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The Coupling of Angular Momentum Vectors in Molecules

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1. INTRODUCTION

As a subject becomes older, and better understood, it is usually possible to present its fundamentals in a simpler form than at the outset. This is true of the rotational distortion of molecular spectral terms. When Hill and I first investigated this problem,[1] we were able to deduce certain rather recalcitrant matrix elements only by adaptation of the results of a somewhat abstruse paper of Dirac's on noncommutative algebra. Since that time, the advent of nuclear spins and quadrupole moments has added to the complexity of molecular coupling problems, and the techniques of microwave spectra reveal hyperfine structures far beyond the possibility of detection twenty-five years ago. A paper by O. Klein,[2] amplified in a dissertation by Casimir,[3] has shown that the Wang secular determinant for the asymmetrical top such as is involved in polyatomic molecules, can be deduced in a simple fashion by means of quantum-mechanical algebra. With this procedure, one can avoid introducing explicit wave functions. Labor is thereby saved, for the use of these functions usually entails a certain amount of computation even though they are expressible in terms of jacobi polynomials. However, these articles of Klein and Casimir did not carry through their method to include the complexities actually found in molecular spectra, notably the fine structures arising from electronic and nuclear spin. It is the purpose of the present paper to show how this can be done. By extending Klein's method, we shall show that to each secular problem arising from the interaction of angular momentum vectors in molecules, there is a mathematically, though not physically, identical coupling problem in molecules. Consequently, the matrices for the molecular secular equations can be obtained from those given in textbooks, such as that of Condon and Shortley on atomic spectra, provided appropriate changes in notation are made. Most physicists are apt to be somewhat better acquainted with atomic than with molecular coupling schemes, and so feel better equipped to handle perturbation problems involving the interaction of angular momenta in atoms than in molecules. Klein's method shows that actually there is no basic difference in complexity in the two cases.

2. THE ANOMALOUS SIGN OF *i* IN KLEIN'S MATRICES

Practically everyone knows that the components of total angular momentum of the molecule relative to axes X, Y, Z fixed in space satisfy commutation relations of the form

$$J_X J_Y - J_Y J_X = iJ_Z, \quad \text{etc.} \tag{1}$$

To avoid constantly writing factors $h/2\pi$, we here, and throughout the paper, suppose angular momentum measured in multiples of the quantum unit $h/2\pi$.

Klein[2] discovered the rather surprising fact that when the total angular momentum is referred to axes mounted on the molecule, which we will denote by x, y, z, the sign of i in the commutation relations is reversed, i.e.,

$$J_x J_y - J_y J_x = -iJ_z. \tag{2}$$

In this connection, it is to be understood that when we say angular momentum *referred* to axes mounted on the molecule, we mean that it is computed in a reference

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* In contributing to this memorial number of *Reviews of Modern Physics* dedicated to John Torrence Tate, I am particularly pleased to write on the subject of the coupling of angular momentum vectors in molecules, for this is a topic on which I was collaborating with E. L. Hill at Minnesota in 1926–27, during Professor Tate's first years at Editor-in-Chief. Although he was not a specialist in our particular field, his interest in our work, and his encouragement of it, were a real assistance. I fondly recall the impromptu office party which J. W. Buchta, then a young instructor, arranged to celebrate Tate's inaugural role as Editor-in-Chief. The subsequent years have certainly more than justified our satisfaction that he accepted this position.

[1] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[2] O. Klein, Z. Physik **58**, 730 (1929).

[3] H. B. G. Casimir, *Rotation of a Rigid Body in Quantum Mechanics*, Dissertation, Leiden, 1931 (published by J. H. Woltjers, The Hague).

system fixed in space, and then projected on axes mounted on the molecule, or in other words,

$$J_x=\lambda_{xX}J_X+\lambda_{xY}J_Y+\lambda_{xZ}J_Z, \qquad (3)$$

where λ_{xX}, λ_{xY}, etc., are the direction cosines connecting the x, y, z and X, Y, Z coordinate systems.

The relation (2) may be established in either one of two ways. One of these is by means of the correspondence principle. This method is given by both Klein and Casimir and will not be repeated here. The other proof, less interesting, but more straightforward, is based on the fact that the direction cosines transform like the components of a vector, and so satisfy commutation relations of the form[4]

$$\lambda_{xX}J_Y-J_Y\lambda_{xX}=i\lambda_{xZ}. \qquad (4)$$

The relations (2) follow from the definition (3) if the left side of Eq. (2) is computed with the aid of Eqs. (4) and (1) and if it is remembered that each direction cosine is equal to its cofactor in the determinant of the direction cosines. We thus have, for example,

$$\begin{aligned}J_xJ_y-J_yJ_x=&(\lambda_{xX}J_X+\lambda_{xY}J_Y+\lambda_{xZ}J_Z)(\lambda_{yX}J_X+\lambda_{yY}J_Y+\lambda_{yZ}J_Z)\\&-(\lambda_{yX}J_X+\lambda_{yY}J_Y+\lambda_{yZ}J_Z)(\lambda_{xX}J_X+\lambda_{xY}J_Y+\lambda_{xZ}J_Z)\\=&(\lambda_{xY}\lambda_{yZ}-\lambda_{xZ}\lambda_{yY})(J_YJ_Z-J_ZJ_Y)-(\lambda_{xX}\lambda_{yZ}-\lambda_{xZ}\lambda_{yX})(J_ZJ_X-J_XJ_Z)\\&+(\lambda_{xX}\lambda_{yY}-\lambda_{xY}\lambda_{yX})(J_XJ_Y-J_YJ_X)-i\lambda_{xX}(-\lambda_{yZ}J_Y+\lambda_{yY}J_Z)-i\lambda_{xY}(\lambda_{yZ}J_X-\lambda_{yX}J_Z)\\&-i\lambda_{xZ}(-\lambda_{yY}J_X+\lambda_{yX}J_Y)+i\lambda_{yX}(-\lambda_{xZ}J_Y+\lambda_{xY}J_Z)+i\lambda_{yY}(\lambda_{xZ}J_X-\lambda_{xX}J_Z)\\&+i\lambda_{yZ}(-\lambda_{xY}J_X+\lambda_{xX}J_Y)\\=&\lambda_{zX}(J_YJ_Z-J_ZJ_Y)+\lambda_{zY}(J_ZJ_X-J_XJ_Z)+\lambda_{zZ}(J_XJ_Y-J_YJ_X)-2i\lambda_{zX}J_X-2i\lambda_{zY}J_Y-2i\lambda_{zZ}J_Z\\=&-i\lambda_{zX}J_X-i\lambda_{zY}J_Y-i\lambda_{zZ}J_Z=-iJ_z.\end{aligned}$$

Substantially, this calculation is mentioned in Casimir's thesis (p. 44). Another, essentially equivalent explicit computation verifying Eq. (2) is also given at the end of Klein's paper, the difference being that eulerian angles are used rather than direction cosines.

3. SIMULTANEOUS ANGULAR MOMENTUM MATRICES WITH ANOMALOUS AND NORMAL SIGNS IN MOLECULAR PROBLEMS

The energy of a molecule whose center of gravity is at rest is approximately separable into the internal energy of the electrons relative to "clamped nuclei," the energy of molecular vibration, and the rotational energy of a rigid body whose constants are obtained by regarding the molecule as built out of an ensemble of rigidly connected nuclei. This fact seems reasonably obvious physically, and also can be demonstrated by a systematic application of perturbation theory.[5] We are concerned primarily with the energy of rotation, whose hamiltonian function is, in general, like that of a symmetrical or asymmetrical top. The angular momentum involved therein is that arising from the rigid rotation of the molecular frame. This is not the same, in general, as the total angular momentum **J** of the molecule, since in the problem of "clamped nuclei," there may be angular momentum due to electronic orbital motion, electron spin, and nuclear spin. The total angular momentum of this character we shall denote by **P**. The notation can be remembered by thinking of the letter **P** as standing for the "partial" angular momentum, i.e., the angular momentum exclusive of that of rigid rotation, which is **J**−**P**. (We overlook for the present the possibility of angular momentum caused by molecular vibration.) The rotational energy or hamiltonian function is thus

$$H=A(J_x-P_x)^2+B(J_y-P_y)^2+C(J_z-P_z)^2. \qquad (5)$$

Here, and elsewhere in the paper, the constants A, B, C have the significance

$$A=\frac{h^2}{8\pi^2I_A},\quad B=\frac{h^2}{8\pi^2I_B},\quad C=\frac{h^2}{8\pi^2I_C},$$

in term of the principal moments of inertia I_A, I_B, I_C of the molecule. The C term is wanting if the molecule is diatomic or collinear.

The important thing now to be noted is that P_x, P_y, P_z satisfy commutation relations with the normal sign of i, so that

$$P_xP_y-P_yP_x=iP_z. \qquad (6)$$

That the normal sign of i enters in Eq. (6) is a consequence of the fact that the angular momentum **P**, unlike **J**, can be regarded as measured relative to, rather than referred to, axes mounted on the molecule. In other words, **P** can be computed with an origin of

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[4] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 59. Usually, the commutation relations analogous to Eq. (4) are given for the components of a vector, rather than direction cosines so that X, Y, Z rather than λ_{xX}, λ_{xY}, λ_{xZ} occur in Eq. (4). However, since the principal axes are determined by nuclear coordinates, the direction cosines can, except for a normalization factor, be regarded as linear functions of the coordinates of the various nuclei. Since the commutation relations are unaffected by taking linear combinations, and since the normalization factor is an invariant which commutes with all components of angular momentum, we are hence justified in using Eq. (4) for the direction cosines.

[5] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

velocity fixed in the molecular frame rather than in space.

The essential physical reason why there is no anomaly in sign in Eq. (6) is that the internal problem of the motion of electrons and spins is one in which the nuclei are regarded as fixed, and no questions connected with molecular rotation can enter. As far as **P** is concerned, the normal sign applies for the commutation relations either in the fixed or moving system. The mathematical reason for this is that the angular momentum operators associated with **P** are functions only of the "internal" coordinates, i.e., coordinates relative to the molecular frame, and so these operators commute with the eulerian angles or direction cosines which are used to project from the moving coordinate system x, y, z to that X, Y, Z fixed in space, or vice versa, and which are nuclear rather than electronic parameters. It may seem contradictory that in the projection the anomaly creeps in for the total angular momentum **J**, but not the partial angular momentum **P**. The distinction arises because the nuclear masses are regarded as exceedingly large compared with the electron ones. In principle, of course, all particles should be on a par, and the diversity in behavior owes its origin to the fact that the perturbation calculation assumes wave functions which are products of a factor involving the eulerian angles, and one involving the variables for the clamped nuclei problem. This separation is not a rigorous one, though legitimate as the starting point of a perturbation calculation, and would be a poor approximation if nuclei were not heavy.

Let us define the "reversed" internal angular momentum, as a vector of components

$$\tilde{P}_x = -P_x, \quad \tilde{P}_y = -P_y, \quad \tilde{P}_z = -P_z.$$

Then, because of the presence of the minus sign in the definition, the reversed internal angular momentum will satisfy commutation relations with an anomalous sign, so that

$$\tilde{P}_x\tilde{P}_y - \tilde{P}_y\tilde{P}_x = -i\tilde{P}_z. \tag{7}$$

We will also have occasion to use the reverses of various constituents of the internal angular momentum, for example, any sort of spin angular momentum, electronic orbital angular momentum, etc. The reverse will be denoted by tildes, and these reversed angular momenta will all satisfy commutation relations with the anomalous sign.

The point of using the reversed internal angular momenta is that they satisfy the same commutation relations, referred to the molecular axes, as does the total angular momentum. The sign of i is never important as long as one is consistent in the usage, and a consistent anomaly is effectively no anomaly at all. It would, on the other hand, have been completely incorrect to use the same sign in Eq. (1) as in Eq. (2). A consistent behavior in the x, y, z frame, however, is obtained by using the reverses in connection with the internal angular momentum. Essentially, this fact has been noted independently by H. Nielsen,[6] but he did not follow it through with detailed applications in the way that we do.

All components of J commute with those of **P** (or $-$**P**), i.e.,

$$J_x\tilde{P}_y - \tilde{P}_yJ_x = 0, \quad \text{etc.} \tag{8}$$

The relation (8) is very important for our purposes, as it is the basis of our ability to take **J** and $-$**P** as two independent, i.e., commuting vectors for compounding purposes, like, for instance, spin and orbital angular momentum vectors in atomic spectra. Formula (8) is most easily established simply by noting that it is possible to choose systems of representations in which **J** and **P** are described by entirely separate quantum numbers, so that the order of multiplication is immaterial. One can also derive Eq. (8) by starting with the commutation rule $P_XJ_Y - J_YP_X = iP_Z$ for a fixed system of axes. One then obtains Eq. (8) by projecting by means of Eq. (3) (and the analogous formula for **P**), and using Eq. (4), together with the fact that **P** commutes with all the direction cosines λ.

4. CORRESPONDENCE OF SUBTRACTION OF ANGULAR MOMENTUM IN MOLECULES TO ADDITION IN ATOMS

In the mathematics of atomic quantum theory, the transformation, with its Wigner coefficients, etc., is a familiar one from a system of representation in which two angular momentum vectors $\mathfrak{A}$, $\mathfrak{B}$ are separately spaced quantized, to a system in which they are collectively spaced quantized and in which $(\mathfrak{A}+\mathfrak{B})^2$ is diagonal. Precisely this transformation can be applied to take one from a system in which $J_z, \tilde{P}_z$ are each diagonal to one in which $(J_z+\tilde{P}_z)$ and $[J_x+\tilde{P}_x]^2+[J_y+\tilde{P}_y]^2+[J_z+\tilde{P}_z]^2$ are diagonal. However, $J_x+\tilde{P}_x$ is really J_x-P_x, etc., and so the transformation which adds angular vectors in the atomic case subtracts them in the molecular applications.

At this stage, it may seem that in this formal parallelism, it is rather artificial that subtraction appears in the molecular problem rather than addition. Actually, however, it is subtraction which is significant and has a physical basis, since the total angular momentum enters as one of the quantities compounded, and residual angular momenta are obtained by subtraction. If, for instance, it is a good approximation in a diatomic molecule to quantize the molecular angular momentum exclusive of spin contributions (Hund's case *b*), then the quantum number specifying the modulus of the difference **J**$-$**S** is a meaningful one.

We could, of course, have introduced the reversal operation in connection with the total rather than internal angular momentum, and then all the vectors would commute with the normal sign. However, in applying the usual atomic transformations, we would

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[6] H. Nielsen, Revs. Modern Phys. **23**, 90 (1951).

TABLE I. Notation for quantum numbers associated with various types of angular momentum in molecular and atomic spectra. The second entry, i.e., that following the commas, specifies the component of angular momentum parallel to some given axis (axis of figure if there is one) in the molecule, and parallel to some particular spatial axis (for example, that of some external electric or magnetic field) in the atomic case.

	Molecule	Atom
Total angular momentum inclusive of nuclear spin	F, Ω_F	F, M_F
Total angular momentum exclusive of nuclear spin	J, Ω	J, M_J
Total orbital angular momentum	$\mathcal{K}, K$	L, M_L
Electronic orbital angular momentum	L, Λ	L, M_L
Electronic spin angular momentum	S, Σ	S, M_S
Nuclear spin angular momentum	I, Ω_I	I, M_I

When F, Ω_F are identical with J, Ω (no nuclear spin), we use J, Ω.
When $\mathcal{K}$ is identical with J (no electronic spin), we use J.
In diatomic molecules, Λ is identical with K, and we use Λ.
In polyatomic molecules, Ω is identical with K when there is no electronic spin, and then we use K.

be subtracting the total from a partial angular momentum, and it is more convenient and physical to think of subtracting partial from total. For this reason, we have introduced the reversals in such a way as to make all the vectors commute with the anomalous sign, which is effectively no anomaly at all. It is to be emphasized that without arranging things so as to achieve a consistent sign behavior in all the commutation relations, we would have no right to employ the standard transformations. Our reversal procedure is thus a trick which enables us to adapt atomic calculations to molecular problems. In the next sections, we shall show that to every coupling problem in molecular spectra, there is a formally equivalent one in atoms, provided allowance is made for the differences in notation, etc.

5. NOTATION FOR MOLECULAR AND ATOMIC QUANTUM NUMBERS

Before proceding to specific applications, it is perhaps well to display the notation which we will use. This we do in Table I.

All the notation in the atomic case is standard. Some comment is required concerning the use of the quantum number K in molecules. The letter K has commonly been employed in two contradictory ways by the diatomic and polyatomic spectroscopists, *viz.*, to specify the total orbital angular momentum and the axial component thereof. An impasse thus arises in attempts to use a notation which is standard and consistent in a paper which treats both diatomic and polyatomic molecules. We have resolved this dilemma after a fashion by introducing $\mathcal{K}$ for the quantum number for which diatomic spectroscopists employ K. (The notation L is sometimes used for this quantum number in polyatomic molecules,[7] but such a usage is apt to be confusing because the letter L is often needed in connection with the matrix elements of purely electronic orbital angular momentum.) Our procedure is a rather makeshift one, but informal polling of a number of molecular spectroscopists failed to produce any happy suggestions, and our scheme has at least the merit that one can lapse back fairly consistently to standard diatomic or polyatomic usages in cases where confusion from the double role of K does not arise. Namely, most polyatomic molecules have no electron spin, and then J can be used in place of $\mathcal{K}$. In purely diatomic papers, confusion is unlikely to arise if K is used in place of $\mathcal{K}$, since there is no nuclear orbital angular momentum parallel to the axis of figure, and so the letter Λ denotes equally well the electronic or total orbital angular momentum parallel to this axis.

It should be particularly cautioned that in the correlations between atomic and molecular problems established in the following sections, atomic and molecular quantum numbers on the same line of Table I do not usually play parallel roles. Instead the correlations are quite different, as the resemblance between the atomic and molecular problems is more a formal mathematical than a physical one.

6. POLYATOMIC MOLECULES DEVOID OF INTERNAL ANGULAR MOMENTUM

We now turn to various illustrations of our procedure. The simplest example is the polyatomic molecule or asymmetrical top devoid of any internal angular momentum, so that $\mathbf{P}=0$ in Eq. (5). The hamiltonian is thus

$$H = AJ_x^2 + BJ_y^2 + CJ_z^2. \tag{9}$$

This is the case treated in Klein's original paper, and does not have any internal angular momentum to exhibit the point of our reversal trick. Our only addition to this paper is a rather trivial one, and consists in mentioning the mathematically analogous atomic problem. It is that of a single angular momentum vector subject to a crystalline potential of rhombic symmetry. It is imperative that the modulus of this angular momentum vector be a constant of the motion, or in other words correspond to a "good quantum number." Hence, the angular momentum vector is best chosen as one arising from spin, since except in rare earth salts the crystalline field usually spoils the goodness of the orbital quantum number L. The analogy is thus to an atom in an S state with either electronic or nuclear spin angular momentum (but not both, to avoid a two-vector problem). The hamiltonian function of such an atom in a rhombic crystalline field is

$$\mathcal{K} = \alpha S_x^2 + \beta S_y^2 + \gamma S_z^2 \quad \text{or} \quad \mathcal{K} = \alpha I_x^2 + \beta I_y^2 + \gamma I_z^2. \tag{10}$$

Obviously, Eqs. (9) and (10) are similar in structure. Physically, the first hamiltonian function listed in Eq. (10) is encountered in magnetic or microwave studies of manganous or ferric salts[8] (with nuclear spin neglected): the second occurs in the experiments of

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[7] J. Coon, J. Chem. Phys. 14. 665 (1946).

[8] J. H. Van Vleck and W. G. Penney, Phil. Mag. 17, 961 (1934).

Dehmelt and Kruger and of Pound[9] on the coupling of nuclear quadrupole moments to noncubic crystalline electric fields. Let us choose a system of representation in which the z compoment of angular momentum is diagonal; in accordance with Table I, the corresponding quantum number in the molecular case is K, and M_S or M_I in the atomic one. The correlation between the molecular and atomic problems is thus

$$J, K \leftrightarrow S, M_S \quad \text{or} \quad J, K \leftrightarrow I, M_I.$$

The matrix elements of S_x, S_y, S_z and hence of J_x, J_y, J_z are found in any elementary text on quantum theory.[10] The nonvanishing ones are

$$\langle JK|J_z|JK\rangle = K, \tag{11}$$

$$\langle JK|J_x+iJ_y|K+1\rangle = \langle JK+1|J_x-iJ_y|K\rangle = f(J,K), \tag{12}$$

where

$$f(J,K) = [J(J+1)-K(K+1)]^{\frac{1}{2}}. \tag{13}$$

The notation (13) will be used throughout the paper in order to abbreviate a type of expression which occurs very commonly. In accordance with Eq. (2), we have reversed the sign of i in Eq. (12) as compared with the usual formulas; but actually in this connection we need not wory about the sign of i, since, as mentioned in Sec. 3, a consistent anomaly is no anomaly at all. By elementary matrix multiplication, the diagonal matrix elements of the hamiltonian function (9) (with $P=0$) are found to be

$$\langle JK|H|JK\rangle = \tfrac{1}{2}(A+B)J(J+1) + (C-\tfrac{1}{2}A-\tfrac{1}{2}B)K^2, \tag{14}$$

and the nonvanishing off-diagonal elements,

$$\langle JK|H|JK+2\rangle = \tfrac{1}{4}(A-B)f(J,K)f(J,K+1). \tag{15}$$

All the hamiltonian matrices occurring in the present article are hermitian, and so we do not write down elements immediately obtainable by transposition. It is thus to be tacitly understood that

$$\langle JK|H|K+2\rangle = \langle JK+2|H|K\rangle^*, \quad \text{etc.} \tag{16}$$

The secular determinant can immediately be constructed for a given value of J. For given J, there are $2J+1$ values of K, but the secular determinant is of degree lower than $2J+1$ because of factorization. There is an obvious factorization because of the fact that the matrix elements are of the form $\Delta K = \pm 2$, so that even values of K are coupled only with even, and odd with odd. There is also a further factorization by the Wang transformation,[11] which utilizes the symmetry as regards reflection in a plane through two of the principal axes, and which is tantamount to choosing wave functions so that the azimuth angle occurs in a cosine or sine rather than an exponential. The form of the secular determinant after this factorization is readily available in the literature, and so will not be given explicitly here. For large values of J, even with the factorization, the algebraic difficulties are considerable, and a quite extensive literature exists on convenient schemes of approximation,[12] as well as numerical tables of roots for different amounts of asymmetry with moderate values of J.

7. COUPLING OF ELECTRON SPIN IN DIATOMIC MOLECULES NOT IN Σ-STATES

We now turn to a problem where the gist of the reversal trick can really be exhibited—*viz.*, the effect of molecular rotation on spin multiplets in diatomic molecules. This is a problem which was treated by Hill and Van Vleck[1] in 1927 by a superficially quite different method. We assume that the only force acting on the spin is that coupling it to the component Λ of orbital electronic angular momentum parallel to the axis of figure. (The perpendicular component affects the energy only in higher order approximations to be considered in Sec. 8.) Since we are neglecting nuclear spin, we can still use the notation J_x, J_y, J_z for the components of total angular momentum, and we take the z direction along the molecular axis. The hamiltonian function is consequently

$$H = B[(J_x-S_x)^2+(J_y-S_y)^2]+\zeta\Lambda S_z, \tag{17}$$

where ζ is the constant of proportionality of the spin-orbit coupling, and where B has the significance $h^2/8\pi^2 I$ in terms of the molecule's moment of inertia I. We now introduce the reversed spin angular momentum

$$\tilde{S}_x = -S_x, \quad \tilde{S}_y = -S_y, \quad \tilde{S}_z = -S_z$$

and note that

$$J_z = \Lambda - \tilde{S}_z, \tag{18}$$

$$S(S+1) = \tilde{S}_x^2 + \tilde{S}_y^2 + \tilde{S}_z^2, \tag{19}$$

where S is the usual spin quantum number. There is no distinction between the quantum numbers S and $\tilde{S}$, since reversal does not affect the absolute value of a vector. In virtue of Eqs. (18) and (19), it is easily seen that Eq. (17) can be written as

$$H = B[J(J+1)-\Lambda^2] + BS(S+1) - \zeta\Lambda\tilde{S}_z + 2B[J_x\tilde{S}_x + J_y\tilde{S}_y + J_z\tilde{S}_z]. \tag{20}$$

The first line of Eq. (20) can be considered as merely an additive constant, since J, Λ, and S are good quantum numbers for the problem under consideration. The secular problem connected with the hamiltonian function represented by the second line of Eq. (20) is the

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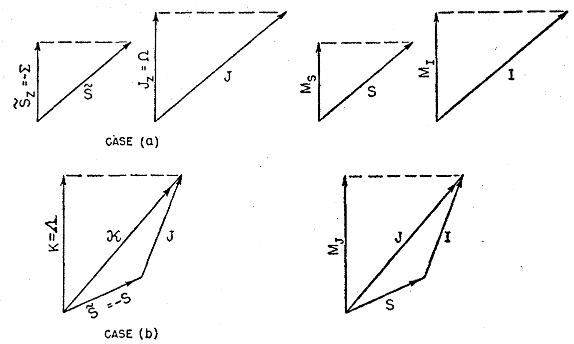
[9] H. G. Dehmelt and H. Kruger, Naturwiss. **37**, 111 (1950); R. V. Pound, Phys. Rev. **79**, 685 (1950).

[10] See, for example, Condon and Shortley, reference 4, p. 48; J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 168.

[11] S. C. Wang, Phys. Rev. **34**, 243 (1929), especially, p. 250.

[12] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943); **12**, 210 (1944); **17**, 826 (1949); G. W. King, J. Chem. Phys. **15**, 820 (1947); S. Golden, J. Chem. Phys. **16**, 78, 250 (1948); **17**, 586 (1949); J. K. Bragg and S. Golden, J. Chem. Phys. **17**, 439 (1949); E. E. Witmer, University of Pennsylvania Thermodynamics Research Laboratory Technical Report "Tabulation of a Function for Calculating the Rotational Energy Levels of a Rigid Polyatomic Molecule" (Navy Contract N6onr-24907) (1950).



Molecule Atom

FIG. 1.

same as that for the Zeeman effect of an atom in an S state with hyperfine structure conforming to the Landé rule.[13] Because of the smallness of nuclear moments, the magnetic field can be regarded as acting only on the electronic spin, and so the hamiltonian function for this atomic problem is

$$H=2\beta\mathfrak{H}S_z+\gamma\mathbf{I}\cdot\mathbf{S}, \tag{21}$$

where β is the Bohr magneton, $\mathfrak{H}$ is the magnetic field, and γ is a constant. The formal correlation of Eq. (20) with Eq. (21) is obtained by taking

$$-\zeta\Lambda\leftrightarrow 2\beta\mathfrak{H},\quad \gamma\leftrightarrow 2B,\quad \tilde{S}\leftrightarrow S,\quad J\leftrightarrow I,\quad \tilde{S}_z\leftrightarrow M_S,\quad J_z\leftrightarrow M_I.$$

It is convenient to set up the secular problem in either one of two schemes of representation as illustrated in Fig. 1. One is that of Hund's case (a), in which the spin is supposed quantized relative to the molecular axis, corresponding to separate spatial quantization of the electronic and nuclear spins, i.e., "complete Paschen-Backing" in the analogous atomic problem. If we use the familiar matrix elements, of structure (11–12), for angular momenta which are individually space-quantized, we see that the diagonal and off-diagonal matrix elements in the present secular problem are, respectively,

$$\langle\Sigma|H|\Sigma\rangle=E_0+\zeta\Lambda\Sigma-2B(\Lambda+\Sigma)\Sigma, \tag{22}$$

$$\langle\Sigma|H|\Sigma+1\rangle=Bf(J,\,\Lambda+\Sigma)f(S,\,\Sigma), \tag{23}$$

where f is defined as in Eq. (13), and E_0 denotes the first line of Eq. (20). The result embodied in Eqs. (22)–(23) is the same as that previously obtained by the writer by use of explicit wave functions.[14] The quantum number $\Sigma=S_z=-\tilde{S}_z$ involved in Eqs. (22) and (23) is that specifying the component of atomic spin along the molecular axis, and $J_z=\Lambda+\Sigma=\Omega$ is the total angular momentum along this axis. Because of the off-diagonal elements (23), neither Σ nor J_z is rigorously a good quantum number. If, however, the spin-orbit coupling is large compared with rotational distortion, the effect of off-diagonal elements is comparatively subordinate, and case (a) quantization is a good approximation. In any event, $\Lambda=J_z+\tilde{S}_z$ is a constant of the motion for the problem under consideration. The analog in the atomic problem is the fact that the component $J_z=I_z+S_z$ of total angular momentum along the direction of the field commutes with $\mathbf{I}\cdot\mathbf{S}$ and so is constant. Note particularly that in the molecular problem the angular momentum Λ which is conserved is that of purely orbital character, or, in other words, the difference between the spin and total angular momentum. On the other hand, in the atomic problem it is the sum of the angular momenta of the two constituents which is conserved. It is because of the reversal procedure that a difference in the molecular problem is able to play the same role as a sum in the atomic one.

The other system of representation in which it is often convenient to formulate the secular determinant is that of case (b). The quantum number $\mathcal{K}$ used in this case has the significance

$$\mathcal{K}(\mathcal{K}+1)=[J_x+\tilde{S}_x]^2+[J_y+\tilde{S}_y]^2+[J_z+\tilde{S}_z]^2=|\mathbf{J}-\mathbf{S}|^2.$$

The corresponding system of representation in the atomic problem is that which diagonalizes the total angular momentum $|\mathbf{I}+\mathbf{S}|^2$ of the atom, and our molecular quantum number $\mathcal{K}$ is formally correlated with the atomic J. The diagonal matrix elements are readily obtainable by the same elementary projection procedure as used for obtaining the Landé g factor when one of the constituents is magnetically inert. The off-diagonal elements are given by Condon and Shortley,[15] as well as in many other places, and are derivable, as there explained, by means of noncommutative algebra. The matrix elements of the hamiltonian function in the present system of representation are thus found to be

$$\langle\mathcal{K}|H|\mathcal{K}\rangle=E_0+B[\mathcal{K}(\mathcal{K}+1)-J(J+1)-S(S+1)]+\zeta\Lambda^2\left[\frac{J(J+1)-\mathcal{K}(\mathcal{K}+1)-S(S+1)}{2\mathcal{K}(\mathcal{K}+1)}\right], \tag{24}$$

$$\langle\mathcal{K}|H|\mathcal{K}+1\rangle=\frac{\zeta\Lambda f(\mathcal{K}+J+1,\,S)f(S,\,\mathcal{K}-J)[(\mathcal{K}+1)^2-\Lambda^2]}{2(\mathcal{K}+1)(2\mathcal{K}+1)^{\frac{1}{2}}(2\mathcal{K}+3)^{\frac{1}{2}}}, \tag{25}$$

where f is defined as in Eq. (13) and E_0 denotes the first line of Eq. (20), Equations (24)–(25) were first given by Hill and Van Vleck.[1]

The most important case experimentally is that of doublets, $S=\frac{1}{2}$. Then the roots of the secular equation are given by the simple formula

$$E=B[(J+\tfrac{1}{2})^2-\Lambda^2]\pm\tfrac{1}{2}[4B^2(J+\tfrac{1}{2})^2+\zeta\Lambda^2(\zeta-4B)]^{\frac{1}{2}}.$$

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[13] L. C. Pauling and S. A. Goudsmit, *The Structure of Line Spectra* (McGraw-Hill Book Company, Inc., New York, 1930), Chapter XI.

[14] J. H. Van Vleck, Phys. Rev. **33**, 481 (1929).

[15] Condon and Shortley, reference 4, p. 64 ff. For present purposes we identify our J, S, $\mathcal{K}$ with their J_1, J_2, J.

This formula can be obtained either from Eqs. (22)–(23) or (24)–(25) by taking $S=\frac{1}{2}$, $\mathcal{K}=J\pm\frac{1}{2}$. Actually, it can be obtained even more simply by the Goudsmit inspection method. Namely, it is comparatively easy to obtain the diagonal elements in either case (a) or (b). Also it is clear that the off-diagonal elements are linear in B in case (a), or linear in ζ in case (b). Once this fact is granted, the off-diagonal elements are uniquely determined when the secular equation is a quadratic, the doublet case, by the requirement that the roots of this equation reduce properly both in the limits corresponding to ideal case (a) and ideal case (b).

8. Λ- AND ρ-TYPE DOUBLING

In the preceding section we neglected the matrix elements of the electronic orbital angular momentum which are perpendicular to the molecular axis. Actually, these elements are present, and destroy the constancy of L_z, or in other words prevent Λ from being rigorously a good quantum number. However, they involve switches in the electronic quantum numbers, and so the resulting perturbation energy has large frequency denominators and is consequently small. The most important effect of these nondiagonal elements is the phenomenon of Λ-type doubling, whereby the degeneracy associated with the ambiguity in sign of Λ is lifted. Also, these elements are a contributing factor in the so-called ρ-type doubling, tripling, in $^2\Sigma$, $^3\Sigma$-states, etc. We shall not attempt to develop the perturbation theory underlying the explicit formulas responsible for these doublings and fine structures, as it is reasonably intricate, and given in detail elsewhere. However, the method of the present paper furnishes immediately the off-diagonal matrix elements which are the starting point of the calculation, and thus avoids the need of introducing explicit wave functions, recursion formulas for jacobi polynomials, etc.

The off-diagonal matrix elements which are responsible for the Λ-doubling are

$$H_\lambda=-2B[J_xP_x+J_yP_y], \tag{26}$$

where $\mathbf{P}$ is the total internal or electronic angular momentum, both spin and orbital (see Eq. (5) with $A=B$, $C=0$; the term $B(P_x^2+P_y^2)$ of Eq. (5) is independent of J and so is an uninteresting constant which we drop). The matrix elements of Eq. (26) can immediately be obtained by essentially the same procedure as employed in the preceding section. The main difference is that $\mathbf{P}^2$ is not a constant of the motion, so that explicit numerical values of the matrix elements of P_x, P_y cannot be written down. However, because of the axial nature of the symmetry in diatomic molecules, the matrix elements of P_x and P_y differ from each other only in being 90° out of phase. Furthermore $J_z+\tilde{P}_z$ commutes with the hamiltonian function, and is rigorously a constant of the motion. The sole eigenvalue of this quantity which concerns us is zero. This conservation theorem expresses the physically rather platitudinous fact that in a diatomic molecule the component of total electronic angular momentum along the molecular axis is purely electronic, so that $J_z+\tilde{P}_z=J_z-P_z=0$. From the preceding statements and the commutation relations (2) and (7) it follows that

$$\begin{aligned}\langle J_z|\,J_y|\,J_z\pm1\rangle&=\mp i\langle J_z|\,J_x|\,J_z\pm1\rangle,\\ \langle\tilde{P}_z|\tilde{P}_y|\tilde{P}_z\pm1\rangle&=\mp i\langle\tilde{P}_z|\tilde{P}_x|\tilde{P}_z\pm1\rangle.\end{aligned}\tag{27}$$

When we use Eq. (27), we see that the matrix elements of Eq. (26) are

$$\langle eJ_z\tilde{P}_z|H_\lambda|e'J_z+1\tilde{P}_z-1\rangle =2f(J,J_z)\langle e\tilde{P}_z|B\tilde{P}_x|e'\tilde{P}_z-1\rangle. \tag{28}$$

Here the letter e symbolizes all electronic quantum numbers other than P_z, and is included in order to indicate that P_x is not, in general, diagonal in electronic quantum numbers. The factor BP_x is written as $\langle|BP_x|\rangle$ rather than $B\langle|P_x|\rangle$ in order to show that the moment of inertia is not diagonal in the electronic quantum numbers; i.e., must be kept inside the integral sign if matrix elements are computed by quadrature from the wave functions.

Since the eigenvalues of J_z and $\tilde{P}_z$ which are involved are the same, the double index notation in Eq. (28) is redundant, and so it is customary to write Eq. (28) in the form[16]

$$\langle e\Omega|H_\lambda|e'\Omega+1\rangle=-2f(J,\Omega)\langle e\Omega|BP_x|e'\Omega+1\rangle, \tag{29}$$

where Ω denotes an eigenvalue of $P_z=J_z=-\tilde{P}_z$.

In case the molecule is devoid of spin, the matrix elements of P_x can be identified with those of L_x. When the molecule is not in a singlet state, the problem of calculating the matrix elements of P_x becomes more complicated, as it is necessary to use an intermediate system of representation which allows for the perturbing effect of spin-orbit interaction and in which L_z and S_z are not separately diagonal. The process of finding these elements is explained in an earlier paper.[16]

It remains for us to point out the secular problem in atomic spectra which is mathematically analogous to the molecular one which we have been considering in the present section. Let us first assume that the molecule has no spin. Then the analogous atomic problem is that of an atom with both spin and orbital angular momentum in a crystalline field of axial symmetry, whose effect is large compared with that of the spin-orbit interaction. The hamiltonian function is then

$$V(r,z)+\gamma\mathbf{L}\cdot\mathbf{S}. \tag{30}$$

In addition, the atom must be in a state $M=0$ of vanishing total angular momentum about the axis of the field. The correlation of the molecular with the atomic problem is as follows:

$$2B\leftrightarrow\gamma,\quad \tilde{L}\leftrightarrow L,\quad -\Lambda\leftrightarrow M_L,\quad J_z\leftrightarrow M_S(M=M_L+M_S=0).$$

The phenomenon of Λ-type doubling in the molecule corresponds in the atom to the lifting by the non-

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[16] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); the phase convention of Eq. (29) of this reference differs by 90° from that of the present Eq. (29) in that we now take P_x rather than P_y to be real.

diagonal elements of the spin-orbit interaction of the degeneracy associated with the pair of levels $L_Z=M_L'$, $S_z=-M_L'$ and $L_z=-M_L'$, $S_z=+M_L'(M_L'\neq 0)$. This degeneracy remains if one retains only the diagonal part γL_zS_z of the spin-orbit interaction in Eq. (30), but is removed when one includes the nondiagonal part, which plays a role analogous to (28).

In case the molecule has spin as well as orbital angular momentum, the corresponding atomic problem is a three-vector one. There is cosine coupling between the three angular momentum vectors, and in addition a strong axial field acting on one of them.

9. COUPLING OF ELECTRON SPIN IN POLYATOMIC MOLECULES

We now turn to a subject which, because of its complexity, probably furnishes the best and most interesting illustration of our method. This is the problem of the coupling of electron spin in polyatomic molecules. Here we may suppose that the diagonal elements of the electronic orbital angular momentum are zero in the "clamped nuclei" problem. Hence, the coupling is only a higher order effect resulting from the influence of excited electronic states and molecular rotation. Our theory applies also to molecules in Σ-states, as here also, only the higher order effects are responsible for the spin multiplets.[17]

The problem consists essentially of two parts: (I) derivation of the effective hamiltonian function from perturbation theory and (II) calculation of the matrix elements once this function has been obtained. The extended Klein technique has a bearing only on (II). In order not to interrupt the continuity of subject matter, we postpone the presentation of (I) until Appendix I. Inclusion of this appendix is desirable, since (I) is a subject which has not been adequately treated in the literature.[18]

The effective hamiltonian function can be taken to be

$$\begin{aligned}H=&A\mathcal{K}_x^2+B\mathcal{K}_y^2+C\mathcal{K}_z^2+a_0(\mathcal{K}_x\tilde{S}_x+\mathcal{K}_y\tilde{S}_y+\mathcal{K}_z\tilde{S}_z)\\&+a[2\mathcal{K}_z\tilde{S}_z-\mathcal{K}_x\tilde{S}_x-\mathcal{K}_y\tilde{S}_y]+b[\mathcal{K}_x\tilde{S}_x-\mathcal{K}_y\tilde{S}_y]\\&+c[\mathcal{K}_x\tilde{S}_y+\mathcal{K}_y\tilde{S}_x]+d[\mathcal{K}_x\tilde{S}_z+\mathcal{K}_z\tilde{S}_x]\\&e[\mathcal{K}_y\tilde{S}_z+\mathcal{K}_z\tilde{S}_y]+\alpha[2\tilde{S}_z^2-\tilde{S}_x^2-\tilde{S}_y^2]\\&+\beta[\tilde{S}_x^2-\tilde{S}_y^2]+\gamma[\tilde{S}_x\tilde{S}_y+\tilde{S}_y\tilde{S}_x]\\&+\delta[\tilde{S}_x\tilde{S}_z+\tilde{S}_z\tilde{S}_x]+\epsilon[\tilde{S}_y\tilde{S}_z+\tilde{S}_z\tilde{S}_y],\end{aligned}\quad(31)$$

where $a_0, a, b, \cdots, \epsilon$ are constants and where

$$\mathcal{K}_x=J_x-S_x=J_x+\tilde{S}_x,\quad A=h^2/8\pi^2I_A,\quad \text{etc.}$$

The notation concerning the quantum numbers associated with angular momentum is that explained in Sec. 5. We continue to assume no nuclear spin, so that the molecule's total angular momentum may be denoted by J rather than F. We have expressed Eq. (31) in terms of $\tilde{S}$ rather than S, since $\mathcal{K}$ and $\tilde{S}$ satisfy similar commutation relations, of the type given in Eq. (2). Note particularly that $J_x^2+J_y^2+J_z^2$ and $\tilde{S}_x^2+\tilde{S}_y^2+\tilde{S}_z^2$ commute with Eq. (31), whereas $\mathcal{K}_x^2+\mathcal{K}_y^2+\mathcal{K}_z^2$ commutes with only the first line of Eq. (31); consequently, J and S are good quantum numbers, whereas $\mathcal{K}$ is not rigorously. (In principle, spin-orbit interaction prevents even S from being strictly a good quantum number, but this effect in unimportant except in very heavy molecules and will be neglected. Such breakdown of Russell-Saunders coupling is less common in molecules than in atoms, since few molecules have atoms of the iron group, etc., in unclosed shells.)

In writing Eq. (31), we have arranged the constants in such a way that each term, other than those on the first line has essentially the rotational transformation properties of a second-degree spherical harmonic.[19] This greatly facilitates our later writing down of the explicit formulas for the matrix elements.

The expression (31) does not represent the same hamiltonian function as that with which one starts, *viz.*,

$$\begin{aligned}H=A(J_x-S_x-L_x)^2+B(J_y-S_y-L_y)^2&\\+C(J_z-S_z-L_z)^2&\quad(32)\\+\text{ spin-orbit and spin-spin interactions.}&\end{aligned}$$

The orbital angular momentum $\mathbf{L}$ and hence the expression (32) are highly nondiagonal in the electronic quantum numbers. Appendix I gives the proof that Eq. (32) can be replaced by Eq. (31) after a perturbation calculation is made to eliminate matrix elements connecting different electronic states. The hamiltonian function (31), unlike Eq. (32), has a secular problem involving only closely spaced states associated with different orientations of the spin and rotational angular momenta relative to the molecular frame.

The general procedure for calculating the constants $a_0, a, \cdots, \epsilon$ is given in Appendix I. The terms having small Roman letters for proportionality factors arise from the combined effect of rotation and spin-orbit interaction. Those having Greek letters come from the second-order effect of spin-orbit interaction. The orders of magnitude of the two types of terms are thus

$$a\sim B\zeta/h\nu,\quad \alpha\sim\zeta^2/h\nu,\quad (B\sim h^2/8\pi^2I),$$

where ζ is the conventional spin-orbit parameter and where $h\nu$ is the order of magnitude of the energy interval between different electronic states. If the molecule is a symmetrical top or is diatomic, great simplification results, as then out of all the constants $a_0, a, \cdots, \epsilon$ only a_0, a, and α are different from zero.

The secular problem in atomic spectra equivalent to

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[17] See, for instance, M. H. Hebb, Phys. Rev. **49**, 610 (1936). The theory of ρ-type tripling is developed in detail in this reference.

[18] Calculations somewhat similar to those in our Appendix I have, however, been made by a different method, and in somewhat less general form by R. S. Henderson, unpublished except as a letter to the editor, Phys. Rev. **74**, 106 (1948). Henderson finds that the theoretical formulas give excellent agreement with the fine structure observed by Coon (reference 7) in ClO_2.

[19] To avoid writing radicals, we do not normalize all the harmonics in the same way; for consistent normalization a factor $(\frac{1}{3})^{\frac{1}{2}}$ would be necessary in the a and α-terms.

Eq. (31) is that of an atom with two spin vectors, say one electronic, one nuclear, each subject to a second-order crystalline potential of rhombic structure, such as $\mu_{11}S_x^2+\mu_{12}S_xS_y+\cdots$, etc. The correlation of the molecular and atomic quantum numbers is then as follows:

$$\tilde{S}\leftrightarrow S,\quad J\leftrightarrow I,\quad \mathcal{K}\leftrightarrow J,\quad K\leftrightarrow M_J. \tag{33}$$

We shall not write down the corresponding atomic hamiltonian function, as it can be obtained by merely making the replacements (33) in Eq. (31) (for example, $\mathcal{K}_x\tilde{S}_y\rightarrow J_xS_y$). To bring out the full generality of the problem, the coupling between the two atomic spin vectors should be anisotropic, $\zeta_{11}S_xI_x+\zeta_{12}S_xI_y+\cdots$, rather than of the conventional "cosine" type $\zeta\mathbf{S}\cdot\mathbf{I}$. The parallelism established in (33) makes the cross terms in (31) correspond to coupling between **J** and **S** rather than **I** and **S**, but this distinction is immaterial as regards mathematical structure since $\mathbf{J}=\mathbf{I}+\mathbf{S}$, and since there are already quadratic terms in S.

Indeed, this corresponding atomic problem comes surprisingly close to being realized in the calculations of Pryce[20] and others on the hyperfine structure of atoms subject to anisotropic powerful crystalline fields which quench the orbital angular momentum. The coupling between the electronic and nuclear spins then becomes anisotropic because the dipolar interaction between the two spins must be averaged over the orbital wave functions, which usually have less than cubic symmetry. Actually, the crystalline field does not act appreciably on the nuclear spin, so that the coefficients of the quadratic terms in I in the hamiltonian function are negligible. However, this fact has no influence on the basic type of complexity of the problem. Of course, the crystalline electric field does not act directly on even the electronic spin in atoms, but does give an effective potential depending on spin alignment because of the indirect repercussions of spin-orbit interaction.

It would be particularly easy to write down the matrix elements of Eq. (31) in a scheme of representation corresponding to case (a) in diatomic molecules, in which the spin and total angular momenta are separately space quantized relative to some axis of reference fixed in the molecule. This corresponds, of course, to separate space quantization of the spins in the related atomic problem. The matrix elements of J would be given by Eqs. (11) and (12), except that the letter Ω must everywhere replace K, since the notation Ω rather than K must be used for J_z in molecules with spin (see Sec. 5). The matrix elements of $\tilde{S}$ would be of similar structure having S, $-\Sigma$ in place of J, K. However, this scheme is not a good starting point physically, because the Coriolis effects of the molecular rotation are far more important than the second-order effects of spin-orbit interactions. It is therefore desirable to set up the matrix elements of Eq. (31) in the $\mathcal{K}$, K system of representation. Here, $\mathcal{K}$ is approximately, but not rigorously a good quantum number. On the other hand, $\mathcal{K}_z$, described by the quantum number K, is a constant of the motion if and only if the molecule has axial symmetry.

Now that a formal correlation with atomic spectra has been established by means of Eq. (33), the matrix elements of Eq. (31) can be calculated by borrowing atomic formulas. The elements of the A, B, C part of Eq. (31) are, of course, simply those of the asymmetrical top, and are given by Eqs. (14)–(15) except for the notational difference that $\mathcal{K}$ now replaces J, inasmuch as the angular momentum involved in the rotational kinetic energy of the molecule is that exclusive of spin. The terms of Eq. (31) containing Greek letters have a quadrupolar structure of the same type form as would result if the electron had a quadrupole moment. The matrix elements of these terms can be obtained by employing the matrices for $\tilde{S}_x$, $\tilde{S}_y$, $\tilde{S}_z$ in the essentially Russell-Saunders system of representation in which $\tilde{S}$, J are compounded to a resultant $\mathcal{K}$; the expressions for $\tilde{S}_x\tilde{S}_y$, $\tilde{S}_x\tilde{S}_z$, etc., are then obtained by multiplying together the matrices for $\tilde{S}_x$, $\tilde{S}_y$, $\tilde{S}_z$. The algebra of this multiplication, though elementary, is rather tedious, and has already been performed by Rubinowicz.[21] The resulting quadrupole amplitudes are given in Condon and Shortley,[22] and can be taken over immediately when appropriate allowance is made for differences in notation and some investigation is made of how the normalization factor is to be chosen. (Normalization is not very clearly discussed by either Rubinowicz or C. and S.) There are, of course, also the more erudite and elegant methods of obtaining quadrupole amplitudes by means of group theory, developed by Brinkman[23] and by Racah.[24] The results are, of course, necessarily the same as those obtained by the more elementary procedure when the normalization is properly made, except for possible differences in the phase conventions.

The matrix elements of the terms in Eq. (31) involving small letters $a, \cdots, e$ can be obtained by multiplication of the matrix elements of the components of $\mathcal{K}$ and S. It is easier to calculate a product of the type $\mathcal{K}_xS_y$ by direct multiplication than one of the form S_xS_y, since in the $\mathcal{K}$ system of representation the matrix elements of $\mathcal{K}_x$ are naturally particularly simple (of structure (11–12) with $\mathcal{K}$ replacing J).

Certain short cuts, however, are available for computing these small letter terms. In the first place,

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[20] M. H. L. Pryce, Nature **164**, 117 (1949); A. Abraham and M. H. L. Pryce, Proc. Phys. Soc. (London) **63A**, 410 (1950); B. Bleaney, Phys. Rev. **78**, 214 (1950).

[21] A. Rubinowicz, Z. Physik **61**, 338 (1930); **65**, 662 (1930).

[22] Condon and Shortley, reference 4, pp. 95, 100, and 252–253. Our $\tilde{S}$, J, $\mathcal{K}$ are correlated with L, S, J in reference 4. We are unable to agree with the rule for finding the phases given on p. 252, as in taking the square root one should not take the modulus of the square root of quantities already squared in their table 4[9]; for example, the $-$ sign given in the third column of the second row of this table applies when one takes $\sqrt{[R(J)-(J+1)]^2}=R(J)-(J+1)$, not $|R(J)-(J+1)|$.

[23] H. C. Brinkman, *Zur Quantenmechanik der Multipolstrahling*, thesis, Utrecht, 1932 (published by Noordhoff, Groningen).

[24] G. Racah, Phys. Rev. **61**, 186; **62**, 438 (1942).

TABLE II. Matrix elements of the hamiltonian function (31), with $S, \mathcal{K}, J$ replaced by I, J, F.

$$\langle JK|H|J\,K\rangle=\tfrac{1}{2}(A+B)[J(J+1)-K^2]+CK^2+\tfrac{1}{2}a_0[J(J+1)+I(I+1)-F(F+1)]+[3K^2-J(J+1)][a\theta(J)+\alpha\rho(J)],$$

$$\langle JK|H|J\,K\pm2\rangle=\tfrac{1}{2}f(J,\pm K)f(J,\pm K+1)[\tfrac{1}{2}(A-B)+(b\mp ic)\theta(J)+(\beta\mp i\gamma)\rho(J)],$$

$$\langle JK|H|J\,K\pm1\rangle=(K\pm\tfrac{1}{2})f(J,\pm K)[(d\mp ie)\theta(J)+(\delta\mp i\epsilon)\rho(J)],$$

$$\langle JK|H|J-1\,K\rangle=\tfrac{3}{2}K(J^2-K^2)^{\frac{1}{2}}[a\varphi(J)+\alpha\chi(J)],$$

$$\langle JK|H|J-1\,K\pm2\rangle=\pm\tfrac{1}{4}f(J,\pm K)g(J-1,\pm K)[(b\mp ic)\varphi(J)+(\beta\mp i\gamma)\chi(J)],$$

$$\langle JK|H|J-1\,K\pm1\rangle=\tfrac{1}{4}(J\pm2K+1)g(J,\pm K)[(d\mp ie)\varphi(J)+(\delta\mp i\epsilon)\chi(J)],$$

$$\langle JK|H|J-2\,K\rangle=\tfrac{3}{2}g(J,K)g(J,-K)\alpha\psi(J),$$

$$\langle JK|H|J-2\,K\pm2\rangle=\tfrac{1}{4}g(J,\pm K)g(J,\pm K+2)[\beta\mp i\gamma]\psi(J),$$

$$\langle JK|H|J-2\,K\pm1\rangle=\pm\tfrac{1}{2}(J^2-K^2)^{\frac{1}{2}}g(J,\pm K+1)[\delta\mp i\epsilon]\psi(J),$$

where

$$f(x,y)=[(x-y)(x+y+1)]^{\frac{1}{2}},\qquad g(x,y)=[(x-y)(x-y-1)]^{\frac{1}{2}},$$

$$\theta(J)=\frac{J(J+1)+I(I+1)-F(F+1)}{2J(J+1)},\qquad \rho(J)=\frac{3R(J)[R(J)-1]-4J(J+1)I(I+1)}{2J(J+1)(2J-1)(2J+3)},$$

$$\varphi(J)=-\frac{[P(J)Q(J-1)]^{\frac{1}{2}}}{J(2J-1)^{\frac{1}{2}}(2J+1)^{\frac{1}{2}}},\quad \chi(J)=\frac{[R(J)-(J+1)]\varphi(J)}{(J-1)(J+1)},\quad \psi(J)=\frac{[P(J-1)P(J)Q(J-2)Q(J-1)]^{\frac{1}{2}}}{2J(J-1)(2J-1)(2J+1)^{\frac{1}{2}}(2J-3)^{\frac{1}{2}}},$$

with

$$P(J)=(J-F+I)(J+F+I+1),\quad Q(J)=(I+F-J)(J+F-I+1),$$

$$R(J)=J(J+1)+I(I+1)-F(F+1)=-2\mathbf{I}\cdot\mathbf{J}$$

unlike the capital letter and Greek terms, they have no elements of the form $\Delta\mathcal{K}=\pm2$, inasmuch as $\mathcal{K}_x$, $\mathcal{K}_y$, $\mathcal{K}_z$ are diagonal in $\mathcal{K}$, and S_x, S_y, S_z have $\Delta\mathcal{K}=0$, ±1. Hence, the small letter terms have $|\Delta\mathcal{K}|\leqq1$. The elements which are diagonal in $\mathcal{K}$ can be obtained by projecting $\tilde{S}$ along $\mathcal{K}$. Thus, for example, one obtains

$$\mathcal{K}_z\tilde{S}_z=\frac{\mathcal{K}_z(\mathcal{K}_x\tilde{S}_x+\mathcal{K}_y\tilde{S}_y+\mathcal{K}_z\tilde{S}_z)\mathcal{K}_z}{\mathcal{K}(\mathcal{K}+1)}=\frac{\mathcal{K}_z\mathcal{K}_z[\mathcal{K}(\mathcal{K}+1)+S(S+1)-J(J+1)]}{2\mathcal{K}(\mathcal{K}+1)}.$$

It still remains to compute the matrix elements of the type $\Delta\mathcal{K}=\pm1$. The a_0 term has no elements of this type, as it is a scalar product diagonal in $\mathcal{K}$. Because of the similar rotational transformation characteristics of the corresponding small letter and Greek terms in Eq. (31), it suffices to compute one of the terms $a, \cdots, e$. The others will differ only by factors depending solely on $\mathcal{K}$, K which are precisely the same as for the alphabetically corresponding Greek terms, already computed by using the known results on quadrupoles. The easiest term to compute is $a[2\mathcal{K}_z\tilde{S}_z-\mathcal{K}_x\tilde{S}_x-\mathcal{K}_y\tilde{S}_y]$, whose nondiagonal elements in $\mathcal{K}$ are the same as those of $3\mathcal{K}_z\tilde{S}_z$, inasmuch as $\mathcal{K}_x\tilde{S}_x+\mathcal{K}_y\tilde{S}_y+\mathcal{K}_z\tilde{S}_z$ is diagonal in $\mathcal{K}$. Essentially, $\mathcal{K}_z\tilde{S}_z$ has been computed in obtaining the expression (25), which differs from $\mathcal{K}_z\tilde{S}_z$ only by having an extra factor $-\zeta$ and in having the notation Λ rather than K (compare Eq. (20)).

Instead of giving the matrix elements obtained by this procedure immediately, we defer writing them down until Table II of Sec. 10, where they are all given, however, in notation appropriate to the case that the spin is nuclear rather than electronic. We do this because the formulas are most likely to be used in the nuclear case in view of the interest in nuclear quadrupole moments and of the comparative rarity of polyatomic molecules with nonvanishing electronic spin. The formulas of Table II, however, apply equally well to the present, electronic case, if a simple change in notation is made, *viz.*, the replacement of the letters on the right side of (34) by those on the left.

10. COUPLING OF NUCLEAR SPIN IN MOLECULES DEVOID OF ELECTRONIC SPIN

We now turn to molecules possessing nuclear spin. For simplicity, we assume that the molecule has only one nucleus with spin, and that it has no resultant electronic spin angular momentum, as is true for the vast majority of molecules. The mathematical problem is then precisely the same as that considered in the preceding section, the only difference being that the spin has a nuclear rather than electronic origin. Hence, all the theory and results of Sec. 9 are applicable, provided only that the following change in notation is made:

$$S,\ J,\ \mathcal{K},\ K\leftrightarrow I,\ F,\ J,\ K. \tag{34}$$

Except for this change in notation, the effective hamiltonian is still given by Eq. (31) (see Appendixes I and II). Since the interaction of nuclear spin with the molecule is comparatively weak, it is natural to use a system of representation which diagonalizes the total angular momentum J of the molecule exclusive of nuclear spin. By means of the method described in Sec. 9, it is found that in this system the matrix elements have the values given in Table II.

Matrix elements in which J increases rather than decreases have not been written down, but can be obtained by using the hermitian property (see Eq. (12)). In forming the conjugate, the expressions a_0, a, b, $\cdots$, ϵ can all be taken as real. The negative sign entering in some of the elements of the type $\Delta J = \pm 1$ is a matter of phase convention and is employed to conform to the usage of Condon and Shortley.

The matrix elements given above are more general and complete than needed for most purposes. In the first place, the molecule may have an axis of symmetry (for example, NH_3 or a diatomic molecule). Then all elements nondiagonal in K vanish.

Regardless of whether the molecule has any particular symmetry, elements nondiagonal in J may be neglected in the first approximation if the coupling of the spin to the molecular frame (terms involving the constants $a, b, \cdots, \epsilon$) is small compared with the rotational energy. Since this coupling arises only in virtue of higher order effects of magnetic interaction, such a neglect is usually pretty well warranted. However, we have included the elements nondiagonal in J, since sometimes high accuracy may be required and since, furthermore, accidental degeneracies may sometimes make nondiagonal elements abnormally important.

Ordinarily, it is convenient to start a perturbation calculation for the effect of spin coupling in a system of representation which diagonalizes the purely rotational energy. The secular determinant for the asymmetrical top factors twice: *viz.*, once according to the evenness or oddness of K and once again after the Wang transformation[11] is made to wave functions which are either even or odd (and thus noncombining) with regards to reflection in a principal plane containing the z axis. The inclusion of the magnetic spin coupling energies can spoil the rigor of both factorizations, for the principal axes for the spin quadratic forms in Eq. (31) are not, in general, the same as principal axes of inertia. (One can see this, for instance, from the fact that substitution of an isotope can rotate the axes of inertia, but does not change the quadrupolar terms $\alpha, \cdots, \epsilon$.) However, the only elements of this spin interaction which enter in the first approximation of perturbation theory are those which are of the form $\Delta J = 0$; $\Delta K = 0, \pm 2$ and which connect states of like Wang symmetry. We omit giving details of the procedure for transforming the matrix elements from the K system of representation to the Wang scheme and finally to that which diagonalizes the asymmetrical top part of the energy. This procedure is fairly straightforward and has been described in detail many places in the literature.[25]

As far as we know, this is the first time that all the matrix elements have been explicitly listed, inclusive of both those of quadrupolar ($\sim I_z^2$) and dipolar ($\sim J_z I_z$) structure. It is, however, true that the quadrupolar elements which are most important for most problems have been given by Bardeen and Townes[26] and by Bragg,[25] and the dipolar terms which are diagonal in J have been computed in largely unpublished work of Henderson.[27] The methods previously employed to obtain the matrix elements are different from the one which we use, which in our opinion is the simplest. Most writers[28] compute the matrix elements in a system of representation in which I and J are separately space quantized relative to axes fixed in space, and then pass to the F, M_F system by using an argument of Casimir's[29] based on the invariance of the diagonal sum and predictions of group theory concerning the mode of dependence on F. Our method frees us from the need of invoking the M_I, M_J system as an initial step, although the difference in ultimate labor is small.

There is a vital difference between the nuclear and electronic cases concerning the significance of the constants $\alpha, \cdots, \epsilon$. Nuclei have bona fide quadrupole moments rather than merely terms of quadrupolar structure resulting from the second-order effects of the magnetic dipole moment (called henceforth "pseudo-quadrupolar terms").

If only the bona fide quadrupole effect is present, the constants $\alpha, \cdots, \epsilon$ have the following values:

$$\alpha = D\left(2\frac{\partial^2 V}{\partial z^2} - \frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right), \qquad \beta = 3D\left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right), \tag{35}$$

$$\gamma = 6D\partial^2 V/\partial x \partial y, \qquad \delta = 6D\partial^2 V/\partial z \partial x, \qquad \epsilon = 6D\partial^2 V/\partial y \partial z$$

with

$$D = eQ/12I(2I-1).$$

Here, eQ is the quadrupole moment of the nucleus, as defined by Casimir[29] and by the nuclear physicists at Columbia. The meaning of this definition, and the derivation of Eqs. (35), which is elementary, are given in Appendix II.

Besides the bona fide quadrupole effect, the pseudo-quadrupolar one is also present. The theory in Appendix I is developed explicitly for the higher order effects of electronic spin, but applies equally well to the nuclear case if the magnetic moment be ascribed to the nucleus rather than electron. Thus, if the pseudo-quadrupolar effect alone is operative, the constants $a_0, a, b, \cdots, \epsilon$ have values which can be calculated by the procedure given in Appendix I, but with the modification (34) in notation and with g, β interpreted as nuclear g factors and magnetons (see note 35).

Actually, of course, the bona fide and pseudo-quadrupolar effect are simultaneously present, and so the

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[25] J. K. Bragg, Phys. Rev. **74**, 533 (1948); S. Golden and J. K. Bragg, Phys. Rev. **75**, 735 (1949); G. B. Knight and B. T. Feld, Phys. Rev. **74**, 354 (1948).

[26] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

[27] R. S. Henderson, Phys. Rev. **74**, 106, 626 (1948).

[28] In the calculations which the writer made in 1946, and which were quoted in a short paper by Dailey, Kyhl, Strandberg, Van Vleck, and Wilson, Phys. Rev. **70**, 984 (1946), the quadrupole matrix elements were found by squaring out those given in reference 1 in the case (b) system of representation. The present paper is essentially a refinement of our earlier work, as it led to the discovery of how to adapt the Klein procedure.

[29] H. B. G. Casimir, "On the Interaction between Atomic Nuclei and Electrons," Prize essay published by Teyler's *Tweede Genootschap* (Haarlem, 1936).

actual values of the constants $\alpha, \cdots, \epsilon$ will be the sum of the values calculated from the two types of effects separately. As Foley[30] and Wick[31] have emphasized, care must be exercised that the pseudo contribution is not important when the quadrupole moment is deduced from the observed dependence on quantum numbers under the assumption that only the bona fide mechanism is operative. Fortunately, the correction for the pseudo effect is usually quite inconsequential if the electronic states are widely spaced.

Ordinarily, the "dipolar" terms (type $a_0, \cdots, e$ in Eq. (31)), which arise from interaction of the nuclear magnetic moment with the molecular rotation, are relatively unimportant. Evidence for a dipolar contribution has, however, been found in the microwave spectrum of ammonia.[27]

11. OTHER PROBLEMS AMENABLE TO THE METHOD

There are other, more complicated problems which can be treated by the present method. The advantages of our procedure probably increase somewhat with the complexity of the model, but these other problems involve too much detail to be appropriately elaborated upon here. Most of them are of the type where the molecule has two (or more generally n) spin angular momentum vectors, for example, simultaneous electronic and nuclear spins, or two nuclei with spins. Such problems are formally reducible to atomic ones involving the coupling of three (or more generally $n+1$) angular momentum vectors. Because of the dipole-dipole form of the interaction between magnetic moments, and also because the coefficients A, B, C in Eq. (5) are unequal, the coupling will, however, be less isotropic than the cosine or scalar product type usually encountered in atomic spectra.

The coupling problems connected with vibrational angular momentum are also amenable to the present method.[32]

12. INTENSITIES, AND BEHAVIOR IN EXTERNAL FIELDS

So far, we have discussed only frequencies, but not intensities, a factor of almost equal significance in the analysis of many experiments. At first sight, it seems that our method is inherently incapable of giving information about intensities in rotational fine structures (P, Q, R branches, etc.), for its very essence is that it enables one to work only with axes mounted on the molecule, without the need of referring to any fixed in space. Physically, it is obvious that the rotational frequencies cannot enter in the fourier components or matrix elements of the electric or magnetic moment relative to axes travelling with the molecule. Mathematically, this truism is expressed by the fact that the moment μ commutes with the total angular momentum when both are referred to axes mounted on the molecule, as it can be shown that μ satisfies commutation relations similar to those of Eq. (8) for the internal angular momentum $\mathbf{P}$. However, if our method has been used to solve the secular problem of the energy levels, the intensities can be computed in a straightforward manner by the following procedure.

The Z component of dipole moment in a fixed coordinate system is given in terms of the components μ_x, μ_y, μ_z measured relative to axes mounted on the molecule by the relation,

$$\mu_Z=\lambda_{Zx}\mu_x+\lambda_{Zy}\mu_y+\lambda_{Zz}\mu_z, \tag{36}$$

where the λ's are direction cosines. Suppose that the starting point of the perturbation or secular calculation is some given standard system of representation. Then μ_x, μ_y, μ_z are matrices known from the "internal" characteristics of the molecule and are independent of how it is oriented in space. For example, the matrix elements of electric moment involve only the electronic quantum numbers e. The matrix elements of the direction cosines can be calculated in this scheme of representation by known kinetimatical and quantal principles. This can be done without group theory or wave functions (one of the aims of our approach); in fact, essentially the λ's were calculated by Dennison[33] in one of the early papers based on the purely Born-Heisenberg formulation of quantum mechanics. By taking the direct product of matrices, the elements of Eq. (36) can then be found. The initial system of representation is not the appropriate final one, but one can transform to this and so find the relevant amplitude $S\mu_Z S^{-1}$. The important thing is that solution of the energy problem gives one the transformation matrix S. Of course, Eq. (36) gives only the Z component of intensity, but the total can be found from spectroscopic stability or standard formulas for the relative intensities of Zeeman components.

Similarly, the secular problems connected with electric and magnetic fields can be formulated even in our method. Consider, for example, the Stark effect. The extra term added to the hamiltonian function is then proportional to (36), and its matrix elements can be calculated by the procedure explained above. The important thing is that the equatorial quantum number M_J (M_F in nuclear problems) enters the secular problem only as a parameter, since the hamiltonian function is diagonal in M_J if the direction of the field is taken as

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[30] H. M. Foley, Phys. Rev. **72**, 504 (1947).

[31] G. C. Wick, Phys. Rev. **73**, 51 (1948).

[32] In fact, in the papers of W. H. Shaffer, H. H. Nielsen, and L. H. Thomas on the rotation-vibration energies of tetrahedrally symmetric molecules, the transformations between different systems of representation are obtained by a procedure which is implicitly equivalent to our method, although the Klein commutation rules are not mentioned as such. [Phys. Rev. **56**, 895, 1051 (1939).]

[33] D. M. Dennison, Phys. Rev. **28**, 318 (1926). For greater detail see Casimir's thesis (reference 3), or his paper in Z. Physik **59**, 623 (1930), in which, however, he says there are several algebraic errors.

that of space quantization. Oftentimes, it is a sufficient approximation to retain only terms diagonal in the total angular momentum. The extra term in the hamiltonian function is then merely $\mathfrak{F}(\mu\cdot\mathbf{J})M_J/(J^2+J)$ $(\mathfrak{F}=\mathfrak{E}$ or $\mathfrak{H})$ and $\mu\cdot\mathbf{J}$, being rotationaly invariant, can be calculated purely from the internal secular problem.

APPENDIX I. THE EFFECTIVE HAMILTONIAN CAUSED BY HIGHER ORDER EFFECTS OF MAGNETIC INTERACTION

We assume that there may be several electrons with spins, but no nuclear spins. The hamiltonian arising from the interaction of these spins with the electronic and nuclear orbital motions, and with each other is[34,35]

$$H=(g\beta/c)\Sigma_K\Sigma_j(Z_Ke)[(\mathbf{r}_j-\mathbf{r}_K)\times(\tfrac{1}{2}\mathbf{v}_j-\mathbf{v}_K)]\cdot\mathbf{s}_j+(g\beta/c)\Sigma_{k>j}(-e)[(\mathbf{r}_j-\mathbf{r}_k)\times(\tfrac{1}{2}\mathbf{v}_j-\mathbf{v}_k)]\cdot\mathbf{s}_j$$
$$+g^2\beta^2\Sigma_{k>j}\cdot r_{jk}{}^{-5}[-3(\mathbf{s}_j\cdot\mathbf{r}_j-\mathbf{r}_k)(\mathbf{s}_k\cdot\mathbf{r}_j-\mathbf{r}_k)+(\mathbf{s}_j\cdot\mathbf{s}_k)r_{jk}{}^2]. \quad (37)$$

Here small and capital subscripts refer respectively to electrons and nuclei. The Landé g factor is 2, and β is the Bohr magneton $he/4\pi mc$. The velocities $\mathbf{v}$ are to be computed relative to a fixed coordinate frame. The first and second terms arise respectively from the interactions of the spins with nuclear and with inter-electronic fields. The factors $\frac{1}{2}$ come from the Thomas correction. The third term is the dipole-dipole coupling between spins.

We must now distinguish between the parts of Eq. (37) which affect the energy in the first and second approximations of perturbation theory. These parts we call H_1 and H_2, respectively. In H_1 (but not H_2 which is larger because electrons have higher velocities than nuclei), it is allowable to average over the orbital motions of the electrons. The terms which contribute to H_1 are those having nuclear velocities as factors, and the spin-spin interaction. The nuclear velocity $\mathbf{v}_K$ is sensibly the same as $\boldsymbol{\omega}\times\mathbf{r}_K$, where $\mathbf{r}_K$ is the radius vector from the center of gravity, and $\boldsymbol{\omega}$ is the angular velocity of rigid rotation. If x, y, z denote principal axes, then ω_x, ω_y, ω_z can be replaced by $\mathcal{K}_x/I_A$, $\mathcal{K}_y/I_B$, $\mathcal{K}_z/I_C$ where $\mathcal{K}_x$, $\mathcal{K}_y$, $\mathcal{K}_z$ are the components of the molecules angular momentum exclusive of spin. (The contributions of the electronic orbital angular momentum to the total angular momentum can be disregarded in this connection, as this kind of angular momentum is highly oscillatory and makes no contribution in the mean.) Referred to any set of axes, an expression of the form $-3(\mathbf{s}_j\cdot\mathbf{r}_j-\mathbf{r}_k)(\mathbf{s}_k\cdot\mathbf{r}_j-\mathbf{r}_k)r_{jk}{}^{-2}+\mathbf{s}_j\cdot\mathbf{s}_k$ will be a linear combination of the five expressions

$$2s_{zj}s_{zk}-s_{xj}s_{xk}-s_{yj}s_{yk},\quad s_{xj}s_{xk}-s_{yj}s_{yk},\quad s_{xj}s_{yk}+s_{yj}s_{xk},\quad s_{xj}s_{zk}+s_{xk}s_{zj},\quad s_{yj}s_{zk}+s_{zj}s_{yk}. \quad (38)$$

We will prove later that, as long as we are interested only in matrix elements entering, in the spin and rotational fine structure of a given nondegenerate electronic state, the matrix elements of the five quantities (38) are proportional to those of

$$2S_z{}^2-S_x{}^2-S_y{}^2,\quad S_x{}^2-S_y{}^2,\quad S_xS_y+S_yS_x,\quad S_xS_z+S_zS_x,\quad S_yS_z+S_zS_y. \quad (39)$$

From the above it follows that H_1 has the structure,

$$H_1=\Sigma_{q,\,q'=x,\,y,\,z}\,\mathcal{K}_qS_{q'}+\Sigma_{p=1\cdots5}\,\alpha_pT_p, \quad (40)$$

where the $a_{qq'}$ are constants with $a_{qq'}=a_{q'q}$, and where we have used $T_1,\cdots,T_5$ abbreviations for the five expressions (39).

We must now consider the effect of the remaining or H_2 part of (37). In addition, we will include the cross term in $\mathbf{S}$ and $\mathbf{L}$, which we denote by H_3, which arises because the energy of rigid rotation is really $A[(\mathcal{K}_x-L_x)^2+B(\mathcal{K}_y-L_y)^2+C(\mathcal{K}_z-L_z)^2$, rather than $A\mathcal{K}_x{}^2+B\mathcal{K}_y{}^2+C\mathcal{K}_z{}^2$. The form of H_2+H_3 is

$$H_2+H_3=\Sigma_j[\eta_{xj}s_{xj}+\eta_{yj}s_{yj}+\eta_{zj}s_{zj}]-2AL_x\mathcal{K}_x-2BL_y\mathcal{K}_y-2CL_z\mathcal{K}_z. \quad (41)$$

Here η_{xj}, η_{yj}, η_{zj}, L_x, L_y, L_z are matrices which are independent of the spin and rotational quantum numbers, and all of whose elements are nondiagonal in the electronic quantum numbers e. So Eq. (41) has no effect in the first approximation of perturbation theory. In the second approximation, Eq. (41) gives rise to an "effective hamiltonian" for the secular problem associated with the rotational and spin fine structure of the given electronic state under consideration. It is usually a good approximation to divide the quantum numbers into two categories, *viz.*, the "high frequency" quantum numbers, whose effect on the energy is large, and the low frequency ones whose influence upon the energy is relevant only when fine structures are considered. In the problems of the present

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[34] See, for instance, W. Heisenberg, Z. Physik **39**, 514 (1926).

[35] In the present appendix, we do not explicitly give the calculation for the case when the free spins are nuclear rather than electronic. However, in broad outline, the present procedure also applies to the nuclear case, and it is not hard to see that the form of dependence of the final effective hamiltonian on the spin and rotational angular momentum vectors is the same as in the electronic case, except, of course, for the difference (34) in notation. When dealing with nuclear spins, one should consider the small letters in Eq. (37) as referring to nuclei, and the capitals to electrons. Of course, the factors $-e$ and Ze are then interchanged; the g factors depend on k and must be taken inside the summation signs. Also, because of the reversed significance of the letters, one uses the approximation $\mathbf{v}_k=\omega\times\mathbf{r}_k$ rather than $\mathbf{v}_K=\omega\times\mathbf{r}_K$.

paper, i can be identified with the pair of quantum numbers $\mathcal{K}$, K or Σ, K (depending on the system of representation employed), and l includes not only the electronic orbital quantum numbers 0 but also the quantum number S which specifies the total spin of the molecule. In the present article, we are concerned entirely with the secular problem associated with variable values of the index i but fixed l. General perturbation theory[36] shows that the effective hamiltonian for problem which results from going to the second approximation and eliminating the leading terms nondiagonal in j, has matrix elements given by

$$\langle il|H_{\mathrm{eff}}|i'l\rangle=\sum_{i'',l'}\frac{\langle il|H_{2+3}|i''l'\rangle\langle i''l'|H_{2+3}|i'l\rangle}{h\nu_{l'l}}. \tag{42}$$

Here it is assumed that the effect of the index i on the frequency denominators can be neglected in comparison with that of l. In our problems we may assume the Russell-Saunders system of representation to be a good approximation, as magnetic forces are usually small compared to electrostatic. Then the matrices $\eta_{xk}, \cdots, L_x, \cdots$ will involve only orbital quantum numbers, and the matrices s_{xk} will involve, besides the quantum number associated with the index i, the spin quantum number S. The initial and final values of S for any spin vector (regardless of whether it is the total spin, or that of only one electron) cannot differ by more than unity. From these observations it is seen that it is possible to decompose Eq. (42) into spin and orbital factors, but it must be cautioned that, in general, the dependence of the frequency denominators on S cannot be disregarded. Thus, the part of Eq. (42) involving, say, the product $s_{zi}s_{zj}$ can be written as

$$\Sigma_{i''}\Sigma_{S'}C_{S'}\langle Si|s_{zj}|S'i''\rangle\langle S'i''|s_{zk}|Si'\rangle, \tag{43}$$

where $C_{S'}=\Sigma_{0'}\langle 0|\eta_{zj}|0'\rangle\langle 0'|\eta_{zk}|0\rangle/h\nu_{0'S';0S}$.

The next step is to note that matrix elements of the type

$$\Sigma_{i''}\{2\langle Si|s_{zj}|S'i''\rangle\langle S'i''|s_{zk}|Si'\rangle-\langle Si|S_{xj}|S'i''\rangle\langle S'i''|S_{xk}|Si'\rangle-\langle Si|S_{yj}|S'i''\rangle\langle S'i''|S_{yk}|Si'\rangle\} \tag{44}$$

are (even without summing over S'), the same as those of

$$\langle i|2S_z^2-S_x^2-S_y^2|i'\rangle, \tag{45}$$

except for a proportionality factor independent of i, i'. Those familiar with group theory will recognize this as a consequence of the transformation properties of second-order spherical harmonics; without using group theory, the proportionality of (44) and (45) can be verified by explicit multiplication of matrix elements.[37] A similar proportionality, with the same factor, holds for expressions similar to (44) but having one of the other four structures listed in Eq. (39). Summation over S' establishes the proportionality between Eqs. (38) and (39) utilized in earlier parts of the proof, but for the present purposes the dependence of $C_{S'}$ on S' requires use of our proportionality lemma in unsummed form. There is also proportionality, but with a different factor, between a scalar product $s_{xj}s_{xk}+s_{yj}s_{yk}+s_{zj}s_{zk}$ and the constant $S_x^2+S_y^2+S_z^2=S(S+1)$. In connection with the K, s type of terms, we use the fact that the elements of s_{xj}, s_{yj}, s_{zj} diagonal in S are proportional to those of S_x, S_y, S_z. In consequence there are analogous proportionality theorems applicable to K, S terms of structures corresponding to (44) or (45).[38] Thus, the elements of $2\mathcal{K}_zs_{zj}-\mathcal{K}_xs_{xj}-\mathcal{K}_ys_{yj}$, diagonal in S are, except for a common factor, the same as those of $2\mathcal{K}_zS_z-\mathcal{K}_xS_x-\mathcal{K}_yS_y$.

From Eqs. (42) and (43) it follows that the effective hamiltonian resulting from the second-order perturbation calculation behaves essentially like a quadratic form in the various components of angular momentum $s_{xj}, \cdots \mathcal{K}_z$. When the terms in this form are grouped so as to correspond to the five types of structures (45), and the invariant scalar product $(\mathbf{S}\cdot\mathbf{S})$ (along with analogous structures in $\mathcal{K}$, S) and when the proportionality theorem of the preceding paragraph are utilized, it is seen that this hamiltonian does indeed have the form represented by the terms a_0, a, b, $\cdots$, ϵ of Eq. (31). We have not included the invariant term proportional to $S_x^2+S_y^2+S_z^2$ in Eq. (31) since it is only a trivial additive constant. On the other hand, the a_0 term of (31) is contributed by the scalar product $(\mathcal{K}_x\tilde{S}_x+\mathcal{K}_y\tilde{S}_y+\mathcal{K}_z\tilde{S}_z)$. The constants a_0, a, $\cdots$, ϵ can all be taken to be real. This follows from the fact that the

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[36] See, for instance, Sec. 48c on what is termed "Van Vleck's method" in E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1939). The calculations of the present appendix are in substance the application and amplification of this method for the case that the original hamiltonian is the direct product of orbital and spin matrices. They thus represent essentially the same procedure as that which the writer utilized in a paper on relaxation times [Phys. Rev. **57**, 440 (1940)], and which was independently developed and described more fully by M. H. L. Pryce, Proc. Phys. Soc. (London) **63**, 25 (1950).

[37] See, for instance, Condon and Shortley, reference 4, p. 64. It is to be emphasized that the proportionality theorems hold only if one is careful to decompose the quadratic form properly into the various harmonics. The matrix elements of s_{zj}^2 do not, for instance, have the same structure as those of S_z^2 (take, for example, $s_j=\frac{1}{2}$, $S=1$ then s_{zj}^2 is a constant matrix, but S_z^2 is not). The proportionality has, except for difference in notation, been essentially verified in Table II of Sec. 10 (after, however, summing over the intermediate states), for the matrix elements of Table **II** diagonal in I have the same dependence on K as though $\tilde{S}$, and $\mathcal{K}$ were both replaced by J in (31).

[38] The terms of the K, S type result from the cross product $H_2\cdot H_3$ in Eq. (42). Terms of the K^2 or H_3^2 type merely alter slightly the effective rotational constants of the molecule, and are of no particular interest for our purposes.

orbital functions can all be chosen to be real, and that consequently the orbital matrices η_{xj}, η_{xk}, $\cdots$, L_x, $\cdots$, L_z involved in (43) can all be taken to be pure imaginaries, because of the factor $h/2\pi i$ in momentum operators. From this type of argument it also follows that the final quadratic form will involve no antisymmetric structures such as, $S_xS_y-S_yS_x$ etc.

We must not forget that besides the contributions to a, $\cdots$, ϵ coming from the second-order mechanism discussed in the preceding paragraph, there are also the contributions of the first-order terms H_1 given in Eq. (40), i.e., the magnetic fields caused by the rotation of the bare nuclei and the spin-spin coupling. It should be cautioned that the order of the perturbation theory has nothing necessarily to do with the magnitude of the terms. In molecules with loosely bound electrons, (40) is, in fact, apt to be overshadowed by the second-order effect.[39] We do not give very explicit formulas for the coefficients a_0, $\cdots$, ϵ and have contented ourselves with indicating how they can be worked out. Usually, little can be done with explicit numerical constants, since not enough is known about electronic wave functions. The factors entering in the proportionality theorems depend on exactly how many unpaired electrons there are in the atom, the resultant spin, etc. We have developed the theory for a quite comprehensive model, in order to show that (31) holds very generally.

APPENDIX II. THE EFFECTIVE HAMILTONIAN ARISING FROM THE BONA FIDE NUCLEAR QUADRUPOLE MOMENT

We imagine that the nucleus has a continuous charge distribution devoid of a dipole moment[40] and expand its energy in a electrostatic potential V through terms of the second order:

$$V=V_0+(\partial^2V/\partial x'^2)\int\int\int\rho x'^2dv +\tfrac{1}{2}(\partial^2V/\partial z'^2)\int\int\int\rho z'^2dv. \tag{46}$$

Here x', y', z' are coordinates mounted on the nucleus, with origin at its center, and with the z' direction its axis of symmetry. Because of this symmetry, the integrals involving x'^2 and y'^2 are equal, and those involving $x'y'$, $y'z'$, $x'z'$ vanish. (Even if geometrically the nucleus does not have axial symmetry, the averages come out as indicated because of the very rapid precession about the nuclear spin axis, the effective axis of symmetry. The precession frequency corresponds to matrix elements nondiagonal in I; and, of course, the excitation energy required to change the resultant spin of the nucleus would be enormous.) If we utilize the fact that the potential satisfies Poisson's equation, and drop uninteresting terms which are rotation invariant, Eq. (46) is the same as

$$V=V_0+\frac{1}{12}\left[2\frac{\partial^2V}{\partial z'^2}-\frac{\partial^2V}{\partial x'^2}-\frac{\partial^2V}{\partial y'^2}\right]e\mathcal{Q} \tag{47}$$

with

$$e\mathcal{Q}=\int\int\int\rho[2z'^2-x'^2-y'^2]dv. \tag{48}$$

We must now express the derivatives of the potential in terms of coordinates fixed in the molecule, by using transformation relations of the type

$$\partial^2V/\partial z'^2=\Sigma_{p,\,q=x,\,y,\,z}\,\lambda_{z'p}\lambda_{z'q}\partial^2V/\partial p\partial q.$$

The matrix elements of $\lambda_{z'x}$, $\lambda_{z'y}$, $\lambda_{z'z}$ differ from those of I_x, I_y, I_z only by a factor $1/(I^2+I)^{\frac{1}{2}}$, and so Eq. (47) becomes

$$\begin{aligned}V=V_0+\alpha[2I_z^2-I_x^2-I_y^2]+\beta[I_x^2-I_y^2]\\ +\gamma[I_xI_y+I_yI_x]+\delta[I_xI_z+I_zI_x]\\ +\epsilon[I_yI_z+I_zI_y],\end{aligned} \tag{49}$$

where α, $\cdots$, ϵ have the values given in Eq. (35). The expression eQ used in Eq. (35) is $[(2I-1)/(2I+2)]e\mathcal{Q}$. We define eQ in this fashion in order to secure agreement with the standard definition[41] of the quadrupole moment, which, is so normalized that the quadrupolar energy is[42]

$$V=V_0+\frac{1}{12}\left[2\frac{\partial^2V}{\partial z^2}-\frac{\partial^2V}{\partial x^2}-\frac{\partial^2V}{\partial y^2}\right]eO, \tag{50}$$

in a state when the nuclear spin is individually space quantized as parallel or antiparallel as possible relative to a fixed direction of axial symmetry. This procedure is tantamount to integrating in this state in the unprimed rather than primed axis system and one obtains eQ rather than $e\mathcal{Q}$ if one replaces x', y', z' by x, y, z in Eq. (48). From (35) and the fact that $I_x^2+I_y^2+I_z^2=I(I+1)$ we see that (50) is indeed the eigenvalue of (49) for the state $I_z=\pm I$ if the symmetry is such that only α is nonvanishing.

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[39] See Wick, reference 31, and Z. Physik **85**, 4 (1933); Nuovo cimento **10**, 118 (1933).

[40] See E. M. Purcell and N. F. Ramsey, Phys. Rev. **78**, 807 (1950); J. H. Smith, thesis, Harvard University.

[41] For a comparison of the normalization schemes which different writers have used to define the quadrupole moment, see B. T. Feld, Phys. Rev. **72**, 1116 (1947). In the 1946 paper of Dailey, Kyhl, Strandberg, Van Vleck, and Wilson (reference 28) the quadrupole moment was defined as $I(I+1)$, rather than $(2I-1)/(2I+2)$ times the integral (48), (giving an extra factor 8 for the case $I=1$ of NH_3). This definition, though not standard and hence now abandoned, correlates quadrupolar energy in the simplest way with the squares of the angular momentum matrices.

[42] The bracketed factor in Eq. (50) is usually written as $3\partial^2V/\partial z^2$. This is allowable if V satisfies Laplace's equation. Actually, it satisfies Poisson's, and use of the form with $3\partial^2V/\partial z^2$ is allowable only if one excludes from V the contribution from the part of the charge distribution which overlaps the nucleus.