THE INTERPRETATION OF BAND SPECTRA, PARTS I, IIa, IIb. ADDITIONS AND CORRECTIONS*

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STRICTLY, Eqs. (3*a*), (4*a*), and (6) should read

$$B_v = B_e - \alpha_e(v+1/2) + \cdots = B_0 - \alpha v + \cdots, \text{ etc.} \qquad (3a)$$

$$D_v = D_e + \beta_e(v+1/2) + \cdots = D_0 + \beta v + \cdots, \text{ etc.} \qquad (4a)$$

$$\cdots \alpha_e = (6B_e^2/\omega_e)\ (2b^*+1) \cdots. \qquad (6)$$

Fig. 1. In Fig. 1 and elsewhere, $D_e = U(\infty) - U(r_e)$ should be distinguished from $D \equiv D_0 = U(\infty) - E(v=0)$.

P. 67. After Eq. (6), it should be noted (cf. Ref. 12*b*, also T. Hori, Zeits. f. Physik, **62,** 352, 1930) that examples where α_e and $x_e\omega_e$ are negative have now been found.

Pp. 92–95. In connection with the discussion on pp. 92–95, it should have been pointed out that the "strong field" and the "weak field" cases of Fig. 10 respectively correspond to Hund's cases *a* and *c* (in case *a*, the effect of the electric axis is strong, in case *c* it is weak, compared with the coupling between the *L* and *S* vectors).

Pp. 95, 107. On p. 95, the last sentence in the text ("The $^3\Sigma$ levels of $O_2 \cdots$") is incorrect and should be omitted. The same is true of the last sentence in the first paragraph of p. 107, beginning "(It may be recalled $\cdots$)."

P. 115. In the third from last paragraph, the recommended symbols should read "T^e or T_e" instead of "T^e," and "$\Delta G(v+1/2) = G(v+1) - G(v)$," instead of "$\Delta G(v) = G(v+1/2) - G(v-1/2)$."

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Pp. 99–100. The following changes will remove some errors, and improve the discussion in other respects:

P. 99, fifth line from bottom, replace "We have $\cdots = -2O\rho$," by" We then have $\overline{N^2} = O^2 + \overline{G^2} + \phi^r(K)/B_v$, where $\phi^r(K)/B_v = -2\overline{O \cdot G} = -2O\rho$.

P. 100, second to fifth line, delete one sentence beginning "If the rotation $\cdots$."

P. 100, replace second ("Now substituting $\cdots$") and third paragraph by the following *three* paragraphs:

The existence of a ρ implies that the motion of the L^* vector has been altered by the rotation. This change is the beginning of a transition from case *b'*, where L^* precesses around the electric axis, to case *d'*, where it precesses around the axis of rotation (cf. next section). Corresponding to the beginning "uncoupling" of L^* from the electric axis, we expect in general an alteration of F^{el}, so that we may set $F^{el} = F_0^{el} + \phi^{el}(K)$.

* For Parts I, IIa, IIb, see Reviews of Modern Physics **2**, 60–115 (1930).

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

$$F=F_0{}^{el}+F^v+B_v[K(K+1)-\Lambda^2+\overline{G^2}]+\phi_i(K)+D_vK^2(K+1)^2+\cdots \quad (29)$$

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 $F_0{}^{el}+F^v$.

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. If the uncoupling is small, this function takes the form $\phi(K)\sim\delta K(K+1)$, so that the coefficient of $K(K+1)$ in Eq. (29) becomes $B_v+\delta=B_v{}^x$ instead of B_v; usually $\delta<<B_v$, 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. If the uncoupling is larger, $\phi(K)$ takes the form $\phi(K)=\kappa+\epsilon K+\delta K(K+1)+\cdots$; when such a term is added to $B_vK(K+1)$, the sum may be expressed in the form $\kappa+B_v{}^xK^x(K^x+1)$, 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 often found in the analysis of band spectra.[12]

P. 100, last two lines, replace $-\delta_i$, $-\delta_a$, $-\delta_b$, by $+\delta_i$, $+\delta_a$, $+\delta_b$.

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On p. 110 it is stated that Eq. (41), which is obtained by expanding Eq. (37) as a power series in the parameter A/B_v, represents a good approximation to Eq. (37) for a range of A/B_v values corresponding well to case b and extending, roughly, from -2 to $+6$. Eq. (41), neglecting terms in A^2, A^3, $\cdots$, is then used in obtaining Eqs. (42) and (43)–(44), which are then shown to agree with Eqs. (34) and (35). Unfortunately this procedure is unjustified except for a much more limited range of A/B_v values (say from $A/B_v=-\frac{1}{2}$ to $+\frac{1}{2}$; even here the approximation is not too good). Although the *type of coupling* of the quantum vectors is essentially that corresponding to case b for the entire range of A/B_v values from -2 to $+6$, except for the lowest J values,—and for a larger A/B_v range for high J values—the departures of the *energy* values from those of the limiting case b or b' ($A=0$), and especially the doublet separations $F_1(K+\frac{1}{2})-F_2(K-\frac{1}{2})$, can be correctly represented only by using the Hill and Van Vleck formula Eq. (37).

In the same way, the item (1) at the bottom of p. 106 and the terms $A\Lambda^2/K(K+1)$ in Eqs. (33) and (36) and $A\Lambda^2/2K$ or $A\Lambda^2/2(K+1)$ in Eqs. (34) and (35), are adequate only for a very limited range of A/B_v values close to $A=0$. In other cases, these expressions should be replaced by others derived by subtracting Eq. (32), with $f(K, J-K)$ set equal to zero, from Eq. (37). Of course for Σ states ($\Lambda=0$) Eqs. (33)–(36) are correct if we merely drop the terms in $A\Lambda^2$.

The physical reason for the invalidity of Eqs. (33)–(36) and (41)–(44) for $\Lambda>0$ and A/B values not close to zero is as follows. Eqs. (33)–(36) make allowance for the departures from case *b* toward case *a* only by adding a *magnetic* energy term (energy of interaction of Λ and spin)—, item 1, foot of p. 106. But actually the effect of these departures on the *kinetic* energy (given in case *b* by $B_v K(K+1)+\cdots$) is usually a good deal more important. This kinetic energy correction is accurately included, together with the magnetic energy correction, in Eq. (37), but not in Eqs. (33)–(36) or (42)–(44), and these corrections are not even convergently represented by the expansion Eq. (41), except for very small A/B_v values.

Eq. (37) does not, however, include the small correction term in γ which appears in Eqs. (33)–(36) and (41)–(44). The inclusion of this term in the form given in Eq. (33) appears to be justified so long as the coupling is essentially that of case *b*. Eqs. (33) and (36) may then be rewritten

$$f(K,\ J-K)=\psi(A,\ \Lambda,\ K)+\tfrac{1}{2}\gamma\left[J(J+1)-K(K+1)-S(S+1)\right]$$
$$+w(K,\ J-K) \tag{33}$$

$$\Delta f(K)=\Delta\psi(K)+\gamma(K+\tfrac{1}{2}) \tag{36}$$

where ψ is a function of A, Λ, and K which vanishes for $\Lambda=0$ and which may be determined for $\Lambda>0$ and $S=\frac{1}{2}$ by means of Eq. (37).