

V. MAGNETIC RESONANCE

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A. THEORY OF SIDEBANDS IN THE SPECTRA OF COHERENTLY MODULATED SYSTEMS

The basic theory of sidebands that are produced when a system is modulated by a periodic external field was developed by Karplus¹ and applied by him and others to Stark modulation in microwave spectroscopy and to Zeeman modulation in nuclear magnetic resonance (NMR). We have extended this theory to the general case in which any term in the Hamiltonian of a system is periodically modulated. The extension considers the possibility that the system Hamiltonian $\mathcal{H}(t)$ may change during the course of modulation in such a way that

$$[\mathcal{H}(t), \mathcal{H}(t')] \neq 0.$$

The main result may be stated as follows: If $V \cos \omega t$ is the effect of the (weak) radiation field that causes transitions between instantaneous states m and n of the system, the absorption corresponding to $n \rightarrow m$ in the unperturbed system is proportional to

$$g(\omega_{mn}, \omega; t) = \sum_{k=-\infty}^{\infty} V_{mn}^{(k)} e^{-ik\omega_s t} f(\omega_{mn} - k\omega_s, \omega; t),$$

where $V_{mn}^{(k)}$ is the k^{th} Fourier coefficient in the expansion of $V_{mn}(t)$, ω_s is the frequency of modulation of some external field that affects the system, and f is the line shape function defined by Karplus.¹ This result may be physically stated as follows: Each absorption line of the unmodulated system responds independently to modulation. The system of sidebands of each line can be computed according to the classical theory of frequency modulation by considering the variation of line intensity and frequency under adiabatic changes in the external field, with time considered parametrically. Thus all that is required to compute the entire sideband behavior is the computation of the static spectrum for every instantaneous value of the applied modulating field.

We have used this theory to calculate the form of the absorption and dispersion modes of the first several sidebands as viewed through lock-in detectors operating at the first several harmonics of the modulation frequency for cases in which the

- (a) Zeeman effect
- (b) quadrupole coupling
- (c) chemical shift
- (d) scalar spin-spin coupling
- (e) dipolar coupling

in nuclear resonance spectra are modulated by a periodic external field. These results

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are being applied in our experiments on electric field effects in NMR spectra.²

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References

1. R. Karplus, Phys. Rev. 73, 1027 (1948).
2. Quarterly Progress Report No. 72, Research Laboratory of Electronics, M. I. T., January 15, 1964, pp. 59, 61.