

This Week's Citation Classic

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Saika A & Slichter C P. A note on the fluorine resonance shifts.

J. Chem. Phys. 22:26-8, 1954.

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It is shown that the large range of fluorine magnetic resonance shifts among different fluorine compounds arises from the valence p electrons. The linear dependence on the ionic character of the bond is also explained. [The SCI® indicates that this paper has been cited in over 345 publications since 1961.]

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"When I was with H.S. Gutowsky at the University of Illinois, an appealing experiment by him¹ remained to be challenged. The experiment showed that the fluorine resonance shifts are linearly dependent upon the electronegativity of the atom bonded to the fluorine, and, furthermore, they cover a much wider range of 10^{-3} than the proton shift range of 10^{-5} . While planning to tackle the problem, I learned that C.P. Slichter in the physics department had an ingenious idea that p electrons must be responsible for the large shifts in fluorine.

"I set out to coin his idea quantum mechanically according to the general theory for the nuclear magnetic shielding by Ramsey.² The theory, as it

stands, is not readily applicable to individual cases, requiring some penetrating simplifications. In the absence of an external static field, the orbital angular momentum is quenched in molecules, but on application of a static field, p electrons will be polarized to a certain extent. Even a slight difference in the degree of this polarization is expected to produce an appreciable effect on the second-order paramagnetic term. Therefore, the diamagnetic term was entirely left out of consideration. Also, the paramagnetic term from other atoms was neglected because of its $1/r^3$ falling off. The problem then was reduced to an atomic one. In this model, one p electron is considered as missing from the closed shell for the covalently bonded fluorine, giving rise to a large paramagnetic shift of 14×10^{-4} . On the other hand, the paramagnetic term would vanish for the completely ionic F⁻ because of the filled shell. These considerations that the shift is dependent upon the fraction of the unbalanced p electrons gave an explanation for its linear dependence on the ionic character of the bond.

"Now, after almost 30 years, I repeated the calculation by many-body perturbation theory,³ applying Ramsey's expression as it stands. The result has been found to be in quantitative agreement with experiment, but the essential features of our previous model have survived. This simplicity together with its general applicability to molecules with p or d valence electrons may be one of the reasons why the paper has been highly cited. The story is reminiscent of a certain merit of the non-computer age."

1. Gutowsky H S & Hoffman C J. Nuclear magnetic shielding in fluorine and hydrogen compounds. *J. Chem. Phys.* 19:1259-67, 1951.
2. Ramsey N F. Magnetic shielding of nuclei in molecules. *Phys. Rev.* 78:699-703, 1950.
3. Iwaf M & Saika A. Electron correlation effects on magnetic properties of molecules. *J. Chem. Phys.* 77:1951-60, 1982.