CC/NUMBER 18
APRIL 30, 1984

This Week's Citation Classic™

Ramsey N F. Magnetic shielding of nuclei in molecules.
Phys. Rev. 78:699-703, 1950.
[Department of Physics, Harvard University, Cambridge, MA]

An expression is developed for the magnetic shielding of a nucleus by the induced circulation of the electrons in a molecule. The expression consists of a first term similar to that in atomic diamagnetism and a second term that corresponds to second order paramagnetism. [The *SCI*® indicates that this paper has been cited in over 540 publications since 1955.]

Norman F. Ramsey
Department of Physics
University of Virginia
Charlottesville, VA 22901
and
Department of Physics
Harvard University
Cambridge, MA 02138

February 14, 1984

"My interest in the problem of magnetic shielding in molecules arose from my activities in developing highly accurate molecular beam magnetic resonance methods to measure the magnetic moments of nuclei in molecules. These methods proved to be so effective that the accuracies of the results were not limited by the methods of measurement but by the uncertainties in the magnetic shielding of the nucleus by the electrons in a molecule. When a magnetic field is applied to an atom, there is an induced circulation of the electrons about the nucleus which produces a magnetic field at the nucleus so the net magnetic field there is somewhat less than that applied, i.e., there is magnetic shielding of the nucleus.

"Willis Lamb[1] had developed a simple theory of magnetic shielding of nuclei in atoms based on his recognition that the effect of an applied magnetic field on a single atom is merely to induce a simple circular motion of the electrons about the nucleus at the Larmor angular frequency $\omega_L = eH/2mc$. Although Lamb's theory was valid for atoms, it was clear even by symmetry that it could not be applied to a molecule since there was no single point to serve as the obvious center for the circular motion. Should the center be one of the nuclei and if so which one? Should it be some intermediate point or was the motion more complicated than circular?

"In my PhD research some years earlier, I had used Van Vleck's elegant theory[2] of molecular magnetic susceptibility and Wick's theories[3,4] of rotational magnetic moments and spin rotational interactions, so I hoped that these theories might serve as useful models in developing a theory of magnetic shielding. Such, indeed, proved to be the case.

"I showed in the paper that the magnetic shielding consisted of two major terms: one was similar to the Lamb expression for nuclear shielding in atoms while the other, often called second order paramagnetism, existed only for molecules. Although I gave a general expression for the second order paramagnetism term, that term is difficult to evaluate and many subsequent papers have been directed toward its evaluation for different molecules by various appropriate methods. I also showed in the paper that the second order paramagnetism term could be experimentally evaluated in those few cases where the interaction energy of the nuclear magnetic moment with the rotational angular momentum had been measured.

"The primary reason that the paper has become one of the most cited is that it provides the fundamental theoretical basis for all later work on nuclear magnetic shielding and on the chemical shifts of nuclear magnetic resonances (NMR) that have made NMR such a powerful tool for analysis in chemistry, physics, and biology. For a recent reference, see *Principles of High Resolution NMR in Solids*."[5]

1. **Lamb W E, Jr.** Internal diamagnetic fields. *Phys. Rev.* 60:817-19. 1941. (Cited 160 times since 1955.)
2. **Van Vleck J H.** *The theory of electric and magnetic susceptibilities.* Oxford: Clarendon Press. 1932. 384 p.
3. **Wick G C.** Magnetic moment of a rotating hydrogen molecule. *Z. Phys.* 85:25-8. 1933.
4. --------------. On the magnetic field of a rotating molecule. *Phys. Rev.* 73:51-6. 1948. (Cited 70 times since 1955.)
5. **Mehring M.** *Principles of high-resolution NMR in solids.* Berlin: Springer-Verlag, 1983. 342 p.