

Van Vleck J H. The dipolar broadening of magnetic resonance lines in crystals.
Phys. Rev. 74:1168-83, 1948. [Harvard University, Cambridge, MA]

The so-called method of moments in quantum mechanics is used to calculate the mean square line width in magnetic resonance on the assumption that the line width is caused by dipolar interaction. The article also includes a discussion of the phenomenon of so-called 'exchange narrowing.' [The SC[®] indicates that this paper has been cited over 1015 times since 1961.]

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"This is not my most profound or imaginative paper. The reason that it is referred to so often is that it was published in the early days of nuclear magnetic resonance which has developed into a very powerful investigative tool both for physicists and chemists. It was thus somewhat of a pioneer article, but at the same time has continued to be relevant.

"My paper was entirely theoretical in character, and was motivated by some experimental measurements which my colleague Professor Purcell was making of the dependence of the width of the magnetic resonance lines of LuF on the direction of the applied magnetic field. Accurate calculation of the line shape is a problem of prohibitive difficulty but I showed that the mean square line width is something which can be very easily computed (also, with increasing difficulty, the mean fourth, mean sixth...power of the breadth). This

procedure is usually called the method of moments. The reason that this is a feasible procedure is the invariance of the trace or diagonal sum in quantum mechanics, which enables one to calculate mean values without knowing the individual eigenfunctions and eigenvalues.

"The method of moments was not new at the time I wrote this paper. I had already employed it in other articles on other problems. In particular it had been introduced by I. Waller in a 1932 paper which I quoted, and in which he used it to calculate the dipolar broadening of spectral lines.¹ However, Waller was interested in the case where the Zeeman splitting (i.e., the splitting of the line in the magnetic field) is small compared to the line width, whereas this is not so in the case of magnetic resonance. Instead it is necessary to truncate the Hamiltonian function, i.e., omit certain terms in the dipolar interaction which give rise to satellites instead of broadening the line. It is this truncation which was the new feature of my paper, and which was responsible for its utility.

"The article also discusses how exchange coupling (the Heisenberg exchange effect) in paramagnetic resonance makes the line breadth at half power smaller than one would calculate on the basis of the mean square line width and an assumed Gaussian or Lorentzian line shape. That this is the case is because the exchange coupling enhances the fourth but not the second moment. This concept of exchange narrowing was presented, earlier in a brief paper by Gorter and myself.²

1. Waller I. Über die Magnetisierung von paramagnetischen Kristallen in Wechselfeldern.
Zeitsch. Physik. 79:370-388, 1932.

2. Gorter C J & Van Vleck J H. The role of exchange interaction in paramagnetic absorption.
Phys. Rev. 72:1128-9, 1947.