PHYSICAL REVIEW VOLUME 137, NUMBER 2A 18 JANUARY 1965

Fine Structure Constants of Metastable H_2 in the $c\,^3\Pi_u$ State*

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(Received 31 August 1964)

The expectation values of *spin-orbit* (A_1) *spin-other-orbit* (A_2) and *spin-spin* (B_0 and B_2) interactions have been evaluated over the electronic wave function for the $c^3\Pi_u$ state of H_2. $A_1=5.737$ kMc/sec, $A_2=-9.8$ kMc/sec, $B_0=-1.33$ kMc/sec, and $B_2=-3.84$ kMc/sec. These values agree well with those obtained from Lichten's experimental fine-structure splittings. The electronic wave function used is a linear combination of Heitler-London-type and ionic-type wave functions. By expressing the gradient operators as components of a spherical tensor, the *spin-other-orbit* interaction can be expressed as a linear combination of irregular solid spherical harmonics of the first order, while the space part of the *spin-spin* interaction consists of irregular solid spherical harmonics of the second order. The method of expansion and evaluation of these irregular solid spherical harmonics for a two-electron system is discussed in detail. The small second-order perturbations due to the nearby rotational states are also calculated.

INTRODUCTION

HYDROGEN, to a good approximation, is a pure Hund's case b^1 diatomic molecule. The angular momentum **N**, which is a resultant of the angular momentum of nuclear rotation (**O**) and the electronic-orbital-angular momentum along the figure axis (**Λ**), is a constant of motion. Half of the rotational levels, namely the levels of even N for *para* H_2 and the levels of odd N for *ortho* H_2, of the $c^3\Pi_u$ state are metastable[2] having a lifetime of the order of milliseconds. These levels can only decay to the levels of the dissociative $b^3\Sigma_u^+$ state via "forbidden predissociation"[3,4] (perturbation due to *spin-orbit* and *spin-spin* interactions). Lichten[5] has measured the fine-structure splittings and the g_J's of the $N=2$ state of *para* H_2 to a high accuracy using a molecular-beam magnetic-resonance method. The fine- and hyperfine-structure splittings and the g_F's of the $N=1$ state of *ortho* H_2 have been measured recently by Lichten and Brooks.[6] It is therefore of great theoretical interest to study the properties of these states. Recently, Fontana[7] has studied the fine structure splittings using a united-atom model; Frey and Mizushima[8] have calculated the hyperfine structure of *para* H_2; Browne[9] has calculated its electronic wave function and constructed a potential curve; Chiu[3] has studied the spin-orbit and spin-spin interactions between $c^3\Pi_u$ and $b^3\Sigma_u^+$ states and consequently the relative lifetime of the fine-structure levels of $c^3\Pi_u$ state. In this paper we calculate the fine-structure coupling constants due to spin-orbit, spin-other-orbit, and spin-spin interactions[10] by using an electronic wave function which is a linear combination of Heitler-London-type and ionic-type wave functions (see Sec. 2).

1. ELECTRON MAGNETIC INTERACTIONS

The Hamiltonian $\mathbf{H}'$ we are considering here is that due to spin-orbit, spin-other-orbit and spin-spin interactions of two electrons in a hydrogen molecule. For matrix elements which are diagonal in total electron spin S only, one can write $\mathbf{H}'$ (in atomic units) as follows[11]:

$$\mathbf{H}'=\frac{\alpha^2}{4}\biggl[\left(\frac{1}{r_{1a}^3}+\frac{1}{r_{1b}^3}\right)\mathbf{L}_1+\left(\frac{1}{r_{2a}^3}+\frac{1}{r_{2b}^3}\right)\mathbf{L}_2+\frac{3}{r_{12}^3}(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_2-\mathbf{p}_1)\biggr]\cdot\mathbf{S}+\frac{\alpha^2}{r_{12}^3}\biggl[(\mathbf{S}_1\cdot\mathbf{S}_2)-\frac{3(\mathbf{S}_1\cdot\mathbf{r}_{12})(\mathbf{S}_2\cdot\mathbf{r}_{12})}{r_{12}^2}\biggr],\qquad(1.1)$$

where α is the fine-structure constant. The subscripts a and b refer to the two nuclei, and 1 and 2 refer to the two electrons. **L** and **p** are the orbital angular momentum and the linear momentum of the electron. $\mathbf{S}_1$, $\mathbf{S}_2$, and **S** are the spins of the two electrons and their resultant. The expectation value of $\mathbf{H}'$ for the molecular state[12] consisting of the electronic state $c^3\Pi_u$, rotational state N, and fine-structure level J, is expressed as follows (after a proper transformation from a space-fixed coordinate system into a moving molecular co-

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* This work was supported by a grant from the National Science Foundation.

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[1] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1955).

[2] W. Lichten, Phys. Rev. **120**, 848 (1960).

[3] W. Lichten, Bull. Am. Phys. Soc. **7**, 43 (1963).

[4] L. Y. C. Chiu, J. Chem. Phys. **40**, 2276 (1964).

[5] W. Lichten, Phys. Rev. **126**, 1020 (1962).

[6] W. Lichten and P. Brooks (private communications). (The measurements are in progress.)

[7] P. Fontana, Phys. Rev. **125**, 220 (1962).

[8] D. A. Frey and M. Mizushima, Phys. Rev. **128**, 2683 (1962).

[9] J. C. Browne, J. Chem. Phys. **40**, 43 (1964).

[10] Preliminary results were presented in a communication, Lue-Yung Chow Chiu, J. Chem. Phys. **41**, 2197 (1964).

[11] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1957), 0. 181. See also Refs. 4 and 7.

[12] Here we neglect to average over the vibrational states. The averaging over the electronic state is to be taken at the equilibrium internuclear distance only.

ordinate system)[4,6]:

$$E'=(J,N,{}^3\Pi_u|\mathbf{H}'|J,N,{}^3\Pi_u)$$

$$=\frac{AC}{2N(N+1)}+\{(N^2+N-3)B_0+(\tfrac{3}{2})^{1/2}N(N+1)B_2\}$$

$$\times\frac{3C(C+1)-8N(N+1)}{4N(N+1)(2N-1)(2N+3)},\quad(1.2)$$

where

$$C=J(J+1)-N(N+1)-2;\quad A=A_1+A_2;$$
$$A_1=(\alpha^2/4)\langle(1/r_{1a}^3+1/r_{1b}^3)L_{1z}+(1/r_{2a}^3+1/r_{2b}^3)L_{2z}\rangle$$

is the spin-orbit coupling constant and $A_2=(3\alpha^2/4)\times\langle[(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_2-\mathbf{p}_1)]_z/r_{12}^3\rangle$ is the spin-other-orbit coupling constant; and $B_0=\alpha^2(4\pi/5)^{1/2}\langle Y_2^0(\mathbf{r}_{12})/r_{12}^3\rangle$ and $B_2=\alpha^2(4\pi/5)^{1/2}\langle Y_2^2(\mathbf{r}_{12})/r_{12}^3\rangle$ are the spin-spin coupling constants. These coupling constants are the expectation values[12] over the electronic wave function of the $c^3\Pi_u$ state. The subscript z here refers to the component along the molecular figure axis. If one neglects other higher order effects which have been discussed by Lichten,[5] these coefficients can be determined from measured energy separations by using Eq. (1.2), and they are shown in Table I. Fontana[7] has estimated these coefficients by using a hydrogenic (united-atom) model. With this simple estimate plus an error[13] of a factor of 2 too small in the spin-spin interaction part of the Eq. (1.2), he has obtained good agreement with the experimental energy separations.

2. ELECTRONIC WAVE FUNCTION

The electronic wave function of the $c^3\Pi_u$ state used here to evaluate the coupling constants is a linear combination of a Heitler-London-type wave function with coefficient C_H and an ionic type with coefficient C_I, and is expressed as follows:

$$\Phi=\tfrac{1}{2}C_H(1-\mathbf{P})[1s\sigma_a(1)2p\pi_b(2)+1s\sigma_b(1)2p\pi_a(2)]$$
$$+\tfrac{1}{2}C_I(1-\mathbf{P})[1s\sigma_a(1)2p\pi_a(2)+1s\sigma_b(1)2p\pi_b(2)],$$

where $1s\sigma_a(1)$ and $2p\pi_b(2)$ are the normalized Slater-type atomic orbitals, e.g.,

$$(2\zeta)^{n+1/2}(2n!)^{-1/2}r^{n-1}e^{-\zeta r}Y_l^m(\theta,\phi),$$

of electrons 1 and 2 centered on nuclei a and b, respectively. σ and π refer to the projection of the orbital-angular momentum (0 and 1) along the molecular-figure axis. The operator $\mathbf{P}$ permutes electrons 1 and 2. The wave function Φ is therefore antisymmetric with respect to interchange of the two electrons. It is also antisymmetric with respect to the inversion[14] of the electronic coordinates (*ungerade*). For a given set of values of orbital exponents, $\zeta_{1s\sigma}$ and $\zeta_{2p\pi}$, the values of C_H and C_I are obtained by a variational principle so as to minimize the total energy E of H_2 in a $c^3\Pi_u$ state. Their values are as follows:

$$\zeta_{1s\sigma}=1.24108,\ \zeta_{2p\pi}=0.50282,\ C_H=0.5612,\ C_I=0.2808,$$

and $E=-0.71879$ atomic units (a.u.) at equilibrium internuclear distance $R_e=1.96080$ a.u.

3. TWO-ELECTRON OPERATORS AND THEIR EXPANSIONS

Spin-spin and spin-other-orbit interactions are the operators involving the relative coordinates of two electrons. To evaluate their expectation values over the product of single-electron orbital wave functions, one has in general[15] to expand the operators into a series of products of one-electron operators. The two-electron operators $Y_2^0(\mathbf{r}_{12})/r_{12}^3$ and $Y_2^2(\mathbf{r}_{12})/r_{12}^3$ which appear in the spin-spin interaction are irregular solid spherical harmonics of the second order. The space part of spin-other-orbit interaction can be expressed as a linear combination of the irregular solid spherical harmonics of the first order, $Y_1^1(\mathbf{r}_{12})/r_{12}^2$ and $Y_1^{-1}(\mathbf{r}_{12})/r_{12}^2$ (see below). We therefore use Chiu's[16] general formula to expand the irregular solid spherical harmonics of any order n for the two-electron system as follows: For $r_2>r_1$ we have

$$\frac{Y_n^k(\mathbf{r}_{12})}{r_{12}^{n+1}}=\sum_{l=n}^{\infty}\sum_{m=-l}^{l}(-)^lF(l,n,k,m)\frac{r_1^{l-n}}{r_2^{l+1}}$$
$$\times Y_{l-n}^{k-m}(\mathbf{r}_1)Y_l^m(\mathbf{r}_2),\quad(3.1)$$

and for $r_1>r_2$ we have

$$\frac{Y_n^k(\mathbf{r}_{12})}{r_{12}^{n+1}}=\sum_{l=n}^{\infty}\sum_{m=-l}^{l}(-)^{l+n}F(l,n,k,m)\frac{r_2^{l-n}}{r_1^{l+1}}$$
$$\times Y_{l-n}^{k-m}(\mathbf{r}_2)Y_l^m(\mathbf{r}_1),\quad(3.2)$$

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[13] This error has been pointed out in Ref. 4, footnote 20.

[14] The inversion is achieved by a rotation of 180° around the z axis (which gives -1 for the π state) followed by a reflection in the x-y plane (which is equivalent to interchanging nuclei a and b).

[15] A convolution theorem for Fourier transforms has recently been introduced by F. P. Prosser and C. H. Blanchard [J. Chem. Phys. **36**, 1112 (1962)] to evaluate two-center integrals. M. Geller [J. Chem. Phys. **39**, 853 (1963); **40**, 2309 (1964)] has applied it to the integrals where two-electron operators (e.g., irregular spherical harmonics) are involved. In this case one uses the proper Fourier transform of the operator (instead of expanding it). The region $r_1=r_2$ is included in the transform and no extra delta-function term is needed. Although this method is very elegant, it can treat Coulombic-type two-center integrals only, and furthermore, it is rather difficult to treat all cases with generality.

[16] Y. N. Chiu, J. Math. Phys. **5**, 283 (1964).

where

$$F(l,n,k,m)=[4\pi(2l)!/(2n)!(2l-2n+1)!]^{1/2}\times C(l-n,l,n;k-m,m) \quad \text{and} \quad |k|\leq n;$$

$C(l-n,l,n;k-m,m)$ is the Clebsch-Gordan coefficient[17]; and $\mathbf{r}_1$ and $\mathbf{r}_2$ refer to the same origin. The above expansion can be centered on either nucleus a or nucleus b. When $n=2$, we have the expansion for the space part of the spin-spin interaction. In this case a delta-function term,[18] $-(4\pi/3)Y_2^k(\mathbf{r}_1)\delta(\mathbf{r}_1-\mathbf{r}_2)$, should be included to take care of the region $r_1=r_2$. Although such a delta-function term will contribute zero value when evaluated over a triplet-state wave function, it must be included during the process of calculating each individual two-center integral, for it is evident that two-center integral of the delta-function term alone will give different values depending on whether the delta function is to be centered on a or b. Consequently, the integral which excludes the delta-function term will take on different values depending on whether the operator is expanded on center a or center b. The series expansions in (3.1) and (3.2) will be truncated after the integration over the angular coordinates of one of the electrons. The remaining two-center[15] and one-electron integrals were evaluated numerically on an IBM-7094 computer using Barnett and Coulson's[19] method of expanding the exponential function of center a into that of center b (or vice versa). In the case of an exchange-type integral i.e., $\langle u_a(1)v_b(2), \mathbf{H}'v_a(2)u_b(1)\rangle$ (where both electrons are spread out over the orbitals centered on both a and b), the angular coordinates of one of the electrons cannot be integrated to truncate the series. We use Mulliken's[20] approximation to convert the above exchange-type integral into a linear combination of hybrid-type integrals, i.e., $\langle u_a(1)v_b(2), \mathbf{H}'v_a(2)u_a(1)\rangle$, and $\langle u_b(1)v_b(2), \mathbf{H}'v_a(2)u_b(1)\rangle$, where one can integrate analytically coordinates of one of the electrons (electron 1 in this case). Such an approximation is estimated to give an uncertainty of less than 10% for each individual integral,[21] but over all it will give an uncertainty of only a little more than 1% (less than 2%) to the expectation value.

Now we consider the space part of the spin-other-orbit operator. It can be expressed as follows (using the relation $\mathbf{p}=-i\boldsymbol{\nabla}$):

$$\frac{3\alpha^2}{4}\frac{[(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_2-\mathbf{p}_1)]_z}{r_{12}^3} =\frac{3\alpha^2}{4}\left(\frac{4\pi}{3}\right)^{1/2}\left\{\frac{Y_1^1(\mathbf{r}_{12})}{r_{12}^2}[\nabla_1^{(-1)}-\nabla_2^{(-1)}] +\frac{Y_1^{-1}(\mathbf{r}_{12})}{r_{12}^2}[\nabla_2^{(1)}-\nabla_1^{(1)}]\right\}, \quad (3.3)$$

where

$$\nabla_1^{(1)}=-\frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial x_1}+i\frac{\partial}{\partial y_1}\right), \quad \nabla_1^{(-1)}=\frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial x_1}-i\frac{\partial}{\partial y_1}\right)$$

and

$$\nabla_1^{(0)}=\frac{\partial}{\partial z_1}$$

are the gradient operators expressed as the components of a first-rank spherical tensor. $Y_1^1(\mathbf{r}_{12})/r_{12}^2$ and $Y_1^{-1}(\mathbf{r}_{12})/r_{12}^2$ are irregular solid spherical harmonics of the first order and they can be expanded according to (3.1) and (3.2). The operation of the above spherical gradients on Slater-type orbitals (Sec. 2) can be expressed as follows by using Rose's[22] gradient formula.

$$\begin{aligned}\nabla^{(k)}[r^l e^{-\zeta r}Y_l^m(\mathbf{r})] &=-(2l+1)^{1/2}\{(l+1)^{1/2}C(l+1,1,l;m+k,-k)\\ &\quad\times(\zeta r^l e^{-\zeta r})Y_{l+1}^{m+k}(\mathbf{r})+l^{1/2}C(l-1,1,l;m+k,-k)\\ &\quad\times[-\zeta r^l+(2l+1)r^{l-1}](e^{-\zeta r})Y_{l-1}^{m+k}(\mathbf{r})\}, \end{aligned}\quad (3.4)$$

where $k=1, 0, -1$, and $C(l\pm1,1,l;m+k,-k)$ is the Clebsch-Gordan coefficient.[17] It will be of greater convenience to regroup the operators in (3.3) into the following:

$$\frac{3\alpha^2}{4}\left(\frac{4\pi}{3}\right)^{1/2}\left\{\left[\frac{Y_1^1(\mathbf{r}_{12})}{r_{12}^2}\nabla_1^{(-1)}-\frac{Y_1^{-1}(\mathbf{r}_{12})}{r_{12}^2}\nabla_1^{(1)}\right] +\left[\frac{Y_1^{-1}(\mathbf{r}_{12})}{r_{12}^2}\nabla_2^{(1)}-\frac{Y_1^1(\mathbf{r}_{12})}{r_{12}^2}\nabla_2^{(-1)}\right]\right\}. \quad (3.5)$$

Both brackets in the above expression are therefore Hermitian. Because of the symmetry between the two terms in each bracket, cancellation arises when these operate on the product wave functions (Slater orbitals) and consequently the integrals are simpler to evaluate.

4. PERTURBATIONS BY OTHER ROTATIONAL STATES

The energy separation between rotational states is about 10^3 times larger than the fine-structure separation. The second-order energy correction $E^{(2)}$ due to

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[17] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1957), p. 76–77.

[18] R. M. Pitzer, C. W. Kern, and W. N. Lipscomb, J. Chem. Phys. **37**, 267 (1962); see also Ref. 16, footnote 18.

[19] M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. (London) **A243**, 221 (1951); *Methods in Computational Physics*, edited by B. Alder (Academic Press, Inc., New York, 1963), Vol. 2, p. 95 and p. 155.

[20] R. S. Mulliken, J. Chim. Phys. **46**, 500 and 521 (1949); K. Rudenberg, *ibid.* **19**, 1433 (1951).

[21] The quoted uncertainty limit 10% for the Mulliken's approximation here was obtained by comparing the results of an exact calculation of all the hybrid-type integrals involved with the approximate calculation of the same integrals.

[22] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1961), p. 124.

the perturbation from nearby rotational states via fine-structure interactions is therefore very small. The off-diagonal matrix elements[4] (for *para* H_2 of even N level and *ortho* H_2 of odd N level) are the following:

$$(J,N-1,{}^3\Pi_u|\mathbf{H}'|J,N,{}^3\Pi_u)=-\left[\frac{(J+N+2)(J-N+2)(J+N-1)(N-J+1)}{(N+1)(2N+1)(N-1)(2N-1)}\right]^{1/2}\times\left\{\tfrac{3}{4}[N^2+1-J(J+1)]\left[\frac{B_0}{N}-\frac{B_2}{\sqrt{6}}\right]+\frac{N^2-1}{2N}A\right\}\quad(4.1)$$

and

$$(J,N+1,{}^3\Pi_u|\mathbf{H}'|J,N,{}^3\Pi_u)=-\left[\frac{(J+N+3)(J-N+1)(J+N)(N-J+2)}{(N+2)(2N+3)(N)(2N+1)}\right]^{1/2}\times\left\{\tfrac{3}{4}[N(N+2)-(J-1)(J+2)]\left[\frac{B_0}{N+1}+\frac{B_2}{\sqrt{6}}\right]+\frac{N(N+2)}{2(N+1)}A\right\}.\quad(4.2)$$

The $\mathbf{H}'$ here is defined in (1.1) and does not connect states of $N=0$ and $N=1$.[23] By substituting the calculated values of A, B_0, and B_2 (see Table I) into (4.1) and (4.2), we obtain the correction $E^{(2)}$ on fine-structure levels as follows:

For $N=2$ of *para* H_2 we have

$$E^{(2)}(J=3)=-0.30\text{ Mc/sec},\quad E^{(2)}(J=2)=-1.7\text{ Mc/sec},\quad E^{(2)}(J=1)=0.13\text{ Mc/sec};\quad(4.3)$$

and for $N=1$ of *ortho* H_2 we have

$$E^{(2)}(J=2)=-0.42\text{ Mc/sec},\quad E^{(2)}(J=1)=-7.9\text{ Mc/sec},\quad E^{(2)}(J=0)=0.\quad(4.4)$$

A typical fine-structure splitting is of the order of 5 kMc/sec; these corrections contribute only about 0.1% or less.

TABLE I. Fine-structure coupling constants of the $c^3\Pi_u$ state of H_2.

Coupling constants[a]	Calc. (kMc/sec)	Expt. (kMc/sec)[b]	Expt. (kMc/sec) with $E^{(2)}$ correction[c]
A_1	$+5.737$	...	...
A_2	-9.8	...	...
$A=A_1+A_2$	-4.1	-3.822144	-3.82249
B_0	-1.33	...	...
B_2	-3.84	...	...
$B_0+(6)^{1/2}B_2$	-10.8	-12.40410	-12.4079

[a] A_1 is due to spin-orbit interaction; A_2 is due to spin-other-orbit interaction; B_0 and B_2 are due to spin-spin interaction.

[b] Calculated from Lichten's experimental fs splittings (Ref. 5) using Eq. (1.2).

[c] Measured fs splittings were corrected by perturbations from the nearby rotational states (Sec. 4).

5. RESULTS

The calculated coupling constants A_1, A_2, A, B_0, and B_2 which are defined in Eq. (1.2) are presented here in Table I. These constants were evaluated at the equilibrium internuclear distance instead of being averaged over the vibrational wave function. The failure to average over the vibrational state was estimated by Lichten[5] to give an uncertainty of 5%, which is larger than all the other higher order effects in their contributions to the fine-structure splittings. In the last column of Table I, the measured fine-structure splittings were first corrected by the second-order energy due to perturbations from nearby rotational states (see Sec. 4), and then substituted in Eq. (1.2) to obtain the coupling constants. These values are very close to the values in the column to the left where no corrections were made.

ACKNOWLEDGMENTS

The author is indebted to Professor W. Lichten, who sponsored this research for his continued interest, encouragement, and useful comments. She wishes to thank Dr. Y. N. Chiu for fruitful discussions throughout the course of this work. She is also grateful to Mrs. E. Schwartz for her help in computing the electronic wave function, and Dr. W. Huo for the use of subroutines of special functions.

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[23] It is evident from (4.1) and (4.2) that the spin-orbit interaction does not connect $N=0$ and $N=1$ states. For the case of spin-spin interaction where the operator is a second-rank tensor, the triangular relation for vector coupling $\Delta(2,N,N')$ cannot be satisfied for $N=0$ and $N'=1$ [see Ref. 4, Eq. (3.5) and footnote 15]. The matrix element therefore vanishes.