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The Rotational Magnetic Moments of H_2, D_2, and HD Molecules*

The Rotational Radiofrequency Spectra of H_2, D_2, and HD in Magnetic Fields

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The radiofrequency spectra of H_2, D_2, and HD molecules have been obtained for transitions corresponding to reorientations of the rotational angular momenta of the molecules. From these spectra the rotational magnetic moments of H_2, HD, and D_2 molecules in the first rotational states are found to be $+0.8787\pm0.0070$, $+0.6601\pm0.0050$, and $+0.4406\pm0.0030$ nuclear magneton, respectively, all of the moments being positive. The relative values are good to 0.2 percent and to this precision they are in the ratio 4 : 3 : 2 as expected theoretically. The rotational magnetic moment of H_2 in the second rotational state was found to be just twice that in the first. From the rotational moment values, the high frequency contribution to the diamagnetic susceptibility of H_2 is deduced to be $(0.093\pm0.007)\times10^{-6}$ per mole. Certain molecular interaction constants, including the interaction of the quadrupole moment of the deuteron with the inhomogeneous electric field of the molecule, are also obtained. The results are in complete agreement with similar measurements from the nuclear reorientation spectrum. Furthermore, the dependence upon orientation of the diamagnetic susceptibility of the hydrogen molecule in the first rotational state can be found. It is such that $\xi_{\pm1}-\xi_0=-(4.5\pm2.0)\times10^{-31}$ per molecule.

INTRODUCTION

THE molecular beam magnetic resonance method[1–3] was originally designed for the measurement of nuclear magnetic moments, but since rotational magnetic moments of molecules are of the same order of magnitude the method may be directly applied to the measurement of these moments as well. The chief difference is that a different ratio of frequency to magnetic field must be used so that resonance minima corresponding to reorientations of the rotational angular momenta instead of the nuclear spins may be observed. In addition to the rotational magnetic moments of the molecules, certain molecular interaction constants can be evaluated from the present experiments and compared with values of the same constants as found by Kellogg, Rabi, Ramsey, and Zacharias.[1,2] These constants measure the interaction energies of the nuclear magnetic moments with the rotational magnetic field of the molecule, the mutual interaction energy of the two nuclear magnetic moments with each other, and—most important of all—the interaction energy of the deuteron quadrupole moment[2,4] with the inhomogeneous electric field of the molecule. A still different constant measuring the dependence of the diamagnetic susceptibility of a hydrogen molecule upon its orientation can also be found.

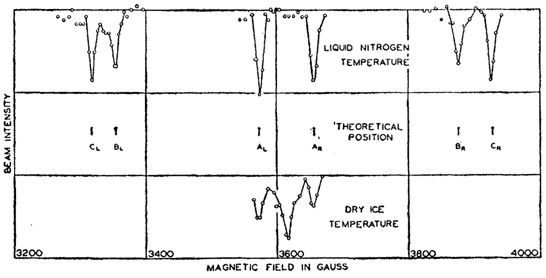

FIG. 1. The radiofrequency spectrum of H_2 corresponding to transitions in which the rotational angular momentum changes its orientation. The oscillator frequency is 2.4198 megacycles and the oscillating field about 10 gauss ($I_F=3.5$ amp.).

The only previous measurements of rotational magnetic moments are those of Estermann and Stern,[5] who found by measurements on para-H_2 molecules in rotational state $J=2$ that the rotational magnetic moment was between 0.8 and 0.9 nuclear magneton per rotational quantum number. The present experiment not only pro-

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[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. **56**, 728 (1939).

[2] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. **57**, 677 (1940).

[3] I. I. Rabi, S. Millman, P. Kusch, and J. R. Zacharias, Phys. Rev. **55**, 526 (1939).

[4] J. M. B. Kellog, I. I. Rabi, N. F. Ramsey, Jr., and J. R· Zacharias, Phys. Rev. **55**, 318 (1939).

[5] I. Estermann and O. Stern, Zeits. f. Physik **85**, 17 (1933).

vides a much more accurate measurement of the rotational magnetic moment of H_2 by an entirely different method, but is also applied to D_2 and HD molecules and can be used to determine the signs as well as the magnitudes of the moments. Furthermore, the rotational magnetic moments of H_2 both in the first and in the second rotational states can be separately measured, whence the proportionality of the magnetic moment to the rotational angular momentum may be experimentally tested. This proportionality was assumed by Estermann and Stern[5] in their determination of the magnetic moment of the proton and is predicted theoretically by Wick,[6, 7] but up to now no experimental evidence has been obtainable.

METHOD AND APPARATUS

The method used in this experiment is that described by RMKZ[3] and KRRZ.[1, 2] As the latter authors have pointed out, the molecular beam magnetic resonance method may be regarded as a means of obtaining the absorption and stimulated emission spectra of molecules at radiofrequencies. Thus, the minima of beam intensity in the accompanying curves occur when the oscillator frequency f_0 is equal to the Bohr frequency, $\nu=\Delta E/h$, of the molecule, where ΔE is the energy difference corresponding to any two orientation states of the molecule between which the transitions are allowed, that is, states for which the total magnetic quantum numbers differ by an amount $\Delta M=\pm 1$. Hence by observations of the positions of these resonance minima the dependence of the energy of the molecule on its orientation may be deduced. When, as in the present experiment, the reorientation transitions occur in the presence of a homogeneous magnetic field, the energy depends upon the values of the nuclear and rotational magnetic moments of the molecule as well as upon certain interaction constants within the molecule; so, from the observed radiofrequency spectrum, the magnetic moments and the interaction constants may be deduced.

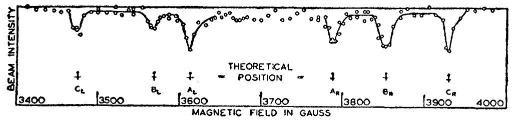

FIG. 2. The radiofrequency spectrum of D_2 corresponding to transitions in which the rotational angular momentum changes its orientation. The oscillator frequency is 1.2410 megacycles and the oscillating field about 14 gauss ($I_F=4.8$ amp.). The temperature is that of liquid nitrogen.

A group of resonance minima may be obtained corresponding to reorientations either of the nuclear or of the rotational angular momentum, i.e., to a change either of m_I or m_J. Experiments of the former type have been done by KRRZ[1, 2] in measuring nuclear moments, whereas the present experiments are limited to changes of m_J from which the rotational magnetic moments are obtainable.

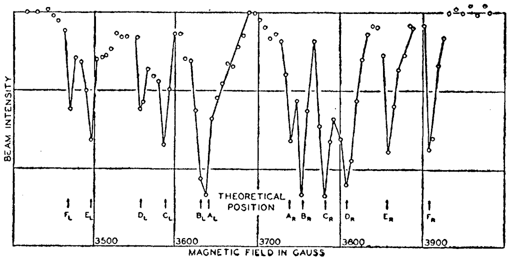

FIG. 3. The radiofrequency spectrum of HD corresponding to transitions in which the rotational angular momentum changes its orientation. The oscillator frequency is 1.850 megacycles and the oscillating field about 12 gauss ($I_F=4$ amp.). The temperature is that of liquid nitrogen.

The molecular beam apparatus used for this work is that which has already been fully described by KRRZ.[1] Since the present observations were taken with the same apparatus that was used in the proton and deuteron nuclear magnetic moment measurements the same magnet calibration could be used. As a check that the magnet had not changed, measurements of the nuclear magnetic moments were made during the course of the rotational measurements and were found to agree with the earlier measurements. In this way values of the rotational magnetic moments relative to a value of the proton moment of 2.785 nuclear magnetons were obtained to a greater precision than the precision of the absolute calibration of the magnetic field.

RESULTS

The experimental results on the groups of resonance minima corresponding to $\Delta m_J=\pm 1$

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[6] G. C. Wick, Zeits. f. Physik **85**, 25 (1933).

[7] G. C. Wick, Nuovo Cimento **10**, 118 (1933).

TABLE I. *Magnetic fields at which* H_2 *rotational resonances should occur for a fixed oscillator frequency* $f_0=\mu_{R-H_2}H_0/h$. $H''=\langle\mu_P/r^3\rangle_{Av}$, $\alpha=\mu_{R-H_2}/2\mu_P$, *and* $k=(\xi_{\pm1}-\xi_0)/2\mu_{R-H_2}$. *The numerical evaluations of the small second-order terms come from KRRZ's values of* H' *and* H''.

Δm_J	m_I	MAGNETIC FIELDS		NUMERICAL VALUE OF SECOND ORDER
		FIRST ORDER	SECOND ORDER	
$0\to1$	1	$H_0-\frac{1}{\alpha}H'+\frac{3}{5\alpha}H''+kH^2$	$+\frac{1}{\alpha}\frac{(3H''/5-H')^2}{H(1-\alpha)}$	$+\frac{338}{H}$
$0\to1$	0	$H_0\quad-\frac{6}{5\alpha}H''+kH^2$	$+\frac{1}{\alpha}\frac{(3H''/5-H')^2}{H(1-\alpha)}$	$+\frac{338}{H}$
$0\to1$	-1	$H_0+\frac{1}{\alpha}H'+\frac{3}{5\alpha}H''+kH^2$	$+\frac{6H''}{5\alpha}\frac{(3H''/5+2H')}{H(1-\alpha)}$	$+\frac{23{,}180}{H}$
$-1\to0$	1	$H_0-\frac{1}{\alpha}H'-\frac{3}{5\alpha}H''-kH^2$	$+\frac{6H''}{5\alpha}\frac{(3H''/5+2H')}{H(1-\alpha)}$	$+\frac{23{,}180}{H}$
$-1\to0$	0	$H_0\quad+\frac{6}{5\alpha}H''-kH^2$	$+\frac{1}{\alpha}\frac{(3H''/5-H')^2}{H(1-\alpha)}$	$+\frac{338}{H}$
$-1\to0$	-1	$H_0+\frac{1}{\alpha}H'-\frac{3}{5\alpha}H''-kH^2$	$+\frac{1}{\alpha}\frac{(3H''/5-H')^2}{H(1-\alpha)}$	$+\frac{338}{H}$

are shown in Figs. 1, 2, and 3 for H_2, D_2, and HD. Approximate values of the rotational magnetic moments (good to about 1.5 percent) can be obtained by merely using the values of the oscillator frequencies and of the magnetic fields at the centers of the groups of minima in the formula for the Larmor precession frequency ($\nu=\mu H/Jh$). However, because of the asymmetry of the curves, accurate determinations of the rotational magnetic moments as well as determinations of the interaction constants of the molecules depend on the detailed nature of the interaction functions as is discussed in subsequent paragraphs.

That the resonance minima shown in the accompanying diagrams correspond to changes of the rotational m_J is indicated by the following results: (1) that unlike the nuclear cases these groups of resonance minima do not correspond to magnetic moments common to either H_2 and HD or D_2 and HD, (2) that a new minimum arises in the center of the group of H_2 minima when the temperature is raised so that a higher rotational state is excited, (3) that the magnetic moments observed with H_2, HD, and D_2 are approximately inversely proportional to the moments of inertia of the molecules as expected theoretically for rotational magnetic moments, and (4) that this assumption makes possible a correct theoretical prediction of the separations of the various minima in a single group.

It is easily possible to account for the number of observed resonance minima in Figs. 1, 2, and 3. All but one of the curves are taken with the source at liquid nitrogen temperature at which, because of the low moments of inertia of hydrogen molecules, most of the molecules are in the zeroth or first rotational state.[1] Since it is impossible to change the value of m_J when the rotational quantum number, J, equals zero, the only molecules of interest are those for which J equals one. In the cases of H_2 and D_2, where the two nuclei are identical, the quantum-mechanical symmetry conditions require that the only varieties of molecules that can have $J=1$ are ortho-H_2 and para-D_2, for both of which the total nuclear spin, I, equals one. Therefore with H_2 and D_2 at liquid nitrogen temperature the only molecules concerned in the experiment are those with $I=1$ and $J=1$, whence there are nine energy levels corresponding to all allowed orientations of I and J and between these energy levels six different transitions corresponding to $\Delta m_J=\pm1$ can occur. This is the reason that six resonance minima are observed for H_2 and D_2 at liquid nitrogen temperature. The additional H_2 minimum which appears when dry ice is placed in the source trap is due to molecules of para-H_2 with $I=0$ which are partially excited to rotational state two at the higher temperature. Since $I=0$, there is no spin-spin or spin-rotational interaction so only a single new peak is produced.

TABLE II. *Magnetic fields at which* D_2 *rotational resonances should occur for a fixed oscillator frequency* $f_0=\mu_{R-D_2}H_0/h$. $S_D=1/5(H''+H''')$, $H'=\langle\mu_D/r^3\rangle_{Av}$, $H'''=-5e^2qQ/4\mu_D$, $\alpha=\mu_{R-D_2}/\mu_D$, *and* $k=(\xi_{\pm1}-\xi_0)/2\mu_{R-D_2}$. *The* C_i*'s are as in KRRZ.*[2] *The numerical evaluations of the small second- and third-order terms come from KRRZ's values of* H' *and* S_D.

Δm_J	m_I	Magnetic Fields: First Order	Second Order	Third Order	Numerical Values of Second and Third Orders
$0\leftrightarrow1$	1	$H_0-\frac{1}{\alpha}H'$	$+\frac{3}{\alpha}S_D+kH^2$	$+\frac{1}{\alpha}C_2'$	$+\frac{8{,}050}{H}$
$0\leftrightarrow1$	0	H_0	$-\frac{6}{\alpha}S_D+kH^2$	$+\frac{1}{\alpha}C_2'-\frac{2}{\alpha}C_3$	$+\frac{8{,}050}{H}+\frac{14{,}140{,}000}{H^2}$
$0\leftrightarrow1$	-1	$H_0+\frac{1}{\alpha}H'$	$+\frac{3}{\alpha}S_D+kH^2$	$+\frac{1}{\alpha}C_2-\frac{1}{\alpha}C_2'-\frac{1}{\alpha}C_3$	$+\frac{41{,}300}{H}+\frac{7{,}070{,}000}{H^2}$
$-1\leftrightarrow0$	1	$H_0-\frac{1}{\alpha}H'$	$-\frac{3}{\alpha}S_D-kH^2$	$+\frac{1}{\alpha}C_2-\frac{1}{\alpha}C_2'+\frac{1}{\alpha}C_3$	$+\frac{41{,}300}{H}-\frac{7{,}070{,}000}{H^2}$
$-1\leftrightarrow0$	0	H_0	$+\frac{6}{\alpha}S_D-kH^2$	$+\frac{1}{\alpha}C_2'+\frac{2}{\alpha}C_3$	$+\frac{8{,}050}{H}-\frac{14{,}140{,}000}{H^2}$
$-1\leftrightarrow0$	-1	$H_0+\frac{1}{\alpha}H'$	$-\frac{3}{\alpha}S_D-kH^2$	$+\frac{1}{\alpha}C_2'$	$+\frac{8{,}050}{H}$

For HD where the nuclei are not identical, there is no symmetry restriction so the number of states with $J=1$ is eighteen, corresponding to all possible orientations of the spins of the two nuclei and of the rotational angular momentum. Between these eighteen states twelve different transitions with $\Delta m_J=\pm1$ can occur, which correspond to the twelve observed resonance minima.

By making the same assumptions as were made by KRRZ,[1,2] that is, by assuming the only interaction energies within the molecule to be a spin-spin magnetic interaction energy, a spin-rotational magnetic interaction energy, and the interaction of a deuteron electrical quadrupole moment with the inhomogeneous electric field of the molecule, it is possible to account not only for their results but also quite well for the present ones. Such agreement should be expected since the present experiments concern merely different transitions between the same set of energy levels. However, if in addition to their assumption, one takes into account the diamagnetic interaction energies of the molecules with the external field, the agreement between theory and experiment is even better, being perfect to well within the experimental error. This new assumption amounts to adding a term $-\frac{1}{2}\xi_{m_J}H^2$ to the Hamiltonian where ξ_{m_J} is the diamagnetic susceptibility of the molecule in the rotational state J when the rotational magnetic quantum number is m_J. This term gives rise to a displacement of the rotational resonance minima because of the dependence of the diamagnetic susceptibility ξ_{m_J} upon m_J, ξ_{m_J} clearly being least in magnitude when the line of the nuclei and hence the electron distributions are most nearly parallel to the field ($m_J=0$) and greatest when they are most nearly perpendicular to the field ($m_J=\pm J$). This added term of course does not affect the agreement already obtained by KRRZ,[1,2] since m_J and hence ξ_{m_J} is unaltered in these transitions whence its effect cancels out. With this assumption added to those of KRRZ the Hamiltonian of a diatomic molecule in a magnetic field **H** becomes (apart from terms independent of orientation)

$$\mathfrak{H}=-\boldsymbol{\mu}_1\cdot\mathbf{H}-\boldsymbol{\mu}_2\cdot\mathbf{H}-\boldsymbol{\mu}_R\cdot\mathbf{H}-H_1'(\boldsymbol{\mu}_1\cdot\mathbf{J})-H_2'(\boldsymbol{\mu}_2\cdot\mathbf{J})$$
$$+\frac{1}{r^3}\left\{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2-\frac{3(\boldsymbol{\mu}_1\cdot\mathbf{r})(\boldsymbol{\mu}_2\cdot\mathbf{r})}{r^2}\right\}-\tfrac{1}{2}\xi_{m_J}H^2 \qquad (1)$$
$$+\sum_{k=1}^{2}\frac{e^2q_kQ_k}{2I_k(2I_k-1)J(2J-1)}\times\{3(\mathbf{I}_k\cdot\mathbf{J})^2+\tfrac{3}{2}\mathbf{I}_k\cdot\mathbf{J}-\mathbf{I}_k^2\mathbf{J}^2\},$$

where $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the nuclear magnetic moments, $\boldsymbol{\mu}_R$ the rotational magnetic moment, **J** the rotational angular momentum in units of

TABLE III. *Magnetic fields at which* HD *rotational resonances should occur for a fixed oscillator frequency* $f_0=\mu_{R\text{-HD}}H_0/h$. $S=\langle 2\mu_P\mu_D/5r^3\rangle_{\text{Av}}$, $E=H'''/5=+e^2qQ/4\mu_D$, $\alpha_P=\mu_{R\text{-HD}}/\mu_P$, $\alpha_D=\mu_{R\text{-HD}}/\mu_D$, *and* $k=(\xi_{\pm1}-\xi_0)/2\mu_{R\text{-HD}}$. *The numerical evaluations of the small second- and third-order terms come from KRRZ's values of* H_P', H_D', S, *and* E.

Δm_J	m_P	m_D	MAGNETIC FIELDS		
			FIRST ORDER	SECOND ORDER	THIRD ORDER
$0\leftrightarrow 1$	$\frac{1}{2}$	1	$H_0-\frac{1}{\alpha_P}H_P'-\frac{1}{\alpha_D}H_D'+\frac{3}{\alpha_D}S-\frac{3}{\alpha_D}E+kH^2$	$+\frac{16{,}300}{H}$	$+\frac{2{,}650{,}000}{H^2}$
$0\leftrightarrow 1$	$\frac{1}{2}$	0	$H_0-\frac{1}{\alpha_P}H_P'+\frac{6}{\alpha_D}E+kH^2$	$+\frac{32{,}220}{H}$	$-\frac{590{,}000}{H^2}$
$0\leftrightarrow 1$	$\frac{1}{2}$	-1	$H_0-\frac{1}{\alpha_P}H_P'+\frac{1}{\alpha_D}H_D'-\frac{3}{\alpha_D}S-\frac{3}{\alpha_D}E+kH^2$	$+\frac{394}{H}$	$+\frac{2{,}470{,}000}{H^2}$
$0\leftrightarrow 1$	$-\frac{1}{2}$	1	$H_0+\frac{1}{\alpha_P}H_P'-\frac{1}{\alpha_D}H_D'-\frac{3}{\alpha_D}S-\frac{3}{\alpha_D}E+kH^2$	$+\frac{47{,}000}{H}$	$-\frac{7{,}150{,}000}{H^2}$
$0\leftrightarrow 1$	$-\frac{1}{2}$	0	$H_0+\frac{1}{\alpha_P}H_P'+\frac{6}{\alpha_D}E+kH^2$	$+\frac{35{,}300}{H}$	$-\frac{10{,}430{,}000}{H^2}$
$0\leftrightarrow 1$	$-\frac{1}{2}$	-1	$H_0+\frac{1}{\alpha_P}H_P'+\frac{1}{\alpha_D}H_D'+\frac{3}{\alpha_D}S-\frac{3}{\alpha_D}E+kH^2$	$+\frac{19{,}400}{H}$	$-\frac{9{,}850{,}000}{H^2}$
$-1\leftrightarrow 0$	$\frac{1}{2}$	1	$H_0-\frac{1}{\alpha_P}H_P'-\frac{1}{\alpha_D}H_D'-\frac{3}{\alpha_D}S+\frac{3}{\alpha_D}E-kH^2$	$+\frac{19{,}400}{H}$	$+\frac{9{,}850{,}000}{H^2}$
$-1\leftrightarrow 0$	$\frac{1}{2}$	0	$H_0-\frac{1}{\alpha_P}H_P'-\frac{6}{\alpha_D}E-kH^2$	$+\frac{35{,}300}{H}$	$+\frac{10{,}430{,}000}{H^2}$
$-1\leftrightarrow 0$	$\frac{1}{2}$	-1	$H_0-\frac{1}{\alpha_P}H_P'+\frac{1}{\alpha_D}H_D'+\frac{3}{\alpha_D}S+\frac{3}{\alpha_D}E-kH^2$	$+\frac{47{,}000}{H}$	$+\frac{7{,}150{,}000}{H^2}$
$-1\leftrightarrow 0$	$-\frac{1}{2}$	1	$H_0+\frac{1}{\alpha_P}H_P'-\frac{1}{\alpha_D}H_D'+\frac{3}{\alpha_D}S+\frac{3}{\alpha_D}E-kH^2$	$+\frac{394}{H}$	$-\frac{2{,}470{,}000}{H^2}$
$-1\leftrightarrow 0$	$-\frac{1}{2}$	0	$H_0+\frac{1}{\alpha_P}H_P'-\frac{6}{\alpha_D}E-kH^2$	$+\frac{32{,}220}{H}$	$+\frac{590{,}000}{H^2}$
$-1\leftrightarrow 0$	$-\frac{1}{2}$	-1	$H_0+\frac{1}{\alpha_P}H_P'+\frac{1}{\alpha_D}H_D'-\frac{3}{\alpha_D}S+\frac{3}{\alpha_D}E-kH^2$	$+\frac{16{,}300}{H}$	$-\frac{2{,}650{,}000}{H^2}$

$h/2\pi$, $\mathbf{I}_k$ the nuclear angular momentum in units of $h/2\pi$, $\mathbf{r}$ the radius vector between the two nuclei, Q_k the quadrupole moment of the kth nucleus, q_k the gradient of the electric field at the position of the kth nucleus divided by the charge of an electron, H_1' and H_2' the spin rotational interaction constants and essentially measures of the rotational magnetic fields at the positions of the nuclei, and ξ_{m_J} the diamagnetic susceptibility of the molecule in rotational state J, m_J.

From their Hamiltonian and the ordinary perturbation theory, KRRZ[1,2] have obtained expressions for the energies of the different molecular states when $J=1$ to the approximation of the third order perturbation theory. The energy expressions needed here are merely those of KRRZ with the above diamagnetic term added. These energy expressions may be differenced subject to the restriction $\Delta m_J=-1$ and from these differences and from the relation $hf_0=\Delta E$, expressions for the predicted fields at which resonance minima should occur may be obtained. These expressions for H_2, D_2, and HD molecules in the first rotational state are given in Tables I, II, and III, respectively, the notation being that of KRRZ[1,2] whenever possible. The numerical expressions for the small second- and third-order perturbations are based on the values of the interaction constants obtained by KRRZ. It should be noted that all the first-order corrections are symmetrical about H_0 so the second-order corrections are important in that they account for the observed asymmetry of the results.

From the expressions of the tables and from the values of the interaction constants found by KRRZ[1,2] in the nuclear resonance experiments, the theoretical positions of the resonance minima may readily be predicted subject to the assumption of appropriate values for the μ_R's and $\xi_{\pm 1}-\xi_0$, the only remaining adjustable constants. When this is done, excellent agreement with the observations is obtained. This agreement makes possible an identification of the quantum numbers associated with each resonance minimum and shows the complete consistency of these results with those of KRRZ. The quantum numbers to be identified with each minimum are given in Tables IV, V, and VI, the correlation between these tables and the curves being the designation letters A_L, etc. The best determinations of the experimental positions of the resonances are also given in these tables.

After this identification has once been made, the process may be performed in the reverse direction and the experimental results used to evaluate the various interaction constants. The values so found not only provide a check upon the values of the same quantities as obtained from the nuclear resonance minima, but in some cases, like H_2 where the separations in gauss of the rotational minima are about seven times greater than the separations of the nuclear minima, the determinations can be made more accurately from the rotational than from the nuclear experiments. This evaluation has been performed by equating the theoretical resonance positions of Tables I, II, and III to the corresponding observed positions listed in Tables IV, V, and VI and by solving for the desired constants by the method of least squares. The values of the various quantities obtained in this way are as follows:

(a) For H_2 in the first rotational state when $f_0=2.420$ megacycles: $H_0=3613.1$ gauss, $H'=26.8\pm 0.3$ gauss, $H''=33.9\pm 0.3$ gauss, and

$$\xi_{\pm 1}-\xi_0=-(3.9\pm 2.5)\times 10^{-31}$$

per molecule;

TABLE IV. *Observed positions of* H_2 *rotational resonances and comparison with theory when* $f_0=2.420$ *megacycles. The theoretical positions are based on the values of* H_0, H', H'', *and k evaluated from these data by the method of least squares.*

Δm_J	m_I	DESIGNATION OF MINIMUM	EXPERIMENTAL POSITION OF RESONANCE (GAUSS)	THEORETICAL POSITION (GAUSS)
$0\Leftrightarrow 1$	1	A_L	3573.0	3572.9
$0\Leftrightarrow 1$	0	B_L	3354.3	3354.7
$0\Leftrightarrow 1$	-1	C_R	3920.3	3919.6
$-1\Leftrightarrow 0$	1	C_L	3319.3	3319.7
$-1\Leftrightarrow 0$	0	B_R	3871.3	3871.5
$-1\Leftrightarrow 0$	-1	A_R	3653.6	3653.5

(b) For D_2 in the first rotational state when $f_0=1.2410$ megacycles: $H_0=3696.2$ gauss, $H'=13.7\pm 0.8$ gauss, $S_D=19.55\pm 0.20$ gauss, and

$$\xi_{\pm 1}-\xi_0=-(5.1\pm 2.5)\times 10^{-31}$$

per molecule;

(c) For HD in the first rotational state when $f_0=1.850$ megacycles: $H_0=3677.4$ gauss, $H_D'=20.5\pm 1.5$ gauss, $H_P'=20.23\pm 0.5$ gauss, $S=11.70\pm 0.5$ gauss, $E=17.30\pm 0.3$ gauss, and

$$\xi_{\pm 1}-\xi_0=-(4.6\pm 3.5)\times 10^{-31}$$

per molecule.

The number of observed resonance minima exceeds the number of available parameters, but

TABLE V. *Observed positions of* D_2 *rotational resonances and comparison with theory when* $f_0=1.2410$ *megacycles. The theoretical positions are based on the values of* H_0, H', S_D, *and k evaluated from these data by the method of least squares.*

Δm_J	m_I	DESIGNATION OF MINIMUM	EXPERIMENTAL POSITION OF RESONANCE (GAUSS)	THEORETICAL POSITION (GAUSS)
$0\Leftrightarrow 1$	1	A_R	3787.3	3786.8
$0\Leftrightarrow 1$	0	C_L	3473.6	3473.9
$0\Leftrightarrow 1$	-1	B_R	3849.4	3849.5
$-1\Leftrightarrow 0$	1	B_L	3565.1	3565.2
$-1\Leftrightarrow 0$	0	C_R	3922.6	3922.8
$-1\Leftrightarrow 0$	-1	A_L	3610.5	3610.0

TABLE VI. *Observed positions of* HD *rotational resonances and comparison with theory when* $f_0=1.850$ *megacycles. The theoretical positions are based on the values of* H_0, H_P', H_D', *S, E, and k evaluated from these data by the method of least squares.*

Δm_J	m_P	m_D	DESIGNATION OF MINIMUM	EXPERIMENTAL POSITION OF RESONANCE (GAUSS)	THEORETICAL POSITION (GAUSS)
$0\Leftrightarrow 1$	$\frac{1}{2}$	1	D_L	3556.5	3557.1
$0\Leftrightarrow 1$	$\frac{1}{2}$	0	A_R	3737.7	3736.1
$0\Leftrightarrow 1$	$\frac{1}{2}$	-1	E_L	3499.6	3499.4
$0\Leftrightarrow 1$	$-\frac{1}{2}$	1	B_L	3631.8	3629.2
$0\Leftrightarrow 1$	$-\frac{1}{2}$	0	F_R	3906.5	3906.6
$0\Leftrightarrow 1$	$-\frac{1}{2}$	-1	C_R	3779.9	3780.8
$-1\Leftrightarrow 0$	$\frac{1}{2}$	1	C_L	3583.2	3584.9
$-1\Leftrightarrow 0$	$\frac{1}{2}$	0	F_L	3469.6	3467.9
$-1\Leftrightarrow 0$	$\frac{1}{2}$	-1	B_R	3750.0	3750.9
$-1\Leftrightarrow 0$	$-\frac{1}{2}$	1	E_R	3857.1	3855.6
$-1\Leftrightarrow 0$	$-\frac{1}{2}$	0	A_L	3631.8	3636.4
$-1\Leftrightarrow 0$	$-\frac{1}{2}$	-1	D_R	3806.5	3806.3

the consistency of the results is shown by a comparison of the experimental positions of the resonance minima with the theoretical positions predicted with the above values of the interaction constants. This comparison is given both on the graphs and in the last two columns of Tables IV, V, and VI. It will be seen that the agreement between theory and experiment is excellent—good to about one part in eight thousand for H_2 and D_2. Although the agreement in the case of HD is worse, it is still very good (about one part in two thousand). That the agreement should be worse in this case is not surprising since the experimental observations were by far the most difficult for HD. This was due to the fact that the rotational moment being reorientated was less than one-fourth the magnitude of the proton moment which occurred in the same molecule. Hence a sufficiently strong inhomogeneous field to throw out reoriented molecules caused all the molecules to make such large excursions because of the proton moment that many nonreoriented molecules were lost, which made the observable intensity of the resonance minima very weak. In fact, the average depth of an HD rotational resonance minimum of Fig. 3 was less than one percent of the total beam intensity. As this refocusing difficulty occurred for all the rotational measurements in a greater or lesser degree, here, unlike the nuclear case, no fundamental significance can be attached to the measured intensities of the resonances.

It will be noted that whereas most of the above quantities have been measured to a high precision, such is not true of $\xi_{\pm 1}-\xi_0$. This is due to the fact that at the magnetic fields of the experiments this term only slightly affects the positions of the resonance minima (1.8 gauss out of 3600 gauss at the most). At the time the experiments were performed it was not realized that such a quantity as $\xi_{\pm 1}-\xi_0$ could be obtained from the results, so there was no special effort to make the observations under the most favorable conditions. It is hoped that at some future date the experiments will be carried out at a much higher frequency and field where this diamagnetic effect, which varies as H^2, will be relatively much stronger.

From the frequencies, from the least-squares values of H_0 listed above, and from the relation

$$\mu_R = Jf_0h/H_0 \tag{2}$$

the values of the rotational magnetic moments of the molecules are obtained. These values are $\mu_{R-\mathrm{H}_2}=0.8787\pm 0.0070$, $\mu_{R-\mathrm{D}_2}=0.4406\pm 0.0030$, and $\mu_{R-\mathrm{HD}}=0.6601\pm 0.0050$ nuclear magneton. The moment values here quoted are relative to a value of the nuclear moment of the proton of 2.785 nuclear magnetons.[1] The relative values should be accurate to 0.2 percent although the absolute values of the moments, like the absolute value of the proton moment, are subject to an error of possibly 0.7 percent due to possible errors in the absolute calibration of the magnetic field.[1] Except for the evaluation of the effect of the second-order perturbations which slightly shift the centers of gravity of the groups of resonance minima, the determinations of the rotational magnetic moments are completely independent of the above detailed theory of the molecular interactions. So even if this theory were completely wrong, which is very highly improbable in view of the extensiveness of its experimental verification, the rotational magnetic moments should be correctly evaluated to an accuracy of at least 1.5 percent. Although the most accurate evaluation of the rotational magnetic moments comes as above from the observed value of H_0/f_0, an independent check of the values can be obtained from the separations of the different minima in the group. From Tables I, II, and III it will be noted that the separations of the minima depend on the ratios $\alpha=\mu_R/\mu_D$, etc. Therefore the agreement of the values of interaction constants obtained in this experiment with those obtained in the nuclear experiments indicates that the μ_R's have been correctly chosen.

It should be noted that, in the theoretical prediction of the resonance minima positions given above, it was implicitly assumed that the μ_R's were positive. Had the μ_R's been negative there would have been no change in the predicted positions as far as the first-order perturbations are concerned since by Tables I, II, and III the first-order energy perturbations are symmetrical about H_0. However, the direction of the shift due to the second-order perturbation and hence the nature of the asymmetry would have been

TABLE VII. *Summary of results. The notation is in agreement with Table XII of KRRZ.*[2] *The quantity in parenthesis in the* μ_D/r^3 *column is the value obtained by multiplying* μ_P/r^3 *by* μ_D/μ_P. *It is used in obtaining* $5e^2qQ/4\mu_D$ *from the* D_2 *observations. The first quantity for* H' *in* HD *is its value at the position of the proton and the second is at the position of the deuteron.*

MOLECULE	μ_R (N. M.)	$\langle\mu_P/r^3\rangle_{Av}$ (GAUSS)	$\langle\mu_D/r^3\rangle_{Av}$ (GAUSS)	SPIN-ORBIT CONSTANT $=H'$ (GAUSS)	$5e^2qQ/4\mu_D$ (GAUSS)	χHF (10^{-6} PER MOLE)	$\xi_{\pm1}-\xi_0$ (10^{-31} PER MOLECULE)
H_2 when $J=1$	0.8787 ± 0.0070	$33.9\ \pm0.3$		$26.8\ \pm0.3$		0.094 ± 0.007	-3.9 ± 2.5
H_2 when $J=2$	1.757 ± 0.014 or $2(0.8786\pm0.0070)$						
D_2 when $J=1$	0.4406 ± 0.0030		(10.42)	$13.7\ \pm0.8$	87.36 ± 1.2	0.093 ± 0.007	-5.1 ± 2.5
HD when $J=1$	0.6601 ± 0.0050	34.21 ± 1.5	10.26 ± 0.40	20.23 ± 0.5 $20.5\ \pm1.5$	86.50 ± 1.5	0.093 ± 0.007	-4.6 ± 3.5
Average of H_2, D_2, and HD						0.093 ± 0.007	-4.5 ± 2.0

reversed. Therefore, the existence of the slight second-order asymmetry of the experimental curves makes possible a determination of the sign of the rotational magnetic moments. In all three cases the rotational magnetic moments are found to be positive.

One of the most significant results of this experiment is obtained by a comparison of the H_2 resonance minima with the source at liquid nitrogen and at dry ice temperatures, respectively, as shown in Fig. 1. At dry ice temperatures, in addition to the six resonance minima found for H_2 at the lower temperature, where the only nonzero rotational state is the state one, a seventh minimum appears midway between the two central minima of rotational state one. This minimum may be assumed to be due to the second rotational state of H_2 which, though unexcited at liquid nitrogen temperature, is partially excited at dry ice temperature. Since only para-H_2 may be in the second rotational state and since para-H_2 has a zero resultant nuclear spin, there is no spin-spin or spin-rotational interaction so only a single unperturbed resonance minimum is obtained from which the rotational magnetic moment may be directly deduced from Larmor's formula. The magnetic moment as thus obtained is $1.757\pm0.014 = 2(0.8786\pm0.0070)$ nuclear magnetons or just twice the rotational moment of rotational state one. This result may also be obtained directly by observing that the new peak due to the second rotational state falls midway between the two central peaks of the first rotational state, which by Table I are unaffected by the second-order perturbations. Therefore, μ_R/J must be the same for $J=1$ and $J=2$ to within the experimental error of 0.2 percent in the determination of ratios of magnetic moments; in other words, as far as the first two rotational states of H_2 are concerned the rotational magnetic moment is proportional to the rotational angular momentum.

As a check upon the consistency of the results, observations were made upon H_2 at half the frequency and consequently at half the value of the magnetic field used in the published curves. The results are completely consistent with those at the higher frequency. Also the rotational magnetic moments of H_2 and D_2 molecules were measured with an earlier form of the present apparatus in which the path of the beam in the radiofrequency field was only 2.7 cm long in contrast to the present 13.5 cm length. Because of the shortness of the field and the smallness of the beam intensity, it was necessary to use a much stronger oscillating magnetic field whence the resolving power of the apparatus was much less (the half-widths of the resonance minima are proportional to the strength of the oscillating magnetic field[8]). For this reason it was impossible to resolve the individual peaks and there was consequently a much greater uncertainty in the evaluation of the magnetic moments than now. However, the moments could be determined with an estimated error of two percent and these values were reported.[9] The earlier measurements agree with the present ones to within the former's estimated error.

DISCUSSION OF RESULTS

A summary of the results obtained in this experiment is given in Table VII. Those quantities which have also been measured by KRRZ are $\langle\mu_P/r^3\rangle_{Av}$, $\langle\mu_D/r^3\rangle_{Av}$, H', and $5e^2qQ/4\mu_D$. The

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[8] I. I. Rabi, Phys. Rev. **51**, 652 (1937).

[9] N. F. Ramsey, Jr., Phys. Rev. **55**, 595(A) (1939).

portion of Table VII pertaining to these quantities may be directly compared with Table XII of KRRZ.[2] It will be seen that the agreement is excellent, being well within the estimated experimental error in all cases. This agreement and the close agreement between theory and experiment in Tables IV, V, and VI provide very strong evidence for the validity of the theory on which this work is based and in particular for the quadrupole moment of the deuteron. A full discussion of this agreement, a final averaging of all the experimental results including those of this paper, and a computation of the deuteron quadrupole moment from the final average of the quantity $5e^2qQ/4\mu_D$ is contained in the paper of KRRZ[2] and will consequently not be discussed further here.

The observed value of the rotational magnetic moment of H_2 falls within the limits 0.8 to 0.9 nuclear magneton per rotational quantum number set experimentally by Estermann and Stern.[5] It also agrees with the much wider theoretical limits set by Wick.[6,7] The uncertainty of Wick's result arises from the sensitiveness of the computed rotational magnetic moment to the nature of the electron wave function of the molecule that is used, the predicted moment being $+0.36$ nuclear magneton with Wang wave functions and $+0.93$ nuclear magneton with another wave function of Wick's invention. It is perhaps worth emphasizing that the observed rotational magnetic moment for H_2 is much different from that which would be obtained if the electrons were a rigid charge distribution which rotated with the same angular velocity as the nuclei. Such a naive theory would predict[10] a rotational magnetic moment in the state $J=1$ of -3 nuclear magnetons which is much different in magnitude and opposite in sign from the observed result, the electron contribution to the magnetic moment from this theory being over thirty times greater than its experimental value. The necessity for a theory such as Wick's in which the electron contribution to the rotational magnetic moment is much less than on the rigid body model is thus evident.

The result that the rotational magnetic moment of H_2 is proportional to its angular momentum would be completely obvious if the electrons were assumed to behave as a rigid charge distribution, but, as just pointed out, this assumption is necessarily false. However, the proportionality of the rotational magnetic moment to J is also predicted by Wick's theory. As this prediction is the most important application[7] of the theory, its direct experimental proof in these experiments is particularly useful.

The experimental values of the rotational magnetic moments of H_2, HD, and D_2 as listed in the preceding section are in the ratio 3.994 : 3.000 : 2.003; that is, to within the experimental error of 0.2 percent they are in the ratio 4 : 3 : 2 or in the inverse ratio of the reduced masses of the molecules. Since the rotational angular velocities in the first rotational state are inversely proportional to the reduced masses the experiment shows that the rotational magnetic moments are proportional to the rotational angular velocities in a comparison of H_2, HD, and D_2 molecules. That such should be the case would certainly be expected in a comparison of H_2 and D_2 molecules; however, that it should be so in a comparison of H_2 with HD is not immediately apparent, for not only are the angular velocities of the two molecules different but so also are the positions of the axes about which the molecules rotate, since the center of mass of the HD molecule is not midway between the two nuclei. Still even for this case if the electrons behaved as a rigid charge distribution attached to the nuclei the rotational magnetic moment would be proportional to the rotational angular velocity, since for a rigid molecule with zero total charge and with central symmetry of the charge distribution the rotational magnetic moment is invariant to the position of the axis of rotation. That the magnetic moment should be inversely proportional to the reduced mass for unsymmetrical molecules like HD is on the basis of Wick's theory not immediately obvious. In fact, to make it so the electron contribution to the moment of HD must be more than twice as great as its contribution to H_2 even though the rotational angular velocity is less. This, however, may be proved as is shown in the appendix to the present paper where the general expression for the rotational magnetic moments of H_2, D_2, and HD molecules is derived.

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[10] R. Frisch and O. Stern, Zeits. f. Physik **85**, 25 (1933).

Although the 4 : 3 : 2 ratio of the rotational magnetic moments holds to within the estimated experimental error of 0.2 percent in the determination of the ratios of moments, the discrepancy is very near the maximum experimental error and seems fairly persistent. It is in the direction that the moments of the lighter molecules are slightly less than would be expected. Such a discrepancy could probably be explained as the effect of the zero state vibrational motion of the molecule upon the mean separation of the nuclei. A quantitative calculation of the magnitude of the effect was not attempted.

From the theory of Wick or from the more general theory given in the appendix it is possible from the experimental measurement of the rotational magnetic moments to evaluate the high frequency term[11] of the ordinary diamagnetic susceptibility of H_2, D_2, and HD molecules. This is due to the fact that the summation in Eq. (6) of the appendix is just exactly the same as the summation which occurs in the theory of the diamagnetic susceptibility of molecules.[9] In fact, a comparison of the two shows that (in the notation of Van Vleck and the appendix)

$$\chi_{\text{mole}-\text{HF}}=\frac{e^2L\rho^2}{12mc^2}\left(1-\frac{2M_1M_2}{(M_1+M_2)M}\frac{\mu}{J}\right). \quad (3)$$

So with the observed values of the rotational moments, the high frequency term in the diamagnetic susceptibility of H_2, D_2, and HD are as listed in Table VII, the average value being

$$\chi_{\text{mole}-\text{HF}}=0.093\pm0.007\times10^{-6} \text{ per mole.}$$

This result may be subject to a somewhat larger error than 0.007 due to possible inaccuracies in the perturbation theories on which the calculation is based. The result calculated from Wang wave functions by Van Vleck and Frank[12] of $\chi_{\text{mole}-\text{HF}}=0.51\times10^{-6}$ thus appears to be about five times too big. However, if instead of the Wang wave function another H_2 wave function, used first by Wick,[6,7] is used in the calculation, the theoretical value for the high frequency part of the susceptibility may be made to drop even below the above experimental value.

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APPENDIX

Theoretical expression for the rotational magnetic moments of H_2, D_2, *and* HD *molecules.*—Although Wick's treatment[6,7] applies only to a symmetrical molecule, it may readily be extended to the case of a molecule one of whose nuclei is of mass M_1 and the other of M_2 with the result that the rotational magnetic moment of the molecule in rotational state J is, in nuclear magnetons,

$$\mu=\frac{(M_2^2+M_1^2)M}{M_1M_2(M_1+M_2)}J-\frac{2}{m\rho^2}\frac{(M_1+M_2)M}{M_1M_2}\left[\sum{}'\frac{|(0|M_{\xi 0}|n)|^2}{E_n-E_0}\right]J, \quad (4)$$

where M is the mass of the proton, m the mass of the electron, and ρ the distance between the nuclei. $(0|M_{\xi 0}|n)$ is a matrix element for the nonrotating molecule of the electronic angular momentum about an axis through the center of mass of the molecule and perpendicular to the internuclear line. Since the angular momentum is about the center of mass of the molecule and not about a point midway between the two nuclei, the quantity in brackets is different for HD than H_2 or D_2. The first term in the above expression is the nuclear contribution to the rotational magnetic moment and the second is the electron contribution, neither of which alone is inversely proportional to the reduced mass. To make possible a comparison of the H_2 and HD results the electronic angular momenta must be expressed about an axis which is the perpendicular bisector of the line joining the two nuclei. This transformation of the quantity in

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[11] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibility* (Oxford Press, 1932), p. 276.

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

the brackets can be performed with the aid of the invariance properties of the diamagnetic susceptibility shown by Van Vleck.[11] (It should be noted that the symmetry of the molecule is such that $|(0|M_{\xi 0}|n)|^2=\frac{1}{2}|P(0,n)|^2$ where $P(0, n)$ are the total angular momentum matrix elements used by Van Vleck.) The result is

$$\mu=\frac{(M_2^2+M_1^2)M}{M_1M_2(M_1+M_2)}J-\frac{2}{m\rho^2}\frac{(M_1+M_2)M}{M_1M_2}\left[\sum{}'\frac{|(0|M_{\xi c}|n)|^2}{E_n-E_0}\right]J-\frac{1}{\rho^2}\frac{(M_1+M_2)M}{M_1M_2}\left[\sum(\langle r_0^2\rangle_{\mathrm{Av}}-\langle r_c^2\rangle_{\mathrm{Av}})\right]J, \quad (5)$$

where $(0|M_{\xi c}|n)$ is the matrix element of electron angular momentum about an axis which is the perpendicular bisector of the line joining the two nuclei and is consequently the same for H_2, D_2, and HD except for second-order effects and where $\langle r_0^2\rangle_{\mathrm{Av}}$ and $\langle r_c^2\rangle_{\mathrm{Av}}$ are the mean square distances of the electron distribution from the center of mass and the midpoint of the molecule, respectively. However, if d is the separation of the midpoint from the center of mass $\langle r_0^2\rangle_{\mathrm{Av}}-\langle r_c^2\rangle_{\mathrm{Av}}=d^2$. From this and the value of $d=\frac{1}{2}(M_2-M_1)/(M_1+M_2)$ the above equation reduces to

$$\mu=\frac{(M_1+M_2)M}{2M_1M_2}\times\left\{1-\frac{4}{m\rho^2}\left[\sum{}'\frac{|(0|M_{\xi c}|n)|^2}{E_n-E_0}\right]\right\}J, \quad (6)$$

whence μ_R should be inversely proportional to the reduced mass as found experimentally.

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On the Spinor Equations for Particles with Arbitrary Spin and Rest Mass Zero

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The spinor equations for arbitrary spin and rest mass zero are examined in some detail. Fierz has shown that for all values of the spin $f(>\frac{1}{2})$ there exists only two "really" independent plane wave solutions instead of $(2f+1)$ when the rest mass is not zero. Fierz later showed, in rather a complicated way, that these two plane waves correspond to components of spin $\pm f$ along the momentum vector of the wave. We will arrive here at the same result but in a much simpler and more direct way.

INTRODUCTION

M. FIERZ[1] has given a detailed discussion of the spinor wave equations for particles with arbitrary spin proposed by Dirac.[2] Fierz showed that when the rest mass is zero there is a certain degeneracy of the equations, and that for a given spin f there are only two really independent plane wave solutions instead of $(2f+1)$. The interpretation of this was not given in his first paper. In a subsequent paper,[3] however, he discusses the rest mass zero case in more detail, and arrives at the result that the two plane waves correspond to axial spins $\pm f$ about the momentum vector of the plane waves. His work is rather complicated. Here we will arrive at the same result in a much simpler way. For coherence it is necessary to give here some of the work appearing in Fierz's paper. The first section will be largely a restatement of Fierz's results, although the notation I will use will be slightly different. The second section will contain a detailed study of the rest mass zero case. In the present discussion no distinction will be made between the cases of integral and half-odd spin.

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[1] M. Fierz, Helv. Phys. Acta **12**, 3 (1939).

[2] P. A. M. Dirac, Proc. Roy. Soc. **A155**, 47 (1936).

[3] M. Fierz, Helv. Phys. Acta **13**, 45 (1940).