MAGNETIC RESONANCE

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Magnetic Resonance

Principles and Applications

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INTRODUCTION TO MAGNETIC RESONANCE
Principles and Applications

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Editor's Foreword

Undergraduate teaching in physics is going through a phase of rapid evolution. On the frontier of physics new information is literally pouring in, new perspectives are opening up, and new concepts emerging. For the beginning student, the distance to be covered from the freshman year to graduate research work is constantly expanding.

Professional education in physics must therefore deal with the very real problem of the need for thoughtful condensation of the material presented, and the question of what may and should reasonably be achieved in four years of undergraduate instruction.

It is generally agreed, on the one hand, that a thorough presentation of the fundamentals of both classical and elementary quantum physics is essential. On the other hand, it is understandably desirable to involve the student in the excitement offered by the many interesting new developments in all fields of physics. The discussion of such new topics would provide the student with an opportunity to observe the actual growth process of science: new experiments, new techniques, and the attempts to relate new results to existing or emerging theoretical views. The study of the well-established, introductory subjects of physics appears to lack these exciting aspects and to offer little room for the display of creativity, except as a historical fact.

It has at last been recognized that this need not entirely be so; that in fact the close ties between the traditional and the modern can be exploited to establish relationships between the classical subjects and current endeavors (e.g., classical mechanics and space navigation, wave optics and radar interferometry, etc.). To develop such links wherever they exist and to put the essential parts of the traditional subjects in a modern perspective is an urgent and rewarding task. There is clearly no general agreement about the manner in which a broad subject can be reduced to its essentials, or what these essentials are, in the context of undergraduate education. The great variety of educational situations will naturally give rise to a diversity of approaches. Interested teachers will find their own challenge and excitement in experimenting with various alternatives. The recent burgeoning of such introductory undergraudate texts as the Feynman lectures, the Berkeley physics course, and the Massachusetts Institute of Technology introductory physics texts bear witness to the interest that has been aroused by the problem of bringing the fundamentals of physics to the undergraduate in a novel way.

Therefore, a new series entitled *Modern Physics Monographs* has been undertaken which intends to continue this process. This series will present material for the post-introductory undergraduate courses, that is for those normally given in the junior and senior years. At this level, there exist on the one hand courses of a specialized nature, which offer the undergraduate student an introduction to the great diversity of topics of physical science, ranging from particle physics to nuclear, atomic, solid state, plasma, and astrophysics, to name but a few. On the other hand, in these two years, basic subject matter previously touched upon may be deepened and extended; indeed, many curricula carry such a "second round" covering the fundamentals again at a more advanced level.

There is an infinite variety of ways to organize this more advanced and specialized material. We hope that the *Modern Physics Monographs* series will help to provide the lecturer in the field with additional flexibility in choosing his course material and, if he is inclined to experiment, enable him to bring into his course topics not generally covered in standard textbooks. In addition, the student will have access to a variety of inexpensive collateral reading material.

For these very reasons, the books of this series are *not* intended to be textbooks, but rather monographs, that is, works that cover a more restricted area in a space of approximately 100 to 250 pages. They contain problems with and without answers, and could either supplement existing texts or be used in groups as a replacement for a single text.

The editor is aware of the fact that the presentation of a modern physics topic on an elementary level is a major didactic challenge for the writer, and so all attention is being given to publish texts that will be readable, informative, and helpful to the student. Critical comments from all interested parties are invited, and suggestions for additional texts of general interest will be welcomed.

Felix Villars

Cambridge, Massachusetts
April 1970

Preface

It is a very common and educationally healthy practice for an undergraduate physicist to do some work in a research laboratory or an advanced teaching laboratory of "research grade." Today, in contrast to twenty years ago, even the student at relatively small colleges and universities participates in research experiments or in experiments only slightly removed (in time and difficulty) from active research. The largest problem facing such students is often not just to find suitable literature to introduce them to the work of the laboratory, but to perceive what relationship a particular experimental activity has with other experiments, with other branches of physics, other branches of science, and most important of all to the student, with the concepts, information, and techniques taught in formal course work. This book is intended to serve as a supplementary text in formal courses on the undergraduate level in atomic physics, solid state physics, and even nuclear physics. It should be regarded as collateral reading material for some experiments in advanced undergraduate laboratories, and for students with summer jobs or informal laboratory "courses" in active research labs. It may also be regarded as an interim text for the beginning graduate student who might not be quite conversant enough in quantum mechanics to manage the introductory graduate level texts, such as the ones by Pake and by Slichter.

I have written from the bias of a "magnetic resonator" working in solid state physics, and as such intended the approach to the material in Chapter 3 to represent the style or point of view that will aid the student in acquiring a useful grasp of the diverse applications of magnetic resonance. In general no command of the formal apparatus of quantum mechanics is required of the reader, although I have not hesitated to introduce some quantum mechanical explanations in parallel with classical or semiclassical ideas when it seemed appropriate. However, for the most part I have tried to exploit the classical concepts of frequency modulation and random walk as introduced in Chapter 3, and have been to some extent influenced in my choice of subjects by the possibility of their explanation in terms of these concepts.

There was another reason for leaning so heavily on this conceptual crutch. The research laboratory engaged in any area of activity acquires a cryptic language of its own, which is spoken in the laboratory and at blackboard discussion but which seldom receives, these days, an imprimatur of respectability by surviving to the journal article stage. By then the ideas have become fully dressed in the elegance and precision of theoretical physics, and consequently they are hard for the student to find. In my judgment, the most characteristic qualitative idea introduced by applications of magnetic resonance is the concept of motional narrowing, and therefore I have made the complementary approaches of random walks and frequency modulation central to the book. I have also digressed whenever it seemed appropriate to indicate the application of these ideas in other areas of physics.

Somewhat apologetically I must call attention to the absence of any explicit treatment of the vast and important field of electron paramagnetic resonance in solids. I simply found that with the exception of exchange narrowing, which *is* discussed, I could not write on such subjects as g shifts, crystal field splittings, and spin Hamiltonians in the same context and with the same language that I believe unifies the rest of the book. In particular, I could not think of any way to discuss the subjects without using much more quantum mechanics than I thought appropriate. That may be the fault of my own background, since I learned whatever I do know about EPR *after* acquiring the standard skills in quantum mechanics, rather than before, as was the case when I was first introduced to NMR. For electron paramagnetic resonance, I can think of no way to simplify or clarify the introductions to the subject by Pake and by Slichter, so I have chosen to omit it entirely.

I hope students with a variety of objectives will be able to use this book without necessarily reading all of it. Chapter 1 is basic to everything, but it duplicates material which often appears in classical mechanics courses, and which should appear in all atomic or modern physics courses. Those interested in magnetic resonances in excited states may proceed directly to the relevant parts of Chapter 6. Those interested in optical pumping should get the main ideas of Chapters 2 and 3 in mind before tackling Chapter 6. (And then such students should proceed to the excellent collection of important papers assembled in a reprint volume by Bernheim.) For students whose interest is in applications to solid state physics, the first four chapters are all relevant. Chapter 5 is in its entirety an illustrative example, an attempt to mashall a large part of the previous material to describe the results of fifteen years of magnetic research on simple metals, mainly the alkalis.

There are a few problems at the end of each chapter. Most are easy and quantitative in nature, chosen to advance my opinion that quantitative as well as qualitative understanding is essential. A few problems serve the time-honored role of introducing new material the author believed interesting or important, but could not gracefully fit into the text. In most cases, I have chosen references by applying the criterion that the student should be directed to the next most accessible place he should look to find something rather than to the most complete discussion, or to the original work. I did not make a special effort to avoid reference to the original work, however, particularly when it is readable. A brief paragraph or two at the end of each chapter has been written with the above standard in mind: namely, that the reference given should be the next place for the student to go.

I think it will be obvious to any physicist who glances at this book and knows Professor Charles P. Slichter that it owes a great debt to him. I should also acknowledge that I learned about the usefulness of the explicit application of the language of frequency modulation from Professor Hans Dehmelt. The colleagues and students who contributed to my education in the nearly fifteen years since my association with Professors Slichter and Dehmelt are so numerous they can only be thanked *en masse*. Mrs. Kate Ellis and Mrs. Lillian Horton typed a draft and the final manuscript with great dispatch and unfailing cheerfulness. The production of the book was kept on schedule with the cooperation of Miss Nancy Ann Chinchor, who lightened the tedious task of reading the galley proofs.

Robert T. Schumacher

Pittsburgh, Pennsylvania
April 1970

Contents

CHAPTER 1

Basic Principles

Historically, experimental investigations into the quantum properties of angular momentum and magnetic moments followed the same course that now seems to be the most natural in introducing the subject conceptually. This first chapter is concerned with the concepts and the experiments on isolated atomic systems with angular momentum, which began with the molecular beam experiments of Stern in the 1920's and which lead naturally into the magnetic resonance experiments of Rabi in the 1930's. The material is probably familiar to all students with the background of an introductory course in modern physics. However, it is recommended that even students with confidence in their command of the subject study the chapter, if only to identify special terminology and points of view relied upon in later chapters. The student who finds the quantum mechanical references of Section 1-4 somewhat obscure should repair to the brief Appendix for some help, at least in the mathematical manipulations of the quantum mechanics of the spin $\frac{1}{2}$ system in magnetic fields.

1-1. DEFINITIONS

A system consisting of a mass undergoing circular motion about a fixed point in a plane has *angular momentum.* If the mass carries electrical charge, it has a *magnetic moment* that is proportional to the angular momentum. It is comforting to know that such simple statements are true in general for quantum mechanical systems, and that, for *magnetic dipole* moments, the proportionality factor is a scalar. The theorem stating this is an application of a powerful and ubiquitous statement known as the Wigner–Eckart theorem. We are concerned with angular momenta of various atomic, nuclear, and elementary particle systems. Table 1-1 shows the conventional symbols used for most of the systems in which we are interested. When the discussion is about an abstract angular momentum vector, we usually use the vector symbol **J**, which serves also as the total angular momentum of an atom.

Table 1-1
Conventional Symbols for Angular Momenta

System	Symbol
single electron spin	$\mathbf{S}$
electron orbit	$\mathbf{L}$
atom	$\mathbf{J} = (\mathbf{L} + \mathbf{S})$
nucleus	$\mathbf{I}$
atom including nucleus	$\mathbf{F} = \mathbf{I} + \mathbf{J}$

We also find it convenient to consider the angular momentum vector symbols to be dimensionless, and to display the units in which angular momentum is measured explicitly. The fundamental unit is, of course, $h/2\pi = \hbar$, Planck's constant. Thus, the Wigner–Eckart theorem states simply

$$\boldsymbol{\mu} = \gamma\hbar\mathbf{J} \tag{1-1}$$

where γ, the *gyromagnetic ratio* (more rationally, the magnetogyric ratio) is the scalar promised by the theorem. Now, if one pursues the example of the opening paragraph, the factor γ can be calculated immediately. The angular momentum is $|\hbar\mathbf{J}| = |\mathbf{r} \times m\mathbf{v}| = mr^2\omega$, where $\mathbf{r}$ is the orbit's radius, ω the angular frequency, m the mass, and $\mathbf{v}$ the velocity. The magnetic moment, in Gaussian units, is $\boldsymbol{\mu} = i\mathbf{A}/c$, where $A = \pi r^2$ is the orbit's area; the vector is perpendicular to the orbital plane, as in the case of the angular momentum. Thus,

$$\frac{iA}{c} = \frac{i\pi r^2}{c} = \frac{q\omega r^2}{2c} = \frac{J\hbar q}{2mc} \tag{1-2}$$

If the particle is an electron with charge $e = -4.8 \times 10^{-10}$ esu, and mass $m = 9.1 \times 10^{-28}$ g, the gyromagnetic ratio, $\gamma = e/2mc$, is related to the Bohr magneton:

$$\beta_0 = \frac{e\hbar}{2mc} = \hbar\gamma = -0.927 \times 10^{-20} \text{ ergs/G}$$

For nuclei, it is convenient to define a nuclear Bohr magneton

$$\mu_0 = \frac{|e|\,\hbar}{2Mc} = 5.05 \times 10^{-24} \text{ ergs/G}$$

where M is the proton mass.

Electrons, protons, neutrons, and μ mesons have intrinsic angular momentum. Atoms and nuclei of interest to us are compound systems, the total angular momentum and magnetic moment of which are still proportional by the Wigner–Eckart theorem, but the proportionality factor of which depends on the details of the system. Those details are conventionally absorbed into a *g factor*, or *spectroscopic splitting factor*. This factor is g_J, the Landé g factor for atoms, or $g = 2.000\ldots$, according to the Dirac equation, for electrons and μ mesons. We define the nuclear g factor by analogy. For the most part, it remains an experimental parameter characterizing nuclear moments, since, in most cases, nuclear theory is not yet able to provide better than rough estimates of its magnitude. In general, then, the expression

$$\boldsymbol{\mu}_J = g_J\left(\frac{e}{2mc}\right)\hbar\mathbf{J} = g\beta_0\,\mathbf{J} = \gamma_e\,\hbar\mathbf{J}$$

or (1-3)

$$\boldsymbol{\mu}_I = g_I\,\mu_0\,\mathbf{I} = \gamma_n\,\hbar\mathbf{I}$$

gives the relation between $\boldsymbol{\mu}$ and $\mathbf{J}$, or $\mathbf{I}$, and it defines g. Equation (1-3) also defines the gyromagnetic ratio γ, which is now $g(e/2mc)$ for a system with intrinsic angular momentum (spin). Tables, particularly the most commonly encountered tables of nuclear moments, publish a quantity called "the magnetic moment in units of the Nuclear Bohr magneton." The maximum projection of $\mathbf{J}$ along any axis occurs for the state $M_J = J$. The magnetic moment is $\boldsymbol{\mu}_J = g\beta_0\,\mathbf{J}$, and the published number is gJ.

1-2. ENERGY IN AN EXTERNAL MAGNETIC FIELD: SPATIAL QUANTIZATION

The energy E of a magnetic moment μ in an external field[1] $\mathbf{H}$ is given by the familiar expression

$$E = -\boldsymbol{\mu}\cdot\mathbf{H} \tag{1-4}$$

or, in terms of the angular momentum,

$$E = -\,g\beta_0\,Hm_J \tag{1-5}$$

[1] In a vacuum it does not matter whether one uses H or B for the magnetic field if the quantities are expressed in Gaussian units. Strictly speaking, one should use B, but conventionally most of the literature uses H, a practice that we follow. Occasionally it is important to make the distinction in solid state physics applications, and then it is well established that the *correctly calculated* B is to be used.

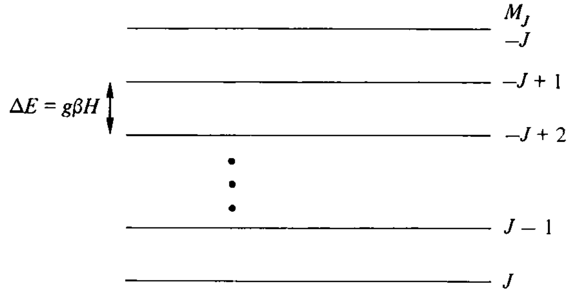

Fig. 1-1 Energy-level diagram for spin of angular momentum **J** in magnetic field **H**.

where m_J is the projection of **J** on **H**. Quantum mechanics restricts m_J to the $2J+1$ integral or half-integral values. The energy-level diagram corresponding to Eq. (1-5) is shown in Fig. 1-1.

1-3. STERN–GERLACH EXPERIMENT

The application of a magnetic field H removes the $2J+1$ degeneracy of the magnetic sublevels, as we have seen. Although these states are no longer degenerate, the energy differences between them are very small. In a field of 10^4 G, Eq. (1-5) corresponds to an energy separation of 1 cm^{-1} or about 10^{-4} eV for electron moments, 10^{-4} cm^{-1} or 10^{-8} eV for nuclear moments. This energy difference must be perceived against a background of 200 cm^{-1} or 0.025 eV of thermal energy at room temperature and several electron volts of energy for atomic transitions. Until the early 1920's, the consequences of spatial quantization had been manifested primarily through the Zeeman effect and the Faraday and other magneto-optic effects. The Zeeman effect was incompletely understood prior to the discovery of electron spin, and the quantitative relation of spatial quantization to the Faraday effect was obscure.

The reality of spatial quantization was demonstrated in a particularly graphic fashion by the Stern–Gerlach experiment, successfully performed in 1922. If a beam of neutral atoms passes through a homogeneous magnetic field, it is undeflected by that field, even though the magnetic degeneracy is lifted. But if the field is not spatially homogeneous, there is a net force on the moments in the beam that is given by the expression

$$\mathbf{F} = (\boldsymbol{\mu} \cdot \nabla)\mathbf{H} = \mu_x \frac{\partial \mathbf{H}}{\partial x} + \mu_y \frac{\partial \mathbf{H}}{\partial y} + \mu_z \frac{\partial \mathbf{H}}{\partial z} \qquad (1\text{-}6)$$

There is a component of this force that is constant while the moment is in the gradient, and it produces a deflection of the beam that is proportional to μ_z. To see that, choose the following simplest possible field gradient. See Fig. 1-2. The beam travels in the x direction with the

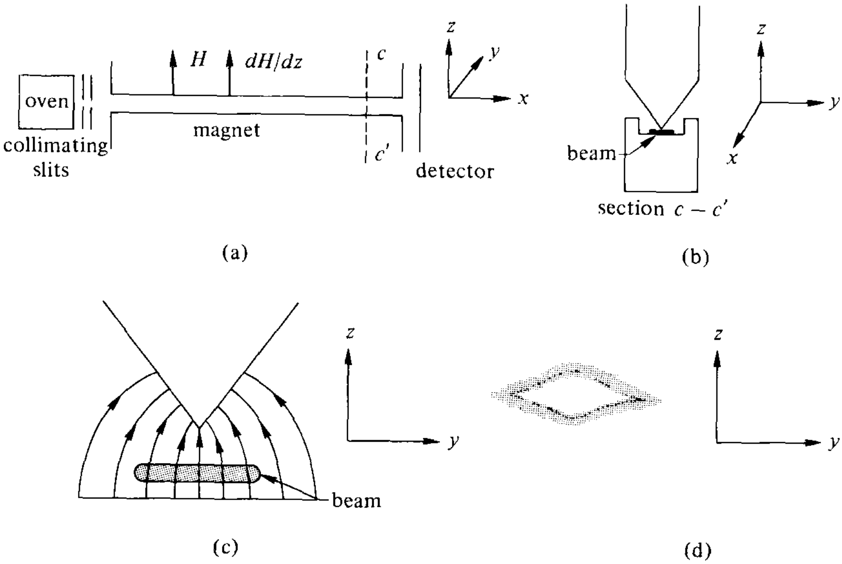

Fig. 1-2 Schematic representation of Stern–Gerlach apparatus. (a) Arrangement of main components: oven, collimating slits, magnet, and detector. (b) Cross section $c - c'$ of (a). (c) Enlarged view of beam and magnetic field in region of the beam. (d) Appearance of film deposited on substrate in original experiments of Stern.

field arranged so that $H_x = 0$. The field is principally in the z direction. All derivatives of H with respect to x vanish, and, in the beam region, both $\nabla \cdot \mathbf{H} = 0$ and $\nabla \times \mathbf{H} = 0$ are satisfied. The components of Eq. (1-6) are

$$F_x = 0 \qquad F_y = \mu_y \frac{\partial H_y}{\partial y} + \mu_z \frac{\partial H_y}{\partial z} \qquad F_z = \mu_y \frac{\partial H_z}{\partial y} + \mu_z \frac{\partial H_z}{\partial z} \tag{1-7}$$

Furthermore, let the beam lie in the symmetry plane $y = 0$, where $H_y = 0$ (Fig. 1-2c). Then $\partial H_y/\partial z = 0$, and, since $\nabla \times \mathbf{H} = 0$, $\partial H_z/\partial y = \partial H_y/\partial z = 0$. Since $\nabla \cdot \mathbf{H} = 0$, $\partial H_y/\partial y = -\partial H_z/\partial z$, Eq. (1-7) reduces to

$$F_x = 0 \qquad F_y = -\mu_y \frac{\partial H_z}{\partial z} \qquad F_z = \mu_z \frac{\partial H_z}{\partial z} \tag{1-8}$$

In the next section, we emphasize in great detail that the magnitude of the field H_z produces a torque $\boldsymbol{\mu} \times \mathbf{H}$, causing a precession about $\mathbf{H}$ (which is virtually entirely H_z at the beam coordinate) such that μ_z is constant and μ_y oscillates about an average value of zero. So the only component of the force that produces a net deflection is in the z direction, and it may be written in terms of the magnetic quantum number as $F_z = m_J g\beta_0(\partial H_z/\partial z)$. The presence of m_J means that the beam splits into $2J + 1$ components. The first experiment was done on silver (partly because the deposit could be easily "developed"), and two components were seen, as illustrated in Fig. 1-2d.[2] We now know that $2J + 1 = 2$ requires $J = \frac{1}{2}$, and that the ground state of the silver atom is an orbital S state with a single electron of spin $\frac{1}{2}$. The first experiment was done prior to the discovery of electron spin, but the result was not interpreted as requiring half-integral spin since it was assumed silver had an orbital angular momentum $L = 1$ and the $m_L = 0$ state was not allowed in old quantum theory.

Even in its simplest form the experiment has several components, none trivial, so that molecular beam experiments have long been known as the most difficult in atomic physics. The experimental problems to be solved include a high enough vacuum so that a typical beam atom can traverse the apparatus without colliding with a residual gas molecule in a meter or more of flight. The source, usually an oven with a small hole, must produce a well-collimated beam. The field gradient must be as large as possible, but the magnetic field itself cannot change too abruptly in time as sensed by the moving magnetic moment that passes from the fieldfree region to a region of maximum field gradient, and then out again to a fieldfree region before striking the detector. Finally, some device must detect, with considerable spatial resolution, the beam intensity. The modern solution of these problems is discussed in detail in the definitive monograph on molecular beams by Ramsey [2]. A somewhat briefer discussion appears in another standard reference in the field of magnetic resonance, Kopfermann's *Nuclear Moments* [3]. Among the refinements particularly useful when two Stern–Gerlach apparatuses are put in series for the standard molecular beam resonance experiment (Section 1-4) have been velocity selectors between the oven and the field region so all molecules in the beam receive the same deflection. Sophisticated universal detectors, which partially ionize the beam and send it through a simple mass spectrometer before it registers on the ultimate detector, have also

[2] The student will find it an amusing exercise in the propagation of errors to watch for illustrations such as Fig. 1-2 in which the beam is traveling in the y direction, transverse to the long dimension of the apparatus. As far as I can determine, the first such incorrect illustration appeared in A. Sommerfeld's *Atombau und Spectrallinien* [1], in all editions subsequent to 1923. It is reproduced in many texts of that school, but it also still appears in texts published in the United States as recently as 1967.

been developed. (See references listed at the end of the chapter for more discussion of experimental techniques.)

The Stern–Gerlach technique, by itself, reached its pinnacle of usefulness under the direction of Stern, particularly with the aid of Otto Frisch and I. Estermann. Although the resonance method of Rabi did prove to offer unheard of precision compared to the nonresonant experiments, the basic technique did provide a few triumphs beyond the first demonstration of spatial quantization. One of these was the discovery of the anomalous g factor of the proton (i.e., that $g_p = 5.59\ldots$ rather than $g = 2.000\ldots$, as expected from the Dirac theory of a spin $\frac{1}{2}$ particle). The initial report of this work appeared in *Nature* in 1933 [4], and it is a model of elegant brevity. The student who understands it, sentence by sentence, has a good working grasp of many of the necessary fundamentals of modern physics.

It should be emphasized that the Stern–Gerlach apparatus is a very useful practical example of a quantum mechanical state selector, or beam polarizer. The separated beams of moments of that energy from the field gradient region, each characterized by its own m_J, are polarized. The apparatus may be reversed in function and a partially or fully polarized beam sent in. Its trajectory in the apparatus is determined by the state function (i.e., the m_J level) of the constituents of the beam, so the apparatus now functions as an analyzer. These functions are important to understand and distinguish in following the magnetic resonance experiment of Rabi. A comprehensive discussion is given in volume 3 of the *Feynman Lectures on Physics* [5].

1-4. THE RABI MAGNETIC RESONANCE EXPERIMENT

If a Stern–Gerlach apparatus can be a state selector, it can also be an analyzer. What could be more natural than to put two of them in series, with some experiment in between? In the 1930's, Rabi, who had done postdoctoral work under Stern at Hamburg, performed the first magnetic resonance experiment and made the first precision nuclear magnetic moment measurement, in a homogeneous magnetic field between a polarizer and analyzer. Figure 1-3 shows two inhomogeneous fields, produced by the conventionally designated A and B magnets, with the homogeneous C magnet between them. In the C region, the magnetic resonance experiment causes transitions between magnetic quantum levels. Consider a $J = \frac{1}{2}$ system. Figure 1-3 shows the polarizer and analyzer with field gradients in the same direction. Also, care is taken that the direction of the field H itself always points in the same direction. At the end of the polarizer, one of the two separated beams may be deflected or stopped by a baffle, leaving a beam of pure $m_J = \frac{1}{2}$ particles, for instance,