

Dependence of Magnetic Shielding of Nuclei upon Molecular Orientation

NORMAN F. RAMSEY

Harvard University, Cambridge, Massachusetts

(Received February 8, 1951)

An expression is calculated for the dependence of the magnetic shielding of nuclei in linear molecules upon the magnetic quantum number of the molecule. The expression for the dependence upon orientation is shown to consist of two different terms. The first of these is directly related to the spin-rotational magnetic interaction constant of the molecule. Since the interaction is known experimentally in the important case of molecular hydrogen, this term can directly be evaluated from the experimental measurements. The other term is proportional to $(3\zeta^2 - r^2)/r^3$ averaged over the electron coordinates in the molecule. This term can be calculated from the wave function of the hydrogen molecule. For molecular hydrogen, the dependence of the nuclear shielding upon the molecular orientation is in principle measurable. Such a measurement, combined with the theory of the paper, provides an important check on the molecular hydrogen wave function.

I. INTRODUCTION

IN an earlier paper,¹ the theory of magnetic shielding of nuclei in molecules was presented. In that paper, the magnetic shielding expression was averaged over all orientation states of the molecule, since such averaging automatically takes place in the high precision measurements by the methods of nuclear resonance absorption² and induction.³ However, in molecular beam resonance experiments, particularly with molecular hydrogen,^{4,5} the nuclear moments are separately measured in states with different magnetic quantum numbers for the rotational angular momentum. Therefore, there is need for a theory of the dependence of the magnetic shielding of the molecule upon the rotational magnetic quantum number. For simplicity, the discussion will be limited to $^1\Sigma$ linear molecules, since experimentally molecules of this type are those of greatest interest.

II. THEORY

In Eq. (9) of the previous paper¹ it was shown that the shielding constant σ_λ for a molecule in orientation λ was given by

$$\sigma_\lambda = (e^2/2mc^2)(0\lambda|\sum_k(x_k^2 + y_k^2)/r_k^3|0\lambda) + \mu_0 \sum_{n\lambda'}' [1/(E_n - E_0)] [H_{0\lambda n\lambda'} L_{n\lambda' 0\lambda} + L_{0\lambda n\lambda'} H_{n\lambda' 0\lambda}], \quad (1)$$

where the quantities are defined in the previous paper.

If for λ one writes σ when the molecule has its axis perpendicular to the magnetic field and π when the axis is parallel, and if ξ , η , and ζ form a cartesian coordinate system attached to the molecule with the ζ -axis being along the internuclear line and with origin at the nucleus for which the shielding is calculated, the above

gives

$$\sigma_\sigma = (e^2/2mc^2)(0|\sum_k(\xi_k^2 + \zeta_k^2)/r_k^3|0) + \mu_0 \sum_{n\lambda'}' [1/(E_n - E_0)] [H_{0\sigma n\lambda'} L_{n\lambda' 0\sigma} + L_{0\sigma n\lambda'} H_{n\lambda' 0\sigma}], \quad (2)$$

$$\sigma_\pi = (e^2/2mc^2)(0|\sum_k(\xi_k^2 + \eta_k^2)/r_k^3|0). \quad (3)$$

In the last equation the complicated second set of terms does not enter because a linear molecule is cylindrically symmetric about its axis as a result of which L has only diagonal matrix elements about that axis since by definition it is then proportional to the ζ -component of orbital angular momentum. From Eq. (18) of the previous paper,¹ and with the notation of Eq. (19) of that paper, (2) above can be expressed as

$$\sigma_\sigma = \frac{e^2}{2mc^2} \left(0 \left| \sum_k \frac{\xi_k^2 + \zeta_k^2}{r_k^3} \right| 0 \right) - \left(\frac{e^2}{4mc^2} \right) \left(\frac{I}{M\mu_N} \right) \left(\sum_i \frac{2Z_i M \mu_N}{I a_i} - \frac{H_r}{J} \right). \quad (4)$$

If σ_{JM} is the average value of σ_λ when the molecule is in a rotational state specified by total rotational angular momentum quantum number J and rotational magnetic quantum number M ,

$$\sigma_{JM} = A v_{JM}(\sigma_\lambda) = A v_{JM}(\sin^2\theta_\lambda \sigma_\sigma + \cos^2\theta_\lambda \sigma_\pi) \quad (5)$$

as in Eq. (15) of the earlier paper.¹ For any specified rotational state wave function of the average of $\sin^2\theta_\lambda$ and $\cos^2\theta_\lambda$ may readily be evaluated. Alternatively, (5) may be rewritten as

$$\sigma_{JM} = \frac{2}{3}\sigma_\sigma + \frac{1}{3}\sigma_\pi - \frac{1}{3}(\sigma_\sigma - \sigma_\pi) A v_{JM}(3 \cos^2\theta_\lambda - 1). \quad (6)$$

For a rotator, however,⁶

$$A v_{JM}(3 \cos^2\theta_\lambda - 1) = -\frac{2}{(2J-1)(2J+3)} \{3(\mathbf{J})_z^2 - \mathbf{J}^2\}, \quad (7)$$

⁶ H. A. Bethe, *Handbuch der Physik*, Vol. 24, p. 557, Eq. (65.38).

¹ N. F. Ramsey, *Phys. Rev.* **78**, 699 (1950).

² Purcell, Torrey, and Pound, *Phys. Rev.* **69**, 37 (1946).

³ F. Bloch, *Phys. Rev.* **70**, 460 (1946).

⁴ Kellogg, Rabi, Ramsey, and Zacharias, *Phys. Rev.* **57**, 691 (1940).

⁵ Kolsky, Phipps, Ramsey, and Silsbee, *Phys. Rev.* **79**, 883 (1950); **80**, 843 (1950).

where \mathbf{J} is the rotational angular momentum vector in units of \hbar and $(\mathbf{J})_z$ is the component of this vector in the direction of the magnetic field. Therefore,

$$\sigma_{JM} = \frac{2}{3}\sigma_\sigma + \frac{1}{3}\sigma_\pi + \frac{2}{3(2J-1)(2J+3)} \times \{3M^2 - J(J+1)\} \{\sigma_\sigma - \sigma_\pi\}. \quad (8)$$

From the combination of Eqs. (3), (4), and (8), together with the fact that the problem is symmetrical in ξ_k and η_k , while r_k^2 is the sum of ξ_k^2 , η_k^2 , and ζ_k^2 , one obtains

$$\begin{aligned} \sigma_{JM} / \left(\frac{e^2}{3mc^2} \right) &= \left(0 \left| \sum_k \frac{1}{r_k} \right| 0 \right) \\ &+ \left(\frac{3M^2 - J(J+1)}{2(2J-1)(2J+3)} \right) \left(0 \left| \sum_k \frac{3\xi_k^2 - r_k^2}{r_k^3} \right| 0 \right) \\ &- \left(\frac{3M^2 - J(J+1)}{2(2J-1)(2J+3)} + \frac{1}{2} \right) \left(\frac{I}{M\mu_N} \right) \\ &\times \left(\sum_i \frac{2Z_i M \mu_N}{I a_i} - \frac{H_r}{J} \right). \quad (9) \end{aligned}$$

Equation (9) gives the desired dependence of the shielding on the orientation of the molecule. If Eq. (9) is averaged over all values of M_J , the previously derived shielding formula is obtained.

The case of greatest interest experimentally is that of $J=1$, in which case (9) gives

$$\begin{aligned} \frac{\sigma_{1,\pm 1} - \sigma_{1,0}}{e^2/3mc^2} &= \frac{3}{10} \left(0 \left| \sum_k \frac{3\xi_k^2 - r_k^2}{r_k^2} \right| 0 \right) \\ &- \frac{3}{10} \left(\frac{I}{M\mu_N} \right) \left(\sum_i \frac{2Z_i M \mu_N}{I a_i} - H_r \right). \quad (10) \end{aligned}$$

As discussed in the previous paper,¹ the second terms in Eqs. (4), (9), and (10) in the case of molecular

hydrogen can be completely determined experimentally from the measured values⁵ of the spin-rotational interaction constant H_r and from the known values of the other fundamental quantities involved. With the numerical values used in the analogous step in the previous paper, except with the improved value⁵ of 13.40 ± 0.04 gauss for $H_r \mu' / MJ$, (10), for example, becomes

$$\begin{aligned} \sigma_{1,\pm 1} - \sigma_{1,0} &= \frac{e^2}{10mc^2} \left(0 \left| \sum_k \frac{3\xi_k^2 - r_k^2}{r_k^3} \right| 0 \right) \\ &- (0.339 \pm 0.005) \times 10^{-5}. \quad (11) \end{aligned}$$

III. CONCLUSION

Although a completely theoretical evaluation of the magnetic shielding of a nucleus in a linear molecule of a given rotational state from Eq. (9) would be very difficult in general, the work is tremendously simplified in those cases for which the second term in (4) can be experimentally evaluated from a measurement of H_r . In particular, for molecular hydrogen, where H_r is known, the difference $\sigma_{1,\pm 1} - \sigma_{1,0}$ is given by (11). A sensitive measurement of the difference of the apparent nuclear magnetic moment of hydrogen in the rotational states of magnetic quantum number 0 and ± 1 should determine $\sigma_{1,\pm 1} - \sigma_{1,0}$. Equation (11) shows that such a determination directly gives an experimental value for the average value of the quantity $\sum_k (3\xi_k^2 - r_k^2) / r_k^3$. This quantity is closely similar to $\sum_k (3\xi_k^2 - r_k^2) / r_k^5$ which must be calculated theoretically in determining the deuteron quadrupole moment from the experimental data. Consequently, a precision measurement of the difference $\sigma_{1,\pm 1} - \sigma_{1,0}$ would provide a valuable experimental check on the wave function used to calculate the deuteron quadrupole moment from the experimental data. In some molecular beam experiments now in progress at Harvard⁵ the difference $\sigma_{1,\pm 1} - \sigma_{1,0}$ should be experimentally observable, though it should not be measured with precision in the present apparatus.