PERTURBATIONS IN THE CA I SPECTRUM

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PROEFSCHRIFT TER VERKRIJGING VAN DEN
GRAAD VAN DOCTOR IN DE WIS- EN
NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DEN
RECTOR MAGNIFICUS DR J. A. J. BARGE,
HOOGLEERAAR IN DE FACULTEIT DER
GENEESKUNDE, VOOR DE FACULTEIT DER
WIS- EN NATUURKUNDE TE VERDEDIGEN
OP DONDERDAG 20 JANUARI 1938, DES
NAMIDDAGS TE 4 UUR, DOOR

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AAN HEN DIE MIJN STUDIE MOGELIJK GEMAAKT HEBBEN

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CONTENTS.

INTRODUCTION.

We have tried to explain the anomalous behaviour of the relative positions of singlet and triplet in the D-series of the Ca I spectrum. In the simple theory, described in the §§ 1 and 2 the distance between singlet and triplet is given by two times the exchange integral. In general we may expect this integral to have a positive sign, while to explain the observed positions in the D-series it would have to be alternatingly positive and negative. We have tried to account for this anomaly by investigating the perturbations of levels of othter configurations, viz. the ^1D levels of the $3d^2$ and the $4p^2$ configurations.

First, however, we discuss in § 3 the effect of perturbations of the D-series of Mg and Cd which are of a simpler type and where in this way the anomalous position of the singlet relative to the triplet can be explained. In § 4 we discuss on the basis of Russell and Shenstone's considerations on this subject the general effect of perturbations in the Ca I spectrum.

In § 5 we will see that our numerical calculations give a positive sign for the exchange integral for the whole D-series of Ca I. In § 6 we then calculate with a rough appoximation for the wave functions of the $3d^2$ and the $4p^2$ configurations the effect of the perturbations. The resulting displacements for the levels were much too large.

In § 7 we discuss the cause of this disagreement. The positions of the perturbing levels are not experimentally known, but were calculated theoretically from the positions of the ^3P levels of the same configurations. We first try to get agreement with experiment by only varying these positions. This, however, proves to be impossible. But, with a position of the ^1D level of the $4p^2$ configuration calculated semi-empirically from the positions of the ^3P level and of the probable ^1S level of this configuration and with altered values for the matrix elements, it is possible to get agreement for the members of the series from $4s\ 4d$ onwards. Agreement for the $4s\ 3d$ level is not obtained in this way, but a probable reason for this is given. In § 8 we discuss the anomalies in the *S*-series.

In §§ 9, 10 and 11 we give more in detail the calculation of the wave functions, of the perturbation matrices and of the matrix elements.

The circumstance mentioned above that the matrix elements had to be changed could theoretically be traced back to the fact that the one electron wave functions in the p^2 and d^2 configurations certainly cannot be the same as in the $4s\ 4p$ and the $4s\ 3d$ configurations, as had originally been assumed. This is discussed in § 12.

Although we have not succeeded in calculating the modified wave functions with the precision required for our problem, it can hardly be doubted that the experimentally observed positions of singlet and triplet in the *D*-series of Ca can be interpreted as a perturbation from the $4p^2$ and the $3d^2$ configurations.

CHAPTER I.

THE SPECTRUM OF AN ATOM WITH TWO VALENCE ELECTRONS.

§ 1. *Theory of an atom with two valence electrons.*

In the following we shall consider the energy states that may exist in an atom with two valence electrons, when these electrons are excited. We neglect the influence of the valence electrons on the completed inner shells. The valence electrons then will move in the electric field, given by the nucleus and the inner shells, which field may be represented by a central field with potential energy *V(r)*. The wave equation for the valence electrons becomes then, when we use Hartree's atomic units

$$\Delta_1 \psi + \Delta_2 \psi + 2\left(E - V(r_1) - V(r_2) - \frac{1}{r_{1,2}}\right)\psi = 0, \tag{1}$$

where Δ_1 and Δ_2 are the Laplace operators in the space of the first and the second electron, $r_{1,2}$ is the distance between the electrons and $\psi(x_1 \ldots z_2)$ is a function of the six coordinates of both electrons, normalized to unity.

To get a first approximation of the wave functions, we omit the interaction between the electrons *); the problem then can be separated and represented by the product

$$\varphi_1(x_1, y_1, z_1) \, . \, \varphi_2(x_2, y_2, z_2)$$

of the wave functions of the two independent electrons, φ_1

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*) In reality the interaction between the valence electrons is already to some extend implied in $V(r_1)$ and $V(r_2)$ (these two functions need not even be the same) but this is not of any importance for the following. For more particulars about this see 2).

and φ_2 being normalized to unity and satisfying an equation of the form

$$\Delta \varphi_a + 2(E - V(r))\varphi_a = 0.$$

We can write the solution of this equation in the form

$$\varphi_a = \frac{R_a(r_a)}{r_a} Y_{lm}(\vartheta_a, \varphi_a), \tag{2}$$

where R_a depends only on the distance r_a of the electron A from the nucleus and $Y_{lm}(\vartheta_a, \varphi_a)$ is a normalized spherical harmonic ($l = 0,1,2,\ldots$; $m \leq l$). The quantum number of the angular momentum of the electron is given by l and of its component in the direction of the z-axis by m. When l has the values $0,1,2,\ldots.$ we say that the electron is in an $s,p,d,\ldots.$ state.

Until now we have not introduced the spin of the electron. This may be done, when we neglect the interaction between spin and orbit, by multiplying the orbital part of the wave function with a function of the spin only. We will call this function u when the direction of the spin is parallel, and v when it is anti-parallel to the z-axis.

Now the product $\psi_1(x_1\,.)\cdot\psi_2(x_2\,.)$ of the wave functions of the electrons inclusive of the spin is not yet a true wave function as this has to be anti-symmetrical in the coordinates of orbit and spin of both electrons. The real normalized wave functions become

$$\frac{1}{\sqrt{2}}\Big(\psi_1(x_1\ldots.)\cdot\psi_2(x_2\ldots.) - \psi_2(x_1\ldots.)\,\psi_1(x_2\ldots.)\Big),$$

$\psi_1(x_1\,.)$ being the wave function, with the spin, of the first electron.

The ground state of the atom is when both electrons are in the lowest possible s-state. We get the normal term series when one of the electrons remains in this state, while the other is excited to a higher state. When this electron is in an $s,p,d,\ldots$ state, then the resulting angular momentum for the orbital motion of the electrons L is also $0,1,2,\ldots.$ and the atom is in an $S,P,D,\ldots$ state. As regards to the spins, there are still two possibilities. They may be parallel; in this case the resulting spinmoment is 1, the state is a triplet, as there are three possible values for the resulting total impulsmoment J. The other possibility is that they are anti-parallel; then the resulting spinmoment is 0, and we get a singlet.

The other, so called anomalous terms, arise when both electrons are excited. When one of them has the orbital impusmoment l_1 and the other l_2, then the resulting impulsmoment can have the values $l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$. For the spins there are in general the same possibilities as above, so that we have a triplet and a singlet state for every value of L. The only exception is in the case of two equivalent states; then Pauli's principle limits the number of possibilities.

In the case of the normal terms we can easily find the wave functions belonging to singlet and triplet states. We have seen that the wave function as a whole has to be anti-symmetrical. Now the wave function is a product of a part depending on the orbit only and a part depending on the spin only. An anti-symmetrical wave function may arise from a symmetrical orbital part combined with an anti-symmetrical part from the spin, or from an anti-symmetrical part from the orbit and a symmetrical from the spin. For the spin, there are possible one anti-symmetrical function $\frac{1}{\sqrt{2}}\left(u(1)v(2)-v(1)u(2)\right)$ and three symmetrical ones $u(1)\,u(2)$, $v(1)\,v(2)$, and $\frac{1}{\sqrt{2}}\left(u(1)\,v(2)+v(1)\,u(2)\right)$ so that we get for the four possible wave functions

$$\left.\begin{array}{l} \frac{1}{\sqrt{2}}\left(\varphi_1(1)\,\varphi_2(2)+\varphi_2(1)\,\varphi_1(2)\right).\ \frac{1}{\sqrt{2}}\left(u(1)\,v(2)-v(1)\,u(2)\right) \\ \text{and} \\ \frac{1}{\sqrt{2}}\left(\varphi_1(1)\,\varphi_2(2)-\varphi_2(1)\,\varphi_1(2)\right).\left\{\begin{array}{l} u(1)\,u(2) \\ v(1)\,v(2) \\ \frac{1}{\sqrt{2}}\left(u(1)\,v(2)+v(1)\,u(2)\right). \end{array}\right. \end{array}\right\} \quad (3)$$

The three wave functions that come last belong to the triplet state and it is seen directly that they have the same energy, as the energy operator in our appoximation only contains the orbital coordinates and the only difference in these functions is in the part, which does not contain these coordinates.

In the case of the anomalous terms it is not so simple to write down the wave functions 1). According to what was said above we can directly write down wave functions which give a definite value of M_l, as this is the sum of the values of m_l for each electron; the same holds also for M_s. But in general several combinations of two m_l values give the same value for M_l, corresponding to the fact that for all states with $L \geqq M_l$ one component of the multiplet has this same M_l value. The wave functions with this same value for M_l will give an energy matrix which is not yet a diagonal matrix. To diagonalize it we have to transform from the wave functions of the M_l -space to the L-space; the new wave functions are linear combinations of the original ones, each belonging to a definite value of L.

§ 2. *Energy difference between singlet and triplet.*

We will now calculate the energy difference between singlet and triplet term belonging to the same member of the normal series 2). The only energy difference can come from the term $\frac{1}{r_{1,2}}$ in the energy operator which alone contains the coordinates of both electrons. As the spin functions are normalized to unity, we get for the energy of the singlet state of the part $\frac{1}{r_{1,2}}$ of the energy operator *)

$$\int \frac{1}{r_{1,2}} \cdot |\varphi_1(1)|^2 \cdot |\varphi_2(2)|^2 \, d\tau_1 \, d\tau_2 + \int \overset{*}{\varphi_1}(1) \, \overset{*}{\varphi_2}(2) \frac{1}{r_{1,2}} \varphi_2(1) \, \varphi_1(2) \, d\tau_1 \, d\tau_2$$

while for the triplet state

$$\int \frac{1}{r_{1,2}} \cdot |\varphi_1(1)|^2 \cdot |\varphi_2(2)|^2 \, d\tau_1 \, d\tau_2 - \int \overset{*}{\varphi_1}(1) \, \overset{*}{\varphi_2}(2) \frac{1}{r_{1,2}} \varphi_2(1) \, \varphi_1(2) \, d\tau_1 \, d\tau_2,$$

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*) When $r_{1,2}$ is given in Hartree's atomic units, this formula gives also the energy in these units. In all the following formulae we have made use of these units.

where $d\tau_1$ and $d\tau_2$ are the elements of volume in the space of the first and the second electron. From this follows for the difference in energy between singlet and triplet the expression

$$2 \int \overset{*}{\varphi_1}(1)\, \overset{*}{\varphi_2}(2)\, \frac{1}{r_{1,2}}\, \varphi_2(1)\, \varphi_1(2)\, d\tau_1\, d\tau_2 = 2K, \tag{4}$$

where K is called the exchange integral.

We now will integrate K over the angular variables. To this end we recall that according to § 1 (2), we may put for the wave functions

$$\varphi_1 = \frac{R_1(r)}{r}\, Y_{oo}(\vartheta, \varphi),$$

$$\varphi_2 = \frac{R_2(r)}{r}\, Y_{lm}(\vartheta, \varphi).$$

We develop $1/r_{1,2}$ in spherical harmonics, which gives

$$\frac{1}{r_{1,2}} = \frac{1}{r_a} \sum_{l'} \left(\frac{r_b}{r_a}\right)^{l'} \sum_m \frac{4\pi}{2l'+1}\, Y^*_{l'm}(\vartheta_1\, \varphi_1)\, Y_{l'm}(\vartheta_2, \varphi_2),\ (r_a > r_b).$$

On substituting this, we get, after integration over the angular variables,

$$K = \frac{2}{2l+1} \int_0^\infty r_1^{\,l}\, R_1(r_1)\, R_2(r_1)\, dr_1 \int_0^\infty \frac{1}{r_2^{\,l+1}}\, R_1(r_2)\, R_2(r_2)\, dr_2. \tag{5}$$

The factor two proceeds from the fact that we have written down only the integral for $r_1 < r_2$, and the part for $r_1 > r_2$ gives once more the same value.

Whether the singlet lies above or below the triplet depends on the sign of K. Now it can be shown [3]) that, when we have a wave function, which is not wholly and improbably different from a hydrogen function, we may expect K to be positive. The way of reasoning to make this probable may be indicated as follows: The only way in which the integrand of the second integral can be negative is, when in the first integration the sign of the integrand in a given point is different from the sign of the integral up to that point. Coming from infinity at first the integrand does not differ markedly from 0, then, when we get a perceptible value, integral and integrand will have the same sign, till we come to the first node. When we have passed this point, at first this will not be the case. As the integrand contains the product of two different wave functions one possibility is that their nodes do not lie in the same region. Then, as the maximum value of the product before and after the node will be of the same order of magnitude, the integrand will increase rapidly in absolute value owing to the negative power of r in the denominator; the integral then decreases rapidly, till again integral and integrand have the same sign. We expect, owing to the rapid decrease of the integral, that this negative part will be smaller than the preceding positive part. When the nodes of both wave functions lie in about the same region, the negative part of the integrand, which lies between them, cannot take on a considerable value. As the same reasoning holds for their next nodes we expect that the whole integral will take a positive value. This would have as consequence that singlet lies above the triplet. Experimentally this is very often the case, but numerous exceptions occur.

The first possibility for an explanation of these exceptions would be to see, whether interaction with the inner closed shells can alter the energy difference between singlet and triplet.

Slater[1]) has shown that an interaction of this kind does not have this effect. To see this we have to bear in mind that in reality we have a wave function depending on the coordinates of all n electrons. This wave function can approximately be written as a Slater-determinant of the wave functions of the separate electrons. For the singlet we find for this function, when we have developed in the elements of two columns

$$ {}^{1}\Phi = \frac{1}{n!\sqrt{2}} \sum_{a,b} (a,b) \left\{ \psi(a)\chi(b) + \chi(a)\psi(b) \right\} \left\{ u(a)v(b) - v(a)u(b) \right\} $$

and for one of the components of the triplet term in the same way

$$ {}^{3}\Phi = \frac{1}{n!} \sum_{a,b} (a,b) \left\{ \psi(a)\chi(b) - \chi(a)\psi(b) \right\} u(a)\,u(b), $$

where the summation has to be taken over all possible combinations of a and b, for $a < b$; (a,b) denotes the Slater-determinant for $(n-2)$ inner electrons that does not contain the coordinates of electron a and electron b; ψ and χ are the wave functions for the outer electrons. We now write down the expectancy values of $1/r_{pq}$. This is, in the case of the singlet a sum of the integrals of expressions of the form

$$\frac{1}{r_{p,q}} \cdot (a,b). \} \psi(a)\, \chi(b) + \chi(a)\, \psi(b) \{ \} u(a)\, v(b) - v(a)\, u(b) \{.$$
$$(c,d). \} \psi(c)\, \chi(d) + \chi(c)\, \psi(d) \{ \} u(c)\, v(d) - v(c)\, u(d) \{,$$

and in case of the triplet

$$\frac{1}{r_{p,q}} (a,b). \} \psi(\mathrm{a})\, \chi(b) - \chi(a)\, \psi(b) \{ u(a)\, u(b).$$
$$(c,d). \} \psi(c)\, \chi(d) - \chi(c)\, \psi(d) \{ u(c)\, u(d).$$

As may be easily seen, this gives a result differing for singlet and triplet only in the case of $a=c=p$ and $b=d=q$ and the sum of these expressions just gives the energy difference between singlet and triplet, as we have calculated it above without taking into account the interaction with the inner shells.

The other possibility is that the anomalous position of the singlet relative to the triplet is caused by a perturbation of one or both levels [3]).

Two states, the eigenfunctions of which in first approximation are represented in the way described above by means of one one-particle wave function for each electron, perturb each other when the energy matrix belonging to these states is not a diagonal matrix. When the wave functions of the two states are φ_1 and φ_2 the true wave functions may be written in the form $\psi = a\, \varphi_1 + b\, \varphi_2$. The constants are given by the equations

$$(H_{11} - E)\, a + H_{12}\, b = o$$
$$H_{21}\, a + (H_{22} - E)\, b = o$$

where $H_{ab} = \int \varphi_a\, H_{op}\, \varphi_b\, d\tau$, when H_{op} is the energy operator, and E is the energy of the perturbed state. These equations only have a solution when

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = o$$

From this equation we can determine E, for which we find two values, $E = \frac{H_{11} + H_{22}}{2} \pm \sqrt{\frac{(H_{11} - H_{22})^2}{4} + H^2_{12}}$. Each of these values gives us a set a,b and a corresponding ψ. When the perturbation is small each ψ may be described as the perturbed wave function of one of the states originally described by the φ-function. From the formulae follows easily that the perturbing states repel each other.

States can be characterized as odd or even from whether $\Sigma\, l$ is odd or even. Only states of the same parity can perturb each other, since the energy operator does not change after reflection with respect to the origin.

We have neglected the spin orbit coupling. Since in that case the operators **J**, **L** and **S** commute with the energy operator there can only be interaction between states with the same value for J, L and S.

A perturbation of a term, of one of the normal series (first approximation wave function φ_1) can in this way be caused by a term of an anomalous series (first approximation wave function φ_2). We have seen that generally a given configuration gives rise to both a triplet and a singlet term of a certain sort — in this case a relative displacement of singlet and triplet can be effected by a difference in their interaction with the foreign level and also the singlet-triplet splitting of the perturbing levels may be of influence. In the case of two equivalent electrons there exist only either a singlet or a triplet; in this case the perturbation affects only terms of one multiplicity; a marked change in the relative position of singlet and triplet terms of the normal series may be the result.

§ 3. *Perturbations of the D-series in Mg and Cd.*

The interaction with another configuration is used by Bacher[3]) to explain the anomalous relative position of the ^1D and ^3D-terms of Mg. In this case the singlet lies below the triplet for all the terms of the normal series. The Mg atom contains 12 electrons; 8 of them fill up the $1s$, $2s$ and $2p$ shell; the other two are, in the D-series, in a $3s$ and nd state *). The $3p^2$ configuration gives the lowest anomalous terms. This configuration contains a ^1D-term and no ^3D-term **) The ^1D-term is not known experimentally with certainty, but Bacher can calculate its position theoretically by means of the wave functions and the position of the ^3P-term, which is known. The other anomalous configurations will give terms, which lie much further away, so we may limit ourselves to the influence of the $3p^2$ configuration.

With the wave functions for the electrons in the $3s$ and $3d$ state Bacher first calculates the exchange integral for the $3s$ $3d$ state and finds indeed a positive value. He now calculates the position of the ^1D term of the $3p^2$ configuration and its interaction with the singlet term of the $3s$ $3d$ configuration. For this the wave functions of the ^1D and ^3P terms are required. As the $3p^2$ configuration contains only a ^1S, a ^3P and a ^1D term these wave functions can be written down directly, for we are sure that the wave function with $M_l = 2$, $M_s = 0$ represents the ^1D state, while the function with $M_l = 1$, $M_s = 1$ represents a ^3P state.

With these wave functions he finds for the expectancy value of the part $1/r_{1,2}$ of the energy operator, which alone gives rise to the energy difference between the ^3P and the ^1D states, after integrating over the angular coordinates,

$$R_d - \tfrac{1}{5} R_e = \text{energy of the } {}^3P\text{-state}$$

$$R_d + \tfrac{1}{25} R_e = \text{energy of the } {}^1D\text{-state},$$

and for the complete set of four matrix elements of $1/r_{1,2}$ corresponding to a transition between the ^1D states of the $3s$ $3d$ and the $3p^2$ configuration

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*) In accordance with the usual notation, the number preceding the letter indicating the value of l of the electron, gives the principal quantum number.

**) The suffixes 1 and 3 denote the multiplicity of the term.

$$\begin{array}{c|cc} & 3s\,3d & 3p^2 \\ \hline 3s\,3d & R_a - \frac{1}{5} R_b = H_{11} & +2\sqrt{\frac{1}{15}}\, R_c = H_{12} \\ 3p^2 & +2\sqrt{\frac{1}{15}}\, R_c = H_{21} & R_d + \frac{1}{25} R_e = H_{22}, \end{array} \qquad (6)$$

where

$$R_a = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_b} R_{3s}^{\ 2}(r_1)\, R_{3d}^{\ 2}(r_2);\ R_b = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_a^{\ 2}}{r_b^{\ 3}} R_{3s}(r_1)\, R_{3d}(r_1)\, .\, R_{3s}(r_2)\, R_{3d}(r_2);$$

$$R_d = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_b} R_{3p}^{\ 2}(r_1)\, R_{3p}^{\ 2}(r_2);\ R_e = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_a^{\ 2}}{r_b^{\ 3}} R_{3p}^{\ 2}(r_1)\, R_{3p}^{\ 2}(r_2);$$

$$R_c = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_a}{r_b^{\ 2}} R_{3s}(r_1)\, R_{3p}(r_1)\, R_{3d}(r_2)\, R_{3p}(r_2)$$

r_a is the smaller, r_b the larger of r_1 and r_2. When Bacher calculates the value of these integrals with his wave functions he finds: $R_b = 10190$ cm^{-1}, $R_e = 25620$ cm^{-1}, $R_e = 29940$ cm^{-1}. The value of R_e places the ^1D level at —3365 cm^{-1}, far above the ionization-potential. When he calculates the position of the levels after the perturbation he finds that the singlet lies about 4000 cm^{-1} below the triplet, whereas its actual position is only 1500 cm^{-1} below. On repeating his calculations with the same wave functions we found for R_e the value 21340 cm^{-1} instead. This places the singlet at 15992 cm^{-1}, which is 2280 cm^{-1} below the triplet; a much closer agreement.

Now we want to estimate the influence of this perturbation on the following members of the normal ^1D sequence. We can do this with fair accuracy, without calculating the matrix elements of $1/r_{1.2}$ with the wave functions corresponding to the electron configurations of these members. We may suppose, indeed, that the form of the wave functions is the same for all d-electrons in that particular region, which alone contributes appreciably to the matrix elements, this contribution coming from a region in the r-coordinate where we still have a reasonable magnitude of the wave function of the s-electron. In classical theory, this is that part of the orbit, which lies inside the orbit of the *s*-electron. The larger the principal quantum number, the better the supposition that this part is the same for different *d*-electrons will cover the truth. The probability of finding the *d*-electron at a distance from the nucleus smaller than the radius of the orbit of the *s*-electron equals the time the electron needs to travel along this part of its orbit in proportion to the time of revolution. As the former time is approximately the same for all the *d*-electrons, this probability will be proportional to the inverse of the time of revolution, which time is proportional to n^{*3},n^* being the effective quantum number defined as $n^* = \sqrt{R/T}$, where R is the Rydberg constant and T is the term value. On the other hand the probability of finding the electron in a given place is proportional to the square of the wave function, so that calling the wave function ψ_d we find $\psi_d \backsim n^{*-3/2}$. As the form of the wave function is the same in the region which contributes to the integrals R_b and R_c their values are only different because of the normalization; we find for them $R_b \backsim \psi_d^2 \backsim n^{*-3}$; $R_c \backsim \psi_d \backsim n^{*-3/2}$.

By means of these formulae we can calculate these integrals for the higher members of the n^1D series, when we know them for 3^1D. With these values we get the following positions of the perturbed levels, which are given in the following table

n	^1D (cal.)	$n\,^3D - n\,^1D$ (cal.)	$n\,^3D - n\,^1D$ (exp.)
3	15992	—2277	—1554
4	9641	—2102	—1058
5	6389	—1685	— 660
6	4534	—1305	— 420
7	3352	— 999	— 279
8	2521	— 781	— 193
9	2017	— 609	— 137
10	1624	— 488	— 99
11	1326	— 390	— 76
12	1103	— 319	— 61

(I)

All values in this table are given in cm^{-1}. The first column gives the principle quantum number for the d-electron, the second the position of the ^1D level as it has been calculated, the third and the fourth respectively the difference between singlet and triplet as following from the positions of the levels, as we have calculated them and as they are experi-

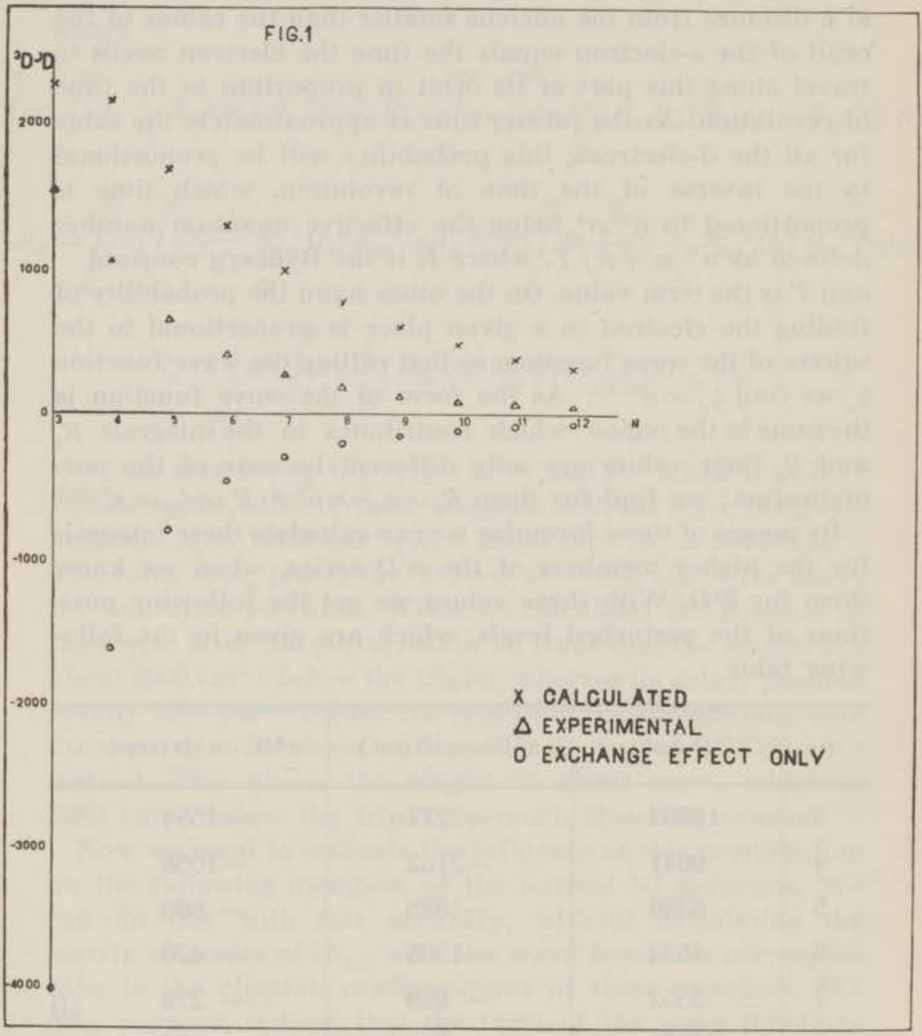

Fig. 1. The difference between ^3D and ^1D levels for the normal series of Mg.

mentally given *). Our results are also given in fig. 1. We have plotted for each state the difference between singlet and triplet as we have calculated it, as it is given by experiment and as the exchange integral would give it without perturbation. That the agreement is better for $n=3$, than for the following levels may easily be due to the fact that the method for obtaining the other matrix elements is a very rough one, especially as we start from a $3d$ electron, where our supposition regarding the similarity of different nd-wave functions will be worst fulfilled. The $3d$ function, which has no nodes, cannot be said to behave, for small r-values, in exactly the same way as all the following nd functions which do have nodes. This would mean that the above rough calculation gives us values that are too large when we deduce the matrix elements for the other members of the series from those for the $4s\ 3d$ state. For the exchange integral this would be more marked than for the matrix elements giving the interaction, as the first contains the nd function twice. The true distance between singlet and triplet would then be smaller than the calculated one, exactly what we need to get better agreement with experiment.

For the normal D-terms of Cd the singlet also lies below the triplet. In this case we have not made any numerical calculations but we have estimated the effect of a perturbation by the ^1D-term of the $5p^2$ configuration, which would also here be the principal source of a perturbation. This term is not known, but two members of the ^3P term of the same configuration lie at —1458 cm^{-1} and —2207 cm^{-1}. We can estimate in the same manner as was done in the case of Mg R_b and R_c for the other members of the series, when we know them for one of them. So we have in total three unknown constants: R_b and R_c for the $6s\ 5d$ state and R_a. We can calculate these constants by requiring that the 5^1D, 6^1D, 7^1D term of the series get the correct positions. There remains then to be seen whether we get possible values for these constants and whether with these constants we get a correct position for the last member of the series for which

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*) The term values are taken from 4), the values for the effective quantum numbers from 5).

both singlet and triplet are known, the 8^1D term. We find for the ^1D-term of the $5p^2$ configuration -2656 cm^{-1}, so the ^1D term lies above the ^3P, as we should expect. For the exchange integral we find 92.1 cm^{-1}, a positive value and for $2\sqrt{1/15}.\ R_c$ we find 2725 cm^{-1}. With these values we get for the ^1D level of the $6s\ 8d$ state the position 3264 cm^{-1}, which gives for the separation of singlet and triplet 127 cm^{-1}, while experimentally we find 109 cm^{-1}, a fairly good agreement.

CHAPTER II.

THE CA SPECTRUM.

§ 4. *Perturbed series.*

We will now consider the Ca spectrum more in detail. As regards the relative position of singlet and triplet, there is an anomaly in the D-series. Both singlet and triplet are known for five members and here the singlet lies alternatively above and below the triplet. Since, according to § 2, the exchange integral may be expected to be always positive, we shall try to explain this by a perturbation of the series by one or more corresponding levels of another configuration.

Now this anomaly is not the only indication of a perturbation in the Ca spectrum. From classical theory we know that for two successive members of a series the values of the effective quantum number n^* will differ by one unit and the difference $n - n^*$, called the quantum defect, will in a normal series remain approximately constant. Whenever in a series this is not the case, there is a possibility that this can be explained by a displacement of the levels by a perturbation. In the case of Mg and Cd, where the singlets were supposed to be perturbed, the quantum defect was in accordance with this nearly constant for the triplet and variable for the singlet.

Russell and Shenstone⁶) have investigated with the help of the classical Rydberg formula the perturbed series for a number of atoms, among them Ca. With this formula they can, when they know the position of the perturbing level, estimate the displacement caused by this perturbation in a first approximation; we will use one of their results later on.

The first example they give and which they treat rather extensively, is the ^3D series of Ca. Here, as in some other examples the quantum defect 5) shows a rapid rise of almost one unit. They explain this by supposing that one of the levels included in the series really is the perturbing level and belongs to another configuration. This level will lie in the middle of the region, where the rapid rise is. In the case of the ^3D series of Ca this is the level commonly ascribed to the *4s 9d* state; they suppose that this level belongs to the configuration *3d* 5s (see fig. 2). When this level is left out of the series, the quantum defect of the following members is one unit lower and the result is that the points representing the quantum defect come to lie on a hyperbolic curve, as should be expected when the level ascribed to the *4s 9d* state is in reality a perturbing level.

For the ^1D series the quantum defects lie very irregularly and as only five members of the series are known, Russell and Shenstone do not give any calculations in this case, but only say, that there is possibly a perturbation by the ^1D levels of the configurations $4p^2$, $3d^2$ and *3d 5s*. These levels are not known experimentally, though there have been reported possible positions for the $4p^2$ level and for one of the other two configurations.

As perturbing level for the ^1P series they take at first the level at 12573 cm^{-1}, which they concluded from evidence of the intensities to be foreign to the series and to belong to the configuration *3d 4p*. With this supposition they did not get good agreement of their calculations with experiment, but when they removed the level at 5372 cm—1, ascribed to the configuration *4s 7p*, from the series, as we would conclude from fig. 3, and supposed this level to be the source of the perturbation, they got good agreement.

Of the ^3P series only three members are known; they made calculations with the known level of the *3d 4p* configuration; the ^3P level of the $4p^2$ configuration will not perturb this series, as this configuration is not of the same parity.

The ^3S series shows no perturbation but the ^1S series does

FIG. 2.

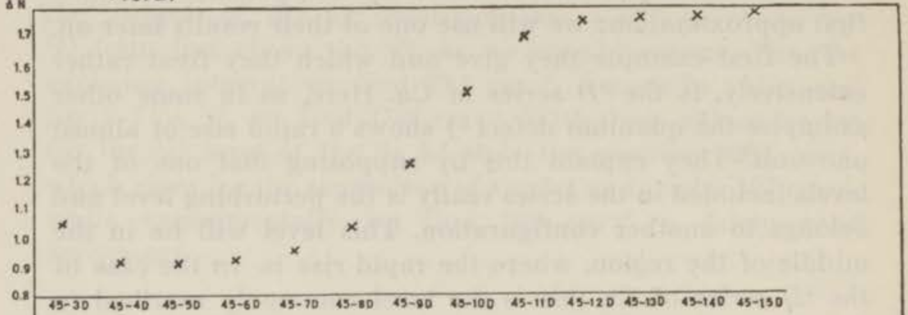

FIG. 3.

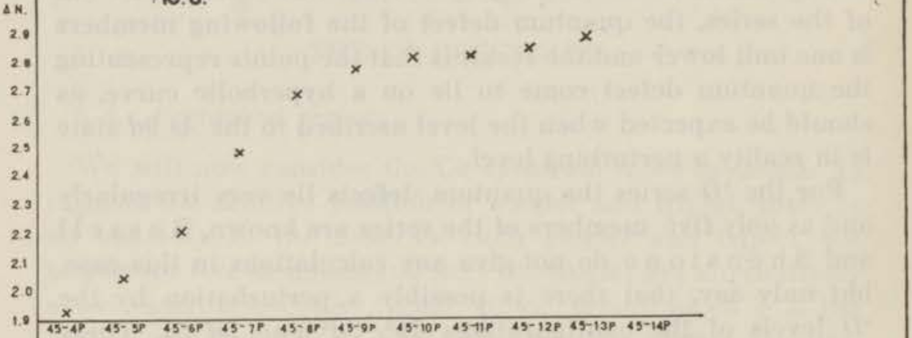

FIG. 4.

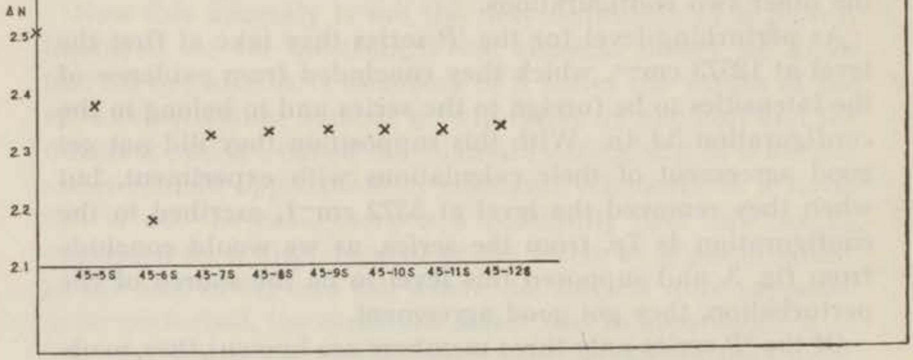

Fig. 2. Δn^* for the ^3D series; the term $4s\,9d$ is the foreign level.

Fig. 3. Δn^* for the ^1P series; the term $4s\,7p$ is the foreign level.

Fig. 4. Δn^* for the ^1S series.

(fig. 4); from the fig. we should suppose the perturbing level to lie near the 4*s* 6*s* level, but somewhat lower. This could be the ^1S level of the $4p^2$ configuration which is reported at 8614 cm^{-1} 4). The calculations they made with this level did not, however, show a good agreement.

The ^3F series does not show a perturbation and the ^1F series is perturbed by a level at 8767 cm^{-1} belonging to the 3*d* 4*p* configuration, with which level they get good agreement with experiment.

In the case of a multiplet, there may be still another indication of the perturbation of a series. We shall consider the differences between the components of the terms of the ^3D series of Ca in the following table 4)

(II)

n	3	4	5	6	7	8	9	10	11
$^3D_1-^3D_2$	13.9	3.6	1.7	1.5	1.8	3.7	10.2	4.2	2.0
$^3D_2-^3D_3$	21.7	5.6	2.8	1.8	2.4	5.2	9.9	7.9	2.5

n denoting as usual the principal quantum number, and ^3D_k the ^3D-term with $j = k$. When we consider the total splitting of the triplets that is, the difference $^3D_1 - {}^3D_3$, we see that from $n = 3$ up to $n = 6$ this difference decreases, then it increases till $n = 9$ and then it decreases again. For an undisturbed series we may expect it to decrease along the whole series.

Now, according to the supposition of Russell and Shenstone, the term indicated with $n = 9$ really belongs to another configuration, which disturbs the other terms of the series; this means that the wave functions of the other terms are not the pure wave functions corresponding to the electron configuration of the normal series, but that they contain also a part that corresponds to the disturbing electron configuration. As the total splitting of the disturbing level is much larger than the splitting of the levels of the series, this means that these levels will show a total splitting that will be larger, than it would be if there were no perturbation. The influence of the perturbation will be greater, when the level lies nearer to the perturbing level and then also the change in the total splitting will be greater; for the levels near the perturbation this might easily dominate over the naturel tendency of this splitting to become smaller and so cause just the observed facts.

A very rough calculation of the magnitude of this effect showed that in this way the course of the total splitting may be represented correctly for the whole series. The method for the estimation was too rough to allow definite conclusions, but only gave an indication that in the case of the ^3D series the hypothesis of Russell and Shenstone may be confirmed by the behaviour of the splitting of the triplet.

§ 5. *Relative position of singlet and triplet for the ^1D-series of Ca.*

We mentioned in the preceding paragraph that for the D-series of Ca the singlet lies alternatively above and below the triplet. To see, whether our supposition regarding the sign of the exchange integral was correct in this special case and, if this proves to be so, whether we then indeed can explain the anomalous position of the singlet relative to the triplet as due to the perturbing term, we have made numerical calculations. To this end we have to know in the first place the wave functions of the electrons, when one of them is in a $4s$ and the other in an nd state. For these, as well as for the other numerical calculations, the results of which are used in this chapter, we refer to Chapter III.

With these wave functions we have first calculated the exchange integrals, the result being given in the folowing table

(III)

	$4s\,3d$	$4s\,4d$	$4s\,5d$	$4s\,6d$	$4s\,7d$
$2K\,(\mathrm{cm}^{-1})$	$+4936$	$+535.2$	$+241.8$	$+135.2$	$+83.0$
$^1D - {}^3D\,(\mathrm{cm}^{-1})$	-1497.3	$+454.3$	-173.8	$+60.8$	-5.7

where K is defined by § 1 (4), so $2K$ is the difference we would find between singlet and triplet without a perturbation. By ${}^1D-{}^3D$ is meant the difference between singlet and triplet, as it is found experimentally[4]), taken positive when the term value of the singlet is larger than that of the triplet.

We see in the first place that, in accordance with our supposition, the sign of the exchange integral is always positive. In fig. (5) we give the experimental positions of singlet and triplet and the position of the singlet, relative to the triplet, as the exchange integral would place it; the difference between this position and the observed one we will now seek to explain by interaction with other levels (in the figure this means that we want the perturbations to displace the levels from the dotted to the full-drawn position). We see that the direction of this displacement is the same for all the members of the series. This was also the case for Mg. (§ 3), but while there the displacement steadily decreased in going to higher members of the series (fig. 1), here we need a displacement that is greater for the $4s\ 6d$ level than for the $4s\ 5d$ level. This is already an indication of the fact, that here the perturbation is not so simple as in the case of Mg. The reason for this is that here we have to expect an interaction with at least two levels.

In the normal Ca spectrum the first D-term lies abnormally low — in the same neighbourhood as the first P-term — and this makes it probable, as we will find confirmed by experiment, that the terms belonging to the configuration $3d^2$ will also lie not very far above the terms, belonging to $4p^2$. Both the d^2 and the p^2 configuration contain a ${}^1D$ term and no ${}^3D$ term. From experiment there are only known the ${}^3P$ terms for both configurations, the ${}^3P$ term of $4p^2$ lying at 10826.7 cm^{-1} and of $3d^2$ at 762.9 cm^{-1}. Though we do not know the positions of the ${}^1D$ levels, we may suppose that they lie in about the same region as the ${}^3P$ levels. Now the ${}^3P$ term of $4p^2$ lies between the ${}^1D$ levels $4s\ 4d$ and $4s\ 5d$ of the normal series, while the ${}^3P$ term of $3d^2$ lies well above all the levels in question. A similar position of the ${}^1D$ levels could just explain the observed facts. In this case the displacement for the ${}^1D$ level of $4s\ 5d$ would be very small, just as we need it,

FIG. 5.

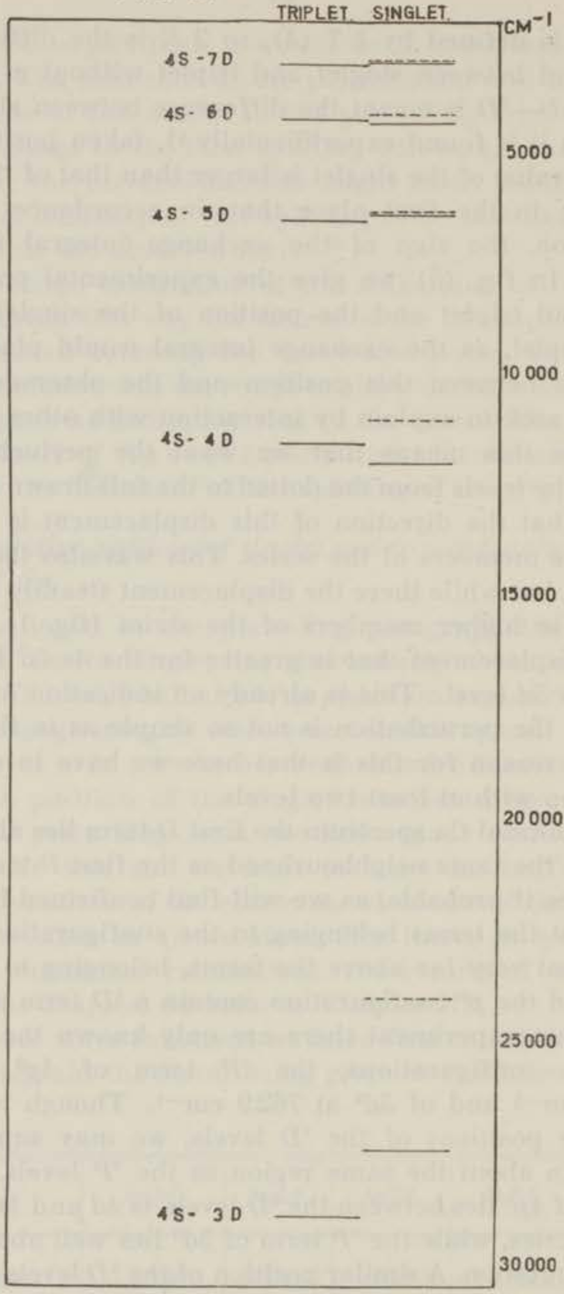

Fig. 5. Energy levels for the Ca *D*-series. The levels of the observed spectrum are drawn full, while the dotted lines indicate the position of the singlet, as it is given by the exchange integral, without other perturbations. Vertically the energy is given in cm^{-1}.

because here, for the first time, the perturbations from both configurations act in the opposite direction. The displacement for the 4*s* 6*d* level could very well be greater again, though generally the displacement caused by a given level tends to diminish, when we go to higher quantum numbers. But then here also the displacement caused by the $4p^2$ level would diminish and, as this acts in the opposite direction, the result might vey well be that in total the displacement in the direction we want is larger in this case.

There is still another configuration that might give rise to a perturbation that would cause an energy difference between singlet and triplet. As we have seen in § 4 the ^3D series is, according to Russell and Shenstone, perturbed by a level at 1849 cm^{-1}, ascribed to the configuration 5*s* 3*d*. This configuration also contains a ^1D level. The inter action matrix, that is the matrix for the part $1/r_{1,2}$ of the energy, can be written down immediately, for we know already the result of the integration over the angular variables, as the angular factors are the same as for the diagonal elements. The results of the integration for the diagonal elements are given in § 2 (5), so with this we find for the interaction matrix

	$4s\,nd,\,^1\mathrm{D}$	$4s\,nd,\,^3D$	$5s\,3d,\,^1D$	$5s\,3d,\,^3D$
$4s\,nd,\,^1D$	$R_a+\frac{1}{5}R_b$	o	$R_A+\frac{1}{5}R_B$	o
$4s\,nd,\,^3D$	o	$R_a-\frac{1}{5}R_b$	o	$R_A-\frac{1}{5}R_B$
$5s\,3d,\,^1D$	$R_A+\frac{1}{5}R_B$	o	$R'_a+\frac{1}{5}R'_b$	o
$5s\,3d,\,^3D$	o	$R_A-\frac{1}{5}R_B$	o	$R'_a-\frac{1}{5}R'_b$

where R_a, R'_a, R_b, R'_b are of the same form as R_a and R_b in § 3, when we substitute the radial functions belonging to the state we consider and when by R_A and R_B are meant

$$R_A = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{1}{r_b} R_{4s}(r_1) R_{5s}(r_1) R_{3d}(r_2) R_{nd}(r_2),$$

$$R_B = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_a^2}{r_b^3} R_{4s}(r_1)\ R_{nd}(r_1)\ R_{5s}(r_2)\ R_{3d}(r_2), \text{ with } r_a < r_b.$$

Now $r_a/r_b < 1$ and R_B contains in the integrand a factor $(r_a/r_b)^2$ more than R_A. The other factors in the integrands are the same, but their arguments are different. Still it seems very probable that R_B, at most, will be of the same order as R^A. On the other hand when, in first approximation, the effect of the energy difference between singlet and triplet in causing a difference in the displacement is neglected, this difference depends only on the relative magnitude of R_A and R_B. In the matrix elements R_B is still multiplied with the factor $^1/_5$; we feel justified in supposing, that $R_A > \frac{1}{5}\ R_B$, and this would mean that the difference between the displacements of singlet and triplet is smaller than the displacement of the triplet term itself. These displacements, as estimated approximately from the calculations of Russell and Shenstone[6]), are given in the following table:

(IV)

	4s 3*d*	4s 4*d*	4s 5*d*	4s 6*d*	4s 7*d*
$\Delta\,^3D\,(\mathrm{cm}^{-1})$	135	66	57	54	72

When we compare these values with the displacements we want (fig. 5), we see that the latter are, except in the case of 4*s* 7*d*, much larger than the displacements given here for the ^3D term and as the difference between singlet and triplet caused by this perturbation is even smaller than these values, we may neglect its influence in first approximation; for the other perturbations, if they give an explanation of the observed facts, have to give much larger displacements.

§ 6. *Effect of the perturbations as calculated with our wave functions.*

We shall now calculate the displacements of the energy levels of the ${}^1D$ series by the perturbations caused by the ${}^1D$ levels of the $4p^2$ and $3d^2$ configurations. To this end we first have to know the matrix elements, giving the interaction between the levels of these configurations and the levels of the normal series. The interaction matrix between the ${}^1D$ states of the $4p^2$ and the $4s\ nd$ configurations is already given in § 3 (6). The calculation of the matrix elements of $1/r_{1,2}$ which give the interaction between the configurations, are for the interaction with the $3d^2$ configuration, given in Chapter III, § 10. We shall now write down the interaction matrix for all three configurations

$$\begin{array}{l|lll}
 & 4s\,nd & 4\,p^2 & 3\,d^2 \\
\hline
4s\,nd & H_{11}=R_a+\frac{1}{5}R_b & H_{12}=+2\sqrt{\frac{1}{15}}\,R_c & H_{13}=-\frac{2}{\sqrt{35}}\,R_k \\
4\,p^2 & H_{21}=+2\sqrt{\frac{1}{15}}\,R_c & H_{22}=R_d+\frac{1}{25}R_e & H_{23}=-\frac{1}{5}\frac{\sqrt{7}}{\sqrt{3}}R_l-\frac{3}{35}\frac{\sqrt{5}}{\sqrt{7}}R_m \\
3\,d^2 & H_{31}=-\frac{2}{\sqrt{35}}\,R_k & H_{32}=-\frac{1}{5}\frac{\sqrt{7}}{\sqrt{3}}R_l-\frac{3}{35}\frac{\sqrt{5}}{\sqrt{7}}R_m & H_{33}=R_f-\frac{3}{49}R_g+\frac{4}{49}R_h
\end{array} \qquad (7)$$

with R_a, R_b, R_c and R_e as given in § 3 (6), only with $3s$ and $3p$ substituted by $4s$ and $4p$ and

$$R_f=\int\limits_0^\infty dr_1\int\limits_0^\infty dr_2\,\frac{1}{r_b}\,R_{3d}{}^2(r_1)\,R_{3d}{}^2(r_2)\,;$$

$$R_g=\int\limits_0^\infty dr_1\int\limits_0^\infty dr_2\,\frac{r_a{}^2}{r_b{}^3}\,R_{3d}{}^2(r_1)\,R_{3d}{}^2(r_2);$$

$$R_h=\int\limits_0^\infty dr_1\int\limits_0^\infty dr_2\,\frac{r_a{}^4}{r_b{}^5}\,R_{3d}{}^2(r_1)\,R_{3d}{}^2(r_2);$$

$$R_k = \int\limits_0^\infty dr_1 \int\limits_0^\infty dr_2 \frac{r_a^{\,2}}{r_b^{\,3}} R_{3d}(r_1)\, R_{4s}(r_1)\, R_{3d}(r_2)\, R_{nd}(r_2);$$

$$R_l = \int\limits_0^\infty dr_1 \int\limits_0^\infty dr_2 \frac{r_a}{r_b^{\,2}} R_{3d}(r_1)\, R_{4p}(r_1)\, R_{3d}(r_2)\, R_{4p}(r_2);$$

$$R_m = \int\limits_0^\infty dr_1 \int\limits_0^\infty dr_2 \frac{r_a^{\,3}}{r_b^{\,4}} R_{3d}(r_1)\, R_{4p}(r_1)\, R_{3d}(r_2)\, R_{4p}(r_2),$$

where $r_a < r_b$. For the energy level of the ^3P term from the $3d^2$ configuration we have found: $R_f + \frac{1}{7} R_g - \frac{4}{21} R_h$.

To calculate these integrals we need, besides the wave functions for the $4s\ nd$ configuration, also those for the $4p^2$ and the $3d^2$ configurations. To obtain these we have used the $4p$ and $3d$ functions for the single electron as calculated when the other of the two electrons is in a $4s$ state; this means that for the potential field in which the electron moves, we take the central field from the nucleus plus the inner electrons, to which field is added the field of the other valence electron when it is in a $4s$ state *).

Actually this is not the field in which the electron moves, but the actual field cannot easily be calculated because of the strong interaction between the electrons. We shall see later on (compare § 7) that the present method of finding wave functions for the $4p^2$ and the $3d^2$ configurations presumably is the cause of considerable errors.

First we have calculated the values of R_e, R_g and R_h, which enabled us to calculate from the observed positions of the ^3P terms the ^1D terms of both configurations. The results were, when we give them in cm^{-1}, which units we use for the comparison with the experiments, R_e = 19710 cm^{-1}, R_g = 42180 cm^{-1}, R_h = 25480 cm^{-1}, which values place the ^1D level of the $4p^2$ configuration at 6097 cm^{-1} and that of the $3d^2$ configuration at 2439 cm^{-1}. We see directly that the level of the $3d^2$ configuration lies indeed above all known

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*) See Chapter III, § 9.

singlet levels of the $4s\ nd$ series, but that the ^1D level of the $4p^2$ configuration lies just above the $4s\ 5d$ level, instead of between the levels of $4s\ 4d$ and $4s\ 5d$, which position we assumed in § 5. The perturbed energy levels we have to calculate from the following equation

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} \\ H_{21} & H_{22}-E & H_{23} \\ H_{31} & H_{32} & H_{33}-E \end{vmatrix} = 0 \qquad (8)$$

where H_{11}, H_{12}, are the matrix elements of energy matrix (7).

From the values of the radial integrals, which we will give in Chapter III, § 11, we have calculated $H_{23} = 2778\ \text{cm}^{-1}$, while the values of H_{12} and H_{13} are given in the following table

(V)

	$4s\ 3d$	$4s\ 4d$	$4s\ 5d$	$4s\ 6d$	$4s\ 7d$
H_{12} (cm^{-1})	7024	5360	3000	2330	1770
H_{13} (cm^{-1})	—2841	—309.8	—246.5	—211.7	—166.8

With these values the perturbation matrix is known and the energy levels can be calculated from an equation of the third degree, which equation we have solved graphically. In the following table we give the difference between singlet and triplet for the series, as it is given experimentally and as it would follow from these calculations, both taken positive when the singlet lies below the triplet

(VI)

(in cm^{-1})	$4s\ 3d$	$4s\ 4d$	$4s\ 5d$	$4s\ 6d$	$4s\ 7d$
^1D—^3D, exp.	—1497.3	+ 454.3	— 173.8	+ 60.8	— 5.7
^1D—^3D, cal.	—2375	+3033	+3124	—599	—64.4

We see at once, when we compare these values with those of the exchange integral, given in table III, that except for the 4*s* 3*d* state, the agreement with experiment is even worse than without the influence of the perturbation.

Now the position of the ^1D level from the $4p^2$ configuration, as we calculated it, can be the reason that our calculations do not show the typical change of sign of the difference ^1D—^3D from the 4*s* 4*d* to the 4*s* 5*d* state. For as we have seen in fig. (5) this corresponds with the fact that for the 4*s* 5*d* state the displacement caused by the perturbation should be very small and we have seen in § 5 that this could be expected when the position of the level from the $4p^2$ configuration was between the levels of the configurations 4*s* 4*d* and 4*s* 5*d*. But a displacement of this level would certainly give no better agreement, for such a displacement would make the difference ^1D—^3D for the 4*s* 4*d* state even greater, so here the disagreement with experiment would become even worse. As to the 4*s* 5*d* state here the difference would get the proper sign, but would remain much too large, as the distance of the perturbing level would not be altered greatly.

So it seems that there are only two alternatives. The first is to suppose that, while the matrix elements giving the interaction between the levels remain as we calculated them, the positions of the perturbing levels differ from the calculated ones; if the position of the ^1D level from the $4p^2$ configuration were in reality much higher than the calculated one, the displacement would become smaller for the first three members of the series. We see at once that in this case the agreement for the 4*s* 3*d* state would be spoiled. The other possibility is to suppose that our approximations for the wave functions of the $4p^2$ and $3d^2$ configurations are so bad that also the value we calculated for the matrix elements, giving the interaction between the levels, are wrong *). In this case, of course, the calculations of the

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*) This would not be in contradiction with the fact that Bacher's results for Mg were fairly correct, as he calculated the wave functions of the $3p^2$ configuration by quite different method, making use of functions of the type proposed by Slater (see [3]) p. 264 and [8]).

positions of the perturbing levels also lose their value. We will now see in the next paragraph to what conclusion both suppositions lead us.

§ 7. *Discussion of the effect of the perturbations, with altered values for the matrix elements.*

The results of the first supposition, namely that only the position of the ^1D level from the $4p^2$ configuration has to be altered, are easy to calculate. The position of this level we can calculate now with the help of equation (7) by substituting for one of the members of the series, besides the other matrix elements, also the energy of this level as the experiments give it. Then we can calculate the perturbation for the other levels in the usual way.

We have seen above that for the configuration $4s\ 3d$ we should not get the correct results in this way. So we used the $4s\ 4d$ level for the calculation of the unknown level because this level has the largest values for the matrix elements, so small errors will here have the least influence. We found for the position of the ^1D level of the $4p^2$ configuration — 19006 cm^{-1}. As the ^3P term of this configuration was given at + 10826.7 cm^{-1}, the difference between ^1D term and ^3P term of the same configuration seems abnormally large.

Still we have calculated the energy with this position for the perturbing level for the other members of the series and the results are given in the following table for the difference between singlet and triplet, where the experimental values are given comparison

(VII)

in cm^{-1}	$4s\,3d$	$4s\,4d$	$4s\,5d$	$4s\,6d$	$4s\,7d$
^1D—^3D, exp.	—1497.3	+454.3	—173.8	+ 60.8	—5.7
^1D—^3D, cal.	—3768	+454.3	+119	+102	+74

We see at once that, though the agreement is somewhat better than previously, the peculiarities of the experimentally given

FIG. 6.

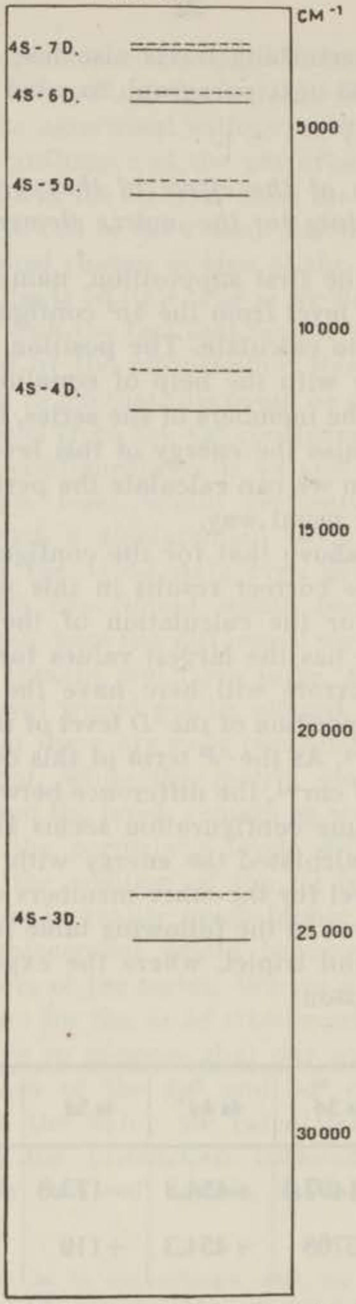

Fig. 6. Energy levels of the ^1D series of Ca. The dotted lines give the undisturbed levels, as calculated with the exchange integral and the drawn lines give the disturbed energy levels, when we suppose that both disturbing levels lie above the levels of the series and that the interaction is the same as is calculated in § 5.

difference between singlet and triplet are by no means accounted for. When we consider fig. 6 which gives the energy levels of the undisturbed ^1D state, as calculated with the exchange integral and of the disturbed levels as calculated here, we see that the displacement of the levels diminishes steadily when we go to higher quantum numbers, whereas the displacement we need has a much more irregular course (fig. 5). So we may conclude that the first supposition not only gives an impossible position for the ^1D level of the $4p^2$ configuration, but also that it does not explain the relative position of singlet and triplet for the normal D series.

We will now discuss the other possibility, namely that the matrix elements giving the interaction between the levels have other values than those calculated in § 6. As in this case the calculations for the positions of the perturbing levels also lose their meaning we shall have to make a supposition about the position of at least one of them in order to be able to make any calculations. In § 5 we have seen that a position of the level belonging to the $4p^2$ configuration between the levels of the $4s\ 4d$ and the $4s\ 5d$ states of the series could explain the experimental facts. Now we have seen in § 4, that the ^1S series shows a perturbation, which could be explained by a perturbation from the ^1S term of the $4p^2$ configuration, taken by experimenters at 8614 cm^{-1}; this level we should theoretically expect at $R_d + \frac{2}{5} R_e$ (see § 8), while the ^1D and the ^3P term of the same configuration lie respectively at $R_d + \frac{1}{25} R_e$ and $R_d - \frac{1}{5} R_e$. When we suppose the level at 8614.2 cm^{-1} to belong indeed to the ^1S term of this configuration, this, together with the knowledge of the ^3P term at 10826.6 cm^{-1}, enables us to calculate the position of the ^1D term, for which position we find 9941.6 cm^{-1}. This position is used as a basis for the following considerations.

In § 3 we have seen that it is possible to calculate the matrix elements, giving the interaction between the levels, for all members of the series, when we know them for one. We have only to assume that, in those distances from the nucleus from which come the chief contributions to our integrals, the form of the wave functions is for all members of the series the same, the only difference being the magnitude, which is inversely proportional to the square root of the normalization integral. In the case of the ${}^1D$ series this is indeed the case, except for the $4s$ $3d$ state. This means that, though the calculation of H_{12} and H_{13}, giving the interaction of the levels of the series with a foreign level, are wrong, they give their relative magnitude correctly. Their true values may then be found by multiplying the old ones with a factor which is the same for all members of the series.

This limits the number of unknown constants to H_{23},H_{33} and to the values of H_{12} and H_{13} for one of the members from the series. It would be possible to determine these constants from the experiments and see what values we get. But as there are only five levels and the level $4s$ $3d$ has to be left out of these considerations, these levels would just suffice to determine these constants and we would have no further verification for the theory. So we only determined H_{12} and H_{13} with the help of the $4s$ $4d$ and $4s$ $5d$ states, supposing the level H_{33} to be the same as given by the first calculations and taking for H_{23}, first, the same value as in the first calculations and, second, a value derived from the first by multiplying with the product of the factors with which we have multiplied H_{12} and H_{13}. These factors are chosen rather arbitrarily, but the choice will enable us to compare the results we get with unvaried H_{23} and with a variation of H_{23} which lies wholly within the range of possibilities.

We remark that for the lowest members of the series, that is for the states $4s$ $3d$ and $4s$ $4d$, the influence of the $3d^2$ configuration is still small; so, when we first determine H_{12} in such a way that the perturbation from the $4p^2$ configuration gives for the $4s$ $4d$ state the right displacement, and then determine the real value of H_{12} when we also take the influence of the $3d^2$ configuration into account the results will not differ greatly. Therefore mistakes in this second interaction will not have much influence. As we indeed do not know the interaction with the $3d^2$ configuration very well, because the position of the ${}^1D$ level is not known exactly, this is rather fortunate, for now we can still be fairly sure that the value we find for H_{12} will be roughly correct.

We have found in this manner H_{12} *(new)* = 0.265 H_{12} *(old)* and H_{13} *(new)* = 2.702 H_{13} *(old)*. The unvaried value of H_{23} was 2778 cm^{-1} and for the varied value we took $H_{23} = 2000$ cm^{-1}. The results with these matrix elements are given in the following table for ^1D—^3D

(VIII)

in cm^{-1}	4*s* 4*d*	4*s* 5*d*	4*s* 6*d*	4*s* 7*d*
^1D—^3D, exp.	+454.3	—173.8	+60.8	— 5.7
^1D—^3D, cal. $H_{23} = 2000$	+454	—174	+41	+150
^1D—^3D, cal. $H_{23} = 2778$	+453	—172	+ 1	+ 77

We see that the results seem somewhat better for $H_{23} = 2000$ cm^{-1}. In fig. (7) we give the positions of the energy levels as given experimentally, the positions of the undisturbed levels determined with the help of the exchange integral and the disturbed levels as calculated here. We see that the displacements are given correctly with our assumptions. That the agreement for the 4*s* 7*d* state is not better might be due to the fact that the exact position of the level from the $3d^2$ configuration which here has considerable influence is not known. Also here interaction with the 5*s* 3*d* state might begin to have a perceptible influence (see § 5).

So far we have not mentioned the 4*s* 3*d* state. We have seen above that here the method for the calculation of the matrix elements H_{12} and H_{13} cannot be expected to give good results and indeed with the matrix elements calculated in this manner we got a displacement that was much too small. On the other hand, when we leave all matrix elements the same as in our original calculations except H_{22} which we give the value corresponding to the new position of the $4p^2$ level we find for ^1D—^3D the value —1928 cm^{-1}, where the experimental value is —1497.3 cm^{-1}. So we now get a dis-

FIG. 7.

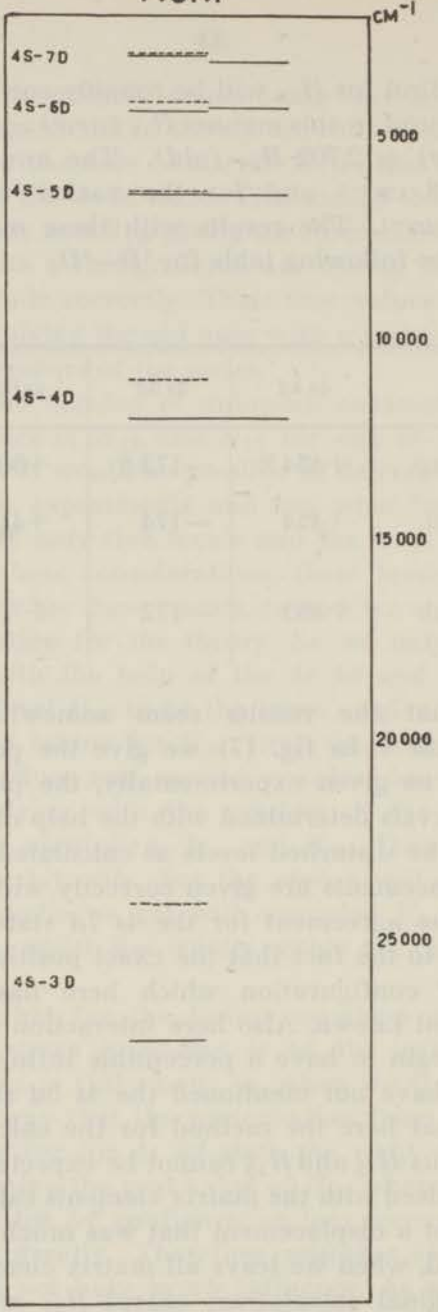

Fig. 7. Energy levels of the ^1D series. The dotted lines give the position of the undisturbed levels, calculated with the exchange integral. Of the full-drawn levels the one to the left gives the experimentally observed level and the one to the right the level as calculated with such values of H_{12} and H_{13} as to give good agreement for the $4s\,4d$ and the $4s\,5d$ states, while H_{23} has also been altered.

placement which is still a little too small, but which at any rate is of the right order of magnitude. As the influence of the $3d^2$ configuration is still very small in this case, we can be sure that the only possibility to get a displacement of the right order of magnitude lies in assuming a value for H_{12} which is at any rate not smaller than the value as we have originally calculated it. In Chapter III § 12 we shall see that it has indeed been possible to construct a modified $4p$ function which at the same time gives H_{12} for the $4s$ $3d$ and $4s$ $4d$ states the correct value; the value of H_{12} for the $4s$ $3d$ state was very susceptible to small variations of this modified wave function, which left that for the $4s$ $4d$ state about uchanged, so that whatever be the influence of the $3d^2$ level we can be sure that it will be possible to find a wave function that gives the correct value for H_{12}.

Although, owing to the fact that the wave functions of the perturbing states are not sufficiently known, it has not been possible to make exact theoretical calculations, we conclude that these perturbations can cause the observed pecularities of the relative positions of singlet and triplet.

§ 8. *The ^1S series.*

In § 4 we have seen that, from the magnitude of the quantum defects, we should conclude that the ^1S terms are perturbed and also that this perturbing level lies in the neighbourhood of the $4s$ $6s$ level. We remarked that this perturbation might be due to the ^1S level of the $4p^2$ configuration, which was indicated at 8614 cm^{-1} and we used this position for the ^1S level in the preceding paragraph to determine the position of the ^1D level of this configuration.

We have made some numerical calculations with this perturbation in order to see, whether this perturbation did indeed explain the observed positions of the levels. From fig. 4 we should conclude that the level $4s$ $6s$ is the most strongly perturbed, due to the fact that this level lies very near to the perturbing one. We planned to make exact numerical calculations for the $4s$ $6s$ state first and then, from these matrix elements to calculate those for the other states, as we did for Mg (see § 3). The wave functions were determined as in the case of the 4*s* *nd* configuration.

The perturbation matrix for the 4*s* 6*s* state is (see § 10)

$$\begin{array}{l|ccc} & 4s\,6s,\,{}^1S & 4s\,6s,\,{}^3S & 4\,p^2,\,{}^1S \\ \hline 4s\,6s,\,{}^1S & R_a + R_b & 0 & \frac{\sqrt{2}}{\sqrt{3}} R_c \\ 4s\,6s,\,{}^3S & 0 & R_a - R_b & 0 \\ 4\,p^2,\,{}^1S & \frac{\sqrt{2}}{\sqrt{3}} R_c & 0 & R_d + \frac{2}{5} R_e, \end{array} \qquad (8)$$

where R_d and R_e are as defined in § 6 (7) and

$$R_a = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \frac{1}{r_b} R_{4s}{}^2(r_1)\, R_{6s}{}^2(r_2);$$

$$R_b = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \frac{1}{r_b} R_{4s}(r_1)\, R_{6s}(r_1)\, R_{4s}(r_2)\, R_{6s}(r_2);$$

$$R_e = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \frac{r_a{}^2}{r_b{}^3} R_{4p}(r_1)\, R_{4s}(r_1)\, R_{4p}(r_2)\, R_{6s}(r_2), \text{ where } r_a < r_b.$$

When there was no perturbation the difference between singlet and triplet would be 2 R_b and the singlet would lie above the triplet when R_b had a positive value.

We then calculated the position of the other ${}^1S$ levels with the help of the values of R_b and R_c of the 4*s* 6*s* state; these values were calculated from their integral expressions by means of the 4*s* and the 6*s* wave functions.

This calculation, however, did not give any satisfactory results, the singlet-triplet splitting becoming about four times too big. We then tried to redetermine R_b and R_c in a semi-empirical way, calculating them from the observed positions in the 4*s* 6*s* and the 4*s* 7*s* states. The results of these calculations are given in table IX

IX

State	4*s* 5*s*	4*s* 6*s*	4*s* 7*s*	4*s* 8*s*	4*s* 9*s*	4*s* 10*s*	4*s* 11*s*	4*s* 12*s*
n^1S-n^3S (exp.)	−1294	−1311.9	−295.8	−105.5	−58.5	−37.8	−25.5	−16.3
n^1S-n^3S (cal.)	+ 285	−1312	−296	−100	−63	−38	−28	−20

Here the difference between singlet and triplet is taken positive, when the singlet has the biggest term value. We see that the agreement with experiment is close except for the 4*s* 5*s* state. The last disagreement might be ascribed to a break-down of the method of determining the values of R_b and R_c from the values of these quantities for another state.

The value of the exchange integral found in this way was about one fourth of the value which we had found originally. As we have here a two *s*-electron problem, it is not so very surprising that with wave functions of a first approximation we do not get correct results. In this case the interaction between the electrons will in fact be strong and insufficiently accounted for by our method of calculating the wave functions (see § 12). In the case of the *S* terms of He it is reported ²) that no agreement at all is obtained with wave functions in first approximation.

CHAPTER III.

NUMERICAL CALCULATIONS.

§ 9. *Calculation of the wave functions.*

The wave functions of the electrons, which we needed to calculate the matrix elements used for the calculations given in the preceding chapter, we have calculated with the W.K.B. method. A detailed description of this method is given by Zwaan ⁷), to whom we refer for all particulars and whose results we have used as far as possible.

To find the wave functions for the 4*s* *nd* state of neutral Ca we have neglected the influence of the *d*-electron on the *s*-electron. This will give us an approximation for the wave function, which will be better the higher the principle quantum number of the *d*-electron is, for higher *n* means greater distance of the two electrons from each other. Zwaan has calculated the potential field of the nucleus and the inner electrons and also the wave function of the 4*s* electron for ionized Ca. With the help of these we can calculate the potential field in which the *d*-electron moves, by adding to the potential field, which Zwaan gives, the field of the 4*s* electron, which field we can calculate because we know the wave function. We can consider this as a first approximation; a second approximation might be obtained in calculating with this wave function for the *d*-electron a new potential field and so a better wave function for the *s*-electron, etc.

The potential field we have calculated in this way for the *d*-electrons could not directly be used for the calculation of the wave functions, as it does not yet satisfy the condition that the phase integral is equal to $n-l-\frac{1}{2}$ for all the states we consider, a condition that has to be satisfied when we use the W.K.B. method (see Zwaan). To obtain a potential field which satisfies this condition we had to alter slightly the calculated potential, in such a way that the condition was fulfilled as well as possible for all states. In the following table we give, in the units used by Zwaan, which differ by a factor 2 in the energy from the units introduced by Hartree, the potential field v (ρ) deduced from Zwaan in which the *s*-electron moves and the field we calculated for the other electron, modified in such a way, as to fulfill the condition for the phase integral

ρ (in units $\frac{\hbar}{me^2}$	$-\rho^2\, v(\rho)$ given by Zwaan for the *s*-electron	$-\rho^2\, v(\rho)$ field in which the second electron moves
0.1	2.88	2.87
0.2	4.71	4.68
0.4	6.52	6.41
0.6	7.37	7.21
0.8	7.83	7.64
1.0	8.20	7.97
1.2	8.44	8.12
1.4	8.68	8.29
1.6	8.80	8.39
1.8	9.06	8.52
2.0	9.45	8.59
2.4	10.51	8.77
2.8	11.88	9.04
3.2	13.42	9.29
4.0	16.49	10.11
5.0	20.32	11.29
6.0		12.40
7.0		14.10

With the potential field given in the second column we have calculated all the wave functions. The results we give in the following table together with the wave function for the 4*s* electron, given by Zwaan

$R(\rho)$ ρ	4*s*	3*d*	4*d*	5*d*	6*d*	7*d*	4*p*	6*s*
0.04	+0.190	+0.000	+0.000	+0.000	+0.000	+0.000	+0.080	+0.187
0.08	+0.071	+0.005	+0.005	+0.005	+0.005	+0.005	+0.199	+0.209
0.16	—0.226	+0.053	+0.056	+0.055	+0.053	+0.053	+0.333	—0.004
0.24	—0.324	+0.173	+0.175	+0.175	+0.171	+0.175	+0.344	—0.251
0.4	—0.074	+0.467	+0.461	+0.462	+0.478	+0.466	+0.098	—0.350
0.6	+0.357	+0.703	+0.699	+0.706	+0.712	+0.701	—0.310	—0.010
0.8	+0.543	+0.833	+0.818	+0.824	+0.818	+0.804	—0.566	+0.372
1.0	+0.495	+0.906	+0.883	+0.875	+0.873	+0.871	—0.631	+0.587
1.2	+0.304	+0.946	+0.896	+0.886	+0.874	+0.862	—0.570	+0.625
1.4	+0.055	+0.938	+0.869	+0.864	+0.839	+0.834	—0.411	+0.523
1.6	—0.198	+0.912	+0.814	+0.779	+0.778	+0.776	—0.206	+0.331
1.8	—0.434	+0.857	+0.727	+0.677	+0.678	+0.678	+0.019	+0.105
2.0	—0.645	+0.800	+0.624	+0.564	+0.561	+0.541	+0.244	—0.138
2.4	—0.956	+0.664	+0.376	+0.302	+0.278	+0.270	+0.650	—0.579
2.8	—1.119	+0.530	+0.114	+0.028	—0.010	—0.028	+0.965	—0.891
3.2	—1.181	+0.435	—0.143	—0.142	—0.302	—0.337	+1.198	—1.052
4	—1.039	+0.361	—0.672	—0.778	—0.849	—0.847	+1.440	—0.966
5	—0.750	+0.287	—1.233	—1.294	—1.351	—1.320	+1.455	—0.147
6	—0.448	+0.223	—1.682	—1.600	—1.581	—1.593	+1.285	+0.597
8	—0.135	+0.125	—2.165	—1.580	—1.359	—1.347	+0.772	+1.521
10	—0.035	+0.065	—2.223	—0.919	—0.452	—0.407	+0.411	+1.440
15	—0.001	+0.011	—1.524	+1.416	+1.766	+1.806	+0.065	—0.925
18			—1.008	+2.324	+1.990	+1.770	+0.019	—2.080
22			—0.344	+2.601	+1.084	+0.318		—2.773
25			—0.275	+2.522	—0.325	—1.024		—2.557
28			—0.162	+2.186	—1.492	—2.008		—1.828
30			—0.095	+1.891	—2.098	—2.362		—1.428
38				+0.844	—3.010	—0.918		—0.424
42				+0.512	—2.828	+0.452		—0.200
45				+0.336	—2.478	+1.479		—0.102
50				+0.156	—1.829	+2.823		—0.032
54					—1.333	+3.336		
58					—0.935	+3.440		
68					—0.341	+2.580		
76					—0.133	+1.660		
82						+1.129		
90						+0.578		
105						+0.154		

Here ρ is given in the units introduced by Hartree and $R(\rho)/\rho$ means the radial part of the wave function (see § 1 (2)). We see that the wave functions of the *d*-electrons from 4*d* onwards are almost equal in the region with $\rho < 8$, beyond which the 4*s* function becomes negligible, a circumstance we have used in § 7. These functions as given above are not yet normalized; we will give their normalization integrals in the following table.

(XII)

State	3*d*	4*d*	5*d*	6*d*	7*d*	4*p*	4*s*	6*s*
$\int_0^\infty R^2(\rho)\,d\rho$	2.01	48.6	115.6	201.1	351.5	9.68	3.86	96.6

As we have already remarked in § 7, we have here calculated the 4*p* function for the configuration 4*s* 4*p*, while we really need it for the configuration $4p^2$. We see that the distance from the nucleus for the 4*p* electron is somewhat greater than for the 4*s* electron, so when the second electron moves in the field of a 4*p* instead of a 4*s* electron it will have a tendency to get nearer to the nucleus. As we will see in § 12 the real wave function for the $4p^2$ configuration, which we estimated from the values we need for the matrix elements, is indeed displaced in this sense.

§ 10. *Pertubation matrices.*

In § 3 we have seen that for the $4p^2$ configuration we can directly write down the wave functions for the ^3P and the ^1D states and so we can also write down immediately the energy of these states and then also the interaction with the normal ^1D series. But for the ^1S state of this configuration and for the $3d^2$ configuration this is not the case. Here the final wave functions are a combination of the original ones (see § 1), which combination has to diagonalize the energy matrix.

We will first calculate the wave function and at the same time the energy that comes from $1/r_{1,2}$ for the ^1D and the ^3P states of the $3d^2$ configuration. This configuration contains a

${}^1S$,a ${}^3P$,a ${}^1D$,a ${}^3F$ and a ${}^1G$ state. We can construct immediately, as a Slater determinant of the wave functions of the two electrons, a wave function with a given total value of M_l and M_s and of their sum M_j. All states with $L > M_l$ and $J > M_j$ can be represented by a wave function with these values of M_l and M_s, so in order to make things as simple as possible we shall take M_j equal to the value of J for the state of which we want to know the energy.

Here as we want the ${}^1D$ state, we shall consider all wave functions with $M_j = 2$. As for one of the ${}^3P$ states also $J = 2$, these wave functions will also represent this ${}^3P$ state. We will now first write down what states of the $3d^2$ configuration can be represented by a wave function with $M = 2$. We give in the following table the values of m_l and m_s for each electron in all combinations that give for M_j a resultant value 2 — as we have equivalent electrons, states which proceed from each other by the exchanging of the electrons are counted as the same state. We find

XIII

	1	2	M_s	M_l
1	$({}^1/_2, 0)$	$({}^1/_2, 1)$	1	1
2	$({}^1/_2, -1)$	$({}^1/_2, 2)$	1	1
3	$({}^1/_2, 1)$	$(-{}^1/_2, 1)$	0	2
4	$({}^1/_2, 0)$	$(-{}^1/_2, 2)$	0	2
5	$(-{}^1/_2, 0)$	$({}^1/_2, 2)$	0	2
6	$(-{}^1/_2, 1)$	$(-{}^1/_2, 2)$	-1	3

where the first column numbers the states, the second gives the values for m and m_s, (a,b) signifying that m_s has the value a and m_l the value b, the third gives M_s and the fourth M_l.

The wave functions corresponding to these states give for the part $1/r_{1 \cdot 2}$ of the energy the matrix, which we give below after integration over the angular and the spin coordinates

$$
\begin{array}{c|cccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 \\
\hline
1 & A & M & 0 & 0 & 0 & 0 \\
2 & M & B & 0 & 0 & 0 & 0 \\
3 & 0 & 0 & D & N & -N & 0 \\
4 & 0 & 0 & N & E & C & 0 \\
5 & 0 & 0 & -N & C & E & 0 \\
6 & 0 & 0 & 0 & 0 & 0 & F
\end{array}
$$

with $A = R_f + \frac{1}{49} R_g - \frac{6}{49} R_h, \qquad E = R_f - \frac{4}{49} R_g + \frac{2}{3.49} R_h,$

$$B = R_f - \frac{2}{49} R_g - \frac{13}{3.49} R_h, \qquad F = R_f - \frac{8}{49} R_g - \frac{1}{49} R_h,$$

$$D = R_f + \frac{1}{49} R_g + \frac{16}{441} R_h, \qquad M = \frac{6}{49} \frac{\sqrt{3}}{\sqrt{2}} R_g - \frac{10}{3.49} \frac{\sqrt{3}}{\sqrt{2}} R_h,$$

$$N = \frac{2}{49} \frac{\sqrt{3}}{\sqrt{2}} R - \frac{10}{441} \frac{\sqrt{3}}{\sqrt{2}} R_h, \qquad C = -\frac{4}{49} R_g - \frac{5}{3.49} R_h,$$

with R_f, R_g and R_h as they are defined in § 6 (7). When we diagonalize this matrix we find the energies for the ^3P, ^1D, ^3F and ^1G states and the wave functions for these states. In this way we have found for the contribution of $1/r_{1,2}$ to the energy of ^3P and ^1D state:

$$\textit{energy from } 1/r_{1,2} \textit{ for } {}^3P = R_f + \frac{1}{7} R_g - \frac{4}{21} R_h,$$

$$\textit{energy from } 1/r_{1,2} \textit{ for } {}^1D = R_f - \frac{3}{49} R_g + \frac{4}{49} R_h.$$

As to the wave functions, we are only interested in that of the ^1D state, which we need for the calculation of the interaction with the ^1D levels of the other configurations. We have found for it $\psi_{^1D} = \frac{\sqrt{3}}{\sqrt{7}}(3) - \frac{\sqrt{2}}{\sqrt{7}}(4) + \frac{\sqrt{2}}{\sqrt{7}}(5)$, where by (3), (4), and (5) are signified the wave functions of the states 3, 4, 5 as given in table XIII. The interaction as calculated with this wave function is given in § 6 (7).

Secondly, in § 8 we have used the interaction matrix of the ^1S state of the $4p^2$ configuration with that of the $4s\ 6s$ configuration. In the same manner as above we calculate the matrix elements belonging to $1/r_{1,2}$, this time for the states with $M_j = 0$. As we need only the ^1S state and as there are no matrix elements between states with different M we need only to consider states with $M_l = 0$. We give these states in the following table where the meaning of the symbols is the same as above

XIV

	1	2	M_s	M_l
1	$(^1/_2, 1)$	$(-^1/_2, -1)$	0	0
2	$(-^1/_2, 1)$	$(^1/_2, -1)$	0	0
3	$(^1/_2, 0)$	$(-^1/_2, 0)$	0	0

The matrix elements for $1/r_{1,2}$ which we found with the wave functions corresponding to these states are, after integration over the angular and the spin coordinates

	1	2	3
1	$R_d + \frac{1}{25} R_e$	$-\frac{6}{25} R_e$	$\frac{3}{25} R_e$
2	$-\frac{6}{25} R_e$	$R_d + \frac{1}{25} R_e$	$-\frac{3}{25} R_e$
3	$\frac{3}{25} R_e$	$-\frac{3}{25} R_e$	$R_d + \frac{4}{25} R_e$,

where R_d and R_e are defined in § 3 (6), only with $3p$ substituted by $4p$. After diagonalization of this matrix we found for the wave function of the ^1S state: $\psi_{1S} = \frac{1}{\sqrt{3}}\Big((3) - (4) + (5)\Big)$, and with this wave function we have calculated the interaction matrix given in § 8 (8).

§ 11. *Calculation of the matrix elements.*

In Chapter II we have used the numerical values of several radial integrals. We will now give some particulars about their calculation. All integrations had to be carried out graphically. In the first place, there are the exchange integrals K, the numerical values of which are given for the ^1D series in table III and for the 4*s* 6*s* state in § 8. The definition of K is given in § 2 (5). In fig. 8 we give the integrand of K for the 4*s* 4*d* state; we do not give it for the other members of the series, as it is for these of exactly the same type. We see that this integrand is precisely as was predicted in § 2, when we wanted to show that we expected for K a positive value.

FIG. 8.

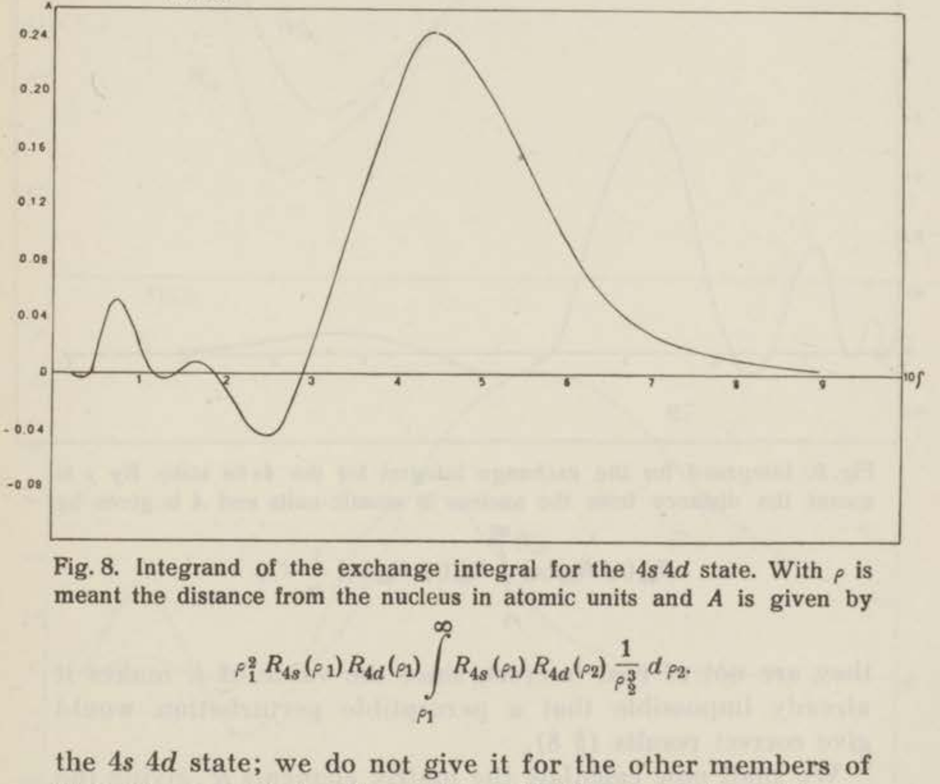

Fig. 8. Integrand of the exchange integral for the 4*s* 4*d* state. With ρ is meant the distance from the nucleus in atomic units and A is given by

$$\rho_1^2 R_{4s}(\rho_1) R_{4d}(\rho_1) \int_{\rho_1}^{\infty} R_{4s}(\rho_1) R_{4d}(\rho_2) \frac{1}{\rho_2^3} d\rho_2.$$

This is not the case for the integrand of K for the 4*s* 6*s* state, which we give in fig. 9, though also here there results a positive value for K. We never get here a considerable negative value for the integrand; this is due to the fact that, as we see in table XI, the 4*s* and the 6*s* function are for the values of ρ that come into account here very well in phase. We will not give more particulars about the other radial integrals that come into consideration for the 4*s* 6*s* state, as they are not of real interest, since the value of *K* makes it already impossible that a perceptible perturbation would give correct results (§ 8).

FIG.9.

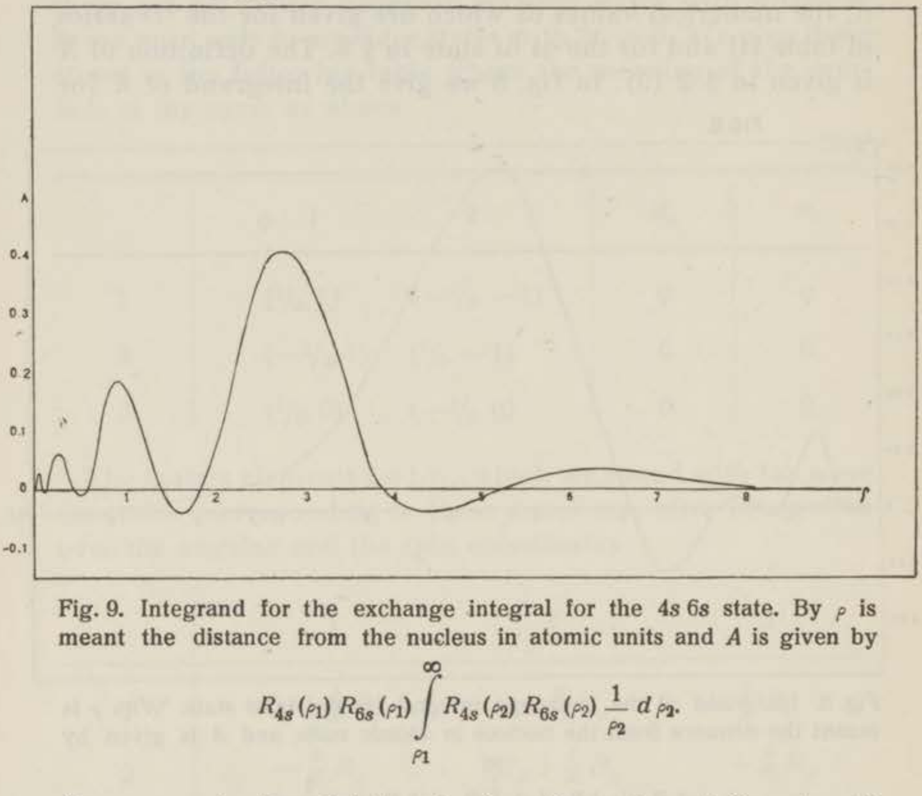

Fig. 9. Integrand for the exchange integral for the 4*s* 6*s* state. By ρ is meant the distance from the nucleus in atomic units and *A* is given by

$$R_{4s}(\rho_1)\, R_{6s}(\rho_1) \int_{\rho_1}^{\infty} R_{4s}(\rho_2)\, R_{6s}(\rho_2)\, \frac{1}{\rho_2}\, d\rho_2.$$

We shall now calculate the matrix elements R_c giving the interaction with the $4p^2$ configuration; R_c was defined in § 3 (6). In order to calculate it we have to devide it into two integrals R_c' and R_c'', defined for the 4*s* 3*d* state as

$$R_c' = \int_0^{\infty} d\rho_1 \cdot \rho_1\, R_{3d}(\rho_1)\, R_{4p}(\rho_1) \int_{\rho_1}^{\infty} d\rho_2 \frac{1}{\rho_2^2} R_{4s}(\rho_2)\, R_{4p}(\rho_2) \text{ and}$$

FIG.10.

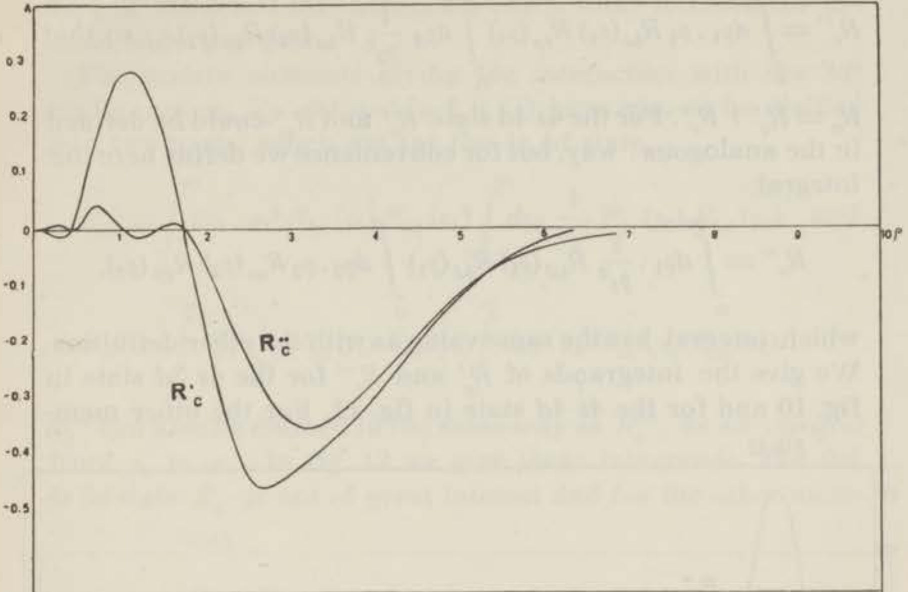

FIG.11

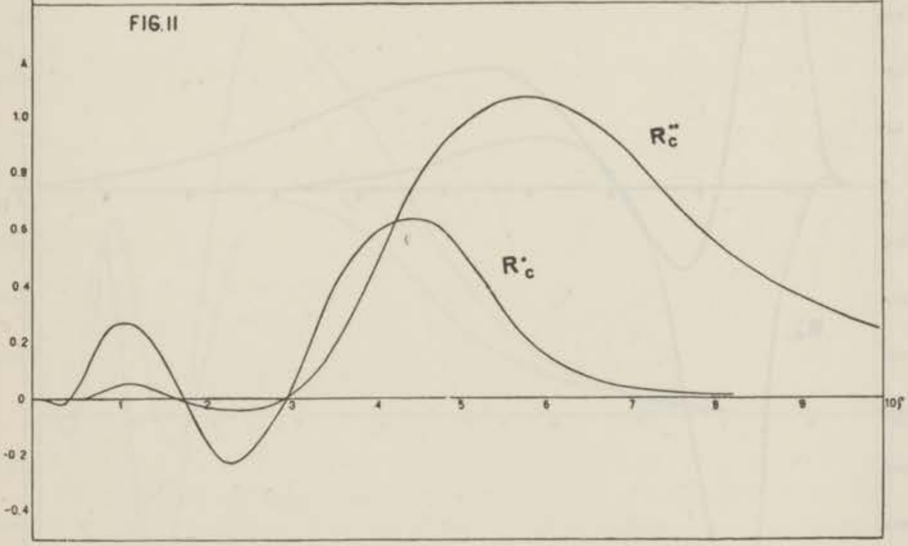

Fig. 10. Integrands of R_c and R_c for the 4*s* 3*d* state. By ρ is meant the distance from the nucleus in atomic units, and by *A* the integrand as defined in the text.

Fig. 11. Integrands of R'_c and R''_c for the 4*s* 4*d* state, where ρ is the distance from the nucleus given in atomic units and *A* is the integrand as defined in the text.

$$R_c'' = \int_0^\infty d\rho_1 \cdot \rho_1 \, R_{4s}(\rho_1) \, R_{4p}(\rho_1) \int_{\rho_1}^\infty d\rho_2 \, \frac{1}{\rho_2^2} \, R_{3d}(\rho_2) \, R_{4p}(\rho_2), \quad \text{so that}$$

$R_c = R_c' + R_c''$. For the 4*s* 4d state R_c' and R_c'' could be defined in the analogous way, but for convenience we define here the integral

$$R_c'' = \int_0^\infty d\rho_1 \cdot \frac{1}{\rho_1^2} \, R_{4p}(\rho_1) \, R_{4d}(\rho_1) \int_0^{\rho_1} d\rho_2 \cdot \rho_2 \, R_{4s}(\rho_2) \, R_{4p}(\rho_2),$$

which integral has the same value as with the other definition. We give the integrands of R_c' and R_c'' for the 4*s* 3*d* state in fig. 10 and for the 4*s* 4*d* state in fig. 11. For the other mem-

FIG.12.

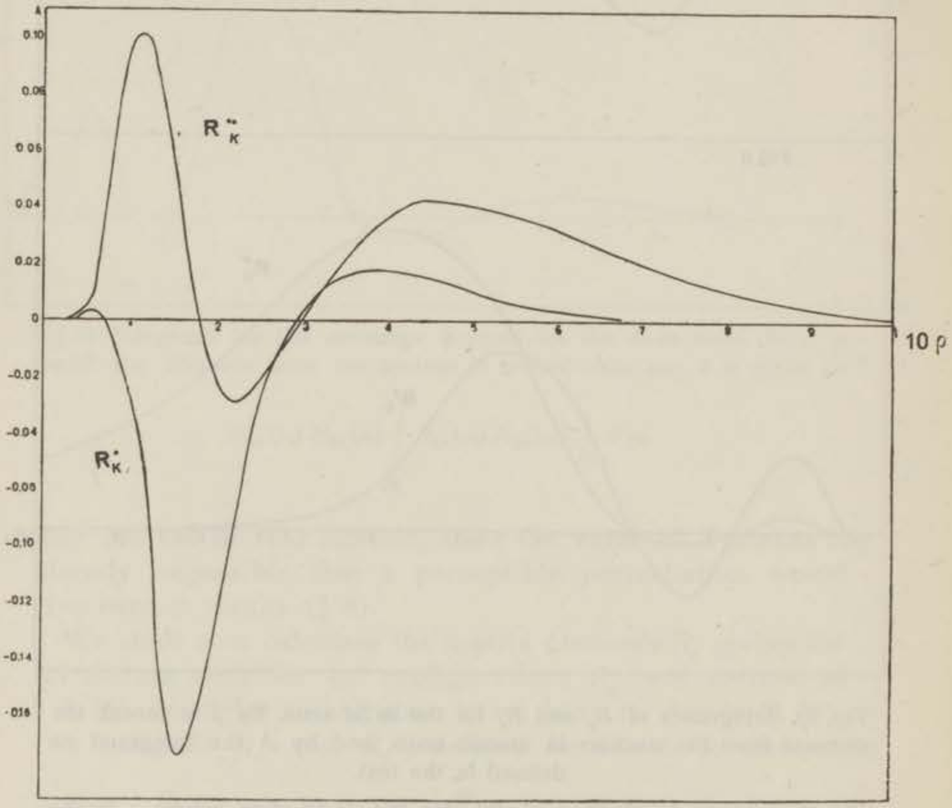

Fig. 12. Integrands of R'_k and R''_k for the 4*s* 4*d* state where, ρ is the distance from the nucleus and *A* is the integrand as defined in the text.

bers of the series the integrands are similar to those for the 4*s* 4*d* state (see § 7).

The matrix elements giving the interaction with the $3d^2$ configuration, R_k, defined in § 6 (7) have also to be divided into two parts, which are for the 4*s* 4*d* state

$$R_k' = \int_0^\infty d\rho_1 \cdot \rho_1^2 R_{3d}(\rho_1) R_{4d}(\rho_1) \int_{\rho_1}^\infty d\rho_2 \frac{1}{\rho_2^3} R_{4s}(\rho_2) R_{3d}(\rho_2) \text{ and}$$

$$R_k'' = \int_0^\infty d\rho_1 \frac{1}{\rho_1^3} R_{3d}(\rho_1) R_{4d}(\rho_1) \int_0^{\rho_2} d\rho_2 \cdot \rho_2^2 R_{4s}(\rho_2) R_{3d}(\rho_2).$$

R_k'' can also be defined in the same way as R_c'', as an integral from ρ_1 to ∞. In fig. 12 we give these integrands. For the 4*s* 3*d* state R_k is not of great interest and for the other mem-

FIG.13.

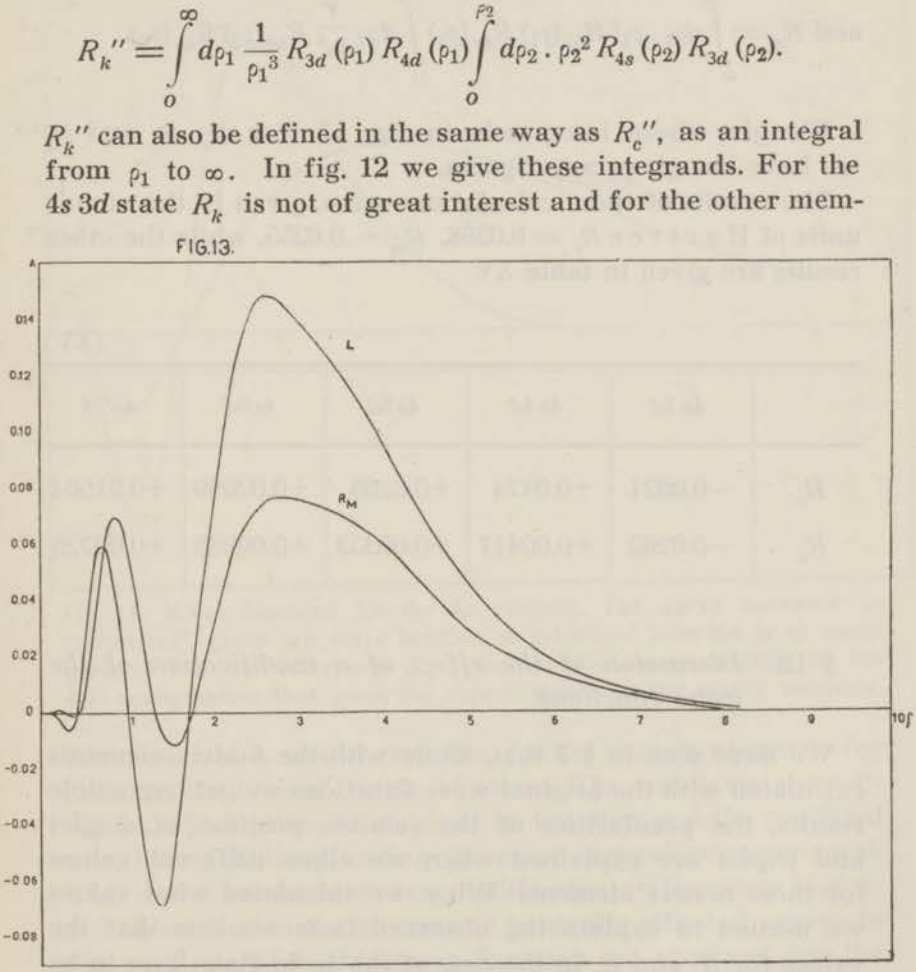

Fig. 13. Integrands of R_l and R_m, where ρ is the distance from the nucleus and *A* the integrand as defined in the text.

bers of the series the integrands are again similar to those for the $4s$ $4d$ *state.*

There remain the integrals R_l and R_m, also defined in § 6 (7). We find for them

$$R_l = 2\int_0^\infty d\rho_1 \cdot \rho_1 R_{3d}(\rho_1) R_{4p}(\rho_1) \int_{\rho_1}^\infty d\rho_2 \frac{1}{\rho_2^2} R_{3d}(\rho_2) R_{4p}(\rho_2),$$

and $$R_m = \int_0^\infty d\rho_1 \cdot \rho_1^3 R_{3d}(\rho_1) R_{4p}(\rho_1) \int_{\rho_1}^\infty d\rho_2 \frac{1}{\rho_2^4} R_{3d}(\rho_2) R_{4p}(\rho_2).$$

We give these integrands in fig. 13. For R_e, R_g and R_h we have not given any figures.

The results of these calculations were, given in the atomic units of Hartree $R_l = 0.0368$, $R_m = 0.0255$, while the other results are given in table XV

(XV)

	$4s\,3d$	$4s\,4d$	$4s\,5d$	$4s\,6d$	$4s\,7d$
R_c	-0.0621	$+0.0474$	$+0.0265$	$+0.02059$	$+0.01564$
R_k	-0.0262	$+0.00417$	$+0.00332$	$+0.00285$	$+0.00225$

§ 12. *Discussion of the effect of a modification of the wave functions.*

We have seen in § 7 that, while with the matrix elements calculated with the original wave functions we get impossible results, the pecularities of the relative position of singlet and triplet are explained when we allow different values for these matrix elements. When we calculated what values we needed to explain the observed facts we saw that the values for R_c and R_k in the case of the $4s$ $4d$ state have to be strongly altered, while the value of R_c for the $4s$ $3d$ state has to remain almost unaltered. On the other hand we have seen in § 9 that the wave functions for the $4p$ and the $3d$ electrons of the $4p^2$ and the $3d^2$ configurations might easily differ from the calculated ones so that the real wave function of the $4p^2$ state would bring the electrons nearer to the nucleus.

We have tried to construct a modification of the wave function which would give the desired matrix elements for both the $4s$ $4d$ and the $4s$ $3d$ states. The result we show in fig. 14, which gives the original $4p$ function and the modified one, both functions having the same normalization integral. This new wave function is a modification in the sense indicated above that is the electron is generally situated nearer to the nucleus. With this wave function we obtained for the $4s$ 4d state, in Hartree's units, $R_c = 0.0122$, whereas according to § 7 we want $R_c = 0.0126$; for the $4s$ $3d$ state we find

FIG.14.

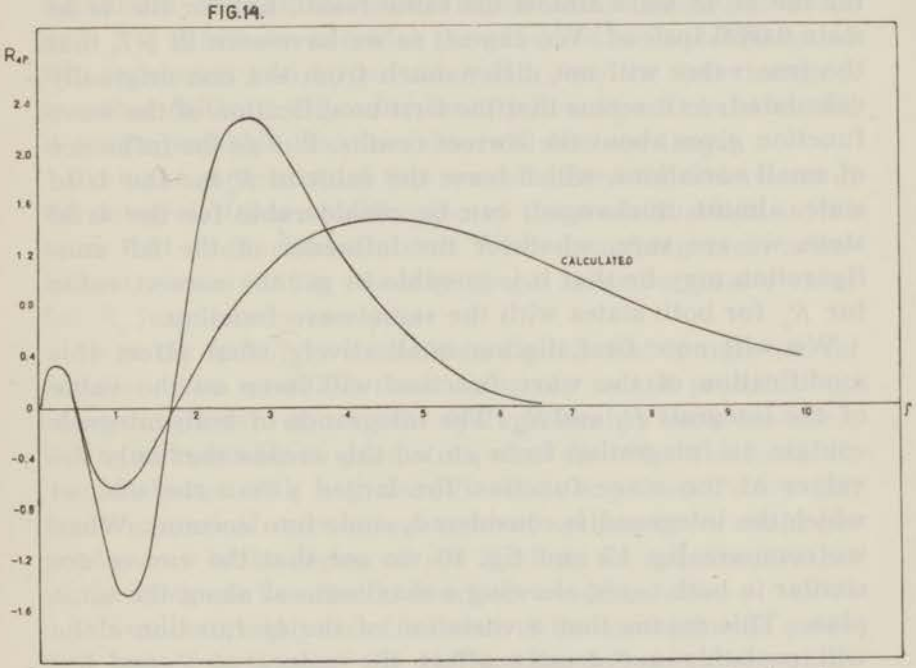

Fig. 14. Wave functions for the $4p$ electron. The curve indicated as "calculated" gives the wave function as calculated from the $4s$ $4p$ configuration and the other one gives the modified wave function for the $4p^2$ configuration that gives the correct values for the matrix elements.

$R_c = 0.0668$, whereas originally we had $R_c = 0.0621$, so here the matrix element has not been strongly altered.

The value of R_c for the 4*s* 3*d* state is, however, very sensitive with respect to a small change in the modified 4*p* function. In fact when we calculated R_c with a wave function, which was modified in a slightly different way, we obtained for the 4*s* 4*d* state almost the same result, but for the 4*s* 3*d* state 0.0896 instead. We expect, as we have seen in § 7, that the true value will not differ much from the one originally calculated; so it seems that the first modification of the wave function gives about the correct results. But as the influence of small variations, which leave the value of R_c for the 4*s* 4*d* state almost unchanged, can be considerable for the 4*s* 3*d* state, we are sure, whatever the influence of the $3d^2$ configuration may be that it is possible to get the correct value for R_c for both states with the same wave function.

We will now first discuss qualitatively what effect this modification of the wave function will have on the value of the integrals R_l and R_m. The integrands of both integrals contain an integration from ρ to ∞; this means that only the values of the wave function for larger ρ than the one, at which the integrand is considered, come into account. When we compare fig. 13 and fig. 10 we see that the curves are similar in both cases, showing a maximum at about the same place. This means that a variation of the 4*p* function alone will probably not greatly affect the values of R_l and R_m, at any rate not in the same measure as R_c of the 4*s* 4*d* state.

As to the wave function of the $3d^2$ configuration, it has little sense to try and construct here also a modification of the wave function, which would give the correct results for the matrix elements R_k; owing to the fact that we do not know the position of the perturbing level, we cannot tell exactly what values for the matrix elements are required. Furthermore, as any value for the matrix element of the 4*s* 3*d* state will do, this state cannot, as in the case of the 4*p* function, give us a test for the usefulness of the modification. Lastly, owing to the fact that the 3*d* function has no nodes, it is more difficult to construct a plausible modification.

The only thing we can say here is that, in contrast to the

$4p$ function, here the maximum value of the wave function lies nearer to the nucleus than that of the $4s$ function, so we may expect that this maximum for the true wave function comes further away. When we consider fig. 12 we have to bear in mind that the integrand of R_k' contains an integration from ρ to ∞ and that of R_k'' one from 0 to ρ. Originally the maximum value of the wave function was situated at about $\rho = 1.4$. When we consider the effect of a displacement of this maximum to a larger value of ρ, we see that though it is rather difficult to predict exactly how R_k will behave, still it seems probable that its value will become larger.

To make more sure of this we calculated the behaviour of the integrals for a modification of the wave function in the sense that was indicated above. Without making exact calculations we saw that in this way we got indeed a greater value for R_k just as was needed.

As to R_l and R_m we see from fig. 13 that if only the $3d$ function was modified these integrals would probably increase. As, however, also the $4p$ function has been modified, it was not possible to predict in what direction the integrals would change with both modifications together. To try and make numerical calculations seemed useless as we could not predict how in the region of $\rho = 3$, where the maximum value of the integrals lies, the $3d$ function would behave.

It would certainly be of interest to try to obtain the modified wave functions of the $4p^2$ and the $3d^2$ states by strictly theoretical methods.

To conclude we recall that in the case of the S series the use of the first approximation wave functions for the individual s-electrons gave wrong results for the matrix elements (§ 8). In this approximation we have neglected the influence of the $6s$ electron on the $4s$ electron; in contrast to the case of the $4s\ np$ and the $4s\ nd$ states this reaction of the outer valence electron on the inner one may be considerable. Indeed, when we consider the wave functions we see that the large value of the exchange integral is due to the fact that the wave functions are very well in phase in the region from which comes the chief contribution to our integral (§ 11). Interaction between the electrons would change this, since they repel each other. The effect of this would surely be that we get a smaller value for the exchange integral, i. e. just the kind of change that is required by the semi-empirical considerations (§ 8).

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SAMENVATTING.

Dit proefschrift is een poging de anomalien in de relatieve ligging van de singulet en de triplet termen bij de *D*-serie van het Ca I spectrum te verklaren. Het energie verschil tussen singulet en triplet term wordt in de elementaire theorie gegeven door tweemaal de plaatsruilings integraal. In het algemeen kan verwacht worden, dat het teken van deze integraal positief is; in dit geval zal de singulet boven de triplet liggen. Bij de Ca *D*-serie is dit niet het geval; hier ligt afwisselend de singulet term boven en onder de triplet. Een mogelijkheid voor een verklaring van een „verkeerde" ligging van singulet ten opzichte van triplet is aangegeven door Bacher. Hij verklaart deze in het geval van de $3s\ 3d$ term van Mg door de storende invloed van een andere configuratie. De vraag was nu, of bij het Ca de experimentele feiten op een dergelijke wijze verklaard zouden kunnen worden.

In het eerste hoofdstuk worden eerst de formules voor de afstand tussen singulet en triplet gegeven. Vervolgens wordt besproken welke oorzaken er kunnen zijn voor een „verkeerde" ligging van singulet en triplet. Hierbij wordt tevens aangetoond dat wisselwerking van de beide buiten electronen met de afgesloten binnenschillen geen invloed op deze afstand uitoefenen.

Vervolgens wordt de veronderstelling van Bacher besproken en met behulp van een ruwe methode uit de matrix elementen van de ene term die voor de overige *D* termen van het Mg geschat. De resultaten, die we op deze wijze gevonden hebben zijn enigszins in overeenstemming met de experimenten. De afwijking kon wat richting betreft begrepen worden uit de wijze waarop de matrix elementen geschat waren. Op deze wijze wordt ook de *D* serie van het Cd behandeld en ook hier zijn de resultaten bevredigend.

In het tweede hoofdstuk gaan we over tot het Ca. Eerst wordt het stuk van Russell en Shenstone besproken, waar deze met behulp van de effectieve quantumgetallen de invloed van een storing op een hele serie bespreken. Vervolgens worden de resultaten van onze berekeningen besproken. Voor de plaatsruilingsintegralen worden positieve, voor de hele serie regelmatig afnemende, waarden gevonden. Vervolgens wordt aangegeven welke configuraties een storende invloed zouden kunnen uitoefenen en, in tegenstelling met het Mg, komen hiervoor twee configuraties in aanmerking, de $4p^2$ en de $3d^2$ configuratie. In § 6 wordt dan de storingsrekening uitgevoerd en we vinden, dat de resulterende verschuivingen veel te groot zijn. In § 7 worden de resultaten gegeven met nieuwe waarden voor de matrix elementen. We zien, dat het mogelijk is met gewijzigde waarden voor de golffuncties van de $4p^2$ en de $3d^2$ configuraties overeenstemming met de experimenten te krijgen.

Vervolgens worden in § 8 de anomalien in de S-serie besproken. Deze kunnen hier met behulp van een storing van de ^1S term op semi-empirische wijze verklaard worden. Weliswaar gaven de zuiver theoretische berekeningen met behulp van de golffuncties hier niet de juiste resultaten. Dit kon echter ook niet verwacht worden, daar reeds uit de litteratuur bekend was, dat in het geval van S termen met golffuncties, die een eerste benadering voorstellen, geen overeenstemming van de theorie met de experimenten te verwachten is [2]).

In het derde hoofdstuk worden de numerieke berekeningen gegeven. In § 9 wordt in het kort de methode, volgens welke de eigen-functies berekend zijn, beschreven; tevens wordt aangegeven wat de oorzaak kan zijn van het feit, dat we met de golffuncties van de $4p^2$ en de $3d^2$ configuraties slechte resultaten kregen. Vervolgens worden in de §§ 10 en 11 de storings matrices afgeleid en de berekening van de matrix elementen gegeven.

In § 12 worden de wijzigingen van de golffuncties der $3d^2$ en $4p^2$ configuraties besproken. In het geval van de $4p^2$ configuratie hebben we een gewijzigde golffunctie geconstrueerd en gezien dat we met deze golffunctie goede resultaten krijgen voor de hele serie.

STELLINGEN

I

Het is mogelijk uit het thermo-electrisch gedrag van een metaal boven het sprongpunt te voorspellen, dat het metaal bij verdere afkoeling super geleidend zal worden.

W. H. Keesom en C. J. Matthijs, Physica, Jan. 1938.

II

De verhandeling van F. Bopp, Zeitschr. für Physik. **9**, 10, 1937, bevat geen essentieel nieuwe gezichtspunten over het wezen der super geleiding.

III

Ten onrechte maken J. Stark en K. Steiner bij hun metingen gebruik van een galvanometer met korte slingertijd.

J. Stark en K. Steiner, Phys. Zeitschr. **38**, 277, 1937.

IV

Het is ondoelmatig de toestand van een super geleider met ingevroren krachtlijnen para magnetisch te noemen.

J. Stark, Phys. Zeitschr. **38**, 269, 1937.

V

Ten onrechte betitelt K. F. Niessen de eerste twee termen van de reeks van Euler-Mac Laurin met de naam „erweiterte Eulersche Formel".

K. F. Niessen, Physica, **1**, 783, 1934.

VI

Het verdient aanbeveling de storing van een spectraal serie te onderzoeken in een geval waar de eigen functies in een voldoende benadering berekend kunnen worden.

VII

De door Bacher gegeven berekening van de ligging der $3s\,3d$ termen bij Mg is onjuist.

F. Bacher, Phys. Rev. **43**, 264, 1933.

VIII

Het ontbreken van philosophische vorming wordt door vele studenten in de exacte vakken als een leemte gevoeld. Het is onjuist te menen, dat hieraan niet dient te worden tegemoet gekomen.