

## Theory of Molecular Hydrogen and Deuterium in Magnetic Fields\*

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The hamiltonian of a diatomic homonuclear molecule in a magnetic field is discussed. Included in the hamiltonian are the effects of the nuclear and rotational magnetic moments interacting with the external magnetic field, magnetic shielding, molecular diamagnetism, the spin-spin magnetic interaction of the two nuclei, the interaction of the nuclear magnetic moments with the field due to the rotation of the molecule, and the interaction of nuclear electric quadrupole moments. Perturbation theory expressions for the energy of  $H_2$  and  $D_2$  in the first rotational state are obtained in both strong and weak field limits. The secular equation is numerically solved for intermediate fields. Curves are given showing the theoretical dependence of the energy and the transition frequencies upon the field.

### I. INTRODUCTION

IN the original molecular beam studies of hydrogen and deuterium by Kellogg, Rabi, Ramsey, and Zacharias<sup>1-3</sup> that led to the discovery of the deuteron quadrupole moment, the measurements were made only in strong external magnetic fields. Consequently the theory of the energy levels and transition frequencies was limited to a perturbation treatment in which the interactions within the molecule were assumed small in comparison with the interaction of the nuclear moments with the external magnetic field.

However, as a confirmation of the assumed nature of the interaction and as a means of increasing the precision of the measurement of the interaction constants within the molecule, experiments have recently been made by Kolsky, Phipps, Ramsey, and Silsbee<sup>4-6</sup> in the limit of weak and intermediate values of the magnetic

field. The present paper contains the theory of the energy levels and transition frequencies relevant to weak, strong, and intermediate field experiments with  $H_2$  and  $D_2$  molecules in the first rotational state. Magnetic shielding effects which were neglected in the earlier discussion are included in the present one.

### II. THE HAMILTONIAN

The hamiltonian for a homonuclear  $^1\Sigma$  diatomic molecule in a magnetic field  $\mathbf{H}$  may be taken as

$$\begin{aligned} \mathcal{H}/h = & -[1 - \sigma_i(\mathbf{J})]a\mathbf{I} \cdot \mathbf{H}/H \\ & - [1 - \sigma_J(\mathbf{J})]b\mathbf{J} \cdot \mathbf{H}/H - c\mathbf{I} \cdot \mathbf{J} \\ & + \frac{5d}{(2J-1)(2J+3)} \{3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}\mathbf{I} \cdot \mathbf{J} - \mathbf{I}^2\mathbf{J}^2\} \\ & - \frac{5f}{3(2J-1)(2J+3)} \{3(\mathbf{J} \cdot \mathbf{H})^2/H^2 - \mathbf{J}^2\} - g \quad (1) \end{aligned}$$

where  $\mathbf{I}$  is the resultant spin angular momentum in units of  $\hbar$  and  $\mathbf{J}$  is the molecular rotational angular momentum in units of  $\hbar$ .

The first term in (1) corresponds to the interaction of the nuclear magnetic moments with the external magnetic fields and  $a$  is defined by

$$a = \mu_i H / i\hbar \quad (2)$$

TABLE II. Nonvanishing matrix elements of  $\mathcal{H}$  in  $Fm$  representation.

$F$	$m$	$F'$	$m'$	$(Fm   \mathcal{H}   F'm')/h$
2	$\pm 2$	2	$\pm 2$	$\frac{1}{2}d - c \mp a \mp b$
2	$\pm 1$	2	$\pm 1$	$\frac{1}{2}d - c \mp \frac{1}{2}a \mp \frac{1}{2}b$
1	$\pm 1$	1	$\pm 1$	$-(5/2)d + c \mp \frac{1}{2}a \mp \frac{1}{2}b$
2	0	2	0	$\frac{1}{2}d - c$
1	0	1	0	$-(5/2)d + c$
0	0	0	0	$5d + 2c$
1	$\pm 1$	2	$\pm 1$	$\frac{1}{2}(a-b)$
2	$\pm 1$	1	$\pm 1$	$\frac{1}{2}(a-b)$
2	0	1	0	$(a-b)/3^{\frac{1}{2}}$
1	0	2	0	$(a-b)/3^{\frac{1}{2}}$
0	0	1	0	$(a-b)2^{\frac{1}{2}}/3^{\frac{1}{2}}$
1	0	0	0	$(a-b)2^{\frac{1}{2}}/3^{\frac{1}{2}}$

TABLE I. Nonvanishing matrix elements of  $\mathcal{H}$  in  $m_I m_J$  representation.

$m_I$	$m_J$	$m_I'$	$m_J'$	$(m_I m_J   \mathcal{H}   m_I' m_J')/h$
$\pm 1$	$\pm 1$	$\pm 1$	$\pm 1$	$\mp(1 - \sigma_{i1})a \mp(1 - \sigma_{J1})b - c + \frac{1}{2}d - \frac{1}{3}f - g$
$\pm 1$	0	$\pm 1$	0	$\mp(1 - \sigma_{i0})a - d + \frac{2}{3}f - g$
0	$\pm 1$	0	$\pm 1$	$\mp(1 - \sigma_{J1})b - d - \frac{1}{3}f - g$
$\pm 1$	$\mp 1$	$\pm 1$	$\mp 1$	$\mp(1 - \sigma_{i1})a \pm(1 - \sigma_{J1})b + c + \frac{1}{2}d - \frac{1}{3}f - g$
0	0	0	0	$2d + \frac{2}{3}f - g$
$\pm 1$	0	0	$\pm 1$	$-c + \frac{3}{2}d$
0	$\pm 1$	$\pm 1$	0	$-c + \frac{3}{2}d$
0	0	$\pm 1$	$\mp 1$	$-c - \frac{3}{2}d$
$\pm 1$	$\mp 1$	0	0	$-c - \frac{3}{2}d$
$\mp 1$	$\pm 1$	$\pm 1$	$\mp 1$	$3d$

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<sup>1</sup> Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939). In the present paper, these authors are frequently referred to as KRRZ.

<sup>2</sup> Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940). In the present paper, these authors are frequently referred to as KRRZ.

<sup>3</sup> N. F. Ramsey, Phys. Rev. **58**, 226 (1940). The signs of  $k$  in the first three tables of this reference are reversed.

<sup>4</sup> Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **79**, 883 (1950).

<sup>5</sup> Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **80**, 483 (1950).

<sup>6</sup> Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **82**, 1061 (1951).

TABLE III. Perturbation theory in strong fields.  $C_2$ ,  $C_2'$ , and  $C_3$  are second- and third-order perturbations and are defined by

$$C_2 = [(c + \frac{3}{2}d)^2 + (9/2)d^2]/(a-b)$$

$$C_2' = (c - \frac{3}{2}d)^2/(a-b)$$

$$C_3 = (c + \frac{3}{2}d)^2(c - (9/2)d)/(a-b)^2.$$

The state designation is the same for H<sub>2</sub> and D<sub>2</sub>.

State	$m_I$	$m_J$	Energy/h
A/L	$\mp 1$	$\mp 1$	$\pm(1-\sigma_{i1})a \pm (1-\sigma_{j1})b - c + \frac{1}{2}d - \frac{1}{3}f - g$
B/K	$\mp 1$	0	$\pm(1-\sigma_{i0})a - d + \frac{2}{3}f - g \pm C_2'$
C/G	$\mp 1$	$\pm 1$	$\pm(1-\sigma_{i1})a \mp (1-\sigma_{j1})b + c + \frac{1}{2}d - \frac{1}{3}f - g \pm C_2 - C_3$
D/F	0	$\mp 1$	$\pm(1-\sigma_{j1})b - d - \frac{1}{3}f - g \mp C_2'$
E	0	0	$2d + \frac{2}{3}f - g + 2C_3$

where  $\mu_i$  is the magnetic moment of one of the nuclei and  $i$  the corresponding nuclear spin. The factor  $[1 - \sigma_i(\mathbf{J})]$  arises from the magnetic shielding of the nucleus by the molecule. As shown by Ramsey<sup>7,8</sup>

$$\sigma_i(\mathbf{J}) = \frac{2}{3}\sigma_\sigma + \frac{1}{3}\sigma_\pi + (\sigma_\sigma - \sigma_\pi)[2/3(2J-1)(2J+3)] \times \{3(\mathbf{J} \cdot \mathbf{H})^2/H^2 - \mathbf{J}^2\} \quad (3)$$

where  $J$  is the quantum number of the total rotational

TABLE IV. Perturbation theory in weak fields.  $K_2$  and  $K_2'$  are second-order perturbations defined by

$$K_2 = (a-b)^2/(2c-3d)$$

$$K_2' = 2(a-b)^2/3(c+(15/2)d).$$

The third-order perturbations vanish.

H <sub>2</sub> state	D <sub>2</sub> state	F	m	Energy/h
A/L	A/L	2	$\mp 2$	$-c + \frac{1}{3}d \pm (a+b)$
B/F	D/K	1	$\mp 1$	$c - (5/2)d \pm \frac{1}{2}(a+b) + \frac{1}{3}K_2$
C	C	0	0	$2c + 5d + K_2'$
D/K	B/F	2	$\mp 1$	$-c + \frac{1}{3}d \pm \frac{1}{2}(a+b) - \frac{1}{3}K_2$
E	G	1	0	$c - (5/2)d + \frac{1}{3}K_2 - K_2'$
G	E	2	0	$-c + \frac{1}{2}d - \frac{1}{3}K_2$

angular momentum and  $\sigma_\sigma$  is the magnetic shielding constant for a magnetic field applied perpendicular to the internuclear axis while  $\sigma_\pi$  is the shielding constant for fields parallel to the internuclear axis. Theoretical expressions for  $\sigma_\sigma$  and  $\sigma_\pi$  have been given by Ramsey.<sup>8</sup>

The second term in (1) provides for the interaction of the molecular rotational magnetic moment with the external magnetic field and  $b$  is defined by

$$b = \mu_J H / Jh \quad (4)$$

TABLE V. Assumed values for constants in secular equations. The constants are given in kilocycles per second.

Constant	H <sub>2</sub>	D <sub>2</sub>
$a$	4.258H	0.6536H
$b$	0.6717H	0.3368H
$c$	113.8	8.783
$d$	57.68	25.24

<sup>7</sup> N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

<sup>8</sup> N. F. Ramsey, Phys. Rev. **83**, 540, 659 (1951).

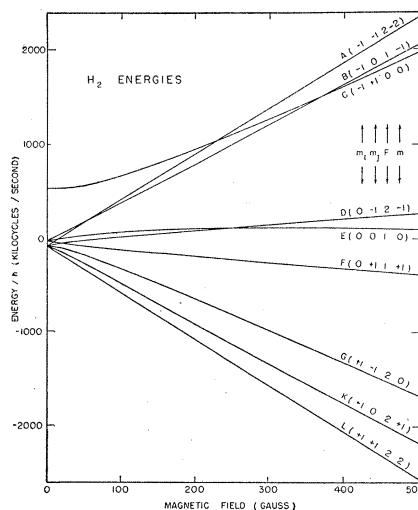


FIG. 1. Energies of H<sub>2</sub> states as functions of magnetic field.

where  $\mu_J$  is the magnetic moment due to the rotation of the molecule in rotational state  $J$ . The third term corresponds to the spin rotational magnetic interaction and  $c$  is related to the quantity  $H'$  of KRRZL<sup>2</sup> by

$$c = \mu_i H' / ih. \quad (5)$$

The fourth term in (1) includes the combination of the spin-spin magnetic interaction of the two nuclei with each other together with the interaction of any nuclear electrical quadrupole moment with the variation of the molecular electric field in the vicinity of the nucleus. That these two separate phenomena combine in this way in homonuclear molecules is shown by KRRZL<sup>2</sup> who also show that for computation of matrix elements diagonal in  $J$  and in  $I$ , the quantum number of the total spin angular momentum,  $d$  can be expressed

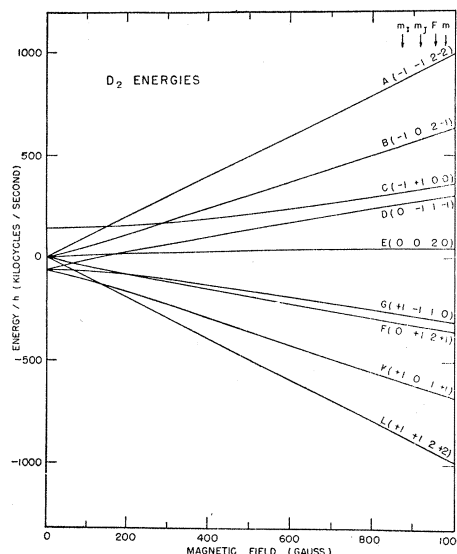


FIG. 2. Energies of D<sub>2</sub> states as functions of magnetic field.

TABLE VI. Numerical solution of secular equation for H<sub>2</sub>. The energy divided by  $\hbar$  is given in kilocycles per second for the designated state in the indicated magnetic field. Magnetic field (gauss).

State ( $m_l m_s J F m$ )	0	5	10	20	60	100	140	180	220	260	300	400	500
A(-1-1 2-2)	-84.96	-60.31	-35.66	13.6	210.8	408.0	605.2	802.4	999.6	1197	1394	1887	2380
B(-1 0 1-1)	30.38	-16.62	-0.37	36.69	201.2	370.2	539.9	709.9	880.1	1050	1221	1647	2072
C(-1+1 0 0)	516.0	516.4	517.6	522.2	569.1	653.2	759.3	879.0	1006	1138	1273	1618	1969
D(0-1 2-1)	-84.96	-74.09	-65.69	-53.45	-20.8	3.71	34.9	62.1	89.2	116.2	143.0	210	278
E(0 0 1 0)	-30.54	-28.96	-24.17	-11.63	40.51	65.06	82.84	93.09	99.34	103.3	106.3	109.8	112.1
F(0+1 1+1)	-30.40	-41.27	-49.69	-61.9	-94.6	-122.8	-150.3	-177.5	-204.5	-231.5	-258.5	-325.5	-393
G(+1-1 2 0)	-84.90	-86.75	-90.84	-106.1	-138.4	-172.8	-211.4	-251.3	-294.8	-340.8	-397.8	-467.2	-549.4
K(+1 0 2+1)	-84.96	-98.74	-115.0	-152.0	-216.7	-316.7	-485.7	-775	-1170	-1716	-2436	-3417	-4787
L(+1+1 2+2)	-84.96	-109.6	-134.3	-183.6	-260.8	-380.8	-578.0	-972	-1470	-2167	-3134	-4507	-6350

as

$$dh = \left\langle \frac{\mu_i^2}{i^2 r^3} \right\rangle \frac{I(I+1) + 4i(i+1)}{5(2I-1)(2I+3)} - \frac{eQ\partial^2 V^e / \partial z_0^2}{10i(2i-1)} \left[ 1 - \frac{I(I+1) + 4i(i+1)}{(2I-1)(2I+3)} \right] \quad (6)$$

where  $r$  is the distance between the two nuclei,  $Q$  is the deuteron quadrupole moment,  $V^e$  is the potential from the charges external to a small sphere surrounding the nucleus and  $z_0$  is along the internuclear axis of the molecule. The quantity  $\partial^2 V^e / \partial z_0^2$  is related<sup>9</sup> to the quantity  $q$  of KRRZ<sup>2</sup> by

$$\partial^2 V^e / \partial z_0^2 = -eq(2J+3)/J. \quad (7)$$

The last two terms in (1) are for the diamagnetic interaction of the molecule with the external magnetic field. If  $\xi_\sigma$  is the magnetic susceptibility of the molecule for a field perpendicular to internuclear axis and  $\xi_\pi$  is the susceptibility parallel to that axis

$$f = (\xi_\sigma - \xi_\pi)H^2/5h \quad (8)$$

and

$$g = (\frac{1}{3}\xi_\sigma + \frac{1}{6}\xi_\pi)H^2/h. \quad (9)$$

The form of diamagnetic interaction given in (1), (8), and (9) arises from averaging the  $\sin^2\theta$  of Ramsey's paper<sup>10</sup> on diamagnetic interaction in the same manner as in his later paper<sup>9</sup> on magnetic shielding. Theoretical

expressions for  $\xi_\sigma$  and  $\xi_\pi$  have been given.<sup>10</sup> The quantity  $f$  is related to the quantities  $\xi_{\pm 1}$ ,  $\xi_0$ , and  $k$  previously used by Ramsey<sup>3</sup> by<sup>10</sup>

$$f = H^2(\xi_{\pm 1} - \xi_0)/2h = H^2 k \mu_J / Jh. \quad (10)$$

In principle, the magnetic shielding which arises in the spin-spin magnetic interaction should also be included.<sup>†</sup> However, this correction has been negligibly small in all experiments so far and consequently is omitted here. However, when the external magnetic field is so weak that the spin-spin magnetic interaction is comparable to the interaction of either spin with the magnetic field, the diamagnetic correction for the external field is comparably small. Consequently, for consistency in approximations as well as for simplification, all diamagnetic corrections will be omitted in magnetic fields sufficiently low that a perturbation treatment in the high field approximation is not adequate.

The cases of greatest experimental interest<sup>1,3,6</sup> are molecular hydrogen and deuterium in the first rotational state for both of which  $I=J=1$ . In these cases the subscripts H and D can be used to designate hydrogen and deuterium and

$$d_H h = \langle 4\mu_H^2 / 5r^3 \rangle = (2/5)2\mu_H H_H'' \quad (11)$$

$$d_D h = \left\langle \frac{2\mu_D^2}{5r^3} \right\rangle + \frac{1}{10} \frac{\partial^2 V^e}{\partial z_0^2} = (2/5)\mu_D(H''_D + H'''_D) = 2\mu_D S_D \quad (12)$$

TABLE VII. Numerical solution of secular equation for D<sub>2</sub>. The energy divided by  $\hbar$  is given in kilocycles per second for the designated state in the indicated magnetic field. Magnetic field (gauss).

State ( $m_l m_s J F m$ )	0	10	20	50	100	200	300	400	600	800	1000
A(-1-1 2-2)	3.84	13.74	23.65	53.36	102.9	201.9	301.0	400.0	598.1	796.2	994.2
B(-1 0 2-1)	3.84	8.84	13.92	29.66	57.39	116.8	179.0	242.6	371.3	500.9	631.1
C(-1+1 0 0)	143.8	143.8	143.9	144.6	147.2	157.0	172.6	192.7	241.9	297.4	356.0
D(0-1 1-1)	-54.32	-49.41	-44.59	-30.62	-8.83	30.80	67.60	103.2	172.6	240.9	308.9
E(0 0 2 0)	3.84	3.91	4.06	5.21	8.76	18.11	26.66	32.96	40.51	44.31	46.30
F(0+1 2+1)	3.84	-1.08	-5.90	-19.87	-41.65	-81.28	-118.1	-153.6	-223.0	-291.4	-359.4
G(+1-1 1 0)	-54.33	-54.41	-54.68	-56.54	-62.61	-81.80	-105.9	-132.4	-189.1	-248.4	-309.0
K(+1 0 1+1)	-54.32	-59.32	-64.40	-80.14	-107.9	-167.3	-229.5	-293.0	-421.7	-551.4	-681.6
L(+1+1 2+2)	3.84	-6.06	-15.97	-45.68	-95.20	-194.2	-293.3	-392.3	-590.4	-788.5	-986.6

<sup>9</sup> B. T. Feld, Phys. Rev. **72**, 1116 (1947).<sup>10</sup> N. F. Ramsey, Phys. Rev. **78**, 221 (1950).<sup>†</sup> Note added in proof.—The effect of magnetic shielding on the nuclear spin-spin interaction is discussed in a letter by Ramsey and Purcell now in course of publication in *The Physical Review*.

TABLE VIII. Transition frequencies for allowed transitions in the strong field limit. The transition designation is the same for H<sub>2</sub> and D<sub>2</sub>.

Transition	$m_I$	$m_J$	$m_I'$	$m_J'$	Transition frequency
AD/FL	-1/0	±1	0/+1	±1	$(1-\sigma_{i1})a \pm (-c + \frac{3}{2}d) + C_2'$
DG/CF	0/-1	±1	+1/0	±1	$(1-\sigma_{i1})a \mp (c + \frac{3}{2}d) + C_2 - C_2' \pm C_3$
BE/EK	-1/0	0	0/+1	0	$(1-\sigma_{i0})a \mp 3d + C_2' \mp 2C_3$
AB/KL	±1	-1/0	±1	0/+1	$(1-\sigma_{j1})b \pm (-c + \frac{3}{2}d) \mp f - C_2'$
BC/GK	±1	0/-1	±1	+1/0	$(1-\sigma_{j1})b \mp (c + \frac{3}{2}d) \pm f - (C_2 - C_2') \pm C_3$
DE/EF	0	-1/0	0	0/+1	$(1-\sigma_{j1})b \mp 3d \mp f - C_2' \mp 2C_3$

where  $H''$ ,  $H'''$ , and  $S_D$  are identical with the corresponding quantities used by KRRZ.<sup>1-3</sup>

### III. THE ENERGY MATRICES

From (1) the energy matrices can be calculated. This will be done only for  $I=J=1$ , since this is the case of greatest interest.

The energy matrix will first be written in the  $m_I m_J$  representation which is most appropriate to strong external fields. To simplify the writing one can let  $\sigma_{i0}$  be the magnetic shielding of the nucleus when  $m_J=0$  and  $\sigma_{i1}$  when  $m_J=\pm 1$ . Then, from (3)

$$\sigma_{i0} = \frac{2}{5}\sigma_\sigma + \frac{3}{5}\sigma_\pi, \quad \sigma_{i1} = \frac{4}{5}\sigma_\sigma + \frac{1}{5}\sigma_\pi. \quad (13)$$

The nonvanishing matrix elements of  $(m_I m_J | \mathcal{H} | m_I' m_J')$  with the aid of the tables in KRRZ<sup>2</sup> can be shown to have the values given in Table I.

Alternatively one can use the  $F, m$  representation which is most appropriate to very weak magnetic fields where  $F$  is the total quantum number of the resultant angular momentum  $\mathbf{F}$  which equals  $\mathbf{I} + \mathbf{J}$  and  $m$  is the magnetic quantum number of  $\mathbf{F}$ . In the weak field limit to which this representation is most appropriate the diamagnetic corrections are very small and indeed are comparable to the diamagnetic correction to the spin-spin magnetic interaction which has already been omitted because of its small size. Therefore, all diamagnetic corrections are omitted in the matrix elements. In the evaluation of some of the matrix elements from (1), the tables of Feld and Lamb<sup>11</sup> are useful. The nonzero matrix elements  $(Fm | \mathcal{H} | F'm')$  have the values given in Table II.

TABLE IX. Transition frequencies for allowed transitions in weak field limit. Primes on the designation for the transition indicates a transition with  $\Delta m=0$ .

Transition H <sub>2</sub>	D <sub>2</sub>	$F$	$m$	$F'$	$m'$	Transition frequency
CB/CF	CD/CK	0	0	1	±1	$c + (15/2)d \mp \frac{1}{2}(a+b)$
CE'	CG'	0	0	1	0	$c + (15/2)d$
BA/FL	DA/KL	1	±1	2	±2	$2c - 3d \mp \frac{1}{2}(a+b)$
BD'/FK'	DB'/KF'	1	±1	2	±1	$2c - 3d$
BG/FG	DE/KE	1	±1	2	0	$2c - 3d \pm \frac{1}{2}(a+b)$
ED/EK	GB/FG	1	0	2	±1	$2c - 3d \mp \frac{1}{2}(a+b)$
EG'	GE'	1	0	2	0	$2c - 3d$
BE/FE	DG/KG	1	±1	1	0	$\pm \frac{1}{2}(a+b)$
AD/LK	AB/LF	2	±2	2	±1	$\pm \frac{3}{2}(a+b)$
DG/KG	BE/FE	2	±1	2	0	$\pm \frac{1}{2}(a+b)$

<sup>11</sup> B. T. Feld and W. Lamb, Phys. Rev. 67, 15 (1945).

### IV. PERTURBATION THEORIES

Perturbation theory calculations appropriate to the high field limit have been carried out by KRRZ with the omission of the magnetic shielding and diamagnetic interaction terms. When these are included, one obtains for the energies of the nine states the expressions given in Table III, where perturbations up to third order are included. For the simplification of the correlation of the states in the strong field limit to those in the weak field limit, each state is designated with a capital letter which is used for the same state in the low field limit. The notation  $A/L$ , used when plus or minus ( $\pm 1$ ) signs are employed, indicates that the upper choice of sign goes with state  $A$  while the lower goes with state  $L$ .

In the weak field limit, the energy levels can be calculated from the energy matrix of Table II. The results to third-order perturbation theory are given in Table IV. Corresponding to the fact that the  $Fm$  and  $m_I m_J$  quantum numbers are differently correlated to each other in the H<sub>2</sub> and D<sub>2</sub> cases because of the numerically different values of the parameters, the state designations are different in the H<sub>2</sub> and D<sub>2</sub> cases.

### V. SOLUTION OF SECULAR EQUATION

For intermediate values of the magnetic field, the secular equation must be solved. For reasons mentioned previously, the magnetic shielding and diamagnetic interaction terms will be omitted in the calculation of the secular equation. From either Table I or II the solutions of the secular equations become

$$W_{A/L}/h = \pm a \pm b - c + \frac{1}{2}d \quad (14)$$

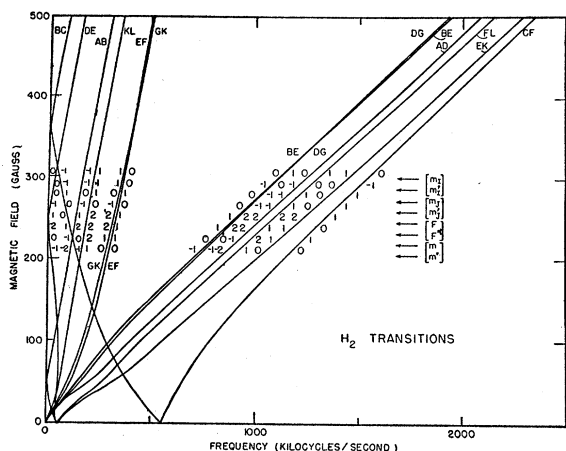


FIG. 3. Frequencies of  $H_2$  transitions that are allowed in the strong field limit. Curves that are dashed along the lower halves indicate forbidden transitions in the weak field limit whereas the full curves indicate allowed transitions in the weak field limit.

$$W_{B/K}/h = \frac{1}{2}(\pm a \pm b - 2d) \pm \frac{1}{2}[(a-b)^2 + 4(-c + \frac{3}{2}d)^2]^{\frac{1}{2}} \quad (15)$$

$$W_{D/F}/h = \frac{1}{2}(\pm a \pm b - 2d) \mp \frac{1}{2}[(a-b)^2 + 4(-c + \frac{3}{2}d)^2]^{\frac{1}{2}} \quad (16)$$

and  $W_C$ ,  $W_G$ , and  $W_E$  are the three roots of the cubic equation

$$(W/h)^3 - (2c + 3d)(W/h)^2 - [(a-b)^2 + c^2 + 45d^2/4 + cd](W/h) + 2(a-b)^2d - \frac{1}{2}(d-2c)(-5/2d+c)(5d+2c) = 0. \quad (17)$$

$W_C$  is the root which in the high field limit approaches  $(a-b)h$  while  $W_G$  approaches  $(-a+b)h$ .

Although, the cubic equation can, in principle, be solved analytically, in practice it is more convenient to leave it in the above form and to solve the cubic numerically. This has been done for  $H_2$  and  $D_2$ . The

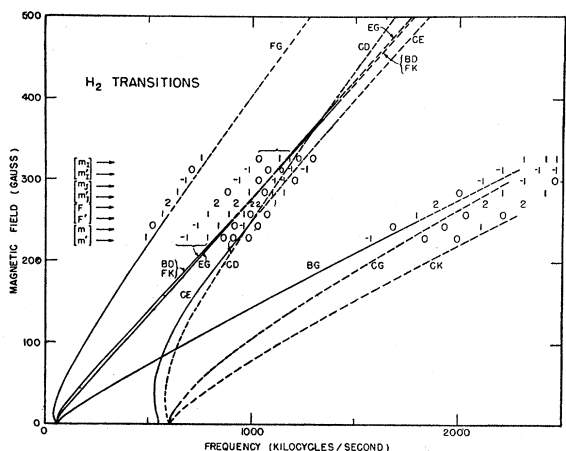


FIG. 4. Frequencies of  $H_2$  transitions that are forbidden in the strong field limit. Curves that are dashed along the lower halves indicate forbidden transitions in the weak field limit whereas the full curves indicate allowed transitions in the weak field limit.

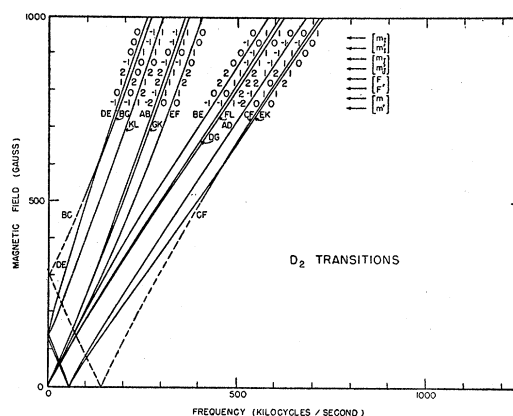


FIG. 5. Frequencies of  $D_2$  transitions that are allowed in the strong field limit. Curves that are dashed along the lower halves indicate forbidden transitions in the weak field limit whereas the full curves indicate allowed transitions in the weak field limit.

constants assumed for  $a$ ,  $b$ ,  $c$ , and  $d$  are given in Table V. These are the best values obtainable from the experiments of Kolsky, Phipps, Ramsey, and Silsbee.<sup>4-6</sup>

The results of these calculations are plotted in Figs. 1 and 2. Since in interpreting the experiments, more accuracy is often needed than that available from the curves, the numerical results obtained are also tabulated in Tables VI and VII.

## VI. RESONANCE FREQUENCIES

In the high field limit, expressions for the transition frequencies can be obtained by differencing the energies of Table III. The results are given in Table VIII. Only transitions allowed in strong fields ( $\Delta m_I = \pm 1$ ,  $\Delta m_J = 0$ , or  $\Delta m_I = 0$ ,  $\Delta m_J = \pm 1$ ) are listed. The transition from state  $A$  to state  $D$  is designated as  $AD$ .

In the low field limit, expressions for the transition frequencies can be obtained by differencing the energies of Table IV. The results for the allowed transitions

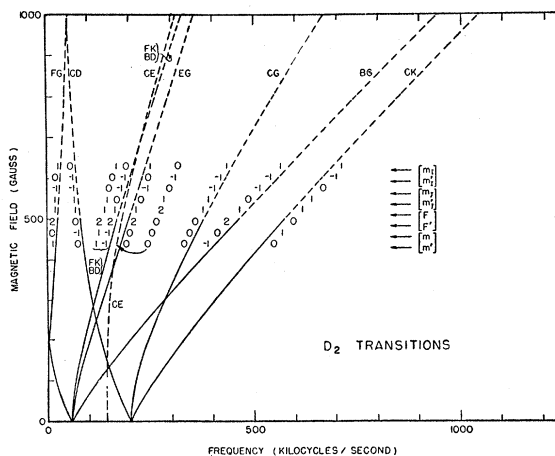


FIG. 6. Frequencies of  $D_2$  transitions that are forbidden in the strong field limit. Curves that are dashed along the lower halves indicate forbidden transitions in the weak field limit whereas the full curves indicate allowed transitions in the weak field limit.

( $\Delta F=0, \pm 1, \Delta m=0, \pm 1$ ) are given in Table IX. A prime added to the transition designation as  $CE'$  indicates a transition for which  $\Delta m=0$ . The oscillating field inducing such transitions must be parallel to the external field.

In intermediate fields the transition frequencies can be obtained by differencing the values of Tables VI and VII. The results of such a procedure are plotted in Figs. 3, 4, 5, and 6. Lines which are dotted along

either their upper or lower halves indicate transitions forbidden in either the strong or weak field limit. The quantum numbers associated with each transition can be obtained by correlating the quantum numbers with the transition designation with the aid of Tables III and IV.

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### Superposition of Configurations in the Ground State of He I\*

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To obtain some understanding of the role played by various configurations in configuration interaction, the Hylleraas six-term expression for the ground-state wave function of He I has been expanded in series of orthogonal functions. To determine the degree of dependence of the coefficients of the expansion on the specific function used for the ground state, the Hylleraas three-term expression was also expanded. Two sets of orthogonal functions were used. One set consisted of orthogonalized symmetrized product type wave functions where the functions for the individual electrons were found from a Hartree self-consistent field without exchange. The second set consisted of orthogonalized variationally determined analytic wave functions. The results emphasize the large number of configurations which would have to be considered if the Hylleraas wave function were to be represented with high accuracy. After  $1s^2$  the largest contributors among the configurations considered were  $2p^2$  and  $2s^2$ .

IT has long been recognized<sup>1</sup> that the method of the self-consistent field involves three principal approximations: (a) the neglect of relativity effects, (b) the neglect of exchange effects, and (c) the neglect of the nonseparability of the wave functions. Relativity effects should be small for the lighter atoms. Exchange effects have been extensively investigated, principally by Hartree using Fock's equations. The inclusion of exchange improves the wave functions considerably and usually improves the energies somewhat. However, something is left to be desired. For example in O, O<sup>+</sup>, and O<sup>++</sup> the average difference between the observed and the calculated energies for the three lowest states are found to be 0.188, 0.088, and 0.114 respectively in units of the ionization energy of hydrogen when self-consistent field wave functions without exchange are used with Slater's integrals.<sup>2</sup> If wave functions with exchange are employed, the values obtained are 0.198, 0.086, and 0.080 with no improvement in the ratio of the multiplet separations.<sup>3</sup> To obtain further improve-

ment one may attempt to remove the approximation involved in the neglect of the nonseparability of the wave functions. This has usually been done by considering the effects of superposition of configurations. A number of calculations of this sort have been made.<sup>4</sup> In general some improvement in multiplet separations has been obtained when superposition was included but in the two most thorough treatments of such effects by self-consistent field methods, the work of Hartree<sup>3</sup> on O, O<sup>+</sup>, and O<sup>++</sup> and the work of Jucys<sup>5</sup> on C, the results were disappointing. Hartree, by the superposition of  $1s^2 2p^{a+2}$  on  $1s^2 2s^2 2p^a$ , obtained for the average difference between the observed and calculated energies for the same lowest states of O, O<sup>+</sup>, and O<sup>++</sup> mentioned above 0.180, 0.108, and 0.090 respectively using wave functions with exchange to determine the effects of the configuration interaction. The ratio of the multiplet separations was considerably improved for O and somewhat improved for O<sup>+</sup> and O<sup>++</sup>. Jucys, by superposing  $1s^2 2s^2 2p^2$ ,  $1s^2 2p^4$ ,  $1s^2 2s^2 2p^3 p$ , and  $1s^2 2s^2 2p^2 3s$  for CI reduced the average difference between the observed

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