

resonance peaks with the new method are only 0.6 as broad as the corresponding ones with conventional method and the same length of magnetic field. (2) Unlike the earlier methods, with the new method the sharpness of the peak is not reduced by non-uniformities of the constant field since from (11) and (12) above it is only the space average value of the energies which is important. The field must still be fairly uniform along the height of the beam, but this is much more easily achieved experimentally than is uniformity along the length. This advantage of the new method is particu-

larly important and in many cases makes possible an increase in precision of a factor of twenty or more. (3) The new method is more convenient and effective at very high frequencies where the wave-length may be comparable to the length of the region in which the energy levels are investigated. (4) The new method may be applied to study energy levels of a system in a region into which an oscillating field cannot be introduced; for example, the Larmor precession frequency of neutrons can be measured while they are inside a magnetized iron block.

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Magnetic Shielding of Nuclei in Molecules*

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An expression is developed for the magnetic field at a nucleus resulting from the application of an external magnetic field to a polyatomic molecule which has no resultant electron orbital or spin angular momenta in the absence of the external field. The field at the nucleus is not the same as the externally applied field because of the field arising from the motion of the electrons in the molecule. The expression for the electron contribution to the magnetic field is shown to consist of two parts. The first is a simple term that is similar to the diamagnetic correction developed by Lamb for atoms. The second is a complicated one arising from second-order paramagnetism and is analogous to the term dependent on the high frequency matrix elements in the theory of molecular diamagnetism. Under certain circumstances the second-

order paramagnetic term can become quite large. Since both of these terms are altered when the same nucleus is in different molecules, they at least partially and perhaps completely explain the chemical effect that has been reported by various observers in measurements of nuclear moments. For linear molecules, the second-order paramagnetic term is shown to be directly related to the experimentally measurable spin-rotational magnetic interaction constant of the molecule. This relation is particularly valuable in the important case of molecular hydrogen where it is shown that the correction for second-order paramagnetism is -0.56×10^{-6} . When this is added to the Lamb-type term as calculated by Anderson, the total magnetic shielding constant for molecular H_2 becomes 2.68×10^{-6} .

I. INTRODUCTION

IN measurements of nuclear magnetic moments, a correction must be made for the magnetic field arising from the motions of the molecular electrons which are induced by the externally applied field. For example, the application of the external magnetic field produces a diamagnetic circulation of the electrons, which in turn produces a magnetic field at the nucleus, so that the resultant field in which the nuclear Larmor frequency is measured differs from the applied field by a small but important amount. Since this shielding field is proportional to the external field it cannot be distinguished from it merely by varying the external field. Until recently the correction has been made in accordance with a theory developed by Lamb.¹ This theory is strictly applicable only to atoms since it depends on the spherical symmetry of the electric field of the nuclear electrical potential. With the precision available in nuclear moment experiments up until recently, this method of correction has been adequate

even though most of the experiments have been performed with molecules instead of atoms. This has been true because the diamagnetic correction in light molecules like hydrogen is so small as to have been negligible, while in molecules with heavy nuclei the diamagnetic correction is caused chiefly by the innermost electrons and for these the problem is approximately an atomic one. However, the atomic approximation is no longer adequate in treating present experiments. The precision of experiments with light nuclei such as hydrogen has become so great (better than one part in a million) that the diamagnetic correction (27 parts in a million in H_2) is important. Furthermore, with heavier nuclei the ratios of the resonance frequencies for the same nucleus in different molecules have been measured with high precision and discrepancies have been found by various observers²⁻⁴ that are sometimes called the chemical effect. The change in different molecular compounds of the electronic magnetic fields described in this paper will at least be an important

* This work was partially supported by the joint program of the ONR and AEC.

¹ W. Lamb, *Phys. Rev.* **60**, 817 (1941).

² W. D. Knight, *Phys. Rev.* **76**, 1260 (1949).

³ W. C. Dickinson, *Phys. Rev.* **78**, 339 (1950).

⁴ F. Bloch (private communication).

contributor to this chemical effect and may well be its complete explanation.

As with the theory of the ordinary diamagnetism and second-order paramagnetism of molecules as discussed by Van Vleck,⁵ the diamagnetic shielding of a molecule differs from that of a single atom in two ways, as was pointed out by Ramsey⁶ in an earlier communication. (1) The electron distribution to be used in calculating the diamagnetic correction of the Lamb¹ type is altered by the presence of the other atoms with their associated electrons in the molecule. (2) In a molecule the electrical potential is no longer spherically symmetric; hence Larmor's theorem no longer applies directly in the manner implicitly assumed in Lamb's derivation of the atomic correction. Thus an additional term arises corresponding to second-order paramagnetism. This term is analogous to the term dependent on the orbital moments' high frequency matrix elements in the theory of molecular diamagnetism discussed by Van Vleck.⁵ Physically it corresponds in part to the fact that the presence of attracting centers from several different massive nuclei prevents a simple circular diamagnetic circulation of the electrons about any one nucleus. Under certain circumstances the second-order paramagnetism terms can become quite large. General expressions for both of these terms are derived in the present paper together with a simplified method, in the case of linear molecules, for evaluating the second-order paramagnetism term from the experimentally measurable spin-rotational magnetic interaction constant. Although the magnetic field from the electrons in the molecule can in principle be either in the same direction as the externally applied field or in the opposite direction, in most cases it is in the opposite direction. Therefore, the term magnetic shielding will be used in this paper to describe the resultant of the diamagnetic and paramagnetic effects even though negative shielding is a possibility.

II. POLYATOMIC MOLECULES

Consider a polyatomic molecule in a ground state which in the absence of an external field has no resultant

electron spin or electron orbital angular momentum. Most nuclear moment measurements made by any of the various nuclear resonance techniques are made with such molecules. Since the nuclei of the molecule are massive compared to the electrons, the nuclei can be treated classically to a very good approximation. In particular, in the first phases of the calculation it will be assumed that the nuclei are approximately stationary attracting centers for the electrons in an orientation specified by the subscript λ . If one wished to avoid this simplification, he could do so by following procedures analogous to those used by Van Vleck⁵ in the theory of molecular magnetism. As is discussed in greater detail by Van Vleck⁵ and Wick,⁷ the effects of electron spin can be omitted in the subsequent discussion; except in cases of accidental degeneracies, the magnetic shielding fields from the electron spin should be of a higher order of smallness than the other contributions calculated here. This omission considerably simplifies the subsequent equations, with no change in most of the significant results. If it were desired, the methods used here could be generalized to include the electron spin explicitly.

If the magnetic shielding constant applicable to a certain nucleus in the molecule is desired, it can be obtained most easily by assuming that all other nuclei have zero magnetic moments and that the nucleus concerned has a magnetic moment of magnitude μ and of the same direction as the externally applied field, H . The energy of the molecular system in the presence of μ and H can then be calculated, and all terms whose dependence on μ and H is linear in the product μH can be collected together and called W_λ' . Let σ_λ be the desired magnetic shielding constant; i.e., if an external magnetic field of unit strength is applied, the magnetic field at the nucleus from the electron motions has a component $-\sigma_\lambda$ parallel to the applied field. If W_λ' were known, then σ_λ could be obtained from the energy relation

$$W_\lambda' = \sigma_\lambda H \mu. \quad (1)$$

Let V be the electrostatic potential energy function for the electrons, \mathbf{A} be the vector potential from the nuclear magnetic moments and from the external magnetic field, $(-e)$ be the charge on the electron, and the remaining notation be that used by Van Vleck.⁵ Then the Hamiltonian of the electronic system is

$$\mathcal{H} = \sum_k (1/2m) [(p_{xk} + eA_{xk}/c)^2 + (p_{yk} + eA_{yk}/c)^2 + (p_{zk} + eA_{zk}/c)^2] + V. \quad (2)$$

With the assumptions of the preceding paragraph and with the origin of the coordinates chosen at the nucleus for which the shielding constant is desired, one has

$$A_x = -\frac{1}{2}Hy - \mu y/r^3, \quad A_y = \frac{1}{2}Hx + \mu x/r^3, \quad A_z = 0. \quad (3)$$

With these values and with the replacement of the p 's by the usual differential operators, (2) becomes

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(1)} + \mathcal{H}^{(2)},$$

⁵ J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

⁶ N. F. Ramsey, *Phys. Rev.* **77**, 567 (1950).

⁷ G. C. Wick, *Phys. Rev.* **73**, 51 (1948).

where

$$\mathfrak{H}^{(0)} = -\sum_k (\hbar^2/2m_k) \nabla_k^2 + V, \quad \mathfrak{H}^{(1)} = -\sum_k (H + 2\mu/r_k^3) m_{zk}^0, \quad \mathfrak{H}^{(2)} = (e^2/8mc^2) \sum_k (H + 2\mu/r_k^3)^2 (x_k^2 + y_k^2), \quad (4)$$

with

$$m_{zk}^0 = -(e\hbar/2mci)(x_k \partial/\partial y_k - y_k \partial/\partial x_k). \quad (5)$$

Therefore, by the usual second-order perturbation theory and with the selection of those terms of the second-order perturbation energy which are linear in the product $H\mu$, one obtains

$$\sigma_\lambda = W_\lambda'/H\mu = (e^2/2mc^2)(0\lambda | \sum_k (x_k^2 + y_k^2)/r_k^3 | 0\lambda) - 2 \sum_{n\lambda'} [1/(E_n - E_0)] [(0\lambda | \sum_k m_{zk}^0 | n\lambda') (n\lambda' | \sum_k m_{zk}^0/r_k^3 | 0\lambda) + (0\lambda | \sum_k m_{zk}^0/r_k^3 | n\lambda') (n\lambda' | \sum_k m_{zk}^0 | 0\lambda)]. \quad (6)$$

For purposes of later comparison with Wick's⁷ theory of rotational magnetic moments, Eq. (6) can be expressed in a somewhat different form. By virtue of the Hermitian character of m_{zk}/r_k^3 , one can write

$$\begin{aligned} (n\lambda' | \sum_k m_{zk}^0/r_k^3 | 0\lambda) &= \frac{1}{2} [(n\lambda' | \sum_k m_{zk}^0/r_k^3 | 0\lambda) + (0\lambda | \sum_k m_{zk}^0/r_k^3 | n\lambda')^*] \\ &= -(e\hbar/4mci) \sum_k \int \left[(x/r^3) \left(\psi_{n\lambda'}^* \frac{\partial \psi_{0\lambda}}{\partial y} - \psi_{0\lambda} \frac{\partial \psi_{n\lambda'}^*}{\partial y} \right) - (y/r^3) \left(\psi_{n\lambda'}^* \frac{\partial \psi_{0\lambda}}{\partial x} - \psi_{0\lambda} \frac{\partial \psi_{n\lambda'}^*}{\partial x} \right) \right]_k d\tau \\ &= [1/(2c)] \int \sum_k (\mathbf{r}_k \times \mathbf{j}_{n\lambda'0\lambda k}/r_k^3)_z d\tau = \frac{1}{2} H_{n\lambda'0\lambda}, \end{aligned} \quad (7)$$

where

$$\mathbf{j}_{n\lambda'0\lambda k} = (ie\hbar/2m)(\psi_{0\lambda}^* \nabla_k \psi_{n\lambda'} - \psi_{n\lambda'} \nabla_k \psi_{0\lambda}^*). \quad (8)$$

With this and with

$$\sum_k (0\lambda | m_{zk} | n\lambda') = -(e\hbar/2mc) \sum_k (0\lambda | L_{zk} | n\lambda') = -\mu_0 L_{0\lambda n\lambda'},$$

one obtains

$$\sigma_\lambda = (e^2/2mc^2)(0\lambda | \sum_k (x_k^2 + y_k^2)/r_k^3 | 0\lambda) + \mu_0 \sum_{n\lambda'} [1/(E_n - E_0)] [H_{0\lambda n\lambda'} L_{n\lambda'0\lambda} + L_{0\lambda n\lambda'} H_{n\lambda'0\lambda}]. \quad (9)$$

In experiments with the resonance absorption and nuclear induction methods, the measurements are made with molecules of all orientations. Consequently (6) and (9) for these experiments must be averaged over all orientations of the molecule. In such an average the x , y , and z coordinates must all be equivalent. Then if Av_λ indicates an average over all orientations, one has

$$\text{Av}_\lambda [\sum_k (0\lambda | x_k^2/r_k^3 | 0\lambda)] = \frac{1}{3} (0 | 1/r_k | n),$$

so

$$\begin{aligned} \text{Av}_\lambda \sigma_\lambda &= (e^2/3mc^2) (0 | \sum_k 1/r_k | 0) - 2 \text{Av}_\lambda \sum_{n\lambda'} [1/(E_n - E_0)] [(0\lambda | \sum_k m_{zk}^0 | n\lambda') (n\lambda' | \sum_k m_{zk}^0/r_k^3 | 0\lambda) \\ &\quad + (0\lambda | \sum_k m_{zk}^0/r_k^3 | n\lambda') (n\lambda' | \sum_k m_{zk}^0 | 0\lambda)], \end{aligned} \quad (10)$$

or

$$\sigma = (e^2/3mc^2) (0 | \sum_k 1/r_k | 0) + \mu_0 \text{Av}_\lambda \sum_{m\lambda'} [1/(E_n - E_0)] [H_{0\lambda n\lambda'} L_{n\lambda'0\lambda} + L_{0\lambda n\lambda'} H_{n\lambda'0\lambda}]. \quad (11)$$

The first term in either (10) or (11) is the same as Lamb's¹ complete expression for the diamagnetic shielding of single atoms. The second term arises from the lack of spherical symmetry of the electrical potential. The magnitude of the second term is quite comparable with that of the first. In fact, it serves to cancel off most of the contribution to the shielding by the electrons that are tightly bound to another nucleus in a distant part of the molecule. For this reason when

the difficult sums in (10) or (11) cannot be evaluated an approximation to the shielding is obtained by merely evaluating the first term over just the electrons of the atom containing the nucleus; that is, by using Lamb's correction for the atom containing the nucleus. This procedure, however, would be very unsatisfactory in a molecule like H_2 where the fields of the two protons are of comparable magnitudes at most electron locations. It is also unsatisfactory in accounting for the chemical

effect²⁻⁴ that has recently been observed in comparing the resonance frequencies of the same nucleus in different molecules. Both the first and the second terms of (10) will be altered in different molecules, and they will not necessarily be altered by exactly canceling amounts. This might be particularly true if one of the molecules had a low energy excited state for which the matrix elements in (10) did not vanish, since then $1/(E_n - E_0)$ would be large and a large second-order paramagnetism would be expected.

In (10) there is apparently a separation into two quite distinct terms of which one seems to be a simple diamagnetic term and the other a second-order paramagnetic term. However, it should be noted that these two terms are very closely related and that the separation is largely artificial. In particular, the above choice of the origin of coordinates at the nucleus where the field is desired and the selection of the arbitrary constant in the vector potential of H as in Eq. (3) make the first term in (10) correspond to a simple circular diamagnetic circulation of the electrons about the nucleus of interest. Had a different choice been made, for example, had the choice been such that the first term corresponded to a simple diamagnetic circulation of the electrons about some other point of the molecule, then both the diamagnetic term and the second-order paramagnetism term would have been altered. Of course, no physical difference can result from such a change so the two terms are necessarily altered in exactly compensating fashions. The magnitudes assigned to the physically indistinguishable diamagnetic term and second-order paramagnetic term are, however, altered. This property of (10) is closely analogous to a similar dependence of the diamagnetic and second-order paramagnetic terms of the magnetic susceptibility of a molecule on the choice of coordinate origin, even though the sum of the two terms is shown by Van Vleck⁵ to be invariant to the choice of the origin.

The numerical evaluation of the summation in (10) would be extremely difficult for most molecules since the summation depends on the wave functions of the excited states of the molecule. The calculation can be somewhat simplified if one estimates somehow an average value for $E_n - E_0$ as was done by Van Vleck and Frank⁸ in their calculation of the diamagnetism of molecular hydrogen. If ΔE is the average value of $E_n - E_0$, then (10) becomes

$$\sigma = (e^2/3mc^2)(0|\sum_k 1/r_k|0) - (4/\Delta E)Av_\lambda[(0\lambda|\sum_{jk} m_{zj}^0 m_{zk}^0 / r_k^3 |0\lambda)]. \quad (12)$$

If

$$\mathbf{m}_k^0 = m_{zk}^0 \mathbf{i} + m_{yk}^0 \mathbf{j} + m_{xk}^0 \mathbf{k} \quad (13)$$

then taking Av_λ as in the previous averaging,

$$\sigma = (e^2/3mc^2)(0|\sum_k 1/r_k|0) - (4/3\Delta E)(0|\sum_{jk} \mathbf{m}_j^0 \cdot \mathbf{m}_k^0 / r_k^3 |0). \quad (14)$$

Although this approximate form depends only on the ground state wave function, it is nevertheless very difficult to evaluate reliably since it depends on the second derivative of the wave function and is consequently very sensitive to errors in this derivative. This was clearly shown by Wick⁹ who found that by taking two somewhat different wave functions in his calculations on the rotational magnetic moment of H_2 he could obtain results for a term analogous to the last one in (14) which differed from each other by more than a factor eight.

III. LINEAR MOLECULES

Although calculation of the summation in (10) would be extremely difficult for most molecules, in the case of $^1\Sigma$ linear molecules this summation can be directly related to the spin-rotational magnetic interaction constant which has been experimentally measured in certain cases. If F_λ represents the summation in (11), if for λ one writes σ when the molecule has its axis perpendicular to the field and π when the axis is parallel, and if θ is the angle between the nuclear axis and the z axis, one has

$$Av_\lambda(F_\lambda) = Av_\lambda(\sin^2\theta_\lambda F_\sigma + \cos^2\theta_\lambda F_\pi) = \frac{2}{3}F_\sigma + \frac{1}{3}F_\pi = \frac{2}{3}F_\sigma. \quad (15)$$

F_π vanishes in the above since a linear molecule is cylindrically symmetric about its axis, as a result of which $\sum_k m_{zk}^0$ has only diagonal matrix elements along the axis of symmetry. With (15), Eq. (11) can be written as

$$\sigma = (e^2/3mc^2)(0|\sum_k 1/r_k|0) + \frac{2}{3}\mu_0 \sum_{n\lambda'} [1/(E_n - E_0)] \times [H_{0\sigma n\lambda'} L_{n\lambda' 0\sigma} + L_{0\sigma n\lambda'} H_{n\lambda' 0\sigma}]. \quad (16)$$

This result may be compared with Brooks'^{9a} Wick's⁷ theories of spin-rotational magnetic interactions. Let H_r be the experimentally observed magnetic field at nucleus r due to the linear molecule rotating with an angular velocity

$$\omega = J\hbar/I, \quad (17)$$

where J is the rotational quantum number and I is the moment of inertia. Let Z_i be the charge on any nucleus of the molecule other than the one at which the shielding constant is desired, and let a_i be its distance from the desired nucleus. Then Wick's result is

$$H_r - \sum_i Z_i e\hbar J / I a_i c = (J\hbar^2/I) \sum_{n\lambda'} [1/(E_n - E_0)] \times [H_{0\sigma n\lambda'} L_{n\lambda' 0\sigma} + L_{0\sigma n\lambda'} H_{n\lambda' 0\sigma}]. \quad (18)$$

⁸ J. H. Van Vleck and A. Frank, Proc. Nat. Acad. Sci. **15**, 539 (1929).

⁹ G. C. Wick, Zeits. f. Physik **85**, 25 (1933).

^{9a} Harvey Brooks, Phys. Rev **59**, 925 (1941).

This can then be substituted into (16) and the resulting expression can be simplified by the introduction of a_0 for the Bohr radius, α for the fine structure constant, and μ_N for the nuclear magneton, $e\hbar/2Mc$, where M is the proton mass. The result, after simplification, is

$$\sigma = \frac{e^2}{3mc^2} \left(0 \left| \sum_k \frac{1}{r_k} \right| 0 \right) - \frac{\alpha^2 a_0 I}{6\mu_N} \left(\sum_i \frac{2Z_i \mu_N}{I a_i} - \frac{H_r}{JM} \right). \quad (19)$$

Although the above derivation of (19) seems to be dependent on the second order perturbation theories, both through its use of Wick's spin-rotational interaction theory and through the shielding theory of the present paper, this particular result can be obtained directly without the necessity for using either of the other derivations directly. This can most easily be done by following a procedure used in another paper by Wick⁹ on rotational magnetic moments. If the molecule were rotating with angular frequency ω and in a magnetic field of just the Larmor value

$$\mathbf{H} = 2m c \omega / e, \quad (20)$$

the molecule would rotate as a completely rigid body, since in a coordinate system rotating with ω the electrostatic field would be constant in time, and, by a simple extension of Larmor's theorem, the rotation of the coordinates would exactly cancel \mathbf{H} . Since the nuclei are at positions where the electric field is approximately zero, the rotational magnetic field at the position of the nucleus is independent of the nuclear velocity; hence to a high degree of accuracy the molecule can be considered as rotating about the nucleus at which the diamagnetic shielding is desired. Then H_r' , the field at the nucleus due to the rotation in the presence of (20), is given by

$$\begin{aligned} H_r' &= - \int [\rho(\omega \times \mathbf{r}) \times \mathbf{r} \cdot \omega / c r^3] dv \\ &\quad - \sum_i [Z_i e (\omega \times \mathbf{a}_i) \times \mathbf{a}_i \cdot \omega / c a_i^3] \\ &= -(e\omega/c) (0\sigma \left| \sum_k (x_k^2 + y_k^2) / r_k^3 \right| 0\sigma) \\ &\quad + \sum_i (Z_i e \omega / c a_i). \quad (21) \end{aligned}$$

The experimental value of H_r can be obtained from (21) by superposing a magnetic field equal and opposite to (20) to cancel it out. Therefore, one has

$$H_r = H_r' + \sigma_e 2m c \omega / e. \quad (22)$$

Furthermore, just as in Eq. (15), the average over all molecular orientations gives

$$\sigma = \frac{2}{3}\sigma_\sigma + \frac{1}{3}\sigma_\pi. \quad (23)$$

The combination of (21)–(23) with Lamb's theory for σ_π then immediately gives the desired (19).

IV. MOLECULAR HYDROGEN

The most important application of (19) is to molecular hydrogen. In this diatomic case (19) becomes

$$\sigma = \frac{e^2}{3mc^2} \left(0 \left| \sum_k \frac{1}{r_k} \right| 0 \right) - \frac{\alpha^2 a_0^2}{6\mu_N} \left(\frac{2Z\mu_N}{a^3} - \frac{\mu' H_r}{MJ} \right) \quad (24)$$

where μ' is the reduced mass of the molecule.

The quantity $H_r \mu' / MJ$ has been experimentally measured in a molecular beam experiment by Kellogg, Rabi, Ramsey, and Zacharias¹⁰ to be

$$H_r \mu' / MJ = (13.66 \pm 0.20) \text{ gauss.}$$

With this and with the current standard values for the other constants in (24),

$$\begin{aligned} \sigma &= (e^2/3mc^2) (0 \left| \sum_k 1/r_k \right| 0) - (0.5291 \times 0.7414^2 / 6 \\ &\quad \times 137^2 \times 5.05) (24.62 - 13.66) \\ &= (e^2/3mc^2) (0 \left| \sum_k 1/r_k \right| 0) - (0.56 \pm 0.01) \times 10^{-5}. \quad (25) \end{aligned}$$

Using Nordsieck's¹¹ wave functions, Anderson¹² has calculated the value of the first term of (25) to be 3.24×10^{-5} . On the other hand, Hylleraas and Skavlem¹³ from different wave functions obtain 3.16×10^{-5} . If Anderson's value is used, σ becomes

$$\sigma = 2.68 \times 10^{-5}. \quad (26)$$

This number can be contrasted to the best previous estimates for σ which were 1.8×10^{-5} and 3.24×10^{-5} . The first of these was obtained by applying Lamb's formula to a single hydrogen atom; Anderson¹² obtained the second by applying Lamb's formula directly to a hydrogen molecule.

The result (26) can be combined with Hylleraas and Skavlem's¹³ value of 5.99×10^{-5} for the σ in He and with Anderson's¹² measured resonance frequency ratio in He³ and H₂ molecules of 0.7617866 to yield a value for the ratio of the nuclear gyromagnetic ratios of $\gamma_{\text{He}^3} / \gamma_p = 0.7617866 [1 + (5.99 - 2.68) \times 10^{-5}] = 0.761812$.

The shielding correction can be calculated from the simplified expression (9) only for linear molecules for which there exist spin-rotational interaction data; e.g., for molecular hydrogen. Since a number of different hydrogenous compounds are used to determine the proton resonance frequency in the various nuclear moment measurements, it is important that some one should compare with high precision the resonance frequencies in these compounds with that in molecular hydrogen. If this is done empirical values for the shielding constant of the protons in the other compounds can be obtained from the above value for H₂.

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¹⁰ Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 691 (1940).

¹¹ A. Nordsieck, Phys. Rev. **57**, 691 (1940).

¹² H. L. Anderson, Phys. Rev. **76**, 1460 (1949).

¹³ E. Hylleraas and S. Skavlem (private communication).