

Theory of Magnetic Resonance in Nitric Oxide*

HENRY MARGENAU AND ALLAN HENRY

Sloane Physics Laboratory, Yale University, New Haven Connecticut

(Received January 24, 1950)

The paper presents a theoretical study of the effect of a magnetic field on the lowest of the ${}^2\Pi_{3/2}$ levels of $\text{N}^{14}\text{O}^{16}$. The molecular Zeeman effect is calculated in detail and found to yield good agreement with experiment. Consideration is given to the energy of interaction, (a), of the spin of the N^{14} nucleus with the total electronic angular momentum in the external field, and (b) of the quadrupole moment of N^{14} with the electric field at the N^{14} nucleus. The last section contains an evaluation of the matrix elements needed in the computation of absolute intensities for the transitions within the ${}^2\Pi_{3/2}$ level.

1. SURVEY

THE splitting of the term ${}^2\Pi_{3/2}$ in the NO molecule, observed by Beringer and Castle,¹ has its origin in the level system schematically represented in Fig. 1 of reference 1. In a magnetic field, the energy of a state with given J takes on as many values as there are magnetic sub-levels characterized by M_J , four in the present instance. This splitting is shown in stage *b* of the figure; it would describe the situation fully if there were no nuclear spin with its associated magnetic moment and no nuclear quadrupole moment.

Before considering the nuclear effects we focus attention once more on stage *b*. The diagram represents a condition commonly known as the weak field case, a condition in which the coupling between the various angular momenta is not disturbed by the external magnetic field. The fields used in the experiments under discussion, having magnitudes below 10,000 oersted, are indeed weak with respect to the internal molecular couplings in the ordinary sense of the word. The scheme of Fig. 1b of reference 1 is therefore adequate.

However, another question concerns the equality of the frequency differences, ν_I , ν_{II} , and ν_{III} . Only for *very* weak fields are they equal. We shall show that under the circumstances of Beringer and Castle's experiments the external field did alter the internal molecular couplings to an extent reflected in an inequality of ν_I , ν_{II} and ν_{III} , though not sufficiently to cause a Paschen-Back effect.

The hyperfine structure of our level with the exclusion of quadrupole effects is shown in stage *c* of Fig. 1 in reference 1. Here the field is strong enough to uncouple **I** and **J** completely, so that M_I and M_J are both good quantum numbers resulting quite accurately in the scheme of levels drawn. Their spacing is the familiar one, but it will be explained in detail in Section 4. We shall demonstrate also, notwithstanding the fact that we are dealing with magnetic dipole transitions, the validity of the usual selection rule, $\Delta M_I = 0$. Thus one is led to expect the nine transitions marked in stage *d* of the figure.

These would be of three different frequencies: $\nu + A/h$, ν , and $\nu - A/h$ if the equality $\nu_I = \nu_{II} = \nu_{III} \equiv \nu$ were true.

The appearance of nine lines is therefore at once an indication of the distortion of the molecular Zeeman levels, of the inequality of the ν 's. Observation shows three similar groups of lines which exhibit two different intervals, one interval of about 27 and one of approximately 100 oersted. One of these must clearly correspond to the difference between successive ν_i , the other to the value of the (hyperfine-structure) constant A . The observed line pattern is indifferent to the assignment of intervals; hence other considerations are necessary to settle this assignment.

We shall see later that the intensities of the lines are given by the formula

$$\text{Int}(M_J \rightarrow M_J - 1) \approx (J + M_J)(J - M_J + 1). \quad (1)$$

Accordingly, the lines associated with ν_{II} should be stronger by a factor 4/3 than those associated with ν_I and ν_{III} . Hence the frequencies $\nu_{II} + A/h$, ν_{II} and $\nu_{II} - A/h$ should be equally strong and slightly more intense than the others. If A were the large interval, we should expect the middle line of each triplet to be of greater intensity; otherwise the middle group of three should contain all the lines of greater intensity. The latter is the alternative present in the measurements. We must conclude, therefore, that the hyperfine-structure constant corresponds to 27 oersted, the separation of about 100 oersted being assignable to molecular distortion. Our detailed calculations, too, will bear this out.

2. THE HAMILTONIAN

The NO molecule presents an instance of Hund's case *a*. Nevertheless it is simpler for the purposes of calculation to employ zero-order state functions corresponding to case *b*, and to treat the interaction which distinguishes the two cases as one of the perturbations. In the initial representation, therefore, the molecular quantum numbers² J , K , S , and Λ and M_J are sharp; as the calculation proceeds, states corresponding to different values of some of these constants are combined in variational fashion.

The perturbing Hamiltonian has the form:

$$\begin{aligned} \mathcal{H}' &= \mathcal{H}_m + \mathcal{H}_n \\ \mathcal{H}_m &= D\Lambda \cdot \mathbf{S} + \mathbf{u}_J \cdot \mathbf{H} \end{aligned} \quad (2)$$

* Supported by the ONR.

¹ R. Beringer and J. G. Castle, Jr., Phys. Rev. 78, 581 (1950).

² The notation follows G. Herzberg, *Molecular Spectra and Molecular Structure I* (Prentice-Hall, Inc., New York, 1939).

$$\mathcal{H}_n = A\mathbf{J} \cdot \mathbf{I} + \mathbf{u}_I \cdot \mathbf{H} + q'. \quad (3)$$

\mathcal{H}_m is the molecular, \mathcal{H}_n the nuclear part of the perturbation. The two differ greatly in magnitude, the contribution of \mathcal{H}_m to the energy differences sought being several hundred times that of \mathcal{H}_n . Of the two terms comprising \mathcal{H}_m , the first accounts for the rotational distortion of the molecule and carries the molecule from case *b* toward case *a*. The term $\mathbf{u}_J \cdot \mathbf{H}$ represents the energy of the electronic magnetic moments \mathbf{u}_J in a magnetic field \mathbf{H} . Customarily it is written in the form

$$g_J \mu_0 \mathbf{J} \cdot \mathbf{H}, \quad (4)$$

and if one consults books on band spectra³ one will find for g_J the formula

$$g_J = \frac{(\Lambda + \Sigma)(\Lambda + 2\Sigma)}{J(J+1)} \quad (4a)$$

as valid for Hund's case *a*. The level studied by Beringer and Castle is of type ${}^2\Pi_{3/2}$, hence $\Lambda = 1$, $\Sigma = \frac{1}{2}$; $J = \frac{3}{2}$, and g_J should be $4/5$. Our work will show that the effective value of g_J will depart appreciably, though not widely, from this ideal value.

We note here that the form (4) is not a suitable one for use on the present occasion because the intermingling of states occurring in the perturbation calculus will cause g_J to be a function of the magnetic quantum number M_J , an incident which deprives this quantity of its usual significance. We must therefore turn to a more detailed analysis of the operator $\mathbf{u}_J \cdot \mathbf{H}$.

When \mathbf{H} is taken along the *Z* axis, this operator may be expanded to read

$$\mathbf{u}_J \cdot \mathbf{H} = [\mu_0(\Lambda_z + 2S_z) + \mu_n(K_z - \Lambda_z)]H_z.$$

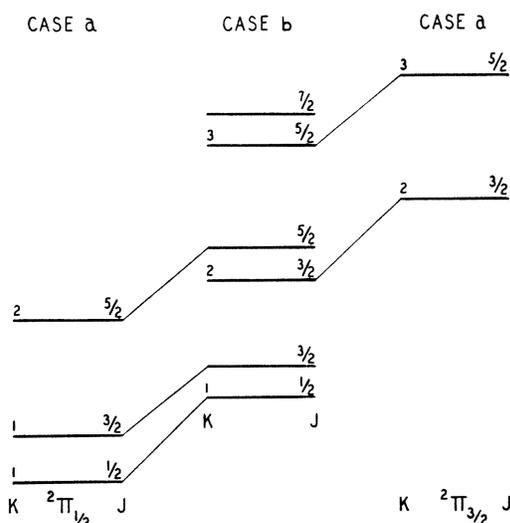


FIG. 1. Relation between level arrangements in case *a* and case *b* [see R. S. Mullikan, *Rev. Mod. Phys.* **2**, 113 (1930)].

³ E.g., W. Jevons, *Band Spectra of Diatomic Molecules* (Cambridge University Press, London, 1932), p. 252.

The quantity $\mathbf{K} - \mathbf{\Lambda}$ is the angular momentum (sometimes called \mathbf{N}) resulting from the slow rotation of the entire molecule, and μ_n is the magnetic moment produced by it. This quantity consists of two parts, $\mu_n' + \mu_n''$, which arise separately from the rotation of the nuclei and of the electrons. A simple consideration shows that μ_n' is a nuclear magneton, multiplied by $N_p/(N_p + N_n)$, the ratio of the number of revolving protons to that of nucleons. On the other hand, μ_n'' is very difficult to calculate, but is known⁴ to cancel part of μ_n' . It is clear, therefore, that the term $\mu_n(K_z - \Lambda_z)H_z$ is quite small in comparison with the remainder of $\mathbf{u}_J \cdot \mathbf{H}$. It will later be seen to be small also relative to the important part of \mathcal{H}_n and will now be ignored. Hence we take

$$\mathcal{H}_m = D\mathbf{A} \cdot \mathbf{S} + \mu_0(\Lambda_z + 2S_z). \quad (5)$$

The matrix elements for this operator have been evaluated by Hill and by Van Vleck.⁵

The three terms composing \mathcal{H}_n (Eq. 3) represent (a) the interaction between the magnetic moment of the N^{14} nucleus ($\mu = 0.403$ nuclear magnetons; I , the nuclear spin quantum number, = 1) and the magnetic field produced by the electrons; (b) the energy of alignment of the nuclear magnet in the external field \mathbf{H} ; (c) the operator q' which represents the interaction between the nuclear quadrupole moment of N and the electronic field. This last effect is very small but, it turns out, just measurable. Nothing is known about the numerical value of the constant A for NO, but we recall from elementary theory its significance:

$$A \approx -\mu_I H_0 / IJ, \quad (6)$$

Here H_0 is the field produced by all electrons in the molecule at the place of the N-nucleus. The experimental data lead to $A = 1.98 \times 10^{-19}$ erg and $H_0 \cong 150,000$ oersteds.

The procedure followed in this paper is to combine "case *a* functions" for the NO molecules so as to diagonalize \mathcal{H}_0 (the unperturbed Hamiltonian) + \mathcal{H}_m , this being the large part of the energy. Then we compute the diagonal energy components corresponding to \mathcal{H}_n in the usual way. The first of these two tasks is performed in Section 3.

Throughout this calculation we have neglected the energy difference resulting from Λ -type doubling. This corresponds to inclusion in \mathcal{H}_m of an operator proportional to $\mathbf{L} \cdot \mathbf{N}$ and requires consideration of electronic states other than the one involved in the lines here studied. The fact that this doubling would not appear in our approximation is of course no guarantee of its

⁴ See G. C. Wick, *Zeits. f. Physik* **85**, 25 (1933).

⁵ E. L. Hill and J. H. Van Vleck, *Phys. Rev.* **32**, 250 (1928); E. L. Hill, *Phys. Rev.* **34**, 1507 (1929).

Equation (3), which is customary and upon which the present treatment will be based, is only approximately true. It will be shown in a later paper that the term $\mathbf{J} \cdot \mathbf{I}$ requires a slight correction which further improves the agreement of our results with experiment.

smallness. Mulliken and Christie,⁶ however, have published parameters from which its size can be computed roughly. The actual splitting should be of the order of 10^{-4} cm^{-1} for the ${}^2\Pi_{3/2}$ term of NO, and this corresponds to about 2 oersted in the experiments of Beringer and Castle. It would thus be on the verge of being measurable if the difference communicated itself somehow *in toto* to the various Zeeman levels. We have not investigated this point in detail.

3. MOLECULAR ZEEMAN EFFECT

In this, the main part of the calculation, we deal with the Hamiltonian $\mathcal{H}_T + \mathcal{H}_m$, which we abbreviate in the present section as \mathcal{H} . Here \mathcal{H}_T is the energy operator for the symmetric top, whose eigenvalues are given by $B[K(K+1) - \Lambda^2] = E_T$. As usual, $B = \hbar/4\pi cI$ and is measured in cm^{-1} . The eigenfunctions of \mathcal{H}_T are characterized by the values of K (and other parameters, to be sure); but since in our case the electron spin $S = \frac{1}{2}$, two values of $\mathbf{J} = \mathbf{K} + \mathbf{S}$ are assignable to every K , namely $K \pm \frac{1}{2}$. This is the degeneracy peculiar to the use of case *b* eigenfunctions, a degeneracy which is removed by the interaction between \mathbf{K} and \mathbf{S} . The eigenfunctions will be written in the form $\psi(K, J)$.

To locate the energies associated with the various quantum numbers we have drawn in Fig. 1 the anatomy of the terms of the NO molecule (without external field) in the neighborhood of the one here selected for study. The central system, labeled case *b*, is the arrangement reflected by our functions $\psi(K, J)$, except that these functions do not take account of the J -splitting indicated in the diagram. As this splitting becomes important (case *a*) the central arrangement transforms itself into the ${}^2\Pi_1$ and the ${}^2\Pi_{3/2}$ systems as shown in the figure. Our interest is in the lowest level on the right. Its ancestor of the case *b* generation has quantum numbers $K=2, J=\frac{3}{2}$, and is degenerate with the level $(2, \frac{5}{2})$. Its closest neighbors are the states $(1, \frac{3}{2})$ and $(3, \frac{5}{2})$; these are important in our variational calculation despite the fact that, in the case *a* scale, one of these states, $(1, \frac{3}{2})$ moves out of the neighborhood of the state in question.

The procedure to be described is suggested by a comparison of the sizes of the various matrix elements $(K, J | \mathcal{H}_m | K', J')$ and by the magnitude of the differences $E_T(K, J) - E_T(K', J')$. Hill⁷ has calculated all matrix elements needed for the present purposes and extensive use is made of his results.

The work proceeds in three steps toward the final approximation.

Step 1.—A linear combination is formed from the functions $\psi(1, \frac{3}{2})$ and $\psi(2, \frac{3}{2})$. Of the two roots of the secular determinant, $|\mathcal{H}_{ij} - E|$ which we will call E_a and E_a' , we select the one which originates at $E_T(2, \frac{3}{2})$ in the absence of the perturbation \mathcal{H}_m , and we call this

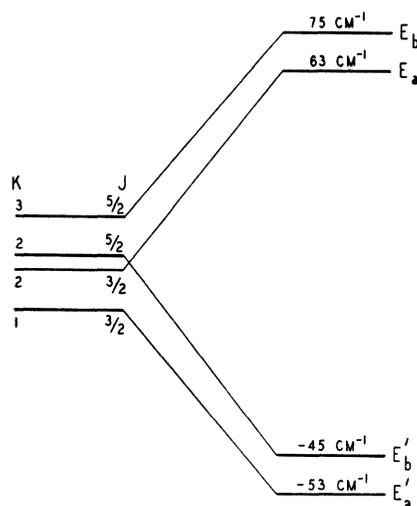


FIG. 2. Behavior of energy levels under perturbation (first stage).

root E_a . The corresponding linear combination shall be ψ_a . Clearly, E_a is a better approximation to the energy we are seeking than is $(2, \frac{3}{2} | \mathcal{H} | 2, \frac{3}{2})$, but it is far from adequate for our purposes.

Step 2.—To improve the accuracy, we first combine the functions $\psi(2, \frac{5}{2})$ and $\psi(3, \frac{5}{2})$ in the same manner in which step 1 combined $\psi(1, \frac{3}{2})$ and $\psi(2, \frac{3}{2})$ to yield ψ_a . In this way, then, two energies, E_b and E_b' , are obtained, and the root selected, E_b , shall be the one closest to E_a . The corresponding linear combination is ψ_b . In completion of step 2, ψ_a is combined with ψ_b , and the combination which reduces to $E_T(2, \frac{3}{2})$ is called ψ , or "the grand ψ ." The corresponding energy is E_{ab} . This E_{ab} is a much better approximation than E_a , but it is not quite good enough. In the absence of an external field, states *a* and *b* do not combine; the improvement just noted has relevance only for the Zeeman effect.

Step 3.—Upon the grand ψ one may impose a perturbation in the manner of the Rayleigh-Schrödinger scheme. In terms of the variational procedure thus far employed this scheme is equivalent to a neglect of all non-diagonal elements in the secular determinant except those in the first row and the first column, ψ being the first state. There is then added to E_{ab} the perturbation

$$\Delta E = \sum_{\lambda} \frac{|\int \psi^* \mathcal{H}_m \psi_{\lambda} d\tau|^2}{E_{ab} - E_{\lambda}} \quad (7)$$

and

$$E = E_{ab} + \Delta E.$$

By ψ_{λ} is meant any function $\psi(K, J)$ which combines with ψ but is not already included in ψ .

The first two steps are illustrated in Fig. 2, intended to show schematically what happens to the various levels under the influence of \mathcal{H}_m . To arrive at the grand ψ , the two states corresponding to the two highest levels, E_a and E_b , were selected because of their prox-

⁶ R. S. Mulliken and A. Christie, Phys. Rev. **38**, 87 (1931).

⁷ E. L. Hill, Phys. Rev. **34**, 1507 (1929).

TABLE I. Calculated magnetic fields (oersteds) and comparison with experimental values.

	H_{II}	$H_{II}-H_I$	$H_{III}-H_{II}$
Step 1	8612.3	17.1	17.5
Step 2	8618.9	127.1	128.6
Step 3	8619.5	105.5	103.1
Experiment	8614.1	105.3	103.0

imity. In his successful work on the Zeeman effect in doublet states, Hill has used what amounts to the procedure here employed up to step 2, although this may not be at once apparent from his language and indeed his formulas. But there is one difference. He combined the states corresponding to E_a and E_b' to obtain the equivalent of the grand ψ . This produces indeed the better approximation for molecules near case b , for then the energies E_a and E_b' fall closer together than they do in NO; in fact the difference E_a-E_b' can be much smaller than E_b-E_a . In our case, however, E_a-E_b' is of the order 100 cm^{-1} while E_b-E_a is less than 10 cm^{-1} . As a consequence, Hill's formula produces in the present instance an approximation inferior to E_{ab} ; it is but little better than E_a alone.

The analytic details of the work need only be summarized, for they are routine matters and involve well-known methods. As to notation, the functions will be labeled

$$\psi(1, \frac{3}{2}) = \psi_1; \quad \psi(2, \frac{3}{2}) = \psi_2; \quad \psi(2, \frac{5}{2}) = \psi_3; \quad \psi(3, \frac{5}{2}) = \psi_4.$$

We recall: $\mathcal{H} = \mathcal{H}_T + \mathcal{H}_m$ and $\mathcal{H}_{ij} = \int \psi_i^* \mathcal{H} \psi_j d\tau$, as usual. One then finds

$$E_a = \frac{1}{2}(\mathcal{H}_{11} + \mathcal{H}_{22}) + (\rho_{12}^2 + 1)^{\frac{1}{2}} \mathcal{H}_{12} \quad (8)$$

with the abbreviation:

$$\rho_{12} \equiv (\mathcal{H}_{22} - \mathcal{H}_{11}) / 2\mathcal{H}_{12}. \quad (8a)$$

The corresponding function is

$$\psi_a = (1 + S_{12}^2)^{-\frac{1}{2}} [\psi_1 + S_{12}\psi_2] \quad (9)$$

with

$$S_{12} \equiv \rho_{12} + (\rho_{12}^2 + 1)^{\frac{1}{2}}. \quad (9a)$$

In a similar manner ψ_b is formed from the functions ψ_3 and ψ_4 ; hence ψ_b and E_b are also given by formulas (8) and (9) provided the subscripts 1, 2 are changed to 3, 4 respectively.

Finally,

$$E_{ab} = (\mathcal{H}_{aa} + \mathcal{H}_{bb}) - (\rho_{ab}^2 + 1)^{\frac{1}{2}} \mathcal{H}_{ab} \\ \psi = (1 + S_{ab}^2)^{-\frac{1}{2}} [-S_{ab}\psi_a + \psi_b]$$

the quantities appearing here being again given by Eqs. (8a) and (9a) with the indicated changes in subscripts. Explicitly,

$$\mathcal{H}_{ab} = (1 + S_{12}^2)^{-\frac{1}{2}} (1 + S_{34}^2)^{-\frac{1}{2}} \\ \times (\mathcal{H}_{13} + S_{34}\mathcal{H}_{14} + S_{12}\mathcal{H}_{23} + S_{12}S_{34}\mathcal{H}_{24}).$$

Only three functions, $\psi(1, \frac{1}{2})$, $\psi(3, \frac{1}{2})$, and $\psi(4, \frac{1}{2})$ form

non-vanishing matrix elements with ψ . The summation in formula (7) has therefore only three terms.

In carrying out the numerical calculations the following values of the constants were adopted: $B_{\frac{1}{2}} = 1.6696\text{ cm}^{-1}$, $B_{3/2} = 1.7200\text{ cm}^{-1}$, $D = 123.8\text{ cm}^{-1}$, and $\mu_0/hc = 4.66846 \times 10^{-5}\text{ (cm oersted)}^{-1}$. The two values of B refer to the $\Pi_{\frac{1}{2}}$ and $\Pi_{3/2}$ states and are taken from Gillette and Eyster.⁸ Our choice of different B 's in the diagonal matrix elements represents a minor refinement which proved to have only a slight effect on the final answer. The constant D is not identical with the doublet splitting of 120.5 cm^{-1} , which is directly measured in the band spectrum. It may be calculated from Hill's formula or, as was done here, from the difference $E_a - E_a'$, this being the doublet splitting. If x is written for $H\mu_0/hc$, all expressions for the energies are of the form

$$\text{constant} + f_1(x) + f_2(M_J, x),$$

the constant being independent of M_J and x , and f_1 independent of M_J . To obtain the energy differences between magnetic states the constant and f_1 are not needed and will not be listed here. The results are given below (M_J is now replaced by M).

Step 1, leading to E_a :

$$f_2 = 0.776495Mx + 0.001963M^2x^2 \\ - 0.0000124M^3x^3 + \dots$$

Step 2, leading to E_{ab} :

$$f_2 = 0.776495Mx + 0.014508M^2x^2 \\ - (0.003859M + 0.000184M^2 - 0.000605M^3 \\ - 0.000021M^4)x^3 + \dots$$

Step 3, leading to $E_{ab} + \Delta E$.

Here ΔE was computed separately for different values of M , since expansion in the form of a power series is not feasible:

$$\Delta E(M = \pm \frac{3}{2}) = 0.000024x^2 + 0.0000020Mx^3 + \dots \\ \Delta E(M = \pm \frac{1}{2}) = 0.005371x^2 - 0.0000284Mx^3 + \dots$$

(Dots indicate omission of terms in higher powers of x .)

Beringer and Castle measure the fields necessary to make the energy differences between magnetic levels equal to the frequency of observation, $\nu_0 = 0.3122\text{ cm}^{-1}$. Hence, to compare the theoretical results with experiment, the differences of our energies (E_a , E_{ab} , and E in the various stages of calculation) for successive M 's must be equated to ν_0 , and each equation must be solved for H . This process leads to the three values H_I , H_{II} and H_{III} tabulated in the first three rows of Table I. Since there is some interest in the manner of convergence of our calculation we have stated the results computed at every stop.

The use of formula (4a) leads to $H_2 = 8359.3$ oersted, with zero values for the difference.

⁸ R. H. Gillette and E. H. Eyster, Phys. Rev. **56**, 1113 (1939).

4. HYPERFINE STRUCTURE

The operator \mathfrak{H}_n contributes the hyperfine structure of the molecular term. In a field of several thousand oersteds \mathbf{I} and \mathbf{J} are completely uncoupled. The nuclear situation corresponds to that of a total Paschen-Back effect, and the correct representation of the state is that in which J, I, M_J and M_I are sharp. The term $\mu_I \cdot \mathbf{H}$ may be written as $(g_I/1840)\mu_0 I_Z H$. Since

$$(M_J M_I | \mathbf{J} \cdot \mathbf{I} | M_J M_I) = M_J M_I$$

and

$$(M_I | I_Z | M_I) = M_I$$

we find

$$E_n = A M_J M_I + (g_I/1840)\mu_0 M_I H \quad (10)$$

to be the energy of the hyperfine levels for the case under consideration, exclusive of the effect of q' in Eq. (3). When account is taken of E_n , we arrive at stage c of Fig. 1 in the preceding paper.

Since the N^{14} nucleus has an electric quadrupole moment, a hyperfine structure resulting from its interaction with the electronic field is to be expected in addition to what we have just calculated.

Employing the customary notation, we have⁹

$$q' = - \frac{eQ \langle \sum_k e_k (3 \cos^2 \theta_k - 1) r_k^{-3} \rangle_{\text{molecule}}}{2J(2J-1)I(2I-1)} U \quad (11)$$

where

$$U = 3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2} \mathbf{I} \cdot \mathbf{J} - I(I+1)J(J+1)$$

Now

$$\langle 3 \cos^2 \theta - 1 \rangle_{\text{molecule}} = \frac{2J}{2J+3} \left[\frac{3(\Lambda + \Sigma)^2}{J(J+1)} - 1 \right] \quad (12)$$

for a molecule typifying Hund's case a , and

$$(M_J M_I | U | M_J M_I) = \frac{1}{2} [J(J+1) - 3M_J^2] [I(I+1) - 3M_I^2]. \quad (13)$$

Hence the quadrupole energy in the J, I, M_J, M_I representation is given by

$$- \frac{eQq}{4(2J-1)I(2I-1)(2J+3)} [J(J+1) - 3M_J^2] \times [I(I+1) - 3M_I^2] \left[\frac{3(\Lambda + \Sigma)^2}{J(J+1)} - 1 \right]. \quad (14)$$

⁹ Equation (11) comes from H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Haarlem, DeErven F. Bohn N.V. 1936). Equation (12) is obtained by a calculation similar to that of J. M. Jauch, *Phys. Rev.* **72**, 716 (1947) and Eq. (13) can be checked by employing matrix elements given in Condon and Shortley. The relationship between θ_k in Eq. (11) and θ in Eq. (12) is given by A. Nordsieck, *Phys. Rev.* **58**, 310 (1940) as $\sum_k e_k (3 \cos^2 \theta_k - 1) r_k^{-3} = (3 \cos^2 \theta - 1) \sum_k \frac{3 \cos^2 \theta_k' - 1}{2r_k^3}$. See this paper for details and notation.

Here

$$q = \sum_k l_k \frac{3 \cos^2 \theta_k' - 1}{r_k^3}.$$

When this effect is added onto the levels in stage c of Fig. 1 of reference 1, stage d results. As is well known, the quadrupole effect causes a departure from the interval rule as illustrated.

5. INTENSITIES

The lines observed by Beringer and Castle arise from transitions in which the magnetic dipole moment changes, the electric moment remaining unaltered. Their intensities are therefore given by the squares of the matrix elements of

$$- \frac{e}{2mc} \mathfrak{M} = - \frac{e}{2mc} (\mathbf{A} + 2\mathbf{S}) - \frac{e}{2Mc} g_I \mathbf{I}.$$

Here M is the mass of a nucleon, while m is the mass of an electron. The last term is therefore negligible.

The operator $\mathbf{A} + 2\mathbf{S}$, like the electric dipole moment, forms a vector of type \mathbf{T} in the terminology of Condon and Shortley.¹⁰ The matrix elements are therefore the same, except for constants, as those for the electric moment vector.

In particular,

$$\Delta M_I = 0$$

for all allowed transitions because \mathfrak{M} commutes with \mathbf{I} when the last term of the former operator is neglected. The intensities become

$$\text{Int} (M_J \rightarrow M_J - 1) = \text{const.} (J + M_J)(J - M_J + 1).$$

This justifies our use of Eq. (1).

An accurate calculation is required for the purpose of comparing the absolute intensities of the measured lines with theory. This involves the computation of the proper matrix elements of \mathfrak{M}_x and \mathfrak{M}_y for the actual molecular states under consideration. We must find

$$(\gamma M | \mathfrak{M}_x | \gamma M \pm 1) = \mp i (\gamma M | \mathfrak{M}_y | \gamma M \pm 1),$$

and take γ to represent the state given by the grand ψ

$$\psi = \psi_\gamma = \sum_{i=1}^4 a_i \psi_i$$

the ψ_i being defined just prior to Eq. (8). It is understood, of course, that the ψ_i are now written in their explicit dependence on the magnetic quantum number M . As to the coefficients a_i , which were used in Section 4 (but not displayed), their values are

$$a_1 = 0.853, \quad a_2 = 0.521, \quad a_3 = a_4 = 0$$

to an approximation sufficiently good for present

¹⁰ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 59 ff.

purposes. We also need the formulas¹¹

$$\begin{aligned}
 & (J, K, M | \mathfrak{M}_x | J, K, M \pm 1) \\
 &= \frac{1}{2} \left\{ \frac{\Lambda^2}{K(K+1)} \frac{J(J+1) - S(S+1) + K(K+1)}{2J(J+1)} + \frac{S(S+1) - K(K+1) + J(J+1)}{J(J+1)} \right\} (J \pm M + 1)^{\frac{1}{2}} (J \mp M)^{\frac{1}{2}} \\
 & (J, K, M | \mathfrak{M}_x | J, K+1, M \pm 1) \\
 &= \frac{\Lambda}{4J(J+1)(K+1)} \left\{ \frac{[(K+1)^2 - \Lambda^2](J - S + K + 1)(J + S + K + 2)(K + S - J + 1)(J + S - K)}{(2K+1)(2K+3)} \right\} (J \pm M + 1)^{\frac{1}{2}} (J \mp M)^{\frac{1}{2}}.
 \end{aligned}$$

When numbers are inserted we obtain for the quantity we are seeking

$$2 | (\gamma M | \mathfrak{M}_x | \gamma M \pm 1) |^2 = 0.386 (J \pm M + 1)(J \mp M). \quad (15)$$

It is interesting to observe that the state ψ_2 contributes

¹¹ These were here derived with the use of the matrix elements given by Reiche and Rademacher, *Zeits. f. Physik* **41**, 453 (1927) and the quantum addition rules for angular momenta.

far less to the intensity than does ψ_1 , as is very evident when the matrix elements are evaluated. An explanation of this apparent anomaly is provided by the vector model which shows state ψ_1 to suffer a large change in magnetic moment on change of M because of the relative orientation of the vectors which constitute M , in contradistinction to the situation in ψ_2 .

The Quantum Mechanics of Localizable Dynamical Systems

T. S. CHANG

Peking University, Peking, China

(Received November 25, 1949)

Expressions for the operators in Dirac's general theory of quantum mechanics of localizable dynamical systems are explicitly constructed and their commutation laws directly worked out (§2). Conditions for the expectation values of dynamical variables or their densities to be independent of the parametrization of the surface are given and it is shown that of the two conjugate field variables in Weiss' theory, one is a parametrization-independent variable and the other is a parametrization-independent density (§3).

Finally it is shown that P^n in Dirac's theory does not have any simple expression other than that given in Weiss' theory. This, together with the results described in the above paragraph, shows that for all practical purposes the two theories are equivalent (§5).

1. INTRODUCTION

IN the quantum mechanical theory of localizable dynamical systems, a wave function is introduced on each space-like surface in the four-dimensional space, and equations are set up for its change as the surface changes. Such a general theory was first given by Dirac,¹ who introduced the deformation operators Π^r , Π^n to describe the changes of the surface and the operators P^r , P^n giving the corresponding changes of the wave function. Conditions which these operators must satisfy were given, and if we call the equation giving the change of the wave function on a surface as the surface changes the wave equation, these conditions are precisely the conditions of integrability of the wave equation.²

For fields whose field equations are derived from the

variation of a Lagrangian, wave equations of the above nature were effectively given by Weiss.³ The exact form of the wave equation and a proof of its integrability were given in two papers by the author.^{4,5} It is easy to construct P^r and P^n from this wave equation and to verify that the conditions for them are satisfied.

In this theory, as well as in Dirac's paper, parametrization of the surface is introduced and the wave function changes as the "parametrized" surface changes. It is thus important to ask whether the expectation values of different dynamical variables at a point P inside a surface S are independent of the parametrization of the surface S . Conditions for such independence of dynamical variables (and their densities) are worked out (§3) and it is found that in Weiss' theory one of the

³ P. Weiss, *Proc. Roy. Soc.* **A156**, 192 (1936).

⁴ T. S. Chang, *Phys. Rev.* **75**, 967 (1949).

¹ P. A. M. Dirac, *Phys. Rev.* **73**, 1092 (1948).

² The relativity requirements on the wave equation were overlooked by Dirac and will be supplied here.

⁵ T. S. Chang, *Chinese J. Phys.* **7**, 265 (1949). This paper contains an extension of Weiss's theory to fields, the Lagrangian of which contains various derivatives of the field quantities.