

Redfield A G. On the theory of relaxation processes.
IBM J. Res. Develop. 1:19-31, 1957. Reprinted with minor revisions in
Advan. Magnetic Reson. 1:1-32, 1965.
[Harvard University, Cambridge, MA]

Relaxation of a spin system by a weak fluctuating perturbation is treated both semiclassically and quantum mechanically. The theory can take account of spatial correlations in a solid, or correlations between different perturbations in a molecule. The relationship between the classical and semiclassical theory, and range of validity, are discussed in detail. [The SCI® indicates that this paper has been cited over 305 times since 1961.]

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"In 1954 I was working on a theory of nuclear spin dynamics in a solid, whose central result was that rapid transverse spin-spin relaxation would be quenched in the presence of a resonant radio frequency field. When rapid transverse relaxation is quenched in this way, slow relaxation can still occur by the influence of residual thermal lattice vibrations, or of conduction electrons in metals. I was looking for a theory to describe such relaxation. The theory of Wangness and Bloch, on relaxation of a single spin-1/2 system,¹ had just appeared but it was not clear to me how to generalize their theory to treat a more complex spin system, or how to take spatial correlations of fluctuations into account.

"About this time I heard Ionel Solomon lecture on his theory of relaxation of a two-spin system, in which he introduced the idea of transitions between states of the spin system which

were not constants of the Hamiltonian, and calculated on these transitions using semiclassical formulae previously derived by Abragam and Pound^{2,3} I realized that Solomon's theory could be expressed more simply in terms of density matrix formalism. I found it straightforward to retrace the steps followed by Abragam and Pound in a rotating frame (interaction) representation, to get an expression for the rate of change of off-diagonal elements of the density matrix under the influence of a semiclassical random perturbation. This theory seemed to me at the time to be a relatively trivial extension of its predecessors, and I might have filed it away if N. Bloembergen had not urged me to develop and publish it.

"This paper has been utilized mostly by scientists interested in interpretation of NMR and EPR experiments, as opposed to those interested in statistical physics per se. Probably such scientists are attracted by the inelegant but transparent notation I used, and also by the generality I achieved. Good notation is an important and often-overlooked part of any theoretical physics work. I was naive in my knowledge of statistical physics, and this led me to use notation and reasoning which could be understood by a wide range of readers. I was also fortunate, being influenced by Solomon's work on hydrogen fluoride, to direct the theory towards chemical as well as solid state applications.

"This work was being done just as high-resolution NMR as a chemical tool was coming of age. With the current general availability of ever-more-sophisticated pulsed NMR equipment it is exciting to watch, at last, detailed measurements on complex molecules, measurements of the type which I contemplated, but could not hope to perform, in my paper written down so long ago."

1. Wangness R K & Bloch F. The dynamical theory of nuclear induction. *Phys. Rev.* 89:728-39, 1953.
2. Solomon I. Relaxation processes in a system of two spins. *Phys. Rev.* 99:559-65, 1955.
3. Abragam A & Pound R V. Influence of electric and magnetic fields on angular correlations. *Phys. Rev.* 92:943-62, 1953.