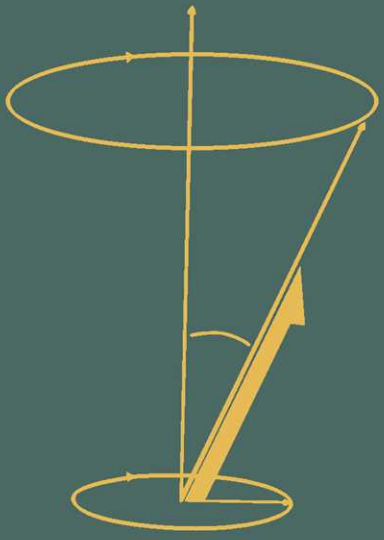
Nuclear Acoustic Resonance



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PREFACE

The authors intend this book to serve as an up–to–date introduction to the field of nuclear acoustic resonance. Although nuclear acoustic resonance is closely related to the well–established field of nuclear magnetic resonance, we take pains to distinguish the characteristics and capabilities of the two fields. The distinction is most marked in the nature of the coupling mechanisms, treated in some detail in Chapter 3 (dynamic electric quadrupole coupling) and Chapter 4 (dynamic Alpher–Rubin coupling); in the experimental techniques, treated in Chapter 7; and in the ease of application of nuclear acoustic resonance to the study of conducting media, treated in many of the applications cited throughout the text. An associated technique, acoustic saturation nuclear magnetic resonance, serves as a bridge between nuclear magnetic resonance and nuclear acoustic resonance; it is treated, albeit in summary form, in Chapter 8.

Emphasis in this text is on fundamentals, both in theory and in experimental techniques. A notable feature of the theory presented by us is the detailed treatment of nuclear electrostatic multipole interactions in terms of the A_{lm} irreducible tensor operators and their application, following Fedders, to the calculation of nuclear acoustic resonance absorption and dispersion (Chapter 3), as well as of line width and relaxation effects (Chapter 5). We also treat in detail the alternative approach, building on the concepts of acoustic impedance and susceptibility for calculating absorption and dispersion in nuclear acoustic resonance, developed by Müller and his colleagues. In an extension of the usual treatment of nuclear dipolar and nuclear quadrupolar interactions, we derive the appropriate expressions for nuclear acoustic coupling in solids via the dynamic hexadecapole moment. Our treatment of dynamic Alpher–Rubin coupling emphasizes the classical approach of Quinn–Buttet–Fedders, but also summarizes the alternative classical and the quantum mechanical approaches of Müller and his colleagues. The extreme sensitivity of acoustic techniques required to observe most nuclear acoustic resonance effects has been achieved by careful application of standard techniques, described in some detail in Chapter 7, and of the SQUID (Chapter 10).

We have had to be selective in citing results, as well as in mentioning important contributors. Probably the most glaring omission is that of R. L. Melcher, a pioneer in the application of NAR to magnetic materials, both in theoretical and experimental aspects, as well as in the use of reflection CW spectrometers for NAR. We encourage the reader to dig deeper in the literature with the aid of the detailed references at the end of each chapter, as well as by utilizing Physics Abstracts. We also have not explored in detail the applications of nuclear acoustic resonance. The final chapter, on

SQUID nuclear acoustic resonance, we feel, points the way most clearly to future research and to novel applications in this field.

The presentation in this book owes much to the contributions of our students and collaborators at Washington University who have worked in the field of nuclear acoustic resonance and in related areas: Janet Brown, R. G. Leisure, R.L. Melcher, J. B. Merry, J. G. Miller, George Mozurkewich, Charles Myles, K. S. Pickens, H. I. Ringermacher, Rebecca Scholz-Hudson, R. E. Smith, Willis Smith, T. H. Wang and Marjorie P. Yuhas. The criticism and advice of our colleagues, George Mozurkewich, P. A. Fedders, J. G. Miller and Yaotian Fu, have been especially valuable. Detailed and very helpful readings of portions of the manuscript were made by R. G. Leisure and Volker Müller. George Mozurkewich did heroic duty in reviewing the entire manuscript. We thank them for their time, insight and patient good humor. We thank Pranoat Suntharothok for her fine contributions to the production and editing of the manuscript. We have benefited from the help and advice of Vicki Jennings and her colleagues at Academic Press.

CHAPTER 1
INTRODUCTION

1. INTRODUCTION

1.1 What is Nuclear Acoustic Resonance?

The nuclei of many atoms have magnetic and electrical properties that are associated with the fact that the nucleus as a whole has an intrinsic angular momentum, or *spin*. The nucleus may be characterized, for example, by a magnetic dipole moment and by an electric quadrupole moment. The static interactions between the magnetic dipole moment and external or internal magnetic fields, and between the electric quadrupole moment and electric field gradients, give rise to energy levels whose separations in frequency characteristically fall into the RF or ultra–high frequency ranges. In the well–known technique of nuclear magnetic resonance, an externally generated RF magnetic field is used to induce transitions among the nuclear spin energy levels by coupling to the nuclear magnetic dipole moment. Thus, in nuclear magnetic resonance, the resonance phenomenon characteristically is accompanied by the absorption (or dispersion) of electromagnetic radiation.

In nuclear acoustic resonance, in contrast, *acoustic* radiation is utilized to induce transitions among the energy levels that characterize the orientation of nuclear spins subjected to external or internal magnetic fields and to electric field gradients. Since the frequency of the acoustic wave usually

falls in the range of 1 MHz to 100 MHz, the convenient terms *ultrasound* and *ultrasonic* are often used to denote the acoustic radiation. Transitions among the nuclear spin energy levels in nuclear acoustic resonance are induced by the ultrasound through modulation of internal interactions involving the magnetic or electric multipole moments of the nucleus.

At first glance, there appear to be marked similarities between the techniques of nuclear acoustic resonance and nuclear magnetic resonance. The energy levels among which transitions are induced are the same. To display the resonance lines, both techniques utilize the variation of an external variable, most often the DC magnetic field or the frequency. The line spectra and the line widths observed by the two techniques are often closely related. The differences between the techniques, however, are equally notable and allow us to view nuclear acoustic resonance as a valuable adjunct to—and occasional substitute for—nuclear magnetic resonance. Although full discussion of these differences must await the detailed treatment of the theory, experimental techniques and characteristic results to be given in the remaining chapters, we may cite immediately two of the most obvious:

(1) The acoustic wave utilized in nuclear acoustic resonance couples energy to the nuclear spin system by the modulation of an *internal* spin–dependent interaction whereas in nuclear magnetic resonance the coupling is always achieved by means of the interaction of an external RF magnetic field with the magnetic dipole moment. In fact, in nuclear acoustic resonance the internal interactions compete to determine which will best serve to couple energy to the spin system from the exciting acoustic wave. Since the nature of the internal interactions depends upon the type of material (for example, magnetic versus nonmagnetic, conducting versus nonconducting) as well as upon the physical environment (*e.g.,* temperature, pressure), one anticipates that much of the physical understanding to be elucidated derives from detailed studies of the nature and properties of the nuclear spin–acoustic wave interaction itself.

(2) There are several classes of materials—most notably bulk metals and alloys—into which electromagnetic waves cannot easily penetrate, whereas there is no inherent difficulty for the passage of ultrasound.

There exist techniques for observing nuclear spin resonance phenomena that combine nuclear magnetic resonance and the use of ultrasound. Among these are acoustic saturation of nuclear magnetic resonance and, in more sophisticated form, double resonance effects that utilize both electromagnetic and acoustic energy. These *combination* spin resonance techniques sometimes include the use of electron spin resonance as detectors of acous-

tic absorption, and these techniques always require electromagnetic excitation of one form or another. The latter feature clearly distinguishes them from nuclear acoustic resonance techniques, in which only acoustic energy is utilized. The combination spin resonance techniques are closely related to nuclear acoustic resonance with respect to the physical understanding obtained, however, and will be treated in some detail.

In the remainder of the present chapter, we attempt a more detailed, though still introductory, description of the three techniques: nuclear acoustic resonance, nuclear magnetic resonance and combination acoustic–electromagnetic spin resonance. Since nuclear magnetic resonance (NMR) is by far the best known of these and the subject of a truly extensive literature, we begin with a very brief review of its fundamentals, and we emphasize—because of their importance to nuclear acoustic resonance—an understanding of the nuclear electric quadrupole interaction and of nuclear spin–lattice relaxation. We end the chapter with an overview of the subjects of acoustic saturation of nuclear magnetic resonance (ASNMR) and, finally, of nuclear acoustic resonance (NAR).

1.2 Nuclear Magnetic Resonance

There exists today an extensive literature on the subject of nuclear magnetic resonance. General and comprehensive treatments are given, for example, in books by *Abragam* [1.1] and by *Slichter* [1.2]. Only topics directly relevant to the subjects of nuclear acoustic resonance and of acoustic saturation of nuclear magnetic resonance are treated in the present, brief review. We restrict our discussion, in order to emphasize essentials, to insulating, non–magnetic solids.

The phenomenon of nuclear magnetic resonance follows directly from the magnetic properties of the nucleus. All nuclei with nonzero angular momentum or spin ($\boldsymbol{I}$) possess a magnetic dipole moment similar to that associated with a classical magnetic dipole. From quantum mechanics we know that the matrix elements of the magnetic moment are proportional to the matrix elements of the total nuclear angular momentum. We can write for the magnetic dipole moment, then,

$$\boldsymbol{\mu} = \gamma \hbar \boldsymbol{I} \ , \tag{1.1}$$

where γ is the gyromagnetic ratio, $\hbar$ is Planck's constant and $|\boldsymbol{I}|$ is in units of $\hbar$. In the presence of an applied DC magnetic field $\boldsymbol{H}_0$, the magnetic moment $\boldsymbol{\mu}$ experiences a torque perpendicular to the plane containing $\boldsymbol{\mu}$ and $\boldsymbol{H}_0$. As in the case of the classical gyroscope, the magnetic moment can be thought of as precessing at an angle θ about the about the axis of a magnetic field (Fig. 1.1). The angular frequency of precession (Larmor

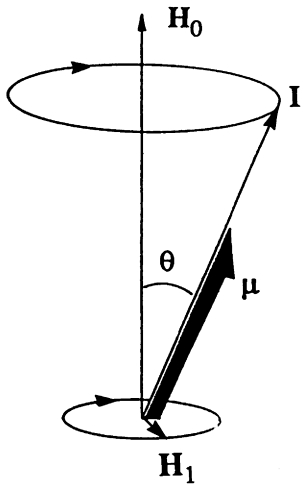

FIGURE 1.1. Gyroscopic precession of a nuclear magnetic moment $\boldsymbol{\mu}$ about the axis of an externally applied magnetic field $\boldsymbol{H}_0$. A rotating magnetic field $\boldsymbol{H}_1$ tends to increase the angle θ between the magnetic moment vector and the field axis.

frequency) ω_0 is given by

$$\omega_0 = -\gamma \boldsymbol{H}_0 \, . \tag{1.2}$$

If an RF magnetic field $\boldsymbol{H}_1$, rotating in the same direction as the nuclear precession, is applied at right angles to $\boldsymbol{H}_0$ and at right angles to the plane of $\boldsymbol{H}_0$ and $\boldsymbol{\mu}$, the effect will be to tip $\boldsymbol{\mu}$ in a direction antiparallel to $\boldsymbol{H}_0$. This corresponds to an absorption of energy from the source of the perturbing field $\boldsymbol{H}_1$. Maximum absorption occurs when the rotational frequency ω of $\boldsymbol{H}_1$ equals the resonant frequency ω_0. For a typical nucleus, the frequency at which resonance occurs in a field of 1 Tesla (10,000 Oe) is $\nu_0 \equiv \omega_0/2\pi \simeq 10\,\mathrm{MHz}$.

It is more useful and more rigorous to treat the nuclear spins as a quantized system. The magnitude of the spin angular momentum $\boldsymbol{I}$, a constant characteristic of stable nuclei, is given by $\sqrt{I(I+1)}$, where I is either integer or half-integer.

The Hamiltonian for a system of isolated spins in a DC magnetic field is given by

$$\mathcal{H}_m = -\boldsymbol{\mu} \cdot \boldsymbol{H}_0 \ . \tag{1.3}$$

The quantities $I(I+1)$ are eigenvalues of the operator $\boldsymbol{I}^2$. The components of $\boldsymbol{I}$ (I_x, I_y, I_z) commute with $\boldsymbol{I}^2$, so that we may specify simultaneously eigenvalues of both $\boldsymbol{I}^2$ and I_z, which we call $I(I+1)$ and m, respectively. A nucleus with spin $\boldsymbol{I}$ may assume only $2I+1$ discrete orientations in the DC magnetic field. These orientations correspond to discrete energy levels characterized by the magnetic quantum number m, corresponding to the projection of $\boldsymbol{I}$ along the direction of the DC magnetic field. The energy levels for isolated nuclear spins in an external DC magnetic field $\boldsymbol{H}_0$ are given by

$$E_m = -mg\mu_n H_0 \ , \quad m = I, I-1 \ldots -I \ , \tag{1.4}$$

where g is the nuclear g factor. $\mu_n = e\hbar/2Mc$ is the nuclear magneton, M is the proton mass, e is the electronic charge and c is the velocity of light.

Application of an RF field $\boldsymbol{H}_1$ of frequency $\omega_0/2\pi$ induces transitions among these energy levels. Under the action of a harmonically varying perturbation the probability per unit time that a nucleus in a state initially characterized by the magnetic quantum number m will be found in a state m' is given quite generally by the expression

$$W = \frac{1}{4\hbar^2}|\langle m'|\mathcal{H}|m\rangle|^2 g(\nu) \ , \tag{1.5}$$

where $\langle m'|\mathcal{H}|m\rangle$ is the appropriate matrix element of the perturbing Hamiltonian, and $g(\nu)$ is a shape function such that $\int_0^\infty g(\nu)d\nu = 1$ and $g(\nu)$ is peaked near the resonant frequency ν_0. For the case in which energy is coupled to the nuclear magnetic moments by a time varying RF magnetic field $\boldsymbol{H}_1$, $\mathcal{H} = -\boldsymbol{\mu} \cdot \boldsymbol{H}_1$ and (1.5) becomes

$$W_M = \frac{\gamma^2 H_1^2}{4}|(m'|I_\pm|m)|^2 g(\nu) \ , \tag{1.6}$$

where $I_+ = I_x + iI_y$, $I_- = I_x - iI_y$ are the *raising* and *lowering* spin operators, respectively. $|(m'|I_\pm|m)|^2$ has a definite value depending upon whether $m' = m+1$ or $m-1$ given by

$$|(m+1|I_+|m)|^2 = (I-m)(I+m+1) \tag{1.7a}$$

$$|(m-1|I_-|m)|^2 = (I+m)(I-m+1) \ . \tag{1.7b}$$

Substituting (1.7) into (1.6), and allowing for the possibility that $\boldsymbol{H}_1$ is not at right angles to $\boldsymbol{H}_0$, we obtain

$$W_{M(\pm 1)} = \frac{1}{4}\gamma^2 H_1^2 g(\nu)(I \mp m)(I \pm m + 1)\sin^2\theta \ , \tag{1.8}$$

where $2H_1$ is the peak amplitude of the RF magnetic field, and θ is the angle that $\boldsymbol{H}_1$ makes with the static magnetic field $\boldsymbol{H}_0$. The allowed transitions under these circumstances are those for which m changes by ± 1 ($\Delta m = \pm 1$). Applying this selection rule to (1.3), one obtains for the resonance condition

$$\hbar\omega_0 = E_{m+1} - E_m = -g\mu_n H_0 \ . \tag{1.9}$$

A pictorial representation of the energy level scheme for a nucleus of spin $I = \frac{1}{2}$ is shown in Fig. 1.2(a), in which N_+ and N_- represent the number of nuclei, respectively, in level $m = +\frac{1}{2}$ and level $m = -\frac{1}{2}$. The absorption of energy from the RF magnetic field as the DC magnetic field (or frequency) is varied is shown schematically in Fig. 1.2(b), in which the center of the absorption line coincides with the resonant field H_0 (or, equivalently, the resonant frequency $\omega_0/2\pi$).

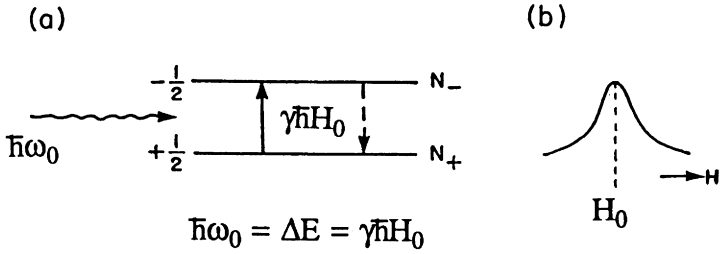

FIGURE 1.2. (a) Energy levels for a nucleus with spin $I = \frac{1}{2}$. (b) A typical nuclear magnetic resonance absorption line.

From quantum mechanics we know that the probabilities for transitions between any two energy levels induced by a time-dependent interaction are equal for transitions up and down. It might appear, then, that for the case illustrated in Fig. 1.2, for example, there would be no net absorption of energy (since a down transition from the higher level, corresponding to a release of energy, might be expected to cancel the absorption of energy in the corresponding up transition). This would indeed be true if the two states were equally populated. If, however, an assembly of nuclei occupying

two states ($I = \frac{1}{2}, m = \pm\frac{1}{2}$) is in thermal equilibrium with a reservoir at a temperature T, the upper of the two states is less densely populated according to the Boltzmann distribution factor

$$N_-^o = N_+^o e^{-\Delta E/k_B T} , \tag{1.10}$$

where k_B is the Boltzmann constant, ΔE is the energy difference between the levels, and N_-^o and N_+^o are the equilibrium populations of the two levels. The population difference $N_+^o - N_-^o$ for DC magnetic fields readily attainable in the laboratory is of the order of parts per million. Because of the greater population of spins in the lower energy state, therefore, there is a net absorption of energy from the source of the RF magnetic field, as shown schematically in Fig. 1.2(b). The mechanism by which the population difference (1.10) is maintained is discussed in Section 1.5. The existence of discrete magnetic energy levels and of a nonuniform distribution of nuclear magnetic moments among these levels leads to a net macroscopic magnetization in the specimen containing these moments. By applying the Boltzmann law, one obtains the expression for M, the net nuclear magnetization per unit volume:

$$M = \frac{N\mu^2}{3k_B T}\left(\frac{I+1}{I}\right) H_0 , \tag{1.11}$$

where N is the number of spins per unit volume. It is this net magnetization that is often measured in nuclear magnetic resonance experiments.

1.3 Nuclear Electric Quadrupole Effects

Nuclei with spin $I > \frac{1}{2}$ possess not only magnetic moments but also electric moments. The lowest nonvanishing nuclear electric moment is the electric quadrupole moment, which is a measure of the departure from spherical symmetry of the charge distribution in the nucleus. The nuclear electric quadrupole moment Q interacts with electric field gradients (inhomogeneous electric fields) that exist at the nucleus due to neighboring electrical charges, such as ions or electrons external to, but associated with, the nucleus. The nuclear electric quadrupole interaction is responsible for at least four phenomena important in nuclear magnetic resonance:

(1) It may affect the nuclear spin magnetic energy level configuration.
(2) Under certain circumstances it gives rise to a set of nuclear spin energy levels—nuclear quadrupole energy levels or pure quadrupole energy levels—even when there is no DC magnetic field present.
(3) It is often responsible for the nuclear spin–lattice relaxation, to be discussed in Section 1.5.

(4) It affects the line width and line shape of the observed resonance. In nuclear acoustic resonance, further, the dynamic nuclear electric quadrupole interaction provides a means of coupling acoustic energy to the nuclear spin system.

Because of its importance in nuclear acoustic resonance, we summarize below some results of the theory of nuclear electric quadrupole interactions. In Chapters 2 and 3, a comprehensive and detailed treatment of these interactions will be given.

The nucleus can be regarded as a small, localized distribution of electric charge with a charge distribution of density $\rho(\boldsymbol{r}_n)$, where $\boldsymbol{r}_n$ is the radial vector from the origin to the element of nuclear charge. If this electric charge is subjected to an electrostatic potential $V(\boldsymbol{r}_n \boldsymbol{r}_e)$ due to charges external to the localized distribution, the electrostatic interaction energy is given by

$$E = \int \rho(\boldsymbol{r}_n) V(\boldsymbol{r}_n \boldsymbol{r}_e) d\tau_{\boldsymbol{r}_n} \ , \tag{1.12}$$

where the integral is over the volume containing the localized distribution and $\boldsymbol{r}_e$ is the radial vector from the origin to the element of electronic charge external to the nucleus. We will show in Chapter 3 that the lowest term in the orientation-dependent part of the electrostatic energy (also, see *Slichter* [1.2]) can be written in operator form as

$$\mathcal{H}_Q = \sum_{ij} Q_{ij} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\boldsymbol{r}=0} \ , \tag{1.13}$$

where i, j stand for x, y or z, respectively, and the derivative is to be evaluated at the origin. The Q_{ij} are the components of the quadrupole moment tensor, which for a nuclear state of spin quantum number I has the following form:

$$Q_{ij} = \frac{eQ}{6I(2I-1)} \left[\frac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I(I+1) \right] \ , \tag{1.14}$$

where $Q = \Sigma_i \rho_i(r)(3\cos^2\theta_i - 1) r_i^2$ is a scalar quantity termed the electric quadrupole moment of the nucleus, and r_i, θ_i are the coordinates of an element of nuclear charge ρ_i with respect to a cylindrical axis. It follows that $Q = 0$ for a spherically symmetric charge distribution, that $Q > 0$ for a prolate, and that $Q < 0$ for an oblate spheroidal distribution.

It is conventional in (1.13) to define

$$V_{ij} \equiv \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\boldsymbol{r}=0} \ . \tag{1.15}$$

The V_{ij} are components of a symmetric, traceless, second-rank tensor, the electric field gradient (EFG) tensor. It is possible to reduce the EFG tensor to a diagonal form by transforming to the principal coordinate system, designated by x, y, z. In this coordinate system, the off-diagonal components of the tensor, $V_{xz} = V_{yz} = V_{xy} = 0$, and the only nonvanishing components are V_{xx}, V_{yy} and V_{zz}. The Hamiltonian can then be written

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)} \sum_{ij} V_{ij} \left[\frac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I(I+1) \right] . \tag{1.16}$$

Even the nonvanishing components are not independent, however, since Laplace's equation is applicable, yielding $V_{xx} + V_{yy} + V_{zz} = 0$. Equation (1.16) then reduces to the form

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} [V_{zz}(3I_z^2 - I^2) + (V_{xx} - V_{yy})(I_x^2 - I_y^2)] . \tag{1.17}$$

In the principal coordinate system, two parameters are thus sufficient to specify the electric field gradient tensor. The usual choice of these parameters is the following:

$$eq = V_{zz}; \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad 0 \leq \eta \leq 1 . \tag{1.18}$$

The scalar quantity η is defined as the asymmetry parameter and is a measure of the departure from axial symmetry. The case $\eta = 0$ corresponds to axial symmetry. The most general type of electric field gradient is uniquely specified by the orientation of the principal axes and by the two parameters q and η.

To evaluate the contribution of the nuclear electric quadrupole interaction to the nuclear energy level configuration, as well as (as we shall see in Section 1.6) its role in coupling acoustic radiation to the nuclear spin system, we require the matrix elements of $\mathcal{H}_Q$ in the (I, m) representation. We consider, in this introductory treatment, only the case of an axially symmetric electric field gradient ($\eta = 0$) and the case in which the nuclear quadrupole interaction is small compared with the interaction energy of the nuclear magnetic moment with the external magnetic field. From conventional quantum mechanical perturbation theory, one obtains the following

nonzero matrix elements [1.1,1.2]:

$$\begin{aligned}(m|\mathcal{H}_Q|m) &= \frac{A}{16}(m|[3I_z^2 - I(I+1)]V_{zz}|m) \\ &= \frac{A}{16}eq[3m^2 - I(I+1)](3\cos^2\theta - 1)/2\end{aligned} \tag{1.19a}$$

$$\begin{aligned}(m \pm 1|\mathcal{H}_Q|m) &= -\frac{A}{16}\sqrt{6}(m \pm 1|(I_\pm I_z + I_z I_\pm)V^{\mp 1}|m) \\ &= -\frac{3}{32}Aeq(2m \pm 1)[(I \pm m + 1) \\ &\quad \times (I \mp m)]^{\frac{1}{2}} \sin\theta\cos\theta\, e^{\pm i\phi}\end{aligned} \tag{1.19b}$$

$$\begin{aligned}(m \pm 2|\mathcal{H}_Q|m) &= \frac{A}{16}\sqrt{6}(m \pm 2|I_\pm V^{\mp 2}|m) \\ &= \frac{3}{64}Aeq[(I \mp m)(I \mp m - 1) \\ &\quad \times (I \pm m + 1)(I \pm m + 2)]^{\frac{1}{2}} \sin^2\theta\, e^{\pm 2i\phi}\ ,\end{aligned} \tag{1.19c}$$

where $A = e^2Q/I(2I-1)$. θ is the angle between the axis of symmetry and the direction of the DC magnetic field, and ϕ is the angle between the projection of the symmetry axis on the xy–plane and the x–axis. The operators $V^{\pm 1}$ and $V^{\pm 2}$ are given in (3.34) and (3.36).

In the high field case ($\mathcal{H}_m \gg \mathcal{H}_Q$) that we are considering, the form of the total Hamiltonian of a nuclear spin that lies in a steady magnetic field and that has a nuclear electric quadrupole coupling is

$$\mathcal{H} = \mathcal{H}_m + \mathcal{H}_Q\ , \tag{1.20}$$

where $\mathcal{H}_m$ and $\mathcal{H}_Q$ have been given previously in (1.3) and (1.17). To obtain the energies to first order in stationary perturbation theory, we use the diagonal terms in $\mathcal{H}_m$ and $\mathcal{H}_Q$ from (1.4) and (1.19a), yielding for the case $\eta = 0$

$$E_m = -\gamma_n\hbar H_0 m + \frac{e^2qQ}{4I(2I-1)}\left(\frac{3\cos^2\theta - 1}{2}\right)[3m^2 - I(I+1)]\ . \tag{1.21}$$

As shown in Fig. 1.3(a), for a nucleus with spin $I = \frac{3}{2}$, in the absence of electric quadrupole coupling, the $2I+1$ nuclear Zeeman energy levels are equally spaced. The effect of the first–order electric quadrupole interaction is to shift these energy levels, thus splitting the single resonance line into