terms in C, which contain the spin-orbit and the spin-other-orbit contributions, imply the interval rule.

The Paschen-Back effect of a distorted ^3P has been treated by Green and Loring,[11] and their simple method may be extended to other triplets. They introduce the empirical zero-field energy differences. In order to obtain an entirely theoretical expression for the Paschen-Back energies, one may substitute the theoretical values of the energies relative to E_{L+1}, in their case $P_1=E_1-E_2$ and $P_0=E_0-E_2$, from (11). In practice, however, one would ordinarily evaluate the integrals C and d from these empirical separations, and the form of the equations in which the empirical values appear directly is the more convenient one.

Thanks are extended to Professors S. Goudsmit, W. V. Houston, and J. B. Green for helpful discussions.

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[11] J. B. Green and R. A. Loring, Phys. Rev. **49**, 632 (1936). Their introductory neglect of the spin-spin term has no effect on their treatment of the Paschen-Back effect.

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Term Formulae for the Configuration d^5

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Term formulae for a configuration of five equivalent d electrons have hitherto not been published. They are given below for the case of Russell-Saunders coupling. A surprising result is that although several terms appear more than once (two ^2G, two ^2F, three ^2D) and are therefore expected to depend irrationally upon the radial integrals, this is only so for two out of the three ^2D terms. For the other of the above terms the secular equation possesses roots linear in the radial integrals. The formulae obtained are able to represent satisfactorily the d^5 terms of Cr II.

FORMULAE representing the distances of the terms arising from a configuration of equivalent d electrons as a function of radial integrals are readily derived by diagonal sum methods as long as each term occurs only once. For d^2 such formulae were given by Slater[1] and for d^3 by Condon and Shortley[2] in which latter case only the sum of the energies of the two ^2D terms was obtained. The separate energies of these terms result without difficulty from a consideration of non-diagonal elements of the energy matrix; they were given by Ufford and Shortley[3] and by Serber,[4] using Van Vleck's[5] method. In the configuration d^4 the doubly occurring terms are more numerous than the others; the complete formulae were given by Ostrofsky.[6]

The energies of the configuration d^5 have hitherto never been published although they are of great importance to the experimental spectroscopist when investigating Cr II and its higher isoelectronic relatives. Also in Mg I and similar spectra can they be expected to be useful since they account for the d^5s^2 configuration as well. In spite of the greater number of magnetic levels (252 compared to 210 for d^4) the computations for d^5 are simpler because of the smaller number of multiply occurring terms (there are two ^2G, two ^2F, and three ^2D).

For these latter the method employed was that described by Condon and Shortley in Section 5^8 of their book.[7] Consider that space of eigenfunctions characterized by the maximum M_SM_L values for which the term pair in question occurs. In this space a complete set of orthonormal unit vectors is given, the unstabilized eigenfunctions $\Phi(m_s{}^1m_l{}^1m_s{}^2m_l{}^2\cdots)$. The proper linear com-

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[1] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[2] E. U. Condon and G. H. Shortley, Phys. Rev. **37**, 1025 (1931).

[3] C. W. Ufford and G. H. Shortley, Phys. Rev. **42**, 167 (1932).

[4] R. Serber, Phys. Rev. **45**, 461 (1934).

[5] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

[6] M. Ostrofsky, Phys. Rev. **46**, 604 (1934). For corrections see paper following this.

[7] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra.*

binations which represent the eigenfunctions Ψ of a term ${}^{2S+1}L$ in that space are known by the angular momentum operator method. It now becomes necessary to find two (or three) more linear combinations of the Φ perpendicular to the Ψ. This can immediately be done provided the $M_S M_L$ space does not have too many dimensions. However, the configurations d^4 and d^5 present cases where the space in question may have such high dimensionality that it may be quite difficult to find additional unit vectors by straightforward methods. In such cases the following procedure has been found useful.

Let the $M_S M_L$ space have n dimensions. In it n unstabilized eigenfunctions Φ_n are available which are orthonormal:

$$(\Phi_i \Phi_j) = \delta_{ij} \quad i, j = 1 \cdots n.$$

By the method of angular momentum operators m stabilized eigenfunctions Ψ_ν have been obtained as linear combinations

$$\Psi_\nu = \sum_{i=1}^{n} a_{\nu i} \Phi_i \quad \nu = 1 \cdots m,\ m < n,$$

where

$$(\Psi_\nu \Psi_{\nu'}) = \delta_{\nu\nu'}.$$

The problem is to find $n-m$ further Ψ functions completing the set. We now write:

$$\Psi_{m+1} = \sum_{\mu=1}^{m} b_\mu \Psi_\mu + c_1 \Phi_1.$$

Orthogonality with all previous Ψ_ν fixes b_μ:

$$b_\mu = -a_{\mu 1} c_1$$

and c_1 is determined by the normalization condition. To get the next unit vector Ψ_{m+2} a different Φ, say Φ_2 will have to be preferred by writing

$$\Psi_{m+2} = \sum_{\mu=1}^{m+1} b_\mu' \Psi_\mu + c_2 \Phi_2.$$

The determination of b_μ' and of c_2 is as before.

This method makes the construction of further unit vectors easy and straightforward. It was used on the 12-dimensional space $M_S = \frac{1}{2}$, $M_L = 2$ of d^5, in which 9 stabilized Ψ were known by the angular momentum operator method and three more had to be found. The secular determinant is only of order 3.

The final formulae are given below; they represent the energies of 16 terms as functions of three radial integrals F_0, F_2, F_4. These latter are, if we denote by $f(r)$ the radial part of the eigenfunctions

$$F_k = F^k / D_k \tag{1}$$

with

$$F^k = 2e^2 \int_0^\infty r^2 dr f^2 r^{-k-1} \int_0^r r'^2 dr' f^2 r'^k \tag{2}$$

and

$$D_0 = 1, \quad D_2 = 49, \quad D_4 = 441.$$

$$\begin{aligned}
{}^6S &= 10\ F_0 - 35\ F_2 - 315\ F_4,\\
{}^4G &= 10\ F_0 - 25\ F_2 - 190\ F_4,\\
{}^4F &= 10\ F_0 - 13\ F_2 - 180\ F_4,\\
{}^4D &= 10\ F_0 - 18\ F_2 - 225\ F_4,\\
{}^4P &= 10\ F_0 - 28\ F_2 - 105\ F_4,\\
{}^2I &= 10\ F_0 - 24\ F_2 - \ 90\ F_4,\\
{}^2H &= 10\ F_0 - 22\ F_2 - \ 30\ F_4,\\
(1){}^2G &= 10\ F_0 - 13\ F_2 - 145\ F_4,\\
(2){}^2G &= 10\ F_0 + \ 3\ F_2 - 155\ F_4,\\
(1){}^2F &= 10\ F_0 - 25\ F_2 - \ 15\ F_4,\\
(2){}^2F &= 10\ F_0 - \ 9\ F_2 - 165\ F_4,\\
(1){}^2D &= 10\ F_0 - \ 4\ F_2 - 120\ F_4,\\
(2,3){}^2D &= 10\ F_0 - \ 3\ F_2 - \ 90\ F_4\\
&\qquad \pm (513\ F_2^2 - 4500\ F_2 F_4 + 20700\ F_4^2)^{\frac{1}{2}},\\
{}^2P &= 10\ F_0 + 20\ F_2 - 240\ F_4,\\
{}^2S &= 10\ F_0 - \ 3\ F_2 - 195\ F_4.
\end{aligned}$$

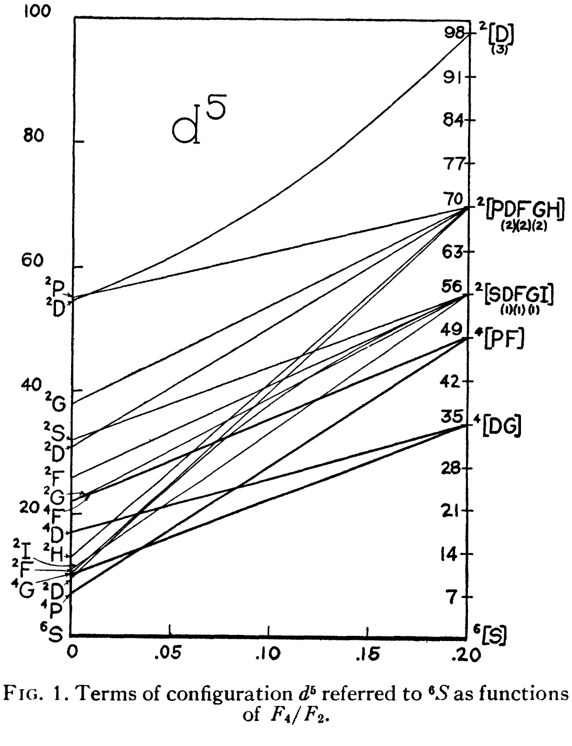

FIG. 1. Terms of configuration d^5 referred to ${}^6S$ as functions of F_4/F_2.

The number in parenthesis in front of a term symbol distinguishes the various terms of equal L and S values that occur. We should like to mention at this time that a standard notation should be provided for such multiply occurring terms, especially since they are so much more numerous in configurations of type f^z. It is evidently inadmissible to use letters a, b, c $\cdots$ here since they serve to label *any* sequence of ${}^{2S+1}L$ terms of equal parity regardless of whether they belong to the same configuration or not.

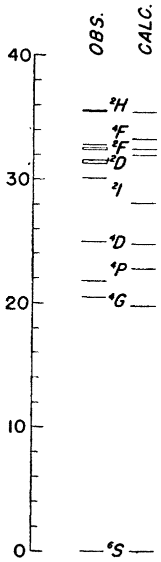

FIG. 2. Comparison with observed d^5 terms in the spectrum Cr II.

Since each element of the energy matrix is linear in the F_k it is to be expected that the energy of a singly occurring term is also linear in the F_k and that the energy of a term pair will contain the square root of a quadratic form in F_jF_k. Similarly a triple of terms is expected to contain the cube root of a form homogeneous of degree 3 in the F. It is therefore remarkable that the two term pairs (1 and 2)${}^2G$ and (1 and 2)${}^2F$ turn out to be rational in the F_k and that the cubic equation for the three ${}^2D$ turns out to have one root, here denoted by (1)${}^2D$, which is also rational. Since the same phenomenon does not occur for any pair of terms in the configuration d^3 or d^4 one is justified in regarding it as a unique feature of d^5. In this connection one is reminded of another fact which simplifies d^5 in comparison with other d^z configurations, namely the vanishing of the spin-orbit interaction constant ζ for all terms. To be sure both results are true only in first approximation.

Comparison of the formulae with experimental values is best carried out by means of the following nomograph scheme. On transparent paper the experimental term distances are marked off along a vertical line. These points are then connected by means of straight lines to a fixed point. Thus on any line parallel to the original vertical line the convergent rays will mark off proportional distances. This transparent graph is then laid on top of Fig. 1 and so adjusted that the straight convergent lines and the curves of Fig. 1 intersect along a vertical line. The two parameters can then be read off. Figure 2 contains a comparison of the formulae with nine terms of d^5 in the spectrum of Cr II. The data were kindly supplied by Dr. C. C. Kiess. A preliminary fit was obtained within a very short time by the graphical method just described. The figure contains a plot of the formulae calculated by setting $F_2 = 1050$ and $F_4/F_2 = 0.0681$.

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