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NUCLEAR MAGNETIC RESONANCE OF SODIUM-AMMONIA SOLUTIONS

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UNIVERSITY OF CALIFORNIA

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Kenneth S. Pitzer

June 1958

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Recently McConnell and Holm¹ studied the nuclear magnetic resonance

¹H.M. McConnell and C.H. Holm, J. Chem. Phys., 26, 1517 (1957).

of sodium ammonia solutions and found a substantial Knight shift for the sodium and nitrogen resonance but no detectable shift in the proton resonance. The last result was surprising and its explanation is the purpose of this paper.

The magnitude of the Knight shift in the nitrogen resonance is quite substantial. McConnell and Holm's results may be stated in terms of $P(X)$, the density of X nuclei at an unpaired electron. They find $P(N) = 4.5 \times 10^{24} \text{ cm}^{-3}$, independent of concentration in the range 50-700 moles of ammonia per mole sodium, and estimate this value to be about 15 % of that expected for a 2 electron on a nitrogen atom.

Since the unpaired electron density on the nitrogen nuclei is substantial, the wave function must pervade the ammonia molecules. The only reasonable explanation of the absence of a Knight shift for the protons is the presence of a node in the wave function at these nuclei. This can easily arise if the odd electron orbitals are 3s-like for nitrogen with the outer node at the N-H bond radius. Such orbitals would be 2p-like the vicinity of the proton.

The central field approximation has proven remarkably successful in the treatment of some properties of molecules such as CH_4 , NH_3 , and H_2O .^{2, 3}

²K. E. Banyard and N.H. March; (a) Acta Cryst. 9, 385 (1956); (b) J. Chem. Phys., 26, 1416; 27, 977 (1957).

³K. Funsbashi and J.L. Nagae, J. Chem. Phys., 26, 407 (1957).

This method uses atom-like wave functions centered on the principal nucleus to describe the electronic distribution of the molecule. Thus Banyard and March^{2a} found, after adjustment of parameters, the following radial functions for NH_3 (in atomic units).

$$R_{1s} = 34.8 e^{-6.715r}$$

$$R_{2s} = 3.94 (1 - 2.955 r) e^{-2.15r}$$

$$R_{2p} = 3.34 r e^{-1.53r}$$

We may obtain an approximation to the next higher energy orbital for NH_3 by solving for the 3rd function in this same system. Since the electron density on any one ammonia molecule is small, there is no need to readjust the inner orbitals. Also the condensed state of the ammonia requires the use of the Wigner-Seitz cell boundary conditions. A radius of 4 (in atomic units, i.e. $2.1 \text{ \AA}$) was selected. The conditions are (1) $d(R_{3s})/dr = 0$ at $r = 4$ and (2) orthogonality to both 1s and 2s functions. These serve to evaluate the three parameters and to yield (normalized within the cell)

$$R_{3s} = 0.55 (1 - 3.253r + 1.42r^2) e^{-0.764r}$$

This function has radial nodes at 0.36 and 1.92. The N-H distance in ammonia is 1.91 in atomic units. Thus the outer node of the 3s-like function comes almost exactly at the location of the protons.

While this function indicates correctly the absence of a significant Knight shift for the proton resonance, it yields considerably too small a shift for nitrogen. However, atomic functions restricted to this analytical form are known by comparison with Hartree functions⁴ to yield too small a

⁴It is also interesting to compare the 2s function for nitrogen given by D.R. Hartree and W. Hartree, Proc. Roy. Soc. London, A193, 299 (1948) with the 2s function for ammonia given by Banyard and March. The radius of the node agrees within 5% but $R(e)$ differs by a factor of 2.

value at $r = 0$, although they agree well in the region of the outer node. Thus a more complex calculation would be required to obtain a significant quantitative comparison with the observed nitrogen shift.