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MAGNETIC SHIELDING OF NUCLEI IN MOLECULES  
BY A VARIATIONAL METHOD\*

by

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ABSTRACT

The accurate measurement of nuclear magnetic moments requires a calculation of the magnetic field at the nucleus arising from the orbital motions of the electrons in the external magnetic field. Lamb<sup>1</sup> has calculated this "magnetic shielding" effect for the case of atoms. Until recently the Lamb theory has been quite adequate for estimating shielding effects in molecules, but the accuracy of recent experiments has indicated the need for a more comprehensive theory. Ramsey<sup>2, 3, 4</sup> has presented such a theory and has discussed its need and application quite thoroughly.

Ramsey's results follow from a second order perturbation treatment of the problem, and as such are difficult to apply since the wave functions of excited electronic states of molecules are seldom available. In the special case of linear molecules, Ramsey showed that the difficult terms could be evaluated experimentally, thus allowing a determination of the magnetic shielding.

In this note we outline a solution of the same problem using the quantum mechanical variation principle. Since all results are in terms of ground state wave functions, such an approach may facilitate a purely theoretical evaluation of shielding constants. As a variation function we take a function of the type suggested by Hylleraas<sup>5</sup> and Hasse<sup>6</sup> and applied successfully to calculation of polarizabilities.

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+ General Electric Co. Fellow, 1953-1954

1. W. Lamb, Phys. Rev. 60, 817 (1941)
2. N. Ramsey, Phys. Rev. 77, 567, (1950)
3. N. Ramsey, Phys. Rev. 78, 699 (1950)
4. N. Ramsey, Phys. Rev. 86, 243 (1952)
5. E. Hylleraas, Z. Physik 65, 209 (1930)
6. H. R. Hasse, Proc. Camb. Phil. Soc., 26, 542 (1930)

To calculate the magnetic shielding at a particular nucleus, we assume with Ramsey<sup>2, 3, 4</sup>: 1) that we have a polyatomic molecule in its ground state, which in the absence of an external field has no resultant electron spin or orbital angular momentum, 2) all other nuclei have zero moment, and 3) the nucleus in question has a moment of magnitude  $\mu$  in the same direction as the applied field  $H$ . We take this to be the  $z$  direction and hold the nuclear skeleton fixed in an orientation specified by the subscript

$\lambda$ . The energy of the electronic system is then calculated and all terms proportional to the product  $\mu H$  are collected and called  $W'_\lambda$ . The shielding constant  $\sigma_\lambda$  is then given by

$$W'_\lambda = \mu H \sigma_\lambda \quad (1)$$

Thus  $\sigma_\lambda$  is so defined that if an external field of unit strength is applied, a magnetic field with component  $-\sigma_\lambda$  parallel to the applied field is induced at the nucleus by the motion of the electrons.<sup>7</sup>

Using the three assumptions mentioned in the previous paragraph, the Hamiltonian of the electronic system<sup>8</sup> may be written with sufficient accuracy in the form

$$\mathcal{H} = -\frac{\hbar^2}{2m} \sum_k \nabla_k^2 + V + \frac{e}{2mc} \sum_k \left( H + \frac{2\mu}{r_k^3} \right) l_{zk} \quad (2)$$

$$+ \frac{e^2}{8mc^2} \sum_k \left( H + \frac{2\mu}{r_k^3} \right)^2 (x_k^2 + y_k^2)$$

where  $l_{zk}$  is the  $z$  component of the angular momentum of the  $k$ 'th electron,

$$l_{zk} = \frac{\hbar}{i} \left( x_k \frac{\partial}{\partial y_k} - y_k \frac{\partial}{\partial x_k} \right)$$

7. For a more detailed discussion of the shielding constant, see Norman F. Ramsey, Nuclear Moments, Wiley & Sons, New York (1953).

8. For a discussion of the complete Hamiltonian of a system in external electromagnetic fields, see J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley & Sons, New York (1954).

Equation (2) implies that the vector potential depends only on the external field and on the nuclear magnetic moment. Since we will use a Hylleraas - Hasse type trial function and will be interested only in energy terms proportional to  $\mu H$ , the parts of the Hamiltonian proportional to  $\mu^2$  and  $H^2$  may be dropped. Thus we use

$$\mathcal{H} = \mathcal{H}_0 + \mu \mathcal{H}_1 + H \mathcal{H}_2 + \mu H \mathcal{H}_3 \quad (3)$$

where

$$\begin{aligned} \mathcal{H}_0 &= -\frac{\hbar^2}{2m} \sum_k \nabla_k^2 + V \\ \mathcal{H}_1 &= \frac{e}{mc} \sum_k \frac{\mathbf{l}_k}{r_k} \\ \mathcal{H}_2 &= \frac{e}{2mc} \sum_k \frac{\mathbf{l}_k}{r_k} \\ \mathcal{H}_3 &= \frac{e^2}{2mc^2} \sum_k \frac{\mathbf{l}_k^2 + 4k^2}{r_k^3} \end{aligned} \quad (4)$$

As a variation function we take

$$\Psi = [1 + \alpha \mu \mathcal{H}_1 + \beta (H \mathcal{H}_2 + \mu H \mathcal{H}_3)] \Psi_0 \quad (5)$$

where  $\Psi_0$  is the normalized ground state wave function satisfying

$$\mathcal{H}_0 \Psi_0 = E_0 \Psi_0 \quad (6)$$

Then

$$E_{(\alpha, \beta)} = \frac{\int \Psi^* \mathcal{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad (7)$$

If we choose  $\alpha$  and  $\beta$  such that

$$\left( \frac{\partial E}{\partial \alpha} \right) = \left( \frac{\partial E}{\partial \beta} \right) = 0 \quad (8)$$

and require that  $\alpha$  and  $\beta$  behave properly as  $\mu$  and  $H$  tend to zero, we will have an approximation of the lowest energy level of

4.

the system in the magnetic field. For small  $\mu$  and  $H$  the result may be expanded in a series in powers of  $\mu$  and  $H$ . The coefficient of the  $\mu H$  term is just the  $\sigma_\lambda$  we seek.

$$\begin{aligned}
 \sigma_\lambda = & (\mathcal{H}_3)_\lambda \\
 & + 2 a_\mu a_H (\mathcal{H}_1 [\mathcal{H}_0, \mathcal{H}_1])_\lambda \\
 & + 2 b_\mu b_H (\mathcal{H}_2 [\mathcal{H}_0, \mathcal{H}_2])_\lambda \\
 & + (a_\mu b_H + a_H b_\mu) (\mathcal{H}_1 [\mathcal{H}_0, \mathcal{H}_2] + \mathcal{H}_2 [\mathcal{H}_0, \mathcal{H}_1])_\lambda \\
 & + (a_\mu + b_H) [(\mathcal{H}_1 \mathcal{H}_2 + \mathcal{H}_2 \mathcal{H}_1)_\lambda - 2(\mathcal{H}_1)_\lambda (\mathcal{H}_2)_\lambda] \\
 & + 2 a_H [(\mathcal{H}_1 \mathcal{H}_1)_\lambda - (\mathcal{H}_1)_\lambda^2] \\
 & + 2 b_\mu [(\mathcal{H}_2 \mathcal{H}_2)_\lambda - (\mathcal{H}_2)_\lambda^2]
 \end{aligned} \tag{9}$$

Here the symbol  $( \quad )_\lambda$  represents the matrix element diagonal in the ground state evaluated with the nuclear skeleton held fixed in the orientation specified by  $\lambda$ , and  $[O, P]$  is the commutator of  $O$  and  $P$ . Also,

$$a_{\mu} = \frac{1}{D} \times \begin{vmatrix} (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} & 2(\kappa_1 \kappa_2) - 2(\kappa_1)_{\lambda}^2 \\ 2(\kappa_2[\kappa_0, \kappa_2])_{\lambda} & (\kappa_1 \kappa_2 + \kappa_2 \kappa_1) - 2(\kappa_1)_{\lambda} (\kappa_2)_{\lambda} \end{vmatrix}$$

$$a_H = \frac{1}{D} \times \begin{vmatrix} (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} & (\kappa_1 \kappa_2 + \kappa_2 \kappa_1)_{\lambda} - 2(\kappa_1)_{\lambda} (\kappa_2)_{\lambda} \\ 2(\kappa_2[\kappa_0, \kappa_2])_{\lambda} & 2(\kappa_2 \kappa_2) - 2(\kappa_2)_{\lambda}^2 \end{vmatrix}$$

(10)

$$b_{\mu} = \frac{1}{D} \times \begin{vmatrix} 2(\kappa_1 \kappa_2) - 2(\kappa_1)_{\lambda}^2 & 2(\kappa_1[\kappa_0, \kappa_1])_{\lambda} \\ (\kappa_1 \kappa_2 + \kappa_2 \kappa_1)_{\lambda} - 2(\kappa_1)_{\lambda} (\kappa_2)_{\lambda} & (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} \end{vmatrix}$$

$$b_H = \frac{1}{D} \times \begin{vmatrix} (\kappa_1 \kappa_2 + \kappa_2 \kappa_1)_{\lambda} - 2(\kappa_1)_{\lambda} (\kappa_2)_{\lambda} & 2(\kappa_1[\kappa_0, \kappa_1])_{\lambda} \\ 2(\kappa_2 \kappa_2)_{\lambda} - 2(\kappa_2)_{\lambda}^2 & (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} \end{vmatrix}$$

where

$$D = \begin{vmatrix} 2(\kappa_1[\kappa_0, \kappa_1])_{\lambda} & (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} \\ (\kappa_1[\kappa_0, \kappa_2])_{\lambda} + (\kappa_2[\kappa_0, \kappa_1])_{\lambda} & 2(\kappa_2[\kappa_0, \kappa_2])_{\lambda} \end{vmatrix}$$

This rather complicated result may be simplified somewhat by referring back to our original assumption that there was no contribution to the vector potential from the orbital motion of the electrons. Various quantum mechanical interpretations of this assumption will give varying degrees of simplification of this result. The absence of orbital angular momentum certainly implies that

$$1) (\mathcal{H}_2)_\lambda = \frac{e}{2mc} (\mathcal{L}_z)_\lambda = 0 \quad (11)$$

and

$$2) (\mathcal{H}_2 \mathcal{H}_2)_\lambda = \frac{e^2}{4m^2 c^2} (\mathcal{L}_z^2)_\lambda = 0$$

Setting these quantities equal to zero in  $\sigma_\lambda$  affords a slight simplification. If we assume, further, that

$$3) [\mathcal{H}_0, \mathcal{H}_2] = \frac{e}{2mc} [\mathcal{H}_0, \mathcal{L}_z] = 0 \quad (12)$$

the result becomes very much simpler. Noting that  $\mathcal{H}_0 \mathcal{H}_2 = \mathcal{H}_2 \mathcal{H}_0$ , exactly,

$$\sigma_\lambda = (\mathcal{H}_0)_\lambda + 12 \frac{(\mathcal{H}_1 \mathcal{H}_2)_\lambda^2}{(\mathcal{H}_2 [\mathcal{H}_0, \mathcal{H}_1])_\lambda} \quad (13)$$

Consistent with  $[\mathcal{H}_0, \mathcal{H}_2] = 0$ , it may be shown that

$$[\mathcal{H}_0, \mathcal{H}_1] = \frac{3e\hbar^2}{m^2 c} \sum_j \frac{r_j \cdot \mathcal{L}_{zj} \nabla_j}{r_j^3} \quad (14)$$

This result, together with the definition of the operators gives, finally,

$$\sigma_\lambda = \frac{e^2}{2mc^2} \left( \sum_j \frac{x_j^2 + y_j^2}{r_j^3} \right)_\lambda + \frac{2e^2}{mc^2 \hbar^2} \frac{\left( \sum_{ij} \frac{1}{r_i^3} \mathcal{L}_{zi} \mathcal{L}_{zj} \right)_\lambda^2}{\left( \sum_{ij} \mathcal{L}_{zi} \frac{r_j \cdot \mathcal{L}_{zj} \nabla_j}{r_j^3} \right)_\lambda} \quad (15)$$

Resonance absorption and nuclear induction methods use molecules of all orientations, so this shielding constant must be averaged over all possible orientations. The first term, corresponding to the Lamb correction, is easily averaged since x, y, and z are identical under such an average. Finally,

$$\sigma = a_{\lambda} \sigma_{\lambda} = \frac{e^2}{3mc^2} \left( \sum_j \frac{1}{r_j} \right) + \frac{2e^2}{mc^2 h^2} a_{\lambda} \frac{\left( \sum_{ij} \frac{1}{r_i^3} l_{zi} l_{zj} \right)_{\lambda}}{\left( \sum_{ij} l_{xi} \frac{r_j \cdot l_{zj} \nabla_j}{r_j^5} \right)_{\lambda}} \quad (16)$$

This result may be compared with the earlier results of Lamb<sup>1</sup> and Ramsey<sup>3</sup>. For atoms, Lamb got

$$\sigma = \frac{e^2}{3mc^2} \left( \sum_j \frac{1}{r_j} \right) \quad (17)$$

Ramsey's result for molecules is

$$\sigma = \frac{e^2}{3mc^2} \left( \sum_j \frac{1}{r_j} \right) - \frac{e^2}{2m^2 c^2} \sum_{\eta \lambda'} \frac{(\langle 0\lambda | \sum_j l_{zj} | \eta \lambda' \rangle \langle \eta \lambda' | \sum_j l_{zj} / r_j^3 | 0\lambda \rangle + (\langle 0\lambda | \sum_j l_{zj} / r_j^3 | \eta \lambda' \rangle) (\langle \eta \lambda' | \sum_j l_{zj} | 0\lambda \rangle)}{E_{\eta} - E_0} \quad (18)$$

where the sum over  $\eta \lambda'$  extends over all excited electronic states.

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