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Quantum Mechanics of a Double Perturbation: Application to the Zeeman Effect of Metastable Hydrogen Molecules*

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A general theorem is derived which applies to any quantum-mechanical system subject to two perturbations H and G . It is shown that the eigenvalues of the system can be found by first solving exactly the secular equation in H . Then the first-order perturbation of the energy by G can be written explicitly without solving for the eigenfunctions. This leads to a simple method for finding the exact Landé g factors for the Zeeman effect of any quantum-mechanical system. These results are applied to the Zeeman effect of the hydrogen molecule in the metastable $c^3\pi_u$ state. Jette and Cahill's theory of the Zeeman effect is extended to cover all magnetic fields. Excellent agreement is found between experimental g factors and theory. At higher magnetic fields, "anti-crossings" are found between pairs of states for which $\Delta J = \pm 1, \pm 2$, $\Delta F = 0, \pm 1, \pm 2$, and $\Delta M_F = 0$. The repulsion between these levels is very small, of the order of a few Mc/sec. This causes the noncrossing rule of von Neumann and Wigner to be violated experimentally. The Landau-Zener theory of level crossings is applied. It is shown that the observed loss of quantization in the molecular-beam experiments is consistent with theory.

I. INTRODUCTION AND HISTORICAL SUMMARY

This paper is concerned with perturbation theory, which is commonly applied to the problem of magnetism in atoms, molecules, nuclei, and solids. Although the lodestone was known to the ancient world, Michael Faraday¹ was the first man to observe and distinguish the two forms of diamagnetism and paramagnetism. Maxwell's macroscopic equations for the electric and magnetic fields were extended to the microscopic world by Lorentz.² Classical electron theory predicted the effect of the surrounding media on the internal electric and magnetic fields of atoms or molecules.^{2,3}

The advent of the precise molecular-beam magnetic-resonance experiments by Rabi and co-workers⁴ made it necessary to consider the magnetic field produced within an atom by its own diamagnetism. Lamb⁵ derived an expression for the diamagnetic shielding in spherically symmetric atoms. The paramagnetic nuclear or electronic moment of an atom interacts so as to produce an energy which is linearly dependent on the external field:

$$E = -\vec{\mu} \cdot \vec{B}. \quad (1)$$

The diamagnetic interaction produces an additional field which is linearly dependent on the external magnetic vector:

$$\vec{B} = \vec{B}_{\text{ext}} + \vec{B}_{\text{int}} = (1 - \sigma) \vec{B}, \quad (2)$$

which effectively reduces the paramagnetic moment by the shielding factor σ . Equivalently, the internal paramagnetic moment produces a polarization of the diamagnetic charge cloud, which interacts with the external field to produce the same result as in Eq. (2). Lamb calculated the shielding factor to be $\sigma = 0.319 \times 10^{-4} Z^{4/3}$, on the basis of the Fermi-Thomas atom model, which gives a shift normally a small fraction of a percent.

The nuclear-magnetic-resonance technique, invented by Bloch *et al.* and Purcell *et al.*,⁶ opened the way to observing the nuclear coupling with external fields in a wide variety of chemical surroundings. Soon it was found that the shielding factor of (2) varied from one molecule to another. Ramsey⁷ developed an extension of Van Vleck's theory of magnetism³ to explain the "chemical shift." He pointed out that the shift can be large when a paramagnetic state is nearby to perturb the diamagnetic state in question.

At that time, Kusch⁸ found a discrepancy of about 0.7% between the magnetic moments of Ga isotopes as measured in nuclear magnetic resonances and molecular-beam experiments, which were done on atoms in the paramagnetic 2P states. Foley⁹ showed that this discrepancy was caused by a partial break-

down in L - S coupling by the nuclear hyperfine interaction. A second-order cross perturbation between the matrix elements of the hyperfine interaction, coupling the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states, and the matrix elements of the applied field caused a deviation in the observed nuclear magnetic moment.

Pryce¹⁰ calculated the second-order cross terms between the spin-orbit interaction and magnetic moment for the spin Hamiltonian¹¹ for electron paramagnetic resonance in crystals. Not only did he find large shifts in the electron magnetic moment, but he found that the field interaction had a tensor form

$$E = \sum_{i,j} g_{ij} S_i B_j. \quad (3)$$

The history of physics is full of surprises caused by unsuspected small admixtures of impurities in wave functions. If a wave function is written as

$$\Psi_0 = a \Psi_1 + b \Psi_2, \quad (4)$$

the expectation value of a perturbation G in the Hamiltonian is given by

$$\langle 0 | G | 0 \rangle = a^2 \langle 1 | G | 1 \rangle + 2ab \langle 1 | G | 2 \rangle + b^2 \langle 2 | G | 2 \rangle. \quad (5)$$

Even with a wave function with an impurity of only 1% ($b^2 = 0.01$), the deviation of the expected interaction in (5) can be 20% ($2ab = 0.20$); or even larger, if the cross term is unusually large.¹²

Well-known examples of such interference terms are Fermi's theory of the perturbation of the alkali doublet line-strength ratios by spin-orbit interaction¹³; Fermi and Segre's explanation of the anomalous hyperfine structure in atoms, caused by small amounts of configuration interaction involving s electron excitation¹⁴; Rarita and Schwinger's explanation of the quadrupole moment of the deuteron¹⁵; and Franken's discovery of interference effects in resonance fluorescence.¹⁶

In the linear Zeeman effect of an atomic system, for a small magnetic field B , the degenerate energy levels of a particular state are given by the expression

$$E(B) = Mg\mu_B B, \quad (3')$$

where E denotes the energy, g is a dimensionless number called the Landé g factor, μ_B is the Bohr magneton ($\mu_B/h = 1.4$ Mc/sec G), M is the z component of angular momentum, and B is the magnetic field in G. In certain cases, the various angular momenta of a system couple in such a way that it is an elementary matter to calculate the g factors. Examples of these coupling cases are L - S and j - j in atoms, and Hund's case a , b , c , and d in molecules. Because of perturbations, the zero-field eigenfunctions of an atomic system are generally a mixture of simple coupling cases. The g factors are very sensitive to this admixture, since interference terms can cause the deviations

from the ideal to be first order in the coefficients. This paper begins with a general theorem on the Zeeman effect and other perturbations, with an application to the particular case of a diatomic molecule in near case b coupling. In particular, this paper is concerned with the Zeeman effect of the hydrogen molecule in the $c^3\pi_u$ state. The discovery¹⁷ of large deviations of experimental Landé g factors from those expected from simple coupling approximations was the original motivation for theoretical studies by Chiu.¹⁸ She calculated the g factors to second order in perturbation theory. Jette and Cahill¹⁹ calculated the Zeeman effect to all orders in the internal interactions of the molecule and gave the linear terms in the dependence on the external magnetic field. Discrepancies between observed and expected intensities in molecular-beam experiments¹⁷ indicated unusual behavior of the energy levels in the high magnetic fields of the deflecting magnets. In order to understand these peculiar experimental results, it was desirable to understand the behavior of the molecule in strong fields. The present paper extends the calculation to the Paschen-Back region.

II. GENERAL RESULT IN PERTURBATION THEORY

Consider a quantum-mechanical system of n states, subject to a Hamiltonian operator \mathcal{H} which is the sum of two terms \mathcal{F} and \mathcal{G} . We consider the case that the matrix \underline{G} is a linear perturbation of the form $\underline{G} = \underline{g}\lambda$, where λ is a parameter. The matrix elements are given by the usual expressions

$$F_{ij} = \int \Psi_i \mathcal{F} \Psi_j d\tau, \quad (6)$$

the "zero-field" Hamiltonian, and

$$G_{ij} = \lambda g_{ij} = \int \Psi_i \mathcal{G} \Psi_j d\tau, \quad (7)$$

the "Zeeman" or "Paschen-Back" terms, where Ψ_i is the i th wave function, i runs from 1 to n , and $d\tau$ is the element of configuration space. We assume all the Ψ 's to be real. The secular equation of the system is

$$\begin{vmatrix} F_{11} + G_{11} - E & F_{12} + G_{12} & \cdots & F_{1n} + G_{1n} \\ F_{21} + G_{21} & F_{22} + G_{22} - E & \cdots & F_{2n} + G_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} + G_{n1} & F_{n2} + G_{n2} & \cdots & F_{nn} + G_{nn} - E \end{vmatrix} = 0. \quad (8)$$

First we turn off the G perturbation, by setting $\lambda = 0$. This gives us the n eigenvalues, which represent the energy levels at "zero field," the n roots of the determinantal equation

$$|F_{ij} - E\delta_{ij}| = 0. \quad (9)$$

We assume no accidental degeneracies, so that all

these levels are distinct. We also assume all matrix elements to be real.

We now try to find a solution of the form $E = E_0 + g\lambda$,

where E_0 is an eigenvalue of (9). We expand the determinant in ascending powers of the expansion parameter λ . Substitution of (7) in (8) gives us

$$\begin{vmatrix} F_{11} - E_0 + (g_{11} - g)\lambda & F_{12} + g_{12}\lambda & \cdots & F_{1n} + g_{1n}\lambda \\ F_{21} + g_{21}\lambda & F_{22} - E_0 + (g_{22} - g)\lambda & \cdots & F_{2n} + g_{2n}\lambda \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} + g_{n1}\lambda & F_{n2} + g_{n2}\lambda & \cdots & F_{nn} - E_0 + (g_{nn} - g)\lambda \end{vmatrix} = \begin{vmatrix} F_{11} - E_0 & F_{12} & \cdots & F_{1n} \\ F_{21} & F_{22} - E_0 & \cdots & F_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} & F_{n2} & \cdots & F_{nn} - E_0 \end{vmatrix} \\ + \begin{vmatrix} g_{11} - g & g_{12} & \cdots & g_{1n} \\ F_{21} & F_{22} - E_0 & \cdots & F_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} & F_{n2} & \cdots & F_{nn} - E_0 \end{vmatrix} \times \lambda + \begin{vmatrix} F_{11} - E_0 & F_{12} & \cdots & F_{1n} \\ g_{21} & g_{22} - g & \cdots & g_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} & F_{n2} & \cdots & F_{nn} - E_0 \end{vmatrix} \times \lambda \\ + \cdots + \begin{vmatrix} F_{11} - E_0 & F_{12} & \cdots & F_{1n} \\ F_{21} & F_{22} - E_0 & \cdots & F_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ g_{n1} & g_{n2} & \cdots & g_{nn} - g \end{vmatrix} \times \lambda + \text{terms of higher order in } \lambda = 0. \quad (10)$$

The first determinant, which is zero order in λ , vanishes because of expression (9). The sum of the remaining n determinants vanishes, if we ignore the higher-order terms in (10). This sum can be written

$$\lambda \sum_{i,j} (g_{ij} - \delta_{ij}g) \mathfrak{F}_{ij} = 0, \quad (11)$$

where \mathfrak{F}_{ij} is the cofactor of the elements $F_{ij} - \delta_{ij}E_0$ of the "zero-field" Hamiltonian matrix, with the diagonal eigenvalue matrix subtracted. We can solve Eq. (11) for the g factor and obtain

$$g = \sum_{i,j} \frac{g_{ij} \mathfrak{F}_{ij}}{\text{Tr}(\mathfrak{F})},$$

where \mathfrak{F} denotes the matrix with elements \mathfrak{F}_{ij} . By the Hermitian character of the real matrix, we have $\mathfrak{F}_{ij} = \mathfrak{F}_{ji}$. This gives us the nice result that

$$g = \text{Tr}(g\mathfrak{F}) / \text{Tr}(\mathfrak{F}), \quad (12)$$

which is exact to all orders in the "zero-field" perturbation \mathfrak{F} and is correct to first order in the

"magnetic field" parameter λ . Thus, it gives the exact g factors. This solution has the advantage of requiring only the n eigenvalues, not the n^2 coefficients of the eigenfunctions, which are the solutions to Eq. (9).²⁰

Although the language of the Zeeman effect has been used in this derivation, the result is clearly a general one for perturbation theory.

III. ZEEMAN EFFECT OF MOLECULES IN CASE b

Jette and Cahill¹⁹ obtained expressions for the diagonal and nondiagonal matrix elements of the magnetic hyperfine-structure (hfs) interaction, for a homonuclear diatomic molecule of arbitrary electronic state and spin in case b , where the "good" quantum numbers are $FM_F IJS\Lambda$. By considering the off-diagonal terms in J , they obtained a wave function

$$\Psi_{FM_F} = \sum_J c_J \psi(FM_F J I), \quad (13)$$

where the sum was over all J values. This wave function was obtained by diagonalization of the hfs matrix which has the following elements¹⁹:

$$\langle \gamma J I; FM_F | \mathfrak{H}_{\text{hfs}} | \gamma J I; FM_F \rangle = \left[\frac{\alpha \Lambda^2}{N(N+1)} \vec{N} \cdot \vec{J} + \alpha_F \vec{J} \cdot \vec{S} + \frac{6}{(2N-1)(2N+3)} \left(\frac{(\vec{N} \cdot \vec{S})(\vec{J} \cdot \vec{N})}{N(N+1)} - \frac{\vec{J} \cdot \vec{S}}{3} \right) \right] \\ \times \left\{ [3\Lambda^2 - N(N+1)]^{\frac{1}{2}} c_{\pm} (-)^N N(N+1)^{\frac{1}{2}} d \right\} \frac{\vec{I} \cdot \vec{J}}{J(J+1)}, \quad (14)$$

$$\langle \gamma J - 1 I; FM_F | \mathfrak{H}_{\text{hfs}} | \gamma J I; FM_F \rangle$$

$$= \frac{M_{J-1,J}}{4J} \left[-\frac{\alpha}{N(N+1)} + \alpha_F + \frac{1}{2} \left(\frac{(S+N-J)(S+J+1-N)}{N^2(2N+1)(2N-1)} - \frac{2N \cdot S}{N^2(N+1)^2} - \frac{(J+S+N+2)(J+N+1-S)}{(N+1)^2(2N+1)(2N+3)} \right) \right]$$

$$\times \left\{ [3\Lambda^2 - N(N+1)]^{\frac{1}{2}} c \pm (-)^N N(N+1)^{\frac{1}{2}} d \right\}, \quad (15)$$

where

$$M_{J-1, J} = \left(\frac{(F+I+J+1)(I+J-F)(F+J-I)(F+I+1-J)(N+S+J+1)(S+J-N)(J+N-S)(N+S-J+1)}{(2J-1)(2J+1)} \right)^{1/2}, \quad (16)$$

$$\vec{J} = \vec{N} + \vec{S}, \quad \vec{F} = \vec{J} + \vec{I},$$

$$\vec{N} \cdot \vec{S} = \frac{1}{2} [J(J+1) - N(N+1) - S(S+1)], \quad \vec{S} \cdot \vec{J} = \frac{1}{2} [J(J+1) + S(S+1) - N(N+1)], \quad (17)$$

$$\vec{N} \cdot \vec{J} = \frac{1}{2} [J(J+1) + N(N+1) - S(S+1)], \quad \vec{I} \cdot \vec{J} = \frac{1}{2} [F(F+1) - I(I+1) - J(J+1)].$$

The diagonal elements of the fine structure are

$$\langle \gamma NSJI; FM_F | \mathcal{H}_{fs} | \gamma NSJI; FM_F \rangle = \frac{\Lambda A \vec{N} \cdot \vec{S}}{N(N+1)} + \frac{[3\vec{N} \cdot \vec{S}(2\vec{N} \cdot \vec{S} + 1) - 4N(N+1)]}{2[N(N+1)(2N-1)(2N+3)]} \{ [N(N+1) - 3\Lambda^2] B_0 \pm (-)^{N+1} \sqrt{\frac{3}{2}} N(N+1) B_2 \}. \quad (18)$$

In the case of very weak magnetic fields, the wave function given by Eq. (13) can be used to calculate the linear Zeeman splittings. The interaction with the external magnetic field is given by

$$\mathcal{H}_Z = g_s \mu_B \vec{S} \cdot \vec{B} + \mu_B \sum_j \vec{I}_j \cdot \vec{B} - g_I \mu_N \vec{I} \cdot \vec{B}, \quad (19)$$

and the energy levels are given by

$$E_{FM_F}(\mathcal{J}) = \sum_{J, J'} C_J C_{J'} \langle \gamma J' I; FM_F | \mathcal{H}_Z | \gamma J I; FM_F \rangle, \quad (20)$$

where \mathcal{J} is used to denote that J is no longer a good quantum number. It is evident from (\wedge) that the

low-field linear Zeeman effect necessitates only use of the matrix elements of \mathcal{H}_Z which are diagonal in F .

IV. GENERAL SOLUTION: NONLINEAR ZEEMAN EFFECT

For higher fields, for which the linear theory no longer holds, it is also necessary to consider matrix elements which are not diagonal in F . It is a relatively straightforward matter to extend Jette and Cahill's evaluation of matrix elements to these cases. By the Wigner-Eckart theorem we have

$$\langle \gamma J' I; F' M_F | g_s \mu_B \vec{S} \cdot \vec{B} | \gamma J I; FM_F \rangle = (-)^{F'-M_F} g_s \mu_B B_z \begin{pmatrix} F' & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \langle \gamma J' I; F' || S || \gamma J I; F \rangle. \quad (21)$$

The reduced matrix element on the right in the uncoupled representation of J and I is

$$\langle \gamma J' I; F' || S || \gamma J I; F \rangle = (-)^{J'+I+F+1} (2F+1)^{1/2} (2F'+1)^{1/2} \begin{Bmatrix} J' & F & I \\ F & J & 1 \end{Bmatrix} \langle \gamma NS; J' || S || \gamma NS; J \rangle, \quad (22)$$

where

$$\langle \gamma NS; J' || S || \gamma NS; J \rangle = (-)^{N+S+J'+1} [(2J'+1)(2J+1)S(S+1)(2S+1)]^{1/2} \begin{Bmatrix} S & J' & N \\ J & S & 1 \end{Bmatrix}. \quad (23)$$

Similarly, the orbital interaction is given by

$$\langle \gamma J' I; F' M_F | \mu_B \sum_j \vec{I}_j \cdot \vec{B} | \gamma J I; FM_F \rangle = (-)^{F'-M_F} \mu_B B_z \begin{pmatrix} F' & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \langle \gamma J' I; F' || \sum_j I_j || \gamma J I; F \rangle, \quad (24)$$

where

$$\langle \gamma J' I; F' || \sum_j I_j || \gamma J I; F \rangle = (-)^{J'+I+F+1} (2F+1)^{1/2} (2F'+1)^{1/2} \begin{Bmatrix} J' & F' & I \\ F & J & 1 \end{Bmatrix} \langle \gamma NS; J' || \sum_j I_j || \gamma NS; J \rangle, \quad (25)$$

$$\langle \gamma NS; J' || \sum_j I_j || \gamma NS; J \rangle = (-)^{N+S+J'+1} [(2J+1)(2J'+1)]^{1/2} \begin{Bmatrix} N & J' & S \\ J & N & 1 \end{Bmatrix} \frac{(2N+1)\Lambda^2}{[N(N+1)(2N+1)]^{1/2}}. \quad (26)$$

The nuclear Zeeman term is given by

$$\langle \gamma J' I; F' M_F | -g_I \mu_N \vec{I} \cdot \vec{B} | \gamma J I; F M_F \rangle = -(-)^{F'-M_F} g_I \mu_N B_z \begin{pmatrix} F' & 1 & F \\ -M_F & 0 & M_F \end{pmatrix} \langle \gamma J' I; F' || I || \gamma J I; F \rangle, \quad (27)$$

$$\langle \gamma J' I; F' || I || \gamma J I; F \rangle = (-)^{J+I+F'+1} \delta_{J',J} (2F+1)^{1/2} (2F'+1)^{1/2} \begin{Bmatrix} I & F' & J \\ F & I & 1 \end{Bmatrix} [I(I+1)(2I+1)]^{1/2}, \quad (28)$$

where there are no off-diagonal terms in J . Note that the convention here, which Jette and Cahill used, follows the usage of nuclear physics, rather than the molecular-beams literature. The g_I factor is unity for a positive nuclear moment of $1 \mu_N$. Hereafter, we shall follow the usual molecular-beams notation, where a nuclear moment of $1 \mu_N$ has a g_I factor of $-(M_0/M_p) = -\frac{1}{1836}$.

Before these expressions are evaluated, it is convenient to lump the matrix elements into different categories. These are listed in the expressions which follow:

$$H_{J J F F}(J F M I) = \langle \gamma J I; F M | \mathcal{H}_Z | \gamma J I; F M \rangle: \\ J' = J, F' = F; \quad (29)$$

$$H_{J J F P}(J F M I) = \langle \gamma J I; F+1 M | \mathcal{H}_Z | \gamma J I; F M \rangle: \\ J' = J, F' = F+1; \quad (30)$$

$$H_{J P F F}(J F M I) = \langle \gamma J+1 I; F M | \mathcal{H}_Z | \gamma J I; F M \rangle: \\ J' = J+1, F' = F; \quad (31)$$

$$H_{J N F P}(J F M I) = \langle \gamma J-1 I; F+1 M | \mathcal{H}_Z | \gamma J I; F M \rangle: \\ J' = J-1, F' = F+1. \quad (32)$$

In general, there are nine different matrix elements with all possible combinations $J' = J, J \pm 1$; $F' = F, F \pm 1$. However, all can be obtained from the five (See Note added in proof.) basic elements [(29-32)] by use of the Hermitian character of H_Z . For example,

$$\langle \gamma J+1 I; F-1 M_F | \mathcal{H}_Z | \gamma J I; F M_F \rangle \\ = \langle \gamma J I; F M_F | \mathcal{H}_Z | \gamma J+1 I; F-1 M_F \rangle \\ = \langle \gamma J'-1 I; F'+1 M_F | \mathcal{H}_Z | \gamma J' I; F' M_F \rangle,$$

where

$$J' = J+1, \quad F' = F-1.$$

Explicit expressions for these quantities can be obtained by evaluating the 3- j and 6- j symbols, and by substituting Eqs. (21), (24), and (27) into Eqs. (19) and (20). The results for the matrix elements diagonal in F have been obtained by Jette and Cahill. We write those elements which are diagonal in J :

$$H_{J J F F}(J F M I) = M B_z \mu_B g_F,$$

where

$$g_F = [F(F+1)]^{-1} (g_J \vec{F} \cdot \vec{J} + g_I \vec{F} \cdot \vec{I}), \\ g_J = [J(J+1)]^{-1} (g_S \vec{S} \cdot \vec{J} + g_N \vec{N} \cdot \vec{J}),$$

where

$$g_N = \Lambda^2 / [N(N+1)], \quad (33)$$

$$g_S = 2.0023,$$

$$g_I = -0.00302;$$

$$\vec{F} \cdot \vec{J} = \frac{1}{2} [F(F+1) + J(J+1) - I(I+1)], \quad (34)$$

$$\vec{F} \cdot \vec{I} = \frac{1}{2} [F(F+1) + I(I+1) - J(J+1)].$$

The matrix elements diagonal in J , but off-diagonal in F , are given by the expression

$$H_{J J F P}(J F M I) = \frac{(g_J - g_I) \mu_B B_z}{2(F+1)} \left(\frac{[(F+1)^2 - M^2] (I+F+J+2) (-I+F+J+1) (I+F-J+1) (I-F+J)}{(2F+1)(2F+3)} \right)^{1/2}. \quad (35)$$

These matrix elements off-diagonal in J , but diagonal in F (previously given by Jette and Cahill) are given by the expression

$$H_{J P F F}(J F M I) = \frac{M B_z \mu_B (g_S - g_N)}{F(F+1) 4(J+1)} \left(\frac{(N+S+J+2) (-N+S+J+1) (N-S+J+1) (N+S-J)}{(2J+1)(2J+3)} \right. \\ \left. \times (I+F+J+2) (-I+F+J+1) (I-F+J+1) (I+F-J) \right)^{1/2}. \quad (36)$$

The matrix elements off diagonal in J and F are of the two types:

$$H_{JNFP}(JFMI) = \frac{\mu_B B_Z (g_S - g_N)}{4J(F+1)} \left(\frac{(N+S+J+1)(-N+S+J)(N-S+J)(N+S-J+1)}{(2J-1)(2J+1)(2F+1)(2F+3)} \right)^{1/2} \times (I+F-J+1)(I+F-J+2)(I-F+J-1)(I-F+J)[(F+1)^2 - M^2]^{1/2}, \quad (37)$$

$$H_{JPPF}(JFMI) = \frac{-\mu_B B_Z (g_S - g_N)}{4(J+1)(F+1)} \left(\frac{(N+S+J+2)(-N+S+J+1)(N-S+J+1)(N+S-J)}{(2J+1)(2J+3)(2F+1)(2F+3)} \right)^{1/2} \times (I+F+J+2)(I+F+J+3)(-I+F+J+1)(-I+F+J+2)[(F+1)^2 - M^2]^{1/2}. \quad (38)$$

The following checks are made on the computations:

(a) Matrix elements diagonal in J are checked to make sure that agreement is achieved with Jette and Cahill.²¹

(b) The entire calculation is done independently by the vector matrix elements listed in Condon and Shortley.²²

(c) Additional checks on the computation are made after the matrix elements are inserted in a computer program. These checks are described in Sec. V.

V. COMPUTER CALCULATIONS: LINEAR ZEEMAN EFFECT

The matrix elements are used to set up a Hamiltonian matrix which is diagonalized by the Jacobi method.²³ The program is written in version 13 of the FORTRAN IV language and the computations are done on the Yale 7090/7094 direct coupled system.

The problem is done by three independent methods:

(a) The matrix elements of the fs and hfs interaction are calculated from the constants and by the method of Jette and Cahill,¹⁹ by use of expressions (14)–(17). The calculated energy levels are compared with the seven experimental energy levels²⁴ of the hydrogen molecule, $c^3\pi_u$; $N=1$; $J=1$, $F=2, 1, 0$; $J=2$, $F=3, 2, 1$; and $J=0$, $F=1$. A best fit is obtained for the constants, which are given in Table I. Then, by a program prepared by Wik,²⁵ Jette and Cahill's method¹⁹ [expression (20)] is used to obtain the g factors from the calculated eigenfunctions. This calculation involves diagonalizing two 1×1 matrices, one 2×2 matrix, and one 3×3 matrix for the $F=3$, $F=0$, $F=2$, and $F=1$ levels, respectively.

(b) The matrix elements of the fs, hfs, and Zeeman interaction are simultaneously diagonalized at each magnetic field to give the 27 Zeeman sublevels of the seven hfs levels. This calculation involves two 1×1 matrices ($M_F = \pm 3$), two 3×3 matrices ($M_F = \pm 2$), two 6×6 matrices ($M_F = \pm 1$), and one 7×7 matrix ($M_F = 0$).

(c) The third method of calculating the Zeeman effect is by inserting the zero-field eigenvalues in expressions (9)–(11).

The computer program for method (b) is checked by several methods. First, it gives the correct energy levels of the completely coupled angular momenta [see Eq. (33)] at low fields. Methods

(a), (b), and (c) give the same Landé g factors with in computer round-off, approximately five decimal places. A comparison of these theoretical g factors with experimental results is given in Table II.

Further checks of method (b) are made by setting the hyperfine constants equal to zero. This decouples I from J completely. At low magnetic fields [$\mu_B B \ll$ (fs separations)], the energy levels agree with the diagonal matrix elements

$$H(JI M_I M_J) = (g_J M_J + g_I M_I) \mu_B B + E(J), \quad (39)$$

where the values of g_J are given in Eq. (35). Finally, the fs constants also are set to zero. This completely decouples the angular momenta \vec{I} , \vec{S} , and \vec{N} . The energy levels agree with the diagonal expression

$$H(NSI M_N M_S M_I) = (g_S M_S + g_I M_I + g_N M_N) \mu_B B, \quad (40)$$

where the values of g_S , g_I , and g_N are given in Eqs. (34).

VI. RESULTS: COMPARISON WITH EXPERIMENT

A conventional diagram of the energy levels of H_2 , $c^3\pi_u$ in an $N=1$ rotational level is shown in Fig. 1. This figure is constructed in the following way. The Landé g factors are calculated for the energy levels by a simple case b coupling model.²⁶ These are given under the heading "first order" in Table II. The linear Zeeman effect [Eq. (3')] is obtained from these g factors and is shown at the left-hand side of the diagram. The energy levels are obtained at high magnetic fields by complete uncoupling of the nuclear and electronic spin. The levels at high field are given in Fig. 1 by Eq. (40),

TABLE I. Fine-structure and hyperfine-structure constants used in this calculation.

Constant	Value (Mc/sec)
A_1	-3717.137
B_0	-1420.458
B_2	-4484.053
a_2	27.900
a_F	449.887
c^a	103.838
d^a	0.000

^aEnergy levels depend only on the difference $\frac{1}{3}c - d$. d was arbitrarily set equal to zero.

TABLE II. Comparison of theoretical and experimental g factors in H_2 , $c^3\pi_u$, orthohydrogen, $N=1$ level.

Level		Calculated g_F		
J	F	Observed g_F	First order ^a	Exact ^b
0	1	-0.170 ± 0.005^c	-0.003	-0.16808
1	0			
	1	0.830 ± 0.005^c	0.624	0.829814
2	2	$0.651 \pm 0.005^{a,c}$	0.624	0.64756
	1	1.85 ± 0.01^c	1.878	1.83749
	2	1.026 ± 0.003^a	1.042	1.01857
3	3	0.833 ± 0.003^a	0.8331	0.83310

^aReference 26. ^bThis work. ^cReference 17.

where the projection of the total angular momentum along the magnetic field is the "good quantum number" $m_F = m_S + m_N + m_I$, and where the internal interaction terms are ignored. The von Neumann-Wigner noncrossing rule²⁷ is used to connect low- and high-field energy levels.

The low-field energy levels can be checked precisely with theory (3'), by studying the Zeeman splitting of transitions of the form $\Delta F = 0, \pm 1$, $\Delta M_F = 0, \pm 1$. These results are shown in Table II. There is a clear discrepancy between experiment and the first-order values in several cases. The exact calculations (see Table II) are in excellent agreement with experiment in all but one case, where the experimental error may be somewhat optimistic.

It is interesting to note that the nuclear g factor of the $J=0, F=1$ level is "shielded" from the bare proton value of -0.00304 to an effective g equal to -0.168 . This enormous distortion is caused by the perturbation of the electronic coupling scheme by the nuclear hfs, and represents a gross exaggeration of the same mechanism as was found in atoms.^{8,9}

The high-field energy levels were not measured by observing radio-frequency transitions. However, the deflecting magnets operate at high fields, at approximately $H = 5000$ G ($\mu_B B/h \approx 7000$ Mc/sec). The use of the correlation supplied in Fig. 1 and the slopes of the high-field energy levels makes it possible to predict the relative intensities of the transitions within a Zeeman multiplet. These are governed by the change in magnetic "moment" μ , where

$$\mu = \frac{dE}{dB} \approx g_S M_S + g_N M_N + g_I M_I, \quad (41)$$

which is obtained from expression (40). There is a clear discrepancy¹⁷ between observed intensities and the predictions of (41).

The computer calculation of the Zeeman effect (see Fig. 2) reveals an apparent violation of the noncrossing rule²⁷ at several values of the magnetic

fields. Careful repetition of the calculations in the very close vicinity of these crossings reveals an extremely small repulsion between some of the levels (see Figs. 3 and 4). These results are summarized in Table III.

Examination of Fig. 2 reveals two types of interactions between energy levels. One type is well illustrated by the levels $J=1; F=0, 1; M_F=0$ at zero field, or the levels $J=0, 1; F=1; M_F=-1$, which "cross" at 7430 Mc/sec. These pairs of levels strongly and visibly repel each other on the gross scale of Fig. 2. The second type of level pairs (listed in Table III) have repulsions of only a few Mc/sec, which are too small to be seen on Fig. 2.

The repulsions are caused by matrix elements of the magnetic field perturbation, $\vec{\mu} \cdot \vec{B}$. This is a vector operator which satisfies the selection rules $\Delta F = 0, \pm 1; \Delta J = 0, \pm 1; \Delta M_F = 0$. The strong repulsions are of this form. The weak repulsions occur in crossings with the quantum numbers which violate the selection rules. Either $|\Delta F| > 1$ or $|\Delta J| > 1$ in all such cases. These repulsions get their strength from the admixture of small impurities of wave functions with different values of F or J . Because the repulsion occurs only in a high order of perturbation, the interactions are

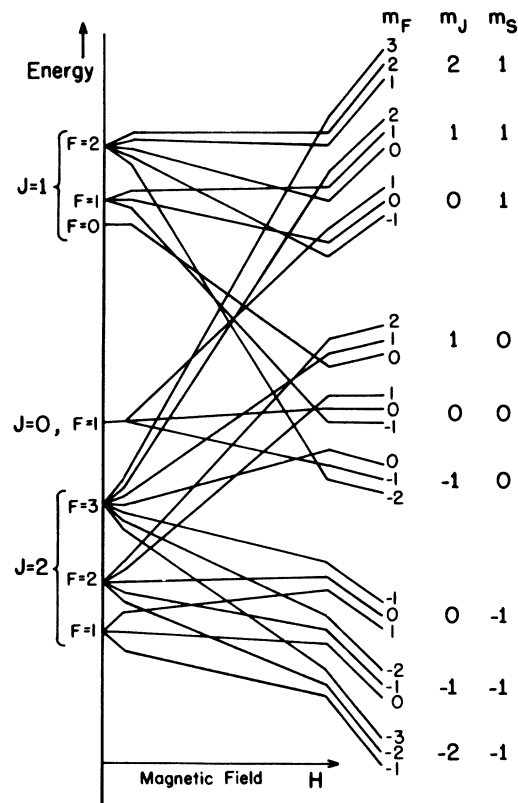


FIG. 1. Correlation diagram, H_2 , $c^3\pi_u$, $N=1$.

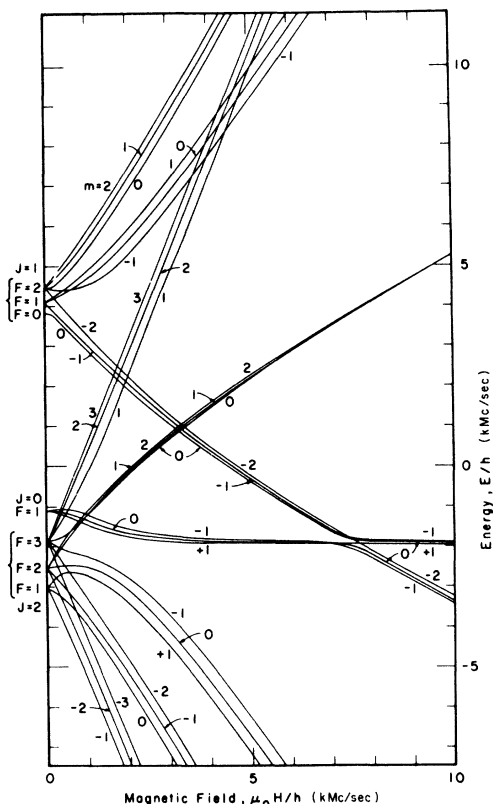


FIG. 2. Energy levels of $H_2, c^3\pi_u, N=1$ in a magnetic field.

weak.

VII. LANDAU-ZENER MODEL

It is evident that the assumption of adiabatic behavior has broken down, because of the extremely close approach of "crossing" energy levels. The occurrence of nonadiabatic transitions is well known in molecular-beam spectroscopy under the term "Majorana transitions." These occur when the magnetic field rotates or oscillates at a frequency comparable to the separation (in frequency

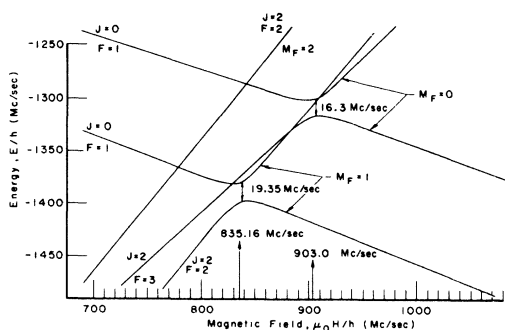


FIG. 3. Avoided crossings of energy levels, $J=0$ and $J=2$. we obtain

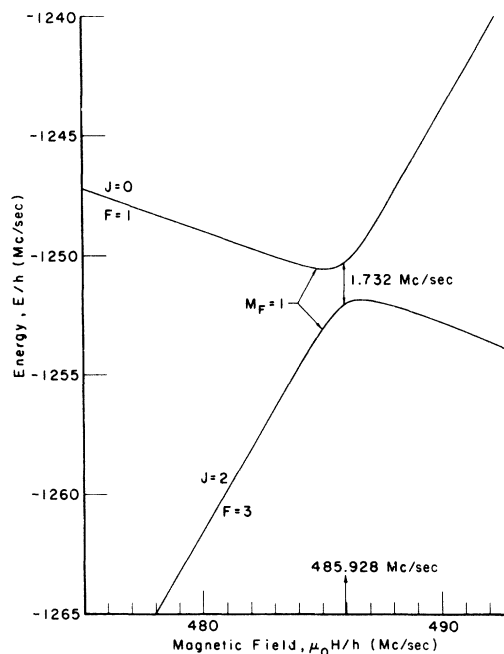


FIG. 4. Avoided crossing of energy levels, $J=0$ and $J=2$.

units) between energy levels.²⁶

The transitions here are of a different type that have not been observed previously in molecular-beam spectroscopy, but are well known in the field of atomic collisions. When two energy levels approach each other rapidly and go through the region of mutual repulsion in a time short compared to the period associated with the energy of repulsion, the transition is "diabatic." That is, the levels cross.

The theory of level crossing has been worked out by Landau, Zener, and Stückelberg.²⁹ The probability of a diabatic transition (crossing) of energy levels between two states S and S' , given by the Landau-Zener formula²⁷ is

$$P = e^{-W},$$

where

$$W = \frac{2\pi(\mathcal{K}_{SS'})^2}{\hbar(dB/dt)(\mu - \mu')}, \tag{42}$$

where $\mathcal{K}_{SS'}$ is the matrix element which produces the repulsion between levels, μ and μ' are the magnetic moments of the two states, and dB/dt is the rate of change of the magnetic field. If we put this expression in units of frequency,

$$\mathcal{K}_{SS'} = hf_{SS'}, \quad \frac{(\mu - \mu')B}{h} = f_S - f_{S'},$$

TABLE III. Repulsions between selected energy levels of H_2 , $c^3\pi_u$, $N=1$ level.

Low-field quantum numbers of diabatic states					Parameters of crossing		Type of transition
J	J	F	F'	$M_F = M_{F'}$	Location $\mu_B B/h$ (Mc/sec)	Repulsion $F_{SS'}$ (Mc/sec)	
0	2	1	3	1	485.93	1.73	Diabatic
0	2	1	2	1	835.16	19.35	Mixed
0	2	1	3	0	903.0	16.3	Mixed
1	2	0	2	0	3262.7	4.6	Diabatic
1	2	1	3	1	5088	5.1	Diabatic
1	0	0	1	0	7381	195.6	Adiabatic
1	0	1	1	-1	7430	201.6	Adiabatic

$$W = \frac{(2\pi)^2 (f_{SS'})^2}{(dB/dt)(d/dB)(f_S - f_{S'})} \quad (43)$$

In the apparatus used in the experiments,²⁴⁻²⁶ the magnetic transition occurs in four regions each ~ 1 mm long, $B \approx 5000$ G in the deflecting magnets, and the molecules travel at a velocity of $\approx 2 \times 10^5$ cm/sec. If we assume a change of moment $\mu - \mu' \approx \mu_B$, then $f_S - f_{S'} \approx 1.5 \times 10^6 B$, and we obtain

$$W \approx 2.5 \times 10^{-15} (f_{SS'})^2, \quad W \approx \left(\frac{1}{40} F_{SS'}\right)^2, \quad (44)$$

where $F_{SS'} = 2 \times 10^{-6} f_{SS'}$ is the minimum separation between states, measured in Mc/sec. We can distinguish three cases:

(a) $W \gg 1$ ($F_{SS'} \gg 40$ Mc/sec). The system obeys the noncrossing rule and the transition is *adiabatic*.

(b) $W \approx 1$ ($F_{SS'} \approx 40$ Mc/sec). The transition is *nonadiabatic*, with an appreciable probability of taking either path after the encounter.

(c) $W \ll 1$ ($F_{SS'} \ll 40$ Mc/sec). The transition is *diabatic*; the system jumps to the other curve with high probability.

VIII. ANALYSIS OF TRANSITION AT 5215 Mc/sec

We can now take a particular case, the 5215-Mc/sec transition. This is between the states $J=1, F=1$ and $J=0, F=1$. There are four transitions of the form $\Delta M_F = \pm 1$, shown in Table IV, along with the high-field ($\mu_B B/h \approx 7000$ Mc/sec) moment changes which would be expected in the

deflecting magnets. Transitions 1 and 2 have essentially no adiabatic changes in magnetic moment. These transitions would be unobservable, if only adiabatic transitions occurred. *The experimental observation of appreciable intensities for these transitions is unambiguous evidence of nonadiabatic transitions.* The change in moments which occur with diabatic transitions are in closer agreement with experiment. However, it is clear that the transitions are not completely diabatic, either.

To see why the transitions are neither diabatic nor adiabatic, it is instructive to follow the individual states through the crossings on Fig. 2 (see Table III). The levels $J=1, F=1, M_F=1, 0$ both have high magnetic moments, regardless of what happens in the transition regions. The states $J=0, 1; F=1, M_F=-1$ have zero or slightly negative magnetic moments up to 7500 G,³⁰ and are adiabatic at all transitions.

Only the states $J=0, F=1, M_F=0, 1$ need be considered. The transition at $\mu_B B/h = 485.9$ Mc/sec is diabatic, so that both levels reach the crossings at 835 and 903 Mc/sec. Both of these are mixed, which ensures that neither the adiabatic nor diabatic hypotheses are correct. Since the transition at 3262 Mc/sec is diabatic, there is an appreciable probability that both states end together on the curves with approximately unit slope. Since the moments for these curves differ by a large amount from those for all other states, these states can be expected to give observable transitions. Because of the mixed character of

TABLE IV. 5215-Mc/sec transition.

Transition		1	2	3	4
$J=1, F=1, M=$		-1	0	0	1
$J=0, F=1, M=$		0	-1	1	0
Change in magnetic moment (μ_B)	Adiabatic	-0.02	1.57	0	2.97
	Diabatic	-0.40	2.04	1.47	1.59
Relative observed intensities		17	24	12	20

the transitions involving these states, the lines will be weaker than those of purely adiabatically allowed transitions. Table IV reveals that these two levels are just those that participate in transitions 1 and 3, which had the anomalously high intensity. In the case of transition 4, it can be shown that the nonadiabatic behavior of the state $J=0$, $F=1$, $M=0$ would act to *weaken* the line intensity. Since this line has the largest adiabatic moment change and is yet not the strongest line, the theory again agrees with observed intensity.

IX. CONCLUSIONS

The presence of nonadiabatic transitions has

been experimentally observed in a molecular beam experiment. Theoretical calculations are in good qualitative agreement with experimental results. In general, such transitions can be predicted on the basis of the Landau-Zener model, which treats the case of "anticrossings" between pairs of energy levels.³¹

Note added in proof. There is an additional matrix element

$$H_{J'FP}(JFM) = \langle \gamma J+1I; F+1M | \mathcal{H}_Z | \gamma JI; FM \rangle :$$

$$J' = J+1, F' = F+1.$$

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W. W. Smith for pointing out this alternative approach.

²¹In Eq. (4.12) of Jette and Cahill, the diagonal term in the nuclear moment interaction with the magnetic field should read $g_I(\mu_N/\mu_B) \vec{F} \cdot \vec{I}$.

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³¹Avoided crossings similar to the cases discussed in the present article are to be expected in any atomic, molecular, or solid-state system with hfs and fs levels which cross. The term "anticrossings" was coined by T. G. Eck, L. L. Foldy, and H. Wieder, *Phys. Rev. Letters* **10**, 239 (1963), who first observed the effect of these near crossings on resonance fluorescence. For further discussion and other cases of anticrossings see H. Wieder and T. G. Eck, *Phys. Rev.* **153**, 103 (1967); K. C. Brog, T. G. Eck, and H. Wieder, *ibid.* **153**, 91 (1967); L. C. Himmel and P. R. Fontana, *ibid.* **162**, 23 (1967); P. Hiismäki and P. Jauho, *Phys. Letters* **21**, 516 (1966). The author is indebted to William Wing for drawing his attention to many of these references.