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# This Week's Citation Classic

**Freeman R & Anderson W A.** Use of weak perturbing radio-frequency fields in nuclear magnetic double resonance. *J. Chem. Phys.* 37:2053-73, 1962. [Varian Associates, Instrument Division, Palo Alto, CA]

**This paper describes what happens in a high resolution nuclear magnetic resonance (NMR) spectrum when a single line is irradiated with a second radiofrequency field, $B_2$, of low intensity. Transitions which share a common energy level with the irradiated transition split into doublets. [The *SCI*® indicates that this paper has been cited over 315 times since 1962.]**

Ray Freeman
Physical Chemistry Laboratory
Oxford University
Oxford OX1 3QZ
England

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"In the early-1960s double resonance methods were just being introduced into high resolution NMR spectroscopy, using relatively strong irradiation fields, $B_2$, to decouple or 'wash out' multiplet structure. Our paper examines what happens when only a very weak $B_2$ is employed such that only one NMR transition is directly affected. This use of a gentle touch in just the right place has earned the name 'spin tickling' but we were too circumspect to use this term in the article.

"The splitting observed in a spin tickling experiment can be thought of as arising from a non-crossing rule of energy levels (mixing in previously forbidden zero-quantum and double-quantum transitions). It is therefore formally analogous to Fermi resonance in infrared spectroscopy, and nowadays there are parallels in microwave and laser spectroscopy. Zero-quantum transitions are insensitive to broadening by the spatial inhomogeneity of the applied magnetic field while double-quantum transitions are doubly sensitive. This explains one of the curious effects which we observed—some doublets were well resolved while others were poorly resolved since the component lines were acquiring some of the character of these multiple-quantum transitions.

"My coauthor, Wes Anderson, deserves the major part of the credit for this discovery. Our collaboration came about in the following way. I had been using double resonance to determine relative signs of spin coupling constants, and had been trying to understand the mechanism of double resonance experiments in general. There was a pioneering paper by Bloom and Shoolery[1] which described decoupling experiments in a two-spin system containing $^{19}F$ and $^{31}P$ nuclei. My attempt to translate their observations into the context of proton-proton double resonance led to a prediction which seemed intuitively quite wrong—that distinctly different effects would be observed depending on whether one chose to irradiate the high-field or the low-field multiplet. This apparent paradox was resolved by David Whiffen,[2] who realized that it was an artifact of the field sweep mode used in all spectrometers at that time, but this prompted us to attempt some theoretical calculations of frequency-sweep double resonance spectra and to build an internally referenced field/frequency locked spectrometer.

"I had been planning to take some sabbatical leave and it seemed natural to choose to spend it with Anderson at Varian Associates in California, since he was a world authority on NMR instruments and double resonance techniques. Only a day or two after my arrival I found myself giving a seminar on double resonance experiments, and it was followed by some penetrating questions from the audience, in particular one from Harry Weaver (now at Hewlett Packard) which sparked off the idea that 'tickling' a single transition might be a useful experiment to try. Anderson went on to work out the entire scheme of possible double resonance experiments[3] and we then proceeded to study spin tickling in some detail. His typical thoroughness probably accounts for the fact that the resulting publication was fairly complete in its coverage, which may explain its frequent citation. For further reading, see *Fourier Transform N.M.R. Spectroscopy*."[4]

1. **Bloom A L & Shoolery J N.** Effects of perturbing radiofrequency fields on nuclear spin coupling. *Phys. Rev.* 97:1261-5, 1955.
2. **Freeman R & Whiffen D H.** The effect of a second radiofrequency field on high resolution proton magnetic resonance spectra. *Proc. Phys. Soc. London* 79:794-807, 1962.
3. **Anderson W A & Freeman R.** Influence of a second radio frequency field on high resolution nuclear magnetic resonance spectra. *J. Chem. Phys.* 37:85-103, 1962.
4. **Shaw D.** *Fourier transform N.M.R. spectroscopy.* Amsterdam: Elsevier, 1976. 357 p.