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SOME RELATIONSHIPS BETWEEN SINGLETS AND TRIPLETS IN THE SPECTRA OF TWO ELECTRON SYSTEMS

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Abstract

The Darwin-Pauli treatment of the electron is applied to the Schroedinger equation for a two electron system. The results show that the division into singlets and triplets is justified only as a limiting case. Expressions are derived which give the position of the levels, the Zeeman effect pattern, and the intensities of the lines when the division into singlet and triplet cannot strictly be made. These expressions are shown to give the observed facts of several spectra.

THE work of Heisenberg[1] on resonance in quantum mechanics has made it possible, in principle, to calculate the spectrum of any complex atom. The difficulties involved are the purely mathematical ones of finding the solutions of the Schroedinger equation. There will be given here some results which show the amount of information which can be secured from a simple perturbation calculation.

The problem treated is that of two electrons in an arbitrary central field, with the restriction that one electron is in an s orbit. By the use of the Darwin-Pauli[2] treatment of the "spinning electron" it is possible to determine the energy levels with and without a magnetic field, in the first approximation. The levels without the field show to what extent a division into a singlet and a triplet system is justified, while the levels with the field show the deviations from the Landé g-formula which are to be expected. The calculated transition probabilities then show that the observed intensity of the intercombination lines is usually due to the metastability of the upper level.

1. *The Schroedinger equation.* The characteristic functions of the problem will be functions of four independent variables for each electron. There are the three space coordinates of the electron and the "spin" variable. These functions, in the zero approximation, may be written in the usual way as products of four functions of one variable only. The function of the coordinates is $R_{ln}P_l^m$, where R is a function of the radius only, and P is a spherical harmonic defined by

[1] W. Heisenberg, Zeits. f. Physik **38,** 411 (1926).

[2] Pauli, Zeits. f. Physik **43,** 624 (1927); Darwin, Proc. Roy. Soc. **A116,** 227 (1927).

$$P_l^m=(l-m)!\,\sin^m\theta\left(\frac{d}{d\cos\theta}\right)^{l+m}\frac{(-\sin^2\theta)^l}{2^l l!}e^{im\phi} \tag{1}$$

n, l, and m are the quantum integers and satisfy the conditions $l<n$, $-l\leqq m\leqq l$. The function S of the spin variable is peculiar in that the variable itself is discontinuous and can take only two values which we may designate by subscripts S_α and S_β. The function $|S_\alpha|^2$ represents the probability that the moment of the electron is parallel to the field, while $|S_\beta|^2$ represents the probability that the electron is pointing in the opposite direction. The normalization is given by

$$|S_\alpha|^2+|S_\beta|^2=1 \tag{2}$$

In a strong magnetic field, with a given energy, either S_α or S_β is equal to one and the other is zero. It is this function for a strong magnetic field which is to be used here, since the total function is written as a sum of products of the independent coordinate and spin functions.

The Hamiltonian function as an operator may be written in three parts so that

$$H\psi=H^0\psi+H'\psi+H''\psi=E\psi \tag{3}$$

where H^0 includes the ordinary kinetic and potential energy with relativity, in the central field. H' is the electrostatic interaction of the two electrons, i.e.,

$$H'=e^2/r_{12} \tag{4}$$

while

$$H''=\frac{h^2}{16\pi^2}\frac{Ze^2}{m_0^2c^2}\frac{1}{i}\sum_{j=1,2}\frac{1}{rj^3}(k\cdot s)_j+\mu\sum_{j=1,2}\left\{(\mathcal{H}\cdot s)_j-(\mathcal{H}\cdot k)_j\right\} \tag{5}$$

The subscripts $_1$ and $_2$ indicate that the operation is to be carried out on the coordinates of the first or second electron only. The components of k are

$$k_x=y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\,;\qquad k_y=z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\,;\qquad k_z=x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x} \tag{6}$$

and

$$\mu=\frac{eh}{4\pi m_0c}\,.$$

s is a vector operator which operates on S only and is defined by the relations

$$\begin{aligned} s_xS_\alpha&=S_\beta & s_xS_\beta&=S_\alpha\\ s_yS_\alpha&=iS_\beta & s_yS_\beta&=-iS_\alpha\\ s_zS_\alpha&=S_\alpha & s_zS_\beta&=-S_\beta. \end{aligned} \tag{7}$$

This Hamiltonian neglects the magnetic interaction between the two electrons and between each electron and the orbit of the other. These, however, are quantities of the order $1/Z$ compared with H'', so that for elements of high atomic number their effect should be small. The Z here is not, of course, the true atomic number, but is the atomic number which is effective for the multiplet separation.

2. *The secular equation.* The results of the perturbation H' are known from Heisenberg's[1] work on helium. The characteristic functions of the space coordinates divide into two groups, symmetric and antisymmetric in the two electrons. The energy levels corresponding to these two groups differ by

$$\gamma X = \int H' R_{0n'} P_0^0(1) R_{ln} P_l^m(2) R_{0n'} P_0^0(2) R_{ln} P_l^m(1) d\tau \tag{8}$$

where we define γ by

$$\gamma = \frac{h^2}{16\pi^2} \frac{Ze^2}{m_0^2 c^2} \int R_{ln}^2 \frac{1}{r^3} d\tau$$

With each of these functions may be combined the four possible spin functions. Of the eight groups of functions which result, only the four which are antisymmetric in the two electrons are permitted. Because of this known effect of the perturbation H', it is convenient to take as the functions of the unperturbed system the four functions:

$$\begin{aligned}
\phi_1 &= (1/2)\left\{P_0^0(1)P_l^m(2)+P_0^0(2)P_l^m(1)\right\}\left\{S_\alpha(1)S_\beta(2)-S_\beta(1)S_\alpha(2)\right\}\\
\phi_2 &= (1/2^{1/2})\left\{P_0^0(1)P_l^{m-1}(2)-P_0^0(2)P_l^{m-1}(1)\right\}S_\alpha(1)S_\alpha(2)\\
\phi_3 &= (1/2)\left\{P_0^0(1)P_l^m(2)-P_0^0(2)P_l^m(1)\right\}\left\{S_\alpha(1)S_\beta(2)+S_\beta(1)S_\alpha(2)\right\}\\
\phi_4 &= (1/2^{1/2})\left\{P_0^0(1)P_l^{m+1}(2)-P_0^0(2)P_l^{m+1}(1)\right\}S_\beta(1)S_\beta(2).
\end{aligned} \tag{9}$$

The radial function which is common to all four is not written. The zero approximation for the perturbed system is given by a linear combination of these four

$$\psi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + a_4\phi_4 \tag{10}$$

The secular equation may then be written as the determinant[3]

$$\begin{vmatrix}
X+\omega m-\epsilon & 1 & -m & 1\\
1 & 2\dfrac{\omega(m+1)+m-1-\epsilon}{(l+m)(l-m+1)} & 1 & 0\\
-m & 1 & \omega m-\epsilon & -1\\
1 & 0 & -1 & 2\dfrac{\omega(m-1)-m-1-\epsilon}{(l-m)(l+m+1)}
\end{vmatrix} = 0 \tag{11}$$

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[3] This determinant is not in its original form. The original form may be obtained by multiplying the second row and second column by $-(1/2^{1/2})(l+m)^{1/2}(l-m+1)^{1/2}$ and the fourth row and fourth column by $(1/2^{1/2})\,(l-m)^{1/2}(l+m+1)^{1/2}$.

where $\omega=\mu/\gamma$ and $\gamma\epsilon=\Delta E$. This really represents a selection of four functions out of all those having the same energy on account of the degeneracy in m. However if the secular equation is written for all the functions with the same value of l, the determinant can be divided into a number of determinants such as (11).

When ω^2 and higher powers are neglected the roots of this equation are

$$\begin{aligned}
\epsilon_1&=\frac{1}{2}(X-1)+\frac{1}{2}\left\{(X+1)^2+4l^2+4l\right\}^{1/2}+\omega m\left\{1+\frac{[(X+1)^2+4l^2+4l]^{1/2}-X-1}{2(l^2+l)[(X+1)^2+4l^2+4l]^{1/2}}\right\}\\
\epsilon_2&=l+\omega m\frac{l+2}{l+1}\\
\epsilon_3&=\frac{1}{2}(X-1)-\frac{1}{2}\left\{(X+1)^2+4l^2+4l\right\}^{1/2}+\omega m\left\{1+\frac{[(X+1)^2+4l^2+4l]^{1/2}+X+1}{2(l^2+l)[(X+1)^2+4l^2+4l]^{1/2}}\right\}\\
\epsilon_4&=-l-1+\omega m\frac{l-1}{l}\cdot
\end{aligned} \tag{12}$$

3. *The interval rule.* The roots in (12) give the interval rule for triplets, for when $|X|\gg l$ and $\omega=0$

$$\epsilon_1=X\,;\quad \epsilon_2=l\,;\quad \epsilon_3=-1\,;\quad \epsilon_4=-l-1 \tag{13}$$

so that the last three form the triplet with the interval ratio $(l+1)/l$. However, when X is not so large the interval ratio is different and is a function of X. The singlet level, ϵ_1 and the center triplet level, ϵ_3 which has the same inner quantum number, are given by

$$\epsilon_{1,3}=\tfrac{1}{2}(X-1)\pm\tfrac{1}{2}\left\{(X+1)^2+4l^2+4l\right\}^{1/2} \tag{14}$$

Thus as X decreases the center triplet level ϵ_3 moves downward; for $X=0$, ϵ_1 and ϵ_3 coincide with the two outer triplet levels ϵ_2 and ϵ_4; while for $X\rightarrow-\infty$, ϵ_1 has become the center triplet level and ϵ_3 is the singlet level. Thus the division into singlet and triplet has a meaning only when $|X|\gg l$.[4]

Because of the terms neglected in the Hamiltonian function, and because this is only the first approximation for the terms considered, it cannot be expected that Eq. (12) will exactly represent the observations. Table I shows, however, that in a number of representative cases the observations are pretty well given. In this table are given the values of the singlet and triplet terms measured from a zero between the two outer triplet terms. This zero is determined from the values of ϵ_2 and ϵ_4 in Eq. (13). From the values of the two outer triplet levels and the singlet level the third triplet level is determined from the two relations:

$$(\epsilon_1+1)(\epsilon_3+1)=-(l^2+l) \tag{15}$$

$$\epsilon_2-\epsilon_4=2l+1 \tag{16}$$

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[4] Dingle, Proc. Roy. Soc. **A100**, 167 (1922), recognized this in treating mercury as a quartette system.

The last column gives the position of the inner triplet level determined from the usual interval rule.

TABLE I.

Terms	$\gamma\epsilon_1$	$\gamma\epsilon_2$	$\gamma\epsilon_4$	$\gamma\epsilon_3$ obs.	$\gamma\epsilon_3$ calc.	$\gamma\epsilon_3$ norm.
N II P	167	56	−112	−80	−84	−56
N II P	1204	57	−114	−62	−62	−57
N II P	500	58	−115	−68	−70	−58
O III P	5447	125	−250	−132	−130	−125
Si I P	1127	91	−181	−104	−105	−91
Ge I P	1425	522	−1044	−894	−801	−522
Sn I P	1957	1329	−2658	−2385	−2405	−1329
Pb I P	4119	3494	−6988	−6662	−6708	−3494
Cd $1P$	12435	571	−1142	−600	−621	−571
Cd $2P$	1597	82	−163	−92	−90	−82
Cd $1D$	−275	12	−18	−6	−5	−6
Cd $2D$	−228	6	−9	−2	−3	−3
Hg $1P$	12158	2133	−4266	−2498	−2769	−2133
Hg $2P$	649	564	−1127	−979	−1088	−564
Hg $1D$	−60	38	−57	3	34	−19
Hg $2D$	−47	18	−27	−4	4	−9
Hg $3D$	−32	10	−15	−3	5	−5

In the D terms of Cd and Hg the singlet level is below the triplet level. The agreement for these terms in Hg is not very good but the results are qualitatively correct. A more exact treatment of these levels could be given by considering the whole Hamiltonian function, but the part treated here is enough to show the nature of the connection between the singlet and triplet systems.

4. *The Zeeman effect.* The connection between the singlets and triplets is also shown by the Zeeman effect. Eq. (12) shows that when X is large the Landé g-factor[5] gives the separation of the levels in a weak magnetic field. But as X decreases and passes through zero to a large negative value, the singlet level becomes the center triplet level not only with respect to its position, but also with regard to its Zeeman effect. The two outer triplet levels are independent of X with regard to the Zeeman effect as well as with regard to position.

TABLE II

Term	g observed	g from Eq. (12)	g normal
Sn $^1P_1$	1.125	1.123	1.000
Sn $^3P_1$	1.375	1.377	1.500
Pb $^1P_1$	1.150	1.148	1.000
Pb $^3P_1$	1.350	1.352	1.500

Table II gives the observed and calculated g values for tin and lead. The agreement in these cases is very satisfactory. Exact measurements on Cd and Hg do not seem to be available.[6]

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[5] A. Landé, Zeits. f. Physik **15**, 189 (1923).

[6] The observed values are taken from a paper by Goudsmit and Back, Zeits. f. Physik **40**, 530 (1927) in which the limiting cases X large and $X=0$ are discussed.

According to the Landé formula the sum of the g factors of the three members of a triplet is equal to three, and hence if the singlet term is included the sum of the four values is equal to four. Eq. (12) shows that this sum rule is true only when the singlet is included.

5. *Intensities.* After the roots of Eq. (12) are known it is possible to determine the coefficients a_1, a_2, a_3, and a_4. These may be written

$$a_1=\frac{(m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)}{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)}a_3$$

$$a_2=\frac{1}{(2^{1/2})}\,\frac{(l+m)^{1/2}(l-m+1)^{1/2}}{(m-1-\epsilon)}\,\frac{\{(X+2m-2\epsilon)(m+1+\epsilon)+2(l-m)(l+m+1)\}}{\{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)\}}a_3$$

$$a_4=-\frac{1}{(2^{1/2})}\,\frac{(l-m)^{1/2}(l+m+1)^{1/2}X}{\{(X+m-\epsilon)(m+1+\epsilon)+(l-m)(l+m+1)\}}a_3 \tag{17}$$

a_3 is determined from the normalizing relation

$$a_1^2+a_2^2+a_3^2+a_4^2=1.$$

These are for the case $\omega=0$, so they hold for weak fields only.

Table III gives the values of the squares of the amplitudes of the oscillators which represent the transitions. It is simpler to express them in terms of ϵ_1 than in terms of X although this assumes that ϵ_1 is exactly given by Eq. (12). The intensities may be obtained by multiplying by the fourth power of the frequency. The sum rules are seen to hold for all values of X provided the singlet and triplet are considered as forming one system[7] but they hold for these squared amplitudes rather than for the intensities or the transition probabilities.

Here again it is only the two levels with the same inner quantum number which are affected and jumps between the other levels are unaffected. The amplitude squared for the intercombinations between singlets and triplets is roughly inversely proportional to the square of the separation between singlet and triplet systems.[8] The observed intensity of the resonance line in helium and in the alkaline earths is much greater than this.[9] This is due to the fact that the upper level in these cases is metastable except for this transition which has a low probability. The accumulation of atoms in this partly metastable state then makes up for the low transition probability and the line appears with some intensity. This intensity in emission should then decrease with an increase in pressure.

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[7] Kronig, Zeits. f. Physik **33,** 261 (1925) expected the sum rules to include both systems. Ornstein and Burger, Zeits. f. Physik **40,** 403 (1926) showed this experimentally for mercury. The observed values in Table IV are from this work.

[8] See also W. Pauli, Handbuch der Physik, XXIII.

[9] The observations of W. Prokofjew, Zeits. f. Physik **50,** 701 (1928) on the transition probabilities as determined from the anomalous dispersion are in good agreement with the predictions of Table III.

TABLE III

$L=L$ $L=L-1$	ϵ_1 $\quad {}^1L_l$	ϵ_4 $\quad {}^3L_{l-1}$	ϵ_3 $\quad {}^3L_l$	ϵ_2 $\quad {}^3L_{l+1}$	Sum
ϵ'_2 ${}^3(L-1)_l$	$\dfrac{(2l+1)(2l-1)(l+1)}{(\epsilon_1+1)^2+l^2+l}$	$\dfrac{1}{l}$	$\dfrac{(2l+1)(2l-1)(\epsilon_1+1)^2}{l\{(\epsilon_1+1)^2+l^2+l\}}$	$(2l+3)(2l-1)l$	$(2l+1)(2l+1)l$
ϵ'_3 ${}^3(L-1)_{l-1}$	$\dfrac{(2l+1)(2l-1)(l-1)\{(\epsilon_1'+1)(l+1)-l(\epsilon_1+1)\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon_1'+1)^2+l^2-l\}}$	$\dfrac{(2l+1)(2l-1)(\epsilon_1'+1)^2}{l\{(\epsilon_1'+1)^2+l^2-l\}}$	$\dfrac{(2l+1)(2l-1)(l^2-1)\{(\epsilon_1+1)(\epsilon_1'+1)+l^2\}^2}{l\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon_1'+1)^2+l^2-l\}}$		$(2l-1)(2l+1)l$
ϵ'_4 ${}^3(L-1)_{l-2}$		$(2l+1)(2l-3)l$			$(2l-3)(2l+1)l$
ϵ_1' ${}^1(L-1)_{l-1}$	$\dfrac{(2l+1)(2l-1)l\{(\epsilon_1+1)(\epsilon_1'+1)+l^2-1\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{(\epsilon'_1+1)^2+l^2-l\}}$	$\dfrac{(2l+1)(2l-1)(l-1)}{(\epsilon_1'+1)^2+l^2-l}$	$\dfrac{(2l+1)(2l-1)(l+1)\{(\epsilon_1+1)(l-1)-(\epsilon_1'+1)l\}^2}{\{(\epsilon_1+1)^2+l^2+l\}\{\epsilon_1'+1)^2+l^2-l\}}$		$(2l-1)(2l+1)l$
Sum	$(2l+1)(2l-1)l$	$(2l-1)(2l-1)l$	$(2l+1)(2l-1)l$	$(2l+3)(2l-1)l$	

Table IV gives the observed and calculated intensities for a group of mercury lines. This table illustrates the applicability of the expressions in Table III for cases where a division into singlet and triplet is rather arbitrary. The intensities in the second column are calculated for a large separation between singlet and triplets, while those in the fourth column are calculated by Table III.

Table IV.

Hg line	Int. ($X \rightarrow \infty$)	Int. Obs.	Table III
3650	100	100	100
3655	17.9	10.8	10.8
3663	1.2	7.9	1.2
3663	0.		7.0

The proper value of X to use in the computations of Table IV is a bit uncertain due to the lack of exactness in the fit of Eq. (12). The value used is the mean of those determined from ϵ_1 and ϵ_2.

6. These calculations show the rather surprising amount of information which may be derived from a first approximation calculation with the Darwin-Pauli method of treating the electron. It is hoped soon to extend this to more complex systems and especially to remove the restriction that one electron must be in an *s* orbit.

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