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THE INTERPRETATION OF BAND SPECTRA. PARTS I, IIa, IIb

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SYMBOLS AND NOTATION†

The following table is an index and summary of the symbols and notation used in Part I of this review. Some of the symbols used here are different from those customary in papers on band spectra, but are in accordance with an agreement recently arrived at by band spectroscopists, and soon to be published in the Physical Review.* Such changes have been made in order to remove ambiguities inherent in the usual symbols. These ambiguities arose largely as a result of a revised interpretation, in the new quantum theory, of certain coefficients used in the old quantum theory. Thus according to the old quantum theory, B_e was assumed the same as B_0, while according to the new theory, the two quantities are distinct (cf. Eqs. 3, 3*a*); the situation in regard to D_e, r_e and ω_e is similar.

Table I. *Symbols and notation used in Part I.*

(Prime)′; *(Double Prime)*″. These indices are used to distinguish the upper (′) and the lower (″) of two energy levels involved in the production of an absorption or emission line. They may be attached to any symbol, coefficient, quantum number, or function which can differ for different states of a molecule (e.g. v', v'', B', B'', $U'(r)$, $U''(r)$, $x_e'\omega_e'$, $x_e''\omega_e''$, F'^v, F''^v, etc.).

$\mu = m_1m_2/(m_1+m_2)$. (m_1, m_2 are masses of nuclei, μ is "reduced mass").
I = moment of inertia $=\mu r^2$; $I_e=\mu r_e^2$.
r = distance between nuclei,in general; r_e = equilibrium value of r.
$\rho = r/r_e$; $\xi = (r/r_e)-1$.
$U(r)$ = potential energy function for nuclear motions.
a^*, b^*, c^* = coefficients in $U(r)$, —cf. Eqs. (1).
D = energy of dissociation.
E = energy (ergs); E^r = rotational energy.
F = spectroscopic term $=E/hc$ (cm^{-1}).
F^{el}, F^v, F^r = electronic, vibrational, and rotational term (cf. Eq. 5).
$\Delta F^v(v_1, v_2) = F^v(v_2) - F^v(v_1)$ (cf. Eq. 18).
ν = spectroscopic frequency (in cm^{-1}) = difference of two terms $(F'-F'')$.
$\nu^{el} = F'^{el} - F''^{el}$; $\nu^v = F'^v - F''^v$; $\nu^r = F'^r - F''^r$ (cf. Eq. 7).
$\nu^0 = \nu^{el} + \nu^v$ (cf. Eq. 8); $\nu^{00} = \nu^{el} + \nu^v$ for $v'=0$, $v''=0$ (cf. Eqs. 17, 17*a*).
$B_e = h/8\pi^2 c\mu r_e^2$.
$B \equiv B_v = B_e - \alpha(v+1/2) = B_0 - \alpha v$ (cf. Eq. 3*a*).
$\overline{B} = (B'+B'')/2$; $\overline{B}_0 = (B_0'+B_0'')/2$ (cf. Eqs. 15, 16*a*).
$C = B'-B''$; $C_0 = B_0'-B_0''$ (cf. Eqs. 15, 16*a*).
$D \equiv D_v = D_e + \beta(v+1/2) = D_0 + \beta v$ (cf. Eq. 4*a*); for D_e, cf. Eq. 4.
ω_e, $x_e\omega_e$, $y_c\omega_e$, α = coefficients in expression for F as a function of the quantum numbers (cf. Eqs. 5, 6).
$a = \omega_e(1-x)$; $b = x_e\omega_e$ (cf. Eq. 17).
$\bar{a}$, $\bar{b}$ = quantities differing slightly from a, b (cf. Eq. 17*a*).
$c\omega_e$ = frequency of mechanical vibration of nuclei for infinitesimal amplitudes about r_e.
v = vibrational quantum number.
K = rotational quantum number.
$K^* = [K(K+1)]^{1/2}$.

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† Cf. important note on p. 115 in regard to further recommended changes.

* Also cf. the preliminary account in the Discussion on Molecular Spectra, Faraday Society Trans., pp. 628–633, 770–772, and Errata (Sept., 1929); also in book form (Gurney and Jackson, 1930).

P branch = negative branch ($K' = K'' - 1$).

R branch = positive branch ($K' = K'' + 1$).

M = ordinal number ($M = -K''$ in P branch; $M = K'' + 1$ in R branch).

Band; band-line; band-structure; band-system; band-head; electronic bands (cf. p. 68 and 72 for definitions).

Pure rotation bands; vibration-rotation bands (cf. pp. 83–4).

Band sequence; v' and v'' progressions (cf. p. 76).

Perturbations (cf. p. 74).

The following table is a supplement to the above Table I of Part I and is an index and summary of the symbols and notation introduced in Parts II*a* and II*b* but not used in Part I. It also serves to show the relation between the symbols used here—most of which are in accordance with an agreement recently arrived at by band spectroscopists,—and other symbols which are or have been in common use (*the latter are given in brackets*).

TABLE II. *Symbols and notation introduced in Parts IIa and IIb.*

A. Atoms.

n = principal, l = azimuthal, s = spin quantum number (individual electrons).

L = resultant orbital, S = resultant spin, J = resultant total angular momentum quantum number.

M_L, M_S, M = magnetic or electric quantum numbers associated with L, S, J, respectively; M_L, M_S, M = projections of L^*, S^*, J^*, respectively on axis of magnetic or electric field; $M_L\, h/2\pi$, etc., = corresponding angular momenta.

l^*, s^*, L^*, S^*, $J^* = [l(l+1)]^{1/2}$, $[s(s+1)]^{1/2}$, etc.; $l^*h/2\pi$, $s^*h/2\pi$, etc., are the angular momenta corresponding to l, s, etc.

$s, p, d, f, \cdots$ electrons: means $l = 0, 1, 2, 3, \cdots$

$S, P, D, F, \cdots$ states: means $L = 0, 1, 2, 3, \cdots$

A = coefficient of magnetic interaction of L^* and S^* (cf. Eqs. (22), (25), (26), and ref. 33).

co = Larmor precession frequency (magnetic field); g = Landé factor.

Weak and strong fields, definition (cf. ref. 30).

$c\omega_k$ = mechanical frequency associated with any quantum number k($k = L, J, M, K$, etc.): cf. Eq. (23).

B. Molecules

A, ω_k, n, l, s, L, S, l^*, s^*, L^*, S^*, and $s, p, d, f, \cdots$, mean the same as for atoms, except that l and L are usually not good quantum numbers, the corresponding angular momenta being in general not even nearly constant in magnitude.

J^a = same as *atomic* J; J^{a*} = resultant of L^* and S^* in cases where L^* and S^* are very strongly coupled.

Λ, Σ, Ω [usually called i_l or σ_k or σ_l, i_s or σ_s, and i or σ, respectively] = quantum numbers giving respectively the component of orbital, spin, and total electronic angular momentum parallel to the electric axis (cf. p. 93 for exact definitions); $\Lambda h/2\pi$, $\Sigma h/2\pi$, $\Omega h/2\pi$ = corresponding angular momenta.

$\Sigma, \Pi, \Delta, \cdots$ states [formerly called $S, P, D, \cdots$ states] mean $\Lambda = 0, 1, 2, \cdots$; ${}^2\Sigma$, ${}^3\Pi_1$, ${}^4\Pi_{-\frac{1}{2}}$, etc., cf. p. 94.

L_{perp} (cf. p. 98), S_{perp} (cf. p. 105) = component of L^* or S^* perpendicular to electric axis, about which L^* or S^* is precessing; L_{perp} and S_{perp} are not quantum numbers.

$Gh/2\pi$ = total instantaneous component of electronic orbital angular momentum perpendicular to electric axis (cf. p. 98); G is not a quantum number.

$Nh/2\pi$ = instantaneous angular momentum of nuclei (cf. p. 99); N is not a quantum number.

$Oh/2\pi$ [formerly often called $mh/2\pi$] = total angular momentum perpendicular to electric axis, exclusive of spin in Hund's case b (cf. p. 97); O is not a quantum number.

$\rho h/2\pi$ [often called $\epsilon h/2\pi$] = mean value of projection of $Gh/2\pi$ on O axis = mean component of electronic orbital angular momentum along O.

R [Hund's p_r] = rotational quantum number in Hund's case d (cf. p. 101).
K [usually called j_k or p_l or m] = rotational quantum number, inclusive of electronic orbital angular momentum, but not of electronic spin (Hund's cases b, d).
J [formerly often called m] = quantum number of total angular momentum in all cases.
R^*, K^*, $J^* = [R(R+1)]^{1/2}$, etc.; $R^*h/2\pi$, etc., = angular momenta.
δ, ϵ, γ = small coefficients (cf. p. 100, and p. 107, Eq. (33)).
$B^*_{v,\Sigma}$ = (cf. Eq. (46)).
$\phi(K)$; $\phi_i(K)(=\phi_a(K)$ or $\phi_b(K))$; $\phi_i(\Sigma, J)$; $\phi_i(K, J)$: small functions (cf. p. 100 et seq.; p. 105; p. 106; Eq. (32)).
$f(R, K\text{-}R)$; $f(K, J\text{-}K)$; $w(K, J\text{-}K)$: small functions (cf. Eq. (30); Eqs. (32-33)).
F_1, F_2, F_3, F_{1a}, F_{1b}, etc. = term designations in Hund's case b (cf. p. 112–13).
Hund's cases, definitions: Case a, p. 105; case b, p. 106; case b', pp. 97, 108; case c, p. 114; case d, p. 108; case d', pp. 101, 108; case e, p. 114; summary of Hund's cases, p. 115.
Core model (cf. p. 85).
Selection rules (cf. pp. 90, 96).
Vectors are denoted by bold-faced type.

INTRODUCTION

THE theory of the spectra of diatomic molecules has undergone very rapid development in the years since 1925. This has been especially true in respect to our knowledge (1) of the nature of electronic states and quantum numbers, and (2) of the connection between the electronic states of molecules and those of their component atoms on dissociation. Parts I–II, and Part III, of this review are respectively devoted primarily to the first and second of these topics, together with their application to the structure and interpretation of band spectra.

For the sake of simplicity and "Anschaulichkeit," the treatment in Parts I–II is in terms of the *old quantum theory* and repeatedly involves the use of models which, according to the new quantum theory, must not be taken too literally. So far as possible, however, the most essential new results of the new quantum theory,—especially energy relations,—are stated in the text, although their rigorous derivation is not given. In Part III, the new theory will be used more directly.

The possible energy values of a diatomic molecule can be expressed as functions of certain quantum numbers associated with motions of the electrons and nuclei. These quantum numbers usually fall naturally into three groups (*a*) a group which defines to a first approximation the energy, depending on the electronic motions, which the molecule would have if the nuclei could be held stationary (*b*) a single quantum number v which defines the state of vibration of the nuclei (*c*) a group of quantum numbers associated with the rotation of the nuclei and with the finer details of the electronic motions. In the simplest cases,—the so-called $^1\Sigma$ states,—the group (*c*) reduces to a single quantum number K belonging to the rotation of the nuclei[1,2], but in general there are interactions between electron motions

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[1] K is usually called m or j. The reasons for using the symbol K will appear later (cf. pp. 97–106).

[2] Even in $^1\Sigma$ states, K does not represent *exclusively* nuclear rotation, because there is always a rapidly varying electronic orbital angular momentum (cf. J. H. Van Vleck and A.

and nuclear rotation which must be taken into account in the scheme of quantum numbers. It is toward an understanding of these interactions and their consequences for the structure of band spectra that Parts I–II are directed. But we shall begin (Part I) by reviewing the characteristic features, and their important variations, for the structure of a band spectrum corresponding to a transition from one $^1\Sigma$ electronic state[3] to another. In this way we shall be better able to appreciate the characteristic *new* structural features (Part II) which appear in bands involving *other* kinds of electron states.

PART I

THEORY OF ENERGY STATES OF MOLECULE REGARDED AS ROTATING ANHARMONIC OSCILLATOR

Potential energy function. In molecular states of the $^1\Sigma$ type, the (average) angular momentum of the electron system is zero.[2] The motion of the nuclei is in this case essentially a pure rotation around their center of gravity, combined with a vibration along the line joining them. For each electronic state there is a function $U(r)$ which acts like a potential energy for the nuclear motions,[4] and which has a single minimum corresponding to an equilibrium value, r_e, of the distance r between the nuclei. If $U(r_e)$ is taken as zero, $U(r)$ gives the total energy of a molecule whose nuclei are momentarily at rest at distance r apart, and $U(\infty)$ is equal to the energy of dissociation D(cf. Fig.1). The following expansion for $U(r)$, expressed in terms of the quantities $\rho = r/r_e$ and $\xi = \rho - 1 = (r - r_e)/r_e$, has $U(r_e) = 0$ and is convergent for values of r not too far from r_e.[5]

$$U(\rho) = -a^*[-(1/2) + (1/\rho) - (1/2)\rho^2 + b^*\xi^3 + c^*\xi^4 + \cdots] \tag{1}$$

Eq. (1) may also be written as a series in ξ alone (Eq. 1*a*). Eq. 1*a* is readily obtained from Eq. (1) by expanding $1/\rho$ and $1/\rho^2$ in powers of ξ.

$$U(\xi) = a^*[\xi^2/2 - (b^* + 1)\xi^3 - (c^* - 3/2)\xi^4 + \cdots] \tag{1a}$$

Frank, Proc. Nat. Acad. Sci. **15**, 539, 1929). Corresponding to this fact, a term $B_e\overline{G^2}$ ought to be added to the rotational energy function in Eqs. 2a, 2b, or a term $B_v\overline{G^2}$ in Eq. 5 (cf. Part II*b*, Eq. 29, with $\Lambda = 0$). $\overline{G^2}$ represents the mean value of the square of the component of electronic orbital angular momentum perpendicular to the line joining the nuclei. This differs from zero even when the average value of the electronic angular momentum vector is zero.

[3] A molecule is said to be in the same electronic state so long as the group of quantum numbers (*a*) remains constant, no matter how v and K may be varied. But if one or more of the quantum numbers of group (*a*) are changed, it is said to be in a different electronic state.

[4] Cf. E. C. Kemble, National Research Council Bulletin on Molecular Spectra in Gases, p. 293, for a discussion of the physical meaning of the function $U(r)$. (Kemble calls it $V(r)$).

[5] A. Kratzer, Zeits. f. Physik **3**, 289 (1920), but with designations of coefficients as given in appendix 15 of A. Sommerfeld's Atombau and Spektrallinien except that a^*, b^* and c^* are used here in place of a, b, and c of Sommerfeld. [In Sommerfeld's chapter, $-5b^2/2$ appears erroneously in the expression for $x_e\omega_e$ (cf. Eq.. (6) below) where $+5b^2/2$ should be used.] For further details of the energy expansion Eq. (5), cf. E. C. Kemble, Jour. Opt. Soc. Am. **12**, 1 (1926). For a form of $U(r)$ which is capable in many cases of representing this function for *all values* of r, cf. P. M. Morse, Phys. Rev. **34**, 57 (1929).

$U(\xi)$ of Eq. (1*a*) is in practise considerably less rapidly convergent than $U(\rho)$ of Eq. (1), especially for polar molecules. $F(r) = -dU/dr$ is readily obtained from either of the above expressions, for example:

$$-F(\xi) = (1/r_e)(dU/d\xi) = (a^*/r_e)[\xi - 3(b^*+1)\xi^2 - 4(c^* - 3/2)\xi^3 + \cdots]. \qquad (1b)$$

Quantization of rotation. Let us review briefly the application of the quantum theory to the determination of the possible energy states corresponding to the nuclear motions. First let us consider the (idealized) case where the motion is one of rotation without vibration. Let ϕ and P_ϕ respectively represent the angle through which the nuclei have rotated, and the angular momentum. Then, according to the old quantum theory, $\oint P_\phi d\phi = Kh$, where K is any non-negative integer, h is Planck's constant, and the integral is taken over a complete revolution. Since P_ϕ is a constant for a molecule in a definite state, the integral yields $2\pi P_\phi = Kh$, or $P_\phi = Kh/2\pi$. In the new quantum theory, this result is modified to $P_\phi = K^*h/2\pi$, where

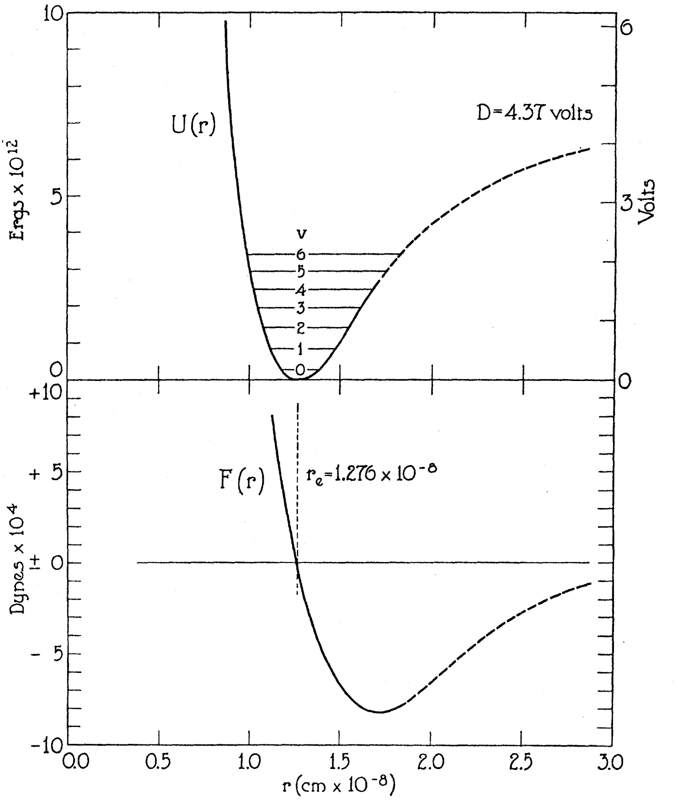

FIG. 1. Potential energy and force functions,—$U(r)$ and $F(r)$,—for nuclear motions, for the normal state of HCl; also a few vibrational energy levels. For r values below 1.8×10^{-8} cm, the curves are drawn in accordance with Eqs. 1, 1*b*; for larger r values, they have been approximately sketched in with the help of Morse's formula.[5]

$K^* = [K(K+1)]^{1/2}$. Our problem is now to express the energy of rotation in terms of K.

The energy of a rotating molecule is mainly kinetic energy, plus a small amount of potential energy resulting from a slight stretching by centrifugal force. If $\dot{\phi}$ is the angular velocity and I is the moment of inertia, the kinetic energy is $I\dot{\phi}^2/2$. If m_1 and m_2 are the masses of the two nuclei and r_1 and r_2 are their respective distances from the center of gravity, we have $I = m_1 r_1^2 + m_2 r_2^2$. The following treatment is simplified by rewriting I in terms of r and the "reduced mass" μ, defined[6] by $\mu = m_1 m_2/(m_1+m_2)$. We then have $I = \mu r^2$, as is easily shown by using the relations $r_1 + r_2 = r$ and (definition of center of gravity) $m_1 r_1 = m_2 r_2$. The potential energy is given to a sufficient approximation, for moderate speeds of rotation where $\xi \ll 1$, by $U = a^*\xi^2/2$ (cf. Eq. 1*a*). The corresponding force is given to a sufficient approximation by $-F = a^*\xi/r_e$ (cf. Eq. 1*b*). By setting $|F|$ equal to the centrifugal force $\mu r\dot{\phi}^2$, an expression for ξ in terms of $\dot{\phi}$ is obtained.[6a] Thus from $a^*\xi/r_e = \mu r\dot{\phi}^2$, putting r_e for r as a sufficient approximation and expressing $\dot{\phi}$ in terms of $P_\phi (P_\phi = I\dot{\phi} = \mu r^2\dot{\phi} \sim \mu r_e^2\dot{\phi})$, we get $\xi \sim P_\phi^2/a^*\mu r_e^2$. For the total energy of rotation we now have

$$E^r = \mu r^2\dot{\phi}^2/2 + a^*\xi^2/2 + \cdots = P_\phi^2/2\mu r^2 + P_\phi^4/2a^*\mu^2 r_e^4 + \cdots$$
$$= P_\phi^2/2\mu r_e^2[1 - 2\xi + \cdots + P_\phi^2/a^*\mu r_e^2 + \cdots] = P_\phi^2/2\mu r_e^2[1 - P_\phi^2/a^*\mu r_e^2 + \cdots]. \quad (2)$$

Substituting $P_\phi = K^*h/2\pi$,

$$E^r = K^{*2}h^2/8\pi^2\mu r_e^2 - K^{*4}h^4/32\pi^4 a^*\mu^2 r_e^4 + \cdots. \quad (2a)$$

Adopting the abbreviations (c = velocity of light)

$$B_e = h/8\pi^2\mu c r_e^2 [= 27.70 \times 10^{-40}/\mu r_e^2] \quad (3)$$
$$D_e = -h^3/32\pi^4 a^*\mu^2 c r_e^4 [= -4B_e^3/\omega_e^2 (\text{cf. Eqs. } 5,\ 6)], \quad (4)$$

Eq. (2*a*) can be written in the form

$$F^r \equiv E^r/hc = B_e K^{*2} + D_e K^{*4} + \cdots = B_e K(K+1) + D_e K^2(K+1)^2 + \cdots \quad (2b)$$

Simultaneous quantization of vibration and rotation. When the new quantum theory is applied to a molecule with zero average electronic angular momentum which is both vibrating and rotating,[7] the complete energy expression[2] is given by

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[6] The correction for the masses of the electrons is too small to need to be included.

[6a] The centrifugal force is $m_1 r_1\dot{\phi}^2$ for nucleus 1, $m_2 r_2\dot{\phi}^2$ for nucleus 2. These are equal (since $m_1 r_1 = m_2 r_2$) and, as is easily shown, each is equal to $\mu r\dot{\phi}^2$.

[7] Old quantum theory, cf. Kratzer or Kemble, l.c., ref. 5; for relations such as Eq. (6) between coefficients in Eq. (5) and molecular constants, cf. Kratzer, l.c. New quantum theory, E. Fues, Ann. der Physik **80**, 367 (1926); **81**, 281 (1926), and A. Sommerfeld's Atombau und Spektrallinien, Wellenmechanischer Ergänzungsband, p. 24. It is probable that $(K+1/2)^2$ should be used rather than $K(K+1)$ in Eq. (5) and in similar equations, but the difference between the two expressions is negligible for practical purposes, and the form $K(K+1)$ gives simpler formulas for the frequencies of band lines.

$$F = F^{el}+F^{v}+F^{r} = F^{el}+(v+\tfrac{1}{2})\omega_e-(v+\tfrac{1}{2})^2x_e\omega_e+(v+\tfrac{1}{2})^3y_e\omega_e+\cdots$$
$$+B_vK(K+1)+D_vK^2(K+1)^2+\cdots \quad (5)$$

F in Eq. (5) means merely E/hc; throughout this review, for reasons of convenience in application to spectroscopic problems, we shall use *term values* (F) in place of corresponding energy values (E). In Eq. (5), F is, somewhat arbitrarily, represented as the sum of three terms, namely, a rotational term F^r which is a function of K (and of v and of the electronic state[8]), a vibrational term F^v which is a function of v (and of the electronic

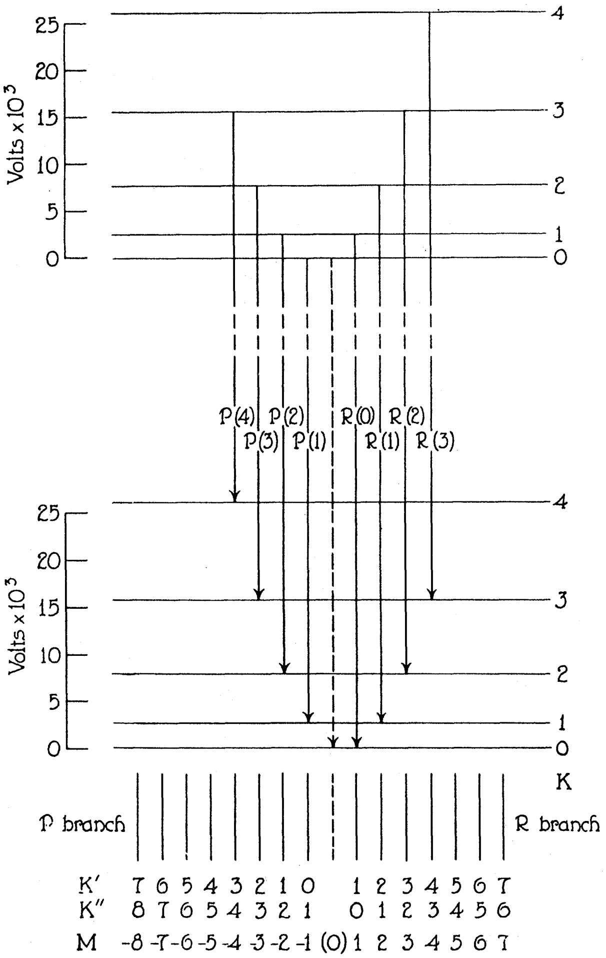

FIG. 2. Relation of rotational energy levels to band structure for the case $B'=B''$ (cf. Eq. 14); B'' is chosen equal to B_0 of normal HCl. The full vertical lines correspond to possible transitions between the two sets of energy levels. The figure shows the conventional method of designating band-lines, and its relation to the M numbering. The frequency which would correspond to $M=0$ (dotted lines in the figure) is not present in the spectrum; this is the so-called "missing line."

state), and an electronic term which is a function of the electronic state only. The quantum numbers v and K can each take on positive integral values, beginning with 0. In Eq. (5), when $v=0$, $F^v=(1/2)\omega_e-(1/4)x_e\omega_e+\cdots\neq 0$; this represents the "zero-point vibrational energy," which cannot be removed from the molecule. It will be noted that F^r is the same in Eq. (5) as in Eq (2b), except for the substitution of B_v and D_v for B_e and D_e (cf. Eqs. 3a and 4a below).[2]

In Eq. (5), $\omega_e \gg x_e\omega_e \gg y_e\omega_e$ in practise, and $\omega_e \gg B_v \gg |D_v|$; for numerical examples, cf. pp. 67, 71, and 75. The "vibrational energy levels" have ordinarily a spacing which decreases slowly with v (cf. Fig. 1), while the "rotational energy levels" have a spacing which increases at first approximately as K^2 (cf. Fig. 2). As a result of $\omega_e \gg B_v$, the members of any set of rotational levels (fixed F^{el} and F^v, variable K) are very much more closely spaced than are the members of a set of vibrational levels (fixed F^{el}, $F^r=0$, variable v); this can be seen by a comparison of Figs. 1 and 2, with due regard to the scales used in these figures. The "electronic levels" (variable F^{el}, with F^v and $F^r=0$) are as a rule even more widely spaced than the vibrational levels, except in the case of highly excited electron orbits which are not very often met with in practise.

In Eq.(5), the coefficients are related theoretically as follows[7] to B_e and D_e of Eqs. (3) and (4) and to the molecular constants r_e, a^*, b^*, and c^* of Eqs. (1), (1a), and (1b).

$$B_v=B_e-\alpha(v+\tfrac{1}{2})+\cdots=B_0-\alpha v+\cdots,\text{ with } B_0=B_e-\alpha/2\ ;\ B_e\gg\alpha \quad (3a)$$

$$D_v=D_e+\beta(v+\tfrac{1}{2})+\cdots=D_0+\beta v\ ;\ B_e\gg|D_e|\gg\beta \quad (4a)$$

$$\omega_e=(1/2\pi c)(a^*/\mu r_e^2)^{1/2}\ ;\ \alpha=(6B_e^2/\omega_e)(2b^*+1)\ ;$$

$$x_e\omega_e=3B_e(1+5b^*+c^*+5b^{*2}/2). \quad (6)$$

In Eqs. (5) and (6), ω_e, times c, is the frequency of vibration of the nuclei for infinitesimal vibrations. Both α and $x_e\omega_e$ of Eqs. (3a), (5), and (6) are positive for all molecular states so far known; ordinarily or perhaps always in practise, $b^*>0$ and $c^*<0$.

Vibrational levels and $U(r)$ *curve.* When ω_e, $x_e\omega_e$, B_0, and α have been determined for any electronic state, as can be done by the analysis of band spectra connected with that state, the quantities r_e, a^*, b^*, and c^* can be computed, and the $F(r)$ and $U(r)$ curves can then be drawn, for r values not too far from r_e. If the dissociation energy D is known, the complete $U(r)$ curve can be approximately sketched in from $r<r_e$ to $r=\infty$. As we shall see later, such $U(r)$ curves are very useful in studying the behavior of the various electronic states of a molecule. Using the values $r_e=1.276\times 10^{-8}$, $a^*=82.87$, $b^*=0.173$ and $c^*=-0.316$, determined from the experimental coefficients[8] $\omega_e=2989.7$, $x_e\omega_e=51.90$, $B_e=10.58$ and $\alpha=0.303$, and the value $D=4.37$ electron-volts, the $U(r)$ and $F(r)$ curves for the normal state of HCl are sketched, using Eq. (1) and Eq. (1b), in Fig. 1. (It should be remarked that the true form of the $F(r)$ curve for HCl is very uncertain

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[8] Cf. W. F. Colby, Phys. Rev. **34**, 53 (1929).

beyond about $r_e = 1.8 \times 10^{-8}$ cm, so that it is probably only qualitatively correct in Fig. 1.) A few of the vibrational energy levels of HCl are drawn on the $U(r)$ diagram in Fig. 1 in accordance with F^v of Eq. (5), assuming $K=0$; the levels $v=0$, 1, 2, and 3 have been observed, while the others are merely calculated.

P. M. Morse[5] has recently given a convenient formula by means of which a *complete* $U(r)$ curve can be computed if r_e, ω_e, and either $x_e\omega_e$ or D, are known. This is applicable only in cases where F^v of Eq. (5) can be fairly accurately represented, as is often but not always true, by $F^v = (v+1/2)\omega_e - (v+1/2)^2 x_e\omega_e$ without further terms. Morse's formula has been used in estimating the form of $U(r)$ for HCl in Fig. 1 for large r values.

ENERGY LEVELS AND SPECTRUM

The wave-number ν of any line in the spectrum of a molecule can be obtained by taking the difference of two terms, one of higher energy (F') and one of lower energy (F''):

$$\nu = F' - F'' = (F'^{el} - F''^{el}) + (F'^{v} - F''^{v}) + (F'^{r} - F''^{r}) = \nu^{el} + \nu^{v} + \nu^{r}. \qquad (7)$$

Usually, but not always, $\nu^{el} \gg \nu^{v} \gg \nu^{r}$, corresponding to the relative energy level spacings of F^{el}, F^{v}, and F^{r} (cf. p. 67). All the spectrum lines associated with a definite pair of electronic states, hence with a definite F'^{el}, F''^{el} and ν^{el}, are collectively called a "*band system.*" This is divided into limited groups of lines called *bands*, each band being associated with a definite pair of vibrational states and quantum numbers (v' and v'') and so with a definite F'^{v}, F''^{v}, and ν^{v}. The *lines* whose arrangement constitutes the *structure* of a band correspond to a variety of values of ν^{r} resulting from various possible pairs of values K', K'' of the rotational quantum number. The various lines are distributed over a limited ν region on both sides of the position, given by $\nu^{el} + \nu^{v}$, where $\nu^{r} = 0$.

We proceed now to a consideration of the structure of band systems which correspond to transitions between $^1\Sigma$ electronic states. We shall divide the discussion into two stages, first assuming ν^{v} = fixed, ν^{r} = variable, so as to obtain an understanding of the structure of individual bands, then later assuming $\nu^{r} = 0$, ν^{v} = variable so as to determine the arrangement of bands in a band system.

The bands of a band system with $\nu^{el} \neq 0$ are "*electronic bands.*" There are also two other types of bands, for both of which $\nu^{el} = 0$, and which lie in the infra-red. These are the "pure rotation bands" and the "vibration-rotation bands." They are of relatively minor interest in the present review, but are considered briefly at the end of Part I.

STRUCTURE OF BAND SPECTRA OF THE SIMPLEST TYPE
($^1\Sigma \rightarrow {}^1\Sigma$ TRANSITIONS)

Structure of individual electronic bands. In a *single band* of the electronic type, ν^{el} and ν^{v} are fixed, while ν^{r} varies. In order to determine the form which ν^r takes as a function of the quantum numbers, we make use in Eq. (7) of the detailed expressions for F' and F'' given by Eq. (5):

$$\nu=\nu^0+F'^r-F''^r=\nu^0+B_{v'}K'(K'+1)+D_{v'}K'^2(K'+1)^2 \\ -B_{v''}K''(K''+1)-D_{v''}K''^2(K''+1)^2+\cdots. \qquad (8)$$

Here ν^0 stands for $\nu^{el}+\nu^v$ of Eq. (7). Now there is an important selection rule which greatly limits the possible transitions and ν values: $(K'-K'')=\pm 1$ only. This is exactly analogous to the selection rule $\Delta l=\pm 1$ for the azimuthal quantum number in line spectra. If in Eq. (8) we put $K'=K''+1$ we get a set of frequencies given by the equation

$$\nu=\nu^0+(B'+B'')(K''+1)+(B'-B''+D'-D'')(K''+1)^2 \\ +2(D'+D'')(K''+1)^3+(D'-D'')(K''+1)^4. \qquad (9)$$

(For simplicity, the subscripts v' and v'' of the B's and D's have been dropped here). The series of lines given by Eq. (9) constitutes the so-called R or *positive* branch; in Eq. (9), K'' can take on the integral values 0, 1, 2, 3, ... Similarly, if we substitute $K'=K''-1$ in Eq. (8), we get the equation of the P or *negative* branch:

$$\nu=\nu^0-(B'+B'')K''+(B'-B''+D'-D'')K''^2-2(D'+D'')K''^3+(D'-D'')K''^4. \qquad (10)$$

In Eq. (10), K'' can take on the integral values 1, 2, 3, ... ($K''=0$ is not possible, because it would imply $K'=-1$). Eqs. (9) and (10) can both be represented by the following Eq. (11) if we substitute $M=K''+1$ in Eq. (9) and $M=-K''$ in Eq. (10); in Eq. (11), $M=+1, +2, +3, \cdots$. give the lines of the R branch, $M=-1, -2, -3, \cdots$. the lines of the P branch. Eq. (11) shows that the two branches form a continuous series, except that a single central line $\nu=\nu^0$, corresponding to $M=0$, is missing.

$$\nu=\nu^0+(B'+B'')M+(B'-B''+D'-D'')M^2+2(D'+D'')M^3+(D'-D'')M^4. \qquad (11)$$

The appearance of a band as recorded, say, on a photographic plate is governed by two factors (1) the arrangement of the lines as given by Eq. (11) and (2) the relative intensities of the lines. The first factor is subject to many variations depending on the relative and absolute values of B', B'', D', and D''. The second factor depends on (*a*) the initial distribution of molecules among rotational states and (*b*) the transition probabilities. In absorption spectra, and in *thermally excited* emission spectra, the initial distribution is that corresponding to thermal equilibrium at some temperature T. In practise, the observed intensity distribution, which depends of course on experimental conditions, is normally approximately of the type to be expected for thermal equilibrium, even when there is no reason to expect such equilibrium.[9] The theoretical intensity expressions, assuming

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[9] Cf. R. T. Birge, Report on Molecular Spectra in Gases, p. 221; R. S. Mulliken, Phys. Rev. **29,** 401 (1927).

thermal equilibrium for the rotational energy distribution in the initial electronic state, are as follows for ${}^1\Sigma \rightarrow {}^1\Sigma$ transitions:[10]

Absorption:

$$\text{Int.} = C(K'+K''+1)e^{-E''^r/kT} = 2C\,|M|\,e^{-[B''M(M-1)+\,.\,.\,.\,]/kT}. \qquad (12)$$

Emission:

$$\text{Int.} = C(K'+K''+1)e^{-E'^r/kT} = 2C\,|M|\,e^{-[B'M(M+1)+\,.\,.\,.\,]/kT}. \qquad (13)$$

Eqs. (12) and (13) take into account both initial distribution and transition probabilities. Eqs. (12) and (13) show that, except for the exponential factor, the Mth line of the P branch should have the same intensity as the Mth line of the R branch. The exponential factor, however (because it involves M, not $|M|$) is for a given $|M|$ somewhat larger in the R than in the P branch for absorption spectra (Eq. 12) but is somewhat larger in the P than in the R branch for emission spectra (Eq. 13). All the features just discussed have been experimentally verified.[9]

We are now ready to consider how the structure of a ${}^1\Sigma \rightarrow {}^1\Sigma$ band may look in various actual cases. Let us first consider the simple case $B' = B''$, with D' and D'' negligibly small. Eq. (11) here simplifies to

$$\nu = \nu^0 + 2BM. \qquad (14)$$

The connection between the spacings of rotational levels (F^r of Eq. 5) and the spacings of lines in a band, for the case $B' = B''$ (Eq. 14), is shown in Fig. 2. In this figure the scale is so chosen that the spacings of the lower set of rotational levels agree with those experimentally determined for the $v'' = 0$ level of the normal electronic state of HCl. (The upper set of levels may then be considered to correspond to some imaginary excited state of HCl). Each band line in Fig. 2 may be regarded as the projection of one of the long vertical lines which connect pairs of energy levels. These vertical lines are spaced from left to right just in accordance with their length, corresponding to the fact that each spectrum frequency is proportional to the interval between the two energy levels involved in its production. The regular progression in the vertical lengths, which is the basis for the regular spacing of spectrum lines given by Eq. (14), should be apparent from the figure.

Fig. 2 also gives a comparison between the M numbering used here and the *conventional notation* which is commonly used for the designation of band lines. For our present descriptive purposes, the M numbering is more convenient than the other numbering, but the latter will be needed later, for more complicated types of bands and in connection with the analysis

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[10] Cf. E. C. Kemble, Phys. Rev. **25**, 1 (1925); D. G. Bourgin, Phys. Rev. **29**, 794 (1927); and Eqs. (2) and (4) of Mulliken, Phys. Rev. **29**, 391 (1927). In Eqs. (12) and (13) above, C varies slightly with K, for large K values (cf. Kemble, l.c.).

To get from the first to the second form of the exponential in Eq. (12), one proceeds as follows. First one substitutes $E''^r = B''K''(K''+1) + \cdots$, then, for the P branch, $K'' = -M$, for the R branch, $K''+1 = +M$. This gives for both branches the same result, $E''^r = B''M(M-1) + \cdots$. A similar method applies in Eq. (13).

of band structure. In the conventional numbering, the value of K'' is given in parentheses, e.g. P (2) corresponds to $K'=1$, $K''=2$, while $R(4)$ corresponds to $K'=5$, $K''=4$.

Fig. 3 shows by means of illustrative examples how the band structure varies with B and T in emission spectra (in absorption spectra, the intensity relations of the P and R branches would be approximately reversed). For large B (small moment of inertia) the band has a very open structure, with few lines widely spaced and with the intensity maxima at small $|M|$ values but relatively far from ν^0. For small B everything is reversed. For small T, the number of strong lines, and the distance of the intensity maxima from ν^0, are relatively small. For large T there are relatively many lines, and the intensity maxima are relatively far from ν^0. In practise, the largest B value is that of the normal state of $H_2(B_0=59.35)$.[10a] The various known states of He_2 all have $B_0 \sim 7$; in the hydrides, B_0 varies from 21 in the normal state of HF to values such as 5.38 for the normal state of HgH and even lower in some other cases. Molecules like N_2, CO, NO have $B_0 \sim 2$. The smallest B_0 value yet definitely determined is that of the excited $^1\Sigma$ level of the I_2 absorption bands ($B_0=0.029$). From these data and an examination of Fig. 3 it is evident that the resolving power needed to analyze the structure of a band varies enormously from one molecule to another.

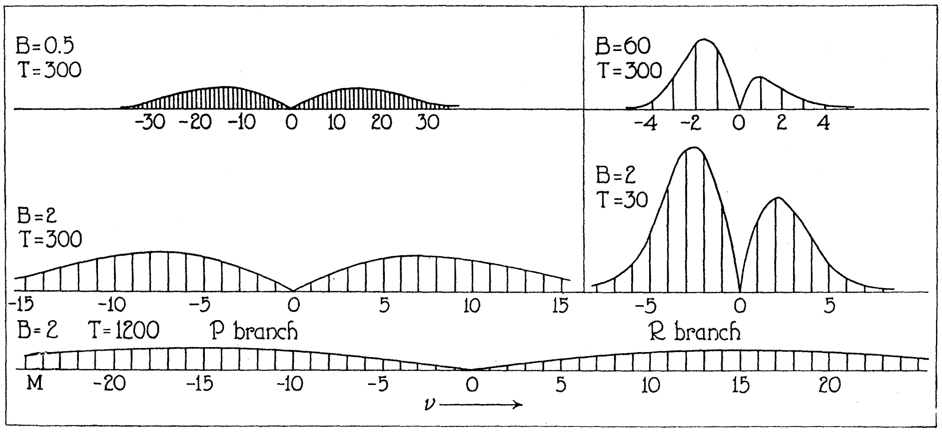

FIG. 3. Effect of numerical values of B and T on structure and intensity distribution (cf. Eqs. 13, 14), for emission bands having $B'=B''$ (headless bands). The numbers are M values. The heights of the lines represent their intensities. For the missing line ($M=0$), the intensity is zero. The law of intensity distribution has been emphasized by drawing envelopes of the individual intensities. All the diagrams are on the same scale, except for the case $B=60$, where both horizontal and vertical dimensions have been reduced to one-fourth what they should be.

The case $B'=B''$ just discussed is one which is only occasionally approximated in practise, except in infra-red bands with $\nu^{el}=0$ (cf. below). In

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[10a] Cf. Birge, Hyman, and Jeppesen, Nature, 1930 (private communication from Professor Birge).

typical band spectra, $B'>B''$ or, somewhat more often, $B'<B''$. In either case Eq. (11) now becomes, still neglecting the D's,

$$\nu=\nu^0+2\bar{B}M+CM^2, \tag{15}$$

where $\bar{B}=(B'+B'')/2$ and $C=B'-B''$. Eq. (15) is plotted in Fig. 4 for several different pairs of values B', B'' (all near 2.0), for the case of emission

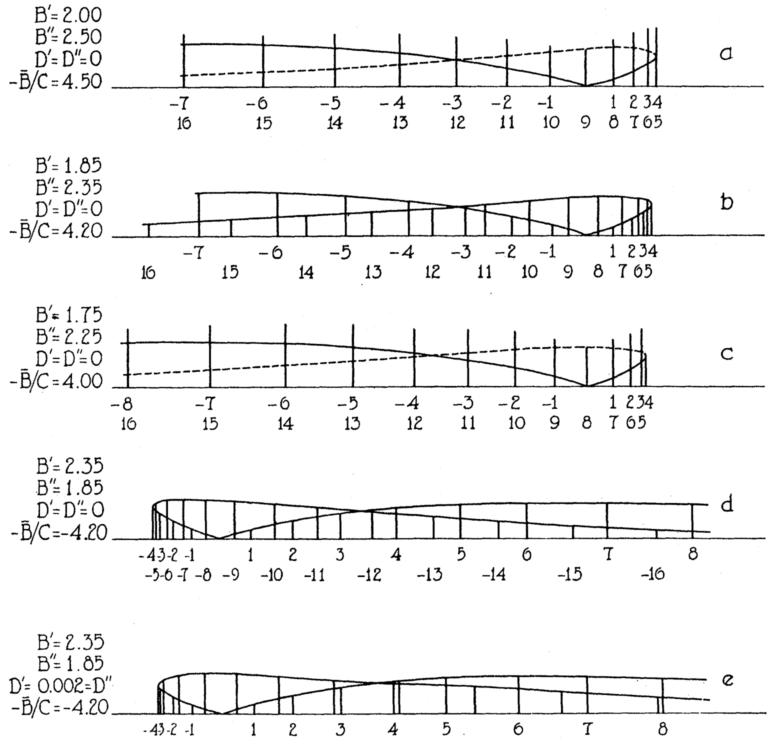

FIG. 4. Band structure types for $B'\neq B''$ (bands with heads) for emission bands with B values near 2 and $T=300°$ absolute (cf. Eqs. 13, 15). The direction of increasing frequency is toward the right. The numbers given under the lines are M values. Negative M values correspond to lines of the negative (P) branch, positive M values to lines of the positive (R) branch. The heights of the lines represent their intensities. In Figs. 4*a* and 4*c*, where lines of two series fall together, each height represents the sum of two intensities; but the separate intensities are also indicated by means of curves which represent the envelopes of the correct intensities for the separate series. [An error has inadvertently been made in the designation at the left of Fig. 4*e*, which should be corrected to read $D'=-0.002=D''$.]

spectra with an initial distribution corresponding to equilibrium at $T=300°$. The way in which the diagrams of Fig. 4 would need to be modified for a different T or a different order of magnitude of the B's can be judged from Fig. 3.

When $B'<B''$ (Fig. 4 *a*, *b*, *c*) the band has a "*head*" on the high frequency side, and is said to be degraded, or shaded, toward longer wave-lengths (or, loosely, toward the red); when $B'>B''$ (Fig. 4 *d*, *e*) there is a head on the low frequency side, and the band is degraded toward shorter wavelengths (or, loosely, toward the violet). The head is usually the most conspicuous part of the band under low dispersion, since there is an accumulation of intensity there. The way in which the formation of a head is related to the relative spacings of the upper and lower rotational energy levels, as determined by B' and B'', can be seen by considering how the lengths of the vertical lines in Fig. 2 would be modified if $B'>B''$, or $B'<B''$, were assumed.

The approximate position of the head is given by taking $d\nu/dM$ in Eq. (15), and then setting $d\nu/dM=0$. This gives $M_{\text{head}}\sim-\overline{B}/C$; also, substituting in Eq. (15), we get ν_{head}:

$$M_{\text{head}}\sim-\overline{B}/C;\ \nu_{\text{head}}\sim\nu^0-\overline{B}^2/C \tag{16}$$

$\overline{B}/C$ may happen to be an integer (Fig. 4*c*) and in this case Eq. (16) is exact for M_{head}, but ordinarily, of course, $\overline{B}/C$ is not integral and the actual M_{head} is the whole number nearest to $-\overline{B}/C$. When $\overline{B}/C$ is a half-integer (Fig. 4*a*) two lines fall together at the head. Whenever $\overline{B}/C$ is either an integer or a half integer, the lines of the series returning from the head coincide exactly with the series of lines which is composed of the lines of the headless branch plus the lines of the head-forming branch before it reaches the head (cf. Figs. 4*a*, *c*). But in the ordinary typical case the lines of the returning series are regularly spaced *between* the remaining lines (cf. Figs. 4*b*, 4*d*). The relations mentioned in the last two sentences are true only so long as $2\,(D'+D'')M^3+(D'-D'')M^4$ of Eq. (11) is negligible. This is always the case for small M values, but when M becomes sufficiently large, the two series eventually cross, and as M increases further they cross repeatedly, as a result of the terms involving the D's and higher coefficients of Eq. (5). A comparison between Figs. 4*d* and 4*e* illustrates the effect of appreciable D's in bringing about the crossing of series; but it should be mentioned that the D's used in Fig. 4*e* are many times larger than would ever actually occur with the given B values.

In the last several paragraphs, we have seen how the structure of a band depends on the values of B' and B'', D' and D''. Now in a band-system, the structure is, slightly at least, different for every band, since B' and B'' are respectively functions of v' and v'' (cf. Eqs. 3*a*, 8, 11). Using Eq. (3*a*) we have

$$B'=B_0'-\alpha'v' \text{ and } B''=B_0''-\alpha''v'', \text{ where } \alpha'<<B_0' \text{ and } \alpha''<<B_0''.$$

Hence in Eq. (16) we have

$$2\,\overline{B}=B'+B''=B_0'+B_0''-\alpha'v'-\alpha''v'', \text{ and } C=B'-B''=B_0'-B_0''-\alpha'v'+\alpha''v'',$$

or

$$M_{\text{head}}\sim-\overline{B}/C=-(\overline{B}_0-\tfrac{1}{2}\alpha'v'-\tfrac{1}{2}\alpha''v'')/(C_0-\alpha'v'+\alpha''v'')\ ;$$
$$\nu_{\text{head}}\sim\nu^0-(\overline{B}_0-\tfrac{1}{2}\alpha'v'-\tfrac{1}{2}\alpha''v'')^2/(C_0-\alpha'v'+\alpha''v''). \tag{16a}$$

Thus $-\overline{B}/C$ varies from one band to another, so that in different bands of the same system any or all of the three types illustrated by Figs. 4*a*, *b*, *c* may occur.

When C_0 is small ($C_0 = B_0' - B_0''$), the variation of the B's with the v's is frequently enough to cause C to occur with ***opposite sign*** for different bands. Bands degraded toward long wave-lengths, headless bands, and bands degraded toward short wave-lengths may then all occur in a single band-system (example, violet CN bands).[11]

In addition to the variations already mentioned, there are sometimes irregularities of various kinds. Frequently there are "*perturbations*" in some of the lines of a band, i.e. displacements from expected position (and intensity). These are explained by the supposition that sometimes in a series of rotational levels, certain levels fail to obey the regular relation expressed by Eq. (5). Another type of irregularity, associated with certain forms of instability of the molecule, is a sudden breaking off of a series of lines, or a progressive broadening of successive lines and gradual fading out, beyond some value of M.

Another kind of departure from the relations discussed above can be expressed by introducing a small linear correction term[12] ϵK in Eq. (5). This disturbs Eqs. (9) and (10) in such a way that the P and R branches have a slight bodily relative shift, so that they can no longer be accurately represented by the single formula of Eq. (11). In Fig. 2 this shift would be equivalent to the use of a slightly different ν^0 (cf. Eq. 14) for the two branches.

Vibrational structure of band systems. Going back to Eqs. (5), (7) and (8), we now assume F'^r, F''^r and ν^r equal to zero in order to study the arrangement of bands in a system, taking the position $\nu^0 = \nu^{el} + \nu^v$ in each band as representative of the band. Neglecting terms in $(v+1/2)^3$, we have from Eqs. (5) and (7),

$$\begin{aligned} \nu^0 = \nu^{el} + \nu^v &= \left[\nu^{el} + \tfrac{1}{2}\omega_e' - \tfrac{1}{2}\omega_e'' - \tfrac{1}{4}x_e'\omega_e' + \tfrac{1}{4}x_e''\omega_e''\right] \\ &\quad + v'\omega_e'(1-x_e') - v'^2 x_e'\omega_e' - v''\omega_e''(1-x_e'') + v''^2 x_e''\omega_e'' \qquad (17) \\ &= \nu^{00} + a'v' - b'v'^2 - a''v'' + b''v''^2. \end{aligned}$$

Usually this equation,— if necessary with additional terms in v^3 and so on,— is adequate to represent accurately the ν^0 values of the bands of a system. Occasionally, however, there are perturbations of some of the vibrational energy levels, so that the ν^0 values for some of the bands show irregular deviations from Eq. (17).

Just as the scale of the structure of individual bands varies with B, which depends on μ and r_e^2, so the scale of the spacing of bands in a band system varies with ω_e, which depends on μr_e^2 and a^* (cf. Eq. 6). Small ω_e results from small a^*, or from large μ or r_e; and conversely. Isotopic molecules are alike in respect to r_e and a^*, but differ in μ and so in ω_e. The largest

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[11] Cf. F. A. Jenkins, Phys. Rev. **31**, 539 (1928).

[12] Cf. R. T. Birge, Report on Molecular Spectra in Gases, p. 171, etc. (CuH Bands). For a theoretical explanation, cf. Part II below, paragraph following Eq. (29).

ω_e known is 4371, for the normal state of H_2; next in size is 4037 for normal HF. Molecules like N_2 and CO have for their stable states values in the neighborhood of 1500–2300. Normal K_2 has $\omega_e=92$; normal I_2 has $\omega_e=128$.

In the analysis of a band system, the position ν_{head} (cf. Eq. 16*a*) is ordinarily measured, rather than the theoretically more important ν^0 of Eq. (17). In fact, it is usually not possible to determine the ν^0 positions without detailed analysis of the structure of a number of the bands. We need therefore a ν_{head} equation. Unless C is unusually small, the distance $\nu_{\text{head}}-\nu^0$ does not vary much from band to band (cf. Eq. 16*a*). Hence the interval $\nu_{\text{head}}-\nu^0$ can be conveniently represented by an expansion of Eq. 16*a* in powers of v' and v''. This contains a constant term $-B_0^2/C_0$ and small terms in v', v'^2, v'', v''^2, $v'v''$, etc.[12a] Approximately, then, the heads of a band system should be given by an equation of the form

$v' \backslash v''$	0		1		2		3		4		5		6		7	Ave. $\Delta F'^v$
0	20646	964	19682	950	18732	929	17803									
	862		862		862		857									861
1	21508	964	20544	950	19594	934	18660	918	17742							
	855		854		857		853		851							854
2	22363	965	21398	947	20431	938	19513	920	18593	904	17689					
	845		848		844		850		846		845					846
3	23208	962	22246	951	21295	932	20363	924	19439	905	18534	890	17644			
	832		840		841		838				837		837			838
4	24040	954	23086	950	22136	935	21201				19371	890	18481	873	17608	
			825		833		831						829		828	829
5			23911	942	22969	937	22032	921	21111				19310	874	18436	
					821		826		825						820	823
6					23790	932	22858	922	21936	908	21028				19256	
							818		817		818					818
7							23676	923	22753	907	21846	894	20952			
									811		811		810			811
8									23564	907	22657	895	21762	883	20879	
											803		804		807	805
9											23460	894	22566	880	21686	
Ave. $\Delta F''^v$		962		948		934		921		906		893		878		

$$\Delta F^v(v'', v''+1)=962.6-14.03\, v''=(\bar{a}''-\bar{b}'')-2\bar{b}''v''; \ \bar{a}''=969.6,\ \bar{b}''=7.01$$

$$\Delta F^v(v', v'+1)=860.9-7.36\, v'=(\bar{a}'-\bar{b}')-2\bar{b}'v'; \ \bar{a}'=864.6,\ \bar{b}'=3.68$$

$$\nu_{head}=20646.4+[864.6\, v'-3.68\, v'^2]-[969.6\, v''-7.01\, v''^2]$$

FIG. 5. Most important part of v' v'' matrix diagram for frequencies of heads of AlO system, showing how the ΔF^v's (cf. Eqs. 18) can be determined, and from them the $\bar{a}$'s, $\bar{b}$'s, and the ν_{head} equation (cf. Eq. 17*a*). (The complete observed spectrum contains heads with v' up to 15 and v'' up to 12: cf. W. Mörikofer, Dissertation Basel, 1925). The frequencies given are experimental values, and for the weaker bands (especially the bands of the sequence $v'-v''=4$) are probably not very accurate, and so give rather irregular ΔF^v's. The ΔF^v and ν_{head} equations given do not correspond to a critical analysis of the data; Fig. 5 is intended to be illustrative rather than complete or exact.

$$\nu_{\text{head}}=\nu^{00}_{\text{head}}+\bar{a}'v'-\bar{b}'v'^2-\bar{a}''v''+\bar{b}''v''^2+\cdots. \qquad (17a)$$

[12a] Cf. R. S. Mulliken, Phys. Rev. **25**, 131 (1925), footnote 29.

Here $\nu^{00}{}_{\text{head}}$ means ν_{head} for the band $v'=0$, $v''=0$, while the $\bar{a}$'s and $\bar{b}$'s are constants differing just slightly from the a's and b's.

The ν^0 or ν_{head} values for the bands of a band system form according to Eqs. (17) and (17*a*) a two-dimensional array, and can be arranged in the form of a matrix. Fig. 5 shows such a matrix for a typical band system (AlO bands), using ν_{head} data as determined by experiment. Each band is characterized by two indices (v', v''); when one speaks of for instance the (3, 1) band, the numbers refer to these indices. There is no strict selection rule which limits the relative values of v' and v'', but the *intense* bands are limited in a way which depends largely on the relative values of ω_e' and ω_e'' (cf. discussion below).

Fig. 6 shows a reproduction of a photograph of the AlO bands, with the heads numbered according to v' and v''. The photograph shows well the grouping of the bands in "*sequences*," i.e. series of bands of constant $(v'-v'')$. It also shows well the $v''=0$ "*v' progression*" and the $v'=0$ "*v'' progression.*" (In a v' progression, v'' is fixed, v' variable; in a v'' progression, v' is fixed, v'' variable). Fig. 6 shows also the relations,—neglecting the error introduced by using ν_{head} instead of ν^0 data,—between the positions of the various bands and the energy levels of the molecule. A careful study of the energy level diagram in connection with Fig. 5 and the photograph will make these relations clear.

From the ν_{head} data in Fig. 5, it is possible to determine the constants $\nu^{00}{}_{\text{head}}$, $\bar{a}'$, $\bar{b}'$, $\bar{a}''$, $\bar{b}''$ of Eq. (17*a*), hence approximately the corresponding constants of Eq. (17). One begins by taking *differences* of adjacent ν_{head} values (cf. Fig. 5). Such differences, which can be read off directly from the spectrum, must according to the theory be equal, except for the slight error caused by the variability of $\nu_{\text{head}}-\nu^0$ from band to band, to differences of the term values of adjacent vibrational energy levels of the molecule. For instance, except for the slight error caused by using ν_{head} data, $\nu(0,0)-\nu(0,1)=F''^v(1)-F''^v(0)\equiv\Delta F''^v(0,1)$. If the bands are correctly arranged in the matrix diagram, $\nu(1,0)-\nu(1,1)$ *also* should be equal to $\Delta F''^v(0,1)$, and we may therefore expect $\nu(0,0)-\nu(0,1)=\nu(1,0)-\nu(1,1)$ within experimental error. The weighted mean of these and other similar intervals $\nu(v_i',0)-\nu(v_i',1)$ may be taken as the best experimental value of $\Delta F''^v(0,1)$. Similarly $\Delta F''^v(1,2)$ can be obtained from the differences $\nu(v_i',1)-\nu(v_i',2)$. The above relations are exemplified in Fig. 5. In an analogous manner, we determine the $\Delta F'^v$'s: e.g. $\Delta F'^v(0,1)=\nu(1,v_i'')-\nu(0,v_i'')$, where $v_i''=0,1,2,\cdots$. The various $\Delta F'^v$ and $\Delta F''^v$ values from the AlO heads are given in Fig. 5. From Eq. (5) with $F^r=0$ we find that the ΔF^v's as obtained from ν^0 data should be quantities of the form

$$\left.\begin{aligned}\Delta F'^v(v',v'+1)&=\omega_e'(1-2x')-2v'x_e'\omega_e'=(a'-b')-2b'v'\\ \Delta F''^v(v'',v''+1)&=\omega_e''(1-2x'')-2v''x_e''\omega_e''=(a''-b'')-2b''v''\end{aligned}\right\}. \qquad (18)$$

The corresponding intervals from ν_{head} data are related in the same manner to the $\bar{a}$'s and $\bar{b}$'s. Thus the averaged intervals of Fig. 5 yield $\bar{a}'$, $\bar{b}'$, $\bar{a}''$, $\bar{b}''$, and, finally, a complete equation of the form of Eq. (17*a*).

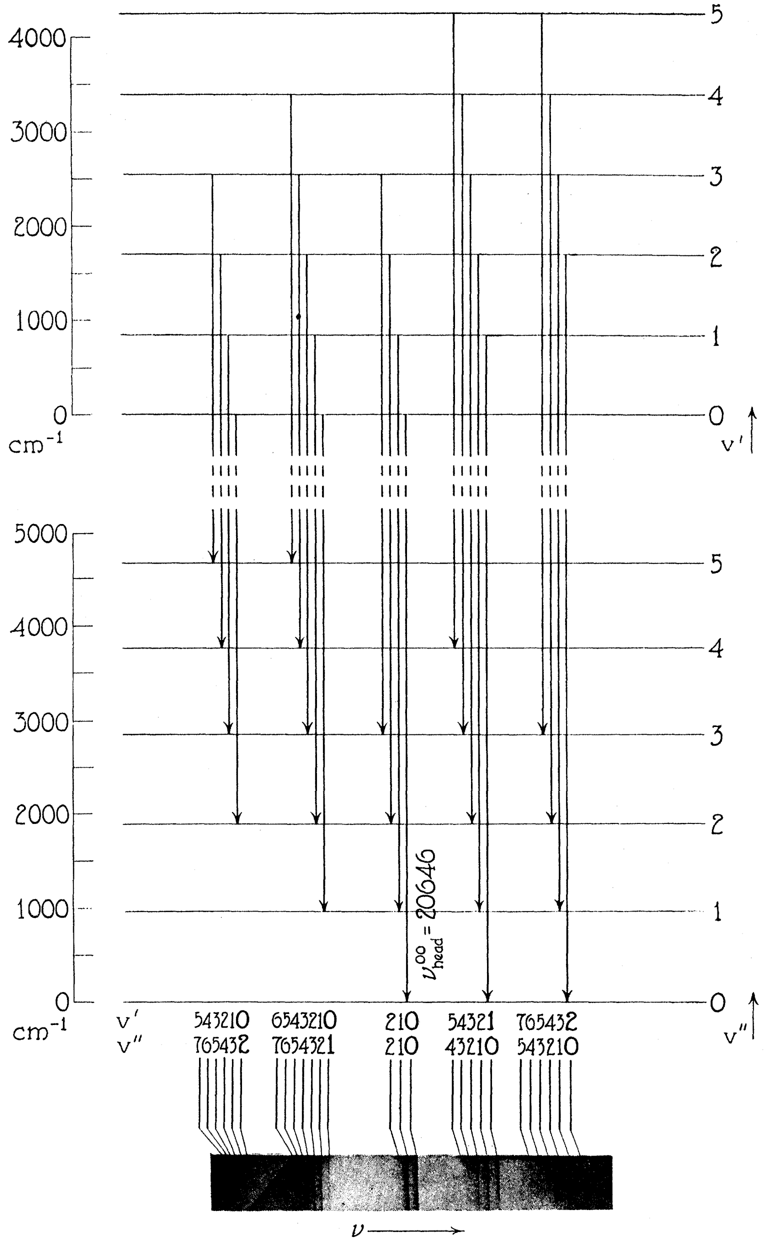

FIG. 6. Relation between vibrational energy levels and spectrum for the AlO band-system. At the bottom of the figure is a reproduction of a photograph showing the actual appearance of these bands as obtained with a prism spectrograph. Above this is a theoretical diagram on a uniform ν scale, with the v' and v'' values of each band. The observed spectrum consists mainly of five sequences of bands ($v'-v''=0, \pm 1, \pm 2$). Various v' and v'' progressions can be readily picked out from the reproduction or the theoretical ν diagram, e.g. the v'' progression with $v'=0$ and the v' progression with $v''=0$. The upper part of Fig. 6 shows a part of the vibrational energy levels of AlO, for each of the two electronic states involved in the AlO bands here considered. The spacings in each set of levels are given by a wave-number scale at the left. The long vertical lines in the figure show how the bands correspond to transitions between vibrational levels (to avoid crowding, these vertical lines have been drawn here for only part of the bands shown in the lower portion of the figure).

The arrangement of bands in Fig. 5 serves to bring out certain criteria which must be fulfilled when a correct assignment of v' and v'' values has been made for a band system. These are: (1), if $b>0$ in Eq. (18), as is true in all cases yet known in practise,[12b] the experimental quantities corresponding to ΔF^v,—both $\Delta F'^v$ and $\Delta F''^v$,—must fulfill the inequalities $\Delta F^v\ (0,1) > \Delta F^v\ (1,2) > \Delta F^v\ (2,3) \cdots$; (2), the matrix diagram (Fig. 5) should, in well developed band systems, be sharply bounded on two sides by two progressions of strong bands, namely the $v'=0$ progression and the $v''=0$ progression. In case the emitting or absorbing molecule has isotopes, there is also a third valuable criterion for the assignment of v values: isotopic molecules give band systems of identical structure but somewhat different scale, with the bands of all isotopes approximately coinciding near $\nu=\nu^{00}$.[13]

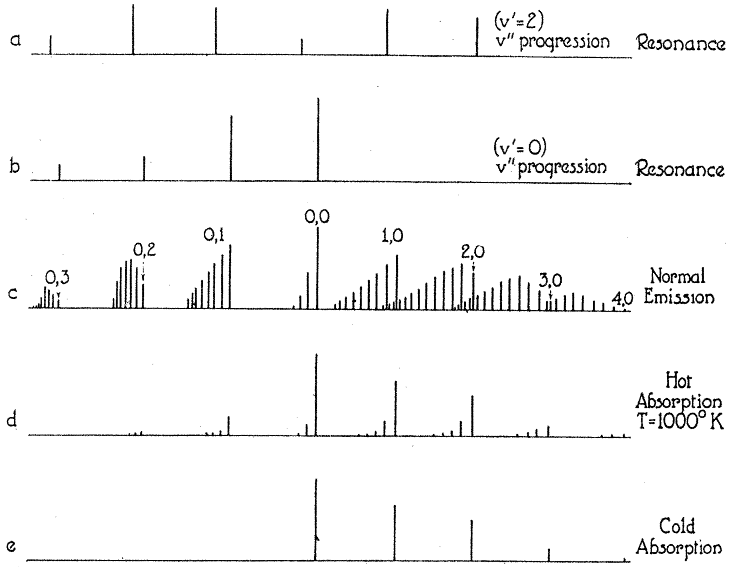

FIG. 7. Effect of initial distribution of molecules among vibrational states on vibrational intensity distribution, for a typical molecule. Each vertical line in the figure represents a band-head; its height is roughly proportional to the intensity of the band. In each band, the band-structure extends from the head toward longer wave-lengths, as in the reproduction in Fig. 6; the extent of this structure would vary, however, with the temperature (cf. Figs. 3, 4). All the diagrams are drawn in accordance with the known vibrational energy levels of the AlO molecule (cf. Fig. 5 for frequency data and Fig. 6 for energy levels and v' and v'' assignments). Absorption and resonance spectra have not yet been obtained experimentally for this molecule, so that the intensities in Figs. 7*a*, 7*b*, 7*d*, and 7*e* have been estimated largely from theoretical considerations; Fig. 7*c*, however, corresponds to the reproduced photograph in Fig. 6. It is of interest to compare the $v''=0$ and $v''=1$, v' progressions in the high-temperature absorption spectrum; the $v'=0$ band is strongest in the $v''=0$ progression, but the $v'=2$ band in the $v''=1$ progression. This difference, which is entirely one of transition probabilities, can be understood by a study of the Type III curves in Fig. 8.

[12b] An exception appears to have been found in LiH (S. Nakamura, Zeits. f. Physik, **59**, 238, 1930.)

[13] Cf. R. S. Mulliken, Phys. Rev. **25**, 119 (1925), or F. W. Loomis, Report on Molecular Spectra in Gases, Chap. V.

We pass now to the question of the relative intensities of bands in a band system. In an emission spectrum, the bands which are developed depend very much on the conditions of excitation, since these govern the initial distribution of the molecules among vibrational levels. Fig. 7*c* represents diagrammatically the intensities of the AlO bands as obtained in emission by running an Al arc in air (cf. reproduction given in Fig. 6). A large range of v' values is present. So far as can be estimated by summation of the photographic intensities of bands originating from each v' value, there are in the arc more molecules with $v'=0$ than with $v'=1$, more with $v'=1$ than with $v'=2$, and so on. This is essentially a high-temperature thermal distribution, and is fairly typical for arc spectra.[14] With other types of excitation (electron impact, chemical reactions, excited atoms, etc.) other v' distributions often occur, e.g. the molecules may be confined to one or more, more or less sharply limited, low values of v'; or moderately high values of v' may be favored rather than low values; and so on.[14] In fluorescent spectra (emission spectra of molecules excited by light absorption) various v' distributions are possible, depending on the exciting wave-lengths and on the molecular constants. An interesting special case is that of "resonance spectra," that is, fluorescent spectra resulting from excitation by *monochromatic* light. Here we have a single value of v' (and of K'), and the emission spectrum consists of a series of bands (or rather, of particular lines of a series of bands) forming a v'' progression (cf. Fig. 7, *a* and *b*).

In absorption spectra, as in emission spectra, one has to consider the initial distribution among vibrational levels, but now this is a v'' distribution instead of a v' distribution. In a typical gas, such as CO, at room temperature, practically all the molecules have $v''=0$, and the absorption spectrum consists of a single v' progression with $v''=0$, as in Fig. 7*e*. This progression consists of bands all,—except the (0, 0) band itself,—on the high frequency side of the (0, 0) band. If the temperature is raised sufficiently, or (even at room temperature) if the molecule has a very small ω_e'' value (e.g., K_2 or I_2), the distribution is shifted so that an appreciable fraction of the molecules has $v''>0$. Additional v' progressions then appear (cf. Fig. 7*d*), so that the spectrum extends toward longer wave-lengths.

The relative intensities of the bands in a system are determined jointly by the initial distribution, as already considered, and by the relative *transition probabilities* as a function of $(v'-v'')$ and of v' or v''. Franck proposed a simple theory for approximately determining the transition probabilities; this was further developed by Condon, and has found many interesting applications in the hands of Franck, Birge and Sponer, and others.[15,16]

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[14] Cf. R. S. Mulliken, Phys. Rev. **25**, 259; **26**, 1 (1925); R. T. Birge, Molecular Spectra in Gases, pp. 135–142; 221, 248–9; G. Herzberg, Ann. der Physik, **86**, 189 (1928); Zeits. f. Physik **49**, 512, 761 (1928); **52**, 815 (1929).

[15] For a review of this work, cf. H. Sponer, Ergebnisse der exakten Naturwissenschaften, Vol. VI, p. 75 (1927); also K. K. Darrow, Chem. Reviews, **5**, 451 (1928).

[16] Intensity distributions and Franck theory, cf. E. U. Condon, Phys. Rev. **28**, 1182 (1926).

Each electronic state of a molecule has, in general, a different $U(r)$ curve, and a different value of ω_e and of r_e. Suppose we consider the transfer of a molecule from one electronic state to a higher one by light absorption. The molecule is assumed initially in some definite vibrational state v''; the rotation of the molecule need not be considered. Franck argued that, to a first approximation, the light quantum acts directly only on the *electron* system of the molecule, the inertia of the nuclei being too great for them to be directly affected. Thus the distance r between the nuclei, also the kinetic energy of the nuclei, should at the first instant be practically unchanged. This condition, in connection with the two $U(r)$ curves involved, suffices to determine the vibrational state after absorption.

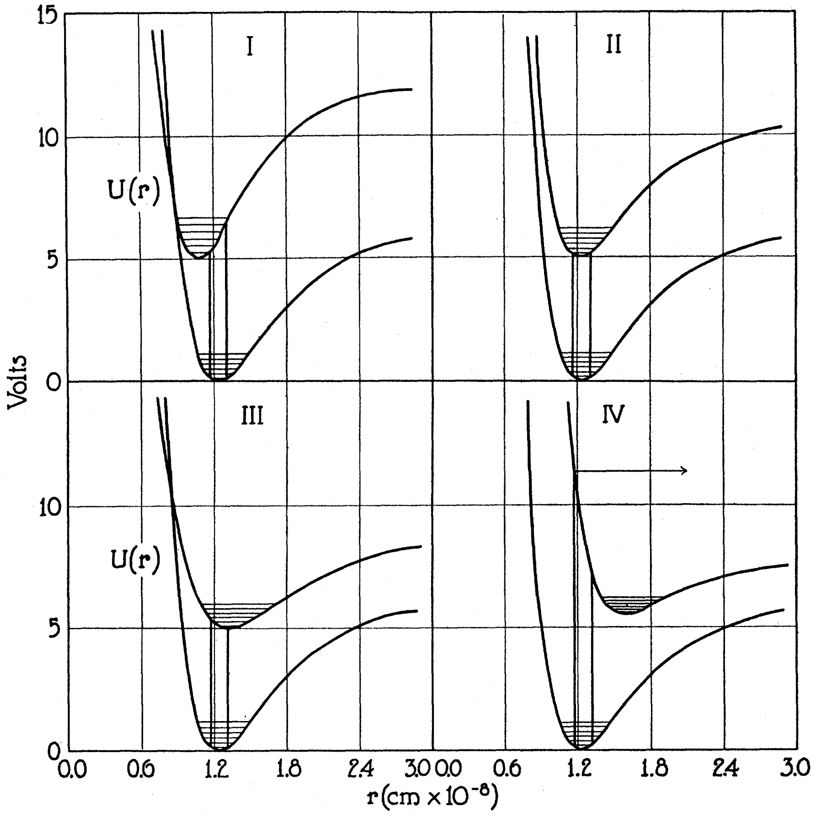

FIG. 8. $U(r)$ curves drawn according to Morse's formula,[5] and in accordance with the relation $r_e^3\omega_e = 3000\times10^{-24}$, for four typical cases. The curves are not those of any actual molecules, but the constants chosen are of approximately the same magnitude as is found for such molecules as O_2. Vertical lines drawn to the $U'(r)$ curves, from $r_{\min}$ and $r_{\max}$ of $v''=0$ of the various $U''(r)$ curves, serve to indicate the most probable v' values resulting from light absorption from $v''=0$. In Case IV, for $r_{\min}$ of $v''=0$, light absorption results in ***dissociation.***

Suppose we start with a molecule having $v''=0$. Its nuclear separation r may be thought of as oscillating between a maximum and a minimum value ($r_{\max}$ and $r_{\min}$). If it happens that $r \sim r_{\max}$ or $r_{\min}$ when the light quantum is absorbed,—as is very probable, since the molecule spends most of its time near these values of r,—the correct state of vibration in the upper electronic state is obtained approximately by vertical projection from the $U''(r)$ curve to the $U'(r)$ curve. Thus in case II of Fig. 8, the molecule initially at $r_{\min}$ of $v''=0$ would find itself, after absorption of the quantum, at $r_{\min}$ of $v'=0$, and would go on with its vibration almost undisturbed by the electron jump. In case III, however, $r_{\min}$ of $v''=0$ is approximately the same as $r_{\min}$ of $v'=2$, and the molecule would probably vibrate with $v'=2$. In case IV, $r_{\min}$ of $v''=0$ corresponds to a point on the $U'(r)$ curve where $U'(r) > U'(\infty)$, and instead of a vibration, we should expect a flying apart of the nuclei (dissociation).

The procedure we have just been using is of course applicable for $r_{\max}$ as well as for $r_{\min}$, for all values of v'', and for all types of $U(r)$ curves, in absorption spectra. It holds equally for emission spectra; in this case we project *downward* from the $U'(r)$ curve. In general, for any given initial v'' (or v') value there are *two* most probable values of v' (or v''), corresponding to the initial positions $r_{\min}$ and $r_{\max}$. Hence for any given v'' (or v'), $(v'-v'')$ has two most probable values. Of course, other values of $v'-v''$ also occur, since the molecule spends part of its time between $r_{\min}$ and $r_{\max}$,[17] and also because the theory is only an approximate one. (That it is necessarily only approximate is evident for instance from the fact that vertical projection from $r_{\min}$ or $r_{\max}$ of a $U''(r)$ curve does not unless by chance hit the $U'(r)$ curve exactly at an energy corresponding to a permitted state of vibration.)

There are various empirical types of intensity distribution for the bands of a band system and, as Condon has shown,[16] these depend, in just the way given by Franck's theory, on the relative forms of the $U'(r)$ and $U''(r)$ curves. Each such type differs characteristically from the others not only in the intensity distribution with respect to v' and v'', but also in the *arrangement* of the bands, and in the appearance of the *band structure*. This threefold relationship can best be understood after an empirical relation which exists between the r_e and ω_e values has been stated. This is as follows: with only a few minor exceptions,[18] there is always, for the different electronic states of a single molecule, a *qualitatively inverse* relation between r_e and ω_e. Quantitatively, this has been expressed in the forms[19]

$$r_e^2\, \omega_e = \text{const.; and, } r_e^3\, \omega_e \sim \text{Const.} \tag{19}$$

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[17] Suppose for example $r''=r_e''$ when the light quantum is absorbed. Here the molecule has kinetic energy equal to $E''^v - U''(r_e'')$ before the jump, and the projection must be made to a point above the $U'(r)$ curve by just this amount.

[18] In the case of two states with nearly equal r_e, the ω_e values are also nearly equal. Here it may happen that the larger ω_e goes with the larger r_e, contrary to the qualitative rule above stated. This is, however, obviously only a minor violation of the rule, and corresponds to the fact that no exact quantitative formulation of the rule can be given. It should also be emphasized that the rule is purely empirical; no theoretical reason for its validity is obvious.

[19] First form, cf. R. T. Birge, Phys. Rev. **25**, 240 (1925); R. Mecke, Zeits. f. Physik **32**, 823 (1925); second form, P. M. Morse, Phys. Rev. **34**, 57 (1929).

Both forms, especially the first, hold fairly well for *different states of a single molecule*. The second form, with *Const.* $=3000\times 10^{-24}$ cm^2, holds fairly well for a wide variety of states, even of *different molecules*, provided the masses of the two atoms are not too unequal (for unequal masses, *Const.* is larger; the largest values are for hydrides, where *Const.*$\sim$6000).

The statements of the previous paragraph can best be elucidated by considering the four typical pairs of $U(r)$ curves depicted in Fig. 8. In Type II of Fig. 8, where $r_e'=r_e''$, we expect $\omega_e'\sim\omega_e''$ according to Eq. (19). Because of $r_e'=r_e''$, we have $B_0'\sim B_0''$ (cf. Eqs. 3, 3*a*); but since $B'=B_0'-\alpha'v'$ and $B''=B_0''-\alpha''v''$, we may have $B'\sim B''$, $B'>B''$ or $B'<B''$ in different bands, depending on the values of α', α'', v', and v''. Thus in the same band system we may find headless or practically headless bands, bands degraded toward long wave-lengths, and bands degraded toward short wave-lengths.—Because of $\omega_e'\sim\omega_e''$, the bands of each sequence are very crowded together or even almost superposed.[20]—Because $r_e'=r_e''$, the sequence $\Delta v=0$ should according to the theory of Franck and Condon be very much stronger than any other sequence, with the sequences $\Delta v=\pm 1$ next in intensity, and so on. (A comparison with the typical band system shown in Fig. 6 will be helpful to the reader in considering the case here under discussion.)—The complete band system should then consist essentially of a strong central group of nearly superposed, headless or practically headless, bands comprising the sequence $(v', v'')=(0,0)$, $(1, 1)$, $(2, 2)$, etc., flanked by two much weaker sequences, likewise composed of nearly superposed bands, the shorter wave-length sequence comprising the bands $(1, 0)$, $(2, 1)$, $(3, 2)$, ... , all degraded toward longer wave-lengths, and the longer wave-length sequence composed of bands $(0, 1)$, $(1, 2)$, $(2, 3)$, $\cdots$ all degraded toward shorter wave-lengths.[21]

For $U(r)$ curves with $r_e'>r_e''$ by a good margin (cf. Type III of Fig. 8) we have $B'<B''$ for all bands of measurable intensity, so that these are all definitely degraded toward longer wave-lengths, like the AlO bands of Fig. 6. Accompanying $r_e'>r_e''$ we have $\omega_e'<\omega_e''$, and the members of each band sequence are now well spread out. At the same time, there are several strong sequences in the band system; the intensity distribution is of a type similar to that of the AlO bands in Fig. 6.

[20] If we had $a'=a''$, $b'=0=b''$ in Eq. (17), all the bands of a sequence would have their ν^0's precisely superposed. Actually, aside from the usual slight difference between a' and a'', the influence of b' and b'' causes successive members of a sequence to be separated. Usually b' and b'' differ greatly even if $a'\backsim a''$. An interesting case sometimes occurs in which (the series of ν^0's of) a sequence turns back on itself,—just like the lines of a band in the series which forms a head. This happens when, say, ω_e' is *slightly* greater than ω_e'' and x_e' is *decidedly* greater than x_e'', as is true in the violet CN bands (cf. F. A. Jenkins, l.c., ref. 11).

[21] If the sequences are *long*, as happens if ω_e is small or if the light source is such as to give large v' values, then the transition from bands degraded toward violet to headless bands and to bands degraded toward red may occur in a single sequence; this actually happens in the violet CN bands (cf. Jenkins, l.c., ref. 11). This is correlated (cf. Eq. 19) with the turning back of the sequences on themselves (ref. 20).

As the difference between ω_e' and ω_e'' increases (passage toward type IV of Fig. 8), each band sequence becomes more and more spread out and more and more overlaps neighboring sequences, until finally the classification into sequences loses its usefulness. At the same time, the intensity becomes distributed over a wider and wider range of v values. The arrangement of bands in the system becomes less obviously regular and the assignment of v' and v'' values more difficult.[22] With $U(r)$ curves as in type IV of Fig. 8, the band system includes bands of very large Δv, and is accompanied by a continuous spectrum corresponding in absorption bands to dissociation by light, or in emission bands to a union of atoms with light emission (examples: visible absorption and recombination spectra of the halogens). Finally, when r_e' and r_e'', and so ω_e' and ω_e'', are very different, we have *only* a continuous spectrum (examples, ultra-violet absorption spectra of the hydrogen and alkali halides).

When $r_e' < r_e''$ as in Type I of Fig. 8, we have a case very similar to that of Type III, except that now all the bands are degraded toward the violet. When the inequality of r_e' and r_e'' is larger, we have cases analogous to Type IV, except that here one has dissociation of a molecule accompanying light *emission* (example, continuous spectrum of H_2), and combination of atoms accompanying light absorption.

A more detailed treatment of the various types of intensity distribution among the bands of a system can be found elsewhere.[14,16]

Structure of $^1\Sigma \rightarrow {}^1\Sigma$ *bands: non-electronic bands.*[23] In Eq. (11), $\nu^0 = \nu^{el} + \nu^v$. If $\nu^{el} = 0$, we have infra-red bands of two types, (*a*) if $\nu^v \neq 0$, vibration-rotation bands; (*b*), if $\nu^v = 0$, pure rotation bands.

The vibration-rotation bands have the same type of structure as electronic bands (cf. Eqs. 11 and 15). The relative intensities of the band lines obey the same relations as electronic bands (cf. Eqs. 12 and 13.) But since $\nu^{el} = 0$, we have $B' = B_0 - \alpha v'$, $B'' = B_0 - \alpha v''$, with the *same* B_0 and α for both vibrational levels involved; hence, since α is small, we have $B' \sim B''$, approximating the cases shown in Fig. 3. But since B' here is always (slightly) less than B'', there is always a slight tendency to form a head on the R branch (cf. Eq. 16).

In vibration-rotation bands we have $x_e' \equiv x_e''$, $\omega_e' \equiv \omega_e''$, so that Eq. (17) becomes

$$\nu^0 = (v' - v'')\omega_e(1 - x_e) - (v'^2 - v''^2)x_e\omega_e. \qquad (20)$$

The relative intensities of different vibration-rotation bands are determined by entirely different factors (cf. below) than in the case of electronic bands. The strongest bands are those for which $v' = v'' + 1$ ("fundamental" bands). The "first harmonic" bands ($v' = v'' + 2$) are very much weaker, the second harmonic ($v' = v'' + 3$) very much weaker still, and so on. Since the infra-red bands

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[22] Criterion (2) of page 78 now fails, since when the inequality of r_e' and r_e'', hence of ω_e' and ω_e'', is large, bands involving low values of both v' and v'', such as (0, 0), (0, 1), (0, 2), (1, 0), (2, 0), (1, 1), etc., are very weak or practically missing.

[23] Cf. W. F. Colby, Report on Molecular Spectra, Chap. III.

are ordinarily observed in absorption at room temperature, we usually have all the molecules in their normal electronic state and so have only a v' progression with $v''=0$. But at high temperatures something like a *band-system* would be possible, and in emission spectra we should expect to have one such system for each different electronic state.

The band intensities in vibration-rotation bands depend, according to the correspondence principle, on the variable part of the *electric moment* of the molecule. Homopolar molecules (H_2, N_2, O_2, etc.), on account of their zero dipole moment, have no vibration-rotation bands (electronic bands they *do* have).

In the pure rotation bands, $B'=B''$, $D'=D''$, and Eq. (11) reduces to

$$\nu=2BM+4DM^3 \tag{21}$$

M has only positive values here. Each band consists of a single series of nearly equally spaced lines. Such bands are best known for ($v''=0$ of the normal states of) the hydrogen halides. We shall not discuss here the relations which govern the intensities of the lines *within a band*, except to note that Eqs. (12) and (13) no longer apply. The intensity of any pure rotation band, *taken as a whole*, depends on the average dipole moment. Homopolar molecules, with zero dipole moment, have no pure rotation bands.

PART II

INTRODUCTION

In Part I we have considered, in summary, the important variations which can occur in the structure of a band spectrum associated with a transition between two $^1\Sigma$ electronic states. We shall now consider, in some detail, what new variations are possible when we have to deal with other than $^1\Sigma$ states. To begin with, it is important to note that these new variations do not directly touch ν^v, but only ν^{el} and ν^r, of Eq. (7). They consist mainly in new complications in the structure of individual bands, often accompanied by multiple values of ν^{el} analogous to atomic multiplets. It is convenient to approach this problem, following the method used by Hund in his fundamental paper on the subject,[24] by a study of a reasonable molecular model in terms of the old quantum theory. The immediate object, which will be followed in Part II, is to learn enough regarding energy relations and electronic quantum numbers to understand and interpret the various types of individual-band structure which occur in practise. Later, in Part III, we shall seek a more complete understanding of electronic quantum numbers and electronic states in molecules, and of their relation to the quantum numbers and states of their atomic dissociation products.

The discussion in Part II falls naturally into three stages: (*a*) a treatment of the problem of the electronic states of an imaginary limiting case which differs from real molecules in that the nuclei are assumed held stationary; (*b*) a consideration of the modifications required in part (*a*) in order

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[24] F. Hund, Zeits. f. Physik 36, 657 (1926).

to take into account the effect of the vibrations and rotations of the nuclei; (*c*) a study of the various types of bands resulting from transitions between electronic states of various types. Parts II*a* and II*b* are given below, while Part II*c* will appear at a later date.

II*a*. THEORY OF MOLECULAR ELECTRONIC STATES FOR THE CASE OF FIXED NUCLEI

Comparison of molecule with atom in strong electric field. A molecule with nuclei assumed held fixed ("frozen molecule") can be regarded (1) as formed from two atoms or ions, each of which, when they come near, acts on the other with a large electric field; or (2) as obtained by dividing the nucleus of an atom into two parts and separating these somewhat, thus producing a modification of the original electric field of the single nucleus, equivalent to the superposition of a suitable correction field upon the original field. We shall here adopt the second point of view as the best means of reaching an understanding of the nature of the electronic states of molecules with nuclei held fixed. In an atom, the motion of any one electron can be treated as a motion in a spherically symmetrical but in general non-Coulombian electric field. The electrons, other than the one under consideration, are regarded as equivalent to a continuous *spherically symmetrical* cloud of negative electricity. (This assumption finds a large measure of justification in the new quantum theory.) This is the so-called core model (atom = core + chosen electron).

The corresponding model for the molecule with fixed nuclei consists in the nuclei plus an electron cloud having *axial* symmetry around a straight line passing through the nuclei. This molecular core-model can be imagined as built up from a suitably chosen atomic core-model by superposing on the central field of the latter a suitable, usually large, axially symmetrical correction field. This correction field must obviously change rather rapidly in both direction and magnitude, both along and at right angles to the axis. Such a correction field is of course quite different from the uniform unidirectional imposed field in the ordinary Stark effect for atoms. Nevertheless the existence of an axial symmetry in both cases is sufficient to make them qualitatively the same, so that the theory of the electronic states of a molecule with fixed nuclei is qualitatively identical with that of an atom in a strong electric field (Stark effect).

We therefore begin by a review of the results of the quantum theory for an atom in the absence of external fields, then, as a useful introduction to a study of the effect of electric fields, we consider briefly the effect of a uniform magnetic field on an atom (Zeeman effect). After that we pass to a more detailed consideration of atoms in axially symmetrical electric fields.

Quantum numbers and electron states of atoms.[25] In the absence of an external electric or magnetic field, the state of an atom can usually be de-

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[25] For a detailed treatment of the theory of atomic spectra, reference may be made to F. Hund, Linienspektren und Periodisches System der Elemente (J. Springer, Berlin, 1927), or to the forthcoming book of L. Pauling and S. Goudsmit (McGraw Hill and Co., 1930).

scribed by giving quantum numbers n, l, and s for each extranuclear electron, and quantum numbers L, S, and J for the atom as a whole.[26] The principal quantum number n can take on values 1, 2, 3, $\cdots$, the azimuthal quantum number l can have values 0, 1, 2, 3, $\cdots$ (s, p, d, f, $\cdots$ electrons), while the electron spin quantum number s always has the value 1/2. In the old quantum theory, l for each electron is obtained by the quantization of the angular momentum P_l of the orbital motion of the electron in the field of the atom core (cf. above), all detailed interactions of the chosen electron with the core electrons being neglected, so that P_l can be treated as a constant. The quantum condition is $\int_0^{2\pi} P_l d\psi = lh$, which gives $P_l = lh/2\pi$. This last relation is replaced, according to the new quantum mechanics, by $P_l = l^* h/2\pi$, where $l^* = [l(l+1)]^{1/2}$. Similarly the angular momentum P_s of spin is given by $P_s = s^* h/2\pi = [s(s+1)]^{1/2} h/2\pi = \sqrt{3}h/4\pi$.

The quantum number L corresponds to an angular momentum $\mathbf{P_L} = \mathbf{L}^* h/2\pi$, where $L^* = [L(L+1)]^{1/2}$. [Bold-face type will be used throughout to indicate vectors.] $\mathbf{P_L}$ is the resultant of the individual $\mathbf{P_l}$'s. Similarly $\mathbf{P_S} = \mathbf{S}^* h/2\pi$, where $S^* = [S(S+1)]^{1/2}$, is the resultant of the $\mathbf{P_s}$'s. Most atoms contain a number of *"closed shells."* Each closed shell has $L=0$ and $S=0$ and therefore contributes nothing to the final resultant L and S of the atom. The latter are therefore determined solely by those electrons which are not in closed shells. If there is just one such electron, as in the alkali metals, then we have simply $L=l$ and $S=s$, where l and s refer to the valence electron.

If there are two electrons (1 and 2), not in closed shells, as in the excited states of the alkaline earth metals, the possible values of L are determined from l_1 and l_2 by the condition $L = l_1 + l_2, l_1 + l_2 - 1 \cdots |l_1 - l_2|$. Corresponding to each such L value, a vector diagram can be drawn representing $\mathbf{L}^*$(or $\mathbf{P_L}$) as a resultant of $\mathbf{l}_1^*$ and $\mathbf{l}_2^*$ (or of $\mathbf{P}_{l_1}$ and $\mathbf{P}_{l_2}$). For S we have $S = s_1 \pm s_2 = 0$ or 1; these two possibilities occur for each of the possible L values. In each case $\mathbf{S}^*$ can be represented as a resultant of $\mathbf{s}_1^*$ and $\mathbf{s}_2^*$.—In case the two electrons are *equivalent* ($n_1 = n_2$ and $l_1 = l_2$), only part of the L, S combinations given by the rules just stated are possible; the allowed pairs of L and S values can always be determined by means of the Pauli exclusion principle.[25]

In an atom with three electrons (1, 2, 3) not in closed shells, the possible L and S values can best be obtained as follows. First we determine as before the possible L and S values for electrons 1 and 2, neglecting 3. In this way we get a variety of possible resultants L_{12} and two possible resultants $S_{12} = 0$ or 1. Now we add the third electron and get as possible values of the final L, $L = L_{12} + l_3, L_{12} + l_3 - 1, \cdots, |L_{12} - l_3|$, there being one such set of resultants for each L_{12}. In many cases this gives two or more equal L values which nevertheless correspond to physically different states. Since $s_3 = 1/2$, we have $S = 1/2$, from $S_{12} = 0$, and $S = 1/2, 3/2$ from $S_{12} = 1$. The two resultants $S = 1/2$ are physically different.—In case two, or all three, of the electrons are equivalent, the possible L, S combinations are fewer.

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[26] The atomic notation used here follows the recommendations in the recent report by H. N. Russell, A. G. Shenstone, and L. A. Turner (Phys. Rev. **33**, 900, (1929)).

Atomic states are commonly classified according to their L values: $S, P, D, F, \cdots$ states respectively have $L=0, 1, 2, 3, \cdots$ The value of the spin S is also indicated, by means of a superscript number placed before the term symbol S, P, or D, etc. This number gives explicitly the "*multiplicity*" m and implicitly the value of $S(m=2S+1)$. Thus ^2S (to be read "doublet S", not "two S") means $L=0$, $S=1/2$, while ^1P("singlet P") means $L=1$, $S=0$; and so on.

For any given pair of values L, S, there are in general several values of the "inner" quantum number J, given by $J=L+S,\ L+S-1, \cdots |L-S|$. $J^*=[J(J+1)]^{1/2}$ is proportional to the resultant angular momentum P_J of the atom $(\boldsymbol{P_J}=\boldsymbol{J}^*h/2\pi)$; each $\boldsymbol{J}^*$ may be considered as a resultant of the vectors $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$. When $L=0$, $J=S$; when $S=0$, $J=L$; in these cases it is not necessary to give J explicitly in the term symbol (examples, ^2S, ^1P); in other cases the value of J is given as a subscript, as for example in $^4P_{\frac{1}{2}}$ $(L=1,\ S=1\frac{1}{2},\ J=\frac{1}{2})$ or in $^4P_{1\frac{1}{2}}$ $(L=1,\ S=1\frac{1}{2},\ J=1\frac{1}{2})$.[27]

The energy of an atom usually depends in first approximation on the n and l values of the individual electrons, next on L and S, and finally on J. In an atomic multiplet level (fixed n's, l's, L, and S, variable J), different values of J correspond to different angles between the vectors $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$. Between $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ there is a magnetic interaction whose energy is proportional to the cosine of the angle between them. The torque exerted by $\mathbf{L}^*$ and S^* on each other causes them to precess (cf. Eq. (23)) around their resultant $\boldsymbol{J}^*$ which, since it represents the total angular momentum of the atom, maintains a fixed direction in space. Their mutual energy is given approximately[28] ($F=\text{term}=E/hc$) by

$$F-F_0=AL^*S^*\cos(\boldsymbol{L}^*,\boldsymbol{S}^*)=(\tfrac{1}{2})A\,[J(J+1)-L(L+1)-S(S+1)] \tag{22}$$

F_0 is the "center of gravity" of the multiplet.[28a] Eq. (22) gives quantitative expression to the Landé interval rule, according to which, in a multiplet level, the spacing of any two sub-levels is proportional to the larger of the two J values concerned; e.g. in a ^4D level, the spacings of the intervals $(^4D_{3\frac{1}{2}}-{}^4D_{2\frac{1}{2}})$, $(^4D_{2\frac{1}{2}}-{}^4D_{1\frac{1}{2}})$, and $(^4D_{1\frac{1}{2}}-{}^4D_{\frac{1}{2}})$ are in the ratio $3\frac{1}{2}:\ 2\frac{1}{2}:\ 1\frac{1}{2}$.

It will be helpful to consider the application of Eq. (22) to ^2P and ^3P states. In ^2P states $(L=1,\ S=\frac{1}{2})$ we have $F-F_0$ equal to $(\frac{1}{2})A$ for the $^2P_{1\frac{1}{2}}$ level $(J=1\frac{1}{2})$, and equal to $-A$ for the $^2P_{\frac{1}{2}}$ level; this gives $\Delta F=1\frac{1}{2}\ A$ for the interval between the two levels. In ^3P (triplet P) states we have $F-F_0=A$

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[27] The above quantum numbers and Eq. (22) are applicable to the so-called Russell-Saunders or normal type of coupling of the quantum vectors $\boldsymbol{l}$ and $\mathbf{s}$. In some cases there is another type of coupling (reference 25) in which, instead of a resultant $\boldsymbol{L}^*=\sum \boldsymbol{l}^*$(vector) and a resultant $\boldsymbol{S}^*=\sum \mathbf{s}^*$ which then form a resultant $\boldsymbol{J}^*$, we have a j and a $\boldsymbol{j}^*$(resultant of $\boldsymbol{l}^*$ and $\mathbf{s}^*$) for each electron (or at least for some electrons), and then $\sum \boldsymbol{j}^*=\boldsymbol{J}^*$.

[28] For further details, cf. Hund's Linienspektren (reference 25), Chaps. III-IV; S. Goudsmit, Phys. Rev. **31**, 946, (1928); S. Goudsmit and C. J. Humphreys, Phys. Rev. **31**, 960 (1928).

[28a] The terms "multiplet" and "multiplet level" are here used, interchangeably, to designate a group of *energy levels* differing only in J (atoms), or in Σ (molecules). The term "multiplet" is also (more appropriately) used to designate a group of *spectrum lines* derived from a pair of multiplet levels.

for $^3P_2$, $-A$ for $^3P_1$ and $-2A$ for $^3P_0$; this gives $\Delta F=3A$ for the over-all width ($^3P_2-{}^3P_0$), and also fulfills the Landé rule for the separate intervals.

Mechanical frequency equation. There is in the classical mechanics an important theorem regarding frequencies of motion. This theorem yields in the old quantum theory the following relation for the frequency $c\omega_k$ associated with any quantum number k (we use $c\omega_k$, rather than ω_k, for frequency, because throughout this review the symbol ω is used to represent a quantity measured in cm^{-1}).

$$c\omega_k=(1/h)(\,|\,\partial E/\partial k\,|\,)=c\,|\,\partial F/\partial k\,| \tag{23}$$

For example, the frequency of precession associated with J is that of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ around their resultant $\boldsymbol{J}^*$; this is obtained by taking $c(\partial F/\partial J)$ in Eq. (22), which gives $cA(J+\frac{1}{2})$.

The reader should be cautioned not to attach too exact a meaning to Eq. (23), especially for low quantum numbers. A quantitative use of Eq. (23) is not permissible in the new quantum mechanics. Qualitatively, however, Eq. (23) is very useful in studying the behavior of vector models such as are used here.

Atoms in magnetic fields. When a uniform external magnetic field is imposed on an atom, $\boldsymbol{J}^*$, instead of remaining fixed in space, precesses around the direction of the field, making with the latter a constant angle θ. This angle is limited to certain values given by $\cos\theta=M/J^*$, where M is a "magnetic" quantum number, which can take on the values $J, J-1, \cdots, -J$. $\boldsymbol{M}h/2\pi$—not $\boldsymbol{M}^*h/2\pi$—represents the component, parallel to the field, of the angular momentum $\boldsymbol{J}^*h/2\pi$. (An analogous relation holds for all angular momenta which are obtained by *projection* on a relatively fixed axis.)

The precession of $\boldsymbol{J}^*$ around the field results from the fact that the latter exerts a torque on $\boldsymbol{L}^*$ and on $\boldsymbol{S}^*$. The effect of the field is, however, different for $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$. In a field of strength H, $\boldsymbol{L}^*$ tends to precess with the Larmor frequency $co=eh/4\pi m$, but $\boldsymbol{S}^*$ with a frequency $2co$(e and m are the charge and mass of the electron). The actual precession of $\boldsymbol{J}^*$ occurs with a compromise frequency gco(cf. below, after Eq. (24)), where g is a factor depending on the values of L, S, and J. When $S=0$ and $L>0$ as in the singlet states ^1P, ^1D, etc., $g=1$; when $L=0$ and $S>0$ as in the S states ^2S, ^3S, etc., $g=2$; in a multiplet state with $L>0$, g is in general different for each value of J. The *energy* of the atom is now given[29] by

$$F-F_0=(\tfrac{1}{2})A\,[J(J+1)-L(L+1)-S(S+1)]+Mgo. \tag{24}$$

Taking $c\,|\partial F/\partial M\,|$ in Eq. (24), in accordance with Eq. (23), we get for the frequency associated with $\boldsymbol{M}$ the value cgo; this represents the frequency around the field.

The compromise precession of $\boldsymbol{J}^*$ around the field exists only so long as the magnetic interaction between $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ is strong enough to preserve their resultant $\boldsymbol{J}^*$ from the disruptive influence resulting from the tendency

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[29] Cf. Hund's Linienspektren (reference 25), Chaps. III-IV.

of the external field to make L^* and S^* precess at different rates. This is true so long as the frequency $cA(J+\frac{1}{2})$ of precession of L^* and S^* about J^* is large compared with the frequency gco of J^* around the external field (it should be remembered that o is proportional to the field strength). If the field is sufficiently strong, J^* is no longer constant and has no quantum significance,[29a] while L^* and S^* precess separately around the field, giving magnetic quantum numbers M_L and M_S ($M_L=L, L-1, \cdots -L$, $M_S=S, S-1, \cdots -S$). The corresponding angular momenta are $M_Lh/2\pi$ and $M_Sh/2\pi$ (not $M_L^*h/2\pi$ and $M_S^*h/2\pi$,—cf. above). The total energy is given by F_0 of Eqs. (22) and (24), plus the magnetic energy oM_L of L^* in the field, the magnetic energy $2oM_S$ of S^* in the field, and the mutual energy AM_LM_S of S^* and L^* (the explanation of this mutual energy term will be clear from the discussion, preceding Eq. (26), of the analogous term in that equation; the "energies" mentioned are of course really all E/hc values):

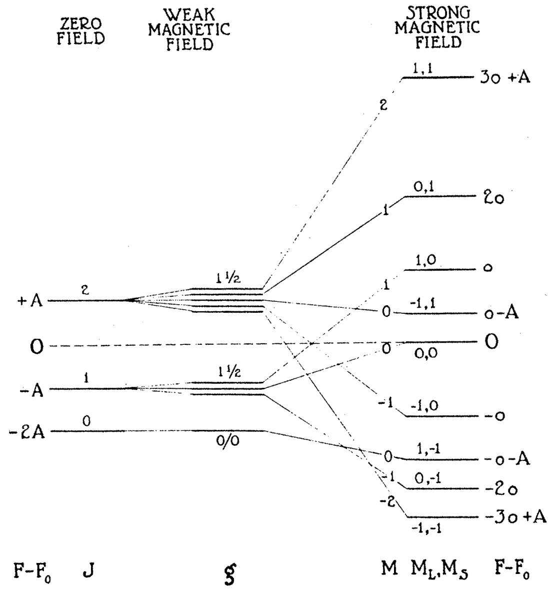

Fig. 9. Energy levels and quantum numbers for a ^3P atom in weak and strong magnetic fields. Energies are expressed by term values F measured from F_0; $F-F_0$ is expressed in terms of A, o, g, M, M_L, and M_S of Eqs. (24) and (25).

$$F-F_0=oM_L+2oM_S+AM_LM_S. \tag{25}$$

It will be noted that the frequencies of L^* and S^* around the field are correctly given as co and $2co$ respectively, by the application of Eq. (23) to Eq. (25).

[29a] On account of the different rates of precession of L^* and S^* in this case, their resultant J^* varies rapidly in direction and magnitude, and J is no longer a quantum number.

In the passage from a "weak" to a "strong" field[30] (Paschen-Back effect), the number of magnetic levels remains unchanged; for each M value in a weak field, there is a corresponding M value (here $M=M_L+M_S$) in a strong field. Fig. 9 shows the transition from weak to strong field [30] for a normal ^3P state ($A>0$ in Eqs. (22), (25)). For weak fields the spacings of the levels are governed by Eqs. (22) and (24), for strong fields by Eq. (25); the proper connections between weak and strong fields are qualitatively established by means of the two rules[29] (*a*) M remains constant during the transition; (*b*) in case there are several levels with the same M, the connections are drawn in such a way that no two levels with the same M cross in the passage from a weak to a strong field.

Selection rules for atoms. In transitions between different states of an atom, changes in some of the quantum numbers are limited by selection rules. In the absence of an external field these are: $\Delta l=\pm 1$ for one electron, $\Delta l=0$ or ± 2 for a second electron (but usually the quantum numbers change for only one electron at a time); $\Delta L=0, \pm 1$; $\Delta J=0, \pm 1$.

In a weak magnetic field, the same selection rules hold, and in addition there is $\Delta M=0, \pm 1$. In the passage to a strong field, the selection rule for J loses its strictness in proportion as J loses its significance. In a strong field, the selection rules for l and L remain strictly applicable, and in addition $\Delta M_L=0, \pm 1$, $\Delta M_S=0$ hold.

Atoms in electric fields. The effects of an axially symmetrical electric field[31] are similar to those of a uniform magnetic field, but differ considerably in some respects. Such a field,—whether or not it is uniform,—tends to make $\boldsymbol{L}^*$ precess[32] around it with a frequency whose magnitude for a given

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[30] The terms "weak" and "strong" field are ordinarily used in a purely relative sense A field is strong or weak according as it is or is not able to break down the coupling of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ which gives $\boldsymbol{J}^*$. Of course the ideal weak or strong field is only *approximated* in practice. The energy levels under the respective headings "weak" and "strong" fields in Figs. 9 and 10 are drawn as if for *ideal* weak and strong fields, although because of space limitations the A values and field strengths assumed in the figures would actually correspond to very poor approximations to these limiting cases.

[30a] In the strong electric field case with $M_L=0$, or with $A=0$ in Eq. (27), there is no magnetic field to orient the spin $\boldsymbol{S}^*$. The latter therefore acts completely independently of the rest of the molecule so that, if external influences are absent, the orientation of its axis (which maintains a fixed direction in space) is purely random. Thus there is no sense in defining M_S, and it is at any rate not a quantum number. (One *can* define M_S if one wishes, although in a real molecule this quantity varies very rapidly in direction and magnitude because of the fact that the molecular electric axis rotates, while the spin axis stands still). It should, however, be pointed out that in passing from the *ideal case* of a strong electric field, with $M_L=0$, to the corresponding energy level in a weak electric field, the spin becomes coupled to the electric axis provided $L>0$ (cf. text, p. 95 and ref. 35).

[31] Cf. Reference 25, Hund's Spektrallinien, p. 76–8 and references there given; also R. S. Mulliken, Phys. Rev. **33**, 746 (1929).

[32] Commonly in molecules the action of the field is even stronger, so that it breaks down the coupling of the $\boldsymbol{l}^*$'s to give $\boldsymbol{L}^*$. In this case, each $\boldsymbol{l}^*$ precesses separately around the field axis. This does not, however, alter the essential qualitative features which exist when $\boldsymbol{L}^*$ precesses around the electric axis. The theory of the latter case is therefore adequate, even if not entirely appropriate, for the present treatment of molecular electron states. In Part

field depends very much on the character of the electron orbits associated with $\boldsymbol{L}^*$. An electric field exerts no direct influence whatever on $\boldsymbol{S}^*$, since $\boldsymbol{S}^*$ corresponds to a so-to-speak disembodied magnetic moment. If the coupling between $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ is strong, however, ("weak" electric field), their resultant $\boldsymbol{J}^*$ orients itself, as in a weak magnetic field, with $\cos\theta = M/J^*$, where M takes any one of the values $J, J-1, \cdots, -J$. M measures the component of angular momentum parallel to the electric axis.

If the action of the external electric field on $\boldsymbol{L}^*$ is strong compared with the interaction of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$, $\boldsymbol{L}^*$ precesses independently of $\boldsymbol{S}^*$ around the field axis,[32] giving $M_L = L, L-1, \cdots, -L$. Although $\boldsymbol{S}^*$ is not acted on by the electric field, it *is* acted on by the magnetic field of $\boldsymbol{L}^*$, even though it is no longer coupled with $\boldsymbol{L}^*$ to give a constant resultant $\boldsymbol{J}^*$. The magnetic field of $\boldsymbol{L}^*$ may be resolved into a fixed component directed along the electric axis, and a precessing component perpendicular to the axis but having an average value zero because of its precession. $\boldsymbol{S}^*$ precesses around the direction of the average magnetic field of $\boldsymbol{L}^*$; but since the latter is parallel to the electric axis, $\boldsymbol{S}^*$ itself precesses, like $\boldsymbol{L}^*$ but for a different reason, about that axis; it gives thus a quantum number M_S whose values range from S to $-S$. The total angular momentum parallel to the electric axis is $\boldsymbol{M}h/2\pi$, where the quantum number M is given by $M = M_L + M_S$.

The energy of $\boldsymbol{S}^*$ in the field of $\boldsymbol{L}^*$ is equal, as in Eq. (22), and with the same value of A, to $AL^*S^*\cos(\boldsymbol{L}^*, \boldsymbol{S}^*)$, except that here one must take the *average* cosine, $\overline{\cos(\boldsymbol{L}^*, \boldsymbol{S}^*)}$; this is equal[33] to $M_L M_S/L^*S^*$. That is,[31]

$$F - F_0 = F(M_L) + AL^*S^*\,\overline{\cos(\boldsymbol{L}^*,\boldsymbol{S}^*)} = F(M_L) + AM_L M_S. \tag{26}$$

In the special case $M_L = 0$, the energy of interaction of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ is zero; here $\boldsymbol{S}^*$ has nothing to orient it and is entirely free, so that M_S has no quantum significance.[30a]

In Eq. (26), $F(M_L)$ corresponds to the energy of L^* in the electric field, expressed as a function of M_L. $F(M_L)$ has the important property that $F(M_L) = F(-M_L)$, i.e. the energy of orientation of $\boldsymbol{L}^*$ in an axially symmetrical electric field depends only on the *magnitude* of $\mathrm{M_L}$. Why this is true can best be understood by thinking of the simple case of an atom with one valence electron, all other electrons being in closed shells. Here $\boldsymbol{L}^*$ is merely $\boldsymbol{l}^*$ of the valence electron, and M_L becomes m_l. Neglecting the spin, whose energy is taken care of by AM_LM_S of Eq. (26), the forces acting on the electron in its orbital motion are purely electrostatic. Hence the energy asso-

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III we shall consider the various coupling cases more thoroughly, including the case of fields so strong as to break down even the quantization of the individual l's, as in the Stark effect of the H atom (*linear* Stark effect). (Cases in which $\boldsymbol{J}^*$, $\boldsymbol{L}^*$, or the $\boldsymbol{l}^*$'s precess all fall under the heading of *quadratic* Stark effects.)

[33] That $L^*S^*\overline{\cos(L^*, S^*)} = M_L M_S$ is most easily seen by writing $L^*S^*\overline{\cos(L^*, S^*)} = \overline{\boldsymbol{L}^* \cdot \boldsymbol{S}^*}$, that is, as the mean value of the scalar product of the vectors $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$. Resolving each of these vectors into components perpendicular and parallel to the electric axis, and noting that each perpendicular component averages zero, the stated result is readily obtained.

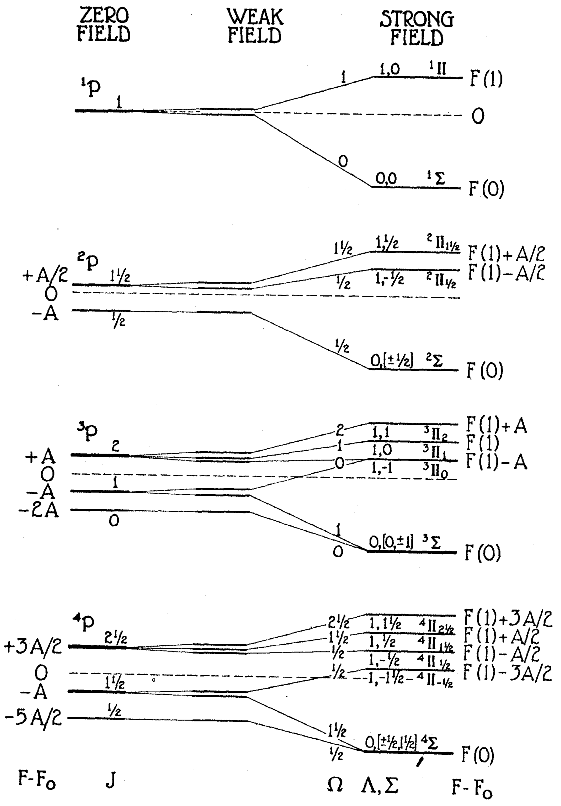

Fig. 10. Energy levels and quantum numbers for ^1P, ^2P, ^3P, and ^4P atoms in weak and strong electric fields.[30] Energies are expressed by giving $F-F_0$ values in accordance with Eq. (27). For zero field, we have $L=1$, with various S and J values. For weak fields, there is also Ω. In strong fields, there is Λ, which in the present examples has the two values 0 and 1 with corresponding $F(\Lambda)$ values,—cf. Eq. (27),—$F(0)$ and $F(1)$. In strong fields, if $\Lambda>0$, there is also a Σ; if $\Lambda=0$, Σ does not exist, but certain virtual values of Σ can be assigned (these are given in brackets in the figure); there is also $\Omega=|\Lambda+\Sigma|$. The quantities $F(0)$ and $F(1)$ have been calculated according to the equation $F(\Lambda)=a[3\Lambda^2-L(L+1)]$. The functions $F(\Omega)$ for weak fields have been calculated according to $F(\Omega)=b_J[3\Omega^2-J(J+1)]$, with a different value of b_J for each J. These equations (cf. W. Pauli, reference 34, p. 252) have no quantitative significance, but are of a form qualitatively suited to represent the effect produced on the terms of an atom by dividing its nucleus into two parts and separating these somewhat (cf. calculations of Morse and Stueckelberg, Phys. Rev. **33**, 932, 1929, in regard to the effect on the He^+ terms of splitting the He nucleus). In the equations given, a and b_J increase with the applied field, or with the degree of separation of the nucleus. Because $F(\Omega)$, like $F(\Lambda)$, depends really on the energy of L^* in the field, b_J, if a is positive, should have a positive value when L^* and J^* make an angle near 0 or π but a negative value when the angle between L^* and J^* is near $\pi/2$. In Fig. 10, a negative value of b_J has accordingly been assumed for $^3P_1$ and $^4P_{1\frac{1}{2}}$ but a positive value in other cases.

ciated with the valence electron, in an orbit of given n and l, depends only on the inclination of the plane of the orbit with reference to the electric axis, and not on the direction of rotation of the electron in its orbit. Now $\pm m_l$ correspond to the same inclination of the orbital plane although they differ in respect to the direction of rotation. Hence the energy is the same for $\pm m_l$. (In a magnetic field, where the magnetic energy depends on the vector velocity, the relations are entirely different: the change from $+m_l$ to $-m_l$ reverses the sign of the energy.) It is easy to see that the same results hold for M_L in the case where $\boldsymbol{L}^*$ is the resultant of several $\mathbf{l}^*$'s.

Further, we have $F(M) = F(-M)$, for both strong and weak fields. For strong fields, this is clear from Eq. (26), since $F - F_0$ is unchanged in the latter if we simultaneously change the signs of M_L and M_S, as is necessary to reverse the sign of M. For weak fields also, where $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ are coupled to give $\boldsymbol{J}^*$, a little consideration shows that the energy of orientation of $\boldsymbol{J}^*$ in the field, depending entirely on the $\boldsymbol{L}^*$ part of $\boldsymbol{J}^*$, is the same for $+M$ as for $-M$.

Fig. 10 shows qualitatively the energy levels for ^1P, ^2P, ^3P, and ^4P atomic states in axially symmetrical electric fields of various intensities.[30] The correlation between the levels in strong and weak fields is effected by means of the M rules stated above in connection with Fig. 9, applied with due regard for the fact that each level with $|M| > 0$ is a level of double statistical weight, corresponding to $\pm M$. It is also important to note that for the strong field cases with $M_L = 0$, M_S and M have no quantum significance,[30a] but that each level with $M_L = 0$ has a statistical weight $2S+1$, equal to the number of M_S values which would exist if there were a magnetic field parallel to the electric axis (the possible M_S values for this hypothetical case are indicated in brackets in Fig. 10). The diagrams are drawn, making use of Eqs. (22) and (27), for the case of so-called normal multiplets ($A > 0$ in Eqs. (22) and (27).[34] The various energy intervals shown in Fig. 10 are, in sign and in relative magnitude, in qualitative agreement with what would be expected if the applied field were obtained by dividing the nucleus of an atom into two parts and separating these somewhat.

Quantum numbers for electron states of molecules (*with fixed nuclei*). Because of the fact that the energy in an axially symmetrical electric field depends on $|M_L|$ and $|M|$ rather than on M_L and M, and because of the importance of $|M_L|$ and $|M|$ in molecules, it is desirable to replace M_L, M_S, and M for the case of an atom in an electric field by new symbols. For a strong electric field we shall use Λ in place of $|M_L|$. At the same time we shall use Σ to represent $\pm M_S$, in such a way that when M_S and M_L have the same sign, Σ is positive, and that when they have opposite signs, Σ is negative. Also, we shall use $\Omega = |\Lambda + \Sigma| = |M|$. (If $\Lambda = 0$, Σ and Ω do

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[34] Cf. O. Stern, Zeits. f. Physik **23,** 476 (1922), and W. Pauli, Handbuch der Physik, Vol. 23, p. 251–2. The corresponding diagrams for inverted multiplets,—$A < 0$, resulting in reversal of the energy order of the components of each multiplet,—are easily constructed. For inverted multiplets, the energy $F(0)$ in the strong field case would also usually lie above the energy $F(1)$, the relations of Fig. 10 being reversed.

not exist as quantum numbers.)[30a] According to these definitions $\Lambda \geqq 0$ always, while Ω takes on values $\Lambda+S$, $\Lambda+S-1, \cdots |\Lambda-S|$. Usually $\Lambda+\Sigma \geqq 0$, but if $S>\Lambda$, $\Lambda+\Sigma$ has one or more negative values so that for a given value of Λ, Ω may take on the same value twice (cf. the case $\Lambda=1$, $S=1\frac{1}{2}$ in Table III and Fig. 10). In a weak electric field, Λ and Σ do not exist as quantum numbers, but $\Omega=|M|$ remains.

The way in which Λ, Σ, and Ω are related to M_L, M_S, and M is shown in Table III for the case $L=1$, $S=1\frac{1}{2}$($^4\Pi$ state, cf. next paragraph and Fig. 10).

TABLE III.

M_L	M_S	M	Λ	Σ	$\Lambda+\Sigma$	Ω	State
$+1$ -1	$+1\frac{1}{2}$ $-1\frac{1}{2}$	$\left.\begin{matrix}+2\frac{1}{2}\\-2\frac{1}{2}\end{matrix}\right\}$	1	$1\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$^4\Pi_{2\frac{1}{2}}$
$+1$ -1	$+\frac{1}{2}$ $-\frac{1}{2}$	$\left.\begin{matrix}+1\frac{1}{2}\\-1\frac{1}{2}\end{matrix}\right\}$	1	$\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$^4\Pi_{1\frac{1}{2}}$
$+1$ -1	$-\frac{1}{2}$ $+\frac{1}{2}$	$\left.\begin{matrix}+\frac{1}{2}\\-\frac{1}{2}\end{matrix}\right\}$	1	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$^4\Pi_{\frac{1}{2}}$
$+1$ -1	$-1\frac{1}{2}$ $+1\frac{1}{2}$	$\left.\begin{matrix}-\frac{1}{2}\\+\frac{1}{2}\end{matrix}\right\}$	1	$-1\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$^4\Pi_{-\frac{1}{2}}$

Molecular multiplets[28a] (*fixed nuclei*). Fig. 10 shows several interesting features which are of importance for the theory of molecular electronic states, since the latter (for fixed nuclei) are of the same nature as the states of atoms in a strong axially symmetrical electric field. First we may note how the strong field atomic levels group themselves in what we may reasonably classify as multiplets,[28a] and which we may correctly take as prototypes of the multiplets which are actually observed in molecular spectra. Each such multiplet has a definite Λ, which has a rôle very similar to that of L in an atomic multiplet; various different orientations of the spin S, each characterized by a definite Σ and giving a definite Ω, comprise the different sublevels of the multiplet; Ω plays a rôle similar to that of J in atomic multiplets. It is therefore natural to designate these multiplets in a manner similar to atomic multiplets, by symbols such as $^1\Pi$, $^2\Sigma$, $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$, etc. In these the superscript gives the multiplicity $m(m=2S+1)$ exactly as for an atomic state, the main letter gives the value of Λ (with Σ, Π, Δ, Φ, $\Gamma, \cdots$ standing respectively for $\Lambda=0, 1, 2, 3, 4, \cdots$), and the subscript gives the value of $\Lambda+\Sigma$ (cf. Fig. 10 for examples). The value of $\Lambda+\Sigma$ rather than that of Ω is chosen for the subscript because it permits one to distinguish readily between physically different levels which have the same value of Ω, such as $^4\Pi_{\frac{1}{2}}$ and $^4\Pi_{-\frac{1}{2}}$ of Fig. 10 and Table III. When $\Lambda+\Sigma \geqq 0$, as usually, Ω is identical with $\Lambda+\Sigma$. For Σ levels we do not use a subscript, since Σ does not exist as a quantum number. For singlet levels subscripts are unnecessary, since Σ has only the one value 0.

Only the following types of electron levels have as yet been identified in practise; these have been found in the analysis of band spectra: $^1\Sigma$, $^2\Sigma$, $^3\Sigma$, $^1\Pi$, $^2\Pi$, $^3\Pi$, $^1\Delta$, $^2\Delta$, $^3\Delta$.

As should be clear from the discussion preceding Eq. (26), the behavior of the spin S in multiplets of the molecular type is very different than in atomic multiplets. As a consequence, the components of each such multiplet (F_0 and Λ fixed) are *equally spaced* (cf. Eq. (26) and definitions of Λ and Σ) according to the law

$$F-F_0=F(\Lambda)+A\Lambda\,\Sigma. \tag{27}$$

This relation is different from the Landé interval rule which holds for ordinary atomic multiplets (cf. Eq. (22)). Nevertheless the order of magnitude of the spacings of the component levels, determined by A of Eq. (22) or (27), is of the same order of magnitude in both cases. Examples of atomic and molecular multiplets may be compared in Fig. 10.

A consideration of the transition from strong to weak fields in Fig. 10 shows some points of interest. Although we may expect molecules to correspond pretty closely to the strong field case of Fig. 10, nevertheless this cannot be strictly true, and we may expect in practice to find some indications of a departure toward the weak field case. For the weak field case, each level with $\Omega>0$ has double statistical weight, because Ω represents $\pm M$; levels with $\Omega=0$, however, have unit statistical weight. For the strong field case, all levels with $\Lambda>0$ have double statistical weight (even if $\Omega=0$), because Λ represents $\pm M_L$. This double weight does not result [in the fixed center problem] in any doubling of the levels, except that in cases with $\Omega=0$, $\Lambda>0$, as $^3\Pi_0$, the level of double weight *does* split in the transition toward the weak field case (cf. Fig. 10).[30] In certain $^3\Pi_0$ levels of N_2 (second positive nitrogen bands) and C_2 (Swan bands), a very small splitting of this kind is actually found, indicating just a slight departure from the strong field case. In the corresponding $^3\Pi_1$ and $^3\Pi_2$ levels there is [for zero rotation], as expected, no splitting.

A somewhat similar state of affairs exists in certain Σ levels. In $^2\Sigma$ levels, no splitting occurs in the passage toward weak fields, but there is another interesting effect: Fig. 10 shows that although Ω is non-existent for the strict[30] strong-field case, an Ω should come into existence as soon as there is a departure toward weak fields.[35] In $^3\Sigma$ levels, passage toward weak fields gives a splitting into a level of double weight with $\Omega=1$ and a level of unit weight with $\Omega=0$; something similar happens with $^4\Sigma$ levels.[35] The $^3\Sigma$ levels of O_2 give evidence of a small splitting of the kind just described.

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[35] It should be pointed out that the splittings just discussed for Σ levels depend on their being derived from atomic levels with $L>0$, like the P levels of Fig. 10. (Σ levels are derivable from every kind of atomic level, since for any L value one obtains Λ values equal to $L, L-1, \cdots, 0$.) For Σ levels derived from S levels, no splitting would occur [for zero rotation], since each S level would give just one Σ level, both the S and the Σ level being single, although of weight $2S+1$ (S=spin); also, Ω would be non-existent in such cases even for weak fields.

Selection rules and electron quantum numbers of molecules. The selection rules for an atom in a weak electric field are the same as those for an atom in a weak magnetic field. In a *strong* electric field the restriction on ΔJ is of course lost in proportion as J loses its significance as a quantum number. Just as in the case of strong magnetic fields, the rules $\Delta M_L = 0, \pm 1, \Delta M_S = 0$ should apply. ($\Delta M = 0, \pm 1$ also holds, but involves no restrictions beyond those already given by the rules for ΔM_L and ΔM_S.) In terms of Λ and Σ, these selection rules become $\Delta\Lambda = 0, \pm 1$ and $\Delta\Sigma = 0$ (also, $\Delta\Omega = 0, \pm 1$); but if $\Lambda = 0$ for one or both of two states between which a transition occurs, only $\Delta\Lambda = 0, \pm 1$ applies.[36] For the spin S we have the rule that intersystem transitions ($\Delta S > 0$) occur only with low intensity; for molecules with nuclei of small charge (H_2, He, He_2), $\Delta S = 0$ is almost a strict selection rule, but when a nucleus of high atomic number is present (e.g., Hg), transitions with $\Delta S = \pm 1$ are fairly intense. There are also other restrictions, especially in the case of symmetrical molecules (e.g., H_2) which will be considered later.

There is an important change in respect to l and L in strong electric fields: the selection rules $\Delta l = \pm 1$ and $\Delta L = 0, \pm 1$ lose their strictness, corresponding to the fact that a strong electric field has a tendency to break down the quantization of L and even of the l's.[32] In molecules J (in the sense in which it is used for atoms, as a resultant of L and S) and L are seldom of importance. Λ and S in molecules take the places which L and S have in atoms as the quantum numbers most characteristic of any multiplet electron level.

IIb. Theory of Molecular Energy Levels; Effects of Molecular Rotation

In Part I, we treated the total energy term F of a molecule as the sum of three parts, F^{el}, F^v, and F^r (cf. Eq. (5)), and determined how the spectrum depends upon the form of F'^v, F''^v, F'^r, and F''^r. The discussion was based on the assumption of a rotational energy of the simple form $F^r = B_v K(K+1) + \cdots$. Actually, this is not quite correct even in the simplest case $\Lambda = 0$, $S = 0$($^1\Sigma$ states); and in general, F^r has a variety of more complicated forms which we have now to consider. F^v, however, is fortunately of the same form $F^v = (v + 1/2)\omega_e + \cdots$ for all types of electronic states, so that practically nothing new needs to be said about it in the following.

In Part II*a*, we have been considering the problem of the states of an atom in a strong axially symmetrical electric field. This problem is qualitatively the same as the problem of two fixed centers (cf. p. 85 above). In the transition to the real molecule we have, so far as nuclear vibration is concerned, only to add the proper expression for F^v to the F^{el} expression of the two-center problem. To take into consideration the rotation of the molecule, however, we have in general to take account of the fact that the latter often disturbs the characteristic angular momentum vectors and quan-

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[36] The selection rules $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0$ are formally more inclusive than $\Delta M_L = 0, \pm 1$, $\Delta M_S = 0$, since $\Lambda = \pm M_L$, and they apparently allow large changes in M_L (and in M_S and in M). There is, however, no real inconsistency, since levels $\pm M_L$ are indistinguishable.

tum numbers of the fixed-center problem. There is in general an interaction between the various electronic angular momenta and the nuclear angular momentum, so that we must consider F^{el} and F^{r}, and the associated quantum numbers, simultaneously. For sufficiently slow rotations, however, (*Hund's case a*), the quantum numbers Λ, Σ, and Ω of the fixed center problem are valid.

Before going into the problem of the interaction of rotation and electronic motions, a few remarks should be of interest in regard to the relative magnitude of the spacings of the component levels in a molecular multiplet as compared with the spacings of the associated vibrational and rotational levels. For most known band spectra, the spacings of the multiplet levels are much smaller than those of the vibrational levels, and often are comparable with those of the rotational levels. A typical example is that of the $^2\Pi$ normal state of NO. Here $A=124$, $\Lambda=1$, $\Sigma=\pm 1/2$ (cf. Eq. (27)), giving a doublet ($^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$) of width $\Delta\nu=A\Lambda=124$. The vibrational levels have a much larger spacing ($\omega_e=1906$). Hence if one plots the energy levels, neglecting the rotation of the molecule, they appear as a series of vibrational levels each of which is double, and in band spectra involving this $^2\Pi$ state one finds double-headed bands. The most widely-spaced molecular multiplet yet known is a $^2\Pi$ state of HgH($\Delta\nu\sim 3700$). Here the spacing of the two components $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ much exceeds the spacing of the vibrational levels ($\omega_e\sim 1980$), so that in the energy level diagram there appear to be two separate sets of vibrational levels, one for $^2\Pi_{\frac{1}{2}}$, one for $^2\Pi_{1\frac{1}{2}}$. Likewise in the spectrum, the bands associated with the $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{1\frac{1}{2}}$ levels appear like independent systems.

Singlet electron states: (*Hund's case b'*).[36a] The simplest types of F^{r} functions and of band structure are those for *singlet* electronic states ($S=0$). Here $\Sigma=0$ and $\Lambda=\Omega$ always. So long as the effect of the nuclear rotation is not too great, Λ is a good quantum number and we have Hund's "case *b'*." Case *b'* is defined in general (cf. p. 108 below) as a case in which the energy of interaction of $\boldsymbol{S}^*$ with the rest of the molecule is practically zero, but in which the energy of orientation of $\boldsymbol{L}^*$ with reference to the electric axis is large enough so that Λ is a good quantum number. When $S=0$, the first condition for case *b'* is automatically fulfilled.

The simplest relations exist in the case of $^1\Sigma$ states ($\Lambda=0$, $S=0$); these have been fully discussed in Part I. In such states the motion of the nuclei is practically one of pure rotation (but see below) with an angular momentum which we shall designate by $\boldsymbol{K}^*h/2\pi$. For $\Lambda>0$, however, the motion is obviously gyroscopic, since we have both angular momentum of nuclear rotation (which we shall call $\boldsymbol{O}h/2\pi$)and electronic orbital angular momentum $\Lambda h/2\pi$. The two last-mentioned angular momentum vectors are perpendicular to each other and precess around their resultant $\boldsymbol{K}^*h/2\pi$, whose direction is fixed in space, since it represents the resultant angular momen-

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[36a] Hund distinguished four important coupling cases which he called *a, b, c, d*; the names *b'* and *d'* given here are applied to certain variants of Hund's *b* and *d*; case *e* is a new case not discussed by Hund.

tum of the entire molecule. The precession frequency is the frequency of the nuclear rotation, since Λ is parallel to the line joining the nuclei and is therefore carried around with them in their rotation (cf. Fig. 11).

Now the resultant angular momentum P of any molecule is always subject to a quantum condition of the form $\int_0^{2\pi} P d\phi = 2\pi P, = k^* h$, where k is a quantum number which has either integral or half-integral values according as S is integral or half-integral. In the case now under discussion, we identify k^* with our K^*, and since $S=0=$integral, we conclude that K is a quantum number which has integral values. As we have already seen for the case of fixed nuclei, Λ is a quantum number whose possible values are the integers 0, 1, 2, · · · ·.

For any definite electronic state, Λ is a constant, while O, which is not a quantum number, takes on various values, given by $(K^{*2}-\Lambda^2)^{1/2}$, such that K can have the values $\Lambda, \Lambda+1, \Lambda+2, \cdots$. For $\Lambda=0$, $O=K^*$. Fig. 11 shows the motion of the nuclei, and the arrangement of the angular momentum vectors, for the case $\Lambda=2$, $K=3$. From the figure it is obvious that the minimum possible value of K is Λ; it may be remarked that, because of the fact that $K^*=[K(K+1)]^{1/2}$, $O>0$ even when $K=\Lambda$ (unless $\Lambda=0$).

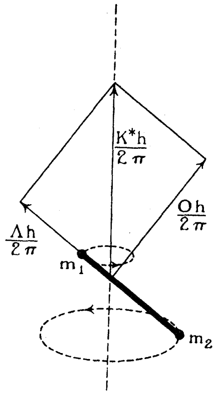

Fig. 11. Vector diagram and nuclear orbits (Hund's case b') for the case $\Lambda=2$, $K=3$, $S=0$ with two unequal nuclear masses ($m_1>m_2$). The figure shows the vector diagram at a moment when the nuclei are in the plane of the paper. During the motion, $\boldsymbol{K}^*$ remains in the plane of the paper, while **Λ** always remains parallel and $\boldsymbol{O}$ perpendicular to the electric axis, i.e. to the line $m_1 \longleftrightarrow m_2$.

The motion of the nuclei is really somewhat more complicated than has been represented in the preceding paragraphs. This is because of the fact that there is a component of electronic angular momentum, which we shall call $\boldsymbol{G}$, perpendicular to the electric axis.[37] $\boldsymbol{G}$ may be thought of as consisting primarily of the rapidly precessing component $\boldsymbol{L}_{\text{perp}}$ of $\boldsymbol{L}^*$ perpendicular to the electric axis, given by the vector equation $\boldsymbol{L}_{\text{perp}}=\boldsymbol{L}^*-\boldsymbol{\Lambda}$ (bold-face type will be

[37] J. H. Van Vleck, Phys. Rev. **31,** 600 (1928); J. H. Van Vleck and A. Frank, Proc. Nat. Acad. Sci. **15,** 539 (1929). Cf. also Hill and Van Vleck (reference 39, especially footnote 24), and Van Vleck (reference 43).

used throughout to indicate vectors) and by the scalar equation $L^2_{perp} = L^{*2} - \Lambda^2$. But strictly, $\boldsymbol{L}^*$ and so $\boldsymbol{L}_{\text{perp}}$ cannot in general be regarded as having even approximately a constant magnitude. In general, $\boldsymbol{G}$ then represents a quantity which varies rapidly in magnitude as well as in direction, corresponding to high frequency interchanges of angular momentum between the electron system and the nuclei, [32],[37] but whose average magnitude is equal to that of $\boldsymbol{L}_{\text{perp}}$. The vector which we have called $\boldsymbol{O}$ includes $\boldsymbol{G}$ as a component, although when K is large, as is commonly true, G is small compared with O. $\boldsymbol{O}$ lies always in the plane determined by $\boldsymbol{K}^*$ and $\boldsymbol{\Lambda}$. $\boldsymbol{O}$ has to satisfy the vector equation $\boldsymbol{O} = \boldsymbol{N} + \boldsymbol{G}$, where we use $Nh/2\pi$ to designate the (instantaneous) angular momentum of the nuclei alone. $\boldsymbol{N}$ is a quantity whose magnitude varies very rapidly, but always in the neighborhood of its mean value, and whose direction also varies equally rapidly, generally within a moderate range, and in such a way as to keep $\boldsymbol{O}$ always in the proper plane and constant in magnitude. N is not a quantum number.

In Part I it was shown (cf. Eq. (12)) that the kinetic energy of rotation, plus potential energy of centrifugal expansion, of a non-vibrating molecule, is given by

$$E^r = P_\phi^2/2\mu r_e^2 - P_\phi^4/2\mu^2 a^* r_e^4 + \cdots$$

P_ϕ is the angular momentum of the nuclei alone. If in this equation we make the substitution $P_\phi = Nh/2\pi$, and also introduce B_e and D_e in accordance with Eqs. (3) and (4) of Part I, we get

$$F^r \equiv E^r/hc = B_e N^2 + D_e N^4 + \cdots$$

This is an accurate expression for the instantaneous energy of rotation even if, as in the case now under consideration, the nuclear angular momentum $Nh/2\pi$ is not a constant. For a vibrating molecule, this becomes (cf. Eqs. (3a), (4a), (5), (6))[38]

$$F^r = B_v N^2 + D_v N^4 + \cdots . \tag{28}$$

We wish now to re-express F^r in terms of quantum numbers. To do this, we first make use of the vector equation $\boldsymbol{N} = \boldsymbol{O} - \boldsymbol{G}$. Taking the scalar product of each side of this equation with itself, we get $N^2 = O^2 + G^2 - 2\,\boldsymbol{O}\cdot\boldsymbol{G}$, where $\boldsymbol{O}\cdot\boldsymbol{G}$ is the scalar product of $\boldsymbol{O}$ and $\boldsymbol{G}$. Since N varies rapidly during each rotation, we need in the F^r equation the mean values $\overline{N^2}$ of N^2 and $\overline{N^4}$ of N^4. We have $\overline{N^2} = O^2 + \overline{G^2} + \phi(K)$ where $\phi(K) \equiv -2\overline{\boldsymbol{O}\cdot\boldsymbol{G}} = -2O\rho$, if ρ is the mean value of the projection of $\boldsymbol{G}$ on $\boldsymbol{O}$.[38a] (It should be noted that O is here constant.) For a given $|\boldsymbol{G}|$, the projection of $\boldsymbol{G}$ on $\boldsymbol{O}$ is obviously equally likely to be positive or negative, except in so far as the motion of $\boldsymbol{G}$ is disturbed by the rotation of the molecule; hence we expect $\rho = 0$ for a rotationless molecule. When the molecule rotates, however, the

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[38] Strictly speaking, there is a continual interchange of energy between vibration and rotation. The expression $E^r/hc = B_v N^2 - D_v N^4 + \cdots$ corresponds to the rotational energy *averaged over a complete vibration* (cf. Birge, Molecular Spectra in Gases, p. 112).

[38a] As used here, ρ has of course an entirely different meaning than in Part I.

symmetry of the motion of the vector **G** is disturbed so that we may expect a ρ, positive or negative, to develop. If the rotation is not too fast, we may reasonably assume $\rho \sim \delta O/2$, where δ is a small constant; then $\phi(K) \sim -\delta O^2$. For the present, however, we shall use the expression $\phi(K)$ without specifying its form.—For $\overline{N^4}$ one readily obtains an expression $\overline{N^4} = O^4 +$ terms of negligible importance.

Now substituting $O^2 = K^{*2} - \Lambda^2$ (cf. Fig. 11), and $K^{*2} = K(K+1)$, we get $\overline{N^2} = K(K+1) - \Lambda^2 + \overline{G^2} + \phi(K)$, and $\overline{N^4} = K^2(K+1)^2 + \cdots$. Substituting in the F^r expression, and adding F^{el} and F^v, we get [38]

$$F = F^{el} + F^v + B_v[K(K+1) - \Lambda^2 + \overline{G^2}] + \phi_i(K) + D_v[K^2(K+1)^2 + \cdots] + \cdots \quad (29)$$

F^v has the same meaning as previously (cf. Part I, Eq. (5)). The small terms given by $B_v(\overline{G^2} - \Lambda^2)$ are of no practical importance, since for any electronic state and v value, they enter as additive constants, which are not separable, in the analysis of band spectra, from the large terms $F^{el} + F^v$.

The "uncoupling term" $\phi(K)$ in Eq. (29) has been written $\phi_i(K)$, because if $\Lambda > 0$ it is double valued $[\phi_a(K)$ and $\phi_b(K)]$, as discussed in the next paragraph. This term often takes the form (cf. second preceding paragraph) $\phi_i(K) = -\delta O^2 = -\delta[K(K+1) - \Lambda^2]$, so that the coefficient of $K(K+1)$ in Eq. (29) becomes $B_v - \delta = B_v^x$ instead of B_v; usually $\delta \ll B_v$, but sometimes δ is large enough so that it needs to be considered if one wishes to determine B_v, B_e, and r_e accurately. Sometimes $\phi_i(K)$ takes the form $\phi_i(K) \sim \epsilon K$, corresponding to a constant ρ (cf. second preceding paragraph), or $\phi_i(K) \sim \epsilon K - \delta K(K+1) + \cdots$; when such a term is added to $B_v K(K+1)$, the sum may be expressed in the form $B_v^x K^x(K^x+1)$, where B_v^x and K^x differ slightly from B_v and K. Thus one gets apparent K values (K^x) differing slightly from integers. Slight deviations of this sort, and probably from this cause, are very commonly found in the analysis of band spectra.[12]

From the discussion on the states of an atom in a strong electric field (cf. pp. 91–3) it may be recalled that each state with $\Lambda > 0$ has a double statistical weight, because Λ really represents two states $\pm M_L$ which happen to have the same energy. In molecules, however, the rotation disturbs this exact coincidence of energies, so that a small splitting occurs,[39] each rotational level becoming a (usually narrow) doublet, whose components may be classified as sub-levels a and b. (In practise, the decision as to which doublet component shall be called a and which b is essentially arbitrary (cf. Part III), i. e. there is no one to one correspondence between the respective letters a and b and any theoretically specifiable properties of the two sub-levels.) The energies involved are given by the two values $\phi_a(K)$ and $\phi_b(K)$ of the small function $\phi_i(K)$. For $\Lambda = 0$, $\phi(K)$ has only a single value. When $\Lambda = 1$, each $\phi_i(K)$, provided the influence of the rotation is not too large, is given by $\phi_i(K) = -\delta_i K(K+1)$; hence the sub-levels a and b differ in respect to the apparent value of $B_v^x (B_{v,a}^x = B_v - \delta_a;\ B_{v,b}^x = B_v - \delta_b)$. This case is illustrated

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[39] Cf. R. S. Mulliken, Phys. Rev. **28,** 1202 (1926); E. Hulthén, Zeits. f. Physik **46,** 349 (1927); R. de L. Kronig, Zeits. f. Physik **46,** 814 (1927); **50,** 347 (1928); E. L. Hill and J. H. Van Vleck, Phys. Rev. **32,** 267–272 (1928); J. H Van Vleck, Phys. Rev. **33,** 484–489 (1929).

in the $^1\Pi$ levels in Fig. 13. For $\Lambda > 1$ the splitting $\phi_a(K) - \phi_b(K)$ is very small.[39] No quantum numbers can be assigned to the sub-levels *a* and *b*, but it is important to emphasize that they do *not* correspond to $+M_L$ and $-M_L$; *each* is really a mixture of $+M_L$ and $-M_L$ in a way which can only be understood and explained in terms of the new quantum mechanics.[39] This kind of doubling of rotational levels we shall designate as Λ-type doubling (formerly called σ-type doubling), because it occurs (for any value of S) in all rotational states where $\Lambda > 0$.

Singlet electron states: Hund's case d′. For the limiting case of fixed nuclei the "uncoupling term" $\phi(K)$ in Eq. (29) vanishes, and with it the Λ-type doubling,—except when $\Lambda = -\Sigma \neq 0$,—cf. $^3\Pi_0$ in Fig. 10. In singlet states of ordinary molecules, the relations which hold for fixed nuclei are only slightly modified by the nuclear rotation, giving small terms $\phi_i(K)$ and a narrow Λ-type doubling (case *b′*). The nature of the term $\phi(K)$, and the reason why it is double-valued when $\Lambda > 0$, can be better understood by a comparison of case *b′* with a condition (case *d′*)[36a] which is close to the opposite limiting case in which the effect of the nuclear rotation is all-important.

For simplicity let us consider the case of a molecule composed of a core with $\Lambda = 0$ and a single outer electron, and let us consider as an example the case in which this outer electron has $l = 1$ and also has some definite value of the principal quantum number n. Then for the molecule in case *b′* we have a $^1\Sigma$ and a $^1\Pi$ state ($\Lambda = 0$ and 1). If the effect of the electric axis is large, l^* precesses very rapidly, the $^1\Sigma$ and $^1\Pi$ states are far apart in energy, each with its own set of (vibrational and) rotational energy levels. Now suppose we consider a series of orbits of increasing principal quantum number n, but all having $l = 1$. As the orbit gets larger, the influence of the electric axis on its energy rapidly gets less; this decreasing relative importance of the electric axis is of the same nature as if, with a *fixed* orbit size, the nuclei were gradually brought together. The rate of precession of l^* and the energy interval beween $^1\Sigma$ and $^1\Pi$ diminish rapidly as the size of the orbit increases. Finally, the rate at which l^* tends to precess around the electric axis becomes small compared with the rate at which the latter is carried around in space by the rotation of the nuclei. The precession of l^* around the electric axis breaks down, and Λ ceases to have any significance as a quantum number.

From the point of view of the electron in its large orbit, the two nuclei are now close together and (with the inner electrons) form a whirling mass whose only distinguishable axis is the axis of rotation of the nuclei (perpendicular to the electric axis). The nuclei rotate (and vibrate) almost as if the outer electron had been removed completely, their rotation being characterized in first approximation by a rotational quantum number R whose possible values are 0, 1, 2, · · · , and by a rotational energy (cf. below, following Eq. (30))

$$F^r = B_v[R(R+1) + \overline{G^2}] + D_v[R^2(R+1)^2 + \cdots] + \cdots$$

[39a] The designations *a* and *b* as used for sub-levels have no connection with the same designations in Hund's cases *a* and *b*.

At the same time the outer electron moves in its orbit in almost the same way as if the nuclei were united. The total energy does, however, usually depend somewhat on the orientation of the plane of rotation of the electron with reference to that of the nuclei; in other words, it depends slightly on the angle between $\boldsymbol{R}^*$ and $\boldsymbol{l}^*$. Hence $\boldsymbol{R}^*$ and $\boldsymbol{l}^*$ give a quantized resultant $\boldsymbol{K}^*$, which, since it represents the resultant angular momentum of the molecule, is fixed in space. K has the values $R+l, R+l-1, \cdots |R-l|$. $\boldsymbol{R}^*$ and $\boldsymbol{l}^*$, exerting a torque on each other, slowly precess about $\boldsymbol{K}^*$. The relations just described are depicted in Fig. 12. Examples of this situation, (*case d′ of Hund*[24]) are found in the higher-quantum singlet [and triplet] electron states of H_2 and He_2.[40] The total energy for Hund's case *d′* is

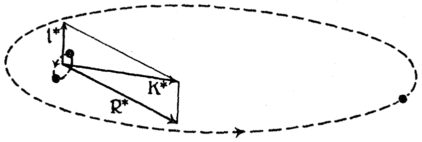

Fig. 12. Vector and orbit diagram for Hund's case *d′*, with $S=0$. The large and the small ellipse respectively represent the orbit of the outer electron and of the nuclei. The vectors $\boldsymbol{l}^*$ and $\boldsymbol{R}^*$, which are intended to be respectively perpendicular to the planes of the large and small ellipses, represent the electronic and nuclear angular momenta. $\boldsymbol{R}^*$ and $\boldsymbol{l}^*$, and with them the corresponding orbit planes, are supposed to be precessing slowly around their resultant $\boldsymbol{K}^*$, which has a fixed direction and magnitude. The figure is drawn for the case of two equal nuclei ($m_1=m_2$), and is directly applicable to the high-quantum singlet states of H_2 and He_2.

$$F=F^{el}+F^{v}+B_v[R(R+1)+\overline{G^2}]+f(R,K-R)+D_v[R^2(R+1)^2+\cdots]+\cdots \quad (30)$$

Here the "coupling term" $f(R, K-R)$ is a small term depending on R and on the relative orientation of $\boldsymbol{l}^*$ and $\boldsymbol{R}^*$. The term $B_v\overline{G^2}$ is needed to take account of the varying perpendicular component of orbital angular momentum of the inner electrons. In general, the inner electrons might also have a Λ, giving $B_v\,[R(R+1)-\Lambda^2+\overline{G^2}]$ in Eq. (30).

The fine structure, corresponding to $f(R, K-R)$ in Eq. (30), in the rotational levels in Hund's case *d′*, is all that remains of the division into states with differents Λ values which exists in Hund's case *b′*. In the limiting case where the coupling of $\boldsymbol{l}^*$ to the electric axis is negligible, even this would disappear and there would be, for each value of l, a single set of rotational levels determined by R alone. Figs. 13 and 14 show, for $l=1$ and $l=2$ respectively, how the energy levels for case *b′* and case *d′* are related.[41] The method of correlation is based on two rules analogous to those used in connection with Figs. 9 and 10. These are, (1) K, representing total angular

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[40] W. Weizel, He_2 bands: Zeits. f. Physik **52,** 175 (1928); **54,** 329 (1929); H_2 bands, Zeits. f. Physik **55,** 483 (1929). He_2 bands, review by W. E. Curtis, in the discussion on Molecular Spectra and Molecular Structure in the Faraday Society Transactions (Sept., 1929).

[41] For a discussion of the energy levels in Hund's case *d* and their relation to Λ-type doubling through the transition to case *b*, cf. Hill and Van Vleck, reference 39, pp. 267–272.

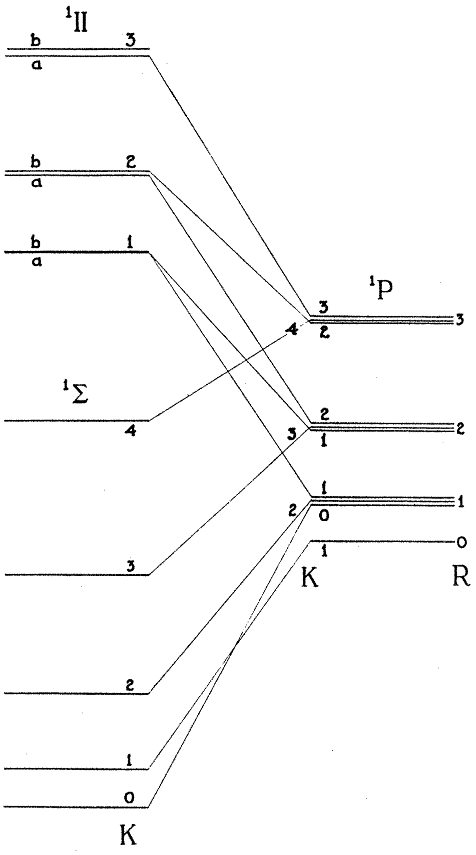

Fig. 13. Relation between case *b′* and case *d′* energy levels for $L=l=1$, $S=0$. In case *b′* we have $\Lambda=0$ ($^1\Sigma$ levels) and $\Lambda=1$ ($^1\Pi$ levels), with $K=\Lambda, \Lambda+1, \cdots$, and with Λ-type doubling in the $^1\Pi$ state; the doublet widths have been assumed proportional to $K(K+1)$, in agreement with both theory and experiment.[43] The $^1\Sigma$ and $^1\Pi$ sets of levels should be imagined as much more widely separated than in the figure. In case *d′* we have $R=0, 1, \cdots$, $K=R$, $R\pm1$; the positions of the three levels $K=R$, $R\pm1$ have been calculated[41] in accordance with certain equations of Hill and Van Vleck (Phys. Rev. **32**, 269, 1928, Eqs. (42) with $k=1$) which are based on the reasonable assumption that the energy of interaction of $\boldsymbol{R}^*$ and l^* is given by $(A\bar{l}^2_{par}$ $+\text{const.})$, where $\bar{l}^2_{par}$ is the average value of the square of the projection of l^* on the electric axis; the levels have been calculated for the case $A=B_v/2$, i.e. $A=B/2$ was substituted in Hill and Van Vleck's formula before making the calculation. The case *b′* levels (here $\bar{l}^2_{par}=\Lambda^2$) correspond to $A\gg B_v$. If A were negative, as it might be, the order of the $^1\Sigma$ and $^1\Pi$ levels would be reversed in case *b′*, and the correlations with case *d′* would be different. In Fig. 13, except for the level $K=0$, the correlations may be expressed as follows: the $^1\Sigma$ levels of case *b′* go over into levels with $K=R+1$ in case *d′*, the $^1\Pi_a$ levels into levels with $K=R$, and the $^1\Pi_b$ levels into levels with $K=R-1$. (It should be remarked that the designations *a* and *b* in Fig. 13 are, as always in the last analysis, arbitrary.)

momentum, remains constant for any level; (2) the members of any group of levels having the same K value never cross one another.—For $l=0$, cases b' and d' would be identical; for $l>2$, correlations similar to those of Figs. 13 and 14 would hold.

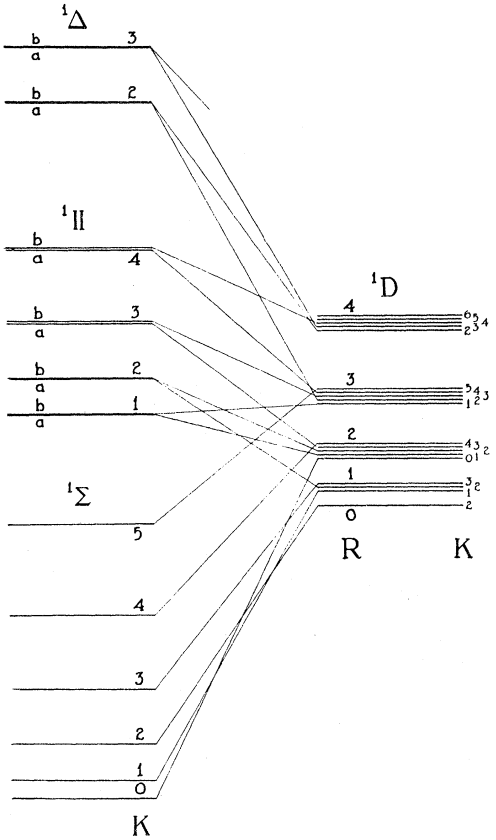

Fig. 14. Relation between case b' and case d' energy levels for $l=2$, $S=0$. This is similar to Fig. 13, except that the uniform spacings of the levels shown here, for fixed R and variable K in case d', have no significance; Hill and Van Vleck give no theoretical formula for the case $l=2$. In agreement with theory and experiment,[43] the Λ-type doublet widths are shown much narrower for the Δ than for the Π levels. If the order of the energy levels $^1\Sigma$, $^1\Pi$, and $^1\Delta$ were inverted in case b', as is possible, the correlations with case d' would be different. In Fig. 14, except for the levels with $K=0$ and 1, the correlation is as follows: $^1\Sigma$ goes into $K=R+2$, $^1\Pi_a$ into $K=R+1$, $^1\Pi_b$ into $K=R$, $^1\Delta_a$ into $K=R-1$, and $^1\Delta_b$ into $K=R-2$. (As in Fig. 13, the designations a and b are essentially arbitrary.) Just such a correlation as this appears actually to exist in the states of the He_2 molecule[40] having $l=2$ for the series electron.

Figs. 13 and 14 show how it is that in Λ-type doubling the a and b sublevels, which would exactly coincide ($\phi_i(K)=0$) for the limiting case of fixed nuclei, must needs separate more and more widely as the disturbance of Λ by the molecular rotation increases,[41] in order to enter into new groupings in case d'.

Multiplet electron states: Hund's case a. In multiplet electronic states ($S>0$) the presence of a spin gives rise to two important coupling cases, Hund's cases a and b;[24] these both degenerate for singlet states into what we have called case b'. In *Hund's case a*[24] the spin S is quantized with reference to the electric axis, because of the magnetic field along this axis produced by Λ. This quantization gives Σ, as discussed in the previous section on the atom in a strong electric field. Case a is possible only if $\Lambda>0$, for reasons previously discussed (cf. ref. 30a). Next we have $\Omega=|\Lambda+\Sigma|$; Ω and $\mathbf{O}$ then form a resultant J^* exactly as Λ and $\mathbf{O}$ formed a resultant $\mathbf{K}^*$ in the case of singlet states (cf. Fig. 11 and accompanying discussion).[41a] J is a quantum number, since it corresponds to the resultant angular momentum of the molecule. It has values Ω, $\Omega+1$, $\Omega+2$, $\cdots$, which are integral or half-integral according as S(and therefore Σ and Ω) are integral or half-integral. (The molecular J is not the same as J for an *atom* except in the fact that each represents a total angular momentum). In complete analogy to Eq. (29), except for the addition of the energy of interaction of Λ and Σ (cf. Eq. (27)) and the occurrence of a term in S_{perp}^2 ($S_{perp}=S^{*2}-\Sigma^2$),[42] the energy is given by

$$F=F_0^{el}+F^v+A\Lambda\Sigma+B_v[J(J+1)-\Omega^2+\overline{G^2}+S_{perp}^2]+\phi_i(\Sigma,J)+D_vJ^2(J+1)^2+\cdots \quad (31)$$

$F_0^{el}+A\Lambda\Sigma$ may be considered to represent electronic energy, different values of Σ, for fixed F_0^{el} and Λ, giving different components of a molecular multiplet. For each such value of Σ there is a set of vibrational and rotational levels. The rotational levels in each set are all double (Λ-type doubling), with two values of $\phi_i(\Sigma, J)$ for each value of Σ and $J[\phi_a(\Sigma, J)$ and $\phi_b(\Sigma, J)]$. The function F^v is found empirically to be practically independent of the value of Σ in a multiplet unless A is very large. Similarly, the coefficients B_v (and presumably also D_v) are almost independent of Σ. (When the conditions of case a are not well fulfilled there is, however, an apparent dependence of B_v on Σ,—(cf. (Eq. 46)). The small functions ϕ_i (Σ, J), unlike the B_v terms, differ greatly according to the value of Σ, the more so the larger A is.[43]

Multiplet states: case b. In Hund's case a, we think of $\mathbf{S}^*$ as precessing around the electric axis with a frequency $c\omega_S=c|\partial F/\partial\Sigma|=cA\Lambda$ (cf. Eq. (23)), making with that axis a constant angle θ such that $\cos\theta=\Sigma/S^*$. The conditions necessary for Hund's case a are well fulfilled so long as

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[41a] But in Hund's case a $\mathbf{O}$ includes $\mathbf{S}_{perp}$ as well as $\mathbf{G}$ as a component (cf. Ref. 42).

[42] Cf. Hill and Van Vleck, reference 39. If $\mathbf{N}h/2\pi$ is the nuclear angular momentum, we have the vector equation $\mathbf{N}=\mathbf{O}-\mathbf{G}-\mathbf{S}_{perp}$. Taking the scalar product of each side with itself, $N^2=O^2+G^2+S^2_{perp}-2\mathbf{O}\cdot\mathbf{G}-2\mathbf{O}\cdot\mathbf{S}_{perp}+2\mathbf{G}\cdot\mathbf{S}_{perp}$. Each of the last two terms has zero as its average value. Therefore for the average value $\overline{N^2}$, using also the relation $O^2=J^{*2}-\Omega^2$, we have $\overline{N^2}=J(J+1)-\Omega^2+\overline{G^2}+\overline{S^2}_{perp}-2\overline{\mathbf{O}\cdot\mathbf{G}}$. Now we write $\overline{S^2}_{perp}$ as S^2_{perp}, since the latter is constant. Proceeding as in the case of Eq. (28), and putting $-2B_v\overline{\mathbf{O}\cdot\mathbf{G}}=\phi_i(\Sigma, J)$, we get Eq. (31).

[43] Theory, J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); compilation of empirical data, R. S. Mulliken, Phys. Rev. **33**, 507 (1929).

$\omega_S \gg \omega_J$, where $c\omega_J$ is the frequency of rotation of the nuclei and therefore of the electric axis. [$c\omega_J$ is obtained by taking $c\,|\partial F/\partial J|$ in Eq. (31): $c\omega_J \sim cB_v(2J+1)$.] But if B_v or J is sufficiently large or A sufficiently small, so that $\omega_S \ll$ (the calculated) ω_J, then the precession of $\mathbf{S}^*$ breaks down, and Σ ceases to exist as a quantum number. [This is similar to the failure of Λ in Hund's case d',—cf. discussion preceding Eq. (30).] Λ, however, still remains quantized, and $\mathbf{\Lambda}$ and $\mathbf{O}$ now form a resultant $\mathbf{K}^*$, around which they precess, in exactly the same manner as for case b' with $S=0$ (cf. Fig. 10, Eq. (29), and accompanying discussion). For the spin, which is here unable to keep up with the (relatively) very rapid precession of $\mathbf{\Lambda}$, the only axis now distinguishable is that of $\mathbf{K}^*$. Parallel to this axis there is usually a small magnetic field (in regard to the cause of this, cf. p. 107 below), and $\mathbf{S}^*$ therefore precesses around $\mathbf{K}^*$. The resultant $\mathbf{J}^*$ of $\mathbf{K}^*$ and $\mathbf{S}^*$ is a vector fixed in space, since $\mathbf{J}^*h/2\pi$ is the resultant angular momentum of the molecule. J is a quantum number, whose possible values are given by $J=K+S,\ K+S-1,\ \cdots\ |K-S|$. K, S, and J here are respectively closely analogous to L, S, and J in an atom (cf. discussion preceding Eq. (22)). For each K value, the group of energy levels associated with it, corresponding to different J values, forms a sort of tiny multiplet. The state of affairs just described is typical of *Hund's case b*.

The energy equation for Hund's case b in multiplet states can be readily obtained by a slight generalization of the Eq. (29) which holds for case b' singlet states. It is only necessary to add to Eq. (29) a small term $f(K, J-K)$ to take account of the energy of interaction of $\mathbf{K}^*$ and $\mathbf{S}^*$, and to replace $\phi_i(K)$ of Eq. (29) by a similar function $\phi_i(K, J)$ which, for any specified K and J, is double-valued [$\phi_a(K, J)$ and $\phi_b(K, J)$] except for $\Lambda=0$, where it is single-valued. The values of $\phi_i(K, J)$, where i is either a or b, in general differ slightly (but only slightly,[43] in marked contrast to the large dependence of $\phi_i(\Sigma, J)$ in case a on the value of Σ) for the $(2S+1)$ different J values associated with a given K value. Thus we have

$$F=F_0^{el}+F^v+B_v[K(K+1)-\Lambda^2+\overline{G^2}] \\ +f(K,J-K)+\phi_i(K,J)+D_vK^2(K+1)^2+\cdots \tag{32}$$

Since for any value of K there are in general $2S+1$ components in the spin fine structure, there are in general altogether either $2S+1$ or $2(2S+1)$ fine structure components for each value of K, according as $\Lambda=0$ or $\Lambda>0$. (When $K<S$, however, there are fewer components.) The relative scales of the two types of fine structure which exist when $\Lambda>0$ differ from one molecule and electron state to another; sometimes the Λ-type doubling (given by $\phi_a-\phi_b$) is coarser than the spin fine structure, sometimes the reverse.

The small term $f(K, J-K)$ in Eq. (32) consists in general of several parts. (1) First we have the energy of interaction of $\mathbf{L}^*$ and $\mathbf{S}^*$ which is given, as in Eqs. (22) and (26), by $AL^*S^*\,\overline{\cos(\mathbf{L}^*, \mathbf{S}^*)}$. This can be written in the form $A\overline{\mathbf{L}^*\cdot\mathbf{S}^*}$, where $\mathbf{L}^*\cdot\mathbf{S}^*$ is the scalar product of the vectors $\mathbf{L}^*$ and $\mathbf{S}^*$. By taking components of $\mathbf{L}^*$ and $\mathbf{S}^*$ along $\mathbf{K}^*$, this expression reduces to $A\Lambda^2(J^{*2}-K^{*2}$

$-S^{*2})/2K^{*2}$.[44] This drops out if $\Lambda=0$. (2) Next we have a small term resulting from the interaction of $\boldsymbol{S}^*$ with the small magnetic field, parallel to $\boldsymbol{K}^*$, which is developed by the rotation of the molecule. This field is that resulting from the forced rotation of the whole electron system of the molecule around $\boldsymbol{K}^*$, modified (but probably usually only to a slight extent) by the field of the rotating nuclei themselves. Assuming that the field is parallel and proportional[44a] to $\boldsymbol{K}^*$, the energy of interaction of $\boldsymbol{S}^*$ with it is given by an expression of the form $\gamma(\boldsymbol{K}^*\cdot\boldsymbol{S}^*)$. This reduces to $((\gamma/2)\ (J^{*2}-K^{*2}-S^{*2})$. This expression should hold provided K is not too large.[45] (3) Finally, as Kramers has shown,[46] there is for $S>1/2$ an energy of interaction $w(K, J\text{-}K)$ of the individual spins which make up the resultant S. For Σ states at least, this energy is proportional to $3\overline{\cos^2\theta}-1$, where θ is the angle between $\boldsymbol{S}^*$ and the electric axis. For ${}^3\Sigma$ states, where there are two individual spins, Kramers finds

$$w(K,+1)=-\epsilon[1-3/(2K+3)]\,;w(K,0)=+2\epsilon\,;w(K,-1)=-\epsilon[1+3/(2K-1)];$$

the states with $J=K\pm1$ form a narrow doublet whose center is separated from the state $J=K$ by an approximately constant energy interval 3ϵ. (The energy $\gamma\boldsymbol{K}^*\cdot\boldsymbol{S}^*$ must also be added, but usually $\gamma<\epsilon$). This case is found experimentally in the ${}^3\Sigma$ normal state of O_2.[46] (It may be recalled that just such a splitting of ${}^3\Sigma$ levels into two components, independently of any rotation of the molecule, was predicted above by a consideration of the states of a ${}^3P$ atom in an electric field: cf. Fig. 10 and p. 95).

From the above, we have

$$f(K,J-K)=(\tfrac{1}{2})\{[A\Lambda^2/K(K+1)]+\gamma\}\{J(J+1)-K(K+1)-S(S+1)\}+w(K,J-K). \quad (33)$$

The last term vanishes (or at least becomes independent of $J-K$) unless $S>1/2$.

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[44] $\boldsymbol{L}^*$ is composed of $\Lambda+\boldsymbol{L}_{perp}$, but $\overline{\boldsymbol{L}_{perp}\cdot\boldsymbol{S}^*}=0$; Λ has a component Λ^2/K^* parallel to $\boldsymbol{K}^*$ (the component perpendicular to $\boldsymbol{K}^*$ gives $\overline{\Lambda_{perpk}\cdot\boldsymbol{S}^*}=0$). (The result is the same even if we recognize that $\boldsymbol{L}^*$ is not a constant, since in *any* case $\overline{\boldsymbol{G}\cdot\boldsymbol{S}^*}\sim0$, if $\boldsymbol{G}$ represents the component of electronic orbital angular momentum perpendicular to the electric axis; thus only the parallel component Λ needs to be considered.) $\boldsymbol{S}^*$ has a component $(J^{*2}-K^{*2}-S^{*2})/2K^*$ parallel to $\boldsymbol{K}^*$.

[44a] Assuming (*a*) that the field is proportional to the component ρ (cf. pp. 99–100) of electronic orbital angular momentum parallel to $\boldsymbol{O}$ developed by the rotation, and (*b*) that ρ is proportional to O for not too large K values (cf. p. 100), we should have, for not too large K values, a field parallel and proportional to O. This may be replaced without serious error by the assumption of a field parallel and proportional to $\boldsymbol{K}^*$ since, except for the smallest K values where the term $\gamma(\boldsymbol{K}^*\cdot\boldsymbol{S}^*)$ is of negligible importance anyway, $\boldsymbol{O}$ and $\boldsymbol{K}^*$ are practically the same. The results obtained from these assumptions are in harmony with the known experimenta data, at least for Σ states (where $\boldsymbol{O}\equiv\boldsymbol{K}^*$).

[45] Cf. E. C. Kemble, Molecular Spectra in Gases, pp. 345–7; R. S. Mulliken, Phys. Rev. **30**, 149 (1927); F. Hund, Zeits. f. Physik **42**, 96 (1927); E. Hulthén, Zeits. f. Physik **50**, 319 (1928); and especially J. H. Van Vleck, Phys. Rev. **33**, 498–500 (1929).

[46] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929). Interpretation of O_2 bands, R. S. Mulliken, Phys. Rev. **32**, 880 (1928).

In the important special case of case *b* *doublet* spectra ($S=1/2$), we have $J=K\pm 1/2$. Substitution in Eq. (33) with the $w(K, J-K)$ term omitted gives

$$f(K,-\tfrac{1}{2})=-A\Lambda^2/2K-\gamma(K+1)/2=-A\Lambda^2/(2J+1)-\gamma(2J+3)/4 \quad (34)$$

$$f(K,+\tfrac{1}{2})=A\Lambda^2/2(K+1)+\gamma K/2=A\Lambda^2/(2J+1)+\gamma(2J-1)/4. \quad (35)$$

The doublet separation, $f(K, +1/2)-f(K, -1/2)$, associated with any value of K is then

$$\Delta f(K)=[A\Lambda^2/K(K+1)+\gamma](K+\tfrac{1}{2}). \quad (36)$$

Multiplet states: *case b′*. It frequently happens that the spin fine structure given by $f(K,J-K)$ is extremely narrow or even quite undetectable. This often occurs in $^2\Sigma$ states, especially for small K values. It is also typical of the triplet states ($S=1$) of H_2 and He_2, where A and γ are very small because of the small charges of the nuclei. (As is well known from theory and from experimental data on atomic spectra, especially for H and He, A is always very small for the lightest elements; while, as Van Vleck has shown,[45] the magnitude of γ is proportional to that of A). When $f(K,J-K)\sim 0$, Eq. (32) becomes practically identical with the equation for singlet states (Eq. (29)) and there is no way of telling empirically whether S is zero or greater; K can then be determined, but not J. In such a case the precession of $\boldsymbol{S}^*$ about $\boldsymbol{K}^*$ is so slow (frequency $=c\{\partial/\partial J[f(K, J-K)]\}$) that $\boldsymbol{S}^*$ may be regarded as practically free, while J becomes practically meaningless as a quantum number. It seems desirable to distinguish this situation as *case b′*.[36a] Case *b′* is merely a form of case *b* in which the interaction of S^* with the rest of the molecule is negligibly small. This condition is automatically fulfilled when $S=0$, as already noted in the discussion of singlet states.

Multiplet states: *cases d and d′*. In spite of the absence of *spin* fine structure, the case *b′* states of H_2 and He_2 often show a rather coarse Λ-type doubling ($\phi_a(K)-\phi_b(K)$ large). This increases with increase in the principal quantum number of the orbit of the outer electron, until finally we pass for very large orbits to *Hund's case d′* as described above in connection with Eq. (30). This happens for both singlet and triplet states ($S=0$ and 1), but there is no practical difference between these cases, since the spin, when present, is essentially free. If there *were* a slight interaction of S with the rest of the molecule, we should expect $\boldsymbol{S}^*$ to orient itself with reference to the resultant $\boldsymbol{K}^*$ of $\boldsymbol{L}^*$ and $\boldsymbol{R}^*$ to give a final resultant $\boldsymbol{J}^*$. We call this last case *d*, and the case in which J does not exist as a quantum number, case *d′*. We return now to cases *a* and *b*.

Doublet states: *transition cases between a and b*. When $\Lambda=0$ (Σ states) or $S=0$ (singlet states), Hund's case *a* is impossible, and case *b* (or *b′*, *d*, or *d′*) is found; when $\Lambda>0$, either *a* or *b* is possible, but one also very frequently finds intermediate cases which do not closely approximate either *a* or *b*. Very often case *a* is approximated for the lowest J values, but case *b* for high J values. For $S=1/2$ (*doublet states*), Hill and Van Vleck[46] have obtained an equation which gives the main term of F^r, plus the interaction term of Λ and $\boldsymbol{S}^*$, exactly for the whole range of intermediate cases. This is

$$F = F_0^{el} + F^v + B_v\{(J+\tfrac{1}{2})^2 - \Lambda^2 \pm \tfrac{1}{2}[4(J+\tfrac{1}{2})^2 - 4A\Lambda^2/B_v + A^2\Lambda^2/B_v^2]^{1/2} + \overline{G^2}\} + \phi_i(J) + \cdots \quad (37)$$

(In Eq. (37), no account has been taken of the energy which corresponds to the small term proportional to γ in Eq. (33). Allowance must therefore be made for this omission when Eq. (37) is applied.) The + and − signs in Eq. (37) give the energy values corresponding to the two orientations of the spin which exist in cases *a* and *b* and in all intermediate cases as well. Neglecting Λ-type doubling, which exists for all levels if $\Lambda > 0$, there are thus just two energy levels for each value of J, except for the lowest value $J = \Lambda - 1/2$, where there is only a single level. We shall now consider the forms which Eq. (37) takes for various values of A/B_v and of J. First we shall consider the special J value $J = \Lambda - 1/2$; then we shall consider the expansion of Eq. (37) for large values of $|A|$, corresponding to case *a*, and after that we shall see what forms it takes for small values of A/B_v (case *b*).

For $J = \Lambda - 1/2$ there is only one energy level (when Λ-type doubling is neglected), as can be seen by consideration of the limiting cases *a* and *b*. For example, in case *a* with $\Lambda = 1$, the value $J = 1/2$ occurs only in the $^2\Pi_{\frac{1}{2}}$ series of levels ($\Sigma = -\frac{1}{2}$, $\Omega = \frac{1}{2}$), and not in the $^2\Pi_{1\frac{1}{2}}$ series ($\Sigma = +\frac{1}{2}$, $\Omega = 1\frac{1}{2}$), because of the restriction $J \geqq \Omega$; for all other J values, however, there is obviously one level in *each* of the two series. Corresponding results hold for *case b* with $\Lambda = 1$: first, we have $K \geqq \Lambda$; then we have $J = K \pm \frac{1}{2}$; $K = \Lambda = 1$ then yields $J = \frac{1}{2}$, $1\frac{1}{2}$, while $K = 2$ yields $J = 1\frac{1}{2}$, $2\frac{1}{2}$, and so on; thus $J = \frac{1}{2}$ occurs only once, but all other J values twice.—For $J = \Lambda - \frac{1}{2}$ the correct energy value is obtained from Eq. (37) by using the upper (+) sign when $-\infty < A/B_v < 2$, and the lower (−) sign when $2 < A/B_v < +\infty$. Eq. (37) then simplifies in both cases to the following form:

$$F(J = \Lambda - \tfrac{1}{2}) = F^{el} + F^v - A\Lambda/2 + B_v(\Lambda + \overline{G^2}) + \phi_i(\Lambda - \tfrac{1}{2}) + \cdots . \quad (38)$$

This expression is identical with that which is obtained for $J = \Lambda - \frac{1}{2}$ from the energy formulas for *either case a* (Eq. (31)) or case *b* (Eqs. (32) and (33), neglecting γ and w in Eq. (33)); this can readily be verified by making the proper substitutions for J, K, S, and Σ in Eqs. (31)–(33).

For large positive values of A (*normal* case *a*) expansion of Eq. (37) gives[47]

$$F = F_0^{el} + F^v \pm (\tfrac{1}{2})A\Lambda + B_v\{J(J+1) - (\Lambda \pm \tfrac{1}{2})^2 + (\tfrac{1}{2}) + \overline{G^2} \pm [(J+\tfrac{1}{2})^2 - \Lambda^2]B_v/A\Lambda + \cdots\} + \phi_i(J) + \cdots \quad (39)$$

For large negative values of A (*inverted* case *a*) expansion gives[47]

$$F = F_0^{el} + F^v \mp (\tfrac{1}{2})A\Lambda + B_v\{J(J+1) - (\Lambda \mp \tfrac{1}{2})^2 + (\tfrac{1}{2}) + \overline{G^2} \mp [(J+\tfrac{1}{2})^2 - \Lambda^2]B_v/A\Lambda + \cdots\} + \phi_i(J) + \cdots . \quad (40)$$

[47] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 261–2 (1928). Eq. (37) as given above differs from the equation given by Hill and Van Vleck in the substitution of B_v for B, and in the addition of the unimportant additive term $B_v\overline{G^2}$ which was dropped by them.

In Eqs. (39) and (40), the upper sign, in each case of a double sign, corresponds to the upper (+) sign in Eq. (37). Bearing in mind that Eqs. (39) and (40) apply only to doublet levels ($S=\frac{1}{2}$), comparison with the equation for case *a* (Eq. 31) shows that the quantities $\pm(\frac{1}{2})$ or $\mp(\frac{1}{2})$ in Eqs. (39) and (40),—*e.g.*, $\pm(\frac{1}{2})$ in $\pm(\frac{1}{2})A\Lambda$ and in $(\Lambda\pm\frac{1}{2})^2$ of Eq. (39),—are to be identified with Σ of Eq. (31), while $+(\frac{1}{2})B_v$ is identified as $B_vS^2_{perp}$ of Eq. (31).

It should be mentioned that equations for triplet states, analogous to Eqs. (39) and (40) for doublet states, are given by Hill and Van Vleck.[46]

The following expansion of Eq. (37) represents a good approximation for a range of values of A/B_v corresponding fairly well to case *b* and extending, roughly, from -2 to $+6$.

$$\begin{aligned}F=F_0{}^{el}+F^v+B_v[(J+\tfrac{1}{2})^2\pm(J+\tfrac{1}{2})-\Lambda^2+\overline{G^2}]\\ \mp[A\Lambda^2/2(J+\tfrac{1}{2})][1-A/4B_v+A\Lambda^2/4B_v(J+\tfrac{1}{2})^2-A^2\Lambda^2/8B_v{}^2(J+\tfrac{1}{2})^2+\cdots]\\ +\phi_i(J)+(\gamma/2)[J(J+1)-K(K+1)-S(S+1)]+\cdots.\end{aligned}\tag{41}$$

The last term in Eq. (41) does not come from the expansion, but has been added (cf. Eq. (33)) in accordance with a remark made above immediately after Eq. (37).

If we neglect the terms in A^2 and A^3, Eq. (41) reduces to the following form which agrees with the case *b* equations (Eqs. (32), (33)), provided, in the case of the upper and lower signs respectively in Eq. (41), we put $J=(K-\frac{1}{2})$ and $J=K+\frac{1}{2}$.

$$\begin{aligned}F=F_0{}^{el}+F^v+B_v[K(K+1)-\Lambda^2+\overline{G^2}]\\ +(A\Lambda^2/2)[\text{times}-1/K(\text{for }J=K-\tfrac{1}{2}),\text{ or times }+1/(K+1)\\ (\text{for }J=K+\tfrac{1}{2})]+\phi_i(K,J)+(\gamma/2)[J(J+1)-K(K+1)-S(S+1)]+\cdots.\end{aligned}\tag{42}$$

In order to see that this agrees with Eqs. (32, 33) it is necessary to complete the substitutions $J=K\mp\frac{1}{2}$ and to put $S=\frac{1}{2}$. This gives

$$\begin{aligned}(J=K-\tfrac{1}{2}):F=F_0{}^{el}+F^v+B_v[K(K+1)-\Lambda^2+\overline{G^2}]\\ -A\Lambda^2/2K-\gamma(K+1)/2+\phi_i(K,-\tfrac{1}{2})+\cdots\end{aligned}\tag{43}$$

$$\begin{aligned}(J=K+\tfrac{1}{2}):F=F_0{}^{el}+F^v+B_v[K(K+1)-\Lambda^2+\overline{G^2}]\\ +A\Lambda^2/2(K+1)+\gamma K/2+\phi_i(K,+\tfrac{1}{2})+\cdots\end{aligned}\tag{44}$$

Eqs. (43) and (44) now respectively agree with Eqs. (32, 34) and (32, 35).

For $A=0$, Eq. (37) takes the form which can be obtained by setting $A=0$ in Eqs. (41) or (42). Rather surprisingly, Eq. (37) takes the *same* form when $A/4B_v=+4$, as can be verified by direct substitution in Eq. (37). For this reason the relations of case *b* are closely approximated when $A/B_v\sim 4$ as well as when $A/B_v\sim 0$. The arrangement of the rotational energy levels is exactly the same for $A/B_v=+4$ as for $A/B_v=0$ except for the two lowest levels. When $A/B_v=0$ these form a close pair $[F_1(\Lambda+\frac{1}{2})$ and $F_2(\Lambda-\frac{1}{2})]$, but when $A/B_v = +4$ the two lowest levels $[F_1(\Lambda-\frac{1}{2})$ and $F_1(\Lambda+\frac{1}{2})]$ are entirely separate, and behave like case *a* levels (cf. Eq. (38) in regard to the state having $J=\Lambda-\frac{1}{2}$). The difference between the two cases can best be seen by reference to Fig. 15, where the BeH levels correspond to $A/4B_v \sim 0$, while the arrangement of the MgH levels ($A/4B_v = +5.7$) is not very far from that characteristic of $A/B_v = +4$.

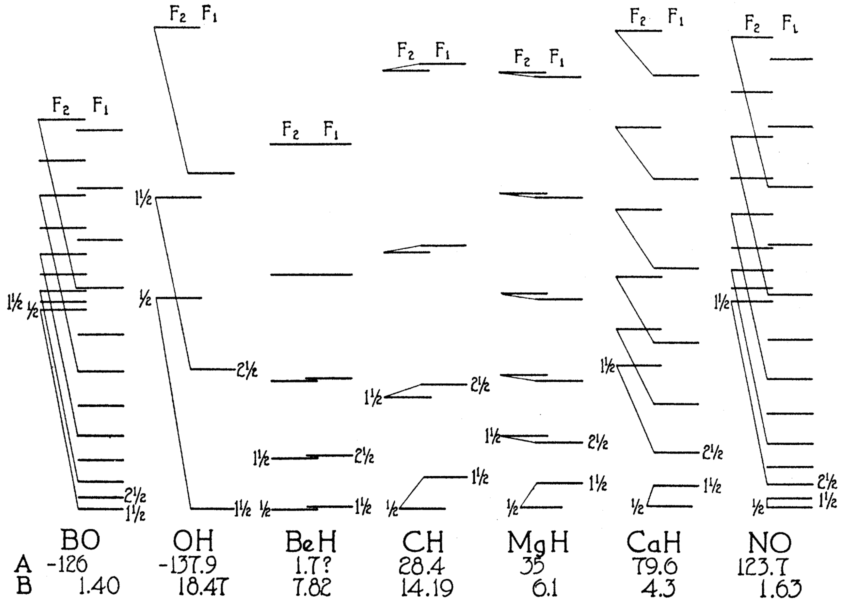

Fig. 15. Rotational energy levels, neglecting Λ-type doubling, for a series of $^2\Pi$ states with a variety of values of B_v and A/B_v (cf. R. S. Mulliken, Phys. Rev. **32**, 391 (1928)). The A values given have been recalculated (cf. R. S. Mulliken, Phys. Rev. **33**, 744 and 747 (1929)). The B values and rotational levels all correspond to $v=0$, except that in the case of NO they are for $v=4$. All the levels are on a uniform scale, with the lowest level placed at zero in each case. The numbers given opposite some of the levels are J values. Pairs of levels (F_1 and F_2) which would in case *b* correspond to the same value of K are indicated by slanting connecting lines. In such pairs, $F_2 > F_1$ when $A/B_v < 0$ or $> +4$, but $F_1 > F_2$ for A/B_v values between 0 and +4 (cf. CH in Fig. 15); corresponding F_1 and F_2 levels fall together when A/B_v is either ~ 0 or $\sim +4$ (cf. BeH for $A/B_v \sim 0$ and MgH for A/B_v near +4).—The level $F(\frac{1}{2})$ is classified as F_2 for $A/B_v < +2$, and as F_1 for $A/B_v > +2$. [Cf. text below, p. 112, for definition of F_1 and F_2 levels.]

Midway between the cases $A/B_v = 0$ and +4 is the characteristic case $A/B_v = +2$. Here Eq. (37) reduces to

$$F = F_0^{el} + F^v + B_v\{(J+\tfrac{1}{2})^2 - \Lambda^2 \pm [(J+\tfrac{1}{2})^2 - \Lambda^2]^{1/2} + \overline{G^2}\} + \phi_i(J) + \cdots. \tag{45}$$

This case is exemplified in the $^2\Pi$ normal state of CH (cf. Fig. 15). Eq. (45) is, accidentally, of practically the same form as, although of different significance than, the Kramers and Pauli equation which formerly was much used in representing the rotational energy functions of molecules.

Multiplet states: correlation of case a with case b energy levels. In case *a* doublet states we have two distinct sets of rotational levels, corresponding to different orientations of the spin; in the one set, $\Sigma=+\frac{1}{2}$ and $\Omega=\Lambda+\frac{1}{2}$, in the other $\Sigma=-\frac{1}{2}$ and $\Omega=\Lambda-\frac{1}{2}$. In case *b*, however, the two orientations of the spin, which give rise to $J=K\pm\frac{1}{2}$, correspond only to narrow doublets. The way in which the orientation of the spin would change in passing from normal case *a* ($A\gg 0$) through case *b* ($A\sim 0$) to inverted case *a*($A\ll 0$) can be followed by a comparison of Eq. (37) with Eqs. (39)–(40) and (41)–(44). For $A\gg 0$, the upper (+) sign of Eq. (37) gives Eq. (39), with $\Sigma=+\frac{1}{2}$, corresponding to $\Omega=\Lambda+\frac{1}{2}$; for $A\sim 0$, it gives Eqs. (41)–(42), and (43), with $J=K-\frac{1}{2}$, and for $A\ll 0$, it gives Eq. (40), with $\Sigma=-\frac{1}{2}$, corresponding to $\Omega=\Lambda-\frac{1}{2}$. Similarly, the lower (−) sign of Eq. (37) corresponds to $\Omega=\Lambda-\frac{1}{2}$ for $A\gg 0$ (Eq. 39), to $J=K+\frac{1}{2}$ (Eqs. 41, 42, 44) for $A\sim 0$, and to $\Omega=\Lambda+\frac{1}{2}$ for $A\ll 0$ (Eq. 40). Thus if, for any specified J value, the spin is roughly speaking parallel (antiparallel) to Λ in inverted case *a*, it becomes parallel (antiparallel) to K in an imagined gradual change to case *b*, but then becomes antiparallel (parallel) to Λ when one passes on to normal case *a*.[48] [In saying that the spin is roughly speaking parallel (or antiparallel) to Λ, we mean merely that $\Sigma=+S=+\frac{1}{2}$ (or $=-S=-\frac{1}{2}$); actually $\mathbf{S}^*$ precesses around Λ with an angle given by $\cos\theta=\Sigma/S^*=(\pm\frac{1}{2})/(\sqrt{3}/2)$. Likewise in saying that the spin is parallel, or antiparallel, to K we mean merely that $J=K+S$, or $J=K-S$.] The single rotational state $J=\Lambda-\frac{1}{2}$ behaves in an exceptional manner, however (cf. Eq. (38)): the spin is antiparallel to Λ in both normal and inverted case *a*, and to K in case *b*. All these relations are indicated in Fig. 16 (cf. also Fig. 15). Fig. 16 also shows the relations between the Λ-type doublets of cases *a* and *b*.

In triplet and other states the correlation of energy levels between normal case *a*, case *b*, and inverted case *a* is analogous to that which holds for doublet states. In triplet states, for example, ($S=1$, $\Sigma=0,\pm 1$), states with $\Omega=\Lambda\pm 1$ in inverted case *a* correspond to case *b* states with $J=K\pm 1$, and these in turn to states with $\Omega=\Lambda\mp 1$ in normal case *a*; while $\Omega=\Lambda$ in inverted case *a* corresponds to $J=K$ in case *b* and to $\Omega=\Lambda$ in normal case *a*.

Classification of rotational levels in multiplet states. The above correlations serve as a convenient basis of classification. The writer has earlier proposed to designate as F_1 levels those levels which correspond to $J=K+S$ in case *b*, as F_2 levels those corresponding to $J=K+S-1$, and so on.[48] Thus for doublets one has F_1 and F_2 levels ($J=K\pm\frac{1}{2}$), for triplets F_1, F_2, and F_3 levels ($J=K+1$, K, $K-1$, respectively), and so on. The classification suggested is useful not only for case *b* but also for intermediate cases between *a* and *b* and even for case *a*. Taking ${}^2\Pi$ states as an example, the ${}^2\Pi_{\frac{1}{2}}$ and ${}^2\Pi_{1\frac{1}{2}}$ states, respectively, of normal case *a*, and the ${}^2\Pi_{1\frac{1}{2}}$ and ${}^2\Pi_{\frac{1}{2}}$ states, respectively, of inverted case *a* would be classified, the former as F_1, the latter as F_2 states[49]

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[48] Cf. R. S. Mulliken, Phys. Rev. **30**, 793–6 and Fig. 1 (1927) for a further discussion.

[49] In doublet states, the level having the special J value $J=\Lambda-\frac{1}{2}$ (e.g. $J=\frac{1}{2}$ in ${}^2\Pi$ states) is classified as an F_2 level for $A<2B_v$ and as an F_1 level for $A>2B_v$, corresponding to the fact of its obvious association with the ${}^2\Pi_{1/2}$ levels in both normal and inverted case *a* (cf. Eq. (38) and Fig. 15).

(cf. Figs. 15, 16). Similarly, normal case *a* $^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$ states, and inverted case *a* $^3\Pi_2$, $^3\Pi_1$, $^3\Pi_0$ states, would be respectively classified as F_1, F_2, F_3. Fig. 15 shows the application of the above classification to a series of typical $^2\Pi$ molecular states.

In addition to the classification F_1, F_2, $\cdots$, which indicates the orientation of the spin, the two sub-levels *a* and *b* which occur (Λ-type doubling) for each such orientation and for each *J* value, may be designated by additional subscripts, thus, F_{1a}, F_{1b}, F_{2a}, F_{2b}, $\cdots$.

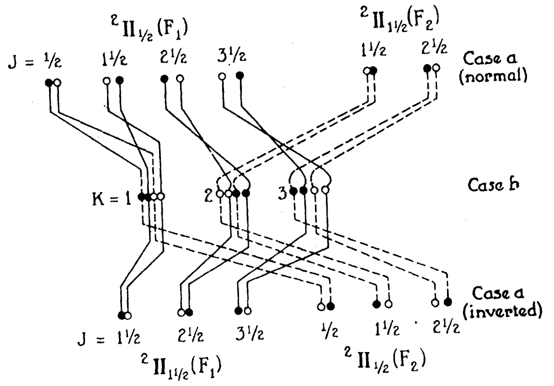

Fig. 16. Correlation of rotational energy levels between Hund's cases *a* and *b* (cf. Van Vleck, p. 496 of reference 43). F_1 levels are connected by means of full lines, F_2 levels by means of dotted lines. Λ-type doublets are shown by the use of full and empty circles (● and ○). In both normal and inverted case *a*, the Λ-type doublets are, according to theory and experiment (reference 43), much wider for $^2\Pi_{\frac{1}{2}}$ than for $^2\Pi_{1\frac{1}{2}}$ states; this is shown in a *qualitatively* correct way in the figure. The crossings of levels belonging to Λ-type doublets, between cases *a* and *b*, are as given by Van Vleck.[43] In case *b*, the Λ-type doublets are of the same width for F_1 and F_2 states; both these and the spin doublets are shown, with exaggerated spacings, in the figure; the spin doublets are drawn in qualitative agreement with the usual relation that the energy is higher for the F_1 than for the F_2 component; the relative spacings of the spin and Λ-type doublets as given for case *b* in the figure are, however, not significant. The various indicated crossings of corresponding F_1 and F_2 levels (same *K*, different *J*) are in agreement with theory and experiment (cf. Fig. 15). [Cf. text, p. 112, for definition of F_1 and F_2 levels.]

Doublet states: comparison of theoretical equations with experimental data for $^2\Pi$ *states.* For a comparison between Hill and Van Vleck's doublet formula (Eq. (37)) and experiment, extensive data are available only for $^2\Pi$ states. Fig. 15 shows the observed energy levels for a number of such states, corresponding to a wide range of *A* values. In most of the examples in this figure, *A* is large enough so that the approximations given by Eqs. (39) and (40) hold, at least for small *J* values. If we let C_Σ represent a suitable (very small) constant whose value depends on Σ, and if we set

$$B_{v,\Sigma}^* = B_v(1 \pm B_v/A\Lambda), \tag{46}$$

with $\pm B_v/A\Lambda$ according as $\Sigma = \pm\frac{1}{2}$, and if we substitute $\Omega = \Lambda + \Sigma$, we get from both Eqs. (39) and (40)

$$F=F_0{}^{el}+F^v+A\Lambda\Sigma+C_\Sigma+B_{v,\Sigma}{}^*[J(J+1)-\Omega^2+(\tfrac{1}{2})+\overline{G^2}]+\phi_i(\Sigma,J)+\cdots. \quad (47)$$

As B_v/A becomes smaller, the two values of $B_{v,\Sigma}{}^*$ both approach B_v, while C_Σ vanishes, and Eq. (47) goes over into Eq. (31). Eqs. (46) and (47) give a satisfactory explanation of the experimental fact[50] (cf. Fig. 15) that in $^2\Pi$ states, if $|A|/B_v$ is fairly large, the rotational levels obey a relation of the *form* of Eq. (31) but with a larger coefficient $B_v{}^*$ for the F_2 than for the F_1 levels. In agreement with the theory, the difference between the $B_v{}^*$ values for the F_2 and F_1 sets of levels is large for the smaller values of $|A|/B_v$ and conversely. Also in agreement with the theory is the fact that $B_v{}^*$ is always greater for the F_2 levels, whether $A<0$, even though these correspond to $^2\Pi_{\frac{1}{2}}$ levels if $A<0$ but to $^2\Pi_{1\frac{1}{2}}$ levels if $A<0$.

According to Hill and Van Vleck's equation (Eq. (37)) the region of A/B_v values from 0 to +4 should show some peculiarities. In this region $F_1(K)>F_2(K)$, whereas elsewhere $F_2(K)>F_1(K)$. The relation $F_1(K)>F_2(K)$ is actually found in the $^2\Pi$ state of CH (cf. Fig. 15 and refs. 48 and 50), for which $A/B_v=+2$ (cf. discussion following Eq. (45)).

Other coupling cases. Besides Hund's cases *a*, *b* and *d*, there are other conceivable modes of coupling of the electronic and nuclear angular momentum vectors. In *Hund's case c*[24] we have $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ coupled to give a resultant $\boldsymbol{J^a}^*$, which then gives a projection $\boldsymbol{\Omega}$ on the electric axis, exactly as in the case of an atom in a weak electric field (cf. Fig. 10). We use J^a instead of J here for the quantum number corresponding to the resultant of $\boldsymbol{L}^*$ and $\boldsymbol{S}$, reserving J as usual for the quantum number corresponding to the resultant angular momentum of the molecule. For the rotating molecule, $\boldsymbol{\Omega}$ and $\boldsymbol{O}$ form a resultant $\boldsymbol{J}^*$, just as in case *a* (cf. p. 105), and the energy is given by an expression of the form

$$F=\{F_0{}^{el}+(\tfrac{1}{2})A[J^a(J^a+1)-L(L+1)-S(S+1)]+F(\Omega)\}+F^v$$
$$+B_v[J(J+1)-\Omega^2+\overline{H^2}]+\phi_i(J)+D_vJ^2(J+1)^2+\cdots. \quad (48)$$

Here H represents the component of electronic angular momentum (including both orbital momentum and spin) perpendicular to the electric axis; $\overline{H^2}$ replaces $\overline{G^2}+S_{perp}{}^2$ of Eq. (31). Hund's case *c* is not yet known in practise. This is because the effect of the electric axis in the case of known molecular states is strong enough to break down the coupling of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ practically completely. We may, however, expect to find examples of Hund's case *c* among the less stable states of molecules containing heavy atoms (for heavy atoms, the coupling of $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ is relatively large).

For very rapid rotations, case *c* should pass continuously into another case, which we may call case *e*, in a manner analogous to the passage of case *b* into case *d*.[36a] In case *e* we assume that $\boldsymbol{L}^*$ and $\boldsymbol{S}^*$ give $\boldsymbol{J^a}^*$ as in case *c*, but that the rotation of the nuclei is so rapid, or the coupling of $\boldsymbol{J^a}$ to the electric axis so small, that Ω no longer exists. Instead we have the nuclei rotating with a quantum number R as in case *d*, then $\boldsymbol{J^a}^*$ and $\boldsymbol{R}^*$ forming a resultant $\boldsymbol{J}^*$ around which they precess. Case *e* has not yet been found in practise.

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[50] Cf. R. S. Mulliken, Phys. Rev. **32**, 389–392 (1928).

Summary of Hund's cases. The various types of coupling which have been discussed above are summarized in Table IV. Under "Projection and composition of vectors" are given first, under "Elements," the symbols corresponding to those quantum vectors or projections of quantum vectors which serve as elements in the building up of the total angular momentum for the case under consideration; when the projection of a vector on the electric axis is important, the vector and its projection are both given, as in the example $\boldsymbol{L}^*$, Λ. Under "Composition", equations are given, which are to be understood as vector equations, showing how the electronic and nuclear angular momentum vectors are compounded.

TABLE IV. *Summary of Hund's Coupling Cases*

Case	Coupling of L^* to electric axis	Coupling of S^* to L^*	Effect of rotation (on S^* or L^* or both)	Projection and composition of vectors		Limitations
				Elements	Composition	
a	large	moderate	small	$L^*, \Lambda; S^*, \Sigma,$ with $\Omega = \lvert \Lambda + \Sigma \rvert$	$\Omega + O(=L^* + S^* + N) = J^*$	$\Lambda > 0, S > 0$
b	large	small	moderate	$L^*, \Lambda; S^*$	$\Lambda + O(=L^* + N) = K^*;$ $K^* + S^* = J^*$	
d	moderate	small	large	$L^*; S^*; R^*$	$R^* + L^* = K^*, K^* + S^* = J^*$	
c	moderate	large	small	$L^* + S^* = J^{a*};$ J^{a*}, Ω	$\Omega + O(= J^{a*} + N) = J^*$	$L > 0, S > 0$
e	small	moderate	large	$L + S = J^{a*}; R^*$	$J^{a*} + R^* = J^*$	$L > 0, S > 0$
b′, d′	Same as *b*, *d*, but $S = 0$, or coupling of S^* to K^* negligibly small.					

As a result of a careful study, made since this review was written, the writer recommends the following changes of notation as compared with the present text; E_e, E_v, and E_r instead of E^{el}, E^v, and E^r; T, T^e, G, and F instead of F, F^{el}, F^v, and F^r; $\Delta G(v)$, defined as $G(v+\frac{1}{2}) - G(v-\frac{1}{2})$, instead of $\Delta F^v(v_1, v_2)$.

The substance of these articles, revised and with additional material, will be subsequently published in book form. The writer will be very grateful to anyone who will call his attention to errors and obscure passages in the present treatment.

The reader will find in Ruark and Urey's new book "Atoms, Molecules, and Quanta" (McGraw-Hill, 1930) an extremely valuable treatment of the subject of molecular spectra.