

## Spin-Orbit and Spin-Spin Interactions in Diatomic Molecules. I. Fine Structure of $H_2^\dagger$

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(Received July 27, 1961)

The fine structure separations of para and ortho  $H_2$  are calculated by assuming that besides the spin-orbit, spin-other orbit, and spin-spin interactions, no other perturbation contributes significantly to the splitting. The interactions are expressed as contractions of irreducible tensors, and the resulting energy separations are obtained by applying the theory of angular momentum to a representation in strict case  $b$  coupling. It is shown that for  $\Pi$  states the  $Y_2^2$  component of the quadrupole-type spin-spin interaction gives nonvanishing matrix elements which arise from the coupling of the electronic states  $\Psi_e(\Lambda=+1)$  and  $\Psi_e(\Lambda=-1)$ . The additional term in the spin-spin interaction yields anomalous

alternations of the fine structure separation from one rotational level to the next, and produces a splitting of the  $J$  levels into a "regular" and an "irregular" component. This splitting is quite different from the usual  $\Lambda$ -type doubling which arises from the interaction of the orbital angular momentum with the rotation of the nuclei. In low rotational states of  $H_2$  the contribution of the  $Y_2^2$  component of the spin-spin interaction is considerably larger than the  $\Lambda$ -type doubling. The theoretical predictions for the fine structure of the  $c^3\Pi_u$  state compare favorably with experimental values.

### I. INTRODUCTION

THE work of Kramers<sup>1</sup> on the fine structure of diatomic molecules in  $\Sigma$  states has been the basis for many subsequent calculations in this field.<sup>2-6</sup> The modified spin-spin Hamiltonian of Kramers, however, cannot be applied to all states of a diatomic molecule since it depends on special symmetries of the system. In particular for  $^3\Pi$  states in case  $b$  coupling, there is an additional term not present in Kramers formula which, especially in  $H_2$ , makes a considerable contribution to the fine structure splitting.

The first measurements of the fine structure splittings of a  $\Pi$  state in  $H_2$  have been made by Foster and Richardson.<sup>7</sup> They observed a splitting of each  $J$  level into a "regular" and "irregular" component, but they were unable to completely resolve the fine structure. Only recently, Lichten<sup>8</sup> resolved the fine structure of the lowest  $N=2$  rotational level of para  $H_2$  by molecular-beam magnetic-resonance techniques. It is apparent from his results that neither the spin-orbit nor the spin-spin interaction alone can explain the observed splittings and level order. Moreover, it is necessary to include the spin-other orbit interaction in order to get the right sign of the spin-axis interaction constant [see Eq. (17) and Eq. (48)].

In the theory presented here it is assumed that only the spin-orbit (including spin-other orbit) and the spin-spin perturbations contribute significantly to the fine structure splitting. The mixing in of other states is negligible and the spin-rotational interaction is quite

small. The perturbation Hamiltonian is obtained from the Pauli approximation of the Breit equation omitting only the contact term in the spin-spin Hamiltonian  $H_s$  which does not contribute to the level splitting.<sup>9</sup> The representation is set up in the Born-Oppenheimer approximation which is justified because of the large proton-electron mass ratio. Also, in this approximation vibrational and rotational states have a definite meaning.

### II. ELECTRONIC WAVE FUNCTION

Since we are dealing here with a homonuclear diatomic molecule, the wave function must exhibit all the required symmetry properties. If we denote by  $\psi$  the normalized product of an invariant function under exchange of electrons, orbits, and spins, and two one-particle eigenfunctions referred to center  $a$  or  $b$ , having orbital quantum numbers  $l_1, m_1$  and  $l_2, m_2$ , and spins  $\alpha$  and  $\beta$ , then the following wave functions satisfy all symmetry requirements:

$$\begin{aligned}\Psi_1 &= (1/\sqrt{8})\{(I+\eta A)(I+\omega O)(I+\sigma S)\}\psi, \\ \Psi_2 &= (1/\sqrt{8})\{(I+\eta A)(I-E)(I+\sigma S)\}\psi, \\ \Psi_3 &= (1/\sqrt{8})\{(I+\omega O)(I-E)(I+\sigma S)\}\psi, \\ \Psi_4 &= (1/\sqrt{8})\{(I+\eta A)(I+\omega O)(I-E)\}\psi.\end{aligned}\quad (1)$$

The symbols  $O$ ,  $A$ ,  $S$ , and  $E$  denote operators which effect the exchange of orbits, atoms, spins, and electrons, respectively, and the operator  $I$  leaves the wave function  $\psi$  unaffected. After multiplying out the expressions of (1) one gets products such as  $\{OAS\}\psi$ , which is a wave function obtained from the original one ( $\psi$ ) by exchanging first the spins, then the atoms, and finally the orbits. The following operator relations can be easily verified by successive operations starting

<sup>†</sup> Work supported by a grant from the National Science Foundation.

<sup>1</sup> H. A. Kramers, *Z. Physik* **53**, 422 (1929).

<sup>2</sup> A. Budo, *Z. Physik* **96**, 219 (1935); **98**, 437 (1936).

<sup>3</sup> M. H. Hebb, *Phys. Rev.* **49**, 610 (1936).

<sup>4</sup> C. Gilbert, *Phys. Rev.* **49**, 619 (1936).

<sup>5</sup> R. Schlapp, *Phys. Rev.* **51**, 342 (1937).

<sup>6</sup> I. Kovacs, *Acta Physica Hungaricae* **10**, 255 (1959); **12**, 67 (1960).

<sup>7</sup> E. W. Foster and O. Richardson, *Proc. Roy. Soc. (London)* **A189**, 175 (1947); **A217**, 433 (1953).

<sup>8</sup> W. Lichten, *Phys. Rev.* **120**, 848 (1960).

<sup>9</sup> H. A. Bethe and E. E. Salpeter: *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press, Inc., New York, 1957), p. 181.

on the right of each product.

$$\begin{aligned} OASE &= I; & OO &= AA = SS = EE = I; \\ OA &= SE; OS &= AE; OE &= AS; OA = AO; SE = ES; \text{ etc.}; \\ ASE &= O; OSE &= A; OAE &= S; OAS = E. \end{aligned} \quad (2)$$

In (1) the symbols  $\eta$ ,  $\omega$ , and  $\sigma$  can assume the values  $+1$  or  $-1$ . If  $(-1)^{l_1+l_2} \times \eta$  is  $+1$  then we have a  $g$  state, and if  $(-1)^{l_1+l_2} \times \eta$  is  $-1$  we deal with a  $u$  state. For  $\sigma = -1$  the wave function describes a singlet state, and for  $\sigma = +1$  the system is in the triplet state. Finally, for  $\omega = +1$  the wave function is even and for  $\omega = -1$  it is odd. In  $\Psi_1$  of (1) the antisymmetry of the wave function which arises from the exchange of the two electrons is not explicitly exhibited and the parameters  $\eta$ ,  $\omega$ , and  $\sigma$  are not independent of each other but have to satisfy the relation

$$\eta\omega\sigma = -1, \quad (3)$$

which insures that

$$E(\Psi_1) = -\Psi_1, \quad (4)$$

and from (1) we also have

$$\begin{aligned} A(\Psi_i) &= \eta\Psi_i; & O(\Psi_i) &= \omega\Psi_i; \\ S(\Psi_i) &= \sigma\Psi_i, & i &= 1, 2, 3, 4. \end{aligned} \quad (5)$$

In addition, the quantization of the orbital angular momentum along the internuclear axis yields

$$\Lambda = m_1 + m_2. \quad (6)$$

Furthermore, the eigenfunctions of  $\Sigma$  states either change sign or remain unchanged under reflection through a plane which contains the internuclear axis. For  $\Lambda \neq 0$ , however, the  $\Psi_i(+\Lambda)$  state is degenerate with the  $\Psi_i(-\Lambda)$  state, and only the following linear combinations satisfy this symmetry requirement.

$$\begin{aligned} \Psi_e^+ &= (1/\sqrt{2})[\Psi(+\Lambda) + \Psi(-\Lambda)], \\ \Psi_e^- &= (1/\sqrt{2})[\Psi(+\Lambda) - \Psi(-\Lambda)]. \end{aligned} \quad (7)$$

In the case of  $H_2$  the total spin of the two electrons is not directly coupled to the electronic state (see Fig. 1) and we shall only use either  $\Psi_1$ ,  $\Psi_2$ , or  $\Psi_3$ , which can be written in terms of products of spin and electronic wave functions.

### III. COUPLING OF THE INTERNAL STATES AND SYMMETRY PROPERTIES OF THE RESULTING WAVE FUNCTION

A comparison of the calculated and observed  $g$  values for  $H_2$  has clearly shown that the coupling of the electron spins to the internuclear axis is very weak and that Hund's case- $b$  coupling rule is very well satisfied<sup>8</sup> (see Fig. 1).

The electron orbital angular momentum is quantized along the internuclear axis with components  $\Lambda = m_1 + m_2$ . The rotational angular momentum  $O$  couples with  $\Lambda$  to form the total orbital angular momentum  $N$  ( $N = \Lambda, \Lambda + 1, \Lambda + 2, \dots$ ). Finally  $N$  and the electron

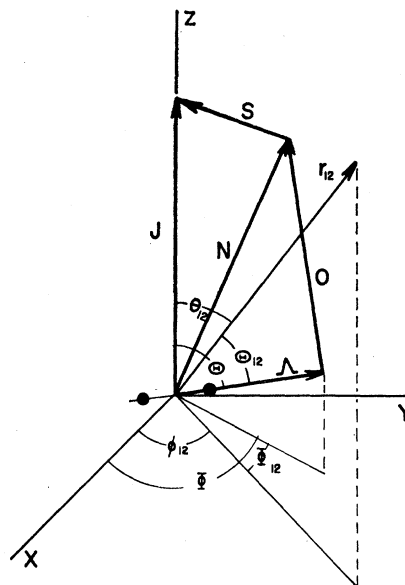


Fig. 1. Vector coupling diagram of the internal states in  $H_2$ . The angles  $\Theta$  and  $\Phi$  describe the position of the molecular coordinate system with respect to axes fixed in space ( $X, Y, Z$ ).

spin  $S$  couple to form  $J$ , the total angular momentum. In the case of ortho  $H_2$ , the interaction of  $J$  with the total nuclear spin  $I = 1$  yields the hyperfine levels  $F = J, J \pm 1$ .

In the following derivation it is assumed that the internal energy can be separated from the rotational motion of the system. In the coordinate system which rotates with the nuclei (molecular coordinate system) the components of the spin angular momentum satisfy the usual commutation relations since the total electron spin depends on the internal coordinates only. The transformation of the total angular momentum  $J$  from the fixed axes to the molecular coordinate system, however, introduces an anomalous sign in the commutation relation of the new components of  $J$ .<sup>10</sup>

If we define the reversed spin angular momentum as

$$S' = -S, \quad (8)$$

then in the molecular system  $S'$  satisfies the same commutation relations as  $J$  and we can use the usual methods to obtain a wave function in the coupled representation which is diagonal in  $J_z = M$  and  $J^2 = (N + S')^2$ .

In view of these remarks we are justified by writing the wave function for a particular fine structure level as

$$\Psi_{JM} = \sum_m C(NS'J; m, M - m) \Psi_{Nm} \Psi_{S', M - m}, \quad (9)$$

where the Clebsch-Gordan coefficient  $C$  is defined as in

<sup>10</sup> For a more detailed discussion of the transformation of angular momenta from a fixed coordinate system to a reference frame which rotates with the molecule see J. H. Van Vleck, *Revs. Modern Phys.* 23, 213 (1951).

reference 11. The wave function  $\Psi_{Nm}$  is expressed in terms of products of the rotational and electronic wave functions.

One can show in a straightforward way that in a homonuclear diatomic molecule the wave function  $\Psi_{Nm}$  can only contain either  $\Psi_e^+$  or  $\Psi_e^-$ , depending on whether  $N$  is even or odd.<sup>12</sup> For a given total nuclear spin  $I$  and symmetry  $g$  or  $u$  of the electronic wave function, the following selection rule can be used to decide which  $\Psi_e$  belongs to a particular rotational state:

$$\left\{ \begin{array}{l} \Psi_e^+ \quad (+1) \\ \Psi_e^- \quad (-1) \end{array} \right\} = \left\{ \begin{array}{l} \text{even } I \quad (+1) \\ \text{odd } I \quad (-1) \end{array} \right\} \times \left\{ \begin{array}{l} g \quad (+1) \\ u \quad (-1) \end{array} \right\} \\ \times (-1)^N, \quad (10)$$

where on the right side the number in the parentheses is to be used to carry out the multiplication. If the product of the three terms is  $+1$  ( $-1$ ), then  $\Psi_e^+$  ( $\Psi_e^-$ ) is assigned to the particular level. Thus, for instance, in the  $\Pi_u$  state of para  $\text{H}_2$  ( $I=0$ ) the  $\Psi_e^+$  belongs to the odd rotational states and  $\Psi_e^-$  to the even rotational states. We shall show in Sec. V that the spin-spin Hamiltonian can connect  $\Psi_e(\Lambda=+1)$  with  $\Psi_e(\Lambda=-1)$  and the application of the selection rule (10) indicates that this term contributes to the even rotational levels with a certain sign and to the odd levels with the opposite sign.

#### IV. SPIN-ORBIT INTERACTION

The Hamiltonian for the spin-orbit and spin-other orbit interaction is obtained from the Pauli approximation of the Breit equation. In the notation of reference 9 we have for a diatomic molecule

$$H_3 = \frac{e^2 \hbar}{2m^2 c^2} \left\{ \left[ \frac{Z_1}{r_1^3} \mathbf{r}_1 \times \mathbf{p}_1 + \frac{Z_2}{|\mathbf{r}_1 - \mathbf{R}|^3} (\mathbf{r}_1 - \mathbf{R}) \right. \right. \\ \left. \left. \times \mathbf{p}_1 - \frac{1}{r_{12}^3} \mathbf{r}_{12} \times \mathbf{p}_1 + \frac{2}{r_{12}^3} \mathbf{r}_{12} \times \mathbf{p}_2 \right] \cdot \mathbf{s}_1 \right. \\ \left. + \left[ \frac{Z_2}{r_2^3} \mathbf{r}_2 \times \mathbf{p}_2 + \frac{Z_1}{|\mathbf{r}_2 + \mathbf{R}|^3} (\mathbf{r}_2 + \mathbf{R}) \times \mathbf{p}_2 \right. \right. \\ \left. \left. - \frac{1}{r_{12}^3} \mathbf{r}_{21} \times \mathbf{p}_2 + \frac{2}{r_{12}^3} \mathbf{r}_{21} \times \mathbf{p}_1 \right] \cdot \mathbf{s}_2 \right\}, \quad (11)$$

where  $\mathbf{r}_1$ ,  $\mathbf{p}_1$  and  $\mathbf{r}_2$ ,  $\mathbf{p}_2$  are the position and momentum vectors of electron 1 and 2 referred to nucleus 1 (with charge  $Z_1$ ) and nucleus 2 (with charge  $Z_2$ ), respectively;  $\mathbf{R}$  is the internuclear separation ( $\mathbf{R}$  originates at nucleus 1 and points to nucleus 2), and  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ . If we intro-

duce the total spin operator  $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$  and the orbital angular momentum operators  $\mathbf{l}_1 = \mathbf{r}_1 \times \mathbf{p}_1$  and  $\mathbf{l}_2 = \mathbf{r}_2 \times \mathbf{p}_2$ , then we can show in a straightforward way that all the matrix elements of (11) using the wave function (9) vanish except the ones obtained from the following reduced Hamiltonian (in atomic units)

$$H_3' = -\frac{\alpha^2}{4} \left[ \left( \frac{Z_1}{r_1^3} + \frac{Z_2}{|\mathbf{r}_1 - \mathbf{R}|^3} - \frac{3}{r_{12}^3} \right) \mathbf{l}_1 \cdot \mathbf{S} \right. \\ \left. + \left( \frac{Z_2}{r_2^3} + \frac{Z_1}{|\mathbf{r}_2 + \mathbf{R}|^3} - \frac{3}{r_{12}^3} \right) \mathbf{l}_2 \cdot \mathbf{S} \right]. \quad (12)$$

For the calculation of the remaining matrix elements it is more convenient to express  $\mathbf{l}_1 \cdot \mathbf{S}$  and  $\mathbf{l}_2 \cdot \mathbf{S}$  as contractions of irreducible tensors. Specifically:

$$\mathbf{l}_1 \cdot \mathbf{S} = (4\pi/3) \sum_{\alpha} (-1)^{\alpha} \mathcal{Y}_1^{-\alpha}(\mathbf{l}_1) \mathcal{Y}_1^{\alpha}(\mathbf{S}), \quad (13)$$

and

$$\mathbf{l}_2 \cdot \mathbf{S} = (4\pi/3) \sum_{\beta} (-1)^{\beta} \mathcal{Y}_1^{-\beta}(\mathbf{l}_2) \mathcal{Y}_1^{\beta}(\mathbf{S}), \quad (14)$$

where the solid spherical harmonics  $\mathcal{Y}_1^{\alpha}(\mathbf{r})$  is defined as

$$\mathcal{Y}_1^{\alpha}(\mathbf{r}) = r Y_1^{\alpha}(\theta, \varphi). \quad (15)$$

All the variables are referred to a coordinate system fixed in space. In terms of (13) and (14) we get for the reduced spin-orbit Hamiltonian

$$H_3' = (\pi\alpha^2/3) \left[ \xi_1(r_1, r_{12}) \sum_{\alpha} (-1)^{\alpha} \mathcal{Y}_1^{-\alpha}(\mathbf{l}_1) \mathcal{Y}_1^{\alpha}(\mathbf{S}) \right. \\ \left. + \xi_2(r_2, r_{12}) \sum_{\beta} (-1)^{\beta} \mathcal{Y}_1^{-\beta}(\mathbf{l}_2) \mathcal{Y}_1^{\beta}(\mathbf{S}) \right], \quad (16)$$

where we have set

$$\xi_1(r_1, r_{12}) = \frac{Z_1}{r_1^3} + \frac{Z_2}{|\mathbf{r}_1 - \mathbf{R}|^3} - \frac{3}{r_{12}^3}, \quad (17) \\ \xi_2(r_2, r_{12}) = \frac{Z_2}{r_2^3} + \frac{Z_1}{|\mathbf{r}_2 + \mathbf{R}|^3} - \frac{3}{r_{12}^3}.$$

The matrix element of (16) in the coupled representation (9) now becomes

$$(JM; N, \Lambda, S | H_3' | JM; N, \Lambda, S) \\ = \frac{\pi\alpha^2}{3} \sum_{m'} \sum_m C(NS'J; m', M-m') C(NS'J; m, M-m) \\ \times \left\{ \sum_{\alpha} (-1)^{\alpha} (Nm' | \xi_1 \mathcal{Y}_1^{-\alpha}(\mathbf{l}_1) | Nm) \right. \\ \times (S, M-m' | \mathcal{Y}_1^{\alpha}(\mathbf{S}) | S, M-m) \\ \left. + \sum_{\beta} (-1)^{\beta} (Nm' | \xi_2 \mathcal{Y}_1^{-\beta}(\mathbf{l}_2) | Nm) \right. \\ \left. \times (S, M-m' | \mathcal{Y}_1^{\beta}(\mathbf{S}) | S, M-m) \right\}. \quad (18)$$

By applying the Wigner-Eckart theorem to the matrix elements on the right of (18) and by introducing the Racah coefficients  $W$ , it can be shown that the matrix

<sup>11</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

<sup>12</sup> See for instance, G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1955), pp. 213, 217, 237-240.

element of (18) reduces to the following expression<sup>13</sup>:

$$(JM; N, \Lambda, S | H'_3 | JM; N, \Lambda, S) \\ = \frac{1}{3} \pi \alpha^2 \{ (N, \Lambda | \xi_1 \mathcal{Y}_1(l_1) | N, \Lambda) + (N, \Lambda | \xi_2 \mathcal{Y}_1(l_2) | N, \Lambda) \} \\ \times (-1)^{N+S-J} [(2N+1)(2S+1)]^{\frac{1}{2}} \\ \times W(NSNS; J1) (S | \mathcal{Y}_1(S) | S). \quad (19)$$

The reduced matrix element  $(S | \mathcal{Y}_1(S) | S)$  can be evaluated directly in the molecular system since it is not affected by the transformation from the coordinate system fixed in space to axes moving with the molecule. Since  $\mathcal{Y}_1(\mathbf{S})$  is a tensor of first rank in the irreducible representation, we have

$$(S | \mathcal{Y}_1(S) | S) = (3/4\pi)^{\frac{1}{2}} [S(S+1)]^{\frac{1}{2}}. \quad (20)$$

The remaining reduced matrix elements in (19), however, first have to be transformed properly to the molecular system. The inverse of the Wigner-Eckart theorem yields

$$(N, \Lambda | \xi_i \mathcal{Y}_1(l_i) | N, \Lambda) = (Nm, \Lambda | \xi_i \mathcal{Y}_1^0(\mathbf{l}_i) | Nm, \Lambda) \\ \times [C(N1N; m0m)]^{-1}, \quad (i=1, 2), \quad (21)$$

and by applying the addition theorem for spherical harmonics we get

$$\mathcal{Y}_1^0(\mathbf{l}_i) = \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} \sum_{\mu} (-1)^{\mu} \mathcal{Y}_1^{-\mu}(\mathbf{l}_i^*) Y_1^{\mu}(\Theta, \Phi) \\ = \sum_{\mu} (-1)^{\mu} \mathcal{Y}_1^{-\mu}(\mathbf{l}_i^*) D_{0\mu}^1(\alpha\beta\gamma), \quad (22)$$

where  $\mathbf{l}_i^*$  is referred to the molecular coordinate system and the variables  $\Theta, \Phi$  are defined in Fig. 1,  $D_{0\mu}^1(\alpha\beta\gamma)$  is a rotation matrix, and  $\alpha, \beta, \gamma$  are the Euler angles defining the orientation of the molecular coordinate system with respect to axes fixed in space.

The rotational wave function in (9) is of the form

$$R(r_N) Y_{N^m}(\theta_N, \varphi_N) = R(r_N) (2N+1)^{\frac{1}{2}} D_{m\Lambda}^N(\alpha\beta\gamma). \quad (23)$$

Using (22) and (23) the matrix element

$$(Nm, \Lambda | \xi_i \mathcal{Y}_1^0(\mathbf{l}_i) | Nm, \Lambda)$$

can now be evaluated in a straightforward way:

$$(Nm, \Lambda | \xi_i \mathcal{Y}_1^0(\mathbf{l}_i) | Nm, \Lambda) = \sum_{\mu} (-1)^{\mu} \langle \xi_i \mathcal{Y}_1^{-\mu}(\mathbf{l}_i^*) \rangle \\ \times C(N1N; m0m) C(N1N; \Lambda\mu\Lambda), \quad (24)$$

and the reduced matrix element becomes

$$(N, \Lambda | \xi_i \mathcal{Y}_1(l_i) | N, \Lambda) = \langle \xi_i \mathcal{Y}_1^0(\mathbf{l}_i^*) \rangle C(N1N; \Lambda 0 \Lambda), \quad (25)$$

since  $C(N1N; \Lambda\mu\Lambda)$  vanishes unless  $\mu=0$ . Finally, substitution of (20) and (25) into (19) and evaluation of the explicit expressions of the Clebsch-Gordan<sup>14</sup> and

<sup>13</sup> For the details of the reduction see reference 11, pp. 115-117; also A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), pp. 110-111.

<sup>14</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1959), pp. 76-77.

Racah<sup>15</sup> coefficients yields the following expression for the diagonal matrix element of the spin-orbit and spin-orbit interaction.<sup>16</sup>

$$(JM; N, \Lambda, S | H'_3 | JM; N, \Lambda, S) \\ = \frac{\alpha^2}{4} \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} [\langle \xi_1(r_{1,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_1^*) \rangle + \langle \xi_2(r_{2,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_2^*) \rangle] \\ \times \frac{\Lambda}{2N(N+1)} [J(J+1) - N(N+1) - S(S+1)] \\ = \frac{\alpha^2}{4} \left(\frac{4\pi}{3}\right)^{\frac{1}{2}} [\langle \xi_1(r_{1,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_1^*) \rangle \\ + \langle \xi_2(r_{2,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_2^*) \rangle] \frac{\Lambda}{N(N+1)} \langle \mathbf{N} \cdot \mathbf{S} \rangle. \quad (26)$$

The second line in (26) is obtained from the relation

$$\langle \mathbf{N} \cdot \mathbf{S} \rangle = \frac{1}{2} [J(J+1) - N(N+1) - S(S+1)], \\ (\mathbf{J} = \mathbf{N} + \mathbf{S}). \quad (27)$$

The off-diagonal matrix elements of the spin-orbit interaction combining different  $N$  states which will be needed in intermediate case- $a$ -case- $b$  coupling can be calculated in an entirely analogous way.<sup>17</sup>

## V. SPIN-SPIN INTERACTION

The Hamiltonian describing the interaction between two electron spins is usually written in the form<sup>1,9</sup>

$$H'_5 = \frac{e^2}{m^2 c^2} \left[ \frac{(\mathbf{s}_1 \cdot \mathbf{s}_2) r_{12}^2 - 3(\mathbf{s}_1 \cdot \mathbf{r}_{12})(\mathbf{s}_2 \cdot \mathbf{r}_{12})}{r_{12}^5} \right], \quad (28)$$

where  $r_{12}$  is the distance between the two electrons.  $H'_5$  differs from the Hamiltonian  $H_5$  of the Pauli approximation of the Breit equation by the omission of the contact term which does not contribute to the fine structure splitting. In order to be able to apply the theory of angular momentum in the calculation of the matrix elements it is necessary to write (28) as a contraction of irreducible tensors. The transformation yields<sup>18</sup>

$$H'_5 = -\alpha^2 \sum_{\mu\nu} \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left[ \frac{(2-\mu-\nu)!(2+\mu+\nu)!}{(1-\mu)!(1+\mu)!(1-\nu)!(1+\nu)!} \right]^{\frac{1}{2}} \\ \times T_1^{\mu*}(\mathbf{s}_1) T_1^{\nu*}(\mathbf{s}_2) \mathcal{Y}_{2^{\mu+\nu}}(\mathbf{r}_{12}), \quad (29)$$

<sup>15</sup> A. Simon, J. H. Vander Sluis, and L. C. Biedenharn, Oak Ridge National Laboratory Report ORNL-1679, 1954 (unpublished).

<sup>16</sup> It should be noted that aside from the expression

$$[\langle \xi_1(r_{1,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_1^*) \rangle + \langle \xi_2(r_{2,r_{12}}) \mathcal{Y}_1^0(\mathbf{l}_2^*) \rangle]$$

the same result can be obtained from a perturbation Hamiltonian which is of the form  $\xi(r) \Lambda \mathbf{n} \cdot \mathbf{S}$ , where  $\mathbf{n}$  is a unit vector along the internuclear axis.

<sup>17</sup> See paper II of this series.

<sup>18</sup> For an expansion of  $H'_5$  in Cartesian coordinates see: T. P. Das and R. Bersohn, Phys. Rev. **115**, 897 (1959).

where we have used atomic units. The tensors  $\mathbf{T}_1(s_1)$  and  $\mathbf{T}_2(s_2)$  are defined such that

$$\mathbf{s}_1 \cdot \mathbf{s}_2 = \hbar^2 \sum_{\beta} (-1)^{\beta} T_1^{-\beta}(\mathbf{s}_1) T_1^{\beta}(\mathbf{s}_2);$$

$$T_1^{\mu*} = (-1)^{\mu} T_1^{-\mu} \quad (30)$$

and

$$\Upsilon_2^{\mu+\nu}(\mathbf{r}_{12}) = \frac{1}{r_{12}^3} Y_2^{\mu+\nu}(\theta_{12}, \varphi_{12}). \quad (31)$$

As in the calculation of the spin-orbit interaction, all variables are referred to a coordinate system fixed in space.

The spin-spin Hamiltonian can be written as a contraction of two quadrupole tensors if we introduce a spin-dependent tensor  $\mathbf{Q}_2(S)$  whose components are defined as

$$Q_2^{-\gamma}(\mathbf{S}) = \sum_{\mu} \left[ \frac{(2-\gamma)!(2+\gamma)!}{(1-\mu)!(1+\mu)!(1-\gamma+\mu)!(1-\mu+\gamma)!} \right]^{\frac{1}{2}}$$

$$\times T_1^{-\mu}(\mathbf{s}_1) T_1^{\mu-\gamma}(\mathbf{s}_2), \quad (\gamma = \mu + \nu). \quad (32)$$

Substitution of (32) into (29) yields

$$H_5' = -\alpha^2 \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} \sum_{\gamma} (-1)^{\gamma} Q_2^{-\gamma}(\mathbf{S}) \Upsilon_2^{\gamma}(\mathbf{r}_{12})$$

$$= -\alpha^2 \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} Q_2(\mathbf{S}) \cdot \Upsilon_2(\mathbf{r}_{12}). \quad (33)$$

The calculation of the matrix element can now be carried out in exactly the same way as in the case of the spin-orbit interaction in Sec. IV. From the coupled representation (9) we get

$$(JM; N, \Lambda', S) | H_5' | JM; N, \Lambda, S)$$

$$= -\alpha^2 (4\pi/5)^{\frac{1}{2}} (-1)^{N+S-J} W(NSNS; J2)$$

$$\times [(2N+1)(2S+1)]^{\frac{1}{2}} (N, \Lambda' || \Upsilon_2(\mathbf{r}_{12}) || N, \Lambda)$$

$$\times (S || Q_2(S) || S). \quad (34)$$

The reduced matrix element  $(N, \Lambda' || \Upsilon_2(\mathbf{r}_{12}) || \Lambda, N)$  can again be evaluated by applying the Wigner-Eckart theorem:

$$(N, \Lambda' || \Upsilon_2(\mathbf{r}_{12}) || N, \Lambda)$$

$$= (Nm; \Lambda' | \Upsilon_2^0(\mathbf{r}_{12}) | Nm; \Lambda) [C(N2N; m0m)]^{-1}, \quad (35)$$

and the application of the addition theorem for spherical

$$\alpha^2 \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} \left\langle \frac{Y_2^0(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle (S || Q_2(S) || S) \frac{2[N(N+1) - 3\Lambda^2] \left[ \frac{3}{4} C(C+1) - N(N+1)S(S+1) \right]}{(2N-1)N(N+1)(2N+3) [(2S-1)S(S+1)(2S+3)]^{\frac{1}{2}}},$$

$$C = J(J+1) - N(N+1) - S(S+1), \quad (40)$$

where we have substituted the explicit expressions of the Clebsch-Gordan and Racah coefficients.<sup>14,15</sup>

For  $\Lambda=1$  ( $\Pi$  states) the spin-spin Hamiltonian can connect  $\Psi(\Lambda=+1)$  with  $\Psi(\Lambda=-1)$  and the resulting

harmonics transforms  $\Upsilon_2^0(\mathbf{r}_{12})$  in the following way (see Fig. 1):

$$\Upsilon_2^0(\mathbf{r}_{12}) = \frac{1}{r_{12}^3} \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} \sum_{\eta} Y_2^{\eta*}(\Theta_{12}, \Phi_{12}) Y_2^{\eta}(\Theta, \Phi)$$

$$= \frac{1}{r_{12}^3} \sum_{\eta} Y_2^{\eta*}(\Theta_{12}, \Phi_{12}) D_{0\eta}(\alpha\beta\gamma), \quad (36)$$

where the Euler angles  $\alpha, \beta, \gamma$  have the same meaning as the ones in Sec. IV. Using (23) and (36) the integration over the triple product of rotation matrices yields

$$(Nm; \Lambda' | \Upsilon_2^0(\mathbf{r}_{12}) | Nm; \Lambda) = \sum_{\eta} \left\langle \frac{Y_2^{\eta*}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle$$

$$\times C(N2N; m0m) C(N2N; \Lambda'\eta\Lambda), \quad (37)$$

and the reduced matrix element of the electronic state becomes

$$(N, \Lambda' || \Upsilon_2(\mathbf{r}_{12}) || N, \Lambda)$$

$$= \sum_{\eta} \left\langle \frac{Y_2^{\eta*}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle C(N2N; \Lambda'\eta\Lambda). \quad (38)$$

All the variables in the remaining matrix element  $\langle Y_2^{\eta*}(\Theta_{12}, \Phi_{12})/r_{12}^3 \rangle$  are expressed in the molecular coordinate system and its expectation value can be obtained from electronic wave functions in the Born-Oppenheimer approximation.

If we substitute (38) into (34) we get for the matrix element of the spin-spin interaction

$$(JM; \Lambda', S; | H_5' | JM; \Lambda, S)$$

$$= -\alpha^2 \left( \frac{4\pi}{5} \right)^{\frac{1}{2}} \sum_{\eta} \left\langle \frac{Y_2^{\eta*}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle (-1)^{N+S-J}$$

$$\times W(NSNS; J2) C(N2N; \Lambda'\eta\Lambda)$$

$$\times [(2N+1)(2S+1)]^{\frac{1}{2}} (S || Q_2(S) || S). \quad (39)$$

For given  $\Lambda'$  and  $\Lambda$  the summation over  $\eta$  is restricted to one term ( $\eta = \Lambda - \Lambda'$ ). Thus in the diagonal matrix elements  $(\Psi(+\Lambda) | H_5' | \Psi(+\Lambda))$  and  $(\Psi(-\Lambda) | H_5' | \Psi(-\Lambda))$  only the  $\eta=0$  term contributes and the matrix element of (39) reduces to

matrix element is of the form

$$-\alpha^2 \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left\langle \frac{Y_{2^{\pm 2}}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle (S \| Q_2(S) \| S) \frac{2\sqrt{3}N(N+1)[\frac{3}{4}C(C+1) - N(N+1)S(S+1)]}{\sqrt{2}(2N-1)N(N+1)(2N+3)[(2S-1)S(S+1)(2S+3)]^{\frac{1}{2}}},$$

$$C = J(J+1) - N(N+1) - S(S+1). \quad (41)$$

The remaining spin-dependent matrix element can be calculated in the following way:

$$(S \| Q_2(S) \| S) = (Sm | Q_2^0(\mathbf{S}) | Sm) [C(S2S; m0m)]^{-1} \\ = \frac{[(2S-1)S(S+1)(2S+3)]^{\frac{1}{2}}}{3m^2 - S(S+1)} \sum_{\mu} \frac{2}{(1-\mu)!(1+\mu)!} \\ \times (Sm; s_1s_2 | T_1^{-\mu}(\mathbf{s}_1)T_1^{\mu}(\mathbf{s}_2) | Sm; s_1s_2), \quad (42)$$

where in the second line we have used the definition (32) of the quadrupole tensor  $Q_2(S)$ . The matrix element on the right side of (42) vanishes for singlet and doublet states. For triplet states, however, we get

$$\sum_{\mu} \frac{2}{(1-\mu)!(1+\mu)!} (Sm; s_1s_2 | T_1^{-\mu}(\mathbf{s}_1)T_1^{\mu}(\mathbf{s}_2) | Sm; s_1s_2) \\ = \frac{2}{3}m^2 - 1, \quad (43)$$

and

$$(1 \| Q_2 \| 1) = (10)^{\frac{1}{2}}/2. \quad (44)$$

If we now combine (44) with (40) and (41) we get the following expressions for the spin-spin interaction.

(1) For  ${}^3\Sigma, {}^3\Delta, \dots$  states:

$$(\Psi_e^{\pm} | H_5' | \Psi_e^{\pm}) = \alpha^2 \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left\langle \frac{Y_2^0(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle \\ \times \frac{[N(N+1) - 3\Lambda^2][\frac{3}{4}C(C+1) - 2N(N+1)]}{(2N-1)N(N+1)(2N+3)}, \quad (45)$$

$$C = J(J+1) - N(N+1) - S(S+1).$$

The result for  ${}^3\Sigma$  states agrees with the expression of Kramers.<sup>1</sup>

(2) for  ${}^3\Pi$  states:

$$(\Psi_e^{\pm} | H_5' | \Psi_e^{\pm}) = \alpha^2 \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left\{ [N(N+1) - 3\Lambda^2] \left\langle \frac{Y_2^0(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle \right. \\ \left. \mp \left(\frac{3}{2}\right)^{\frac{1}{2}} N(N+1) \left\langle \frac{Y_{2^{\pm 2}}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle \right\} \\ \times \frac{\frac{3}{4}C(C+1) - 2N(N+1)}{2(2N-1)N(N+1)(2N+3)}, \quad (46)$$

$$C = J(J+1) - N(N+1) - S(S+1).$$

## VI. FINE STRUCTURE OF THE $c^3\Pi_u$ STATE

In  $\Pi$  states the presence of the matrix element  $(\Psi_e^{\pm}(\Lambda=+1) | H_5' | \Psi_e^{\pm}(\Lambda=-1))$  produces anomalous fine structure separations. In order to get an idea of the importance of this term let us apply the results of the spin-orbit and spin-spin interactions to the  $c^3\Pi_u$  states of para and ortho  $H_2$ , for which there are experimental data available.<sup>7,8</sup>

If we combine (26) and (46), we get for the total fine structure energy of a  ${}^3\Pi$  state

$$E = -\left(\frac{4\pi}{3}\right)^{\frac{1}{2}} [\langle \xi_1 \mathcal{Y}_1^0(\mathbf{l}_1^*) \rangle + \langle \xi_2 \mathcal{Y}_1^0(\mathbf{l}_2^*) \rangle] \\ \times \frac{[J(J+1) - N(N+1) - 2]}{2N(N+1)} \\ + \alpha^2 \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left\{ [N(N+1) - 3] \left\langle \frac{Y_2^0(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle \right. \\ \left. \mp \left(\frac{3}{2}\right)^{\frac{1}{2}} N(N+1) \left\langle \frac{Y_{2^{\pm 2}}(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle \right\} \\ \times \frac{\frac{3}{4}C(C+1) - 2N(N+1)}{2(2N-1)N(N+1)(2N+3)}, \quad (47a)$$

which in Cartesian coordinates becomes

$$E = \frac{\alpha^2}{4} [\langle \xi_1 l_{1z}^* \rangle + \langle \xi_2 l_{2z}^* \rangle] \frac{[J(J+1) - N(N+1) - 2]}{2N(N+1)} \\ + \frac{\alpha^2}{4} \left\{ [N(N+1) - 3] \left\langle \frac{z^2 - r^2}{r^5} \right\rangle \right. \\ \left. \mp N(N+1) \left\langle \frac{x^2 - y^2}{r^5} \right\rangle \right\} \\ \times \frac{\frac{3}{4}C(C+1) - 2N(N+1)}{(2N-1)N(N+1)(2N+3)}, \quad (47b)$$

where we have set

$$\mathbf{r}_{12} = \mathbf{i}(x_1 - x_2) + \mathbf{j}(y_1 - y_2) + \mathbf{k}(z_1 - z_2) = \mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

From the selection rule (10) we deduce that for a  ${}^3\Pi$  state the minus sign in front of the  $Y_2^2$  component of the spin-spin interaction applies to odd rotational levels in para  $H_2$  and to even ones in ortho  $H_2$ , and consequently the plus sign refers to even  $N$  in para  $H_2$  and to odd  $N$  in ortho  $H_2$ . The remaining matrix ele-

ments in (47) can be easily estimated by retaining only the  $1s(1)2p\pi(2)$  and  $1s(1)2p\bar{\pi}(2)$  terms in the wave function of the  ${}^3\Pi$  state, and by using a united atom approximation ( $R=0$ ). In this case only a small fraction of the  $2p$  orbit penetrates the  $1s$  core and we can replace  $\mathbf{r}_{12}$  by  $\mathbf{r}_2$  without introducing a large error.<sup>19</sup> In this approximation we obtain

$$\langle \xi_1 \mathcal{Y}_1^0(\mathbf{l}_1^*) \rangle = 0; \quad \langle \xi_2 \mathcal{Y}_1^0(\mathbf{l}_2^*) \rangle = (3/4\pi)^{1/2} (Z^* - 2) \langle 1/r_2^3 \rangle, \quad (48)$$

$$\left\langle \frac{Y_2^0(\Theta_2, \Phi_2)}{r_2^3} \right\rangle = \left( \frac{5}{4\pi} \right)^{1/2} C(121; \pm 1, 0, \pm 1) \times C(121; 000) \langle 1/r_2^3 \rangle = - \left( \frac{5}{4\pi} \right)^{1/2} \frac{1}{5} \langle 1/r_2^3 \rangle, \quad (49)$$

$$\left\langle \frac{Y_2^{\pm 2}(\Theta_2, \Phi_2)}{r_2^3} \right\rangle = \left( \frac{5}{4\pi} \right)^{1/2} C(121; \mp 1, \pm 2, \pm 1) \times C(121; 000) \langle 1/r_2^3 \rangle = - \left( \frac{5}{4\pi} \right)^{1/2} \frac{\sqrt{6}}{5} \langle 1/r_2^3 \rangle, \quad (50)$$

and

$$\langle 1/r_2^3 \rangle = (Z^*)^3/24, \quad (51)$$

where  $Z^*$  is the effective nuclear charge of the  $1s$  core. Finally, if we substitute (48-51) into (47) we get the following expressions for the fine structure levels of the  $c\,{}^3\Pi_u$  state:

$$E(J=N+1) = \frac{\alpha^2(Z^*)^3}{96} \left\{ - \frac{(2-Z^*)}{N+1} + \left[ \left( \frac{3}{N(N+1)} - 1 \right) \frac{1}{5} \pm \frac{3}{5} \right] \frac{N}{2N+3} \right\}, \quad (52)$$

$$E(J=N) = \frac{\alpha^2(Z^*)^3}{96} \left\{ + \frac{(2-Z^*)}{N(N+1)} - \left[ \left( \frac{3}{N(N+1)} - 1 \right) \frac{1}{5} \pm \frac{3}{5} \right] \right\}, \quad (53)$$

$$E(J=N-1) = \frac{\alpha^2(Z^*)^3}{96} \left\{ + \frac{(2-Z^*)}{N} + \left[ \left( \frac{3}{N(N+1)} - 1 \right) \frac{1}{5} \pm \frac{3}{5} \right] \frac{N+1}{2N-1} \right\}. \quad (54)$$

The plus sign in front of the last term in Eqs. (52)-(54) refers to odd  $N$  in para  $\text{H}_2$  and to even  $N$  in ortho  $\text{H}_2$ , and the minus sign to even  $N$  in para  $\text{H}_2$  and to odd  $N$  in ortho  $\text{H}_2$ . In Fig. 2 we have plotted the fine structure

<sup>19</sup> See for instance, reference 9, Secs. 39-40. For a more accurate wave function of the  $c\,{}^3\Pi_u$  state of  $\text{H}_2$  see A. Ameniya, Proc. Phys.-Math. Soc. Japan 21, 394 (1939).

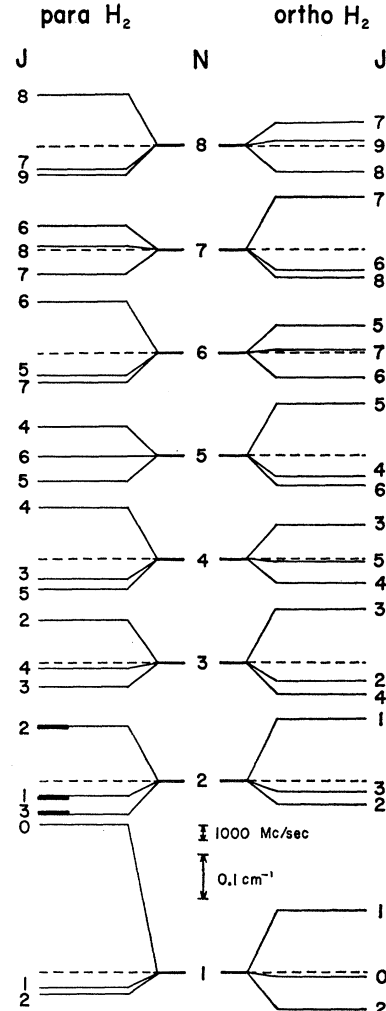


FIG. 2. Fine structure separation of the first eight rotational levels of the  $c\,{}^3\Pi_u$  ( $v=0$ ) state of para and ortho  $\text{H}_2$ . The energy separation of the rotational levels is arbitrary. The heavy lines in the  $N=2$  level of para  $\text{H}_2$  refer to the experimental values of Lichten.<sup>8</sup>

separations of the first 8 rotational levels of para and ortho  $\text{H}_2$ . An effective nuclear charge has been chosen such that the  $J=2 \rightarrow J=3$  energy difference of the  $N=2$  level of para  $\text{H}_2$  agrees with the experimental value of Lichten.<sup>8</sup> The comparison yields a  $Z^*$  of 1.06 which corresponds to almost complete screening ( $Z^* = 1.00$ ). The energy separation of the rotational levels is arbitrary. The heavy lines in the  $N=2$  level of para  $\text{H}_2$  refer to the experimental values of Lichten.<sup>8</sup> In the "regular" levels (even  $N$  in para  $\text{H}_2$  and odd  $N$  in ortho  $\text{H}_2$ ) the contribution of the  $Y_2^2$  component of the quadrupole type spin-spin interaction adds to the one of the  $Y_2^0$  component. The  $J=N$  level is positive, whereas the  $J=N+1$  and  $J=N-1$  levels are negative. In the limit of large  $N$  the  $J=N$  level is 3475 Mc/sec above the center of gravity, whereas the  $J=N+1$  and  $J=N-1$  levels coincide, and the degenerate level is 1738

Mc/sec below the center of gravity. In the "irregular" levels (odd  $N$  in para  $H_2$  and even  $N$  in ortho  $H_2$ ) the  $Y_2^2$  component of  $H_5'$  subtracts from the  $Y_2^0$  component and in the resulting fine structure the  $J=N-1$  level is on top of the  $J=N+1$  and  $J=N$  levels. In the limit of  $N \rightarrow \infty$  the  $J=N$  level is 1738 Mc/sec below the center of gravity and the coinciding  $J=N-1$  and  $J=N+1$  levels are 869 Mc/sec above the center of gravity.

The fine structure of the  $N=1$  level in para  $H_2$ , however, is different, since here  $[3/N(N+1)-1]$  is positive and the two contributions of the  $Y_2^0$  and  $Y_2^2$  components of  $H_5'$  add to give an anomalously large splitting. The fine structure splitting of the  $N=1$  level in para  $H_2$  is very similar to the  $2^3P$  state of helium.

For  $N \geq 4$ , the alternation of the fine structure from one rotational level to the next becomes more pronounced since as  $N$  increases the contribution of the spin-orbit interaction diminishes while the energy of the spin-spin interaction tends to a finite value.

The level scheme of ortho  $H_2$  also applies to the  $^3\Pi_g$  state of  $He_2$ . Mulliken and Monk<sup>20</sup> who measured the fine structure of  $He_2$  noted that the intensity ratio of the two observed lines ending on the regular levels (odd  $N$  in  $^3\Pi_g$  of  $He_2$ ) is 2:1. They also mentioned that the same ratio of the lines ending on the  $N=2$  level is appreciably larger (3:1 to 6:1). If one calculates the ratio of the statistical weight of the upper  $J$  level ( $J=N$ ) in the odd rotational levels to the average weight of the two lower levels ( $J=N-1, J=N+1$ ), one finds that it is 2:1. Furthermore, the intensity ratio of the lines ending on the  $N=2$  level turns out to be

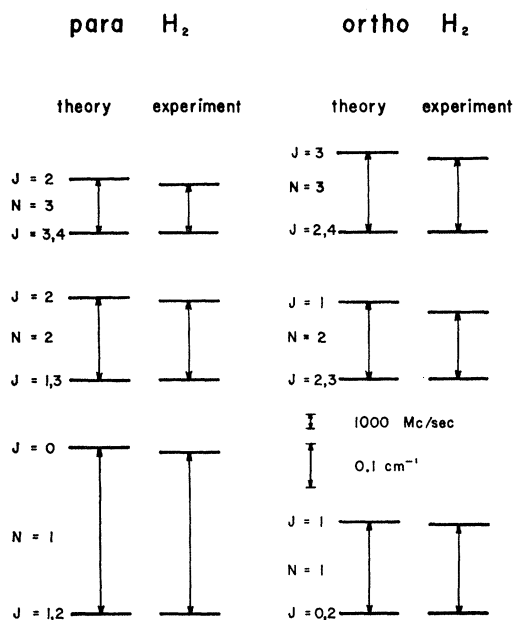


FIG. 3. Comparison of averaged theoretical [Eqs. (52)–(54)] and experimental (reference 7) fine structure separations.

<sup>20</sup> R. S. Mulliken and G. S. Monk, Phys. Rev. 34, 1530 (1929).

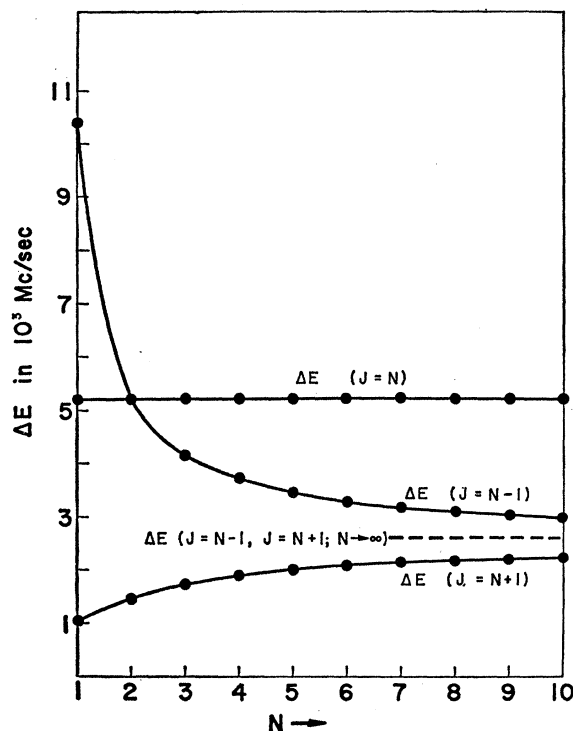


FIG. 4. Energy separations of corresponding "regular" and "irregular" fine structure levels [Eq. (57)].

4:1, which is in agreement with the observation of Mulliken and Monk.

Recently, Mizushima and Frey<sup>21</sup> calculated the fine and hyperfine structure of the lowest rotational level of the  $c^3\Pi_u$  of  $H_2$ . They do not mention to which state of  $H_2$  their results refer, but since only the rotational states of ortho  $H_2$  show a hyperfine structure it is assumed that the results apply to the  $N=1$  level of ortho  $H_2$ . Their predicted transition frequencies are 11 500 Mc/sec ( $J=0 \rightarrow J=2$ ) and 7500 Mc/sec ( $J=1 \rightarrow J=2$ ). Thus neither the level order nor the energy separations agree with our results of Eqs. (48)–(50).

Foster and Richardson<sup>7</sup> have measured the mean fine structure splitting of the first 3 rotational levels of the lowest vibrational state of the  $c^3\Pi_u$  state in para and ortho  $H_2$ . In Fig. 3 their results are compared with the properly averaged theoretical splittings. The rather good agreement seems to indicate that indeed besides the spin-orbit and spin-spin interactions no other perturbation contributes significantly to the fine structure splitting.<sup>22</sup>

The spin-spin interaction does not shift the center of gravity of the fine structure levels, but since the contribution of the  $Y_2^2$  component of  $H_5'$  affects corresponding  $J$  levels of para and ortho  $H_2$  differently,

<sup>21</sup> H. Mizushima and D. A. Frey, Bull. Am. Phys. Soc. 2, 165 (1961).

<sup>22</sup> For an estimate of the contributions of other perturbations see W. Lichten (to be published).



there is an apparent splitting of each fine structure level into a "regular" and "irregular" component. The energy difference between corresponding  $J$  levels of para and ortho  $\text{H}_2$  is given by

$$\Delta E = \alpha^2 \left(\frac{4\pi}{5}\right)^{\frac{1}{2}} \left(\frac{3}{2}\right)^{\frac{3}{2}} \frac{\frac{3}{4}C(C+1) - 2N(N+1)}{(2N-1)(2N+3)} \times \left\langle \frac{Y_2^2(\Theta_{12}, \Phi_{12})}{r_{12}^3} \right\rangle, \quad (55)$$

which in the united atom approximation becomes

$$\Delta E = \alpha^2 \frac{(Z^*)^3 \frac{3}{4}C(C+1) - 2N(N+1)}{40(2N-1)(2N+3)}, \quad (56)$$

or if we separate out the different  $J$  components we get (in a.u.)

$$\begin{aligned} \Delta E(J=N+1) &= \frac{\alpha^2(Z^*)^3}{80} \frac{N}{2N+3}, \\ \Delta E(J=N) &= -\frac{\alpha^2(Z^*)^3}{80}, \\ \Delta E(J=N-1) &= \frac{\alpha^2(Z^*)^3}{80} \frac{N+1}{2N-1}. \end{aligned} \quad (57)$$

In Fig. 4 we have plotted  $\Delta E$  of (57) as a function of  $N$ . For large  $N$  we have  $\Delta E(J=N+1) = \Delta E(J=N-1) = \Delta E(J=N)/2$ . It is seen that the contribution of the  $Y_2^2$  component of  $H_5'$  to the fine structure splitting is sizeable. In low rotational levels the magnitudes of the energies in Fig. 4 are appreciably larger than those caused by the usual  $\Lambda$ -type doubling which arises from the interaction of the orbital angular momentum with the rotation of the nuclei.<sup>23</sup> In addition, the  $N$  dependence of the doubling due to the spin-spin interaction is quite different from the one of the  $\Lambda$ -type doubling which in general increases with increasing  $N$ . In article II we shall investigate this doubling of the  $J$  levels due to  $H_5'$  more intensively. In particular, we shall show that in some  $\Pi$  states of  $\text{N}_2$  the doubling is almost entirely due to the spin-spin interaction.

#### ACKNOWLEDGMENTS

The author is indebted to Professor W. Lichten for his helpful remarks and critical comments. He also wishes to thank Professor R. S. Mulliken and Professor C. C. J. Roothaan for their interest in this research.

<sup>23</sup> G. H. Dieke, *J. Mol. Spectroscopy* **2**, 494 (1958).