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On the Triplets of Helium

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It is well known that the inversion of the helium triplets and their deviation from interval rule are due to the spin-other-orbit and to the magnetic spin-spin interactions (respectively), which may be neglected in comparison with the spin-orbit interaction in treating the spectra of heavy elements. The preliminary calculation of Heisenberg is compared with the correct calculation of Breit for the lowest triplet. The extension to higher triplets, by Araki, is simplified and generalized, and the comparison with experiment is discussed.

I. THE LOW TRIPLET

THE part of the Hamiltonian of a two-electron atom which is attributed to the spins and spin magnetic moments of the electrons may be written[1]

$$\begin{aligned}H''=a\{&\tfrac{1}{2}Z[(\mathbf{s}_1\cdot\mathbf{l}_1)/r_1^3+(\mathbf{s}_2\cdot\mathbf{l}_2)/r_2^3]\\&-(m/\hbar)[(\mathbf{s}_1+\mathbf{s}_2)\cdot(\mathbf{r}_2-\mathbf{r}_1)\times(\dot{\mathbf{r}}_2-\dot{\mathbf{r}}_1)\\&+\tfrac{1}{2}\mathbf{s}_1\cdot(\mathbf{r}_2-\mathbf{r}_1)\times\dot{\mathbf{r}}_1-\tfrac{1}{2}\mathbf{s}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)\times\dot{\mathbf{r}}_2]/r_{12}^3\\&+[\mathbf{s}_1\cdot\mathbf{s}_2-3(\mathbf{s}_1\cdot\mathbf{r}_{12})(\mathbf{s}_2\cdot\mathbf{r}_{12})/r_{12}^2]/r_{12}^3\},\end{aligned}\tag{1}$$

where $a=(e\hbar/mc)^2$. The first line is the part of the familiar "spin-orbit interaction" due to the field of the nucleus (including the "Thomas factor" $\frac{1}{2}$). The second line is the Larmor magnetic contribution to the screening part of the spin-orbit interaction and the spin-with-other-orbit interaction, and the third line contains the corresponding Thomas relativistic terms, which may be said to depend on the acceleration of each electron in the nuclear coordinate system caused by the Coulomb interaction with the other electron.[2] The fourth line is the magnetic spin-spin interaction.

Two prominent papers have treated the low triplet $1s2p\,^3P$ of helium in sufficient detail to include all terms of the interaction (1), and their results stand in some disagreement. Heisenberg's result for the relative energies of the states of the sp triplet, $^3P_2$, $^3P_1$, and $^3P_0$, respectively, is

$$a\langle(1/r^3)_p\rangle_{\text{Av}}\{\tfrac{1}{4}(Z-3)(1,\,-1,\,-2)+(1/16)(1,\,-5,\,10)\},\tag{2}$$

where the terms in $(Z-3)$ arise from the first three lines of (1) and the others from the last line. This result is based on neglect of exchange and on the approximation which considers the domain of the s electron as small, $r_s\rightarrow 0$. The later and more pretentious paper of Breit,[3] whose primary purpose was essentially a derivation of (1) and its consequences from relativistic reasoning analogous to that underlying the Dirac equation for one electron, leads to a triplet splitting given by the relative energies

$$C(0,\,-2,\,-3)-3d(0,\,-2,\,3),\tag{3}$$

where $C=\frac{1}{4}a\int u^*{}_1\{Z(\mathbf{l}_1/r_1^3+\mathbf{l}_2/r_2^3)-3\hbar^{-1}(\mathbf{r}_2-\mathbf{r}_1)\times(\mathbf{p}_2-\mathbf{p}_1)/r_{12}^3\}_z u_1 d\tau$ and

$$d=-\tfrac{1}{4}a\int u^*{}_1\{(r_{12}^2-3z_{12}^2)/r_{12}^5\}u_1 d\tau.$$

Here $\mathbf{l}$ is the operator $\mathbf{r}\times\mathbf{p}/\hbar$, $\mathbf{p}$ being linear momentum, and u_{m_l} is a two-electron wave function of the configuration sp. A refined variational determination of these wave functions and the integrals containing them was carried out in Breit's paper, with quite satisfactory agreement with the observed triplet splitting in He, and presumably also in Li$^+$. For the sake of comparison of (2) with (3), we may specialize (3) to the simple case $r_s\rightarrow 0$, with neglect of exchange. In this case $r_{12}\rightarrow r_2$ and C reduces to $\frac{1}{4}a(Z-3)\times\langle(1/r^3)_p\rangle_{\text{Av}}$, so that the part of (3) involving it agrees with the corresponding part of the triplet splitting given by (2). The angular integration of d introduces a factor

$$\int(1-3\cos^2\theta)\sin^3\theta d\theta/\int\sin^3\theta d\theta=2/5,$$

making $d=-(1/10)a\langle(1/r^3)_p\rangle_{\text{Av}}$. We thus have

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[1] W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

[2] L. H. Thomas, Phil. Mag. **3**, 1 (1926); J. Frenkel, Zeits. f. Physik **37**, 243 (1936); S. Dancoff and D. R. Inglis, Phys. Rev. **50**, 784 (1936).

[3] G. Breit, Phys. Rev. **36**, 383 (1939); **39**, 616 (1932). His integral D_0 is here denoted by $3d$. His integral D, arising from terms in e^4, need no longer concern us.

TABLE I. Diagonal elements of (4) and (5) by trace invariance.

m_l	m_{s_1}	m_{s_2}	(4)	(5)	J	(4)	(5)
1	+	+	1/10	1/16	2	1/10	1/16
0	+	+	−1/5	−1/8	1	−5/10	−5/16
1	+	−	−1/10	−1/16			
1	−	+	−1/10	−1/16			
1	−	−	1/10	1/16	0	10/10	10/16
−1	+	+	1/10	1/16			
0	+	−	1/5	1/8			
0	−	+	1/5	1/8			

the triplet energies

$$a\langle(1/r^3)_p\rangle_{\text{Av}}\{\tfrac{1}{4}(Z-3)(0,\ -2,\ -3)$$
$$+(1/10)(0,\ -6,\ 9)\} \qquad (3')$$

and a separation ratio $({}^3P_2-{}^3P_1)/({}^3P_1-{}^3P_0)=-2/35$. The spin-spin terms of (2) are thus too small by a factor $\frac{5}{8}$. Since (2) has been rather widely quoted in the literature, it has some interest to point out the cause of the discrepancy. This lies in Heisenberg's *assumption* (reference 1, page 551) that the average value of

$$\{\mathbf{s}_1\cdot\mathbf{s}_2-3(\mathbf{s}_1\cdot\mathbf{r})(\mathbf{s}_2\cdot\mathbf{r})/r^2\}/r^3 \qquad (4)$$

obtained by a classical treatment of the vector model, namely[4]

$$-\tfrac{1}{2}\{\mathbf{s}_1\cdot\mathbf{s}_2-3(\mathbf{s}_1\cdot\bar{\mathbf{l}})(\mathbf{s}_2\cdot\bar{\mathbf{l}})\}/r^3 \qquad (5)$$

is valid also in quantum mechanics. His derivation from this point is somewhat indirect because of an appeal to Kronig's work on intensities, but his results may be derived very simply from (5) by use of trace invariance, and of the fact that the diagonal element of (5) for the singlet is zero, in the manner carried out in Table I. The corresponding correct calculation direct from (4), by use of the expression $m_{s1}m_{s2}(1-3\cos^2\theta)$ with $\cos^2\theta=1/5$ for $m_l=1$ and $3/5$ for $m_l=0$, is also carried out in the columns headed (4) in Table I, and the resulting contributions to the triplet splitting of course agree with (3′).

The calculation of Breit shows that the relative importance of the spin-spin term (the ratio d/C) is decreased by a factor $(0.21/0.2)/(0.91/0.5)=0.57$ when exchange and the s electron distribution in He are taken into account. This is so nearly equal to the factor $\frac{5}{8}$ which erroneously appeared in Heisenberg's calculation by neglecting these refinements that the error and neglect nearly annul one another and the results of the two calculations are very similar.

For the sake of a qualitative understanding of the distorted triplets it should be pointed out that the spin-orbit and spin-other-orbit couplings together would in helium make an inverted triplet obeying interval rule. This is manifest in the factor $(Z-3)$, which is negative for helium in the approximate formula (3′). It comes about because the magnitude of the spin-orbit coupling is determined by an effective nuclear charge $Z_{\text{eff}}=(Z-1)e=e$ and is further reduced by the "Thomas factor" $\frac{1}{2}$ because of the acceleration of the electron concerned, while the spin-other-orbit term arises primarily from the orbital motion of the p electron about the "spinning" s electron and its magnitude is determined by a charge $-e$, without any Thomas factor because the s electron is bound to the nucleus and not accelerated. The spin-spin interaction elevates the ${}^3P_0$ more than the ${}^3P_2$, while lowering the ${}^3P_1$, and in the approximation leading to (3′) it is responsible for the entire triplet splitting in Li$^+$, since there the spin-orbit and spin-other-orbit terms just annul one another.

Breit's evaluation of C and d takes into account both exchange and the finite domain of the s electron. The positive part of C, arising from the field of the bare nucleus, is thereby increased from $\frac{1}{2}C_0$ to $1.33C_0$, where $C_0=(R_H/\alpha^2)/24=m(e^4/\hbar c)^2/48$. (The value $\frac{1}{2}C_0$ is obtained by putting $\langle 1/r^3\rangle_{\text{Av}}=(me^2/\hbar^2)^3/[n^3l(l+\frac{1}{2})(l+1)]$ above.) The negative part of C, arising from the interaction of the electrons, is altered somewhat less, from $-1.5C_0$ to $-2.24C_0$. The increase in magnitude is in each case presumably caused mainly by a contraction of the scale of the p wave function, and a corresponding increase in density within and near the "s shell," due to the lowered potential within it. In the inter-electronic

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[4] Here $\bar{\mathbf{l}}$ is the unit vector along $\mathbf{l}$. A diagonal matrix element of $(\mathbf{s}_1\cdot\bar{\mathbf{l}})(s_2\cdot\bar{\mathbf{l}})$ may be obtained by multiplying by the operator l^2, so as to get rid of the unit vectors, taking the diagonal element, and then dividing by the proper value of l^2, which in our case is 2. In the m_l, m_{s_1}, m_{s_2}-representation of Table I, this leads to the evaluation of (5) as $\frac{1}{2}m_{s_1}m_{s_2}(1-3m_l^2/2)$. The mean value (5) may be derived from (4) by a classical treatment of the vector model in that representation thus:

$$\{\mathbf{s}_1\cdot\mathbf{s}_2-3(\mathbf{s}_1\cdot\mathbf{r})(\mathbf{s}_2\cdot\mathbf{r})/r^2\}_{\text{Av}}=s_{z_1}s_{z_2}\{1-3\langle z^2/r^2\rangle_{\text{Av}}\}$$
$$=s_{z_1}s_{z_2}\{1-(3/2)\sin^2(lz)\}$$
$$=s_{z_1}s_{z_2}\{-\tfrac{1}{2}+(3/2)\cos^2(lz)\}\rightarrow(5).$$

term, this increase is only partly compensated by the "incomplete screening," that is, by the fact that circulation of the p electron with an "s shell" is ineffective in the spin-other-orbit coupling. The net effect on C is an increase of 82 percent from $-\frac{1}{2}C_0$ to $-0.91C_0$, only about half of the change in $\langle 1/r^3\rangle_{\text{Av}}$. The effect on the spin-spin integral d is smaller, being a change from $-0.2C_0$ to $-0.21C_0$. The increased density near the s shell would alone make d considerably larger, but the finite spherical domain of the s electron has also a tendency to make d small because it distributes the s electron much more nearly isotropically about important positions of the p electron near the s shell, where $1/r_{12}^3$ may become very large—the integral is a maximum if both electrons are confined to the xy-plane, and is zero if they are isotropically distributed.

II. THE HIGHER TRIPLETS

The calculation of Breit for the low triplet has been repeated by Araki,[5] using slightly different wave functions which allow more polarization of the s distribution, and has also been extended by him to the higher triplets $1s3p\,^3P$ and $1snd\,^3D$. His results for the low triplet slightly improve the agreement with experiment but are not very significantly different from Breit's: the separation ratio $(^3P_2-{}^3P_1)/(^3P_1-{}^3P_0)$ equal to 1/14 rather than 1/7 implies an increase of the ratio d/C of only about 12 percent. With the approximations in the wave functions, probably neither calculation can claim an accuracy much greater than that. Among the higher triplets, Araki found both agreement and disagreement with the partially conflicting experimental data. In attempting to adjudge the seriousness of the disagreement, it is convenient to have at hand also a shorter calculation which is simplified in such a way as to present only those points which seem to be physically most important.

We neglect the interaction with the singlet, as did Breit, since it is small even in the high configurations where the singlet is nearby, and can only depress the central triplet level, decreasing the smaller separation slightly. There is so much less overlapping of the two single-electron wave functions in the configuration $1snd$ that we may treat the ^3D fairly well, and at the same time very simply, by neglecting exchange and the spatial extension of the s electron. So $r_s\rightarrow 0$, as above, and we have only one position vector. We construct Table II for $1snd\,^3D$, by use of (4) and the results of the angular integrations $\langle 1-3\cos^2\theta\rangle_{\text{Av}}=4/7,\ -2/7,\ -4/7$ for d states with $m_l=2, 1, 0$, respectively. The sixth column is obtained from the fourth by trace invariance as before. The spin-orbit and spin-other-orbit contributions are together listed in the seventh column. They alone form an inverted triplet obeying interval rule. The intervals are much distorted, but the inversion remains, when the spin-spin contributions are added (last column). It will be shown below that the ratios of the spin-spin contributions among themselves remain unaltered when one takes into account exchange and the extent of the s wave function. The only change is again a change of the scale of the spin-spin contributions, relative to the scale of the orbital contributions. The reasons for the change are essentially the same as in the ^3P case discussed above, and considerably less change is expected in $1s3d$ than in $1s2p$ because of the smaller overlapping of the single-electron wave functions. This leaves the $^3D_2$ very much nearer to the $^3D_3$ than to the $^3D_1$.

The agreement between the two sets of experimental data,[6,7] and their agreement with the theory, in the low triplet $1s2p\,^3P$ is gratifying. In the next triplet, $1s3p\,^3P$, the calculations of

TABLE II. Splitting of a ^3D in helium. Multiply by $\langle a/r^3\rangle_{\text{Av}}$ to obtain energies.

m_l	m_{s_1}	m_{s_2}	$m_{s_1}m_{s_2}(1-3\cos^2\theta)$	J	spin-spin	$\frac{1}{4}(Z-3)\dot{s}$	Sum
2	+	+	1/7	3	1/7	−1/2	−10/28
2	+	−	−1/7	2	−1/2	1/4	− 7/28
2	−	+	−1/7				
1	+	+	−1/14				
2	−	−	1/7	1	1/2	3/4	35/28
1	+	−	1/14				
1	−	+	1/14				
0	+	+	−1/7				

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[5] G. Araki, Proc. Phys. Math. Soc. Japan **19**, 128 (1937).

[6] W. V. Houston, Proc. Nat. Acad. Sci. **13**, 91 (1927). Professor Houston has kindly pointed out the following misprints: In Fig. 1, the subscripts of $^3D_2$ and $^3D_3$ should be interchanged, as is obvious from the transitions drawn and from selection rules, and in the fifth line of Table I $^3P_0$ should read $^3P_1$, which combines with $^3D_{12}$.

[7] G. Hansen, Verh. d. deutsch phys. Ges. **10**, 5 (1929).

TABLE III. Triplet energies in strong and weak fields.

M_L	M_S	$H'''/(\mu_B H)$	H''	M_J	J	H''	$H'''/(\mu_B H)$
L	1	$L+2$	C_L+d_L	$L+1$	$L+1$	C_L+d_L	$L+2$
L	0	L	$-2d_L$	L	$L+1$	C_L+d_L	$(L+2)L/(L+1)$
$L-1$	1	$L+1$	$C_{L-1}+d_{L-1}$	L	L	$C_{L-1}-C_L+d_{L-1}-3d_L$	$(L^2+L+1)/(L+1)$
L	-1	$L-2$	$-C_L+d_L$	$L-1$	$L+1$	C_L+d_L	$(L+2)(L-1)/(L+1)$
$L-1$	0	$L-1$	$-2d_{L-1}$	$L-1$	L	$C_{L-1}-C_L+d_{L-1}-3d_L$	$(L^3-1)/(L^2+L)$
$L-2$	1	L	$C_{L-2}+d_{L-2}$	$L-1$	$L-1$	$C_{L-2}-C_{L-1}-C_L+d_{L-2}-3d_{L-1}+3d_L$	$(L-1)^2/L$

Araki yield a result intermediate between (3′) and the $1s2p\,^3P$ result, as one would expect by comparing the overlapping in the two configurations, and this disagrees sharply with the observed[8] separations $^3P_2-{}^3P_1=0.165$ cm^{-1}, $^3P_1-{}^3P_0=0.192$ cm^{-1}. Such a separation ratio, with one level almost midway between the other two, would require a ratio $d/C=1/12$, rather than over $\frac{1}{4}$ as calculated, and it is extremely unlikely that any of the approximations of the theory could introduce so large an error in this ratio. Configuration interaction seems to be excluded as a possible cause of the discrepancy, the nearest odd configuration being more than 5000 cm^{-1} distant. This seems to be the only measurement of this triplet available. Araki[5] and others[9] have quoted a supposedly experimental value of its separation ratio by Houston, although he measured only the over-all triplet width and stated what the separations would be if the ratio should be the same as in the lower triplet, a surmise based on Heisenberg's theoretical treatment. A repetition of the measurement would be of interest. In the $1s3d\,^3D$, the earlier analysis of Houston,[6] while apparently painstaking and legitimate, was made in spite of the difficulty that his experiments did not resolve this triplet, and his results may perhaps be said to have been superseded by the later measurements of Hansen,[7] who did succeed in resolving it into two lines, by use of liquid helium. The earlier results placed the $^3D_3$ nearer the $^3D_1$ than the $^3D_2$, a distortion which no plausible modification of the theory could give, while Hansen's separations are $^3D_3-{}^3D_2<0.01$ cm^{-1}, $^3D_2-{}^3D_1=0.04$ cm^{-1}, in accord with theory. In the high triplet $1s4d\,^3D$ no measurement of the separation ratio is available, although here again a surmise from reference 6 has been quoted as experimental.[5, 9] The over-all separations of both the D triplets measured by Hansen agree with results of Araki.

III. DERIVATION FOR A GENERAL TRIPLET

We shall now derive an expression for the triplet splitting in terms of parameters C and d which is valid for any triplet. Other calculations have involved good, but still special, assumptions concerning the wave functions. In order to avoid specialization of the form of the wave function (beyond the properties of a triplet) and in order at the same time to avoid use of the theorems of group theory, we employ the method of comparing coefficients in the secular equations determined in two extreme representations.[10] This requires the calculation of only diagonal matrix elements. Because of the simplicity of the proper functions of the atom in a strong magnetic field (strong enough to make energies much larger than the triplet splitting, but much smaller than the singlet-triplet separation) we consider the secular equations of this Paschen-Back transition.

The wave functions of the triplet are

$$\psi_{M_L M_S}(r_1, r_2, \sigma_1, \sigma_2)=U_{M_L}(r_1, r_2)S_{M_S}(\sigma_1, \sigma_2)$$

with

$$S_{\pm 1}=\delta(\pm\tfrac{1}{2}/\sigma_1)\delta(\pm\tfrac{1}{2}/\sigma_2);$$
$$S_0=\{\delta(\tfrac{1}{2}/\sigma_1)\delta(-\tfrac{1}{2}/\sigma_2)+\delta(\tfrac{1}{2}/\sigma_2)\delta(-\tfrac{1}{2}/\sigma_1)\}/\sqrt{2},$$

where the δ's are the Pauli single-electron spin functions. In this representation we first wish to reduce the diagonal elements of H'' to as few undetermined parameters as possible. The form

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[8] R. C. Gibbs and P. G. Kruger, Phys. Rev. **37**, 1559 (1931).

[9] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill, 1934).

[10] S. Goudsmit, Phys. Rev. **35**, 1925 (1930).

of the usual spin operations,

$$(s_x \pm i s_y)\delta(\pm\tfrac{1}{2}/\sigma)=0,$$
$$(s_x \pm i s_y)\delta(\mp\tfrac{1}{2}/\sigma)=\delta(\pm\tfrac{1}{2}/\sigma),$$
$$s_z\delta(\pm\tfrac{1}{2}/\sigma)=\pm\tfrac{1}{2}\delta(\pm\tfrac{1}{2}/\sigma),$$

is such that only the z component of s_i contributes to a diagonal element of the first three lines of (1), which are linear in the $\mathbf{s}_i$ and may of course be factored in the familiar form $\mathbf{A}\cdot\mathbf{s}=\frac{1}{2}(A_x+iA_y)\times(s_x-is_y)+\frac{1}{2}(A_x-iA_y)(s_x+is_y)+A_zs_z$. Since the matrix element $(M_S|s_{i_z}|M_S)=\frac{1}{2}M_S$ for $i=1$ or 2, we may write the part of the matrix element $(M_LM_S|H''|M_LM_S)$ which arises from the first three lines of (1) in the form

$$\begin{aligned}\tfrac{1}{2}aM_S(M_L|\{\tfrac{1}{2}Z(l_{1z}/r_1{}^3+l_{2z}/r_2{}^3)-(m/\hbar)\\ \times\tfrac{3}{2}[(\mathbf{r}_2-\mathbf{r}_1)\times(\dot{\mathbf{r}}_2-\dot{\mathbf{r}}_1)]_z/r_{12}{}^3\}|M_L)\\ \equiv M_SC_{M_L}.\end{aligned}\quad(6)$$

In the spin-spin terms, the proper value $\frac{1}{4}$ of $\mathbf{s}_1\cdot\mathbf{s}_2$ may be inserted directly, and the spin operations just listed may be used in the last term, to give the part of $(M_LM_S|H''|M_LM_S)$ arising from the last line of (1) in the form

$$\begin{aligned}&\tfrac{1}{4}a(M_L|\{1/r_{12}{}^3-3z_{12}{}^2/r_{12}{}^5\}|M_L)\equiv d_{M_L}\\ &\text{for } M_S=\pm1 \text{ and}\\ &\tfrac{1}{4}a(M_L|\{1/r_{12}{}^3-3(1/r_{12}{}^3-2z_{12}{}^2/r_{12}{}^5)\}|M_L)\\ &\qquad=-2d_{M_L}\quad\text{for } M_S=0.\end{aligned}\quad(7)$$

These energies are listed in the fourth column of Table III for the states of the M_LM_S representation (strong field). The values calculated from them for the JM_J representation, by use of trace invariance and the fact that these "internal" energies depend on J but not on M_J, are listed in the seventh column. In treating the Paschen-Back transition, we also introduce the perturbing energy of an external magnetic field H,

$$H'''=-\mu_B(\mathbf{L}+2\mathbf{S})\cdot\mathbf{H},$$

and list its diagonal elements in Table III. Here μ_B is the Bohr magneton. (The fact, familiar from the vector model, that the Zeeman energies in the weak-field case are proportional to M_J for a given J, may be used together with trace invariance to obtain the last column of Table III from the strong-field case.) Table III gives the energies as one departs from either extreme of the Paschen-Back transition: in the strong-field case we have an expansion to the first order in the small quantity a/H and in the weak field case an expansion to the first order in the small quantity H/a. The intermediate transition of the two levels with $M=L$ is described by the roots E of a quadratic secular equation of the form

$$E^2-(\alpha+\beta H)E+\gamma+\delta H+\epsilon H^2=0.\quad(8)$$

The sum of the last three terms, which do not contain E, is the product of the two roots. The central term δH is determined by the first-order expansion of the roots in either extreme case: using the strong-field energies listed in Table III, we find

$$\delta/\mu_B=L(C_{L-1}+d_{L-1})-2(L+1)d_L$$

and using the weak-field energies we find

$$\begin{aligned}\delta/\mu_B=\{&L(L+2)(C_{L-1}+d_{L-1})\\ &-(L-1)C_L-(2L^2+5L-1)d_L\}/(L+1).\end{aligned}$$

Since the C's are physically independent of the d's, this double determination of δ yields the two relations

$$\begin{aligned}C_{L-1}&=[(L-1)/L]C_L\\ d_{L-1}&=[(L-3)/L]d_L.\end{aligned}\quad(9)$$

Similarly, the cubic equation for the three levels with $M=L-1$ contains a coefficient of E which is equal to the sum of the products of the roots taken two at a time, and the double determination of the term which is linear in H furnishes two additional relations which, by use of (9), reduce to

$$\begin{aligned}C_{L-2}&=[(L-2)/L]C_L\\ d_{L-2}&=[(2L^2-13L+12)/L(2L-1)]d_L.\end{aligned}\quad(10)$$

By use of these relations the triplet energies in the seventh column of Table III may be written in terms of the two integrals C_L and d_L, which we now call simply C and d:

$$\begin{aligned}E_{L+1}&=C+d\\ E_L&=-(1/L)C-[(2L+3)/L]d\\ E_{L-1}&=-[(L+1)/L]C\\ &\quad+[(2L+3)(L+1)/L(2L-1)]d.\end{aligned}\quad(11)$$

For $L=1$, the separations of these levels are of course the same as Breit's result (3). For $L=2$ they are compatible with Table II, and the ratios of the spin-spin terms are not affected by the greater generality. For any value of L, the 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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[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.*