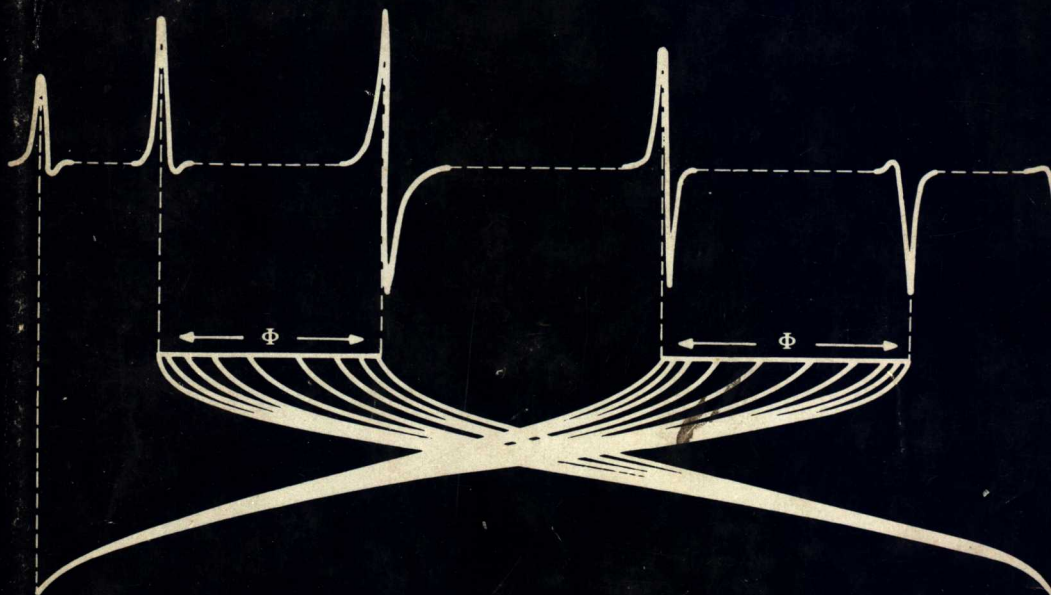


THEORY & APPLICATIONS OF



ELECTRON SPIN RESONANCE

WALTER GORD

TECHNIQUES OF CHEMISTRY. ARNOLD WEISSBERGER, SERIES EDITOR
VOLUME XV. EDITED BY W. WEST

TECHNIQUES OF CHEMISTRY

VOLUME XV—W. West, *Editor*

THEORY AND APPLICATIONS OF ELECTRON SPIN RESONANCE

WALTER GORDY

Duke University

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York · Chichester · Brisbane · Toronto

Copyright ©1980 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

Library of Congress Cataloging in Publication Data

Gordy, Walter, 1909-

Theory and applications of electron spin resonance.

(Techniques of chemistry ; v. 15)

“A Wiley-Interscience publication.”

“Completes Chemical applications of spectroscopy.”

Includes index.

I. Electron paramagnetic resonance spectroscopy.

I. Chemical applications of spectroscopy.

II. Title.

QD61.T4 vol. 15 [QD96.E4] 542'.08]

ISBN 0-471-93162-4 79-12377

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion — Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can be easily recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

The present volume, *Theory and Applications of Electron Spin Resonance* by Walter Gordy, completes *Chemical Applications of Spectroscopy*, edited by W. West and published as Volume IX of the series Technique of Organic Chemistry.

It is a pleasure to recognize Dr. West's never-failing interest in a task he undertook more than twenty years ago. His devotion is matched by the author's willingness to invest time and effort in a treatise commensurate to the great importance of the field.

Authors and editors hope that readers will find the volumes in this series useful and will communicate to them any criticisms and suggestions for improvements.

ARNOLD WEISSBERGER

*Research Laboratories
Eastman Kodak Company
Rochester, New York 14650*

PREFACE

At this advanced stage in the development of electron paramagnetic resonance (epr) an attempt to contain in one volume a comprehensive treatment of it would be foolhardy. No such attempt is made here, but the selection of the limited material to be included has been one of the more difficult tasks involved in the preparation of this volume. Electron magnetic resonance spectroscopy has spread like a forest fire throughout solid-state physics, organic and inorganic chemistry, biochemistry, and biological physics and is now spreading rapidly in pure and applied biology. The power it gives to observe with precision unpaired electrons within condensed matter—liquids and solids—has made it a tool for all scientists, but most particularly for chemists.

Our limited goal has been the explanation of the theory essential for the understanding and interpretation of electron-spin resonance (esr) spectra in condensed matter and its applications to paramagnetic species induced in nonmagnetic or diamagnetic substances by various physical or chemical means. We treat doublet-spin-state spectra of free radicals produced by bond dissociation or molecular ionization and the triplet-state spectra of molecules, of charge-transfer complexes, and of exchange-coupled radical pairs. We include the spectra of ordered species in single crystals; of randomly oriented species in powders, polymers, or glassy solutions; and of tumbling free radicals in liquid solutions. Numerous spectra of various types are interpreted, and the derived parameters tabulated. To a very limited degree, the volume is a source book of selected information that has been gained from esr in the past.

By selection of *electron-spin resonance* as a title rather than the more general term, *electron paramagnetic resonance*, we sought to remove from consideration all problems of gaseous atoms or molecules, in which the orbital angular momentum joins in the resonance. Nevertheless, partly to show what the subject is not, we found it desirable in the introductory chapter to give a brief discussion of the magnetic resonance of free atoms. Although the orbital moments do not directly participate in the resonance motions in the condensed systems that we treat, they do influence to a degree the spin-resonance frequencies through residual spin-orbit couplings. Thus one cannot entirely forget the orbitals in any treatment of esr. The most pronounced effects of orbital moments on electron magnetic resonance occur for the salts of the transition elements, especially for the rare-earth salts. These naturally occurring magnetic species were the first to be investigated with esr and they have been the most thoroughly and extensively studied. Hence

we decided that the most significant containment of our subject material could be made by omission of the transition ions. Their inclusion is rendered superfluous by the lengthy treatise, *Paramagnetic Resonance of the Transition Ions*, by Abragam and Bleaney (Clarendon, Oxford; 1970), probably the two most qualified to write on this topic. To further contain the subject material, descriptions of experimental techniques and instrumentation are not included. Regretably, we had to omit the description of electron-electron nuclear double resonance (ELDOR) and saturation-transfer spectroscopy, which are subjects suitable for individual monographs. Although the basic theory for electron-nuclear double resonance (ENDOR) is developed, its application to the spectra is not specifically illustrated. A recent book, *Electron Spin Double Resonance Spectroscopy*, by Kevan and Kisper (Wiley-Interscience, New York, 1976), is devoted entirely to ENDOR spectroscopy. Saturation-transfer esr spectroscopy, a new technique developed by Larry R. Dalton and his associates, is most useful for observation of the large spin-labeled biological polymers in viscous solutions, a subject of great importance in biophysical and biochemical areas. The powerful electron spin-labeling technique introduced by H. M. McConnell and his associates has developed into an extensive subfield of esr spectroscopy, which we also regret having to exclude from this limited volume.

This book could not have been written without the diligent and effective work of my wife, Vida Miller Gordy, who typed and edited the entire first draft and read and marked the final copy. Mrs. Jean Luffman typed the final manuscript with accuracy and clarity. Many of the illustrations were drawn by Mrs. Dorothy Bailey. The former Duke graduate students and postdoctoral fellows who worked in esr spectroscopy contributed directly or indirectly to this volume through their earlier collaborations with me. I am particularly indebted to Drs. Ichiro Miyagawa, Donald Chesnut, Peter Smith, Howard Shields, Joseph Hadley, William Nelson, F. M. Atwater, and Louis Dimmey, who kindly read parts of this manuscript and made helpful suggestions. During the considerable time required for completion of this volume I have benefited from the kindly encouragement and exceptional patience of Dr. William West. For these courtesies, and for his careful reading of the manuscript, I am sincerely grateful.

WALTER GORDY

Durham, North Carolina
May 1979

CONTENTS

Chapter I	
Introduction	1
Chapter II	
The Spin Hamiltonian	17
Chapter III	
Characteristic Energies and Frequencies	44
Chapter IV	
Line Strengths, Line Shapes, and Relaxation Phenomena	91
Chapter V	
Analysis of Spectra in Single Crystals	150
Chapter VI	
Interpretation of Nuclear Coupling in Oriented Free Radicals	198
Chapter VII	
Relation of the g Tensor to Molecular Structure	305
Chapter VIII	
Randomly Oriented Radicals in Solids	354
Chapter IX	
Free Radicals in Liquid Solutions	442
Chapter X	
Triplet-state ESR	543
Appendix	602
Author Index	605
Subject Index	617

Chapter I

INTRODUCTION

1. Magnetic Resonance of Free Atoms	4
a. The Landé g Factor	4
b. Nuclear-magnetic Interactions	6
2. Description of Atomic Orbitals	11
3. Nature of Resonance in Condensed Matter	12
a. Effects of Chemical Bonds	13
b. Orbital Substates and Effective Orbital Quantum Numbers	15
c. Other Treatments of ESR	15

Electronic paramagnetic resonance, first detected by the Russian scientist Zavoisky [1] in 1945, represents a powerful method for the study of many properties of matter of interest to chemists, physicists, and biologists. The theoretical and experimental methods were developed mostly at Oxford, England by a theoretical group led by M. H. L. Pryce and A. Abragam and an experimental team led by B. Bleaney. The foundation of this field of spectroscopy was provided by the earlier theoretical work on magnetism, notably by J. H. Van Vleck of Harvard, and the experimental measurements on magnetic dispersion, notably by C. J. Gorter at Leyden. General reviews describing these early developments are listed at the end of the chapter [2-10].

Classically, this resonance consists of the Larmor precession of a free electron-spin moment, an atomic or a molecular moment about an externally applied magnetic field. Quantum mechanically, the resonance is described as a transition between Zeeman levels separated by the applied field. The method is not limited to the naturally occurring paramagnetic substances, since electrons can always be unpaired and paramagnetism produced by irradiation or other physical or chemical treatment of nonmagnetic substances. Paramagnetic resonance is commonly observed in solids, liquids, and gases and also in both liquid and solid solutions. Probably no method is more effective for the study of radiation chemistry of the solid state than is electron paramagnetic resonance

or electron spin resonance, commonly designated as epr and esr. Microwave radiation used for observation of the spectra readily penetrates most nonmetallic solids. Increasingly, the epr or esr method is being used to detect trace radicals in organic and biological substances and to study transient radicals in chemical reactions. Essentially all organic chemicals and biochemicals can be studied with this method.

In its purest form, esr corresponds to a flipping over of the free electron-spin vector—along with its associated spin magnetic moment—in an imposed magnetic field. The classical energy of a magnetic dipole moment μ in a magnetic field \mathbf{H} is $-\mu \cdot \mathbf{H}$, or $-\mu_H H$, where μ_H is the component of the dipole moment along the field. The electron-spin moment can have only two components along the field, $\mu_H = \beta$ and $-\beta$, where β is the Bohr magneton. These correspond to the two allowed values of the electron-spin quantum number, $M_S = 1/2$ and $M_S = -1/2$. Thus there are two spin states corresponding to energies βH and $-\beta H$, with energy difference $2\beta H$. More precisely, this energy difference is $g_s \beta H$, where $g_s = 2.0023$ for the completely free electron-spin moment. With the Bohr rule, $h\nu = E_{M=1/2} - E_{M=-1/2} = g_s \beta H$, one finds the esr frequency to be

$$\nu = \frac{g_s \beta H}{h} \quad (1.1)$$

where h is Planck's constant. In the ideal case, where there are no internal interactions but only interactions with the externally applied field, \mathbf{H} , the resonance occurs at a frequency of

$$\nu(\text{in megahertz}) = 2.8024 H(\text{in gauss}) \quad (1.2)$$

It is interesting that this frequency corresponds to the classical Larmor precessional frequency of the spin moment about the field direction.

In actual observation of the resonance one usually leaves the microwave frequency fixed and sweeps through the resonance by varying the strength of the magnetic field imposed. Thus the esr curves traced by the spectrometer represent a plot of intensity of absorption against magnetic field strength at a fixed radiation frequency. At a constant frequency of ν_0 , the resonant field strength is

$$H_0 = \frac{h\nu_0}{g_s \beta} \quad (1.3)$$

The ideal case of the free electron spin is not completely achieved but is closely approached in almost all resonances in molecular free radicals. Thus if one expects to observe the resonance with 3-cm microwaves (10,000 MHz), a field

of the order of 3570 G must be applied. If one wishes to observe it with 1-cm waves (30,000 MHz), a field of the order of 10,700 G is required. Since these fields are easily obtainable in the laboratory, most of the spectra are observed in the microwave region of 1 to 3 cm. Excellent commercial epr spectrometers are now available for observations in this range.

Most of the stable molecules, excluding those containing transition elements, have all their electrons neatly paired so that their spin moments point in opposite directions and mutually cancel. The pairing of electrons was recognized as an important phenomenon in chemical bonding even before it was realized that the electron has a spin moment. Now it is known from the Pauli exclusion principle that two electrons can occupy the same atomic or molecular orbital only when their spin moments are opposed. Thus the two electrons of a fully occupied bonding molecular orbital or of a covalent chemical bond have no resultant electron-spin moment and can have no esr. Only molecules or radicals having an orbital or orbitals occupied by a single (unpaired) electron can exhibit esr. However, one can produce unpaired electrons by breaking chemical bonds or by lifting electrons from paired, singlet-state orbitals into excited triplet states and can then use esr to examine the resulting species.

If the electron spin were sufficiently free to give the simple resonance frequency of (1.1), we could learn that unpaired spins were present and could learn their concentrations, their rates of buildup or decay—but little else. In practice, however, there are always magnetic fields within the paramagnetic substances that interact with the electron-spin moment to perturb the resonance. These internal fields may split the esr into a complex multiplet or may simply alter its width or frequency. Among the most informative of the internal perturbing fields are those arising from nuclear magnetic moments. Internal magnetic fields also arise from orbital motions of the electrons. Although the orbital magnetic moments in molecular free radicals are largely quenched by crystalline electric fields of solids or by strong electric fields along chemical bonds, weak internal fields can be induced by the applied field through admixture of the orbital states. These induced fields displace the resonance slightly from its free-spin value. This displacement is generally anisotropic so that the g factor of (1.1) is most often not a simple constant but a tensor. By evaluating the principal elements of the anisotropic g tensor, one can often learn the symmetry of the internal electric fields and the orientation of certain chemical bonds and orbitals in the free radical or excited molecule.

In the absence of an externally applied magnetic field or of internal interactions, the spin moments will have no preferred direction, and the spins will be randomly oriented. If a uniform magnetic field is imposed on the sample consisting of a magnetic species with $S = 1/2$, the components of spin angular momentum will be resolved along the field, corresponding to the two allowed states, $M_S = 1/2$ (spin up) and $M_S = -1/2$ (spin down). Within an extremely

small fraction of a second after the field is on—the time it takes for the spins to come to thermal equilibrium—slightly more than half the spins are found to be in the state of lower energy, $M_S = -1/2$. For example, such a paramagnetic sample at room temperature in a magnetic field of 3000 G will have approximately 50.05% of its spins in the lower state and 49.95% of its spins in the upper state. This slight difference in population has significant consequences. If there were no difference in population of energy states, spin resonance could not be detected, since a radiation field at the resonant frequency induces transitions between two states in either direction with equal probability. If the population of the two states were equal, as much energy would be emitted as absorbed, and no net effect would be observed. A net absorption occurs only when the population of the lower state is greater.

1. MAGNETIC RESONANCE OF FREE ATOMS

1.a. The Landé g Factor

Although we are concerned here primarily with the magnetic resonance of unpaired electrons in molecular free radicals, or crystals, we can advantageously consider briefly the gross paramagnetic resonance of free atoms, first neglecting nuclear spin effects. Since the electrons in completely filled subvalence shells contribute nothing to the magnetism of the atom, they can be ignored. Each electron has a spin momentum s , a spin magnetic moment μ_s , and (except when in an s orbital) an orbital momentum l and an orbital magnetic moment μ_l . The angular momentum and spin moments are coupled in various ways in different atoms. The most common coupling scheme is the Russell-Saunders coupling, in which the various vectors l_1, l_2 , and so on of the different electrons combine to form a resultant L , and the various spin vectors s_1, s_2 , and so on combine to form a resultant S ; L and S then combine to form a resultant J . The total quantum number J may have integral or half-integral values differing by integers and ranging from $|L + S|$ to $|L - S|$. When there is only one electron outside a closed shell, there is only the coupling between the spin and the orbital motion of that electron, which can combine to give only $j = l + 1/2$, or $j = l - 1/2$. The components of the magnetic moments μ_L and μ_S combine to give a resultant μ_J along J , which can be expressed by

$$\mu_J = -g_J \beta J \quad (1.4)$$

The classical interaction of μ_J with an applied magnetic field H is

$$\mathcal{H} = -\mu_J \cdot H = g_J \beta J \cdot H = g_J \beta H |J| \cos \theta, \quad (1.5)$$

where θ is the angle between J and H . Quantum mechanically, J is resolved along

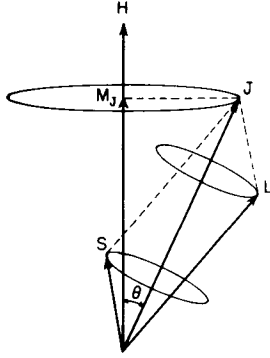


Fig. 1.1 Vector model of an atom in an applied field \mathbf{H} when $g_J \beta \mathbf{J} \cdot \mathbf{H} \ll \lambda \mathbf{L} \cdot \mathbf{S}$ and there is no nuclear coupling.

the applied field with quantized components that in units of \hbar are $M_J = J, J - 1, \dots, -J$. From the vector model of Fig. 1.1, $\cos \theta = M_J/|J|$. Substitution of this value in (1.5) gives the allowed Zeeman energies as

$$E_J = g_J \beta M_J H \quad (1.6)$$

The magnetic resonance frequency corresponding to the transition $M_J \rightarrow M_J \pm 1$ is

$$\nu = \frac{g_J \beta H}{\hbar} \quad (1.7)$$

where $\beta = 5.05038 \times 10^{-24}$ erg/G is the Bohr magneton and g_J is the gyromagnetic ratio or Landé g factor. This well-known formula can be derived easily from the vector model of Fig. 1.1. For example,

$$\mu_J = \mu_L \cos(\mathbf{L}, \mathbf{J}) + \mu_S \cos(\mathbf{S}, \mathbf{J}) \quad (1.8)$$

with $\mu_J = g_J \beta J$, $\mu_L = \beta L$, and $\mu_S = 2\beta S$. This gives

$$g_J = \frac{\beta [\mathbf{L} \cos(\mathbf{L}, \mathbf{J}) + 2\mathbf{S} \cos(\mathbf{S}, \mathbf{J})]}{J} \quad (1.9)$$

From the law of the cosine, $\cos(\mathbf{L}, \mathbf{J}) = (\mathbf{J}^2 + \mathbf{L}^2 - \mathbf{S}^2)/2\mathbf{LJ}$ and $\cos(\mathbf{S}, \mathbf{J}) = (\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2)/2\mathbf{SJ}$. Substitution of the eigenvalues $\mathbf{J}^2 = J(J+1)$, $\mathbf{L}^2 = L(L+1)$, $\mathbf{S}^2 = S(S+1)$ in the cosines, with some rearrangement, yields the Landé g factor for the atom:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (1.10)$$

A case of special interest is that of S states for which $L = 0$, $J = S$, and $g_J = g_S = 2$.

In the preceding Hamiltonian we did not include the spin-orbit interaction $\lambda \mathbf{L} \cdot \mathbf{S}$ because this interaction is so strong that it is not broken down or measurably perturbed by applicable magnetic strengths. A change in $\lambda \mathbf{L} \cdot \mathbf{S}$ associated with a change in the eigenvalues of $J = L + S, L + S - 1, L + S - 2, \dots, -(L + S)$ represents a very large energy change as compared with the Zeeman splitting and corresponds to a change in the electronic state of the atom. Thus in observation of epr spectra of atoms, one can consider \mathbf{J} as well as \mathbf{L} and \mathbf{S} as constants of the motion. Only changes in the resolvable components M_J need be considered.

The conventional labeling of the atomic states signifies the particular values of J , L , and S for the state. For example, L of 0,1,2,3 corresponds to S, P, D, F states. A superscript to the left is added to signify the spin degeneracy $2S + 1$, and a subscript on the right is added to indicate the value of J . For example, the ground state of nitrogen, $^4S_{3/2}$, has $L = 0, S = 3/2, J = S = 3/2$, and hence a Landé g factor $g_J = 2$, from (1.10). Atomic oxygen has a 3P_2 ground state, $L = 1, S = 1, J = S + L = 2$, and $g_J = 3/2$. Atomic fluorine has a $^2P_{3/2}$ ground state with $S = 1/2, L = 1, J = 3/2$, and hence $g_J = 4/3$.

1.b. Nuclear-magnetic Interactions

When the nucleus of an atom has a spin $I \neq 0$, it will have an associated magnetic moment $\mu_I = g_I \beta_I \mathbf{I}$, where g_I is the nuclear g factor and $\beta_I = eh/4\pi Mc$ is the nuclear magneton. This μ_I interacts with the averaged atomic field at the nucleus \mathbf{H}_J that is in the direction of \mathbf{J} . Because interaction with field components perpendicular to \mathbf{J} is canceled by the precessional motions, the nuclear magnetic interaction when no field is applied can be expressed as

$$\mathcal{H}_N = \mu_I \cdot \mathbf{H}_J = A \mathbf{I} \cdot \mathbf{J} \quad (1.11)$$

where A is the nuclear coupling constant between \mathbf{I} and \mathbf{J} . The last expression follows because $\mu_I \sim \mathbf{I}$ and $\mathbf{H}_J \sim \mathbf{J}$. Thus when \mathbf{J} is a constant of the motion, the nuclear interaction is an isotropic $\mathbf{I} \cdot \mathbf{J}$ interaction, in contrast to the tensor interaction in solids, where the spin-orbit coupling is broken down (see Chapter II). For spin values, $I > 1/2$, the nucleus may also have an electric quadrupole moment Q that gives additional coupling to \mathbf{J} . As this interaction is treated in Chapter II, it is omitted here.

In the absence of an external field, \mathbf{I} and \mathbf{J} are thus coupled to form a resultant designated $\mathbf{F} = \mathbf{J} + \mathbf{I}$. Since \mathbf{J} and \mathbf{I} commute, $\mathbf{J} \cdot \mathbf{I} = \mathbf{I} \cdot \mathbf{J}$ and

$$\mathbf{F}^2 = (\mathbf{J} + \mathbf{I})^2 = \mathbf{J}^2 + \mathbf{I}^2 + 2\mathbf{I} \cdot \mathbf{J} \quad (1.12)$$

and hence

$$\mathbf{I} \cdot \mathbf{J} = (1/2) (\mathbf{F}^2 - \mathbf{J}^2 - \mathbf{I}^2) \quad (1.13)$$

Quantum mechanically, the square of the total angular momentum \mathbf{F}^2 has the eigenvalues $F(F + 1)$, and the resolvable components of \mathbf{F} have eigenvalues M_F . In this coupling model, \mathbf{J}^2 and \mathbf{I}^2 are also quantized with $\mathbf{J}^2 = J(J + 1)$ and $\mathbf{I}^2 = I(I + 1)$. Thus \mathcal{H}_N is diagonal in the representation $|F, M_F, J, I\rangle$, and the diagonal element represents the specific energy values

$$E_N = (1/2)A [F(F + 1) - J(J + 1) - I(I + 1)] \quad (1.14)$$

where the F quantum numbers have the values

$$F = J + I, J + I - 1, J + I - 2, \dots, -(J + I)$$

If a weak magnetic field is imposed, one in which the Zeeman energies are much smaller than $A\mathbf{I} \cdot \mathbf{J}$, a resultant \mathbf{F} is still formed by \mathbf{J} and \mathbf{I} . In the vector model of Fig. 1.2, \mathbf{J} and \mathbf{I} precess about \mathbf{F} , and \mathbf{F} precesses more slowly about the direction of the applied field \mathbf{H} . The components of the total angular momentum that are resolvable along a fixed direction in space have the quantized values

$$M_F = F, F - 1, F - 2, \dots, -F$$

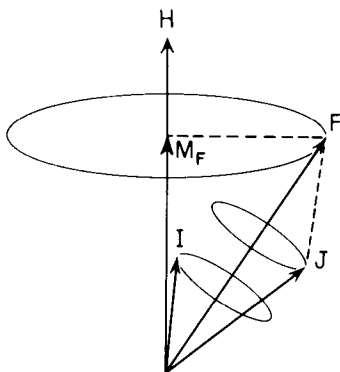


Fig. 1.2 Vector model of an atom in an applied field \mathbf{H} when there is nuclear coupling and $g_I\beta_I\mathbf{I} \cdot \mathbf{H} \ll A\mathbf{I} \cdot \mathbf{J}$ (weak-field case).

The Zeeman Hamiltonian for this weak-field case is

$$\mathcal{H}_M = - \boldsymbol{\mu}_F \cdot \mathbf{H} \quad (1.15)$$

where

$$\boldsymbol{\mu}_F = \mu_J \cos(\mathbf{J}, \mathbf{F}) - \mu_I \cos(\mathbf{I}, \mathbf{F}) \quad (1.16)$$

The components of μ_J and μ_I perpendicular to \mathbf{F} average to zero by the precession of \mathbf{J} and \mathbf{I} about \mathbf{F} . The sign of the last term is negative because μ_J and μ_I are opposed in sign when μ_I is positive. Let us define g_F such that $\boldsymbol{\mu}_F = g_F \beta \mathbf{F}$. Then with $\mu_J = g_J \beta \mathbf{J}$ and $\mu_I = g_I \beta \mathbf{I}$, (1.16) gives

$$g_F = g_J \cos(\mathbf{J}, \mathbf{F}) - g_I \frac{\beta_I}{\beta} \cos(\mathbf{I}, \mathbf{F}) \quad (1.17)$$

With $\cos(\mathbf{J}, \mathbf{F})$ and $\cos(\mathbf{I}, \mathbf{F})$ determined from the cosine law and with $\mathbf{F}^2 = F(F+1)$, $\mathbf{J}^2 = J(J+1)$, $\mathbf{I}^2 = I(I+1)$, (1.17) for g_F becomes

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_I \left(\frac{\beta_I}{\beta} \right) \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} \quad (1.18)$$

where g_J is given by (1.9).

By substitution of $g_F \beta \mathbf{F}$ for $\boldsymbol{\mu}_F$, the Zeeman Hamiltonian, (1.15), can be expressed as

$$\mathcal{H}_M = g_F \beta \mathbf{F} \cdot \mathbf{H} = g_F \beta (F_x H_y + F_y H_y + F_z H_z) \quad (1.19)$$

Since in this weak-field case \mathcal{H}_M is small as compared with \mathcal{H}_N , it can be treated as a perturbation of \mathcal{H}_N . The first-order perturbation is simply an average of \mathcal{H}_M over the wave functions $|F, M_F, J, I\rangle$ of \mathcal{H}_N . This average is

$$E_{M_F} = \langle F, M_F, J, I | \mathcal{H}_M | F, M_F, J, I \rangle \quad (1.20)$$

Since the diagonal elements of F_z are M_F and those of F_x and F_y vanish, this average is

$$E_{M_F} = g_F \beta H M_F \quad (1.21)$$

where g_F is given by (1.18) and $H = H_z$. Alternately, one can express \mathcal{H}_M as $g_F |\mathbf{F}| H \cos(\mathbf{F}, \mathbf{H})$ and then with $\cos(\mathbf{F}, \mathbf{H}) = (F_z/|\mathbf{F}|) = (M_F/|\mathbf{F}|)$ can derive the same formula. The vector-model treatment is equivalent to the first-order perturbation theory. This weak-field Zeeman splitting is superimposed on each of

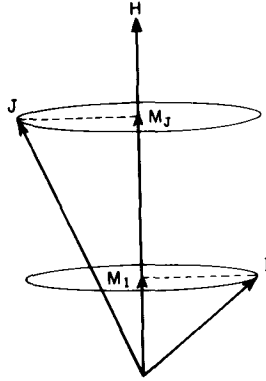


Fig. 1.3 Vector model of an atom in an applied field \mathbf{H} when $g_I\beta_I\mathbf{I}\cdot\mathbf{H} \gg A\mathbf{I}\cdot\mathbf{J}$ (strong-field case).

the nuclear hyperfine levels (corresponding to each value of F) as given by (1.14). Because $(\beta_I/\beta) = 5.446 \times 10^{-4}$, the last term in the g_F of (1.18) can be omitted in approximate treatments.

A second important case occurs when the nuclear $\mathbf{I} \cdot \mathbf{J}$ interaction is much smaller than the $\mathbf{J} \cdot \mathbf{H}$ interaction. In this strong-field or Paschen-Back case, \mathbf{I} and \mathbf{J} do not form a resultant, but each is individually resolved along (or in the vector model of Fig. 1.3, precesses about) the direction of the applied field. The Hamiltonian for the magnetic interaction is

$$\begin{aligned}\mathcal{H}_M &= -\mu_J \cdot \mathbf{H} - \mu_I \cdot \mathbf{H} + A\mathbf{I} \cdot \mathbf{J} \\ &= g_J\beta\mathbf{J} \cdot \mathbf{H} - g_I\beta_I\mathbf{I} \cdot \mathbf{H} + A\mathbf{I} \cdot \mathbf{J}\end{aligned}\quad (1.22)$$

The axis of quantization of both \mathbf{J} and \mathbf{I} is the direction of \mathbf{H} and is chosen as the z axis. In the representation $|J, M_J, I, M_I\rangle$, in which the first two terms are diagonal, the diagonal matrix elements of the last term are AM_JM_I . This follows from the fact that diagonal matrix elements of J_z are M_J and those of I_z are M_I , whereas the diagonal elements of J_x, J_y, I_x , and I_y are zero. Thus the energy values to first order, $\langle J, M_J, I, M_I | \mathcal{H}_M | J, M_J, I, M_I \rangle$, are

$$E_M = g_J\beta HM_J - g_I\beta_I HM_I + AM_JM_I \quad (1.23)$$

where g_J is given by (1.9) and A has the same value as in the weakfield case, (1.14). A more precise treatment, which takes into account the incomplete resolution of the \mathbf{J} and \mathbf{I} along the applied field, has been given by Breit and Rabi [11] for $J = 1/2$ with any value of I . Similar corrections are derived in

Chapter III, Sections 4.b and 4.k for nuclear couplings of doublet-state free radicals in solids.

The selection rules for epr are $\Delta M_J = \pm 1$ and $\Delta M_I = 0$. These rules mean, in effect, that the electronic moment is induced by the microwaves to flip over in the applied field \mathbf{H} , whereas the nuclear moment is not. These selection rules give the epr frequency for the strong-field case as

$$\nu = \frac{g_J \beta H}{h} + \frac{A}{h} M_I \quad (1.24)$$

The nuclear magnetic quantum number M_I can take the values

$$M_I = I, I - 1, I - 2, \dots, -I$$

where I is the nuclear spin value. Thus there are $(2I + 1)$ hyperfine components of the epr transition. These have equal spacing and are of equal intensity when observed under normal conditions of thermal equilibrium. The spacing of consecutive components gives the coupling constant A/h directly. At a constant frequency the “resonant field” values are

$$H_0 = \frac{h\nu_0}{g_J \beta} - \frac{A}{g_J \beta} M_I \quad (1.25)$$

where A is in energy units (ergs). For convenience, A is often expressed in frequency units. When this is done, the last term of (1.25) must be multiplied by h because $A(\text{ergs}) = hA(\text{hertz})$. Thus in magnetic field units the spacing of the hyperfine components is $hA/g_J \beta$, where A is in frequency units (hertz) rather than in ergs.

Figure 1.4 illustrates the energy-level diagrams for the zero-field, weak-field, and strong-field cases for an atom in a $^2S_{1/2}$ state with nuclear spin $I = 1/2$. Although the nuclear magnetic hyperfine splitting differs in the weak- and strong-field cases, the same value of the coupling constant A is obtained from measurements of either of the two types of spectra. Approximately the same value of the nuclear coupling constant is obtained from analysis of esr spectra of atoms in solids where the $\mathbf{L} \cdot \mathbf{S}$ coupling is also broken down, and where neither J nor F is a good quantum number. See Chapter VIII, Section 3 for a treatment of atoms trapped in solids. Theoretical formulas for calculation of A are given in Chapter II. Values of some coupling constants measured from atomic spectra are given in Table A.1. These atomic coupling constants are used in the interpretation of esr hyperfine structure in condensed matter.

This brief discussion of magnetic interactions in free atoms is given as an aid to the understanding of the epr or esr of condensed matter where the para-