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Introduction to Spin, Magnetic Resonance and Polarization

In this chapter, we shall review the mathematical formalism required for the understanding of the spin physics of polarized targets. Particular focus is given to the problems treating the situations that are favorable for obtaining high polarizations: high magnetic field and low lattice temperature.

In the following sections we shall first discuss the concept of the spin and magnetic moment and work out in detail some standard quantum mechanical problems involving these variables. The quantum statistics of a system of spins is then overviewed, before briefly introducing the thermodynamics of spin systems. Most of these can be found in well-known textbooks of quantum mechanics, such as those of Dicke and Wittke [1] and of Landau and Lifshitz [2], and of magnetic resonance, such as Abragam [3], Goldman [4], Abragam and Goldman [5] and Slichter [6]. The main justification for presenting textbook material is that we need to make frequent reference to this basic formalism. Three further reasons are:

(1) to introduce a consistent notation and vocabulary;
(2) to refer uninitiated readers to the basic source literature for further reading; and
(3) to introduce the SI units.

There are differences in the way how some basic entities are defined in the textbooks, and therefore a consistent notation and vocabulary are useful in developing the theory of spin dynamics.

Magnetic resonance is one of the last fields of physics where the old Gaussian units are still commonly used, or they are mixed with the MKSA units, which is a subset of SI units. Because the SI units have been almost exclusively used for more than 25 years in most other fields of physics, we have made an effort to extend this to magnetic resonance. We shall also refer to Appendix A.1 where the SI unit system is compared with CGS Gaussian system (Tables A1.1 and A1.2). In the same appendix the fundamental physical quantities and variables, relevant for magnetic resonance, are defined in Table A.1.3, and the physical constants are listed in Table A.1.4, both in the SI system of units.

The basic results and terminology of this chapter will be used in Chapter 2 to describe various interactions of spin systems in general, and those of electron spin systems more specifically in Chapter 3. The basic groundwork is equally important for dynamic nuclear polarization (DNP) which is the subject of Chapter 4 and for nuclear magnetic resonance (NMR) that is discussed in Chapter 5.

1.1 Quantum Mechanics of Free Spin

1.1.1 Spin

The angular momentum vector **J** has the same units as the Planck constant $\hbar$ and can therefore be expressed for a rigid body as

$$\mathbf{J} = \hbar \mathbf{I}, \tag{1.1}$$

where the vector **I** is called *spin*. The components of **I** are unitless numbers in classical mechanics, whereas in quantum mechanics they are unitless operators performing rotations about the three coordinate axes. Macroscopic rigid bodies can have a large spin, the components of which can be incremented or decremented in steps of 1 that is very small in comparison with the length of **I**, whereas elementary particles have a definite maximum projection I of **I** on any coordinate axis. This maximum projection I is called the *intrinsic spin*, or briefly the spin.

The concept of the intrinsic spin of an elementary particle was controversial until Dirac's relativistic theory of electron became accepted after the experimental discoveries of the positron and of the creation and annihilation of electron-positron pairs. Since then spin has played a fundamental role in particle physics, proving and disproving many theories. The most famous proofs are probably those of the quantum electrodynamics (QED) based on the Lamb shift of atomic hydrogen and on the anomalous magnetic moment of the electron, and the tests of unified electroweak theories based on the accurate measurements of parity violation parameters in atomic, nuclear and high-energy interactions.

It has been suggested that the intrinsic spin may have a still deeper meaning in physics through general relativity [7, 8], possibly explaining the existence of the three types of charged leptons, the electron e, the muon μ and the tau lepton τ.

For the main purpose of this book, we do not need to specify whether the spin of a particle is due to intrinsic angular momentum, or due to the motion of a complex composite system (such as quarks and gluons or partons in a hadron, or nucleons in a nucleus). Landau and Lifshitz [2] discuss this in the context of nonrelativistic quantum mechanics. They note that the law of conservation of angular momentum is a consequence of the isotropy of space in both classical and quantum mechanics. They remark, however, that in quantum mechanics the classical *definition* of the angular momentum $\mathbf{r}\times\mathbf{p}$ of a particle has no direct significance owing to the fact that the position **r** and momentum **p** cannot be simultaneously measured. In other words, neither **r** nor **p** of the constituents has significance for observations of a complex system of particles, with a probe which does not break the structure.

Thus, a stable composite particle, in a definite internal state with given internal energy, has also an angular momentum of definite magnitude J, due to the motion of the constituent particles. This angular momentum can have $2I + 1$ orientations in space. With this understanding of the angular momentum, its origin becomes unimportant, and Landau and Lifshitz [2] thus arrive at the concept of an 'intrinsic' angular momentum which must be ascribed to a particle regardless of whether it is 'composite' or 'elementary'.

When discussing the dynamics of a system made of these composite (in the sense described above) particles, such as nuclei or electrons in a solid lattice built of ions, atoms or molecules, the origin of the angular momentum of the stable composite becomes unimportant; however, a reserve must be made on electronic spins with regard to spin-lattice relaxation, for example.

This 'intrinsic' angular momentum which is not connected with the dynamics of the solid material is called the *spin* to distinguish it from the *orbital angular momentum*. Paramagnetic electrons in a solid are said to possess an *effective spin* when only the lowest magnetic states of the ground-state multiplet are populated; in this case the term 'spin' must be understood as a shorthand notation.

The complete wave function of a particle with a spin depends on the three coordinates of the particle and on the spin variable. The spin variable is a discrete one, and it gives the projection of the intrinsic angular momentum on a selected direction in space. The selection of this direction is often the key problem to be solved. Only in a steady high magnetic field, this direction is parallel or close to the field vector.

1.1.2 Spin and Magnetic Dipole Moment

In classical electromagnetic theory, the magnetic moment[1] $\vec{\mu}$ of a volume containing currents with density $\mathbf{j}_m$ is (see, for example, Ref. [9] p. 130):

$$\vec{\mu} = \frac{1}{2}\int_\tau \left(\mathbf{r} \times \mathbf{j}_m\right) d\tau, \tag{1.2}$$

where $\mathbf{r}$ is the vector pointing to the volume element $d\tau$. If the currents can be considered as charge densities ρ_e moving with a velocity $\mathbf{u}$, the magnetic moment becomes

$$\vec{\mu} = \frac{1}{2}\int_\tau \rho_e \left(\mathbf{r} \times \mathbf{u}\right) d\tau. \tag{1.3}$$

This resembles the mechanical angular momentum

$$\mathbf{J} = \int_\tau \rho_m \left(\mathbf{r} \times \mathbf{u}\right) d\tau \tag{1.4}$$

of mass densities ρ_m moving at a velocity $\mathbf{u}$. If the system is composed of identical particles with mass m and charge e, the gyromagnetic ratio, γ, defined as

[1] As discussed in Appendix A.1, in SI units the unit of magnetic moment is $[\mu] = \mathrm{Am}^2$; the magnetic energy of the dipole is then $E = \boldsymbol{\mu} \cdot \mathbf{B}$, magnetic field being expressed in $[B] = \mathrm{Vs/m}^2 = \mathrm{Tesla}$.

$$\gamma = \frac{\mu}{J}, \tag{1.5}$$

becomes

$$\gamma = \frac{e}{2m} \tag{1.6}$$

for the case where μ and J are parallel.

In classical mechanics there is no general reason why these vectors should be parallel, but in quantum mechanics this is the case for closed systems. However, when adding the quantum mechanical angular momentum vectors of the system, the resultant magnetic momentum vector does not generally align with the angular momentum vector. A way of understanding this is that because the magnetic moment component perpendicular to J cannot be determined simultaneously with that along J (it can be thought to undergo rapid rotation around the axis), the only observable is the projection of μ along J. This gives rise to the structural g-factor, which is particularly important in electron spin resonance.

In the case of a complex structure, the gyromagnetic ratio is written in the terms of the g-factor as

$$\gamma = \frac{ge}{2m}, \tag{1.7}$$

where the factor g contains the entire description of the magnetic structure. For electrons we also often write

$$\gamma = \frac{g\mu_B}{\hbar}, \tag{1.8}$$

where we have introduced the fundamental constant Bohr magneton

$$\mu_B = \frac{\hbar e}{2m_e}. \tag{1.9}$$

We note here that for a negatively charged pointlike particle the gyromagnetic factor and the magnetic moment are always negative. In the literature the symbol β is often used for the Bohr magneton, but we reserve here this symbol for the inverse spin temperature.

Free pointlike charged particles (such as electron or muon) have the g-factor close to the Dirac value $g = 2$. The deviations are often given using an anomalous magnetic moment a defined by

$$g = 2(1+a). \tag{1.10}$$

The deviation can be measured to a high accuracy using a Penning trap for electrons or a storage ring for muons; comparisons with theoretical calculations have given important proofs of QED and QCD and restrained the limits of any substructure of the leptons [10].

As was discussed in the previous subsection, the spin angular momentum variable is a discrete one. Therefore, the magnetic moment projection on the axis of quantization also has only discrete values. This quantum mechanical fact, which will be discussed below in this chapter, is seen in a striking way in magnetic resonance measurements which are the basis of a large industry today.

The gyromagnetic ratio and the magnetic moment can be positive or negative, depending on not only the sign of the charge of the pointlike particle but also the structure of the complex system made of constituents. In this book we shall always assume, however, that the magnetic moment of the nucleus or electron is parallel or antiparallel to its spin angular momentum, depending on the sign of the gyromagnetic ratio:

$$\hat{\vec{\mu}} = \gamma \hbar \hat{\mathbf{I}}, \tag{1.11}$$

where the vectors $\hat{\vec{\mu}}$ and $\hat{\mathbf{I}}$ now are taken as quantum mechanical operators. The three components of these vectors can be mathematically represented by the so-called spin matrices, which will be discussed below.

1.1.3 Spin Operator Algebra

For simplicity, we shall eliminate here the vector notations but maintain the operator symbols with circumflex for a while in order to make the operators clearly distinct from constants. The spin operator $\hat{I}$ thus has the projections $\hat{I}_j\,(j = x, y, z)$ along the three coordinate axes in the same way as the angular momentum operator $\hat{J} = \hbar \hat{I}$. The algebra with operators requires the knowledge of their commutation relations[2] which, for the rotation operators, are obtained by considering infinitesimally small (elementary) rotations about the coordinate axes. For example, by performing a small rotation first around the x-axis and then around the y-axis, and then rotations about the same axes in reverse order and direction, the net result is a small positive rotation about the z-axis. The same can be achieved by comparing small rotations around the x- and y-axes, with rotations made around y- and x-axes. The difference of these two is a small rotation about the z-axis. This can be mathematically represented as a commutation relation

$$\hat{I}_x \hat{I}_y - \hat{I}_y \hat{I}_x \equiv \left[\hat{I}_x, \hat{I}_y\right] = i\hat{I}_z.$$

Cyclic permutation of the subscripts gives the following commutation relations for the spin operator components:

$$\begin{aligned} \left[\hat{I}_x, \hat{I}_y\right] &= i\hat{I}_z, \\ \left[\hat{I}_y, \hat{I}_z\right] &= i\hat{I}_x, \\ \left[\hat{I}_z, \hat{I}_x\right] &= i\hat{I}_y. \end{aligned} \tag{1.12}$$

[2] See, for example, Landau and Lifshitz [2] Chapters IV and VIII, and Dicke and Wittke [1] Chapters 9 and 12.

It is remarkable that these equations, based on the sole assumption that the space is isotropic, result in all the physics of spin. Notably, because the spin components do not commute, only one of them can be measured at a time, and the remaining two being not simultaneously measurable. Some other immediate results are briefly reviewed below.

The square of the 'magnitude' of $\hat{I}$

$$\hat{I}^2 = \hat{I}_x^2 + \hat{I}_y^2 + \hat{I}_z^2 \tag{1.13}$$

commutes with all three components of I as a consequence of Eq. 1.12:

$$\left[\hat{I}^2, \hat{I}\right] = 0, \tag{1.14}$$

i.e. $\hat{I}^2$ and any one of the components of $\hat{I}$ are simultaneously measurable.

Instead of $\hat{I}_x$ and $\hat{I}_y$ it is often more convenient to use the complex combinations

$$\hat{I}_\pm = \hat{I}_x \pm i\hat{I}_y, \tag{1.15}$$

which satisfy, based on Eq. 1.12 directly, the relations

$$\left[\hat{I}_+, \hat{I}_-\right] = 0, \tag{1.16}$$

$$\left[\hat{I}_z, \hat{I}_\pm\right] = \pm\hat{I}_\pm, \tag{1.17}$$

and

$$\hat{I}_\pm \hat{I}_\mp = \hat{I}^2 - \hat{I}_z^2 \pm \hat{I}_z. \tag{1.18}$$

Let us assume that m is the eigenvalue of $\hat{I}_z$:

$$\hat{I}_z \psi = m\,\psi. \tag{1.19}$$

The operators $\hat{I}_\pm$ are now seen to be ladder operators with respect to the eigenvalue m of $\hat{I}_z$, because

$$\hat{I}_z(\hat{I}_+\psi) = \left(m+1\right)\left(\hat{I}_+\psi\right), \tag{1.20}$$

which can be obtained using Eq. 1.17 or Eq. 1.12 directly.

Because of relation 1.14, the eigenfunction ψ can be chosen so that it simultaneously satisfies Eq. 1.19 and

$$\hat{I}^2\psi = a\psi, \tag{1.21}$$

where a is the square of the magnitude (i.e. length squared) of the spin vector, which we shall evaluate now. Firstly, because both expectation values and their sum

$$\left\langle \hat{I}_x^2 \right\rangle + \left\langle \hat{I}_y^2 \right\rangle$$

must be positive, from Eq. 1.13 it is clear that the expectation values of $\hat{I}^2$ and $\hat{I}_z$ satisfy

$$\left\langle \hat{I}^2 \right\rangle \geq \left\langle \hat{I}_z^2 \right\rangle,$$

which gives

$$a \geq m^2. \tag{1.22}$$

As a consequence of Eq. 1.20, the difference $2I$ of the greatest ($+I$) and least ($-I$) possible eigenvalue m of $\hat{I}_z$ must be an integer; I may take then any half-integer[3] value 0, 1/2, 1, 3/2, etc., and

$$m = -I, \ -I+1, \ldots I-1, \ I. \tag{1.23}$$

If m has its maximum value I, then $\hat{I}_+\psi = 0$, and, using Eq. 1.18,

$$\hat{I}_-\hat{I}_+\psi = 0 = \left(\hat{I}^2 - \hat{I}_z^2 - \hat{I}_z\right)\psi; \tag{1.24}$$

from this and Eq. 1.19 with $m = I$, we get

$$a = \left\langle \hat{I}^2 \right\rangle = I\left(I+1\right). \tag{1.25}$$

The eigenvalue of the operator $\hat{I}^2$ is therefore $I(I + 1)$, where I is called the spin quantum number and gives the maximum projection of the spin vector along an axis. Speaking of spin I therefore means speaking of a vector with magnitude $\sqrt{I\left(I+1\right)}$ and maximum projection on any axis of I. For simplicity we shall use in the rest of the book, unless ambiguities or clarity require otherwise, the same symbol I to denote the spin vector operator $\hat{I}$ and the spin quantum number I (or spin in short); possible confusions between these should become clarified by the context.

1.1.4 Matrix Representation of the Spin Operator

A quantum mechanical operator can be represented by a matrix acting upon a state vector which represents the wave function. The elements or components of these have a direct physical significance and can be related to the expectation values of the observables.

The wave function of a particle with spin I has $2I + 1$ components; the squares of the magnitudes of these components give the probability of the magnetic states m. The spin operator in matrix representation has $(2I + 1)\cdot(2I + 1)$ elements

$$\begin{aligned} \left(I_x\right)_{m,m-1} &= \left(I_x\right)_{m-1,m} = \frac{1}{2}\sqrt{\left(I+m\right)\left(I-m+1\right)}, \\ \left(I_y\right)_{m,m-1} &= -\left(I_y\right)_{m-1,m} = \frac{i}{2}\sqrt{\left(I+m\right)\left(I-m+1\right)}, \\ \left(I_z\right)_{m,m} &= m, \end{aligned} \tag{1.26}$$

where m is the magnetic quantum number; the rest of the elements are zero.

[3] The orbital angular momentum operator L can take only integer values of L_z, which is the consequence of restricting the form of the wave function to represent simple orbital motion. This restriction is by no means valid for complex wave functions such as that of the nucleon, whose constituents undergo relativistic motion.

The most important case is spin $I = 1/2$, for which the matrix components of the spin vector operator of Eq. 1.26 are:

$$I_x = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix};$$
$$I_y = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \tag{1.27}$$
$$I_z = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

These 2×2 matrices are called Pauli spin operators, often denoted by $\sigma \equiv 2I$; their direct multiplication gives

$$\sigma^2 = 3 \cdot \mathbf{1}, \tag{1.28}$$

where **1** is the unit matrix

$$\mathbf{1} \equiv \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

Equation 1.28 is clearly compatible with the value given by Eq. 1.25 for I. Moreover, similar direct multiplication yields

$$(\sigma \cdot \mathbf{a})(\sigma \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\sigma \cdot \mathbf{a} \times \mathbf{b}, \tag{1.29}$$

where **a** and **b** are any constant vectors. Furthermore, by replacing **a** and **b** by any unit vector **e** we get immediately

$$(\sigma \cdot \mathbf{e})^{2p} = 1 \tag{1.30}$$

and

$$(\sigma \cdot \mathbf{e})^{2p+1} = \sigma \cdot \mathbf{e}. \tag{1.31}$$

According to relations 1.29–1.31, any scalar polynomial of the components of σ can be reduced to terms independent of σ and to a term linear in σ; furthermore, any scalar function of σ reduces to a linear function, if it can be expanded as a Taylor series. These relations will be used in calculating traces involving the density matrix, without resorting to the so-called high-temperature approximation. This is a very important property of the Pauli spin operator for the theory of DNP at low temperatures, where high polarizations can be obtained.

In the case of $I = 1/2$, both Eqs. 1.25 and 1.28 yield $\langle \hat{I}^2 \rangle = \frac{3}{4}$. If the spin is in a state where one of its components (say, in the z-direction) has its maximum value of $\langle \hat{I}_z \rangle = \frac{1}{2}$, then I_x and I_y have zero expectation values, but $\langle \hat{I}_x^2 \rangle = \langle \hat{I}_y^2 \rangle = \frac{1}{4}$. As will be seen in Section 1.1.6, this can be understood by the precession of the spin vector which makes the components perpendicular to the axis of quantization oscillate sinusoidally.

For spin $I = 1$ we get the matrix representations of the components:

$$I_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix};$$
$$I_y = \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}; \tag{1.32}$$
$$I_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

These will be used explicitly in an example in Chapter 5.

1.1.5 Magnetic Energy Levels

Let us now consider a particle with spin I in a magnetic field B_0, with the field vector lying along the z-axis so that $\mathbf{B}_0 = \mathbf{k}B_0$. The spin is associated with the dipole moment $\hat{\mu} = \hbar\gamma\hat{I}$, where the gyromagnetic factor γ is defined by Eq. 1.6. The magnetic energy of the particle is then (in operator form)

$$\hat{\mathcal{H}} = -\hat{\mu} \cdot \mathbf{B}_0 = -\hbar\gamma B_0 \hat{I}_z, \tag{1.33}$$

and the Schrödinger equation

$$\hat{\mathcal{H}}\psi = E\psi \tag{1.34}$$

has $2I + 1$ eigenvalues

$$E_m = -m\hbar\gamma B_0, \tag{1.35}$$

because the eigenvalues of $\hat{I}_z$ go from $m = -I$ to $m = +I$, as was shown in Eq. 1.23. The magnetic energy level splitting is often visualized as shown by Figure 1.1a.

1.1.6 Larmor Precession

The time-dependent Schrödinger equation

$$\hat{\mathcal{H}}\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{1.36}$$

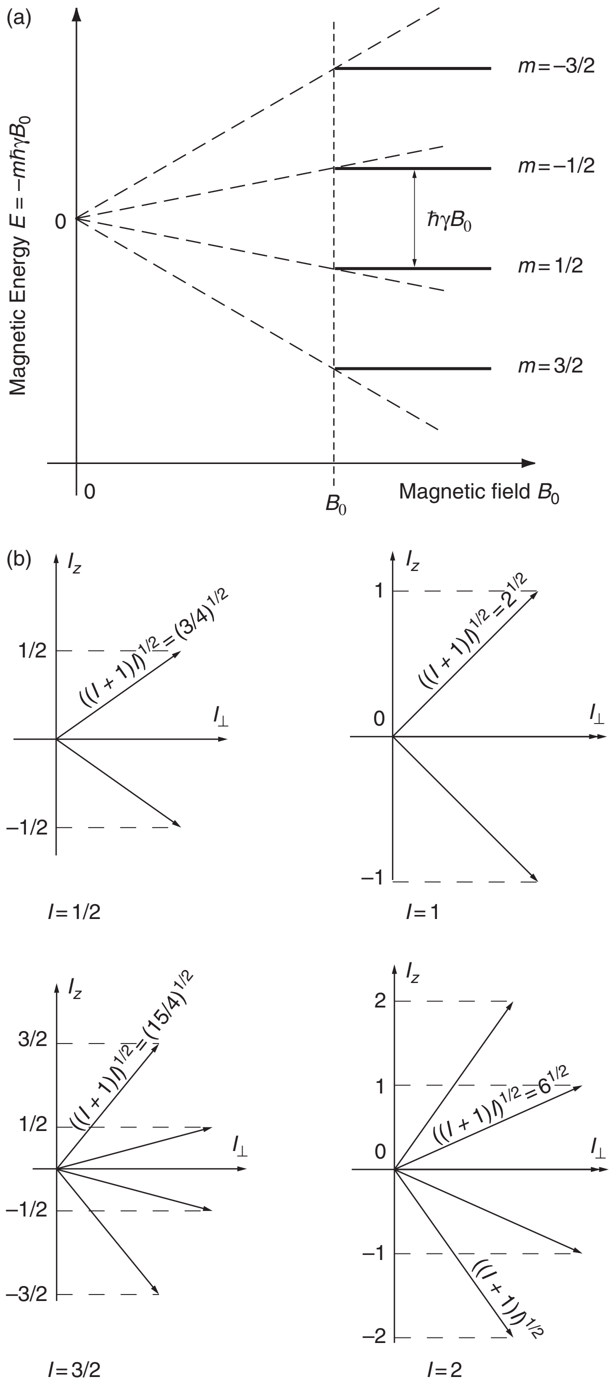

Figure 1.1 (a) The magnetic energy levels for a free particle with spin $I = 3/2$ and gyromagnetic factor γ in a steady magnetic field B_0. (b) The possible projections of the spin of a free particle in a steady field along the z-axis of the field and perpendicular to it, for spins $I = 1/2$, 1, 3/2 and 2. The perpendicular component rotates in its plane with undetermined phase angle