3. *Orbach Process*. If a low-lying spin level exists at an energy Δ above the ground manifold, a Raman process involving that state can dominate the spin-lattice relaxation. In this case τ_1 is predicted to vary as $\exp(\Delta/k_bT)$, from which Δ can be obtained. This process was first described by Orbach and co-workers [14,15].
4. *Other Mechanisms*. Several other mechanisms have been proposed and verified experimentally; most of them are even more complex than the one presented above [9, Chapter 8]. In gases, collisions are an important relaxation mechanism.

10.3 SPIN RELAXATION: BLOCH MODEL

We now turn to another view of spin relaxation, using the famous Bloch equations [16] that describe the time dependence of the total spin magnetization vector **M** (Eq. 1.8) in the presence of static and oscillating magnetic fields externally applied. Here we present only a brief summary of the treatment. Full derivations are available in many standard texts [9, Chapter 2; 17, Sections 3–5; 18, Chapter 11; 19,20]; most of these are developed in the context of NMR; however, the basic theoretical framework is also applicable to EPR.

The Bloch equations are useful because they

1. Furnish a visual and intuitive model, in terms of vectors and torques, of the magnetic-resonance phenomenon. This is especially helpful when an understanding of the effects of microwave pulses in EPR is required (Chapter 11). An introduction to the rotating frame also ensues.
2. Simplify the very complex subject of the spin interaction with the atomic surroundings by gathering together these aspects into just two empirical parameters, the relaxation times τ_1 and τ_2.
3. Serve well to introduce the important concepts of absorption and dispersion.
4. Lead gracefully into the topic of interconversion between two ensembles of different spin-state populations, for example, chemical exchange.
5. Give the reader a feeling for and confidence in the use of ensembles of spins. This can be a helpful preparation for the adoption of the more powerful and complex density-matrix techniques.

The Bloch equations apply to any pair of energy levels, more or less adequately. They do, of course, have limitations in their usefulness. For instance, one cannot employ them to visualize the quantum-mechanical behavior of individual spins. Thus consideration of spin-spin coupling, for example, hyperfine effects, are excluded, as are anisotropies of the medium. Also the effect on the magnetization of the emitted photons, radiation damping [21], is neglected in our formulation. Furthermore, the simplification that only two relaxation parameters are required is not rigorously valid and fails to be exact especially for solids.

10.3.1 Magnetization in a Static Magnetic Field

In the absence of an external magnetic field, the bulk magnetization **M**, if present (Section 1.8), is fixed in space, with components M_x, M_y and M_z in an arbitrary cartesian coordinate system. When the ensemble of magnetic moments is exposed to a static and homogeneous magnetic field **B**, in the absence of relaxation, it is in a dynamic equilibrium.[8] However, here **M** is not fixed in space, moving according to the equation of motion (Eq. B.75)

$$\frac{d\mathbf{M}}{dt} = \gamma_e \mathbf{M} \wedge \mathbf{B} \tag{10.14}$$

where γ_e is the electronic magnetogyric ratio (Section 1.7), equal to $g\beta_e/\hbar$.Taking **B** along **z**, one obtains

$$\frac{dM_x}{dt} = \gamma_e B M_y \tag{10.15a}$$

$$\frac{dM_y}{dt} = -\gamma_e B M_x \tag{10.15b}$$

$$\frac{dM_z}{dt} = 0 \tag{10.15c}$$

The solutions

$$M_x = M_\perp{}^0 \cos \omega_B t \tag{10.16a}$$

$$M_y = M_\perp{}^0 \sin \omega_B t \tag{10.16b}$$

$$M_z = M_z^0 \tag{10.16c}$$

to these equations reveal that **M** precesses about **B** with an angular frequency $\omega_B = -\gamma_e B$ (the classical Larmor frequency) if $M_\perp{}^0$ is non-zero.[9] The longitudinal magnetization M_z is constant. Here the field was taken to be static; the effects of modulating it sinusoidally (as is done in practice) lead to more complex solutions.

Let us now include relaxation effects. If the system is subjected to a sudden change in the magnitude and/or direction of **B**, then M_x, M_y and M_z (referenced to the new field direction) in general relax to their new equilibrium values at different rates. For instance, if the magnetic field is suddenly turned on ($B = 0$ at $t = t_0$), then ΔN initially is 0 and it as well as the component M_z follow an exponential rise with time (Fig. 10.3).

We assume (as is usual) that the transverse components M_x and M_y relax with the same rate constant, which is the inverse of a new characteristic time τ_2 called the

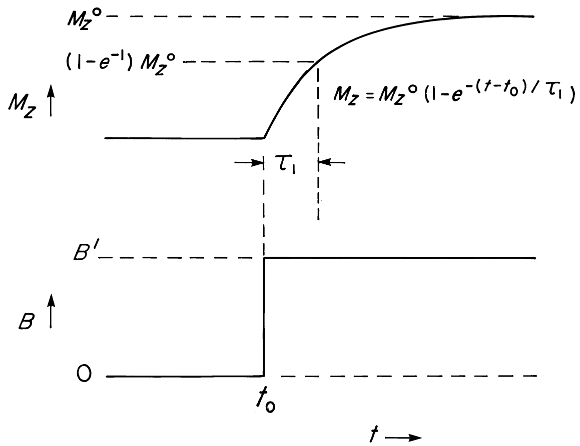

FIGURE 10.3 Behavior of the magnetization M_z when a magnetic field **B** ($\|$**z**) is suddenly increased from zero to a magnitude B' at time $t = t_0$. τ_1 is the appropriate longitudinal relaxation time.

transverse relaxation time. Thus

$$\frac{dM_x}{dt} = \gamma_e B M_y - \frac{M_x}{\tau_2} \tag{10.17a}$$

$$\frac{dM_y}{dt} = -\gamma_e B M_x - \frac{M_y}{\tau_2} \tag{10.17b}$$

$$\frac{dM_z}{dt} = \frac{M_z^0 - M_z}{\tau_1} \tag{10.17c}$$

The solutions of these empirical equations feature the decay of the components M_x and M_y to zero. Note that both τ_1 and τ_2 in the Bloch formulation are empirical bulk (ensemble) properties. The scheme reveals nothing about the physical mechanisms giving rise to these parameters. Note that in the absence of relaxation effects (i.e., τ_1 and $\tau_2 = \infty$), we retrieve Eqs. 10.15.

10.3.2 Addition of an Oscillating Magnetic Field

As noted in Chapter 1, transitions can be induced between the magnetic-energy levels when an oscillating magnetic field $\mathbf{B}_1$ is imposed in a direction perpendicular to **B**. We now assume that, in addition to the static field **B** considered in Section 10.3.1, a sinusoidally varying monochromatic field $\mathbf{B}_1$ is introduced with components

$$B_{1x} = B_1 \cos \omega t \tag{10.18a}$$

$$B_{1y} = B_1 \sin \omega t \tag{10.18b}$$

$$B_{1z} = 0 \tag{10.18c}$$

We take ω to be positive. With the addition of terms for these components, the complete equations of motion (the Bloch equations) are[10]

$$\frac{dM_x}{dt} = \gamma_e(BM_y - B_1 \sin \omega t\, M_z) - \frac{M_x}{\tau_2} \tag{10.19a}$$

$$\frac{dM_y}{dt} = \gamma_e(B_1 \cos \omega t\, M_z - BM_x) - \frac{M_y}{\tau_2} \tag{10.19b}$$

$$\frac{dM_z}{dt} = \gamma_e(B_1 \sin \omega t\, M_x - B_1 \cos \omega t\, M_y) - \frac{M_z - M_z{}^0}{\tau_1} \tag{10.19c}$$

Here γ_e is taken to be the same for the two field directions, $\mathbf{B}$ and $\mathbf{B}_1$. In principle, one can integrate these equations to obtain the functional form of the components of $\mathbf{M}$.

10.3.3 Rotating Frame

Because $\mathbf{M}$ is continuously precessing about $\mathbf{B}$, it is easier to visualize the time dependence of $\mathbf{M}$ if we transform to a coordinate frame that is rotating about $\mathbf{z}$ (azimuthal angle ϕ) at the angular frequency ω with the same sense as that of $\mathbf{B}_1$ (Fig. 10.4), taking the new x axis $\mathbf{x}_\phi$ to be along $\mathbf{B}_1$. The components of $\mathbf{M}$ in this new coordinate frame are called $M_{x\phi}$, $M_{y\phi}$ and M_z (the latter is unaffected by the transformation). The Bloch equations in the rotating frame then are

$$\frac{dM_{x\phi}}{dt} = -(\omega_{\mathrm{B}} - \omega)M_{y\phi} - \frac{M_{x\phi}}{\tau_2} \tag{10.20a}$$

$$\frac{dM_{y\phi}}{dt} = (\omega_{\mathrm{B}} - \omega)M_{x\phi} + \gamma_e B_1 M_z - \frac{M_{y\phi}}{\tau_2} \tag{10.20b}$$

$$\frac{dM_z}{dt} = -\gamma_e B_1 M_{y\phi} - \frac{M_z - M_z{}^0}{\tau_1} \tag{10.20c}$$

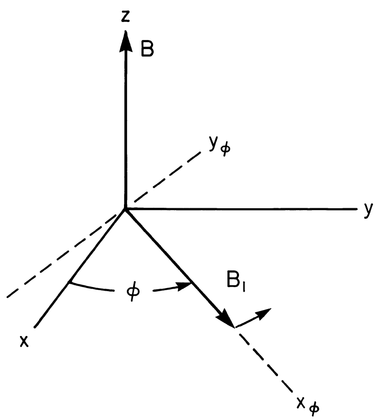

FIGURE 10.4 Diagram showing the rotating frame (dashed lines) in relation to an axis system fixed in space. This frame rotates at the angular frequency ω with the same sense as the rotation of $\mathbf{B}_1$.

where $\omega_B = -\gamma_e B$. Here, the B_1 time dependences present in Eqs. 10.16 are absent.

Note that, much as kinetic energy $\frac{1}{2}mV^2$ depends on what translational coordinate system is being used, the energy of the spin moment in a magnetic field depends on the rotational frame selected; that is, the fields seen by the particle differ. It turns out that the spin temperature T_s and also the spin-lattice relaxation time τ_1 are somewhat dependent on the rotational speed [24]. We shall not dwell here on these sophisticated concepts.

It is useful (Section 10.5.1) to define a complex transverse magnetization

$$M_{+\phi} = M_{x\phi} + \mathrm{i}M_{y\phi} \tag{10.21}$$

Thus Eqs. 10.20*a*,*b* can be combined to yield

$$\frac{dM_{+\phi}}{dt} + \alpha M_{+\phi} = \mathrm{i}\gamma_e B_1 M_z \tag{10.22}$$

where

$$\alpha = {\tau_2}^{-1} - \mathrm{i}(\omega_B - \omega) \tag{10.23}$$

The equation for $M_{-\phi}$, obtained simply by writing the complex conjugate, contains no different information.

10.3.4 Steady-State Solutions of the Bloch Equations

Equations 10.20 are a set of coupled linear differential equations with constant coefficients and can be solved in a straightforward manner. The steady-state solutions are

$$M_{x\phi} = -M_z^0 \frac{\gamma_e B_1(\omega_B - \omega){\tau_2}^2}{1 + (\omega_B - \omega)^2{\tau_2}^2 + {\gamma_e}^2{B_1}^2\tau_1\tau_2} \tag{10.24a}$$

$$M_{y\phi} = +M_z^0 \frac{\gamma_e B_1\tau_2}{1 + (\omega_B - \omega)^2{\tau_2}^2 + {\gamma_e}^2{B_1}^2\tau_1\tau_2} \tag{10.24b}$$

$$M_z = +M_z^0 \frac{1 + (\omega_B - \omega)^2{\tau_2}^2}{1 + (\omega_B - \omega)^2{\tau_2}^2 + {\gamma_e}^2{B_1}^2\tau_1\tau_2} \tag{10.24c}$$

Note that the response $M_{x\phi}$ is in phase with $\mathbf{B}_1$, whereas $M_{y\phi}$ is 90° out of phase. The magnitudes of $M_{x\phi}$ and $M_{y\phi}$ tend to be small compared to that of M_z^0. For sufficiently small values of B_1, the last term in each denominator may be neglected. This power-saturation term predicts that $\mathbf{M}$ vanishes as B_1 (i.e., ρ_ν) increases indefinitely.[11] The steady-state solutions are not appropriate in rapid time-resolved experiments to be discussed later.

The solutions in Eqs. 10.24 apply only for a field $\mathbf{B}_1$ rotating in the same sense as $\mathbf{M}$. The usual experimental setup has $\mathbf{B}_1$ oscillating linearly in the (say) x direction, with components

$$B_{1x} = 2B_1 \cos \omega t \tag{10.25a}$$
$$B_{1y} = 0 \tag{10.25b}$$
$$B_{1z} = 0 \tag{10.25c}$$

and with ω taken to be positive. This can be decomposed into two equal-magnitude and oppositely rotating fields (Fig. 10.5)

$$\mathbf{B}_1 = \mathbf{B}_1(+) + \mathbf{B}_1(-) \tag{10.26a}$$
$$= B_1(\cos \omega t\,\mathbf{i} + \sin \omega t\,\mathbf{j}) + B_1(\cos \omega t\,\mathbf{i} - \sin \omega t\,\mathbf{j}) \tag{10.26b}$$

$\mathbf{B}_1(+)$ rotates in the same direction as the Larmor precession, so that $\omega_B - \omega$ is small and the resonance effects predicted by Eqs. 10.24 are significant. However, $\mathbf{B}_1(-)$ rotates in the opposite direction, and its effects being small are neglected herein. Note that now only half of the radiation-energy density is effective in inducing transitions.

The effects of the imposition of the oscillating field $\mathbf{B}_1$ are often described in terms of dynamic (volume) susceptibilities χ' and χ'' (often called the 'Bloch susceptibilities'). For electrons, in view of Eq. 1.15, we have

$$\mathbf{M} = \chi\mathbf{H} = \chi\mathbf{B}/\kappa\mu_0 \tag{10.27a}$$

that is

$$M_z{}^0 = \chi^0 B/\kappa\mu_0 \tag{10.27b}$$
$$= \tfrac{1}{2} g\beta_e \Delta N^{ss}/V \tag{10.27c}$$

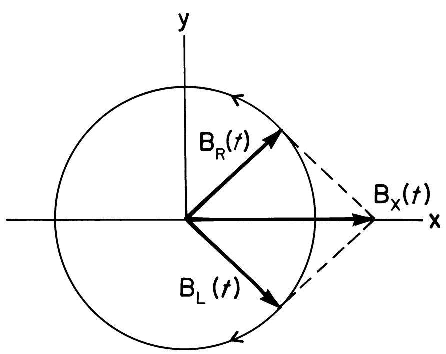

FIGURE 10.5 Resolution of the magnetic excitation field $\mathbf{B}_1$, oscillating with frequency ν along direction $\mathbf{x}$, into two circularly polarized components in plane xy, one rotating clockwise and the other counterclockwise. Static magnetic field $\mathbf{B}$ is located normal to $\mathbf{B}_1$, along $\mathbf{z}$. See Fig. E.4c for a laboratory example, where oppositely rotating magnetic fields of equal frequencies and magnitudes add vectorially to yield a linearly polarized field $\mathbf{B}_1$.

where χ^0 is the static magnetic susceptibility $\kappa\mu_0 N_V g^2\beta_e^{\,2}/4k_bT$ (Eq. 1.17*c*); here T is the temperature of the lattice and N_V is the sample's (spin) volume density. We >consider a medium in which χ and the relative permeability κ are isotropic. Then, consistent with Eqs.10.24 and 10.27*a*, we can define dynamic magnetic susceptibilities via

$$\chi' = +\kappa\mu_0 M_{x\phi}/B_1 \tag{10.28a}$$
$$\chi'' = -\kappa\mu_0 M_{y\phi}/B_1 \tag{10.28b}$$

where B_1 is half the amplitude of the linearly polarized excitation field. Thus

$$\chi' = \chi^0 \frac{\omega_B(\omega_B - \omega)\tau_2^{\,2}}{1 + (\omega_B - \omega)^2\tau_2^{\,2} + \gamma_e^{\,2}B_1^{\,2}\,\tau_1\tau_2} \tag{10.29a}$$
$$\chi'' = \chi^0 \frac{\omega_B\tau_2}{1 + (\omega_B - \omega)^2\tau_2^{\,2} + \gamma_e^{\,2}B_1^{\,2}\,\tau_1\tau_2} \tag{10.29b}$$

These are dimensionless quantities (see Section 1.9). Note that $\chi'' = \chi'/[(\omega_B - \omega)\tau_2]$ and that both depend on B, as well as on B_1 via the power-saturation term.[12] Figure 10.6 illustrates the frequency profile of χ' and χ'' under non-saturating conditions.

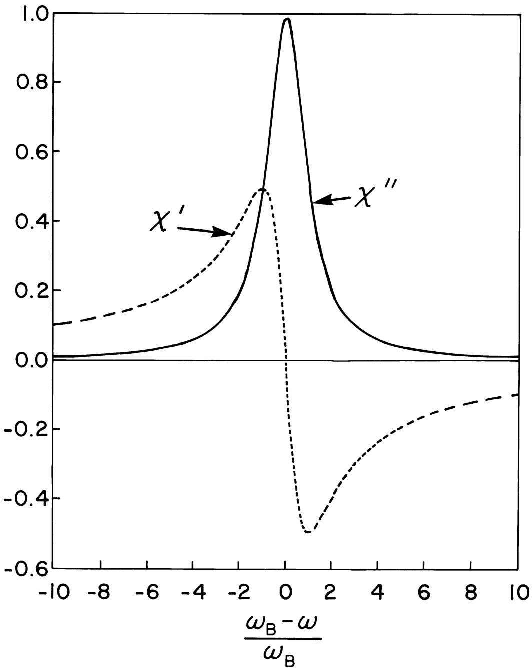

FIGURE 10.6 The *in-phase* (χ') and *out-of-phase* (χ'') components of the dynamic magnetic susceptibility (Eqs. 10.29) versus the angular frequency deviation.

Equations 10.19 are not correct at small fields B (i.e., at $B \leq B_1$) since the susceptibilities in reality do not vanish at $\omega_B = 0$, but rather must be modified in light of the condition expressed in Note 10.

The dynamic susceptibilities χ' and χ'' have definite and important meanings, representing the dispersion and power absorption of the magnetic-resonance transition (see Section F.3.5). The latter is especially important and is the radiative part of $d(-\mathbf{M}^{\mathrm{T}} \cdot \mathbf{B}_{\text{total}})/dt$ (Eqs. 1.8 and 1.14a). It follows [9, Chapter 2; 20] that the power $P_a(\omega)$ absorbed by the magnetic system from the linearly polarized excitation field (Eq. 10.25) is

$$P_a(\omega) = 1 \frac{\omega \, \chi'' {B_1}^2}{\mu_0 V} \tag{10.30}$$

per unit sample volume.[13] Hence, with use of Eq. 10.29b

$$P_a(\omega) = \frac{\pi}{\mu_0} \frac{{B_1}^2}{(1 + {\gamma_e}^2 {B_1}^2 \tau_1 \tau_2)^{1/2}} \omega \; \omega_B \chi^0 Y \tag{10.31}$$

Note that $Y(\omega - \omega_B)$ is a normalized lorentzian function (Table F.1a) and depends on the experimental conditions [i.e., on B_1 via the linewidth $\Gamma = (1 + {\gamma_e}^2 {B_1}^2 \tau_1 \tau_2)^{1/2}/\tau_2$]. The increase in linewidth as saturation sets in can be discussed in terms of 'lifetime broadening'. Increasing the microwave power produces spin transitions at a faster rate and hence decreases the mean spin-orientation lifetime. As B_1 becomes very large, τ_1 becomes proportional to ${B_1}^{-2}$ (Eq. 10.13) and hence Γ becomes insensitive to B_1 (when τ_2 is non-zero).

As long as ${\gamma_e}^2 {B_1}^2 \tau_1 \tau_2 \ll 1$, this saturation term can be neglected, and both P and dP/dB are proportional to ${B_1}^2$. When the absorption line is strongly saturated (${\gamma_e}^2 {B_1}^2 \tau_1 \tau_2 \gg 1$), according to the Bloch theory, both χ' and χ'' decrease with increasing power P_0 (e.g., Fig. F.8a), and P_a becomes constant. However, note that the theory fails when $B_1 > B$ and $\tau_1 \neq \tau_2$, as in solids (see Note 11.6 and Chapter 8 of Ref. 11).

The various equations in this section have been written in terms of ω and $\omega_B = -\gamma_e B$. It has been implied that ω is the continuous variable and ω_B is a constant for the spin species at hand, with resonance centered at a particular value $\omega_r = \omega_B$. In EPR, of course, usually ω is held constant and B is scanned. It is relatively easy to switch to B as the variable,[14] with $\omega = \omega_B$ held fixed; now ω_B is the angular frequency at a particular value B_r of B as given by the resonance condition.

When we switch to field-sweep conditions, the lineshape function, now $Y(B - B_r)$, is a lorentzian with half width at half-height given by

$$\Gamma = \frac{1}{|\gamma_e| \tau_2} (1 + {\gamma_e}^2 {B_1}^2 \tau_1 \tau_2)^{1/2} \tag{10.32}$$

In more recent work, the effect of field modulation on the magnetic field $\mathbf{B}$ appearing in the Bloch equations has been treated successfully, via perturbation theory [27]. Expression for both the absorption and dispersion phenomena are given.