delta/2(2I+1) \pm \tfrac{1}{2}\Delta. \tag{28}$$

The difference between the two energy levels given in Eq. (28) is Δ. Evidently, Δ is the hyperfine spacing between the levels $F = 2$ and $F = 1$ (refer to Fig. 2) at zero magnetic field. In terms of frequency, the value of Δ for ^{85}Rb is 3036 Mc/sec for ^{87}Rb, $\Delta = 6834.7$ Mc/sec and, for ^{133}Cs, $\Delta = 9192.6$ Mc/sec.

The frequency ν of the transition between the levels m_F and m_{F-1} may be found by expanding the last term on the right of Eq. (27) and finding the energy difference $\Delta E = h\nu$. The result is

$$h\nu = -\epsilon g_I \pm \frac{\Delta}{2}\left[\frac{2w}{2I+1} + \frac{2w^2(1 - 2m_F)}{(2I+1)^2} - \frac{w^3}{2I+1} \right.$$
$$\left. + \frac{4(3m_F{}^2 - 3m_F + 1)w^3}{(2I+1)^3} \right]. \tag{29}$$

If w is very small, and g_I is neglected,

$$\nu = g_J eB/(2I+1)(4\pi m), \tag{30}$$

Equation 30 is the same as Eq. (13) since $F = I + \frac{1}{2}$ in Eq. 9.

At field strengths of the order of 30 G (1.5 A in the 1164-turn coil), an oscillating field of frequency 21 Mc will produce resonance for the isotope ^{87}Rb. The oscilloscope trace appears as shown in Fig. 6. Evidently, there is not one but six closely grouped resonances resulting from the six transitions indicated in the diagram. This splitting of the resonance is known as the quadratic Zeeman effect. The maximum difference in frequency is the frequency difference between the transitions $2 \rightarrow 1$, $F=2$, and $-1 \rightarrow -2$, $F=2$. For the first transition, the value of m_F in Eq. 29 is 2, and, for the second transition, $m_F = -1$. The difference in frequency between these two transitions can be calculated theoretically from Eq. 29. The result is

$$|\Delta\nu| = 6\bar{\nu}^2/\Delta', \tag{31}$$

where $\bar{\nu}$ is the average resonant frequency and Δ' is the hyperfine energy separation expressed as a frequency. Clearly, the value of Δ' may be found from Eq. 31 (which happens to be correct to fourth order) if $\Delta\nu$ and $\bar{\nu}$ have been measured. With reasonable care, the error in this procedure may be limited to approximately 3% or less.

VIII. SUGGESTIONS FOR EXPERIMENTS

Six relatively simple experiments are described below.

1. Relaxation Time

An oscilloscope trace such as that shown in Fig. 4 should be obtained. The sawtooth voltage from the oscilloscope should be connected to the 1940-turn coil, and a very small current from the regulated dc power supply should be sent through the 1164-turn coil so that zero magnetic field will occur at the center of the screen. The well depth should be approximately 15 mV and the sweep rate should be 50 msec/cm. It is advisable to heat the cell to 65°C and, then, to allow it to cool to the operating range of 55–60°C. Under no circumstances, should the current through the Varian rubidium lamp exceed 26

mA. An estimate of the relaxation time can be obtained from the rising portion of the oscilloscope trace as the pumping light intensity is reduced.

2. Half Width

If the current in the 1164-turn coil is gradually increased, the relaxation pattern will occur nearer and nearer one end of the sawtooth. Eventually, the pattern moves off screen since the sawtooth is no longer able to produce zero magnetic field. If a signal of frequency approximately 1400 k/sec is now applied to the coils marked L in Fig. 3, an oscilloscope trace similar to that shown in Fig. 5 will be obtained for a current in the 1164-turn coil of 0.1 A. The half width may be measured by noting the change in frequency required to shift the pattern the distance H in Fig. 5.

3. Identification of Isotopes

If the current through the 1164-turn coil is increased, the signal frequency must also be increased to produce resonance. In essence, the value of B in Eq. 13 is increased, and the value of ν is subsequently adjusted to satisfy Eq. 13. The sawtooth current in the 1940-turn coil causes the axial magnetic field to fluctuate slightly at the oscilloscope sweep rate. Equation 13 is satisfied once during the steady rise in each sawtooth cycle. The flux density B' at the center of the solenoid due to the steady current in the 1164-turn coil is

$$B' = \mu_0 Ni/[(L^2+D^2)^{\frac{1}{2}}],$$

where $N=1164$, $L=0.74$ m, and $D=0.23$ m. It is advisable to plot ν versus B'. The intercept on the B' axis is the residual axial field (mainly due to the sawtooth), and the slope of the curve is $g_F(e/4\pi m)$. The value of I can thus be determined, and the particular isotope of rubidium responsible for the resonance may be identified.

4. Hyperfine Energy Level Differences

When the current in the 1164-turn coil is 1.5 A, the magnetic field is strong enough to permit observation of the quadratic Zeeman effect shown in Fig. 6. By measuring the difference

in frequency between the two extreme reso-
nances, a value for the hyperfine spacing between
the two F-levels may be calculated from Eq. 31.

5. Multiple Quantum Transitions

To verify Eq. 14, two signal generators are
needed. One provides a transverse oscillating
field, and the other provides an axial oscillating
field. An additional pair of coils, not shown in
Fig. 3, must be installed. A single quantum
resonant frequency ν far from other resonances
should be selected first. Then, two frequencies,
ν_1 and ν_2, should be used, where $\nu = \nu_1 \pm \nu_2$.
Resonance should be attained for widely varying
values of ν_1 and ν_2.

6. Spin Exchange

If the alkali vapor cell contains cesium 133
($I = \frac{7}{2}$) in addition to rubidium, it may be possible
to observe resonances that are characteristic of
cesium. The cesium atoms may be oriented
through collisions with oriented rubidium atoms.

Such collisions are called spin exchange collisions.
At the proper frequency, the cesium atoms are
disoriented, and resonance may be observed.

GENERAL REFERENCES

1. T. R. Carver, "Optical pumping," Science
141, 599 (August 16, 1963).
2. R. L. de Zafra, "Optical pumping," Am. J.
Phys. **28**, 648 (1960).
3. A. L. Bloom, "Optical pumping," Sci. Am.
(October, 1960).
4. N. F. Ramsey, *Molecular Beams* (Oxford
University, Clarendon Press, 1956).