

Electron Coupled Interactions between Nuclear Spins in Molecules

NORMAN F. RAMSEY

Harvard University, Cambridge, Massachusetts

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In addition to the direct magnetic interaction between two nuclear spins in a molecule, the nuclei can have an effective mutual interaction as a result of the magnetic interactions between each of the nuclei and the electrons of the molecule. Although these indirect interactions are in general small, they are important in many cases, particularly as a result of the fact that the frequent collisions which characterize most nuclear paramagnetic resonance experiments cause the direct interaction to average to zero while this is not so for the indirect. In the present paper, the indirect interactions are evaluated. Contributions arise from a simple diamagnetic term, a closely related second-order orbital paramagnetism term, and terms due to the magnetic interaction of the nuclei with the electron spins. Expressions for each of these terms are given both for the general case and for the spherically symmetric case which arises when there are many collisions. Specific numerical calculations of the various effects are given for hydrogen deuteride. It is shown for HD that the diamagnetic terms are of the order of a few tenths of a cycle per second. On the other hand, if the suitable mean energy of the molecular excited states is given the reasonable value of 1.4 Rydbergs, the electron spin terms are 43 cps in agreement with experiment.

I. INTRODUCTION

A NUMBER of observers¹⁻⁵ have recently found splittings of nuclear resonance lines in molecules that are independent of the strength of the external magnetic field in contrast to magnetic shielding effects⁶ which are proportional to the external magnetic field. Gutowsky, McCall, and Slichter⁴ and Hahn and Maxwell⁵ have independently pointed out that their observed results could empirically be interpreted in terms of an interaction between two nuclei N and N' of the form $h\delta_{NN'}\mathbf{I}_N \cdot \mathbf{I}_{N'}$. Gutowsky, McCall, and Slichter^{3,4} and Drell⁷ attempted to attribute the value of $\delta_{NN'}$ to the effect of the electron orbital motion magnetically shielding⁶ the direct magnetic interaction between the two nuclei, which direct interaction would have averaged to zero in the absence of shielding in experiments with high collision frequencies. Although such an interpretation was qualitatively of the correct form, it gave a value of $\delta_{NN'}$ which in most cases was too small by a factor of ten or more. Ramsey and Purcell⁸ pointed out in a brief note that the magnetic interaction of the nuclei with the electron spin magnetic moments which are in turn exchange coupled together would also give rise to an interaction of the desired form which should in addition be of the observed order of magnitude. As an illustration, they stated a calculated value for δ_{HD} in HD and suggested that experiments be made with HD because of its convenience in calculations.

Recently, the suggested experiments with HD have

been carried out by several independent observers.⁹⁻¹¹ As a result the value of δ_{HD} for HD has been determined as 43 ± 0.5 cps. With the availability of this experimental datum it has appeared desirable to publish some details of the calculation whose results only were reported in the previous note.⁸ In addition, the problem merits a better calculation than the earlier one which was dominantly for the purpose of estimating the order of magnitude of the electron spin mechanism. In particular, in the earlier calculation perturbations by only the lowest triplet molecular state were included and the relatively inaccurate Heitler-London wave functions were used. In the present paper, on the other hand, the contributions of all the excited states are included and James-Coolidge¹² wave functions are used.

Although numerical calculations are made only in the case of HD, the formulas used in the calculation are developed in forms applicable to molecules in general. Likewise, general expressions are obtained for the nuclear spin-spin interaction which occurs as a result of the magnetic shielding by the electron orbital motion even though this effect in the case of HD and many other cases is small compared to the electron spin terms.

In the experiments so far performed, the molecules are subjected to frequent collisions in which case the theory presented below predicts that the electron coupled nuclear spin interactions should be of the form $h\delta_{NN'}\mathbf{I}_N \cdot \mathbf{I}_{N'}$ in agreement with experiment. However, in the general case where there are not frequent collisions, the energy of interactions, $E_{NN'}$, for a specific orientation, λ , of the molecule is

$$E_{NN'} = h\mathbf{I}_N \cdot \mathbf{d}_{NN'} \cdot \mathbf{I}_{N'} + h\delta_{NN'}\mathbf{I}_N \cdot \mathbf{I}_{N'}, \quad (1)$$

⁹ Smaller, Yasaitis, Avery, and Hutchison, Phys. Rev. **88**, 414 (1952).

¹⁰ H. Y. Carr and E. M. Purcell, Phys. Rev. **88**, 415 (1952).

¹¹ T. F. Wimett, private communication.

¹² H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

¹ W. G. Proctor and F. C. Yu, Phys. Rev. **81**, 20 (1951).

² E. L. Hahn, Phys. Rev. **80**, 580 (1950).

³ Gutowsky, McCall, Slichter, and McNeil, Phys. Rev. **82**, 748 (1951), and **84**, 1245 (1951).

⁴ Gutowsky, McCall, and Slichter, Phys. Rev. **84**, 589 (1951).

⁵ E. L. Hahn and D. E. Maxwell, Phys. Rev. **84**, 1246 (1951), and **88**, 243 (1952).

⁶ N. F. Ramsey, Phys. Rev. **77**, 567 (1950); **78**, 699 (1950); and **86**, 243 (1952).

⁷ S. Drell, private communication.

⁸ N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952).

where \mathbf{d} is a tensor of second rank or dyadic whose trace is zero. Due to the vanishing trace of \mathbf{d} , frequent collisions, which average the molecular orientation over all directions, make \mathbf{d} average to zero, so

$$\overline{A_{V\lambda} E_{NN'}} = h\delta_{NN'} \mathbf{I}_N \cdot \mathbf{I}_{N'}. \quad (2)$$

where

$$\mathfrak{S}_1 = \sum_k [\frac{1}{2} m_k] [(\hbar/i) \nabla_k + (e/c) \sum_N \hbar \gamma_N \mathbf{I}_N \times \mathbf{r}_{kN} / r_{kN}^3 + \frac{1}{2} \mathbf{H} \times \mathbf{r}_k]^2 + V + \mathfrak{S}_{LL} + \mathfrak{S}_{LS} + \mathfrak{S}_{SS} + \mathfrak{S}_{SH}, \quad (4)$$

$$\mathfrak{S}_2 = 2\beta\hbar \sum_{kN} \gamma_N \{3(\mathbf{S}_k \cdot \mathbf{r}_{kN})(\mathbf{I}_N \cdot \mathbf{r}_{kN}) r_{kN}^{-5} - \mathbf{S}_k \cdot \mathbf{I}_{N'} r_{kN}^{-3}\}, \quad (5)$$

$$\mathfrak{S}_3 = (16\pi\beta\hbar/3) \sum_{kN} \gamma_N \delta(\mathbf{r}_{kN}) \mathbf{S}_k \cdot \mathbf{I}_N, \quad (6)$$

$$\mathfrak{S}_4 = -\hbar^2 \sum_{NN'} \gamma_N \gamma_{N'} \{3(\mathbf{I}_N \cdot \mathbf{r}_{NN'}) (\mathbf{I}_{N'} \cdot \mathbf{r}_{NN'}) r_{NN'}^{-5} - \mathbf{I}_N \cdot \mathbf{I}_{N'} r_{NN'}^{-3}\}. \quad (7)$$

The squared term of \mathfrak{S}_1 in Eq. (4) above is essentially the same as that used by Ramsey⁶ in discussing magnetic shielding except that for simplicity a specific choice of gauge is made. γ_N is the gyromagnetic ratio of nucleus N and \mathbf{I}_N is the nuclear angular momentum in units of \hbar . \mathbf{r}_{kN} is used to represent $\mathbf{r}_k - \mathbf{r}_N$, where \mathbf{r}_k designates the coordinate of the k 'th electron. \mathfrak{S}_{LL} , \mathfrak{S}_{LS} , \mathfrak{S}_{SS} , and \mathfrak{S}_{SH} designate, respectively, the contributions to the Hamiltonian of the electron orbital-orbital, spin-orbital, electron spin-spin, and electron spin-external field interactions. For singlet molecular states the effects of these terms on the quantities concerned are of higher order.

\mathbf{S}_k is the electron spin angular momentum in units of \hbar . \mathfrak{S}_2 and \mathfrak{S}_3 are the terms for the magnetic interaction between the nuclear spins and the electron spins. \mathfrak{S}_2 is obviously such a term since it corresponds to the classical magnetic interaction energy of two magnetic moments. \mathfrak{S}_3 is less obvious but corresponds to the fact that hyperfine structure interaction does not vanish in an S state as discussed by Fermi;¹³ the form of \mathfrak{S}_3 here used is that of Abragam and Pryce¹⁴ in their discussions of nuclear hyperfine structure in paramagnetic resonance experiments.

\mathfrak{S}_4 is the term for the direct magnetic interaction of the nuclei with each other.¹⁵ To the first order \mathfrak{S}_4 averages to zero in experiments such as nuclear paramagnetic resonance ones in which frequent collisions

$$E_{3NN'} = -2(16\pi\beta\hbar/3)^2 \gamma_N \gamma_{N'} \sum_{nkj} [1/(E_n - E_0)] (0 | \delta(\mathbf{r}_{kN}) \mathbf{S}_k \cdot \mathbf{I}_N | n) (n | \delta(\mathbf{r}_{jN'}) \mathbf{S}_j \cdot \mathbf{I}_{N'} | 0). \quad (9)$$

This is in the form of Eq. (1) provided

$$\begin{aligned} \delta_{3NN'} &= -(2/3h) (16\pi\beta\hbar/3)^2 \gamma_N \gamma_{N'} \sum_{nkj} [1/(E_n - E_0)] (0 | \delta(\mathbf{r}_{kN}) \mathbf{S}_k | n) \cdot (n | \delta(\mathbf{r}_{jN'}) \mathbf{S}_j | 0), \\ \delta_{3NN'} &= -(2/h) (16\pi\beta\hbar/3)^2 \gamma_N \gamma_{N'} \sum_{nkj} [1/(E_n - E_0)] (0 | \delta(\mathbf{r}_{kN}) \mathbf{S}_k | n) (n | \delta(\mathbf{r}_{jN'}) \mathbf{S}_j | 0) - \delta_{3NN'} \mathfrak{S}, \end{aligned} \quad (10)$$

where \mathfrak{S} is the unit dyadic.

In so far as the electron spin-orbital interaction energy and other interactions coupling the electron spins to the molecular orientation are negligible compared to

II. HAMILTONIAN

The Hamiltonian for the molecular system in a magnetic field may be taken as

$$\mathfrak{H} = \mathfrak{S}_1 + \mathfrak{S}_2 + \mathfrak{S}_3 + \mathfrak{S}_4, \quad (3)$$

average the molecule over all orientations, since the expression \mathfrak{S}_4 when averaged equally over all directions gives zero. This, of course, is not true of molecular beam experiments for which it gives an important interaction.¹⁵

The electron coupled nuclear spin-spin interactions are those terms dependent on both \mathbf{I}_N and $\mathbf{I}_{N'}$ which arise when \mathfrak{S}_1 , \mathfrak{S}_2 , and \mathfrak{S}_3 are discussed to the accuracy of second-order perturbation theory.

III. ELECTRON SPIN TERMS

In most cases, the largest contribution to the nuclear spin-spin interaction comes from the mechanism first considered by Ramsey and Purcell⁸ which corresponds to second-order perturbations involving \mathfrak{S}_3 . These terms tend to be the largest because they correspond to the electrons being closest to the nuclei. Let $E_{3NN'}$ represent the energy of interaction between nuclei N and N' by this process. Then by ordinary second-order perturbation theory⁶

$$\begin{aligned} \sum_{N \leq N'} E_{3NN'} \\ = -\sum_n' [1/(E_n - E_0)] (0 | \mathfrak{S}_3 | n) (n | \mathfrak{S}_3 | 0). \end{aligned} \quad (8)$$

Therefore, if one separates out the NN' terms and uses a factor of two because of the terms in which N occurs in the first matrix element and N' in the second and vice versa,

$E_n - E_0$, intermediate sums over excited states which differ only in electron spin configurations can be carried out in which case there is no preferred direction for the above dyadic and, since it is traceless, it vanishes, leaving only δ to yield electron coupled nuclear spin interactions. Of course, even in the absence of the preceding restriction, frequent collisions will reduce the interaction to the form of Eq. (2) as discussed in Sec. I.

¹³ E. Fermi, Z. Physik **60**, 320 (1930).

¹⁴ A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 136 (1951).

¹⁵ N. F. Ramsey, Phys. Rev. **85**, 60 (1952).

For accurate calculations of δ , Eq. (10) should be used. However, such a solution would be extremely difficult because wave functions for the excited mo-

lecular states are required. However, the calculation can be simplified by assuming Δ_3 to be the suitable mean value of $E_n - E_0$ such that

$$\begin{aligned}\delta_{3NN'} &= - (2/3h\Delta_3)(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'}\Sigma_{nkj}(0|\delta(\mathbf{r}_{kN})\mathbf{S}_k|n)\cdot(n|\Sigma_j\delta(\mathbf{r}_{jN'})\mathbf{S}_j|0) \\ &= - (2/3h\Delta_3)(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'}(0|\Sigma_{kj}\delta(\mathbf{r}_{kN})\delta(\mathbf{r}_{jN'})\mathbf{S}_k\cdot\mathbf{S}_j|0).\end{aligned}\quad (11)$$

A similar approximate relation can be obtained for \mathfrak{d} .

The electron spin enters in \mathfrak{S}_2 as well as \mathfrak{S}_3 . In a second-order perturbation calculation strictly analogous to the above, the terms in \mathfrak{S}_2 only give

$$\delta_{2NN'} = - (2/3h)(2\beta\hbar)^2\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\{3(\mathbf{S}_k\cdot\mathbf{r}_{kN})\mathbf{r}_{kN}\mathbf{r}_{kN}^{-5} - \mathbf{S}_k\mathbf{r}_{kN}^{-3}\}|n)\cdot(n|\{3(\mathbf{S}_j\cdot\mathbf{r}_{jN'})\mathbf{r}_{jN'}\mathbf{r}_{jN'}^{-5} - \mathbf{S}_j\mathbf{r}_{jN'}^{-3}\}|0), \quad (12)$$

and

$$\mathfrak{d}_{2NN'} = - (2/h)(2\beta\hbar)^2\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\{3(\mathbf{S}_k\cdot\mathbf{r}_{kN})\mathbf{r}_{kN}\mathbf{r}_{kN}^{-5} - \mathbf{S}_k\mathbf{r}_{kN}^{-3}\}|n)(n|\{3(\mathbf{S}_j\cdot\mathbf{r}_{jN'})\mathbf{r}_{jN'}\mathbf{r}_{jN'}^{-5} - \mathbf{S}_j\mathbf{r}_{jN'}^{-3}\}|0) - \delta_{2NN'}\mathfrak{S}.$$

In the present case, unlike the preceding one, even if the electron spin orbital interaction is negligible, $\mathfrak{d}_{2NN'}$ will in general have a nonvanishing value because of the direct dependence of the matrix elements on molecular orientation. On the other hand, frequent collisions as discussed in Sec. I will lead to a zero average value of \mathfrak{d} in this case as well as in the preceding. For purposes of approximate calculation, Eq. (12) can be

reduced to a form analogous to Eq. (11), in which the wave functions of the excited electronic states are not required provided a suitable mean effective energy Δ_2 of the excited states is assumed.

There remain the possibility of cross terms between \mathfrak{S}_2 and \mathfrak{S}_3 . Selection of these terms in the preceding manner leads to

$$\delta_{23NN'} = - (64\beta^2\hbar/9)\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\delta(\mathbf{r}_{kN})\mathbf{S}_k|n)\cdot(n|\{3(\mathbf{S}_j\cdot\mathbf{r}_{jN'})\mathbf{r}_{jN'}\mathbf{r}_{jN'}^{-5} - \mathbf{S}_j\mathbf{r}_{jN'}^{-3}\}|0), \quad (13)$$

and

$$\mathfrak{d}_{23NN'} = - (64\beta^2\hbar/3)\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\delta(\mathbf{r}_{kN})\mathbf{S}_k|n)(n|\{3(\mathbf{S}_j\cdot\mathbf{r}_{jN'})\mathbf{r}_{jN'}\mathbf{r}_{jN'}^{-5} - \mathbf{S}_j\mathbf{r}_{jN'}^{-3}\}|0) - \delta_{23NN'}\mathfrak{S}.$$

It should be noted in this case that if the electron spin is only weakly coupled to the molecular orientation $\delta_{23NN'}$ (not $\mathfrak{d}_{23NN'}$) vanishes, since the quantity in the first-matrix element has no orientation dependence to prevent the quantity in the second-matrix element from averaging zero. As a result, if there are also frequent collisions, the entire average contribution from the cross terms vanishes.

There remains the possibility of electron spin dependent cross terms between \mathfrak{S}_1 and either \mathfrak{S}_2 or \mathfrak{S}_3 ,

but as \mathfrak{S}_1 does not perturb the electron spin states, its matrix elements vanish between those states for which \mathfrak{S}_2 and \mathfrak{S}_3 have their matrix elements unless there is a strong electron spin-orbital coupling.

IV. ELECTRON ORBITAL TERMS

The only terms in \mathfrak{S}_1 that depend upon the \mathbf{I}_N 's in the absence of an external magnetic field are one of the following:

$$\begin{aligned}\mathfrak{S}_1^{(1)} &= \Sigma_{kN}2(e\hbar/2m_k c i)\hbar\gamma_N(\mathbf{I}_N \times \mathbf{r}_{kN}/r_{kN}^3) \cdot \nabla_k \\ &= - \Sigma_{kN}2\gamma_N\mathbf{I}_N \cdot \mathbf{m}_{kN}^0/r_{kN}^3,\end{aligned}\quad (14)$$

$$\begin{aligned}\mathfrak{S}_1^{(2)} &= \Sigma_{kNN'}(e^2\hbar^2/2m_k c^2)\gamma_N\gamma_{N'}(\mathbf{I}_N \times \mathbf{r}_{kN}/r_{kN}^3) \cdot (\mathbf{I}_{N'} \times \mathbf{r}_{kN'}/r_{kN'}^3) \\ &= \Sigma_{kNN'}(e^2\hbar^2/2m_k c^2)\gamma_N\gamma_{N'}\mathbf{I}_N \cdot [\mathfrak{S}\mathbf{r}_{kN'} \cdot \mathbf{r}_{kN} - \mathbf{r}_{kN'}\mathbf{r}_{kN}]r_{kN}^{-3}r_{kN'}^{-3} \cdot \mathbf{I}_{N'}.\end{aligned}\quad (15)$$

Then if Eq. (8) is applied to these and the terms dependent on \mathbf{I}_N and $\mathbf{I}_{N'}$ are selected as was done previously, where

$$\begin{aligned}\mathfrak{d}_{1NN'} &= a\mathfrak{d}_{1NN'} + b\mathfrak{d}_{1NN'}, \quad \delta_{1NN'} = a\delta_{1NN'} + b\delta_{1NN'}, \\ a\delta_{1NN'} &= (4/3h)\gamma_N\gamma_{N'}(0|\Sigma_k(e^2\hbar^2/2m_k c^2)\mathbf{r}_{kN'} \cdot \mathbf{r}_{kN}\mathbf{r}_{kN}^{-3}\mathbf{r}_{kN'}^{-3}|0), \\ b\delta_{1NN'} &= -(8/3)\hbar^2\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\mathbf{m}_{kN}^0\mathbf{r}_{kN}^{-3}|n)\cdot(n|\mathbf{m}_{jN'}^0\mathbf{r}_{jN'}^{-3}|0), \\ a\mathfrak{d}_{1NN'} &= (2/h)\gamma_N\gamma_{N'}(0|\Sigma_k(e^2\hbar^2/2m_k c^2)[\mathfrak{S}\mathbf{r}_{kN'} \cdot \mathbf{r}_{kN} - \mathbf{r}_{kN'}\mathbf{r}_{kN}]r_{kN}^{-3}r_{kN'}^{-3}|0) - a\delta_{1NN'}\mathfrak{S},\end{aligned}\quad (16)$$

and

$$b\mathfrak{d}_{1NN'} = - (8/h)\hbar^2\gamma_N\gamma_{N'}\Sigma_{nkj}[1/(E_n - E_0)](0|\mathbf{m}_{kN}^0\mathbf{r}_{kN}^{-3}|n)(n|\mathbf{m}_{jN'}^0\mathbf{r}_{jN'}^{-3}|0) - b\delta_{1NN'}\mathfrak{S}.$$

V. APPLICATION TO HYDROGEN DEUTERIDE

Numerical calculations of the above quantities may be carried out for the molecule HD. Since the experimental observations so far have been on molecules subjected to frequent collisions, only the δ 's in the above equations need be calculated for comparison with the present experiments.

For terms arising from \mathfrak{S}_3 , if the orbital and spin wave functions are assumed separable in the ground state with primes designating the former and double primes the latter, Eq. (11) gives

$$\delta_{3\text{HD}} = - (4/3h\Delta_3) (16\pi\beta\hbar/3)^2 \gamma_H \gamma_D (O' | \delta(\mathbf{r}_{1\text{H}}) \cdot \delta(\mathbf{r}_{2\text{D}}) | O') (O'' | \mathbf{S}_1 \cdot \mathbf{S}_2 | O''), \quad (17)$$

where the extra factor of two arises from the double summation over the two electrons. Since

$$(O'' | \mathbf{S}_1 \cdot \mathbf{S}_2 | O'') = (O'' | \frac{1}{2} \{ \mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 \} | O'') = -\frac{3}{4}, \quad (18)$$

Eq. (17) gives

$$\delta_{3\text{HD}} = (1/h\Delta_3) (16\pi\beta\hbar/3)^2 \gamma_H \gamma_D (O' | \delta(\mathbf{r}_{1\text{H}}) \delta(\mathbf{r}_{2\text{D}}) | O') \quad (19) \\ = (64\beta^2 \hbar \gamma_H \gamma_D / 9\Delta_3) |\psi|^2_{1\text{H}2\text{D}},$$

where $|\psi|^2_{1\text{H}2\text{D}}$ is the probability density for the first electron to be on the proton while the other electron is on the deuteron.

The matrix element in the preceding equation is of a form that is easy to evaluate with the James-Coolidge¹² wave function for the hydrogen molecule. The result of such an evaluation is

$$(0 | \delta(\mathbf{r}_{1\text{H}}) \delta(\mathbf{r}_{2\text{D}}) | 0) = 0.0600/a_0^6, \quad (20)$$

where $a_0 = \hbar^2/me^2$. With this value and with numerical expressions for the other quantities,

$$\delta_{3\text{HD}} = 55.8/\Delta_3 \text{ cps}, \quad (21)$$

where Δ_3 is expressed in Rydberg units.

The problem of selecting Δ_3 is, however, difficult. Indications of its possible range of values, however, are provided by the following results. For the internuclear spacing of $1.4 a_0$, the lowest triplet state as calculated by James, Coolidge, and Present¹⁶ is 0.67 Rydberg above the ground state, whereas the energy required to ionize the molecule doubly, while the internuclear spacing is maintained, is 3.77 Rydbergs. For the analogous mean quantities, Δ , in the theories of the electronic contributions to the rotational magnetic moments and to the spin-rotational magnetic interaction, Brooks¹⁷ has selected 1.97 and 1.1 Rydbergs, respectively. For lack of other means of determining Δ_3 it

seems best to use the results of the subsequent paragraphs that all other contributions to δ are approximately 3 cps whence the experimental residual value of 40 cps can be used to determine Δ_3 . With this procedure a value of $\Delta_3 = 1.4$ Rydbergs in Eq. (21) yields the residual value of 40 cps for $\delta_{3\text{HD}}$. The value of 1.4 Rydbergs is reasonable in view of its above indicated possible range, though from one point of view it appears to be slightly high since the occurrence of the δ -functions would suggest that the low-lying states should be much more effective than the high.

An alternative expression to Eq. (19) without the assumption of a mean value Δ_3 is possible if it is merely assumed that for the two electron problem the spin and orbital wave functions are separable in the ground and excited states with the spin wave functions being expressible in the usual fashion.¹⁸ With this assumption and with n''' representing an antisymmetric orbital wave function of the excited molecule, it is easy to show that

$$\delta_{3\text{HD}} = (2/\hbar) (16\pi\beta\hbar/3)^2 \gamma_H \gamma_D \sum_{n'''} [1/(E_{n'''} - E_0)] \\ \cdot (O' | \delta(\mathbf{r}_{1\text{H}}) | n''') (n''' | \delta(\mathbf{r}_{2\text{D}}) | O). \quad (22)$$

If adequate wave functions for the higher electronic states should ever become available, this would be the most suitable expression for determining $\delta_{3\text{HD}}$ and for investigating the difficulty mentioned at the end of the preceding paragraph.

In one respect Eq. (22) has a surprising behavior. If the two nuclei in HD were pulled apart approaching the case of two isolated hydrogen atoms, the value of $E_{n'''} - E_0$ would approach zero for the lowest antisymmetric orbital state,⁷ whence the contribution of this term would go to infinity making δ infinitely large for two isolated hydrogen atoms, contrary to reason. The explanation of this paradox is that Eq. (22) and the other similar equations are valid only in so far as the perturbations giving rise to them are small compared to the electronic separation of the states; that is, they are valid only in so far as the magnetic interaction between the electrons and the nucleus is small compared to the energy difference between the singlet and triplet states. The latter is not true for two almost isolated hydrogen atoms.

The expression for $\delta_{2\text{HD}}$ can be simplified from Eq. (12) by the assumption of a mean excitation energy Δ_2 analogous to Eq. (11), by the assumption that the spin and orbital wave functions are separable, and by the assumption that $\mathbf{S}_1 = -\mathbf{S}_2$ in the electronic ground state. The result of these assumptions is

$$\delta_{2\text{HD}} = (1/3h\Delta_2) (2\beta\hbar)^2 \gamma_H \gamma_D [(0 | \{ 3\mathbf{r}_{1\text{H}}\mathbf{r}_{1\text{H}}\mathbf{r}_{1\text{H}}^{-5} - \mathfrak{S}_{1\text{H}}^{-3} \} : \{ 3\mathbf{r}_{2\text{D}}\mathbf{r}_{2\text{D}}\mathbf{r}_{2\text{D}}^{-5} - \mathfrak{S}_{2\text{D}}^{-3} \} | 0) \\ + (0 | \{ 3\mathbf{r}_{1\text{H}}\mathbf{r}_{1\text{H}}\mathbf{r}_{1\text{H}}^{-5} - \mathfrak{S}_{1\text{H}}^{-3} \} : \{ 3\mathbf{r}_{1\text{D}}\mathbf{r}_{1\text{D}}\mathbf{r}_{1\text{D}}^{-5} - \mathfrak{S}_{1\text{D}}^{-3} \} | 0)]. \quad (23)$$

If the last dyadic multiplication is carried out the result is a second Legendre polynomial in the angle be-

tween $\mathbf{r}_{1\text{H}}$ and $\mathbf{r}_{1\text{D}}$ which can be re-expressed with the aid of the spherical harmonic addition theorem¹⁹ with the

¹⁶ James, Coolidge, and Present, *J. Chem. Phys.* **4**, 194 (1936).

¹⁷ H. Brooks, *Phys. Rev.* **59**, 925 (1941); **60**, 168 (1941); and private communication.

¹⁸ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 344.

¹⁹ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), p. 53.

result given in the second part of the next equation. In addition, if one makes the restrictive assumption that the electronic wave functions consist of sums of terms which are products of factors each of which depends on the coordinates of a single electron in a cylindrically symmetric fashion, the first dyadic product can be simplified since the simplification of cylindrical sym-

metry can be applied to each dyadic separately. This assumption is applicable to the wave functions of Heitler-London,¹⁸ Wang,¹⁸ and Nordsieck²⁰ but not to those of Newell²¹ and James and Coolidge.¹² With these simplifications and with θ_1 being the angle between \mathbf{r}_{1H} and the internuclear axis, θ_2 between \mathbf{r}_{2D} and the axis, θ_3 between \mathbf{r}_{1D} and the axis, Eq. (23) becomes

$$\delta_{2HD} = (1/3h\Delta_2)(2\beta\hbar)^2\gamma_H\gamma_D[(0|\{3\cos^2\theta_1-1\}r_{1H}^{-3}\{3\cos^2\theta_2-1\}r_{2D}^{-3}|0) + 3\pi(0|\{\cos^2\theta_1-1\}r_{1H}^{-3}\{3\cos^2\theta_3-1\}r_{1D}^{-3}|0)]. \quad (24)$$

An approximate evaluation of this expression with Heitler-London wave functions and with $\Delta_2=1.4$ Rydbergs indicates that δ_{2HD} is approximately 3 cps. However, a better evaluation of this based both on better wave functions and fewer approximations would be highly desirable. The contribution to δ_{HD} of δ_{23HD} can be neglected by the argument in Sec. III.

There remains only the term δ_{1HD} . The first term for this as given in Eq. (16) can be approximately evaluated with Heitler-London wave functions with the result that δ_{1HD} is approximately -0.1 cps. The author has been told that Drell⁷ in an independent calculation has reached a result of the same magnitude. Since the calculation is an approximate one and since the very small value is achieved by two terms of six times this size almost canceling each other, the actual interaction for δ_{1HD} might be of either sign and as large as 0.5 cps, but it is probably smaller and of the order of 0.1 cps.

The term δ_{1HD} is more difficult to evaluate. Even if a mean energy Δ_1 for the excited states is assumed to reduce Eq. (16) analogously to Eq. (11), mean values of an expression involving second derivatives of the ground-state wave function are required; as discussed by Wick,²² such expressions are difficult to evaluate accurately. However, an indication of its probable magnitude can be inferred from the facts that in the analogous cases of diamagnetic susceptibility,^{2,23} and magnetic shielding⁶ the second-order paramagnetism terms are 3 percent and 21 percent, respectively, as

large as the corresponding simple diamagnetic terms. It is therefore probable that the second-order paramagnetism terms are no larger than about half a cycle per second in the case of HD.

VI. CONCLUSIONS

In the case of HD, by far the largest contribution to the electron coupled interaction between nuclei is due to the electron spin terms as in Eqs. (10), (12), and (21) with the electron orbital terms probably accounting for less than 1 cps out of the observed 43 cps. With different molecules, on the other hand, the electron orbital contributions may be relatively much larger, in which case Eqs. (15) and (16) must be evaluated.

It should be noted that all of the effects calculated in the present paper are proportional to the product $\gamma_N\gamma_{N'}$. Consequently a measurement of the nuclear spin-spin interaction constant $\delta_{NN'}$ in molecules which differ only in consisting of different isotopes of the same element would be of great value in confirming that the observed interactions are indeed magnetic ones as assumed in the present paper. A slight departure from strict proportionality to $\gamma_N\gamma_{N'}$ might be expected in two molecules differing isotopically due to different amplitudes of zero-point vibration²⁴ and to different electronic reduced masses, but these should be relatively small departures.

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²⁰ A. Nordsieck, Phys. Rev. **58**, 310 (1940).

²¹ G. F. Newell, Phys. Rev. **78**, 711 (1950).

²² G. C. Wick, Z. Physik **85**, 25 (1933).

²³ N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1952).

²⁴ N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).