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Atomic Eigenfunctions and Energies

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In §1, the calculation of the nondiagonal elements of electrostatic interaction is sketched. In §2, attention is called to the fact that the matrix elements of L_x (the x-component of orbital angular momentum), as calculated between spherical harmonic eigenfunctions taken with positive phase, are negative when m_l is $+$ and positive when m_l is $-$. The calculation of eigenfunctions in LS coupling has always been done using only positive matrix elements of L_x. This amounts effectively to using a zero-order scheme in which one takes spherical harmonic eigenfunctions with negative phase for positive odd values of m_l, and positive phase for all other values. In §3 the calculation of first order energies for configurations which give more than one multiplet of a kind is considered, and explicit formulas given for the electrostatic energies and magnetic splitting of the two ^2D's of d^3. The results are shown to compare satisfactorily with the observed data. The second ^2D is predicted in general to be extremely high and inverted.

In this paper we wish to calculate the separate energies and intervals of multiplets which occur more than once in a configuration. For this purpose we need the nondiagonal elements of the matrix of electrostatic interaction, which are given in §1. Since this matrix must be obtained algebraically, we discuss in §2 the interpretation, in terms of algebraic functions, of the eigenfunctions in LS coupling which have been found by various investigators. This consideration is necessary because of a question of phase to which attention has not hitherto been called. We then proceed in §3 to discuss the energy levels and separations, calculating in detail the two ^2D's of d^3.

§1. Matrix Elements of Electrostatic Interaction[1]

We shall first sketch the calculation of the matrix of the electrostatic interaction

$$G = \sum_{i>j=1}^{N} \frac{e^2}{r_{ij}} = \sum_{i>j=1}^{N} g(i, j) \tag{1.1}$$

in the zero-order scheme. In this scheme the eigenfunction belonging to the state $A = (a^1, a^2, \cdots a^N)$ will be the antisymmetric combination

$$\psi(A) = +\,(N!)^{-\frac{1}{2}} \sum_{P} (-1)^p P u_1(a^1) u_2(a^2) \cdots u_N(a^N), \tag{1.2}$$

where P represents a permutation of quantum numbers relative to electron indices, and p has the parity of P. Here the symbol $u_i(a^j)$ indicates the one-

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[1] The contents of this section are not original, although they have never been published in detail. The reduction of the nondiagonal elements to the form (1.5) and the calculation of the table of c's were done over a year ago by Slater and his students at Harvard and M.I.T., and by Condon and the writers at Princeton. This fact is noted by Inglis, Phys. Rev. **38**, 862 (1931), footnote 7.

electron central field eigenfunction for electron i with the j^{th} set of quantum numbers $n^j l^j m_l^j m_s^j$:

$$u_i(a^j) = [R_i(n^j l^j)/r_i]\Theta_i(l^j m_l^j)\Phi_i(m_l^j)\delta(\sigma_i, m_s^j). \tag{1.3}$$

The angle factors are given by the formulas

$$\left.\begin{aligned} \Theta(lm_l) &= +\left[\frac{2l+1}{2}\,\frac{(l-|m_l|)!}{(l+|m_l|)!}\right]^{\frac{1}{2}} \sin^{|m_l|}\theta \frac{d^{|m_l|}}{d(\cos\theta)^{|m_l|}} P_l(\cos\theta), \\ \Phi(m_l) &= +(2\pi)^{-\frac{1}{2}}e^{im_l\phi}. \end{aligned}\right\} \tag{1.4}$$

These are given explicitly because their exact form will be essential in §2. The sign of the eigenfunction (1.2) is determined by the order of listing the quantum numbers, and we shall adopt for convenience the following standard order.[2] The individual sets will be listed first in increasing order of n values; sets with a particular n will be arranged in increasing order of l values; those with a particular nl will be listed in decreasing order of the m_l values; and the set with $m_s = +\frac{1}{2}$ will be listed before that with $m_s = -\frac{1}{2}$ in case the two sets agree in regard to n, l, and m_l.

In this scheme the diagonal elements of G have been given by Slater.[3] The nondiagonal elements are easily obtained from formulas given by Condon.[4] Since G is diagonal with respect to $M_L = \Sigma m_l$ and $M_S = \Sigma m_s$, there will be no component between two states of the same configuration which differ in regard to just one individual set. If the two states differ in regard to two sets, A having the sets a, b, while A' has the sets a', b', this matrix element is given by

$$\begin{aligned}(A|G|A') = \pm\Big[&\iint \bar{u}_1(a)\bar{u}_2(b)g(1, 2)u_1(a')u_2(b')d\tau_1 d\tau_2 \\ &- \iint \bar{u}_1(a)\bar{u}_2(b)g(1, 2)u_1(b')u_2(a')d\tau_1 d\tau_2\Big],\end{aligned}$$

where the sign is to be chosen as in note 4. The general integral with four different quantum numbers which occurs here may be shown to be reducible to the form

$$\begin{aligned}&\iint \bar{u}_1(a)\bar{u}_2(b)g(1, 2)u_1(c)u_2(d)d\tau_1 d\tau_2 \\ &\quad = \delta(m_s^a, m_s^c)\delta(m_s^b, m_s^d)\delta(m_l^a + m_l^b, m_l^c + m_l^d) \\ &\qquad \cdot \sum_k c^k(l^a m_l^a; l^c m_l^c)c^k(l^b m_l^b; l^d m_l^d)R^k(n^a l^a n^b l^b; n^c l^c n^d l^d)\end{aligned} \tag{1.5}$$

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[2] Used by Shortley, Phys. Rev. **40,** 185 (1932). See esp. pp. 194, 195.

[3] Slater, Phys. Rev. **34,** 1293 (1929).

[4] Condon, Phys. Rev. **36,** 1121 (1930). These formulas must be supplemented by a determination of sign given in reference 2. The rule is as follows: To the matrix component between two states, $\psi(A)$ and $\psi(A')$, differing in regard to one or two individual sets, one prefixes + or − according to the parity of the permutation which changes the set A' from its standard order to the order in which the equal elements in A and A' occupy the same places.

where

$$c^k(lm_l;\, l'm_l') = \left(\frac{2}{2k+1}\right)^{1/2} \int_0^\pi \Theta(k,\, m_l - m_l')\Theta(lm_l)\Theta(l'm_l') \sin\theta d\theta \qquad (1.6)$$

$$R^k(n^al^an^bl^b;\, n^cl^cn^dl^d)$$
$$= e^2 \int_0^\infty \int_0^\infty \frac{r_<^{\,k}}{r_>^{\,k+1}} R_1(n^al^a)R_2(n^bl^b)R_1(n^cl^c)R_2(n^dl^d)dr_1dr_2. \qquad (1.7)$$

Slater's a's, b's, F's and G's are special cases of these c's and R's, namely

$$\left.\begin{aligned} a^k(l^am_l^a;\, l^bm_l^b) &= c^k(l^am_l^a;\, l^am_l^a)c^k(l^bm_l^b;\, l^bm_l^b) \\ b^k(l^am_l^a;\, l^bm_l^b) &= [c^k(l^am_l^a;\, l^bm_l^b)]^2 \end{aligned}\right\} \qquad (1.8)$$

$$\left.\begin{aligned} F^k(n^al^a;\, n^bl^b) &= R^k(n^al^an^bl^b;\, n^al^an^bl^b) \\ G^k(n^al^a;\, n^bl^b) &= R^k(n^al^an^bl^b;\, n^bl^bn^al^a). \end{aligned}\right\} \qquad (1.9)$$

Hence the c's may be obtained by taking the square roots of the b's as given by Slater and Condon and Shortley[5] except for sign.[6] It is easily seen that the R's which will be obtained within a configuration will always reduce to F's and G's.

§2. THE EIGENFUNCTIONS FOR LS COUPLING

The direct method of finding eigenfunctions in LS coupling is to proceed according to the definition of this scheme as one in which $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, and either L_z, S_z, or $\boldsymbol{J}^2$, J_z are diagonal. This method, which has been discussed by Johnson,[7] consists in finding the matrices of $\boldsymbol{L}^2$, $\boldsymbol{S}^2$ (and $\boldsymbol{L}\cdot\boldsymbol{S}$) in the zero-order scheme and diagonalizing them simultaneously. Gray and Wills[8] have given a method which depends essentially on the fact that the matrix of $J_x \pm iJ_y$, where $\boldsymbol{J}$ is any angular momentum, has but one component in each row or column, so that component connecting the state $\psi(j,\, m_j)$ with the state $\psi(j,\, m_j \mp 1)$. Wigner[9] has given a general formula for the states which result

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[5] Condon and Shortley, Phys. Rev. **37,** 1025 (1931).

[6] The signs are given by Inglis, Phys. Rev. **38,** 862 (1931), footnote 7, for s, p, and d electrons. These are repeated below, together with the signs for f electrons. To get c^k the square root of b^k is to be taken with the positive sign except for the following values of $(l^am_l^a;\, l^bm_l^b;\, k)$, for which it is to be taken negative:

$(1\pm1;\, 2\pm2;\, 3)$
$(2\pm2;\, 3\pm2;\, 3)$
$(2\pm1;\, 3\pm3;\, 5)$
$(2\quad 0;\, 3\pm3;\, 3)$
$(1\pm1;\, 3\pm2;\, 4)$
$(2\pm2;\, 2\pm2;\, 2)$
$(3\pm3;\, 3\pm3;\, 2)$
$(3\pm3;\, 3\pm1;\, 6)$
$(3\pm2;\, 3\quad 0;\, 2)$
$(1\pm1;\, 2\pm1;\, 3)$
$(2\pm2;\, 3\pm1;\, 1)$
$(2\pm1;\, 3\pm2;\, 5)$
$(2\pm2;\, 3\mp1;\, 3)$
$(1\pm1;\, 3\pm1;\, 4)$
$(2\pm2;\, 2\pm1;\, 4)$
$(3\pm3;\, 3\pm3;\, 6)$
$(3\pm3;\, 3\quad 0;\, 4)$
$(3\pm2;\, 3\quad 0;\, 4)$
$(1\pm1;\, 2\quad 0;\, 1)$
$(2\pm2;\, 3\pm1;\, 5)$
$(2\pm1;\, 3\pm1;\, 5)$
$(1\pm1;\, 1\pm1;\, 2)$
$(1\pm1;\, 3\quad 0;\, 2)$
$(2\pm2;\, 2\quad 0;\, 2)$
$(3\pm3;\, 3\pm2;\, 4)$
$(3\pm2;\, 3\pm2;\, 4)$
$(3\pm1;\, 3\pm1;\, 6)$
$(2\pm2;\, 3\pm3;\, 3)$
$(2\pm2;\, 3\quad 0;\, 3)$
$(2\pm1;\, 3\quad 0;\, 1)$
$(1\pm1;\, 3\pm3;\, 4)$
$(1\pm1;\, 3\mp1;\, 2)$
$(2\pm1;\, 2\pm1;\, 4)$
$(3\pm3;\, 3\pm1;\, 2)$
$(3\pm2;\, 3\pm1;\, 6)$
$(3\pm3;\, 3\mp1;\, 4)$

[7] M. H. Johnson, Phys. Rev. **39,** 197 (1932).

[8] Gray and Wills, Phys. Rev. **38,** 248 (1931). The sign of the imaginary i as we use it is reversed from that in Gray and Wills, in accordance with the more usual convention.

[9] Wigner, *Gruppentheorie*, p. 206.

from the addition of any two angular momentum vectors, and the determination of eigenfunctions using this formula has been discussed by Bartlett.[10]

All of these methods depend in the last analysis on the values of the matrices of L_x, L_y, L_z and S_x, S_y, S_z for one-electron eigenfunctions. If one calculates algebraically the matrix of L_x using the functions (1.3), one finds[11]

$$\bar{u}(nlm_lm_s)L_xu(nl,\, m_l-1,\, m_s) = \pm\,[(l+m_l)(l-m_l+1)]^{1/2}\begin{cases} + \text{ for } m_l \leqq 0. \\ - \text{ for } m_l > 0. \end{cases} \tag{2.1}$$

Now ever since they were first calculated by Born, Heisenberg, and Jordan[12] all matrix elements of the x-component of an angular momentum vector have usually been taken as real and positive, in particular in references 7, 8, 9, 10. Of course, this is satisfactory as long as one uses matrix methods and is consistent in the determination of the matrices of other observables; but before one may calculate a matrix, such as that of the electrostatic interaction, purely algebraically, one must determine what this choice of positive sign implies in the phase of the eigenfunctions. Suppose we designate by $v(nlm_lm_s)$ the system of one-electron eigenfunctions for which the matrix of L_x is given by

$$\bar{v}(nlm_lm_s)L_xv(nl,\, m_l-1,\, m_s) = +\,[(l+m_l)(l-m_l+1)]^{1/2} \text{ for all } m_l. \tag{2.2}$$

Then the v's will be related to the u's by the scheme

$$\begin{aligned} &\cdots\cdots && \cdots\cdots \\ v(nl,\ \ 3,m_s) &= -\,u(nl,\ \ 3,m_s) \\ v(nl,\ \ 2,m_s) &= +\,u(nl,\ \ 2,m_s) \\ v(nl,\ \ 1,m_s) &= -\,u(nl,\ \ 1,m_s) \\ v(nl,\ \ 0,m_s) &= +\,u(nl,\ \ 0,m_s) \\ v(nl,-1,m_s) &= +\,u(nl,-1,m_s) \\ &\cdots\cdots && \cdots\cdots \end{aligned} \tag{2.3}$$

(or this same scheme with signs reversed). Here the signs alternate for positive values of m_l, but are all positive for negative values.

The matrix of L_y is given in terms of that of L_x, in any scheme by the relation

$$(m_l|\,L_y\,|m_l') = e^{i(\pi/2)(m_l'-m_l)}(m_l|\,L_x\,|m_l').$$

The matrices of S_x and S_y are the same in the u scheme and the v scheme since they are diagonal with respect to m_l. Hence the matrix of any function of $\boldsymbol{L}$ and $\boldsymbol{S}$ as calculated using positive angular momentum matrix components is correct for the v scheme.

This means that all eigenfunctions in LS coupling heretofore published have been in terms of zero-order functions in the v scheme and not in the more

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[10] Bartlett, Phys. Rev. **38**, 1623 (1931).

[11] See, for instance, Brillouin, Jour. de Physique **8**, 74 (1927).

[12] Born, Heisenberg, and Jordan, Zeits. f. Physik **35**, 557 (1925).

logical u scheme. This distinction is essential when one calculates the matrix of electrostatic interaction, for example; if one fails to note this one will obtain matrices of electrostatic interaction which are not at all diagonal in LS coupling.[13]

As an example we may take the case of p^3, as calculated by Johnson using positive matrix components. If we use a notation $m_l^{\pm}$,in which we write $+$ for $m_s = +\frac{1}{2}$, $-$ for $m_s = -\frac{1}{2}$, the zero order states for $m_j = \frac{1}{2}$ are

$$\begin{array}{ll} \text{I}\ (1^-0^+0^-) & \text{III}\ (1^+0^+ -1^-) \\ \text{II}\ (1^+1^- -1^-)^{14} & \text{IV}\ (1^+0^- -1^+) \end{array}$$
$$\text{V}\ (1^-0^+ -1^+).$$

In terms of these states the eigenfunction for ${}^2D_{5/2}$ $(M_J = \frac{1}{2})$ as given by Johnson is

$${}^2D_{5/2} = (1/5)^{1/2}\text{I} - (1/5)^{1/2}\text{II} + (1/10)^{1/2}\text{III} - (4/10)^{1/2}\text{IV} + (1/10)^{1/2}\text{V}.$$

This state must be interpreted, if we let $\mathcal{A}$ represent the antisymmetrizing operator $+(N!)^{-\frac{1}{2}}\ \Sigma_P(-1)^p\ P$ which occurs in (1.2), as

$$\begin{aligned} {}^2D_{5/2} = {} & (1/5)^{1/2}\mathcal{A}v_1(1^-)v_2(0^+)v_3(0^-) - (1/5)^{1/2}\mathcal{A}v_1(1^+)v_2(1^-)v_3(-1^-) \\ & + (1/10)^{1/2}\mathcal{A}v_1(1^+)v_2(0^+)v_3(-1^-) - (4/10)^{1/2}\mathcal{A}v_1(1^+)v_2(0^-)v_3(-1^+) \\ & + (1/10)^{1/2}\mathcal{A}v_1(1^-)v_2(0^+)v_3(-1^+). \end{aligned}$$

In terms of the u scheme this becomes, according to (2.3)

$$\begin{aligned} {}^2D_{5/2} = {} & -(1/5)^{1/2}\mathcal{A}u_1(1^-)u_2(0^+)u_3(0^-) - (1/5)^{1/2}\mathcal{A}u_1(1^+)u_2(1^-)u_3(-1^-) \\ & - (1/10)^{1/2}\mathcal{A}u_1(1^+)u_2(0^+)u_3(-1^-) + (4/10)^{1/2}\mathcal{A}u_1(1^+)u_2(0^-)u_3(-1^+) \\ & - (1/10)^{1/2}\mathcal{A}u_1(1^-)u_2(0^+)u_3(-1^+). \end{aligned}$$

It is here, of course, not the sign of the whole expression, but the relative change of sign of the second term, which is significant. In the same way one must interpret all eigenfunctions which have been calculated using positive angular momentum matrices.

If one wishes to calculate eigenfunctions directly in the u scheme, one must substitute the values (2.1) instead of (2.2) in the formulas given by Johnson for the matrices of $\boldsymbol{L}^2$ and $\boldsymbol{L}\cdot\boldsymbol{S}$. For the Gray-Wills' method one must use the formulas

$$\begin{aligned} & (L_x - iL_y)u(lm_l) \\ & \qquad = \pm\ [(l + m_l)(l - m_l + 1)]^{1/2}u(l, m_l - 1) \quad \begin{cases} + \text{ for } m_l \leqq 0 \\ - \text{ for } m_l > 0 \end{cases} \\ & (L_x + iL_y)u(lm_l) \\ & \qquad = \pm\ [(l - m_l)(l + m_l + 1)]^{1/2}u(l, m_l + 1) \quad \begin{cases} + \text{ for } m_l < 0 \\ - \text{ for } m_l \geqq 0 \end{cases} \end{aligned} \tag{2.4}$$

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[13] Failing to note this will in general affect the calculation of transition probabilities, but not in the particular case of transitions in which one electron jumps from p to s, as calculated by Ufford, Phys. Rev. **40**, 974 (1932).

[14] This state is the negative of Johnson's II because of the different order of listing the quantum numbers.

which have signs chosen in accordance with (2.1). When using Wigner's formula for the addition of an l electron to an ion of resultant orbital momentum l^i, the sign of the coefficient[15] $(l^i l L\ M_L | l^i l\ m_l{}^i\ m_l)$ must be changed when $m_l = +1, +3, \cdots$. This is because an electronic function which is different in the u and v schemes is combined with an ionic function which is equivalent in the two schemes in the sense of (2.3). In adding L and S to obtain eigenfunctions in the $LSJM_J$ scheme, Wigner's coefficients are used as given by his formula without change of sign, since the initial states are now independent of the scheme used in obtaining them. The changes given in this paragraph are required only when it is desired to calculate eigenfunctions directly using positive phases for all of the one-electron functions, the other alternative being the calculation using v's throughout.

§3. FIRST-ORDER ENERGIES FOR CONFIGURATIONS WHICH GIVE MORE THAN ONE MULTIPLET OF A KIND

We shall now discuss the calculation of the first-order energies for configurations which give more than one multiplet characterized by the same values of L and S; at the same time giving the detailed results for the configuration d^3, which gives two ^2D's, and is the simplest and most completely analyzed configuration of this type.

The electrostatic energy of any multiplet occurring only once in a configuration may be obtained very simply by the diagonal sum method outlined by Slater,[3] without having to calculate any eigenfunctions or to use nondiagonal elements of electrostatic interaction in the zero-order scheme. When several multiplets of a kind occur, however, this method gives only the sum of the energies. In order to separate the energies, one must solve a secular equation connecting a group of eigenfunctions representing the multiplets of one kind. This is most easily explained by an illustration: the case of the two ^2D's of d^3. Consider the highest M_L and M_S values which belong to a ^2D. These are $M_L = 2$, $M_S = \frac{1}{2}$. The zero-order states of d^3, which are characterized by $M_L = 2$, $M_S = \frac{1}{2}$ are, in the notation of §2,

$$\begin{array}{llll} A & \mathcal{A}u_1(2^+)u_2(2^-)u_3(-\,2^+) & B & \mathcal{A}u_1(2^+)u_2(1^+)u_3(-\,1^-) \\ C & \mathcal{A}u_1(2^+)u_2(1^-)u_3(-\,1^+) & D & \mathcal{A}u_1(2^-)u_2(1^+)u_3(-\,1^+) \\ E & \mathcal{A}u_1(2^+)u_2(0^+)u_3(0^-) & F & \mathcal{A}u_1(1^+)u_2(1^-)u_3(0^+)\,. \end{array}$$

In terms of these zero-order functions one must determine two orthogonal eigenfunctions for ^2D, which will then be characterized by $M_L = 2$, $M_S = \frac{1}{2}$. A convenient way of doing this is to find by any of the methods of §2 the eigenfunctions for all the other multiplets which have states $M_L = 2$, $M_S = \frac{1}{2}$ (namely $^2H_{2,1/2}$, $^2G_{2,1/2}$, $^2F_{2,1/2}$ $^4F_{2,1/2}$) and then to choose two functions orthogonal to these and to each other. The following were obtained by this procedure:

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[15] This is Wigner's coefficient $s_{Lm_l{}^i m_l}{}^{(l^i l)}$, formula (27) p. 206, *Gruppentheorie*. For example in Wigner's table, page 208, the signs in the column $\nu = 1$ should be changed, when $\mu = m_l{}^i$, $\nu = m_l$.

$$\begin{aligned} {}^2D^a{}_{2,1/2} &= \tfrac{1}{2}[-A+B-C+E] \\ {}^2D^b{}_{2,1/2} &= (84)^{-1/2}[-5A-3B-C+4D-3E-2(6)^{1/2}F]. \end{aligned} \qquad (3.2)$$

The matrix of electrostatic energy for these states becomes[16]

$$\begin{array}{c|cc} & a & b \\ \hline a & 3F_0+7F_2+63F_4 & 3(21)^{1/2}(F_2-5F_4) \\ b & 3(21)^{1/2}(F_2-5F_4) & 3F_0+3F_2-57F_4 \end{array} \qquad (3.3)$$

which has for its eigenvalues the energies

$$\epsilon = 3F_0+5F_2+3F_4 \pm (193F_2{}^2-1650F_2F_4+8325F_4{}^2)^{1/2}. \qquad (3.4)$$

This formula then gives the electrostatic energies of the two ${}^2D$ multiplets. The eigenfunctions for these multiplets, for $M_L=2$, $M_S=\frac{1}{2}$, may now be obtained. If we write the eigenfunction for either of them as $\alpha\,{}^2D^a{}_{2,1/2}+\beta\,{}^2D^b{}_{2,1/2}$, we find

$$\begin{aligned} \alpha &= \left[\left(\frac{3F_0+7F_2+63F_4-\epsilon}{3(21)^{1/2}(F_2-5F_4)}\right)^2+1\right]^{-1/2} \\ \beta &= -\frac{3F_0+7F_2+63F_4-\epsilon}{3(21)^{1/2}(F_2-5F_4)}\,\alpha. \end{aligned} \qquad (3.5)$$

Now since this is the only state with $M_J=5/2$, this state is identical with the state ${}^2D_{5/2}$, $M_J=5/2$. The eigenfunctions for the other values of J and M_J may be obtained from this by the Gray-Wills' procedure, and the whole matrix of magnetic interaction[17] calculated. This procedure leads, however, only to secular equations which are too complicated to be solved. In all the analyzed d^3 configurations the magnetic interaction is very small compared to the electrostatic, so that one can consider it merely as a small perturbation on the electrostatic levels; hence it will suffice to calculate the diagonal elements of magnetic interaction in the $LSJM_J$ scheme. The use of the diagonal sum rule together with the Landé interval rule enables all of these elements to be readily calculated[18] for multiplets which occur only once in a configuration; but for multiplets occurring more than once this method gives only the sums of the magnetic energies. For the state (3.5) one obtains by direct calculation the value

$$\begin{aligned} ({}^2D_{5/2},5/2\,|\,V^1\,|\,{}^2D_{5/2},5/2) &= [\alpha^2/2-(21)^{1/2}\alpha\beta/3-\beta^2/6]\zeta \\ &= \tfrac{1}{6}[1 \mp (59F_2-435F_4)(193F_2{}^2-1650F_2F_4+8325F_4{}^2)^{-1/2}]\zeta, \end{aligned} \qquad (3.6)$$

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[16] The notation is as in Condon and Shortley,[5] $F_2=(1/49)F^2(nd^2)$, $F_4=(1/144)F^4(nd^2)$, where F^2 and F^4 are as in (1.9).

[17] For the elements of this matrix see Johnson,[7] p. 201, and Shortley,[2] §5. These elements are given with plus signs and must be so used only in the v scheme, as has been done by Johnson.

[18] Pauling and Goudsmit, *Structure of Line Spectra,* §39. The a of this section is our ζ.

where V^1 is the magnetic interaction $\Sigma\xi(r_i)\boldsymbol{L}_i\cdot\boldsymbol{S}_i$, and ζ the radial factor $(nd|\xi(r)|nd)$. The upper sign is to be taken with the upper sign in (3.4), and *vice versa*. From the Landé interval rule we know that the ^2D splitting is 5/2 this quantity, while the other d^3 intervals are given in Table XIII of Pauling and Goudsmit. The sum rule says that the sum of (3.6) for the two ^2D's must be $\frac{1}{3}\zeta$, which is seen to be the case.

We shall now see how these calculations compare with the experimental data. The first instance of d^3 is Russell's[19] $3d^3$ in Ti II, which has been discussed by Condon and Shortley,[5] who have also given the formulas for the electrostatic energies. They found that they could obtain a fairly good fit for this configuration with $F_2=845$, $F_4=54$ $(3F_0=17{,}750)$. If we put these values into (3.4) we find for the energies of the two ^2D's 12,820 and 31,450 cm^{-1}. The only ^2D found by Russell is at 12,710 cm^{-1}, which agrees excellently with our lower ^2D. The position of the second ^2D is predicted 10,000 cm^{-1} higher than any other level of the configuration, which may account for its not being found. The intervals in this configuration are discussed in Pauling and Goudsmit, p. 163. Using, as they do, the ^2H interval as standard, one calculates,

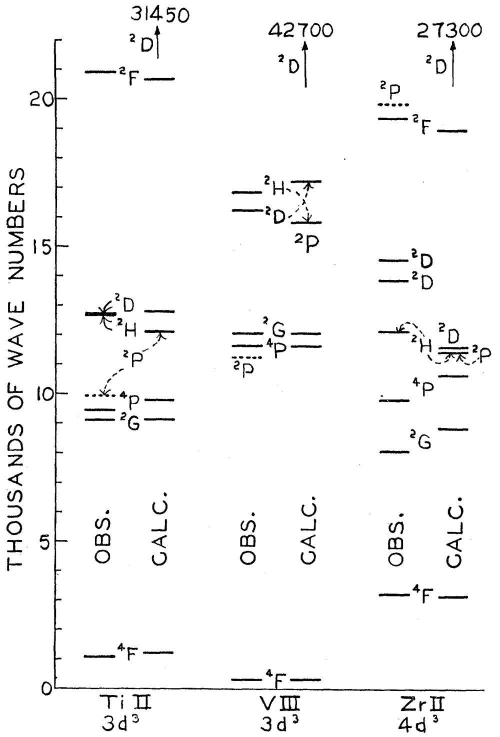

Fig. 1. Energy levels of the configuration d^3. The values for Ti II and Zr II are calculated from the constants given by Condon and Shortley;[5] in V III the constants are chosen to make ^4F, ^4P, and ^2G fit exactly.

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[19] Russell, Astrophys. J. **66**, 283 (1927).

from (3.6) the lower ${}^2D$ interval as 142 cm^{-1}, while the observed value is 129.4. The interval for the higher ${}^2D$ is calculated as -67.7 cm^{-1}.

In the $3d^3$ of V III White[20] has found all the multiplets except ${}^2F$ and one ${}^2D$. The configuration d^3 has the peculiarity that the calculated electrostatic energies for ${}^2H$ and ${}^2P$ are equal. In this instance these energies are not at all equal so that we cannot depend much on ${}^2H$ and ${}^2P$. However if we choose the F's to make the other three multiplets, ${}^4F$, ${}^4P$, ${}^2G$ fit exactly, the ${}^2H$ energy is fairly good (15,869 cm^{-1} calc., 16,906 cm^{-1} obs.) while that of the ${}^2P$ is not (11,327 cm^{-1} obs.). This is in accord with the observation of Condon and Shortley, who in two instances (Ti II and Zr II) found a reasonable fit for ${}^2H$, but not for ${}^2P$. The values of the constants which are obtained in this way are $F_2=1171$, $F_4=83$ $(3F_0=23{,}891)$. These constants give for the values of the two ${}^2D$'s, 17,300 and 42,700 cm^{-1}. The first of these is agreeably close to the ${}^2D$ found by White at 16,317 cm^{-1}; the second is predicted 25,800 cm^{-1} higher than any other level of the configuration, which has a spread of only 16,900 cm^{-1} as analyzed! Hence it is not surprising that this second ${}^2D$ was not found. The intervals as usual agree only roughly. White has remarked that ${}^4F$ fits the interval rule fairly well, and if we use the ζ given by this level, (which is about an average ζ for the configuration), the calculated ${}^2D$ intervals are 248 and -110 cm^{-1}; the first of these is to be compared with the observed interval of 147 cm^{-1}.

For the $4d^3$ of Zr II, in which Kiess and Kiess[21] report two ${}^2D$'s, Condon and Shortley obtain an approximate fit of all levels except ${}^2P$ with $F_2=683$, $F_4=36$ $(3F_0=16{,}000)$. With these values the calculated ${}^2D$'s lie at 11,750 and 27,310 cm^{-1}, with separations of 593 and -309 cm^{-1}, respectively. These separations are calculated using the ${}^2H$, which gives an average value for ζ, as standard. The observed ${}^2D$'s lie at 13,869 and 14,559 cm^{-1} with separations of 734 and 435 cm^{-1}. Hence we must infer that, if these are correctly classified, one of them is very strongly perturbed.

These are all the instances of d^3 which are sufficiently analyzed for comparison with the theory. In general we have seen that the lower ${}^2D$ corresponds well with the one usually observed; the second ${}^2D$ is predicted extremely high and inverted.

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[20] White, Phys. Rev. **33**, 672 (1929).

[21] Kiess and Kiess, Bur. Standards J. Research **5**, 1210 (1930).