

OPTICAL PUMPING

An Introduction

ROBERT BERNHEIM

The Pennsylvania State University

W. A. BENJAMIN, INC.
New York

1965
Amsterdam

Preface

In recent years the words "optical pumping" have been used more and more often, generally in connection with the operation of lasers and masers. However, the concept of optical pumping and the techniques involved have a more general applicability and have been responsible for the success of a large number of fundamental and aesthetically beautiful experiments. Because of this and because it has become evident that an increasing diversity of problems can be investigated with optical pumping, a general survey of the subject seems desirable.

This book contains an elementary discussion of optical pumping techniques and theory suitable for physicists and chemists who wish an introduction to the subject. The first sections of the book describe what optical pumping is and what basic phenomena are involved in an optical pumping experiment. The latter sections of the book are concerned with the application of optical pumping to the investigation of the energy levels of atoms and molecules and with the effect of intermolecular interactions on these energy levels. Most of the discussion is directed at the optical pumping of gases; however, a chapter is included on optical pumping in solids. The emphasis is on the investigation of energy levels, and the application of optical pumping to lasers and masers is only briefly mentioned.

It is not intended that this be an exhaustive review but more a discussion of elementary principles. It is hoped that the inclusion of reprints and a rather complete bibliography will add to the usefulness of this volume.

The author wishes to express his appreciation to the many authors and to the journals for permission to reprint the articles which appear in the last part of this book. Unfortunately, space does not permit the reprinting of all the works that are appropriate for a volume of this sort. As a result, many papers which played important roles in the development of optical pumping could not be included. Likewise, many papers which give the latest experimental and theoretical results do not appear. The articles which are reprinted represent a diverse selection in that some are an extended development of the topics treated in the preceding pages, others contain some thought-provoking ideas on data, while still others represent some of the milestones in the history of optical pumping. The reader will have his own list of favorite papers on this subject, but it is hoped that he will find some of them included here.

ROBERT BERNHEIM

University Park, Pennsylvania
July 1965

Contents

Preface	v
1 Introduction	1
1-1 What Is Optical Pumping?	1
1-2 The Early Experiments in Optical Pumping	1
1-3 Applications of Optical Pumping	2
2 The Optical Pumping Experiment	4
2-1 A Simple Example	4
2-2 Magnetic Resonances	7
2-3 A More General Example	8
3 The Dynamics of Optical Pumping	10
3-1 Pumping and Relaxation in Ground States	10
3-2 Orientation and Alignment	12
3-3 Optical Pumping of Excited States	14
4 Optical Resonance Radiation	18
4-1 Resonance Fluorescence and Line Fluorescence	18
4-2 Absorption of Optical Resonance Radiation	20
4-3 Broadening of Optical Resonance Lines	21
4-4 Self-reversal	22
5 Magnetic Interactions: Zeeman and Hyperfine Splitting	24
5-1 The Hamiltonian	24
5-2 Energy Levels in Weak, Strong, and Intermediate Magnetic Fields	25
5-3 Determination of Hyperfine Constants, g-Factors, and Nuclear Spins by Optical Pumping	26
6 Electric Interactions: Nuclear Electric Quadrupole and Stark Splitting	29
6-1 Nuclear Electric Quadrupole Coupling Constants	29
6-2 Electric Field Gradients in Atoms	30
6-3 Determination of Nuclear Electric Quadrupole Moments	30

6-4	Energy Levels	31
6-5	Stark Effect	32
7	Magnetic Resonance Detection	34
7-1	The Magnetic Resonance Condition	34
7-2	Optical Detection of Magnetic Resonances	36
7-3	Transmitted Radiation through Vapor Cells	37
7-4	Scattered Radiation from Vapor Cells; Change in Polarization	37
7-5	Scattered Radiation from Vapor Cells; Change in Frequency and Selective Reabsorption	37
7-6	Crossed Light Beams	38
7-7	Modulation of Optical Pumping Light	39
7-8	Spin-Exchange Method	39
7-9	Scattered Radiation from Atomic Beams	39
7-10	Deflection of Optically Pumped Atomic Beams	40
7-11	The Bloch-Siegert Shift	40
8	Phenomenological Description of Oriented Systems	42
8-1	Orientation As a Bulk Magnetization	42
8-2	Equations of Motion with Optical Pumping	43
9	Energy Level Crossing Experiments	47
9-1	Principle of the Experiment	47
9-2	Applications	49
10	Spin Exchange	50
10-1	Magnetic Resonance Detection by Spin Exchange	50
10-2	Mechanism for Spin Exchange	52
11	Pressure Shift of the Hyperfine Interaction	54
11-1	Origin of the Pressure Shift	54
11-2	Experimental Results	55
11-3	Theoretical Calculations of the Pressure Shift	56
12	Spin-Relaxation Times	58
12-1	Measurement of Spin-Relaxation Times	58
12-2	Diffusion Coefficients and Spin-Disorientation Cross Sections	59
12-3	The Spin-Relaxation Mechanism	60
12-4	Spin-Disorientation in Molecular Buffer Gases	61
12-5	Spin-Disorientation in Electric Dipolar Buffer Gases	61
13	Chemical Applications of Optical Pumping	63
13-1	Atomic Structure	63
13-2	Intermolecular Interactions	64

CONTENTS

ix

13-3 Chemical Kinetics	64
13-4 Molecular Structure	66
14 Optical Pumping in Solids	68
14-1 Fluorescence in Solids	68
14-2 Optical Detection of Magnetic Resonances in Solids	69
14-3 Application to Masers	70
Bibliography	71

Reprints

1. J. Brossel and A. Kastler, La Détection de la Résonance Magnétique des Niveaux Excités: L'effet de Dépolarisation des Radiations de Résonance Optique et de Fluorescence, *Compt. Rend.* **229**, 1213-1215 (1949) 87
2. A. Kastler, Quelques Suggestions concernant la Production Optique et la Détection Optique d'une Inégalité de Population des Niveaux de Quantification Spatiale des Atomes. Application à l'Expérience de Stern et Gerlach et à la Résonance Magnétique, *J. Phys. Radium* **11**, 255-265 (1950) 90
3. A. Kastler, Optical Methods of Atomic Orientation and of Magnetic Resonance, *J. Opt. Soc. Am.* **47**, 460-465 (1957) 101
4. J. Brossel and F. Bitter, A New 'Double Resonance' Method for Investigating Atomic Energy Levels. Application to Hg $^3P_1$, *Phys. Rev.* **86**, 308-316 (1952) 107
5. W. B. Hawkins, Orientation and Alignment of Sodium Atoms by Means of Polarized Resonance Radiation, *Phys. Rev.* **98**, 478-486 (1955) 116
6. W. Franzen and A. G. Emslie, Atomic Orientation by Optical Pumping, *Phys. Rev.* **108**, 1453-1458 (1957) 125
7. R. H. Dicke, The Effect of Collisions upon the Doppler Width of Spectral Lines, *Phys. Rev.* **89**, 472-473 (1953) 131
8. H. G. Dehmelt, Modulation of a Light Beam by Precessing Absorbing Atoms, *Phys. Rev.* **105**, 1924-1925 (1957) 133
9. W. E. Bell and A. L. Bloom, Optical Detection of Magnetic Resonance in Alkali Metal Vapor, *Phys. Rev.* **107**, 1559-1565 (1957) 135
10. J. N. Dodd and G. W. Series, Theory of Modulation of Light in a Double Resonance Experiment, *Proc. Roy. Soc. (London) Ser. A* **263**, 353-370 (1961) 142

11. P. A. Franken, Interference Effects in the Resonance Fluorescence of 'Crossed' Excited Atomic States, *Phys. Rev.* **121**, 508-512 (1961) 161
12. P. Thaddeus and R. Novick, Optical Detection of Level Crossing in the (5s 5p) $^3P_1$ State of Cd¹¹¹ and Cd¹¹³, *Phys. Rev.* **126**, 1774-1780 (1962) 166
13. E. M. Purcell and G. B. Field, Influence of Collisions upon Population of Hyperfine States in Hydrogen, *Astrophys. J.* **124**, 542-549 (1956) 173
14. H. G. Dehmelt, Spin Resonance of Free Electrons Polarized by Exchange Collisions, *Phys. Rev.* **109**, 381-385 (1958) 181
15. L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., Hyperfine Structure of Hydrogen, Deuterium, and Tritium, *Phys. Rev.* **120**, 1279-1289 (1960) 186
16. P. L. Bender, Effect of Hydrogen-Hydrogen Exchange Collisions, *Phys. Rev.* **132**, 2154-2158 (1963) 197
17. L. C. Balling and F. M. Pipkin, Spin Exchange in a Cesium-Electron System, *Phys. Rev.* **136**, A46-A53 (1964) 202
18. R. Herman, Theory of Spin Exchange between Optically Pumped Rubidium and Foreign Gas Nuclei, *Phys. Rev.* **137**, A1062-A1065 (1965) 210
19. M. Arditi and T. R. Carver, Pressure, Light, and Temperature Shifts in Optical Detection of 0-0 Hyperfine Resonance of Alkali Metals, *Phys. Rev.* **124**, 800-809 (1961) 214
20. G. A. Clarke, Effects of Helium Buffer Gas Atoms on the Atomic Hydrogen Hyperfine Frequency, *J. Chem. Phys.* **36**, 2211-2216 (1962) 224
21. H. G. Dehmelt, Slow Spin Relaxation of Optically Polarized Sodium Atoms, *Phys. Rev.* **105**, 1487-1489 (1957) 230
22. W. Franzen, Spin Relaxation of Optically Aligned Rubidium Vapor, *Phys. Rev.* **115**, 850-856 (1959) 233
23. A. L. Bloom, Spin Relaxation and Line Width in Alkali Metal Vapors, *Phys. Rev.* **118**, 664-667 (1960) 240
24. R. A. Bernheim, Spin Relaxation in Optical Pumping, *J. Chem. Phys.* **36**, 135-140 (1962) 244
25. R. J. McNeal, Disorientation Cross Sections in Optical Pumping, *J. Chem. Phys.* **37**, 2726-2727 (1962) 250
26. R. J. McNeal, R. A. Bernheim, R. Bersohn, and M. Dorfman, Optical Pumping and Chemical Reactions, *J. Chem. Phys.* **40**, 1678-1683 (1964) 252
27. H. G. Dehmelt and K. B. Jefferts, Alignment of the H₂⁺ Molecular Ion by

CONTENTS

xi

Selective Photodissociation. I., <i>Phys. Rev.</i> 125 , 1318–1322 (1962)	258
28. F. Varsanyi, D. L. Wood, and A. L. Schawlow, Self Absorption and Trapping of Sharp-Line Resonance Radiation in Ruby, <i>Phys. Rev. Letters</i> 3 , 544–545 (1959)	263
29. S. Geschwind, R. J. Collins, and A. L. Schawlow, Optical Detection of Paramagnetic Resonance in an Excited State of Cr^{3+} in Al_2O_3 , <i>Phys. Rev. Letters</i> 3 , 545–548 (1959)	264
30. J. Brosel, S. Geschwind, and A. L. Schawlow, Optical Detection of Paramagnetic Resonance in Crystals at Low Temperature, <i>Phys. Rev. Letters</i> 3 , 548–549 (1959)	267
31. N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Observation of a Photon Echo, <i>Phys. Rev. Letters</i> 13 , 567–568 (1964)	269
Index	271

1/ Introduction

1-1 WHAT IS OPTICAL PUMPING?

By "optical pumping" we mean the use of light to produce a population of a set of energy levels of a system which is different from the normal Boltzmann distribution at the temperature of the experiment. The energy levels in question might be magnetic energy levels of an atom in which case the optical pumping would refer to either the orientation or the alignment of the atoms by the light beam. On the other hand, the levels might be electronic states which are to be populated in order to establish conditions for laser action. We should like to begin our discussion with atoms and atomic resonance fluorescence as used for the optical pumping of angular momentum substates. Once this process has been explained, various applications will be discussed.

1-2 THE EARLY EXPERIMENTS IN OPTICAL PUMPING

Since a certain amount of the discussion involves the detection of radio-frequency resonances by using the optical resonance transitions of atoms, it might be appropriate to begin our introduction to optical pumping with mention of the first workers to observe the effect of a radiofrequency field upon atomic optical resonance radiation. There were E. Fermi and F. Rasetti (1925 a, b) and G. Breit and A. Ellett (1925) who observed the change in polarization of the resonance fluorescence of mercury vapor upon change in frequency of an applied alternating magnetic field. From such experiments the

g-factor and lifetime of the excited state could be determined (Mitchell, 1934, p. 271).

In the following years a great deal of experimental work was done with atomic fluorescence. The reader is referred to two excellent books which describe the early theory and the extensive experimental work (Mitchell, 1934; Pringsheim, 1949).

In the late nineteen forties microwave and radiofrequency spectroscopy began to capture the attention of the physicist and chemist. Magnetic resonance, which had been detected in atomic and molecular beams, had been detected in bulk material; molecular rotational transitions and nuclear electric quadrupole interactions were being observed in the microwave spectra of the vapors of various compounds. These new types of experiments produced many advances in the elucidation of atomic and molecular structure. Another motivation for work in these areas was the desire to be able to determine nuclear spins and moments which, at that time, were two of the few quantities that could be obtained experimentally and which could be used in a discussion of nuclear structure. Most of this work in microwave and radiofrequency spectroscopy was directed at measurements upon the ground electronic states of atoms and molecules.

In 1949 Bitter called attention to the possibility of the optical detection of a radiofrequency resonance. However, the particular detection scheme he proposed was shown to be impractical (Pryce, 1950). Also, Brossel and Kastler, (1949; Kastler, 1950; see reprints) proposed a scheme for the optical orientation of atoms and discussed different ways of detecting the orientation. Successful optical pumping experiments were carried out on the $^3P_1$ state of the mercury isotopes by Brossel and Bitter (1952a) and on the ground state of Na^{23} by Brossel, Kastler, and Winter (1952c) and by Hawkins and Dicke (1953).

1-3 APPLICATIONS OF OPTICAL PUMPING

In the years following these early experiments the principles of optical pumping led to valuable developments, both practical and theoretical. Among the practical devices resulting from these concepts have been the development of various types of frequency standards, the maser, the optical maser (laser), and very sensitive magnetometers, to name a few. The contributions to fundamental knowledge are numerous and include the determination of nuclear spins, magnetic moments, and nuclear electric quadrupole moments; very accurate measurements of the electron magnetic moment and a determination of an upper limit to the electric dipole moment of the electron; the determination of nuclear hyperfine interactions and their "pressure shifts"; the determination of hyperfine interactions and g-factors for excited states of atoms; and the determination of diffusion constants, disorientation cross sections, and spin-exchange cross sections for atomic collisions.

As the field developed, experimental techniques were refined, and new effects were observed. The transmission technique of detecting magnetic resonances in the ground state of alkali metal vapors was introduced (Dehmelt, 1957 a, b,

1958 a, b). Energy level crossing techniques were introduced (Franken, 1958b); the energy shift caused by the intensity of the pumping radiation was considered theoretically (Barrat, 1960) and measured experimentally (Cohen-Tannoudji, 1961 a, b, c); optical masers were proposed (Schawlow, 1958) and made to work (Maiman, 1961); and optical harmonic generation has been accomplished (Franken, 1961b).

In the following pages the fundamental concepts of some of these experiments will be described. However, the emphasis will be on those experiments that yield information about the energy levels of the ground and excited states of the systems considered.

2 / The Optical Pumping Experiment

2-1 A SIMPLE EXAMPLE

In order to describe the optical pumping process, we shall first make a few simplifying assumptions which will later be removed. In this example, we shall consider an alkali metal atom which has a $^2S_{1/2}$ ground state and $^2P_{1/2}$ and $^2P_{3/2}$ excited states. The optical transitions between the ground state and these two excited states give rise to the D_1 and D_2 lines, respectively, of alkali metal atomic spectra. For some cases, the D_2 line can be removed from a source of light by means of an interference filter. We shall assume this to be the case for our example.

If an alkali metal atom is placed in a magnetic field H_0 , and if the nuclear spin is neglected, the energy levels of the atom pertinent to D_1 spectral lines will be as shown in Figure 2-1. The spin magnetic moment of the valence electron will interact with the magnetic field with energy:

$$E = g\beta H_0 m_s \quad (2-1)$$

where g is the Lande g -factor, β is the Bohr magneton, and m_s is the magnetic quantum number of the atomic state, having a value of $\pm \frac{1}{2}$ for this example.

Next, consider the experimental arrangement shown schematically in Figure 2-2 and which is typical of one method, originally introduced by Dehmelt (1957a), of optically pumping alkali metal atoms. The vapor cell, usually made from a 250-ml flask, is illuminated by a spectral lamp which emits the D_1, D_2 resonance doublet

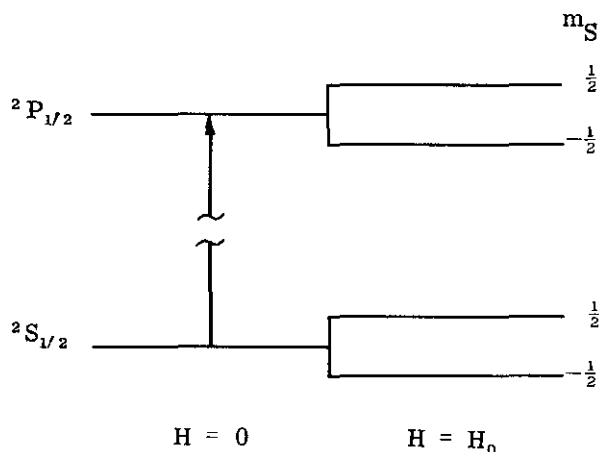


Figure 2-1 Energy levels of a hypothetical atom with a $^2S_{1/2}$ ground state and a $^2P_{1/2}$ excited state.

of the alkali metal atom being studied. The light is collimated or focused with lenses through an interference filter where the D_2 component is attenuated, and through a circular polarizer. The D_1 light then passes through the vapor cell which contains the vapor of the alkali metal species. The cell is usually heated to a temperature that will result in an alkali metal vapor pressure in the region

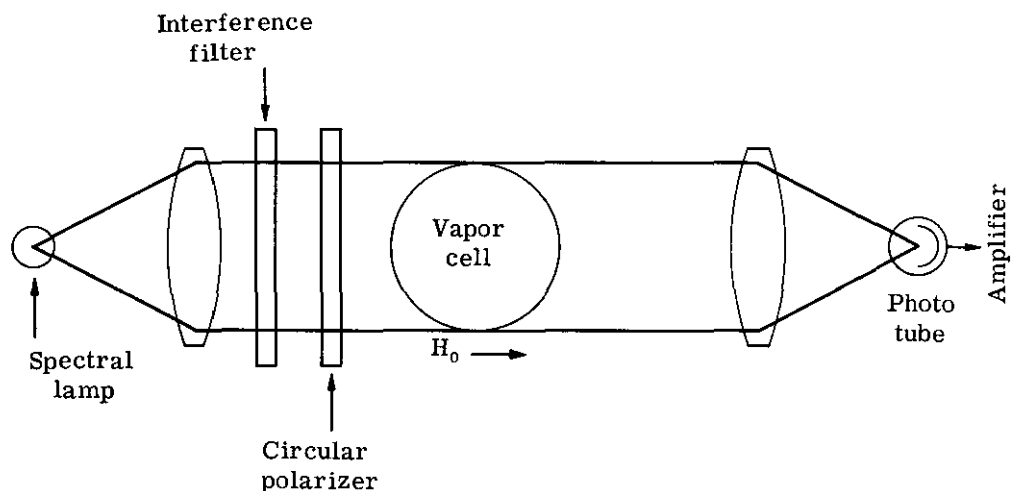


Figure 2-2 Schematic of an optical pumping apparatus that uses transmission detection.

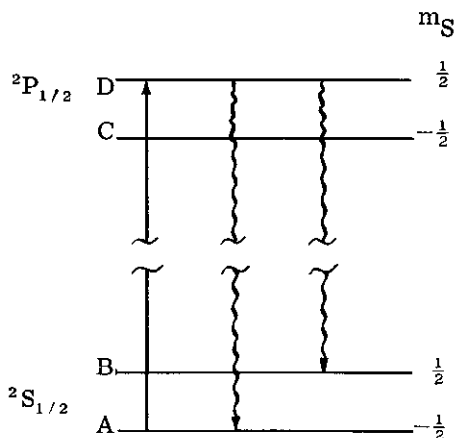


Figure 2-3 Absorption with $\Delta m_S = +1$ and spontaneous emission.

of 10^{-5} mm Hg. Typical operating temperatures are 25°C for Cs, 45°C for Rb, 85°C for K, and 150°C for Na. The vapor cell is placed in a weak magnetic field, H_0 , which is directed along the direction of the light path. The intensity of the D_1 resonance radiation passing through the apparatus can be measured with the photo tube.

What is the effect of the circularly polarized D_1 radiation upon the atoms in the vapor cell with the above experimental arrangement? The well-known result is that the atoms will be excited to the $^2P_{1/2}$ state with a selection rule of $\Delta m_S = \pm 1$. Furthermore, the selection rule will be either $\Delta m_S = +1$ or $\Delta m_S = -1$ but not both. Which one holds will depend upon the direction of the magnetic field with respect to the direction of propagation of the light and the direction of circular polarization. If the electric vector of the light portrays a right-handed helix, the light is said to be right circularly polarized. This type of circularly polarized light is given the notation σ^+ if it produces $\Delta m_S = +1$ transitions.

Inspection of Figure 2-1 reveals that there is only one possible excitation that can take place; this is shown in Figure 2-3. Excitation with $\Delta m_S = +1$ can occur only from energy level A to energy level D. The lifetimes of the $^2P_{1/2}$ states of alkali metal atoms are typically of the order of 10^{-8} sec. If we assume that no disorientation occurs in the excited state of the atom (i.e., that state C is not populated) the atom will fluoresce from state D to states A and B with equal transition probability. For an assembly of atoms the net effect in time will be a transfer of population from state A to state B.

Before the pumping radiation is turned on, the relative populations of states A and B are given by the Boltzmann distribution:

$$\frac{n_B}{n_A} = \exp[-(E_B - E_A)/kT]$$

which in a typical case gives an excess of about 1 part in 10^6 in state A over state B at room temperature for weak magnetic fields. After the pumping radiation is turned on $n_B \gg n_A$, and the final relative population will be determined by such parameters as the pumping light intensity, relative transition probabilities, and the relaxation time. A concentration of atoms in state B corresponds to a net orientation of the angular momentum of the atoms. The process described above is one example of optical pumping, the pumping being a transfer of atoms from one energy level to another.

2-2 MAGNETIC RESONANCES

The intensity of light passing through the apparatus in Figure 2-2 will be a function of the amount of orientation of the atoms in the vapor cell. If 100% of the atoms were optically pumped into state B the alkali metal vapor would no longer be able to absorb the D_1 radiation, and the bulb would become transparent. When states A and B are occupied according to their normal Boltzmann distribution, the vapor will absorb the circularly polarized resonance radiation, and the vapor cell will become opaque to the pumping radiation. Thus, one can detect the amount of orientation by simply observing the intensity of D_1 light passing through the apparatus.

If an oscillating magnetic field is applied perpendicular to H_0 and if the frequency of the oscillating field is

$$\nu_0 = \frac{g\beta H_0}{h} \quad (2-3)$$

i.e., the Larmor frequency of the alkali atom, transitions between states A and B can take place. This frequency will fall in the radiofrequency region if H_0 is of the order of 1 gauss. If the radiofrequency radiation is very intense the occupations of states A and B are equalized and the systems of spin energy levels are said to be saturated.

Since the application of the radiofrequency field causes the population of state A to increase, more D_1 resonance radiation will be absorbed, and the bulb will appear to be opaque. If the frequency of the oscillating field is varied and the intensity of D_1 light passing through the apparatus monitored, one will observe the intensity vs. frequency dependence as shown in Figure 2-4. An absorption

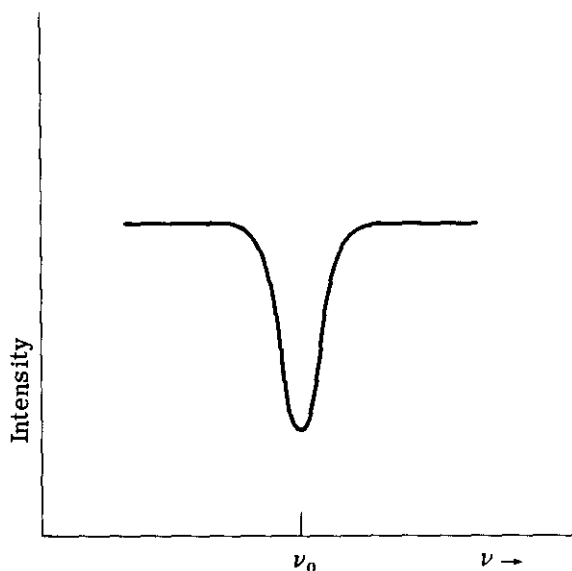


Figure 2-4 Magnetic resonance observed in the intensity of light transmitted through the optical pumping apparatus.

of light corresponding to a transition between states A and B will be observed. The central frequency of this line, ν_0 , can be measured with high accuracy. The above experiment, then, is a way of performing radiofrequency spectroscopy.

2-3 A MORE GENERAL EXAMPLE

One of the simplifications of the above example was that the ground state of the atom consisted of only two levels—the Zeeman levels of the electron-spin magnetic moment interacting with an externally applied magnetic field. More often, the nucleus of the atom will also have spin angular momentum, and the magnetic sublevels of the ground state of the atom are more complicated. In the case of weak external magnetic fields the sublevels are described in terms of F and m_F , where F is the total angular momentum of an atom and m_F is its projection along an external magnetic field.

As an example, we shall consider an atom with nuclear spin $I = \frac{3}{2}$ and electron spin $S = \frac{1}{2}$ (Na^{23} , Rb^{87}). Here, $F = I \pm S$, and the sublevels of the ground state are shown in Figure 2-5 for the atom in a weak magnetic field. Optical pumping can cause population differences between m_F states and between F states. There is now the opportunity of observing transitions between m_F states

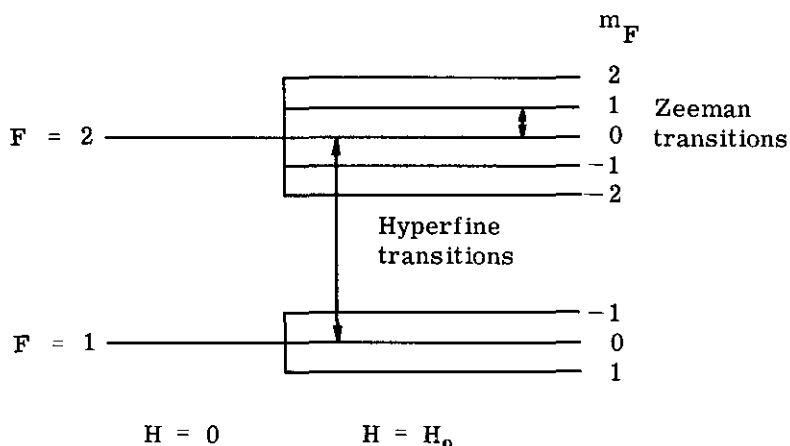


Figure 2-5 Magnetic sublevels of an electronic state of an atom with $L = 0$, $S = \frac{1}{2}$, and $I = \frac{3}{2}$. A positive nuclear moment is assumed.

(Zeeman transitions) and between F states (hyperfine transitions) by applying radio or microwave radiation of the correct frequency to the vapor cell and observing the transmitted light intensity. A discussion of the energy levels and their variation with applied magnetic field is given in Chapter 5.

The extent of the optical pumping or orientation will depend upon several factors. All transitions from the ground-state magnetic sublevels to the excited states must be considered along with their relative transition probabilities. In addition, there exists the possibility of disorientation of the atom in the excited state. Two extreme situations, complete disorientation and no disorientation in the excited state, have been considered by various workers (Franzen, 1957; Hawkins, 1955, 1961). Another factor that influences the extent of orientation is the relaxation among the magnetic sublevels of the ground state. Also, effects arising from the spectral line shape of the pumping radiation must be considered. In the following sections these various contributions to the more general case will be discussed more fully.

3/ The Dynamics of Optical Pumping

3-1 PUMPING AND RELAXATION IN GROUND STATES

We are interested in examining how the occupation of a given magnetic sublevel of the ground state of an atom changes with time. There are two simultaneous rate processes which must be considered: pumping and relaxation. If we let b_{ij} be the probability that the atom will be optically transferred from sublevel i to sublevel j , and w_{ij} be the probability that the atom will be relaxed from sublevel i to sublevel j , then the rate of change of the population of state R will be given by

$$\begin{aligned} \frac{dn_R}{dt} = & + \sum_{i=1}^Q (b_{iR} + w_{iR}) n_i \\ & - \sum_{j=1}^Q (b_{Rj} + w_{Rj}) n_R \end{aligned} \quad (3-1)$$

where n_R is the occupation probability of state R , and it is normalized such that

$$\sum_{R=1}^Q n_R = 1 \quad (3-2)$$

The summation indices i and j are over the magnetic sublevels of the ground

electronic state of the atom which are Q in number. The prime on the summation signs indicates that the terms for $j = R$ and $i = R$ are omitted from the sums. This merely means that processes which take an atom from state R and return it to state R do not change the population of state R .

The first sum in Eq. 3-1 gives the rate at which atoms arrive in state R , whereas the second sum gives the rate at which they leave state R . Equation 3-1 exists simultaneously for each magnetic sublevel, R , of the ground state of the atom. If there are Q sublevels then the set of Eqs. 3-1 plus 3-2 gives $Q - 1$ independent equations. If the transition probabilities b_{ij} and w_{ij} are known the time development of the occupation probability of each state can be computed (Franzen, 1957).

The average probability that the atom will absorb light will be given by

$$B = \frac{1}{Q} \sum_R \sum_j b_{Rj} n_R \quad (3-3)$$

At thermal equilibrium the n_R 's are all nearly equal and Eq. 3-3 can be written

$$B_0 = \frac{1}{Q} \sum_R \sum_j b_{Rj} \quad (3-4)$$

B_0 is now the average absorption probability per unit time per atom for the non-pumped species. When the atoms have been pumped to a certain degree their absorption will be given by Eq. 3-3. B_0 is a function of the initial light intensity and can be estimated from classical dispersion theory.

In order to obtain the detailed time development of the occupation probabilities of the sublevels, several approximations have to be introduced.

The first of these has to do with the relaxation probabilities in Eq. 3-1. The simplest assumption to make is that the w_{ij} are all equal. Then for each w_{ij} in Eq. 3-1

$$w = \frac{1}{QT_1} \quad (3-5)$$

where T_1 is the spin-lattice relaxation time for the system, and Q is the total number of magnetic sublevels of the system.

In the absence of optical pumping radiation

$$\frac{dn_R}{dt} = \frac{-1}{T_1} (n_R - 1/Q) \quad (3-6)$$

In the presence of optical pumping radiation the final time-dependent equations will also be dependent upon whether or not reorientation takes place in the excited

state of the atom. The equations can be written down for two cases: (1) no reorientation in the excited state of the atom and (2) complete reorientation in the excited state (Franzen, 1957). The general equation which holds for both cases is found by using Eq. 3-5 and 3-1:

$$\frac{dn_R}{dt} = - \sum_{j=1}^Q b_{Rj} n_R + \sum_{i=1}^Q b_{iR} n_i - \frac{n_R}{T_1} + \frac{1}{QT_1} \quad (3-7)$$

The b_{ij} are then computed according to whether reorientation or no reorientation occurs in the excited state.

The time development of n_R has been solved for a $I = \frac{3}{2}$, $J = \frac{1}{2}$ system, which is the case for Na^{23} (Franzen, 1957), and for a $I = \frac{7}{2}$, $J = \frac{1}{2}$ system, which is the case for Cs^{133} (Hawkins, 1961). In these papers graphs show quite clearly how the population for each state changes as a function of time for each of the two reorientation cases.

3-2 ORIENTATION AND ALIGNMENT

The distribution of atoms among the magnetic sublevels of the ground state is determined by Eq. 3-7 and by the b_{ij} . The b_{ij} , in turn, are determined by the various matrix elements for absorption and emission of the resonance radiation. These will depend upon the given experimental conditions, i.e., whether circularly or linearly polarized light is used, and the direction of magnetic fields at the absorption cell. Therefore, it is not too surprising that a variety of distributions can be obtained with different experimental conditions. These fall into the two main categories mentioned previously: (1) orientation and (2) alignment.

In optical orientation the atoms are pumped in one direction only with regard to the sign of m_F . The atoms can be concentrated in either the $m_F = +F$ level or the $m_F = -F$ level depending upon whether σ^+ or σ^- excitation is utilized. The result of orientation is a net angular momentum of the sample along the light beam. The sample of oriented atoms can also be conveniently characterized by a magnetization.

In optical alignment the atoms are pumped into the highest and lowest m_F levels simultaneously. In this case the net angular momentum along the light beam is zero, and there is no net magnetization.

For the special case of $Q = 2$, optical alignment techniques are not very useful because the most one would be able to do would be to equalize the populations of the two levels; no large population differences would be possible. For $Q = 2$ and optical orientation, Eq. 3-1 takes the form:

$$\frac{dn_A}{dt} = -(b_{AB} + w_{AB})n_A + (b_{BA} + w_{BA})n_B \quad (3-8)$$

$$\frac{dn_B}{dt} = -(b_{BA} + w_{BA})n_B + (b_{AB} + w_{AB})n_A$$

where the level notation of Figure 2-3 has been used. Neglecting the small Boltzmann difference in population at thermal equilibrium, one obtains in the absence of pumping

$$\frac{dn_A}{dt} = \frac{1}{T_1} (n_A - \frac{1}{2}) \quad (3-9)$$

and in the presence of pumping

$$dn_A/dt = b_{BA}n_B - n_A/T_1 - b_{AB}n_A + \frac{1}{2T_1} \quad (3-10)$$

A similar set of equations holds for dn_B/dt . If the transition probabilities b_{AB} and b_{BA} are known, the equations can be solved for $n_A(t)$ or $n_B(t)$. After a time long compared to the "optical pumping time," τ , a "stationary state" is reached where dn_A/dt and dn_B/dt are both equal to zero, and the Eqs. 3-8 become

$$\frac{n_A}{n_B} = \frac{1 + 2T_1 b_{BA}}{1 + 2T_1 b_{AB}} \quad (3-11)$$

If $b_{AB} = b_{BA}$, optical orientation cannot occur since the ratio n_A/n_B would be unity. In order for optical pumping to take place $b_{AB} \neq b_{BA}$. Two factors will influence the relative magnitudes of b_{AB} and b_{BA} . These will be (1) the matrix elements connecting the sublevels of the ground electronic state with those of the excited electronic state and (2) the amount of reorientation that occurs while the atom is in the excited electronic state.

For the special example illustrated in Figure 2-3 where only atoms in one of the ground state sublevels are excited and where no disorientation takes place in the excited state, i.e., $b_{BA} = 0$, Eq. 3-11 becomes

$$\frac{n_A}{n_B} = \frac{1}{1 + 2T_1 b_{AB}} \quad (3-12)$$

Here again we see that the population difference between levels A and B becomes

larger as T_1 becomes longer. In the case for which Eq. 3-12 holds the transition probability b_{AB} can be replaced by an alternative notation, $1/\tau$, where τ is called the "optical pumping time." Equation 3-12 with this notation becomes

$$\frac{n_A}{n_B} = \frac{1}{1 + (2T_1/\tau)} \quad (3-13)$$

and holds for the steady-state situation. The optical pumping time, then, is associated with the relative transition probabilities between the sublevels of the ground and excited electronic states of the system and the reorientation processes that result from collisions of the atom while it is the excited state.

3-3 OPTICAL PUMPING OF EXCITED STATES

The orientation or alignment of an excited state can be accomplished in two ways. One way is to first populate the excited state and then carry out a pumping scheme similar to that just described for ground states utilizing some still higher excited state. Alternatively, the orientation or alignment can be produced by the same radiation that is used to populate the excited state.

An example of the first procedure is the optical pumping of helium in the 2^3S_1 metastable state (Colegrove, 1960). In this experiment helium atoms are excited from the 2^3S_1 to the 2^3P states as shown in Figure 3-1. Even if the atoms are re-distributed among the 2^3P states before making the transition back to the 2^3S_1 state, an inequality in population distribution of the 2^3S_1 sublevels can be achieved, those levels with the smallest absorption probability having the highest population. If unpolarized resonance radiation is used, optical alignment in the 2^3S_1 state is produced. This experiment has been used for a magnetic-field stabilizing device (Scheerer, 1961), a very sensitive magnetometer, and, more recently, to produce nuclear polarization in He^3 (Colegrove, 1963).

The second type of optical pumping in an excited state is illustrated by the important case of mercury. The very first optical pumping experiment was with mercury vapor (Brossel, 1950, 1952a). Since that time the case of mercury has been exhaustively examined. A typical experimental configuration for the optical pumping of mercury is shown schematically in Figure 3-2. Mercury vapor is irradiated with resonance radiation polarized in the direction of the magnetic field at the vapor cell. The π radiation emitted at right angles to both the incident radiation and the magnetic field passes through an analyzing prism, and its intensity can be measured with a photomultiplier tube. The π resonance radiation causes excitations in which there is no change of components of angular momentum, $\Delta m = 0$. In this way only specific sublevels of the excited state are populated as illustrated in Figure 3-3 for the case of the even isotopes of mercury, i.e., those which have no nuclear spin. The emitted radiation from the $^3P_1$ state is polarized in the same direction as the incident radiation. If a

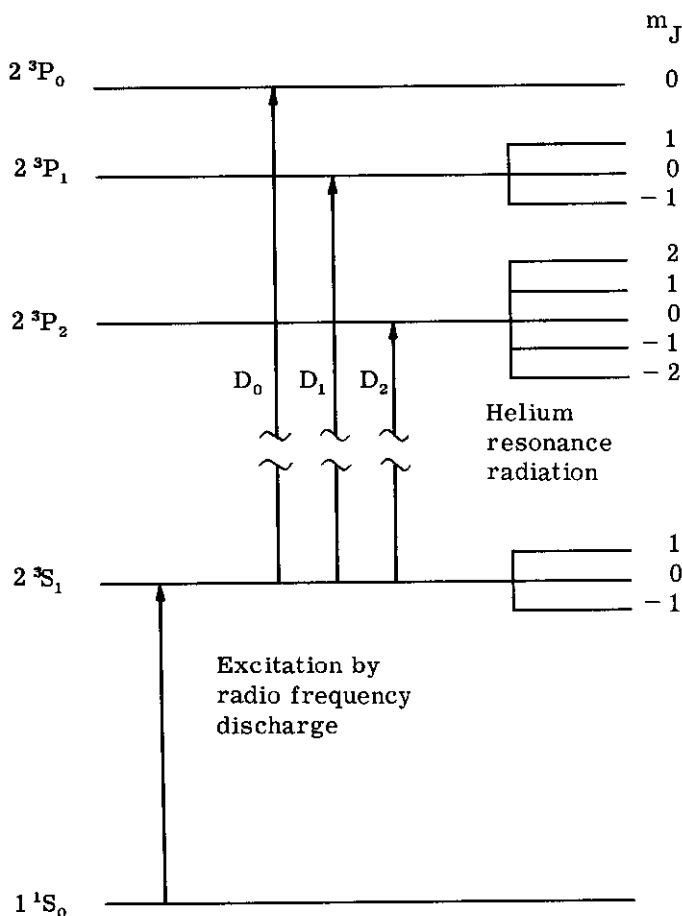


Figure 3-1 Energy levels of the helium atom pertinent to optical pumping in the 2^3S_1 state.

transition is produced between magnetic sublevels of the excited state with an applied radiofrequency field, the emitted radiation will contain some σ light, coming from the $m_J = \pm 1$ states, and the intensity of the π fluorescence from the $m_J = 0$ state will be diminished. This change in intensity of emitted π radiation is, then, a way of detecting magnetic resonances in the excited state of mercury.

The optical pumping of excited states and the detection of magnetic resonances has been accomplished in other substances as well. The nuclear electric quadrupole moment of Zn^{67} has been determined by optical methods in the 4^3P_1 metastable state of zinc (Bochmann, 1957). Experiments have been performed on

excited states of singly ionized helium mainly for the purpose of determining the Lamb shift for that system (Series, 1958a). Experiments on the excited states of the alkali metals are usually done for the purpose of determining the nuclear electric quadrupole interaction and the nuclear electric quadrupole moment. Such an experiment is, of course, impossible for the ground state because of the spherical charge distribution of S-state atoms which produces no electric field gradient at the nucleus and, therefore, no nuclear electric quadrupole interaction. Experiments on the excited states of alkali metal vapors have been performed on

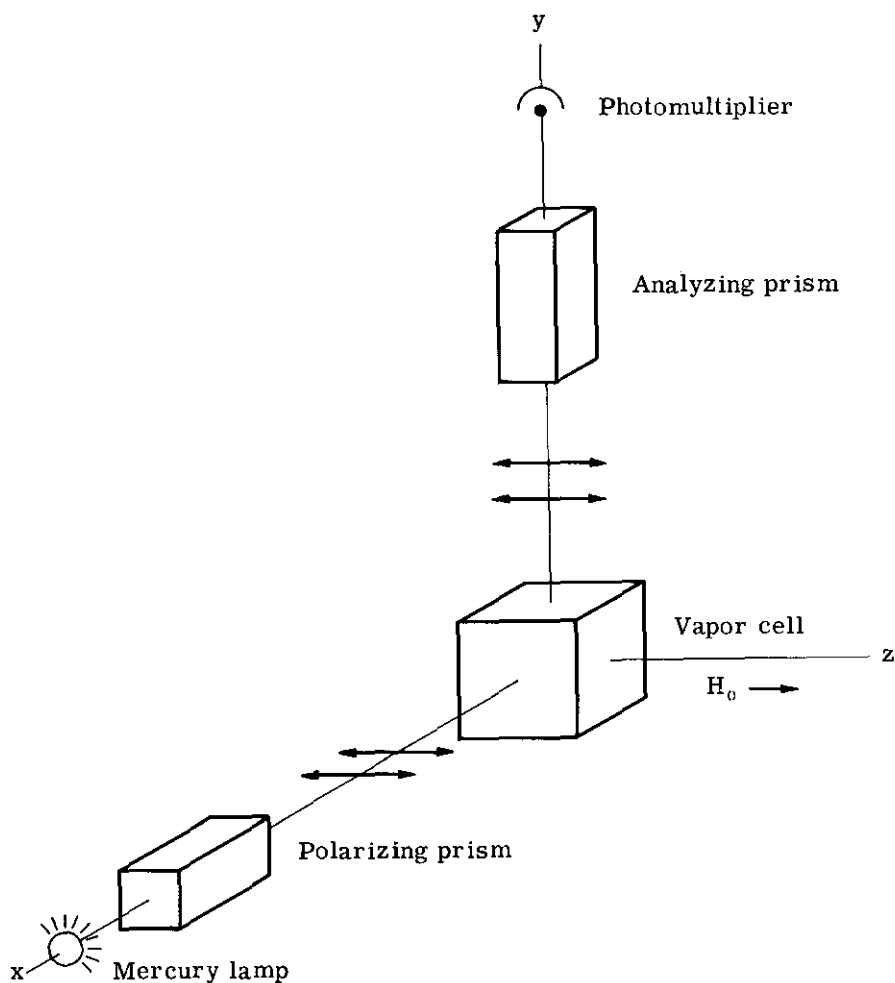


Figure 3-2 Schematic of an apparatus for the optical pumping of the mercury $^3P_1$ state.

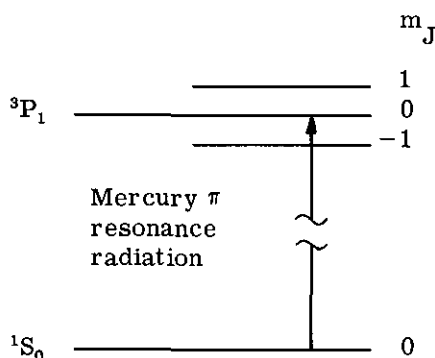


Figure 3-3 Energy levels pertinent to the optical pumping of the $^3P_1$ state of the even isotopes of mercury.

Na^{23} (Krüger, 1958; Sagalyn, 1954), K^{41} (Bucka, 1962a), Rb^{85} and Rb^{87} (K13), and Cs^{133} (Althoff, 1954, 1955; Krüger, 1955b; Bucka, 1956, 1958). It should also be mentioned that the experiments on excited states of atoms were also proposed for atomic beams (Rabi, 1952). Atomic beam experiments have been performed on excited states of Na^{23} (Perl, 1955), and K^{39} (Ritter, 1957).

The nuclear electric quadrupole interaction will be discussed in another section.

In this section we have presented only a very general discussion of the optical pumping process. The reader interested in a careful formalism in terms of the density matrix is referred to the excellent thesis by Cohen-Tannoudji (1962).

4 / Optical Resonance Radiation

4-1 RESONANCE FLUORESCENCE AND LINE FLUORESCENCE

The resonance fluorescence of atoms was first observed in sodium vapor by R. W. Wood about 60 years ago (Wood, 1913). The early explanation of this phenomenon was made on the basis of the classical theory of oscillators whereby light is scattered when its frequency is exactly in tune with a basic frequency of the scattering center. However, the classical theory could not explain the appearance of light of longer wavelengths than that of the exciting light in a fluorescence experiment. For example, it was inconsistent for sodium to emit the yellow D lines when illuminated with ultraviolet light. The advent of the Bohr theory and the concept of emission as a separate process distinct from absorption explained these as well as other anomalous observations in atomic spectra.

Strictly speaking, resonance radiation is produced when an excited state of a system emits light by making a transition to the ground state of the system. This occurs for atoms where there is a single ground electronic state such as is the case for S-state atoms (Hg, Na, Ca, etc.), but for systems which have low-lying electronic states, as is usually the case for atoms with P ground states (Tl, Pb, etc.), both resonance radiation and line fluorescence occur. The resonance transition terminates in the ground state, and the line fluorescence occurs when the transition terminates in a state that lies above the ground state. For an S-state atom, irradiation by the resonance lines produces fluorescence of the same lines, whereas for a P-state atom, irradiation by one of the exciting lines will produce at least two lines in the fluorescence as shown in Figure 4-1.

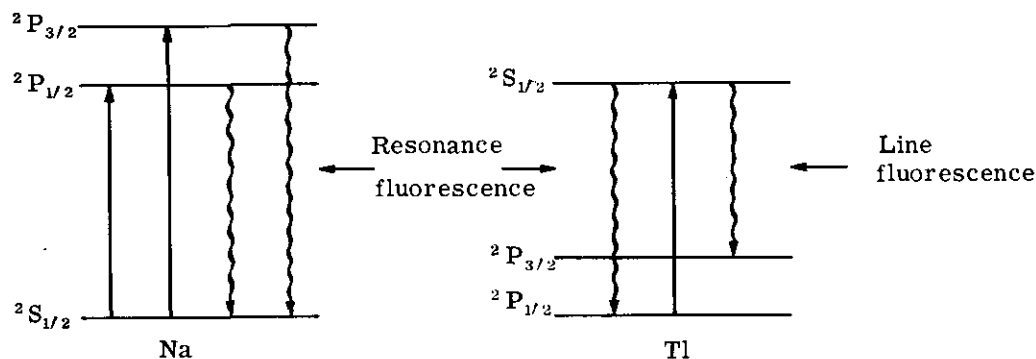


Figure 4-1 Examples showing the difference between resonance fluorescence and line fluorescence.

An exception to our definition of resonance radiation might occur in the case of an atom that has a metastable state. If this state is sufficiently well populated one could have the same situation as described above for resonance radiation where the metastable state is the lower terminus for a resonance transition.

In order to observe resonance fluorescence one needs a light source and a cell containing the vapors of the substance which will absorb the light. This cell, containing the vapors of the unexcited species is sometimes referred to as a "resonance lamp." A typical experimental arrangement for observation of resonance fluorescence is diagrammed in Figure 4-2. The horn shape of the resonance lamp, due to R. W. Wood, prevents internal reflections from complicating the observation of the resonance radiation. In Wood's early experiments with sodium, the light source used for exciting the resonance radiation was a gas flame to which a solution containing a sodium salt was added. This can be done by inserting into the flame a piece of asbestos which has been soaked in a salt solution. In modern experiments the light source is usually a discharge lamp which contains a few

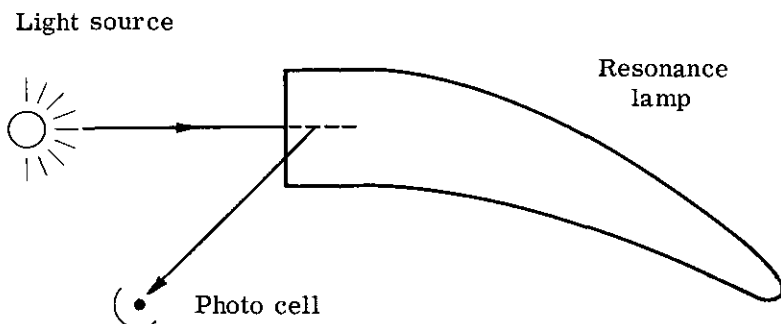


Figure 4-2 Observation of resonance fluorescence.

millimeters pressure of some inert gas and a small quantity of the element whose resonance radiation is required.

It is, of course, beyond the scope of this brief discussion to review all the aspects of resonance light. Instead, only a few topics of immediate consequence to optical pumping will be mentioned, and the reader is referred to the excellent work of Mitchell and Zemansky (1934) on the subject. In addition, a great deal of information concerning experiments with resonance light and about fluorescence and phosphorescence in general can be found in the book by Pringsheim (1949).

4-2 ABSORPTION OF OPTICAL RESONANCE RADIATION

For any spectral absorption line of a gas one can define an absorption coefficient $k(\nu)$ by the relation

$$I(\nu) = I_0 e^{-k(\nu)x} \quad (4-1)$$

where I is the intensity of light of frequency ν transmitted through the absorbing gas, I_0 is the incident light intensity, and x is the thickness of the absorbing

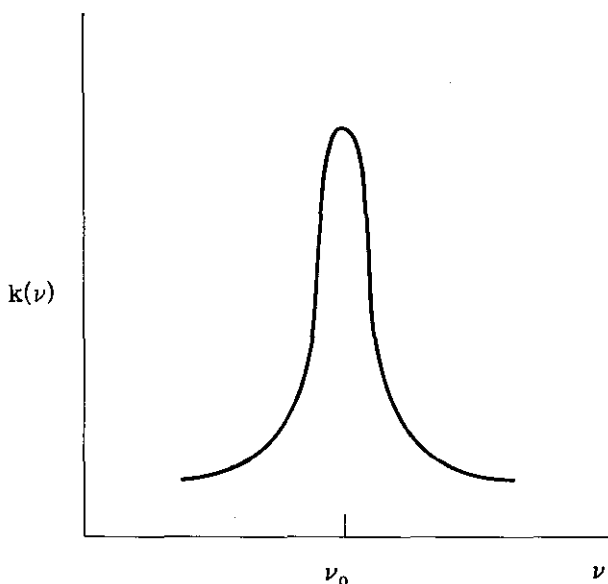


Figure 4-3 Absorption coefficient of a resonance transition.

gas. If one examines $k(\nu)$ as a function of ν one obtains the absorption line shape as shown for an idealized case in Figure 4-3.

Using the Einstein theory of radiation the integral of the absorption coefficient, which determines the line intensity, is given by

$$\int k(\nu) d\nu = \frac{\lambda_0^2 g_2 N}{8\pi g_1 \tau} \quad (4-2)$$

where λ_0 is the wavelength of the center of the line; g_2 and g_1 are the statistical weights of the excited and ground states, respectively; N is the number of absorbing gas atoms per cubic centimeter; and τ is the lifetime of the excited state. The above integral is a constant for a fixed N and can be used to determine τ . However, most tables of spectral lines and transition probabilities describe the line intensity in terms of the oscillator strength, f , defined by a relation due to Landenburg:

$$f = \frac{mc \lambda_0^2 g_2}{8\pi^2 e^2 g_1 \tau} \quad (4-3)$$

where the additional constants are the mass of the electron, m ; the speed of light, c ; and the electronic charge, e . Again, the lifetime of the excited state may be obtained from a measurement of the oscillator strength. However, oscillator strengths and absorption coefficients are sometimes difficult to obtain unambiguously. One must be certain that the spectral line is not broadened by mechanisms other than that of the natural lifetime of the excited state. In the next section we mention some of these other mechanisms of line broadening.

4-3 BROADENING OF OPTICAL RESONANCE LINES

The success of an optical pumping experiment very often hinges on differences in the resonance line profile between the light source and the absorbing species. In order to obtain a high degree of orientation in the m_F energy levels of the ground state of an alkali metal atom one wishes to have maximum intensity of the circularly polarized exciting light at exactly the center of the absorbing gas line shape. For certain hyperfine pumping experiments, one hyperfine component in the exciting light must be filtered out. In general, one has to consider and make use of the various sources of broadening of resonance lines.

An arbitrary breakdown of the contributions to spectral line shapes and broadening is as follows:

- Uncertainty broadening due to the natural lifetime of the excited state of the atom;
- Doppler broadening due to the thermal motion of the gas;
- Lorentz broadening due to collisions with foreign buffer gases;
- Holtmark broadening due to collisions with like atoms;

- e. Stark broadening due to collisions with electrons and ions;
- f. Zeeman broadening and splitting due to the presence of magnetic fields;
- g. Hyperfine splitting.

A number of these contributions to the line width can be controlled by the experimental conditions. In the case of Doppler broadening a theoretical correction for its contribution can sometimes be made.

Under certain conditions where one has a dense gas the Doppler width of a magnetic dipole transition can be narrowed by the collisions between gas particles. This effect was calculated by Dicke (1953; see reprint) who found that when the mean free path of the gas is small compared to the wavelength of the transition, a normal Doppler distribution plus a sharp non-Doppler broadened line results. Very narrow lines are, indeed, found in magnetic resonances of gases and in hyperfine transitions in S-state atoms. This effect is present in solids and is also responsible for the narrow lines found in experiments with the Mössbauer effect. Recently, it has been shown that the collision narrowing also occurs in the optical spectra of gases (Rank, 1963).

Another spectral line narrowing process can occur in a system of atoms that has the upper energy level of the resonance transition more densely populated than the lower. This effect is observed in the emission from lasers and masers.

4-4 SELF-REVERSAL

A common occurrence in the production of resonance radiation by a discharge lamp is the self-reversal of the resonance lines. This usually happens when the lamp is too hot or if there is a high pressure of a foreign gas present in the lamp. A hypothetical self-reversed line profile is illustrated in Figure 4-4. In a situation where the excitation occurs in the central portion of a lamp the resonance light will be absorbed by unexcited atoms surrounding the excitation region. In addition, if the excitation region becomes very hot the resonance lines will be

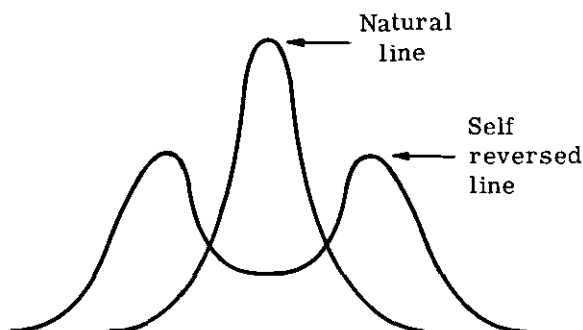


Figure 4-4 Self-reversal.

broadened. Sometimes cooling of the lamp will cause the discharge to be more uniformly distributed. It should be pointed out that only resonance lines, defined as above, will exhibit self-reversal. This fact was used by the early workers in identifying resonance spectral lines.

The production of intense, unreversed, resonance lines for an optical pumping experiment is a matter of considerable concern and has received some attention (Brewer, 1961; Franz, 1963a; Bell, 1961c). The self-reversal problem is quite serious with Rb, Cs, and Hg. If a commercial lamp is used it is helpful to blow air over the discharge bulb; if one makes one's own lamps, care should be taken to assure a clean interior. An inert gas is usually present inside the lamp to support the discharge. If the pressure of this gas is too high, the emitted spectral lines will be broadened. The pressure which gives the best results is a matter of trial and error, although some guides have been established by those who have studied this problem.

5/Magnetic Interactions: Zeeman and Hyperfine Splitting

5-1 THE HAMILTONIAN

The investigation of the Zeeman and hyperfine structure of an atomic state of an atom by the optical pumping method differs from the atomic beam method mainly in detection techniques. Sometimes, the optical pumping experiment is a more simple approach. However, the analysis of the resulting radiofrequency spectrum proceeds along the same lines as in the atomic beam case.

The Zeeman and hyperfine interactions of an atom in an external magnetic field H_0 are described by the Hamiltonian

$$\mathcal{H} = a\mathbf{I} \cdot \mathbf{J} - g_J \beta \mathbf{J} \cdot \mathbf{H}_0 - g_I \beta_N \mathbf{I} \cdot \mathbf{H}_0 \quad (5-1)$$

where $\mathbf{J}$ is the total electron angular-momentum operator composed of the sum of the electron orbital angular momentum, $\mathbf{L}$, and the electron-spin angular momentum, $\mathbf{S}$. $\mathbf{I}$ is the nuclear-spin angular-momentum operator, g_J and g_I are the electronic and nuclear spectroscopic splitting factors, β and β_N are the Bohr and nuclear magnetons, and a is the hyperfine splitting constant. The evaluation of the energy level structure of the system is simplified for either very weak or very strong external magnetic fields, i.e., if either the Zeeman or the hyperfine terms dominate. When the two types of interaction are comparable, the complete secular equation for the system must be solved.

5-2 ENERGY LEVELS IN WEAK, STRONG, AND INTERMEDIATE MAGNETIC FIELDS

In very weak external magnetic fields, **I** and **J** are strongly coupled to form $F = I + J$ and the resultant m_F . The energy levels of the system are given in the Fm_F representation by

$$E(F, m_F) = \frac{a}{2} [F(F+1) - I(I+1) - J(J+1)] - \left[g_J \beta \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} + g_I \beta_N \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} \right] m_F H_0 \quad (5-2)$$

Sometimes the term in the energy expression proportional to $g_I \beta_N$ is neglected due to its small size.

In very strong external magnetic fields, **I** and **J** are not coupled, and the system is described in terms of the separate magnetic quantum numbers m_J and m_I .

$$E(m_J, m_I) = a m_I m_J - g_J \beta m_J H_0 - g_I \beta_N m_I H_0 \quad (5-3)$$

In the intermediate case the appropriate secular equation can be solved in either the F, m_F representation or the m_J, m_I representation. A solution for the case of $J = \frac{1}{2}$ (alkali metal atoms) and arbitrary **I** is given by the Breit-Rabi formula:

$$E(F, m_F) = -\frac{a}{4} - g_I \beta_N m_F H_0 \pm \frac{a}{4} (2I+1) \sqrt{1 + \frac{4m_F}{2I+1} x + x^2} \quad (5-4)$$

where

$$x = \frac{2H_0(g_I \beta_N - g_J \beta)}{a(2I+1)}$$

The (+) sign in Eq. 5-4 is used for $F = I + \frac{1}{2}$, and the (-) sign for $F = I - \frac{1}{2}$.

An example of the energy level structure of an atom with $J = \frac{1}{2}$ and $I = \frac{3}{2}$ and g_I positive is shown in Figure 5-1. This is the level structure one would expect from a Na^{23} atom.

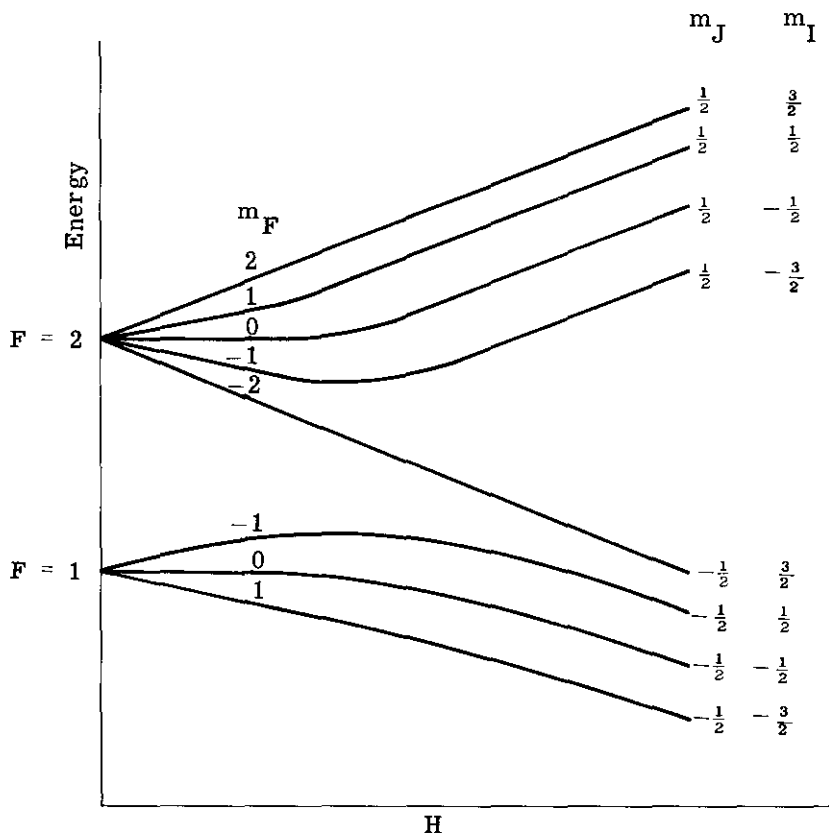


Figure 5-1 Magnetic sublevels of an atom with $J = \frac{1}{2}$ and $I = \frac{3}{2}$ and positive g_I as a function of magnetic field strength, H . Both the F, m_F and the m_J, m_I representations are used to label the energy levels.

If J is greater than $\frac{1}{2}$ or if there are other interactions present, such as the nuclear electric quadrupole interaction, the derivation of the energy levels is complex. The quadrupole coupling interaction will be treated in the next chapter.

5-3 DETERMINATION OF HYPERFINE CONSTANTS, g -FACTORS, AND NUCLEAR SPINS BY OPTICAL PUMPING

As described earlier, optical pumping can be used to produce an orientation or an alignment in the m_F states. It can also be used to populate preferentially one of the hyperfine states. With an oscillator of the appropriate frequency, Zeeman transitions or hyperfine transitions can be induced and can be detected

optically. If the frequency of the oscillator is measured with an electronic counter the energy of the transition can be accurately determined. By performing experiments at different applied magnetic fields the unknown parameters in the preceding energy level expressions can be determined. The unknown parameters are usually one or more of the quantities a , g_I , g_J , and I .

The Hamiltonian as written in Eq. 5-1 represents the sum of the hyperfine interaction, the Zeeman interaction of the electronic moment (spin plus orbital), and the Zeeman interaction of the nuclear magnetic moment. The nuclear g -factor, g_I , and spin I are constants for a given nucleus in its ground state. The electronic g -factor, g_J , for a given atomic state characterized by a value of J is usually thought of as a constant quantity given approximately by the Lande formula

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (5-5)$$

On the other hand, the hyperfine coupling constant a is dependent upon the electronic wave function of the atom and is subject to any perturbations of the wave function that can occur. For atoms with an odd electron in states of zero orbital angular momentum, e.g., $^2S_{1/2}$ states, the hyperfine interaction is proportional to the amount of electron magnetic moment density at the nucleus. This is usually referred to as the Fermi contact interaction and is given by

$$a \mathbf{I} \cdot \mathbf{S} = \frac{16\pi}{3} g_J \beta g_I \beta_N \mathbf{I} \cdot \mathbf{S} \delta(r) \quad (5-6)$$

where the delta-function operator $\delta(r)$ picks out the value of the wave function at the nucleus, $r = 0$. For an atom with one unpaired s electron described by a wave function ψ_0 the energy levels results from Eq. 5-6 are

$$E(m_I) = \frac{8\pi\beta}{3} g_I \beta_N |\psi_0(r=0)|^2 m_F \quad (5-7)$$

If the unpaired electrons are not s electrons they will not have any electron magnetic moment density at the nucleus. However, there will be an electron orbital magnetic moment which, along with the electron-spin magnetic moment, will produce a direct dipole-dipole interaction with the nucleus. In addition, the unpaired electrons can interact with the filled inner shells of s electrons to produce an unpaired moment density at the nucleus. A rigorous evaluation of this latter "core polarization" effect can be quite complicated, but an approximate formula for the hyperfine coupling constant due to dipolar interactions can be derived in a semiclassical fashion (Ramsey, 1956, p. 74).

$$\begin{aligned} a &= \beta \frac{\mu_I}{I} \frac{2L(L+1) \langle \psi_0 | 1/r^3 | \psi_0 \rangle}{J(J+1)} \\ &= \frac{hcR_y \alpha^2 Z^3 g_I}{n^3 (L + \frac{1}{2}) J(J+1) (M/m)} \end{aligned} \quad (5-8)$$

where n is the principal quantum number, R_y is the Rydberg constant ($me^4/4\pi\hbar^3c$), α is the fine structure constant, M/m is the proton-electron mass ratio, and Z is the nuclear charge.

As will be seen in a later section, perturbation of the wave function by nearby molecules or atoms can cause a change in the hyperfine constant. These changes yield information about the intermolecular interaction energies between optically pumped species and buffer species.

6/ Electric Interactions: Nuclear Electric Quadrupole and Stark Splitting

6-1 NUCLEAR ELECTRIC QUADRUPOLE COUPLING CONSTANTS

Nuclei with spin angular momentum $I \geq 1$ can possess a nuclear electric quadrupole moment, Q , which is a measure of the departure from spherical symmetry of the nuclear charge distribution. The nuclear electric quadrupole moment can undergo an electrostatic interaction with any surrounding electronic charges that are present, resulting in a quantization of the components of nuclear-spin angular momentum with respect to the surrounding charge distribution. The form of the interaction energy is such that it vanishes if the surrounding distribution of charges has tetrahedral, cubic, or spherical symmetry. Thus, for an alkali metal atom with a nucleus having an electric quadrupole moment, there will be no quadrupole interaction in the ground or S state, but there is the possibility for a finite interaction in some excited non-S states. This interaction energy is usually expressed in terms of a nuclear electric quadrupole coupling constant, e^2qQ , where e is the electronic charge, Q is the nuclear electric quadrupole moment, and q is the electric field gradient at the nucleus. In actual fact the nuclear electric quadrupole moment and the electric field gradient are tensor quantities, but we deal here with scalar quantities which are related to the

irreducible components of the nuclear electric quadrupole moment and electric field gradient tensors. Q is a constant quantity for a given nucleus in its ground state, but q is a function of the electronic wave function for the particular atomic state being considered. In a molecule, q at the site of a given nucleus would be a function of the electronic distribution about that nucleus due to nonbonding electrons, bonding electrons, and other nuclear charges.

6-2 ELECTRIC FIELD GRADIENTS IN ATOMS

In an atom where the field gradient arises solely from one electron, q is axially symmetric and can be calculated from

$$q = - \int \psi^* \frac{(3 \cos^2 \theta - 1)}{r^3} \psi d\tau \quad (6-1)$$

where ψ is the electronic wave function defined for the state $m_J = J$. The angular factors in Eq. 6-1 cause $q = 0$ for the $^2S_{1/2}$ and $^2P_{1/2}$ states but do yield a finite value of q in the $^2P_{3/2}$ state.

In order to determine experimentally a nuclear electric quadrupole moment it is not only necessary to know the coupling constant e^2qQ , but also the electric field gradient q . In the alkali metal atoms the quadrupole coupling constant is usually measured in the $^2P_{3/2}$ state. However, the field gradient at the nucleus calculated for a single p-valence electron is not the true field gradient. Besides a small relativistic correction (Casimir, 1936) there is an effect which comes from the filled inner shells of electrons in the atom. A filled inner shell would be expected to make zero contributions to q . However, the nuclear electric quadrupole moment can induce a quadrupole moment in these inner shells of electrons which, in turn, interacts with the field gradient due to the valence electron. The total effect of the inner shells is one of shielding or antishielding (depending upon the sign of the effect) of the field gradient due to a valence electron. This effect has been examined by Sternheimer (1956) who finds that the effective field gradient seen by the nucleus is equal to that given by Eq. 6-1 multiplied by a correction factor $[1 - \gamma(R)]$, where $\gamma(R)$ is called the "quadrupole antishielding factor." The aforementioned quadrupole coupling constant would then be expressed as $[1 - \gamma(R)]e^2qQ$ if q is to retain the definition given in Eq. 6-1. Values of $\gamma(R)$ must be obtained by a calculation and require a knowledge of the atomic wave functions.

6-3 DETERMINATION OF NUCLEAR ELECTRIC QUADRUPOLE MOMENTS

In the determination of Q from a measurement of the quadrupole coupling constant one must know both q and $[1 - \gamma(R)]$. Any uncertainty in either q or

$[1 - \gamma(R)]$ will be reflected by an uncertainty in Q . In order to test the reliability of a quadrupole moment determination one can measure the coupling constant in two different electronic states of an atom, calculate $\gamma(R)$ and q for each state, and examine the two resulting values of Q for consistency.

The quadrupole coupling constant can be determined in the excited states of atoms by optical pumping methods. The experimental arrangement is essentially that described in Chapter 3 for the case of mercury. The energy level separations in the excited state are determined by observing the polarization of resonance fluorescence when a radio or microwave frequency oscillating field is applied to the optically pumped atoms. A change in polarization of the fluorescence is observed when the applied oscillating field is in resonance with one of the transitions between the sublevels of the excited state of the atom. Early work of this nature was performed on the $^2P_{3/2}$ state of sodium (Sagaly, 1954). Numerous other elements have been examined by Kopfermann, Bucka, and co-workers at Heidelberg.

6-4 ENERGY LEVELS

With the addition of the nuclear electric quadrupole interaction the Hamiltonian for the atom becomes

$$\mathcal{H} = a\mathbf{I} \cdot \mathbf{J} - g_J \beta \mathbf{J} \cdot \mathbf{H}_0 - g_I \beta_N \mathbf{I} \cdot \mathbf{H}_0 + \frac{b3\mathbf{I} \cdot \mathbf{J} (2\mathbf{I} \cdot \mathbf{J} + 1) - I(I+1)J(J+1)}{4I(2I-1)J(2J-1)} \quad (6-2)$$

where the first three terms on the right have the same definition as given in Eq. 5-1, b is the quadrupole coupling constant, and I and J are the nuclear-spin and total electron angular momentum of the atom, respectively. Often, the terms in Eq. 6-2 can be of comparable magnitude which precludes the use of simple first-order perturbation theory in the derivation of the energy levels of the atom. In such a case the complete secular equation must be solved. On the other hand, when one of the terms is very large or small compared to the others the problem can be treated by perturbation theory. In the case where the hyperfine interaction and quadrupole interactions are comparable and where there are no externally applied magnetic fields the expression for the energy levels becomes (Davis, 1949)

$$E(F) = \frac{aC}{2} + b \frac{3}{8} \left[\frac{C(C+1) - I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \right] \quad (6-3)$$

where $C = F(F+1) - I(I+1) - J(J+1)$. A measurement of the energy level separations would enable one to determine a and b in Eq. 6-3.

A complicating factor that can arise is the broadening of the energy states by the very short lifetime of the excited electronic state of the atom. This lifetime broadening can interfere with the accuracy of the measurement and in some cases prevent the experiment from being performed at all.

6-5 STARK EFFECT

The magnetic sublevels of an atom can also be split by an electric field or Stark effect. The additional term which must be added to the Hamiltonian when an electric field E_z is present is

$$\mathcal{H}_s = e E_z \sum_i z_i \quad (6-4)$$

where e is the electronic charge and z_i is the z component of $\mathbf{r}_i$, the position vector of the i -th electron. In the situation where all the other interactions that have been discussed above are either very large or very small compared to $\mathcal{H}_s$, the Stark effect may be treated with perturbation theory. When this is done for atoms where the ℓ degeneracy has been lifted, i.e., for noncentral Coulomb field atoms, the first-order energy correction is zero and the Stark effect appears in second order, the change in energy being dependent only on the absolute value of m_J :

$$\Delta E(|m_J|) = e^2 E_z \sum_{n,J} \frac{|\langle 0 | \sum_i z_i | n, J \rangle|^2}{E(0) - E(n, J)} \quad (6-5)$$

for an atom whose magnetic sublevels can be described in the m_J representation.

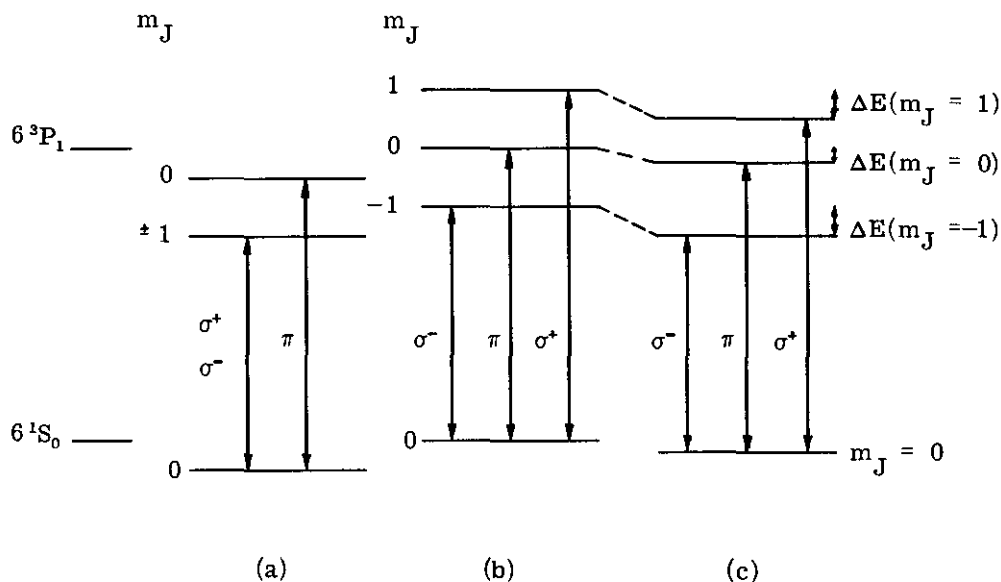


Figure 6-1 (a) Stark splitting of the energy levels of a mercury atom with nuclear spin $I = 0$. (b) Zeeman splitting. (c) Zeeman splitting plus weak Stark effect.

The summation over n and J represents a sum over all excited states of the atom. When the Stark effect becomes comparable to one of the other interactions that splits magnetic sublevels the complete secular equation must be solved.

Optical pumping has been used to investigate the 6^3P_1 state of the mercury atom in an electric field (Blamont, 1954, 1956, 1957a,b). The actual experiment was performed in parallel electric and magnetic fields which produce the energy level splitting shown in Figure 6-1. If a magnetic resonance is observed, using the method described for mercury in Section 7-4 in the next chapter, the resonance line will be split into two lines separated by an energy of 2ϵ , where

$$\epsilon = \Delta E (m_J = 0) - \Delta E (m_J = 1) \quad (6-6)$$

The case where a hyperfine interaction is also present in addition to the Zeeman and Stark effects has also been treated (Blamont, 1957b).

7 / Magnetic Resonance Detection

7-1 THE MAGNETIC RESONANCE CONDITION

Many applications of optical pumping involve the detection of a radio or microwave frequency resonance. Measurement of this frequency allows one to determine a hyperfine, quadrupole, Zeeman, or Stark interaction. Consequently, a few words are in order concerning the magnetic resonance condition, methods of detection, and the effect of oscillating magnetic fields upon the energy level separations themselves.

With the discovery of nuclear and electron magnetic resonance in bulk material shortly after World War II the subject of magnetic resonances received widespread attention and led to developments in physics and chemistry of far-reaching importance. The development and basic theory of magnetic resonances can be found in numerous places. Three recent books (Abragam, 1961; Pake, 1962; Slichter, 1963) are recommended to the reader as sources. Much of the discussion of nuclear and electron resonance phenomena can be carried over directly to their counterpart in optical pumping phenomena.

In a magnetic resonance experiment one is concerned with the reorientation of a component of angular momentum of a species by allowing it to interact with an oscillating magnetic field. If the frequency of the oscillating magnetic field is in resonance with an energy level separation of the species, transitions between the levels can occur. The probabilities of the transitions will follow the magnetic dipole selection rules and will be given by the usual result from first-order perturbation theory:

$$W_{m \rightarrow m'} = \gamma^2 H_1^2 |\langle m' | M_x | m \rangle|^2 \left| \frac{1 - e^{-i \Delta \omega t}}{\Delta \omega} \right|^2 \quad (7-1)$$

where $W_{m \rightarrow m'}$ is the transition probability per unit time from state m to state m' , H_1 is the amplitude of the oscillating magnetic field, γ is the magnetogyric ratio, M_x is the operator corresponding to the x component of angular momentum, and $\Delta \omega$ is given by

$$\Delta \omega = \omega - \omega_0 \quad (7-2)$$

where ω is the frequency of H_1 and ω_0 is the frequency corresponding to the energy level separation. The resonance condition is satisfied for $\omega = \omega_0$.

The classical discussion of magnetic resonance starts with the equation of motion of a magnetic moment μ in a magnetic field $\mathbf{H}$. This is obtained by equating the torque exerted on the magnetic moment to the rate of change of angular momentum, $\mathbf{M}$, of the system:

$$\frac{d\mathbf{M}}{dt} = \mathbf{T} = \mu \times \mathbf{H} \quad (7-3)$$

The ratio of magnetic moment to angular momentum is the magnetogyric ratio γ which, when substituted into Eq. 7-3, yields

$$\frac{d\mu}{dt} = \mu \times (\gamma \mathbf{H}) \quad (7-4)$$

This equation describes the precession of the magnetic moment about the direction of the magnetic field.

In a magnetic resonance experiment the magnetic field $\mathbf{H}$ is composed of a static magnetic field $\mathbf{H}_0$ and an oscillating magnetic field $\mathbf{H}_1(t)$ which is a function of time. Upon introduction of $\mathbf{H}_0$ and $\mathbf{H}_1(t)$, Eq. 7-4 becomes

$$\frac{d\mu}{dt} = \mu \times \gamma [\mathbf{H}_0 + \mathbf{H}_1(t)] \quad (7-5)$$

The magnetic moment now precesses about the resultant field composed of $\mathbf{H}_0$ and $\mathbf{H}_1(t)$. The resultant field is also time-dependent. When the frequency at which $\mathbf{H}_1(t)$ rotates about $\mathbf{H}_0$ is equal to the precessional frequency of the magnetic moment an additional torque is exerted on μ which turns it away from the direction of $\mathbf{H}_0$, and the resonance condition is satisfied. If the frequency of $\mathbf{H}_1(t)$ is different from the Larmor frequency the additional torque will vary with time according to the variation of the relative phases of $\mathbf{H}_1(t)$ and the precession of μ , and the resonance condition is not satisfied.

In order to proceed further with the classical description of magnetic resonance experiments it is useful to transform the equation of motion to a rotating coordinate

system that rotates about the direction of $\mathbf{H}_0$ with an angular frequency identical to that of $\mathbf{H}_1(t)$. In this way the time dependence of $\mathbf{H}_1$ can be eliminated and future mathematical manipulation simplified. This procedure is described in the references mentioned above.

7-2 OPTICAL DETECTION OF MAGNETIC RESONANCES

The role of optical pumping in magnetic resonance experiments is one of creating a situation which makes the detection of the resonance possible under conditions where other methods would fail or would not give accurate information. One factor that must be considered is the concentration of resonant species. In a conventional nuclear magnetic resonance experiment the sensitivity is limited to samples that have of the order of 10^{19} resonant nuclei per cubic centimeter or more. In electron resonance experiments the lower concentration limit is of the order of 10^{12} spins per cubic centimeter. Of course, these numbers are subject to resonance line-width and apparatus design consideration. In optical pumping experiments one can obtain a very high sensitivity. With improved techniques it would be possible to make measurements on systems with 10^6 species per cubic centimeter. The reason for this increased sensitivity is due to the double resonance nature of the experiment. One uses an optical transition to detect a radiofrequency transition, and the extinction coefficient of an optical resonance absorption is extremely high. Therefore, only a very small concentration of absorbing atoms is needed to detect a change in intensity or polarization of the resonance radiation.

Some of the detection schemes have been mentioned earlier in order to illustrate the principles of optical pumping. These plus some additional ways of studying magnetic resonances are summarized in Table 7-1. The techniques separate into two categories: optically pumped vapors and optically pumped atomic beams. Optical pumping of atomic beams is generally worth while for situations that are definitely not tractable by optical pumping of a vapor contained in an absorption cell. Such cases usually occur if the ground state of the atom being studied has a net electronic orbital angular momentum. An optical pumping experiment in which such an atom is placed in an absorption cell with a buffer gas to prevent wall collisions will generally fail owing to fast spin-relaxation processes.

Table 7-1 Methods of Detection of Magnetic Resonances in Optically Pumped Systems

Vapor cells	Transmitted radiation
	Scattered radiation; change in polarization
	Scattered radiation; change in frequency
	Modulation of a crossed light beam
	Modulation of pumping light
	Spin exchange
Atomic beams	Scattered radiation
	Beam intensity

Fast spin relaxation is encountered for these states because the electron orbital motion is easily perturbed by atomic collisions, and the spin angular momentum, being coupled to the orbital angular momentum, will also be affected strongly by collisions, providing a mechanism for relaxation. Such a resonance experiment must then be performed in a time short compared to the time between collisions of the species. This situation can be obtained in an atomic beam or in the case where the lifetime of the state being studied is very short. An example of a species that has been studied by both beam and vapor-cell methods is the $^2P_{3/2}$ state of Na where the nuclear electric quadrupole interaction was measured (Perl, 1955; Sagalyn, 1954). A brief summary of the methods listed in Table 7-1 follows.

7-3 TRANSMITTED RADIATION THROUGH VAPOR CELLS

This method which is due to Dehmelt (1957a) was described in Chapter 2. It marked a major advance in optical pumping techniques because it is simple and easy to use. Its application has been mainly to alkali metal atoms in their ground electronic state. In this experiment the intensity of circularly polarized radiation passing through a vapor cell is dependent upon the degree of orientation of the atomic species. At resonance the degree of orientation changes and, likewise, the intensity of transmitted light. This change can be detected with a photcell. Both Zeeman and hyperfine transitions can be studied in this way.

7-4 SCATTERED RADIATION FROM VAPOR CELLS; CHANGE IN POLARIZATION

This type of experiment is illustrated by the famous case of mercury also described in Chapter 2. The atoms are illuminated with π resonance radiation to produce pumping in the sublevels of the $^3P_1$ state. The intensity of scattered π radiation is monitored at 90° to the incident beam and is a measure of orientation of angular momentum in the $^3P_1$ state. At resonance $\Delta m = \pm 1$ transitions occur in the $^3P_1$ state resulting in a change in the intensity of the scattered π radiation. Since the early proposals by Kastler (1950, 1951) and the experiments by Brossel and Bitter (1952a; see reprint) this technique has been used for the studies of the mercury isotopes and for the excited states of the alkali metals, helium, zinc, cadmium, and some of the alkaline earth metals.

7-5 SCATTERED RADIATION; CHANGE IN FREQUENCY AND SELECTIVE REABSORPTION

In some cases a microwave resonance can be detected by a change in frequency of the scattered light from an atomic system rather than a change in polarization.

The method depends upon the availability of sharp-line light sources and filters which have a narrow band width and uses selective readsoption principles. In one example of this method (Kohler, 1961) use was made of the optical resonance transition in Hg^{198} to excite a transition to the $F = \frac{3}{2}$ level of the $^3\text{P}_1$ state of Hg^{201} . The scattered light was passed through a filter cell filled with Hg^{198} . If transitions to the $F = \frac{5}{2}$ or $\frac{1}{2}$ states of Hg^{201} are induced by microwave radiation, the scattered light can pass through the Hg^{198} filter and be detected with a photomultiplier. This method has also been used by Bucka (1958) in an investigation of the $7\ ^2\text{P}_{1/2}$ level of cesium and for detection of resonances in solids by optical means (Geschwind, 1959; see reprint).

7-6 CROSSED LIGHT BEAMS

The previous methods described above yielded a measure of the z component of angular momentum, M_z . This is a measure of the degree of orientation of the species being studied. Radiofrequency resonances can also be detected by

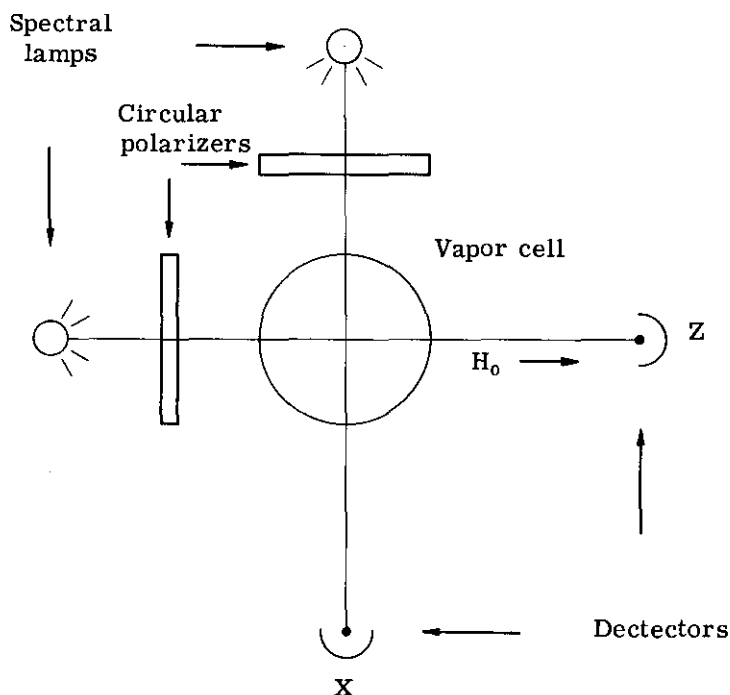


Figure 7-1 Schematic of an experimental arrangement to observe radiofrequency resonances of a vapor in a crossed light beam experiment.

measuring M_x instead of M_z (Bell, 1957). A method for doing this is shown in Figure 7-1 and employs two light beams: a circularly polarized beam in the z direction which optically pumps an alkali metal vapor and which can be used to monitor M_z , and an additional circularly polarized beam in the x direction which is used to monitor M_x . At resonance the x beam is modulated at the Larmor frequency, and the intensity of the modulated signal will depend upon the magnitude of M_x . In addition to monitoring M_x the beam will have two effects: it will tend to produce an orientation in the x direction, and it will produce a relaxation in the z direction. These points have been treated with the Bloch equations by Bell and Bloom (1957) whose experiment was based on a suggestion by Dehmelt (1957b). Other modulation effects have been extensively treated by G. W. Series and co-workers.

7-7 MODULATION OF OPTICAL PUMPING LIGHT

If circularly polarized resonance radiation is applied to a vapor cell at right angles to a magnetic field and if the light intensity is modulated, a change in the total transmitted light intensity can be observed when the modulation frequency is equal to the Larmor frequency of the absorbing species. This method of magnetic resonance detection has been observed and discussed for rubidium, cesium, and helium (Bell, 1961a, b) and also for cadmium (Corney, 1964b, c) and mercury (Dodd, 1963).

7-8 SPIN-EXCHANGE METHOD

The phenomenon of spin exchange will be discussed in Chapter 10. Briefly, spin exchange makes possible the orientation of spin angular momentum of a second species through a coupling interaction with the optically pumped species. Thus, cesium atoms can be oriented if they can collide with oriented rubidium atoms. In a like manner, disorientation can be transmitted by spin exchange and can be optically detected. For example, if one has a vapor cell containing rubidium and cesium with the rubidium being optically pumped, the cesium will be oriented by means of spin exchange. Upon application of a strong radiofrequency field at a cesium resonance the rubidium will be disoriented as well as the cesium, the disorientation being transmitted by spin exchange. One can do radiofrequency spectroscopy experiments on the cesium by detecting changes in the rubidium orientation with an experimental apparatus of the type introduced by Dehmelt (1957a).

7-9 SCATTERED RADIATION FROM ATOMIC BEAMS

Ground-state radiofrequency resonances can also be detected by observation of the scattered resonance radiation from an atomic beam (Hawkins, 1955). One method (Brossel, 1954) uses a beam of sodium atoms which is illuminated by σ^+

resonance radiation in one region to produce an accumulation of sodium atoms in an $m_s = +\frac{1}{2}$ state. In a second region the beam of oriented atoms is irradiated with π light, and the ratio of intensities of σ^+ and σ^- scattered light is measured. This ratio yields the degree of orientation of atoms at that point. If a radiofrequency resonance is excited in between the above two regions, the atomic orientation as measured by the scattered light will change. However, it is more convenient to perform magnetic resonance experiments on the ground states of the alkali metals in vapor-cell experiments rather than beams. Indeed, one can sometimes achieve more narrow magnetic resonance lines in a vapor to which a buffer gas has been added. This effect was predicted by Dicke (1953) and has been observed in numerous experiments.

7-10 DEFLECTION OF OPTICALLY PUMPED ATOMIC BEAMS

Radiofrequency resonances in excited states may also be detected by a combination of atomic beam and optical pumping methods. The nuclear electric quadrupole moment of Na^{23} has been determined by this method. A beam of sodium atoms are first state selected by deflection in a Stern-Gerlach magnet. The beam is then illuminated with optical resonance radiation and sent through a second Stern-Gerlach magnet where the beam is again state selected; the intensity of the beam being a measure of the relative population of the selected state. A radiofrequency field can be applied at the point at which the beam is illuminated, and if transitions between the magnetic sublevels of the excited state are induced during its 10^{-8} sec lifetime the relative population of the selected state will change and can be detected by a change in beam intensity (Perl, 1955). Again, it is possible to make this measurement in a resonance fluorescence experiment.

In experiments where a magnetic resonance transition must be excited during the short lifetime of some excited electronic state, a high flux of radio or microwave frequency photons must be present. This corresponds to a large $H_1(t)$. Otherwise, the excited state will fluoresce before a magnetic resonance transition has occurred. When a magnetic resonance is excited in a ground electronic state the problem is not as serious. However, the mere presence of $H_1(t)$ can perturb the magnetic energy level separations and introduce a small error in some types of experiments (Bloch, 1940). We shall briefly turn our attention to this effect.

7-11 THE BLOCH-SIEGERT SHIFT

In a magnetic resonance experiment transitions between magnetic energy levels are caused by the interaction of the spin system with a magnetic field $H_1(t)$ which oscillates about H_0 at the Larmor frequency. The oscillating magnetic field is composed of two magnetic fields rotating in opposite directions as indicated in Figure 7-2. The spin system interacts with only one of the two rotating fields regardless of whether absorption or stimulated emission is taking place. Which component is effective depends only upon the sign of the g -factor for the spin system involved.

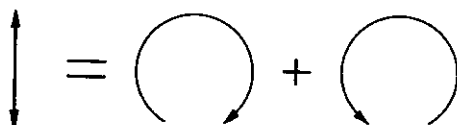


Figure 7-2 Decomposition of a linear oscillating H_1 into two rotating components.

The remaining rotating component of the oscillating H_1 does not participate in causing transitions to occur, but it can have an effect upon the experimental measurement of a resonance frequency. In the early days of atomic beam magnetic resonance there was some concern about this effect. If a resonance frequency were displaced by the presence of this second H_1 component there would be a corresponding error in the determination of the magnetic moment being studied.

In 1940, Bloch and Siegert calculated the effect and showed that the experimental resonance frequency is given by

$$\omega = \omega_0 + \frac{(\gamma H_1)^2}{4\omega_0} \quad (7-6)$$

where ω_0 is the true Larmor frequency. If H_1 (the magnitude of the radiofrequency field) is small the shift is negligible.

Ramsey (1955) has shown that if H_1 is small and if there is an additional field of magnitude H_2 rotating about H_0 with frequency ω_2 , the resonance will occur at

$$\omega = \omega_0 + \frac{(\gamma H_2)^2}{2(\omega_0 - \omega_2)} \quad (7-7)$$

This general result is identical with the Bloch-Siegert result when $\omega_2 = -\omega_0$.

More recently, an additional small shift in the magnetic energy levels has been investigated. This displacement is caused by light itself. The effect has been investigated theoretically (Barrat, 1961a, b, c, e) and has been experimentally observed (Cohen-Tannoudji, 1961a, b, c, 1962). It is also discussed in a review by Kastler (1963a), is referred to as the "lamp shift," and is caused by a reduction of the hyperfine structure of the excited state over that of the ground state.

8/ Phenomenological Description of Oriented Systems

8-1 ORIENTATION AS A BULK MAGNETIZATION

In Chapter 3 expressions were derived for the degree of orientation or alignment of the magnetic moments of a simple system being optically pumped. In the case of optical orientation it is reasonable to characterize the population differences among the magnetic sublevels of the system by a macroscopic magnetization. In addition, relaxation terms are present in the orientation expressions that describe the rate at which the atoms regain their normal Boltzmann distribution among the sublevels.

Since the ensemble of atoms can be characterized by a magnetization and by relaxation it is reasonable that the macroscopic magnetic properties of the system be described by expressions similar to the phenomenological equations of Bloch (1946) which were formulated to describe the motion of nuclear moments in the presence of external magnetic fields. The solutions of these equations would then describe the behavior of the system of optically pumped atoms. The boundary values for the equations could be specified by a given set of experimental conditions.

In the absence of a pumping process or relaxation, the time variation of the magnetization per unit volume $\mathbf{M}$ of an ensemble of atoms is given by an equation similar to Eq. 7-4:

$$\frac{d\mathbf{M}}{dt} = \mathbf{M} \times (\gamma \mathbf{H}) \quad (8-1)$$

where $\mathbf{H}$ is the magnetic field acting on the atoms and γ is the magnetogyric ratio for the magnetic moment of the atom. The magnetogyric ratio is related to the spectroscopic splitting factor, g_F , of the atom, by the relation $\gamma \hbar = g_F \beta$, where β is the Bohr magneton. In the case of nuclear magnetism the Bloch equations are obtained by adding relaxation terms to Eq. 8-1 which then becomes

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{H} - \frac{M_x \mathbf{i} + M_y \mathbf{j}}{T_2} - \frac{M_z - M_0}{T_1} \mathbf{k} \quad (8-2)$$

Here $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors in the laboratory coordinate system, and M_x , M_y , M_z are the components of $\mathbf{M}$ in this coordinate system. M_0 is the z-component value of the magnetization when the ensemble of magnetic moments has achieved a normal Boltzmann distribution. It is assumed that a steady external magnetic field is applied along the $\mathbf{k}$ direction. T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, and describe the rate at which the components of $\mathbf{M}$ relax along their respective directions.

The usual procedure is to solve Eq. 8-2 for M_x , M_y , M_z with particular boundary conditions. These are usually dictated by the experimental conditions and the range of t in which one is interested. $\mathbf{H}$ is generally composed of a steady magnetic field $\mathbf{H}_0$ applied along the $\mathbf{k}$ direction plus a magnetic field $\mathbf{H}_1(t)$ oscillating perpendicular to $\mathbf{k}$ at some frequency ω . The magnitude of $\mathbf{H}_0$ and $\mathbf{H}_1$ plus the frequency ω are experimental variables contained in the expressions for M_x , M_y , and M_z .

8-2 EQUATIONS OF MOTION WITH OPTICAL PUMPING

When optical pumping is also taking place the state populations and, hence, the magnetization are changed from the normal Boltzmann value. This change can be introduced by simply adding the contribution that comes from pumping. If the pumping is such that it changes the total z component of angular momentum of the ensemble of atoms the contributions to be added will be

$$\frac{M_0^P - M_z}{\tau_P} \mathbf{k}$$

where M_0^P is the maximum equilibrium value of M_z while pumping is taking place and τ_P is the "optical pumping time" for this process to occur. It must be noted that M_0^P is a constant determined by three factors: T_1 , the transition probabilities for excitation of the atom, and the intensity of light used for the pumping process. Usually M_0^P is much larger than the normal Boltzmann

$$\frac{d\mathbf{M}}{dt} = \mathbf{M} \times (\gamma\mathbf{H}) \quad (8-1)$$

where $\mathbf{H}$ is the magnetic field acting on the atoms and γ is the magnetogyric ratio for the magnetic moment of the atom. The magnetogyric ratio is related to the spectroscopic splitting factor, g_F , of the atom, by the relation $\gamma\hbar = g_F\beta$, where β is the Bohr magneton. In the case of nuclear magnetism the Bloch equations are obtained by adding relaxation terms to Eq. 8-1 which then becomes

$$\frac{d\mathbf{M}}{dt} = \gamma\mathbf{M} \times \mathbf{H} - \frac{M_x\mathbf{i} + M_y\mathbf{j}}{T_2} - \frac{M_z - M_0}{T_1}\mathbf{k} \quad (8-2)$$

Here $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors in the laboratory coordinate system, and M_x , M_y , M_z are the components of $\mathbf{M}$ in this coordinate system. M_0 is the z-component value of the magnetization when the ensemble of magnetic moments has achieved a normal Boltzmann distribution. It is assumed that a steady external magnetic field is applied along the $\mathbf{k}$ direction. T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, and describe the rate at which the components of $\mathbf{M}$ relax along their respective directions.

The usual procedure is to solve Eq. 8-2 for M_x , M_y , M_z with particular boundary conditions. These are usually dictated by the experimental conditions and the range of t in which one is interested. $\mathbf{H}$ is generally composed of a steady magnetic field $\mathbf{H}_0$ applied along the $\mathbf{k}$ direction plus a magnetic field $\mathbf{H}_1(t)$ oscillating perpendicular to $\mathbf{k}$ at some frequency ω . The magnitude of $\mathbf{H}_0$ and $\mathbf{H}_1$ plus the frequency ω are experimental variables contained in the expressions for M_x , M_y , and M_z .

8-2 EQUATIONS OF MOTION WITH OPTICAL PUMPING

When optical pumping is also taking place the state populations and, hence, the magnetization are changed from the normal Boltzmann value. This change can be introduced by simply adding the contribution that comes from pumping. If the pumping is such that it changes the total z component of angular momentum of the ensemble of atoms the contributions to be added will be

$$\frac{M_0^P - M_z}{\tau_P}\mathbf{k}$$

where M_0^P is the maximum equilibrium value of M_z while pumping is taking place and τ_P is the "optical pumping time" for this process to occur. It must

be noted that M_0^P is a constant determined by three factors: T_1 , the transition probabilities for excitation of the atom, and the intensity of light used for the pumping process. Usually M_0^P is much larger than the normal Boltzmann

distribution, which enables one to neglect the M_0 term for most problems. Equation 8-2 for the optical pumping case now becomes

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{H} - \frac{M_x \mathbf{i} + M_y \mathbf{j}}{T_2} - \frac{M_z \mathbf{k}}{T_1} + \frac{M_0^P - M_z}{\tau_P} \mathbf{k} \quad (8-3)$$

As was mentioned in the previous chapter if $\mathbf{H}$ is composed of a static field $\mathbf{H}_0$ of magnitude

$$H_0 = H_z = -\frac{\omega_0}{\gamma}$$

and a radiofrequency field $\mathbf{H}_1$ of magnitude

$$H_1 = -\frac{\omega_1}{\gamma}$$

rotating at a frequency ω close to ω_0 , an effective static magnetic field $\mathbf{H}_{\text{eff}}$ may be described in a coordinate system which rotates about $\mathbf{H}_0$ at the frequency ω :

$$\begin{aligned} \mathbf{H}_{\text{eff}} &= \left(H_0 + \frac{\omega}{\gamma} \right) \mathbf{k}' + H_1 \mathbf{i}' \\ &= \frac{(\omega - \omega_0) \mathbf{k}' - \omega_1 \mathbf{i}'}{\gamma} \\ &= \frac{\Delta\omega \mathbf{k}' - \omega_1 \mathbf{i}'}{\gamma} \end{aligned} \quad (8-4)$$

where the primes indicate that the unit vectors are now taken in the rotating coordinate system. $\mathbf{H}_{\text{eff}}$ is illustrated in Figure 8-1 for the situation where the rotating coordinate system has the same frequency as does H_1 . In such a case it is convenient to transform Eq. 8-3 to the rotating coordinate system:

$$\begin{aligned} \frac{d\mathbf{M}'}{dt} &= \frac{dM'_x \mathbf{i}'}{dt} + \frac{dM'_y \mathbf{j}'}{dt} + \frac{dM'_z \mathbf{k}'}{dt} \\ &= (M'_x \mathbf{i}' + M'_y \mathbf{j}' + M_z \mathbf{k}) \times (\Delta\omega \mathbf{k} - \omega_1 \mathbf{i}') \\ &\quad - \frac{M'_x \mathbf{i}' + M'_y \mathbf{j}'}{T_2} - \frac{M_z \mathbf{k}}{T_1} + \frac{M_0^P - M_z}{\tau_P} \mathbf{k} \end{aligned} \quad (8-5)$$

Since the coordinate system rotates about $\mathbf{H}_0$, $\mathbf{k}' = \mathbf{k}$ and $M'_z = M_z$, which have been taken into account accordingly in Eq. 8-5. The resulting time variations of the components of magnetization in the rotating coordinate system are

$$\begin{aligned}
 \frac{dM'_x}{dt} &= -\frac{M'_x}{T_2} + \Delta\omega M'_y \\
 \frac{dM'_y}{dt} &= -\Delta\omega M'_x - \frac{M'_y}{T_2} - \omega_1 M_z \\
 \frac{dM_z}{dt} &= \omega_1 M'_y - \frac{M_z}{T_1} + \frac{M_0^P - M_z}{\tau_P}
 \end{aligned}
 \tag{8-6}$$

Equation 8-6 can be solved for a given set of experimental conditions according to the same procedures that have been used in the nuclear magnetic case. However, it must be pointed out that the usual experimental arrangement sometimes utilizes an H_0 which is a fraction of a gauss. This means that H_1 can easily be comparable to H_0 . Under these conditions the validity of the Bloch equations and their solutions must be carefully examined. In these cases T_1 and T_2 become equal, and it would be preferable to modify the Bloch equations such that $\mathbf{M}$ relaxes toward the instantaneous value of $\mathbf{H}$ rather than along fixed component directions of $\mathbf{M}$. In these circumstances the Bloch equations for nuclear magnetism become (Abragam, 1961)

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{H} - \frac{\mathbf{M} - \chi_0 \mathbf{H}}{T_1}
 \tag{8-7}$$

where T_1 is equal to T_2 , and χ_0 is the spin magnetic susceptibility. The validity of the modified Bloch equation in situations where H_0 is low or even equal to zero has been justified experimentally.

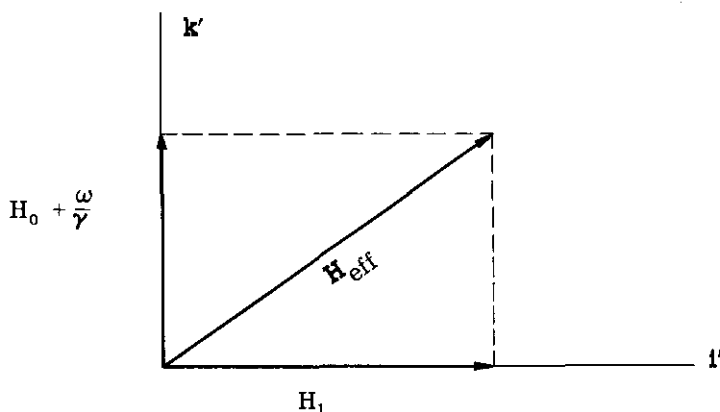


Figure 8-1 Effective magnetic field, H_{eff} , in a rotating coordinate system.

It seems reasonable that in the optical pumping case the production of magnetization by optical pumping may be simply added to Eq. 8-7 as before to yield

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{H} - \frac{(\mathbf{M} - \chi_0 \mathbf{H})}{T_1} + \frac{\mathbf{M}^P - \mathbf{M}}{\tau_P} \quad (8-8)$$

In actual fact the details of the pumping term must be derived for the particular type of experiment being performed. If the orientation is along the z direction defined as along $\mathbf{k}' = \mathbf{k}$ Eq. 8-8 in the rotating coordinate system becomes

$$\begin{aligned} \frac{dM'_x}{dt} &= M'_y \Delta\omega - \frac{M'_x}{T_1} - \frac{\chi_0 \omega_1}{\gamma T_1} \\ \frac{dM'_y}{dt} &= -M'_x \Delta\omega - \omega_1 M'_z - \frac{M'_y}{T'} \\ \frac{dM'_z}{dt} &= \omega_1 M'_y - \frac{M'_z}{T_1} + \frac{\chi_0 \Delta\omega}{\gamma T_1} + \frac{M_z^P - M'_z}{\tau_P} \end{aligned} \quad (8-9)$$

Again, if M_z^P is large, the terms in χ_0 may be neglected. Equation 8-9 can then be solved with the set of boundary conditions dictated by the specific experimental conditions.

The case where two light beams are present, one in the z direction and the other in the x direction, has also been discussed from the phenomenological point of view by Bell and Bloom (1957) to describe experiments in which a high-frequency modulation of a second light beam is observed.

A description of optically oriented systems in terms of the density matrix formalism will not be given here. The reader is referred to the paper by Cohen-Tannoudji (1962) on this subject.

9/Energy Level Crossing Experiments

9-1 PRINCIPLE OF THE EXPERIMENT

In certain cases it is possible to make precision measurements of fine and hyperfine level separations without performing a radiofrequency resonance experiment upon the atom under study. This is achieved by what is called a "level crossing experiment." The angular distribution of the resonance fluorescence of the atom under study is observed as a function of the magnitude of some externally applied magnetic field. If two states involved in the resonance fluorescence cross one another at some magnetic field strength, and if both of the states can participate in the absorption of an incoming photon, the angular distribution of resonance fluorescence will be different than that in the noncrossed states.

Such an experiment was first performed on the helium ($1s2s$) ^3P state and resulted in a redetermination of the $^3P_1 - ^3P_2$ and $^3P_0 - ^3P_1$ fine structure splittings with a high degree of precision (Colegrove, 1959; Franken, 1961a).

The energy levels of the helium states involved in this experiment are shown in Figure 9-1 with the crossing points circled for which the effect exists when the exciting light is unpolarized. The magnetic field at each crossing point can be accurately measured. The fine structure splittings can then be computed. The level crossing phenomenon was discussed by Breit (1933) and more recently by Franken (1961a) and by Rose and Carovillano (1961) who point out that it can be thought of as simply an interference phenomenon between radiation from each of the two states that cross, although it is a one-photon process and not a two-photon process. The amount of interference depends upon the separation between the two states.

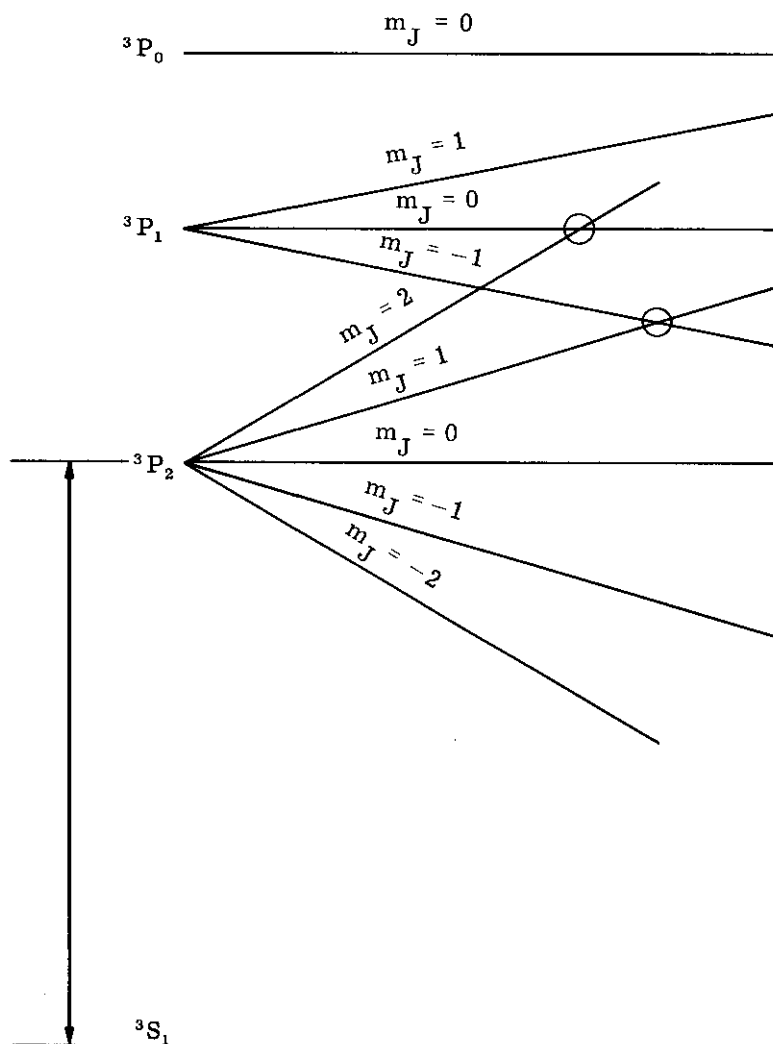


Figure 9-1 Energy level crossing in helium (indicated by circles).

Two extreme cases may be considered to illustrate why the process can be observed: (1) the two states a and b are far apart (resolved), and (2) the two states are exactly crossed. If one examines the rate $R(f,g)$ at which photons of polarization f are absorbed and photons of polarization g are emitted in resonance fluorescence, the following proportionalities hold for $R(f,g)$ for the above two cases:

$$R_{\text{resolved}} \sim |f_{ab} g_{ba}|^2 + |f_{ac} g_{ca}|^2 \quad (9-1)$$

and

$$R_{\text{crossed}} \sim |f_{ab}g_{ba} + f_{ac}g_{ca}|^2$$

where $f_{ab} = \langle a | f \cdot r | b \rangle$, $g_{ba} = \langle b | g \cdot r | a \rangle$, etc. In order for the level crossing to be an observable process, none of the matrix elements may be equal to zero, otherwise R_{resolved} would be the same as R_{crossed} . Therefore, both states must participate in the absorption and re-emission of the resonance radiation being used.

9-2 APPLICATIONS

As might be expected, there are a variety of experimental configurations that might be used, each having its own special consequences. Level crossings with $\Delta m = 0$ or 2 may be observed with unpolarized light whereas $\Delta m = 1$ crossing may be observed with plane polarized light if the direction of polarization is neither parallel nor perpendicular to the externally applied magnetic field. In addition, the line shape of the crossover will be a function of experimental configuration and can vary from a pure Lorentzian to a pure dispersion-type curve depending upon the polarization and scattering angle of the light.

In addition to helium, level crossing techniques have been used to make precision measurements of g_J factors for the $(5s5p) {}^3P_1$ state of Cd^{111} and Cd^{113} (Thaddeus, 1962) and Cd^{107} and Cd^{109} (Thaddeus, 1963). Level crossings have also been used to measure the hyperfine structure of the $(6s6p) {}^3P_1$ state of Hg^{199} and Hg^{201} (Hirsch, 1961; Dodd, 1961a, b).

Recently, the same effect has been observed for states which do not actually cross but which come close together, then repel one another. If the two states are coupled by some interaction they will be prevented from crossing one another. The observation of this "anticrossing" can be made, and a theoretical treatment performed in a fashion similar to that for level crossings (Eck, 1963).

10/Spin Exchange

10-1 MAGNETIC RESONANCE DETECTION BY SPIN EXCHANGE

A very important effect that occurs in optical pumping experiments is the ability of two particles to transfer their spin orientation to one another upon making a collision. If one has two species, A and B, present in a vapor cell, pumping can be produced in B by optically pumping species A, the effect being transferred from species A to species B via spin exchange.

As was mentioned in Chapter 7, optical detection of radio frequency resonances in species B can be accomplished by monitoring their effect upon the absorption of resonance radiation by species A; the effect being transferred by spin exchange. This is experimentally a very powerful tool because one can study an atom for which the proper production, filtering, and polarization of resonance radiation is difficult simply by utilizing a second atomic species for which the proper kind of resonance radiation is easily obtainable.

Dehmelt (1958a; see reprint) introduced this technique to study the spin resonance of free electrons. By utilizing spin exchange between free electrons and optically oriented sodium vapor, he was able to obtain a very precise value of the Lande g-factor for the free electron. This is of considerable interest in testing relationships from quantum electrodynamics such as the ratio of the electron-spin magnetic moment, μ_S , to the Bohr magneton, μ_0 :

$$\frac{\mu_S}{\mu_0} = 1 + \frac{\alpha}{2\pi} - 2.973 \frac{\alpha^2}{\pi^2} + \dots \quad (10-1)$$

Potassium (Franken, 1958a), rubidium (Novick, 1958), and cesium (Dehmelt, 1958b) atoms have been oriented by spin exchange with other optically pumped alkali atoms. Also, the hyperfine interaction has been measured in N^{14} (Holloway, 1958) and N^{15} (Anderson, 1959), in P^{31} (Lambert, 1962), and in H, D, and T (Anderson, 1958, 1960b, 1961; Pipkin, 1962) atoms by using spin-exchange techniques.

In addition, nuclear polarization has been achieved by exchange mechanisms. He^3 nuclei can be oriented by spin exchange with optically pumped Rb atoms (Bouchiat, 1960). He^3 nuclei have also been oriented by a metastability exchange with optically pumped ^3S helium atoms (Colegrove, 1963). The orientation of He^+ ions by spin exchange with optically pumped cesium has been achieved by Dehmelt and Major (1962a) in an ingenious experiment where the ions are trapped in a quadrupolar field whose polarity reverses at a high frequency.

Spin exchange is also important in interpreting the details of state population changes in relaxation processes (Anderson, 1961b).

Experimentally, the same procedures are followed as are used in a conventional optical pumping experiment except that two species are placed in the vapor cell—one is optically pumped directly and the other is pumped by spin exchange with the first species. The second species sometimes is produced by an electrical or radiofrequency discharge. This must be done if one wants to examine free electrons or make measurements on atoms whose stable form is a molecule. For example, H atoms must be produced by dissociation of H_2 molecules. The production of the second species could also be the result of a chemical reaction or of decomposition of a parent substance with ultraviolet light or by particles emanating from radioactive materials.

The optical detection of a radiofrequency resonance in the second species is illustrated by Dehmelt's (1958a; see reprint) experiment on free electrons. Sodium atoms in an argon buffer gas are optically pumped by circularly polarized light. Electrons, produced by a series of 1-msec radiofrequency discharges, were oriented by spin-exchange collisions with the oriented sodium atoms. Resonance disorientation of the free electrons was caused by a radiofrequency field applied to the vapor cell, whose frequency was the same as the Larmor frequency of the electrons. This spin disorientation was transferred to the sodium atoms by spin exchange and was detected as a decrease in intensity of circularly polarized sodium resonance radiation passing through the apparatus.

Dehmelt has discussed the interdependence of the orientation of the sodium atoms and the electrons in the above experiment. It serves to illustrate what factors are important in the spin-exchange process. He finds for the equilibrium orientations p and P of electrons and sodium atoms, respectively,

$$p = \frac{f T_e P_I}{f T_e + F \tau_p + 1}; \quad P = \frac{(f T_e + 1) P_I}{f T_e + F \tau_p + 1} \quad (10-2)$$

where f is the frequency of collision of an electron with sodium atoms and F is the frequency of collision of a sodium atom with electrons. f can be expressed $f = v \sigma_{ex} N$, where v is the mean relative velocity of the two species, N is the

number of sodium atoms per cubic centimeter, and σ_{ex} is the cross section for spin exchange. Likewise, $F = v\sigma_{\text{ex}}m$, where m is the number of free electrons per cubic centimeter. T_e in Eq. 10-2 is the electron relaxation time, and P_I is the equilibrium orientation that can be obtained with the light intensity available for the experiment.

When the electrons are disoriented by a radiofrequency field the effect is the same as a shortening of T_e , hence, a decrease in P . From the amount of change in P the spin-exchange cross section σ_{ex} can be estimated. For electron-sodium interactions it is found that $\sigma_{\text{ex}} = 2.3 \times 10^{-14} \text{ cm}^2$.

10-2 MECHANISM FOR SPIN EXCHANGE

The mechanism for spin exchange has been discussed by Purcell and Field (1956; see reprint), Wittke and Dicke (1956), Glassgold (1963), Bender (1963), and by Balling, Hanson, and Pipkin (1964a, b). Purcell and Field were interested in the effect of spin exchange in establishing the state populations of the hydrogen hyperfine levels and the resulting consequences with respect to 21-cm radio astronomy. Wittke and Dicke were interested in the effects of spin exchange on the relaxation and line width in an experimental redetermination of the hyperfine splitting in the ground state of the hydrogen atom. The spin functions of two colliding hydrogen atoms are represented as being a superposition of singlet and triplet functions. During a collision, a phase shift occurs between the amplitude of the singlet component and the amplitude of the triplet component due to the difference in scattering potential of the two components. The amount of phase shift will depend upon the "hardness" of the collision. It is generally assumed that the phase shift evolves mainly from the singlet state contribution since for this state the potential is attractive and closer distances of approach are involved in producing hard collisions. This means that the centripetal barrier to "hard" collision is lowered. Cross sections for such hard collisions are computed using classical kinematics, and the contributions from collisions that are not hard can be estimated.

A reappraisal of the treatment of Purcell and Field is given by Glassgold who finds that quantum effects are important and that the cross section will be sensitive to the form of the potential for both the singlet and triplet states. Bender has also examined spin-exchange collisions and has calculated the frequency shift in the hydrogen hyperfine interaction arising from hydrogen-hydrogen spin exchange. This effect must be considered in the operation of a hydrogen maser as a frequency standard. Balling, Hanson, and Pipkin have presented a rather complete treatment of spin exchange by means of a density matrix formalism and have applied it to the electron-rubidium spin-exchange experiment.

One uncertainty inherent in any determination of a spin-exchange cross section is the accuracy of the measurement of the vapor density of the substance or substances participating in spin exchange. If one of the species is produced in a

discharge of some kind the problem is particularly acute. In the case of the alkali metals an accurate value of the vapor pressure is needed.

Experimental and theoretical values for σ_{ex} are of the order of 10^{-14} to 10^{-13} cm^2 , i.e., they are of the order of the cross sections for changing momentum of the colliding particles.

11/Pressure Shift of the Hyperfine Interaction

11-1 ORIGIN OF THE PRESSURE SHIFT

Optical pumping makes possible a precision determination of the hyperfine interaction in an atom as discussed earlier. The hyperfine interaction arises mainly from the Fermi contact interaction between the nuclear magnetic moment and the unpaired electron. The Hamiltonian for this scalar interaction is

$$\mathcal{H} = \frac{8\pi}{3} g_N g_e \beta_N \beta \mathbf{I} \cdot \mathbf{S}_i \delta(\mathbf{r}_{iN}) \quad (11-1)$$

where g_N and g_e are the nuclear and electronic g-factors, β_N and β are the nuclear and Bohr magnetons, $\mathbf{I}$ is the nuclear-spin angular momentum, $\mathbf{S}_i$ is the spin angular momentum of electron i , and $\delta(\mathbf{r}_{iN})$ is the Dirac delta function which is zero everywhere except at nucleus N .

Upon solving for the energy, the Fermi contact interaction is found to contribute to the hyperfine interaction an amount

$$E(\text{hyperfine}) = \frac{8\pi}{3} g_N g_e \beta_N \beta m_N m_i \psi_n^2(0) \quad (11-2)$$

where m_N and m_i are the magnetic quantum numbers describing the z component

of angular momentum of the nucleus N and the electron i . $\psi_n^2(0)$ is the wave function of electron i in state n evaluated at the nucleus N . It is assumed here that the interaction is isotropic. We see that, since the hyperfine interaction depends only upon the size of the nuclear magnetic moment and the electron wave function of the atom, it is a constant quantity for an isolated atom.

This presents the possibility of using an optically pumped vapor cell as a frequency standard or "atomic clock" whose base frequency is the hyperfine frequency of the atomic species used. However, it turns out that the hyperfine frequency as measured in such an experiment is dependent upon the pressure of buffer gas present in the vapor cell and upon the temperature of the cell. This is not surprising, as one would expect that during a collision between the atom and a buffer gas particle the wave function of the atom would be highly perturbed and the factor $\psi_n^2(0)$ in Eq. 11-2 would change. When averaged over all types of collisions $\langle \psi_n^2(0) \rangle_{av}$ would be different from $\psi_n^2(0)$ for the isolated atom. This effect is called "the pressure shift of the hyperfine interaction."

In frequency-standard applications one must work in the absence of a buffer gas or with a known pressure of buffer gas in order to correct for the pressure shift. There is also the possibility of using a mixture of buffer gases whose effect upon the wave function and, hence, $\psi_n^2(0)$ would exactly cancel one another.

Although the pressure shift introduces complications in frequency-standard applications, it is in itself an interesting and useful phenomenon. It is a measurable quantity directly related to interatomic interactions, and its interpretation presents another means by which the details of such interactions can be investigated.

11-2 EXPERIMENTAL RESULTS

Table 11-1 shows some representative experimental values of the pressure shift that are available at this time. It is seen that for the rubidium hyperfine interaction very light buffer gases show a positive pressure shift, i.e., an increase in $\langle \psi_n^2(0) \rangle$, while the heavy buffers show a negative pressure shift. Moreover, the variation from one buffer gas to another is smaller for the hyperfine interaction in the hydrogen isotopes than in the alkali metals. In addition, the variation seems to be

Table 11-1 Fractional Pressure Shifts of Hyperfine Frequencies in Various Buffer Gases^a

Buffer	H ^b	D ^b	T ^b	Na ^{23 c}	K ³⁹ (65° C)	Rb ⁸⁷ (25° C)	Cs ¹³³ (30° C)
He	4.80	—	—	73	93	105.3	174.0
Ne	2.88	3.24	3.24	45	52	57.4	70.7
A	-4.77	-4.52	-5.05	3	-1	-7.5	-27.2
Kr	—	—	—	-42	-91	-84.9	-141.4
Xe	—	—	—	-85	—	—	-261.1
H ₂	-0.56	—	—	62	72	96.6	206.7

(continued)

Table 11-1 (continued)

Buffer	H ^b	D ^b	T ^b	Na ²³ ^c	K ³⁹ (65° C)	Rb ⁸⁷ (25° C)	Cs ¹³³ (30° C)
D ₂	—	—	—	—	—	98.0	—
N ₂	—	—	—	49	—	76.1	117
CH ₄	—	—	—	—	—	— 73.2	—
n-C ₅ H ₁₂	—	—	—	—	—	—409.7	—
C(CH ₃) ₄	—	—	—	—	—	—420	—
n-C ₇ H ₁₆	—	—	—	—	—	—614.5	—

^aThe pressure shifts, $1/\nu(\partial\nu/\partial P)_T$, are tabulated in units of $10^{-3}/\text{mm Hg}$. The values are taken from Pipkin (1962), for H, D, and T; Arditi (1958b), and Ramsey (1964b) for Na²³; Bender (1958) for Rb⁸⁷; and Arditi (1958c) and Beaty (1958) for Cs¹³³.

^bPressure measured at 0° C.

^cPressure measured at 295° K.

greater for Cs than for Rb. This is reasonable since one would expect a larger effect upon electrons that are in states of higher principal quantum number and are more easily polarized or distorted by a colliding buffer particle. It would be very interesting to see what the numbers would be for other pumped species such as N and P. Also, it would be valuable to have numbers for other molecular buffer gases, especially those with permanent electric dipole moments.

11-3 THEORETICAL CALCULATIONS OF THE PRESSURE SHIFT

To date, the interpretation of the effect has taken two forms. The first approach, which was used for the alkali metal species, is essentially a parametric one in which empirical data are used to calculate the shift (Margenau, 1959; Herman, 1961; Robinson, 1960). This treatment leads to the result that the change in hyperfine energy for an atom is:

$$\Delta E(\text{hyperfine}) = \Delta E(\text{dispersion}) \left(\frac{1}{\bar{E} + I_2} + \frac{2}{I_1} \right) \varepsilon \quad (11-3)$$

where $\Delta E(\text{hyperfine})$ is the shift in hyperfine energy, $\Delta E(\text{dispersion})$ is the van der Waals energy between the alkali metal atom and the buffer gas particle, and I_1 and I_2 are the ionization energies of the alkali atom and buffer gas particle, respectively. $\bar{E}$ is an average excitation energy of the pumped atom which comes from applying the closure approximation to the second-order energy term arising in the perturbation treatment of the problem. $\bar{E}$ is usually taken as the alkali atom resonance energy or a weighted average of the P states of the alkali atom. ε is the hyperfine energy of the atom in free space and is proportional to $\psi_n^2(0)$.

In order to calculate the fractional pressure shift the expression in Eq. 11-3 must be multiplied by the classical configurational distribution function and

integrated over all possible configurations. This gives

$$\left\langle \frac{\Delta\nu}{\nu_0} \right\rangle = \frac{4\pi N}{h\nu_0} \int_0^\infty \Delta E(\text{hyperfine}) \exp\left\{\frac{-V(r)}{kT}\right\} r^2 dr \quad (11-4)$$

where $\Delta\nu$ is the shift in hyperfine frequency, ν_0 is the true hyperfine frequency, N is the density of buffer particles, and $V(r)$ is the potential energy function between an alkali atom and a buffer gas particle.

One can, for example, assume a Lennard-Jones potential for the interaction, calculate the van der Waals energy, and evaluate the shift from the expression in Eq. 11-4.

A different approach is to evaluate the Fermi contact interaction over the total wave function for the colliding system to obtain the correction to the hyperfine energy. This has been done by Clarke (1962; see reprint) who calculated the first-order perturbation correction to the H-He system. His result is similar to that in Eq. 11-4 except that $\Delta E(\text{hyperfine})/h\nu_0$ is replaced by

$$\frac{\Delta\nu(R)}{\nu_0} = \frac{\langle \psi_{\text{H-He}}(\mathbf{r}_\text{H}, \mathbf{r}_\text{He}, \mathbf{R}) | \sum_{i=1}^3 \mathbf{I}_\text{H} \cdot \mathbf{S}_i \delta(\mathbf{r}_{i\text{H}}) | \psi_{\text{H-He}}(\mathbf{r}_\text{H}, \mathbf{r}_\text{He}, \mathbf{R}) \rangle - \nu_0}{\langle \psi_{\text{H-He}}(\mathbf{r}_\text{H}, \mathbf{r}_\text{He}, \infty) | \sum_{i=1}^3 \mathbf{I}_\text{H} \cdot \mathbf{S}_i \delta(\mathbf{r}_{i\text{H}}) | \psi_{\text{H-He}}(\mathbf{r}_\text{H}, \mathbf{r}_\text{He}, \infty) \rangle}$$

where $\psi_{\text{H-He}}(\mathbf{r}_\text{H}, \mathbf{r}_\text{He}, \mathbf{R})$ is the wave function for the colliding system with inter-nuclear coordinates $\mathbf{R}$ and electron coordinates $\mathbf{r}_\text{H}$ and $\mathbf{r}_\text{He}$ associated with H and He. The operator in each matrix element is the Fermi contact interaction and is summed over each of the three electrons of the system.

Clarke also considered the mass-dependent quantum statistical correction and found it to be quite small ($\sim 4\%$), in disagreement with the then available data for the pressure shift of the hydrogen isotopes. However, a subsequent repeat of the experiments show very little mass dependence of the shift (see Table 11-1) in agreement with Clarke's calculation.

For those interested in interatomic and intermolecular interactions, the pressure shift of the hyperfine interaction will continue to be a valuable parameter.

A similar effect should be observed in accurate measurements of the Zeeman splitting. The pressure shift of the g-factor remains to be measured.