Ch. III MACROSCOPIC ASPECTS OF NUCLEAR MAGNETISM

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nuclear spin system is calculated from (79) and (80) and found to be The power $P=2\omega H_{1X}^{2}$ " dissipated in the coil and provided by the

$$P = |M_d| \frac{H_0}{T_1} \left(1 - \frac{Q_0}{Q} \right). \tag{81}$$

either, a phenomenon known as 'pulling'. Let us write in (67): If $\omega_c \neq |\omega_0|$, the frequency of oscillation ω will not be equal to ω_0 circuit was equal to the frequency ω of the oscillation, that is, to $|\omega_0|$. we implicitly assumed that the frequency $\omega_c = (LC)^{-1}$ of the tuned for the impedance of the tuned circuit containing the nuclear spins, By using the formula (68) rather than the more general formula (67)

$$C\omega = rac{1}{L\omega(1-\delta)}, \quad ext{whence} \quad \delta = rac{\omega^2 - \omega_c^2}{\omega^2} \cong 2rac{\omega - \omega_c}{\omega} \cong 2rac{(\omega - \omega_c)}{\omega_c}.$$

Eqn. (67) can be rewritten

$$Z = L\omega Q(1-\delta) \left[\frac{1+j4\pi Q\eta\chi + jQ\delta}{1+4\pi\eta\chi - j/Q} \right]^{-1}.$$
 (82)

The condition $Z^{-1} = 0$ becomes

$$4\pi Q \eta \chi''(\omega) = -1, \qquad 4\pi \eta \chi'(\omega) = -\delta. \tag{83}$$

From (22) we obtain

$$\chi'(\omega) = -T_2(\omega - |\omega_0|)\chi''(\omega) \cong -T_2(\omega - |\omega_0|)\chi''(\omega_0)$$

$$T_2(\omega - |\omega_0|) = -2Q \frac{\omega - \omega_c}{\omega_c} \cong 2Q \frac{\omega_c - |\omega_0|}{\omega_c}.$$
 (84)

 $2Q/\omega_c T_2$ which except for very low frequencies is very small. The From (84) we see that $|\omega - |\omega_0|$ is smaller than $|\omega - \omega_c|$ by the ratio 'pulling' is thus almost always negligible.

entirely calculable from first principles even in the non-linear region. simpler than most oscillators from a theoretical point of view, since its behaviour, independent of the characteristics of electronic tubes, is We shall conclude by remarking that the nuclear spin oscillator is

steady-state oscillation when the conditions for it have been created such as band width, noise figure, dynamic behaviour in reaching the are outside the scope of this book. that could be pursued by an extension of the methods outlined here Further study (14) of properties of nuclear spin maser oscillators

experimental methods in nuclear magnetism is far from complete. of some interesting but rather special methods such as observation of Thus no mention has been made of super-regenerative methods, nor As already stated at the beginning of this section, this review of

> ponent M_z of the nuclear magnetization (1). the resonance in low fields through a change in the longitudinal com-

problem, is that of the 'spinning' sample. Suppose that the inhomoand will simply mention two rather elegant devices that have been discuss the engineering problems connected with these requirements fields are homogeneity in space and stability in time. We shall not average of all those 'seen' during the motion. Fig. III, 19 shows two within the interval ΔH and will produce an appreciable narrowing of will cause each nuclear spin to 'see' all the values of the applied field ('spinning') of the whole sample at a frequency much higher than Δv , than $\Delta \nu = \gamma/2\pi \times 10^{-3}$ c/s (4 c/s for protons). A macroscopic motion gauss, so that the Larmor frequencies of any two nuclei differ by less geneity ΔH of the field over the sample is smaller than, say, one milliused in that connexion. The first, aimed at solving the inhomogeneity The two main requirements to be met by the magnets producing these fields of several thousands gauss, currently used in nuclear magnetism. signals obtained with and without spinning. the resonance line, the effective field 'seen' by each proton being the We conclude with a few words about the production of the magnetic

curacy of, say, 10^{-8} over long periods of time it may not be necessary order to keep the resonance condition $\omega = |\gamma H_0|$ with a relative acmagnet since its frequency is proportional to the applied field. in practice, would be the use of a maser oscillator operating in the same with varying success. One of the simplest in principle, if possibly not ing them together can be imagined. Several schemes have been tried that H_0 and ω be separately stable to the same extent, if a device lock-In connexion with the stability problem it can be remarked that in

APPENDIX

Proof of the Kramers-Krönig relations

susceptibility $\chi = \chi' - i \chi''$ are very general and apply to many systems besides a magnetization but many other examples can be imagined: \mathcal{E} electric field and nature or of different nature. In nuclear magnetism ${\mathscr E}$ is a magnetic field and Rresponse R(t) can be observed. $\mathscr E$ and R may be physical quantities of the same which a time-dependent excitation $\mathscr{E}(t)$ can be applied, and an output where a assemblies of nuclear spins. Consider a physical system S, with an input at particles on a scatterer and R outgoing flux, etc. R electric polarization, $\mathscr E$ input and R output voltages, $\mathscr E$ incoming flux of The relations (8') between the real and the imaginary parts of the complex

a few general assumptions to be satisfied by the systems S which we consider. tion & is monochromatic. In order to prove the K.-K. relations (8'), we make The very definition of χ implies that the response to a monochromatic excita-

(i) The systems S are linear

explicitly excluded. We mean thereby that if R_1 and R_2 are responses to excitations \mathscr{E}_1 and \mathscr{E}_2 the response to the excitation $c_1\mathscr{E}_1+c_2\mathscr{E}_2$ will be $c_1R_1+c_2R_2$. Saturation is thus

(ii) The systems S are stationary

from (i) and (ii). Let f(t) be the response to the unit impulse excitation $\delta(t)$ and, according to (ii), f(t-t') be the response to $\delta(t-t')$. A monochromatic excitation condition of a monochromatic response to a monochromatic excitation follows If R(t) is the response to $\mathscr{E}(t)$, the response to $\mathscr{E}(t-t_0)$ will be $R(t-t_0)$. The

$$\mathscr{E}(t) = e^{i\omega t} = \int_{-\infty}^{\infty} e^{i\omega t} \delta(t-t') dt'$$

with, because of (i) and (ii), a response

$$R(t) = \int_{-\infty}^{\infty} e^{i\omega t'} f(t - t') dt' = e^{i\omega t} \int_{-\infty}^{\infty} e^{-i\omega t'} f(t') dt'$$
 (85)

which is indeed monochromatic with the same frequency

(iii) The systems S obey the principle of causality

proof of the K.-K. relations. It implies in particular that f(t) (which incidentally for t < 0. Equation (85) can thus be written: is real, being the response of a physical system to a real excitation $\delta(t)$) vanishes If $\mathscr{E}(t) = 0$ for $t < t_0$, R(t) = 0 for $t < t_0$. This assumption is the key to the

$$e^{i\omega t}\int_{0}^{\infty}f(t')e^{-i\omega t'}dt',$$

$$=e^{i\omega t}, \qquad R=\chi(\omega)e^{i\omega}$$

whence, from the definition of
$$\chi$$
,
$$\mathscr{E} = e^{i\omega t}, \qquad R = \chi(\omega)e^{i\omega t},$$

$$\chi = \int_{0}^{\infty} f(t)e^{-i\omega t} dt, \qquad \chi' = \int_{0}^{\infty} f(t)\cos\omega t dt, \qquad \chi'' = \int_{0}^{\infty} f(t)\sin\omega t dt. \quad (86)$$

(1V) Finite total response to a finite total excitation

We define the total excitation and the total response by the relations:

$$egin{align} E_T(t) &= \int\limits_{-\infty}^t \left|\mathscr{E}(t')
ight| dt', \ R_T(t) &= \int\limits_{-\infty}^t \left|R(t')
ight| dt'. \ \end{aligned}$$

from it that f(t) has no singularities, for in the simplest case where $R = \mathscr{E}$, $f(t) = \delta(t)$. It is still possible, however, to state that $|tf(t)| \to 0$ when $t \to 0$, for otherwise the integral $\int_{0}^{\infty} |f(t)| dt$ would diverge. mediately from (iv) that $\int\limits_0^\infty |f(t)|\,dt$ is finite. One should not, however, conclude The condition (iv) requires $R_T(t)$ to be finite if $\mathscr{E}_T(t)$ is finite. It follows im-

> The imaginary part $\chi''(\omega)$ is expected on physical grounds to vanish when ω tends to infinity, for otherwise an infinite absorption of energy by the system would occur. That this is actually so is easily verified from:

$$\lim_{\omega \to \infty} \chi''(\omega) = \lim_{\omega \to \infty} \int_{0}^{\infty} f(t) \sin \omega t \, dt = \lim_{\omega \to \infty} \int_{0}^{\infty} dt \, f(t) \int_{0}^{\omega} t \cos(\omega' t) \, d\omega'$$
$$= \lim_{\omega \to \infty} \frac{1}{2} \int_{0}^{\infty} t f(t) \int_{-\omega}^{\omega} e^{i\omega' t} \, d\omega' \to \pi \int_{0}^{\infty} t f(t) \delta(t) \, dt = 0.$$

A similar calculation shows that $\chi'_{\omega} = \lim_{\omega \to \infty} \chi'(\omega)$ does not necessarily vanish. This was to be expected, for in the simplest case when $\mathscr{E} = R$, $\chi'(\omega) = 1$ for all excitation frequencies. The function $\psi(\omega) = \chi(\omega) - \chi_{\infty}$, where $\chi(\omega)$ is defined by

$$\chi(\omega) = \int_{0}^{\infty} f(t)e^{-i\omega t} dt, \qquad ($$

is a complex function of the real variable ω , which vanishes at both ends of the real axis. According to a general theorem in the theory of analytical functions of a complex variable, the function $\psi(z)$, where the complex variable z replaces ω

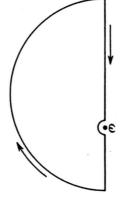


Fig. III, 20. Integration contour.

z. The important point for the validity of this statement is that the integral in principle (iii). Then, applying the theorem of residues to the function in (86), is in half the plane $\operatorname{im}(z) \leqslant 0$ an analytical regular function of the variable (86) is over positive values of t only, which in turn is a consequence of the causality

$$\xi(z) = \psi(z)/(z-\omega)$$

for the contour shown in Fig. III, 20, we find

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega') - \chi_{\infty}}{\omega' - \omega} d\omega' + \pi i \{\chi(\omega) - \chi_{\infty}\} = 0.$$
 (87)

The real and imaginary parts of (87) give respectively

$$\chi'(\omega) - \chi_{\infty} = \frac{1}{\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\chi''(\omega') d\omega'}{\omega' - \omega},$$

$$\chi''(\omega) = -\frac{1}{\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\chi'(\omega') - \chi_{\infty}}{\omega' - \omega} d\omega'.$$

nuclear magnetism. Using the fact that χ' is even and χ'' is odd they are sometimes rewritten as These are the K.-K. formulae in the form (8') most suitable for the study of

$$\chi'(\omega) - \chi_{\infty} = \frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{\chi''(\omega')\omega' d\omega'}{\omega'^{2} - \omega^{2}},$$

$$\chi''(\omega) = -\frac{2\omega}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{\chi'(\omega') - \chi_{\infty}}{\omega'^{2} - \omega^{2}} d\omega'.$$
(88)

As a special case consider a system with a monochromatic absorption response:

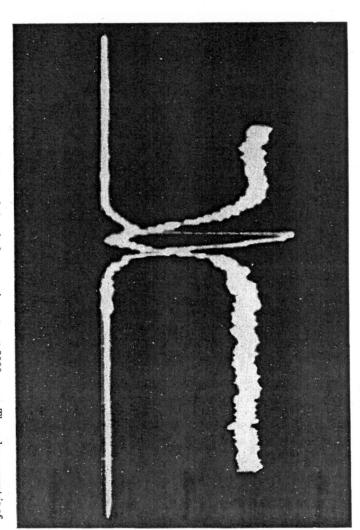
$$\chi''(\omega) = \delta(\omega - \omega_0) - \delta(-\omega - \omega_0) = \delta(\omega - \omega_0) - \delta(\omega + \omega_0). \tag{89}$$
thions (88) give $\chi'(\omega) - \chi = \frac{2}{2} - \frac{\omega_0}{2}$

The relations (88) give
$$\chi'(\omega) - \chi_{\infty} = \frac{2}{\pi} \frac{\omega_0}{\omega_0^2 - \omega^2}$$
, (

slightly damped oscillator, and use these relations as a starting-point to demonhave been possible to start from (89) and (89') obtained as a limiting case of a which is the response of an undamped harmonic oscillator. Conversely, it would strate the K.-K. relations.

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Frg. III, 18. Normal and enhanced signal of protons in water at 3000 gauss. The enhancement is of the order of -50. The scale is different for the two signals as can be seen from the reduced noise on the lower trace.