1

Phenomenological theory of relaxation

1.1 Nuclear magnetic relaxation

In order to establish a microscopic theory of nuclear magnetic relaxation we first study the behaviour of an atomic nucleus in the presence of a constant magnetic field H_0 in a fixed direction, which we take to be the positive z-direction. If the spin vector of the nucleus is the operator $\mathbf{I}$, the nuclear angular momentum operator $\mathbf{m}$ is expressed in terms of $\mathbf{I}$ by (McConnell, 1960; Schiff, 1968)

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

where $\hbar$ is the Planck constant divided by 2π. The measured values of I_z are the eigenvalues of I_z, and these eigenvalues are numbers:

$$-I, -I+1, -I+2, \ldots, I-1, I, \tag{1.2}$$

where I is a positive integer or half-odd integer. We call I the *spin* of the nucleus. Moreover the measured value of the total angular momentum operator $(m_x^2+m_y^2+m_z^2)^{1/2}$ is $\{I(I+1)\}^{1/2}\hbar$.

A nucleus with spin angular momentum $\mathbf{m}$ has a permanent spin magnetic moment $\boldsymbol{\mu}$, given by

$$\boldsymbol{\mu} = \gamma\mathbf{m}, \tag{1.3}$$

where γ is the *gyromagnetic ratio* of the nucleus. This is positive, if $\boldsymbol{\mu}$ and $\mathbf{m}$ are parallel, and it is negative if they are antiparallel. A similar phenomenon occurs in the case of the electron and for it the gyromagnetic ratio is almost exactly the *Bohr magneton* $e\hbar/(2m_e c)$, where e is the electronic charge, m_e the mass of the electron and c the velocity light *in vacuo*. If m_e is replaced by the mass m_p of the proton, we have the *nuclear magneton* β_N:

$$\beta_N = \frac{e\hbar}{2m_p c}. \tag{1.4}$$

The nuclear magnetic moment is often expressed by

$$\boldsymbol{\mu} = g\beta_N\mathbf{I}, \tag{1.5}$$

where g is a dimensionless quantity called the *nuclear g factor*. For the

proton g is 2.7927 and for the neutron it is -1.913, the negative sign indicating that the magnetic moment is in the direction opposite to that of the spin angular momentum. The values of physical quantities will often be taken from Royal Society (1975). The magnetic moment of the proton is 1.4106×10^{-26} J T^{-1}.

For all nuclei the absolute value of g lies between 0.1 and 6 approximately (Pople, Schneider & Bernstein, 1959). Since $m_p = 1836 m_e$, it follows from (1.4) and (1.5) that the ratio of a nuclear magnetic moment to the electron magnetic moment is of order 10^{-3}–10^{-4}. From (1.1), (1.3) and (1.5) we see that

$$\boldsymbol{\mu} = \gamma \hbar \mathbf{I} = g \beta_N \mathbf{I}, \tag{1.6}$$

so that the magnetic moments of different nuclei are specified by the values of their spins and their g factors.

According to classical electrodynamics a nucleus with magnetic moment $\boldsymbol{\mu}$ under the influence of a magnetic field of intensity $\mathbf{H}$ experiences a torque $\boldsymbol{\mu} \times \mathbf{H}$ (McConnell, 1980*b*, p. 2) and therefore its angular momentum $\mathbf{m}$ satisfies

$$\frac{\mathrm{d}\mathbf{m}}{\mathrm{d}t} = \boldsymbol{\mu} \times \mathbf{H}.$$

Hence, from (1.3),

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \gamma(\boldsymbol{\mu} \times \mathbf{H}). \tag{1.7}$$

The Hamiltonian $\mathscr{H}$ for the interaction of the nucleus with the field is given by (Jeans, 1933, p. 377)

$$\mathscr{H} = -(\mu_x H_x + \mu_y H_y + \mu_z H_z).$$

On employing the quantum mechanical equations of motion

$$\frac{\mathrm{d}m_x}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}(\mathscr{H} m_x - m_x \mathscr{H}),$$

etc., and the commutation relations

$$m_y m_z - m_z m_y = \mathrm{i}\hbar m_x,$$

etc. (McConnell, 1960), it is easily seen that (1.7) is valid also in quantum theory.

Suppose that the magnetic field is in the z-direction and that its intensity has the constant value H_0. Then (1.7) yields

$$\frac{\mathrm{d}\mu_x}{\mathrm{d}t} = \gamma \mu_y H_0, \qquad \frac{\mathrm{d}\mu_y}{\mathrm{d}t} = -\gamma \mu_x H_0, \qquad \frac{\mathrm{d}\mu_z}{\mathrm{d}t} = 0. \tag{1.8}$$

Hence

$$\frac{d^2\mu_x}{dt^2} = -\gamma^2 H_0^2 \mu_x, \qquad \frac{d^2\mu_y}{dt^2} = -\gamma^2 H_0^2 \mu_y$$

and by suitably choosing time zero we may express the solution of (1.8) as

$$\mu_x = \mu_\perp \cos \omega_0 t, \qquad \mu_y = -\mu_\perp \sin \omega_0 t, \qquad \mu_z = \mu_\parallel, \tag{1.9}$$

where

$$\omega_0 = \gamma H_0 \tag{1.10}$$

and $\mu_\perp$, $\mu_\parallel$ are constants. Equations (1.9) show that the dipole axis of the nucleus precesses about H_0 with angular velocity $-\omega_0$. We call the motion of the dipole *Larmor precession*, ω_0 the *Larmor angular frequency* and ν_0 defined by

$$\nu_0 = \frac{\gamma H_0}{2\pi} \tag{1.11}$$

the *Larmor frequency*.

The energy of the nucleus in the presence of H_0 is $-\mu_z H_0$, and according to (1.2), (1.6) and (1.10) the energy levels are

$$I\hbar\omega_0, (I-1)\hbar\omega_0, \ldots, -(I-1)\hbar\omega_0, -I\hbar\omega_0. \tag{1.12}$$

In principle these energy levels could be disturbed by the fields of neighbouring nuclei. When we are interested only in liquids that are in steady state thermal motion, the fields of the other nuclei will average out and we may therefore accept (1.12) as providing the energy levels, if H_0 is sufficiently strong. The energy difference between consecutive levels is $\pm\hbar\omega_0$. Hence in order to raise the nuclear spins from one level to the next highest level we should irradiate the nuclei with electromagnetic waves of frequency $|\nu_0|$ given by (1.11). Such a process is called *nuclear magnetic resonance absorption*, and it gives rise to a sharp spectral line. In general the study of magnetic resonance is concerned with observing transitions caused by the field whose frequency corresponds to the Larmor precession of the magnetic nuclei around a constant field. This frequency lies in the radiofrequency (rf) range.

Since we are dealing with steady state motion, the populations of nuclei in the various levels obey the Boltzmann distribution law

$$\frac{\exp[-E_{m'}/kT]}{\sum_{m'} \exp[-E_{m'}/kT]}. \tag{1.13}$$

In the present case the values of the energies $E_{m'}$ are given by (1.12) and let us therefore put

$$E_{m'} = -m'\gamma\hbar H_0, \tag{1.14}$$

where m' assumes the values (1.2). We now consider the case of identical nuclei, their number per unit volume being N. By symmetry the resultant magnetization is in the z-direction. We obtain the magnetization M per unit volume by averaging the magnetic moment $\gamma\hbar m'$ over the energy states and multiplying by N. Hence, we deduce from (1.13) and (1.14) that

$$M = N\frac{\sum_{m'=-I}^{I}\gamma\hbar m'\exp[\gamma\hbar m'H_0/kT]}{\sum_{m'=-I}^{I}\exp[\gamma\hbar m'H_0/kT]}. \tag{1.15}$$

To estimate the magnitude of the exponent we put m' equal to unity, take H_0 equal to 1 T and the nucleus to be a proton so that (Pople *et al.*, 1959, Appendix A) $\gamma H_0 = 2\pi\times 4.258\times 10^7\ \mathrm{s}^{-1}$, put $\hbar = 1.055\times 10^{-34}\ \mathrm{J\,s}$ and $k = 1.381\times 10^{-23}\ \mathrm{J\,K}^{-1}$, thus obtaining for room temperature (300 K)

$$\frac{\gamma\hbar m'H_0}{kT} = \frac{\gamma\hbar H_0}{kT} = 6.813\times 10^{-6}, \tag{1.16}$$

which is very much less than unity. On expanding the exponentials in (1.15) we obtain approximately

$$M = \frac{N\gamma\hbar\sum_{m'=-I}^{I} m'\left(1+\dfrac{\gamma\hbar m'H_0}{kT}\right)}{\sum_{m'=-I}^{I}\left(1+\dfrac{\gamma\hbar m'H_0}{kT}\right)}.$$

Employing the results

$$\sum_{m'=-I}^{I} 1 = 2I+1, \qquad \sum_{m'=-I}^{I} m' = 0,$$

$$\sum_{m'=-I}^{I} m'^2 = \tfrac{1}{3}I(I+1)(2I+1)$$

we find that

$$M = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT}H_0. \tag{1.17}$$

The multiplier of H_0 is the *static nuclear susceptibility*, which we write χ_0, so that

$$\chi_0 = \frac{N\gamma^2\hbar^2 I(I+1)}{3kT}. \tag{1.18}$$

The susceptibility is a macroscopic quantity which is expressed in terms of microscopic quantities by (1.18). Since, from (1.6)

$$\mu^2 = \gamma^2\hbar^2 I(I+1),$$

(1.18) is equivalent to

$$\chi_0 = \frac{N\mu^2}{3kT}. \tag{1.19}$$

This is Curie's law (Curie, 1895), which was established theoretically by Langevin (1905). We see from (1.19) that the susceptibility is positive and therefore, by definition, the collection of nuclei is *paramagnetic*. It is moreover temperature dependent. The decrease in χ_0 resulting from the increase in temperature is due to the increased randomization of the orientations of the dipoles. We also note that, on account of the μ^2-factor in (1.19), the nuclear susceptibilities are of order 10^{-6} to 10^{-8} that of the electron paramagnetic susceptibility.

When there is no external field, $E_{m'}$ vanishes by (1.14). Then the energy levels have equal populations for steady state motion. When the external field H_0 is effective, (1.13) shows that, when a steady state has been attained, the populations of the various energy levels are different. This means that the application of the external field produces changes in the spin orientations, and this in turn produces an increase $-(\mathbf{M}\cdot\mathbf{H}_0)$ of energy per unit volume in the spin system. By (1.17) this quantity is negative and the surplus energy must be dispersed throughout the environment composed of the molecules which constitute the thermal motion. This environment is called the *lattice*; this term is not confined to atoms in a crystal lattice but is applied also to a liquid or a gaseous medium.

We shall now consider some effects of the mutual interactions of identical nuclear spins on each other. If there is no external magnetic field, the ensemble of spins will be in thermal equilibrium, there will be no preferential direction for the spins, and hence $\mathbf{M}$ will be zero. If a constant field $\mathbf{H}_0$ in a fixed direction is applied, this will produce for each spin with magnetic moment $\boldsymbol{\mu}$ an interaction energy $-(\boldsymbol{\mu}\cdot\mathbf{H}_0)$. When thermal equilibrium is attained, the spins will have a Boltzmann distribution deduced from (1.13) by putting $E_{m'} = -(\boldsymbol{\mu}\cdot\mathbf{H}_0)$ and summing over the spins. Thus the spins will be preferentially in states where $(\boldsymbol{\mu}\cdot\mathbf{H}_0)$ has large values, and consequently $\mathbf{M}$ will be in the direction of $\mathbf{H}_0$.

If the field is changed to another fixed value $\mathbf{H}_0'$ in the same direction, the system is disturbed, the orientations of the dipoles will change and the new magnetization $\mathbf{M}'$ per unit volume will have a component $M_\parallel'$ in the direction of $\mathbf{H}_0'$ and a component $M_\perp'$ in a transverse direction. When the system reaches a new steady state of equilibrium, the components will satisfy

$$M_\parallel' = M', \qquad M_\perp' = 0,$$

where

$$M' = \chi_0 \mathbf{H}'_0$$

and χ_0 is given by (1.18). The approach to such a state is called *nuclear magnetic relaxation*. The approach of $M'_{\parallel}$ to its equilibrium value is called *longitudinal relaxation* and the approach of $M'_{\perp}$ to zero is called *transverse relaxation*.

In the nuclear magnetic relaxation processes that we shall investigate a system of particles having spins and magnetic moments is made to interact with a strong constant field in the z-direction and also with a weak time dependent perturbing field, the interaction Hamiltonian involving the particle spins. If M_0 is the value of M_z when equilibrium has been reached, it is frequently found that M_z obeys an equation

$$\frac{dM_z}{dt} = -\frac{M_z - M_0}{T_1}. \tag{1.20}$$

The longitudinal relaxation is caused by the interaction of the spins with the lattice and is therefore often called *spin–lattice relaxation*. T_1 is the *spin–lattice relaxation time* or *longitudinal relaxation time*. Equation (1.20) shows that $M_z - M_0$ tends to zero with e^{-t/T_1}.

While the motion is settling down to its steady state, the individual magnetic particles precess about the z-axis. This precessional motion is influenced by the internal field arising from interactions with spins of neighbouring particles. This internal field does not contribute to the total energy of the system. However, it has the effect that the particles do not all precess with the same angular velocity, and so the transverse components M_x, M_y tend to zero. If there exists an equation

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \tag{1.21}$$

and we are dealing with isotropic media, there will also be an equation

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2}. \tag{1.22}$$

T_2 is called the *spin–spin relaxation time* or *transverse relaxation time*. Similarly transverse relaxation is called *spin–spin relaxation*. For solids it it usually found that $T_1 \gg T_2$, whereas for liquids $T_1 \approx T_2$. The quantities T_1^{-1}, T_2^{-1} are called *relaxation rates*.

1.2 The Bloch equations

We consider the time variations of the components of **M**, the magnetization

per unit volume resulting from a constant magnetic field **H** in a fixed direction. From (1.7) we deduce that

$$\begin{aligned}\frac{dM_x}{dt} &= \gamma(M_y H_z - M_z H_y),\\ \frac{dM_y}{dt} &= \gamma(M_z H_x - M_x H_z),\\ \frac{dM_z}{dt} &= \gamma(M_x H_y - M_y H_x),\end{aligned} \tag{1.23}$$

provided that the interactions of the spins between themselves and with their environment are neglected. Bloch (1946) made two assumptions:

(*a*) In order to include the influence of the neglected interactions we combine (1.20)–(1.22) with (1.23).

(*b*) H_x, H_y, H_z need not be constants.

He thus proposed the *Bloch equations*:

$$\begin{aligned}\frac{dM_x}{dt} - \gamma(M_y H_z - M_z H_y) + \frac{M_x}{T_2} &= 0,\\ \frac{dM_y}{dt} - \gamma(M_z H_x - M_x H_z) + \frac{M_y}{T_2} &= 0,\\ \frac{dM_z}{dt} - \gamma(M_x H_y - M_y H_x) + \frac{M_z - M_0}{T_1} &= 0.\end{aligned} \tag{1.24}$$

These equations are phenomenological but are nevertheless very useful for the study of nuclear induction.

Bloch considered the case of

$$H_x = H_1 \cos \omega t, \qquad H_y = -H_1 \sin \omega t, \qquad H_z = H_0 \tag{1.25}$$

corresponding to a constant rotating rf field $\mathbf{H}_1$ perpendicular to a constant field H_0 and rotating about it in a clockwise direction. He supposed that both H_1 and H_0 are positive and that $H_1 \ll H_0$. On substituting (1.25) into (1.24) we have

$$\begin{aligned}\frac{dM_x}{dt} - \gamma(M_y H_0 + M_z H_1 \sin \omega t) + \frac{M_x}{T_2} &= 0,\\ \frac{dM_y}{dt} - \gamma(M_z H_1 \cos \omega t - M_x H_0) + \frac{M_y}{T_2} &= 0,\\ \frac{dM_z}{dt} + \gamma(M_x H_1 \sin \omega t + M_y H_1 \cos \omega t) + \frac{M_z - M_0}{T_1} &= 0.\end{aligned} \tag{1.26}$$

To discuss (1.26) we transform to a new cartesian coordinate system shown in Fig. 1.1 such that the z'-axis coincides with z-axis, the x'-axis is in the direction of $\mathbf{H}_1$ and consequently the y'-axis makes the angle ωt with the y-axis. We denote by u and v the components of $\mathbf{M}$ in the x'- and y'-directions, respectively, so that

$$\begin{aligned} M_x &= u\cos\omega t + v\sin\omega t, \qquad M_y = -u\sin\omega t + v\cos\omega t, \\ u &= M_x\cos\omega t - M_y\sin\omega t, \qquad v = M_x\sin\omega t + M_y\cos\omega t. \end{aligned} \tag{1.27}$$

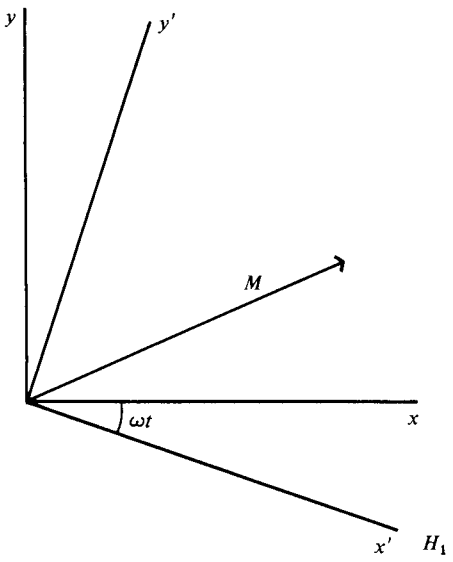
On substitution from (1.27) into (1.26) we deduce that

$$\begin{aligned} \frac{\mathrm{d}u}{\mathrm{d}t} - (\omega_0 - \omega)v + \frac{u}{T_2} &= 0, \\ \frac{\mathrm{d}v}{\mathrm{d}t} + (\omega_0 - \omega)u - \gamma H_1 M_z + \frac{v}{T_2} &= 0, \\ \frac{\mathrm{d}M_z}{\mathrm{d}t} + \gamma H_1 v + \frac{M_z - M_0}{T_1} &= 0, \end{aligned} \tag{1.28}$$

where γH_0 is written ω_0 according to (1.10). If in (1.24) we make the substitutions

$$\begin{aligned} M_x &\mapsto u, \qquad M_y \mapsto v, \qquad M_z \mapsto M_z \\ H_x &\mapsto H_1, \qquad H_y \mapsto 0, \qquad H_z \mapsto H_0 - \frac{\omega}{\gamma}, \end{aligned}$$

Fig. 1.1 The coordinate system with x'-axis in the direction of the constant rotating rf field H_1. The positive third axis is perpendicular to the plane of the paper and upwards.



we obtain (1.28). Thus the Bloch equations hold in the rotating frame for the *effective field* $\mathbf{H}_e$ given by

$$\mathbf{H}_e = H_1\mathbf{i} + \left(H_0 - \frac{\omega}{\gamma}\right)\mathbf{k}, \tag{1.29}$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors in the directions of $0x'$, $0y'$, $0z'$.

The spin–lattice relaxation time in the rotating frame $T_{1\rho}$ is defined as the time of decay of the component of magnetization in the direction of H_e. According to (1.29) this direction makes with $0z'$ an angle θ such that

$$\tan\theta = \frac{\gamma H_1}{\omega_0 - \omega}.$$

The spin–spin relaxation time in the rotating frame is denoted by $T_{2\rho}$. An expression for $T_{1\rho}$ in the case of weak collisions was derived by Jones (1966).

The steady state solutions of (1.28) are found by putting the time derivatives equal to zero, so that we have

$$\begin{aligned} u &= (\omega_0 - \omega)vT_2, \\ v &= -(\omega_0 - \omega)uT_2 + \gamma H_1 M_z T_2, \\ M_z &= M_0 - \gamma H_1 T_1 v. \end{aligned}$$

It is easily found that

$$\begin{aligned} \frac{u}{M_0} &= \frac{\gamma H_1(\omega_0 - \omega)T_2^2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}, \\ \frac{v}{M_0} &= \frac{\gamma H_1 T_2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}, \\ \frac{M_z}{M_0} &= \frac{1 + (\omega_0 - \omega)^2 T_2^2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}. \end{aligned} \tag{1.30}$$

It follows from (1.27) that

$$\begin{aligned} \frac{M_x}{M_0} &= \frac{\gamma H_1 T_2\{(\omega_0 - \omega)T_2 \cos\omega t + \sin\omega t\}}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}, \\ \frac{M_y}{M_0} &= \frac{\gamma H_1 T_2\{-(\omega_0 - \omega)T_2 \sin\omega t + \cos\omega t\}}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}. \end{aligned} \tag{1.31}$$

We use these results to examine the case of a constant external field H_0 in the z-direction and a periodic rf field $2H_1 \cos\omega t$ in the x-direction. This system may be replaced by the H_0 and H_1 fields defined in (1.25) together with an H_1 field rotating with angular velocity $-\omega$. Then, since we are employing a linear theory, we obtain from (1.31)

$$\frac{M_x}{M_0}=\gamma H_1 T_2\left\{\frac{(\omega_0-\omega)T_2\cos\omega t+\sin\omega t}{1+(\omega_0-\omega)^2T_2^2+\gamma^2H_1^2T_1T_2}+\frac{(\omega_0+\omega)T_2\cos\omega t-\sin\omega t}{1+(\omega_0+\omega)^2T_2^2+\gamma^2H_1^2T_1T_2}\right\}. \tag{1.32}$$

Let us now consider resonance effects due to a weak periodic field $2H_1\cos\omega t$. Since the Larmor precession of the spins is clockwise, resonance can arise only from the component of $2H_1\cos\omega t$ which results from the rotation in the clockwise direction. Hence we neglect the second term in the braces of (1.32), and M_x is obtained from the first equation of (1.31). Introducing from (1.10), (1.17) and (1.18)

$$\gamma H_0=\omega_0, \qquad M_0=\chi_0 H_0, \tag{1.33}$$

where χ_0 is the static nuclear susceptibility, we have

$$M_x=\frac{\chi_0\omega_0H_1T_2\{(\omega_0-\omega)T_2\cos\omega t+\sin\omega t\}}{1+(\omega_0-\omega)^2T_2^2+\gamma^2H_1^2T_1T_2}. \tag{1.34}$$

Then writing

$$M_x=2H_1\cos\omega t\,\chi'(\omega)+2H_1\sin\omega t\,\chi''(\omega) \tag{1.35}$$

we see from (1.34) and (1.35) that

$$\chi'(\omega)=\frac{\frac{1}{2}\chi_0\omega_0(\omega_0-\omega)T_2^2}{1+(\omega_0-\omega)^2T_2^2+\gamma^2H_1^2T_1T_2}, \tag{1.36}$$

$$\chi''(\omega)=\frac{\frac{1}{2}\chi_0\omega_0T_2}{1+(\omega_0-\omega)^2T_2^2+\gamma^2H_1^2T_1T_2}. \tag{1.37}$$

If we put

$$\chi(\omega)=\chi'(\omega)+i\chi''(\omega), \tag{1.38}$$

where we call $\chi(\omega)$ the *complex magnetic susceptibility*, then (1.35) may be expressed as

$$M_x=\mathrm{Re}(2H_1\chi(\omega)\,e^{-i\omega t}),$$

where Re denotes (real part of).

We return to the rotating system of Fig. 1.1 in order to derive an expression for the time rate of absorption of energy per unit volume. Employing the expression $\boldsymbol{\mu}\times\mathbf{H}_1$ for the torque exerted on a magnetic moment $\boldsymbol{\mu}$ by $\mathbf{H}_1$ we see from (1.27) that $\mathbf{H}_1$ produces on the nuclear spin system a torque of moment $-vH_1$ per unit volume about the positive z-axis. If $\phi=-\omega t$, the angle through which the x'- and y'-axes have turned about the z-axis, the work done per unit volume by H_1 is $-vH_1\phi$. Since we are concerned with steady motion, $\mathrm{d}v/\mathrm{d}t$ vanishes and the rate of work done is $vH_1\omega$; in other words, the power absorbed by the system is $vH_1\omega$. From (1.30), (1.33) and (1.37) the *power absorption* $b(\omega)$ is given by