ON THE QUANTUM THEORY EXPLANATION OF THE ANOMALIES IN THE 6th AND 7th PERIODS OF THE PERIODIC TABLE

BY

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Introduction.

It is well known that the family of rare earths in the 6th period of the periodic table occupies an anomalous position, as no homologous family is found in the other periods. According to Bohr's theory the appearance of the rare earth family is a natural consequence of the gradual development of the group-structure of the electronic distribution in the atom. In fact the appearance of this family is attributed to the completion of the four-quantum group by the addition of the 4th sub-group. According to the theory we should expect an analogous family in the 7th period of the periodic table corresponding to the addition of the 4th subgroup to the five-quantum group. The non-appearance of such a family among the known elements must be attributed to the different conditions in the atom during the development of the 4- and 5-quantum groups, which brings about a relative delay in the development of the latter group. It is the object of the present paper to examine this point by a closer investigation of the fields of force in the atom which are responsible for the binding of electrons.

Fues[1] and Hartree[2] have already treated the interatomic fields of force by showing that it is possible to ac-

[1] E. Fues, Zs. für Phys. *11*,364, 1922; *12*,1, 1923; *13*,211, 1923; *21*,265, 1924.

[2] D. R. Hartree, Proc. Camb. Phil. Soc. 21,625, 1923.

count for X-ray levels by comparison with stationary orbits
in a central field. Especially Fues[1] showed how the field
corresponding to Caesium (the first element in the 6th
period) did not yet allow the binding of electrons belonging
to the 4th subgroup of the 4-quantum group, but that the
conditions for this binding are so nearly fulfilled, that such
electrons must be expected to appear in the atoms of
elements in the early part of the 6th period. In order to
investigate the above anomaly Urey made an investgation
of the central fields of the atoms in the 7th period by the
same method as that used by Fues. This calculation
predicted in accordance with the observed structure of the
periodic table, that the conditions for the appearance of
the fourth group of the 5-quantum group are not yet fulfilled
in uranium.

The difficulty of the theoretical explanation of the fine
structure in X-ray levels left these considerations not quite
satisfactory. The difficulty has, however, been removed by
the recognition of the magnetic moment to be attributed
to each electron, and by the establishment of a rational
quantum mechanics. This development at the same time
suggested some modifications in the calculation and the
work has therefore been continued by Sugiura with the
result that it is possible to obtain satisfactory support for
the above conclusions as regards the explanation of the
anomaly in the periodic table.

§ 1. *X*-Ray levels and central orbits.

In the analysis of spectral problems it has been useful
to compare the binding of each electron in the atom with

[1] E. Fues, Zs. für Phys. 21,265, 1924.

the stationary states of an electron in a central field of force. It was assumed that these states could be represented by mechanical orbits of the electron picked out among the continuous multitude of such orbits by means of the so-called quantum rules. In the case of central orbits these rules may be written in the form:

$$\int_0^\cdot p_r \, dr = n_r h \, , \qquad \int_0^{2\pi} p_\varphi \, d\varphi = 2\pi p_\varphi = n_\varphi h \qquad (1)$$

where p_r and p_φ are the generalised momenta conjugated to the polar coordinates r and φ, while h is Planck's constant and n_r and n_φ are integers, the so-called radial and azimuthal quantum number. In the case of a Coulomb field, where the orbits are Keplerian ellipses, the energy depends only on the sum $n = n_r + n_\varphi$, which is denoted as the principal quantum number. In the interior of the atom this number will in the well known way determine the strength of the electron-binding to the first approximation, and the group of electrons corresponding to the same value of n forms what is called the n-quantum group. When completed, this group contains $2n^2$ electrons. The sub-division of the group structure is intimately connected with the appearance of two quantum numbers in the theory of central orbits. Thus corresponding to the n different types of n-quantum orbits we recognize n-subgroups of each group. The orbit corresponding to each such subgroup is denoted by the symbol n_k, where the subordinate quantum number k takes the values 1 to n. A completed subgroup contains $4k-2$ electrons. As regards the interpretation of X-ray levels it is as well known possible to characterize the levels, known as K, L, M, by the principal quantum numbers 1, 2, 3. For a time a difficulty consisted in cor-

relating the multiplicity of these levels in a unique way with the sub-ordinate quantum number k. In fact the appearance of the so-called "screening" and "relativity" doublets in the levels suggested the necessity of correlating two values k_1 and k_2 to each level, each referring to certain features of the theory of central orbits.[1] Recently, however, all difficulties have been removed by the introduction of the idea of the spinning electron.[2] On classical mechanics the orbit of a spinning electron in a central field will not be plane, but can be described as a plane central orbit performing a precession round a fixed axis in space. As a consequence each level which would correspond to given values of n and k is generally split up in two levels. The theory shows that such a pair of levels will form a "relativity" doublet, their distance apart being just equal to the distance which on Sommerfeld's theory of the influence of the relativity modifications on the stationary states of a hydrogen-like atom, would appear between two n_k levels, corresponding to successive values of k. Only the level corresponding to the first subgroup ($k = 1$) is not split up, but shifted in the direction of the n_2 level. Moreover the theory explains that the distance between two neighbouring levels, corresponding to successive values of k, will just be a screening doublet. Due to this development of the theory it is now possible from the observed levels to deduce a simpler system of levels which would correspond to an imagined atom, in which the influence of the relativity modification and of the electronic spin on the binding of the electrons

[1] N. BOHR and D. COSTER, Zs. für Phys. 12, 342, 1923.

[2] G. E. UHLENBECK and S. GOUDSMIT, Nature, 117, 264, 1926; F. R. BICHOWSKY and H. C. UREY, Proc. Nat. Acad. of Sciences 12, 80, 1926; L. H. THOMAS, Nature, 117, 514, 1926; W. HEISENBERG and P. JORDAN, Zs. für Phys. 37, 263, 1926.
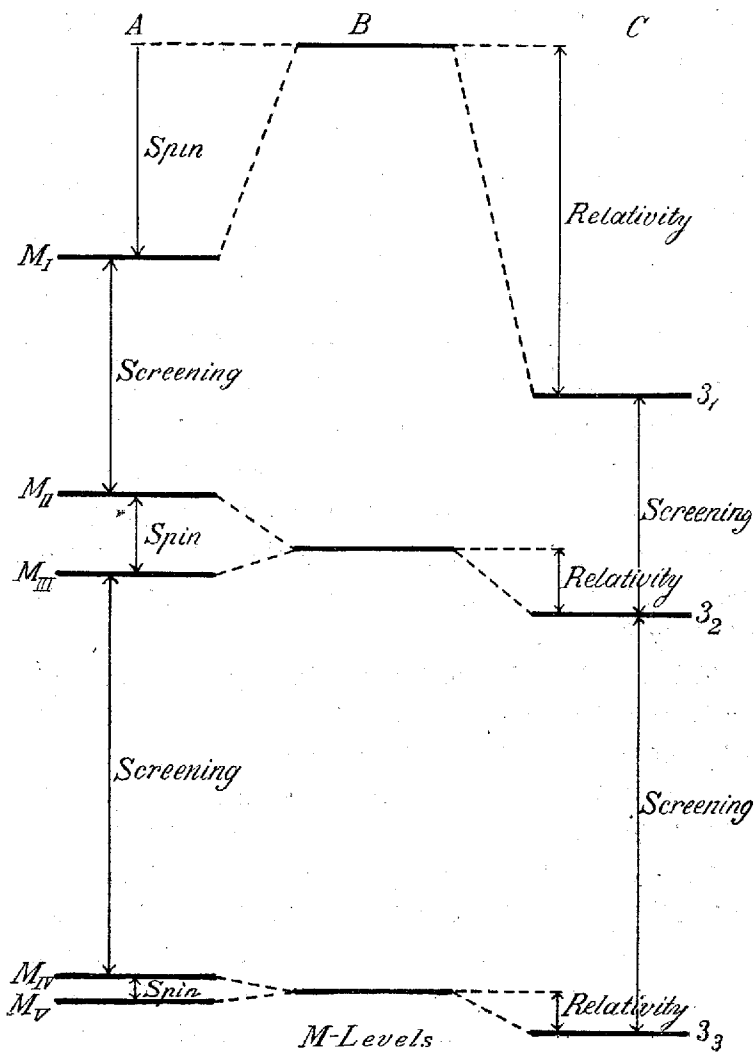
Fig. 1.

were absent. This procedure is illustrated by the accompanying figure referring to the M-levels. In column A is given a complete scheme corresponding to the theoretical interpretation of the observed levels. In column B the

system of levels is given which would appear if only the spin were neglected. Column C illustrates the levels in absence of the relativity modifications. It is easily found that the reduction of the levels in question with a degree of approximation sufficient for our purpose may be obtained by taking the distances between two neighbouring n_k levels equal to the observed screening doublets, and by fixing the absolute values of the n_n level by subtracting from the smallest term observed (in Fig. 1 M_V) a quantity equal to $\frac{R}{N^4} \cdot \frac{1}{4} \cdot \alpha^2 (N-s)^4$ which on Sommerfeld's theory appears as the first approximation of the relativity correction for a circular n-quantum orbit. Here R is Rydberg's constant, $\alpha = \frac{2\pi e^2}{ch}$ and s a screening constant, which for the K-level ($n = 1$) may be taken equal to 1, and for the L-levels, M-levels etc. equal to the empirical screening constant in the smallest relativity doublet.

This simplification of the problem by reduction of the levels may be considered as quite rational both from the point of view of the empirical laws governing the multiplicity of X-ray levels and from the quantum-mechanical analysis of the effect of electronic spin and relativity modifications on hydrogenlike spectra.[1] A comparison of the system of reduced levels with the atomic model, however, is, according to the modern development of the quantum theory, strictly speaking no mechanical problem. Nevertheless the above mentioned close analogy between the reduced level structure and the system of stationary states to be expected from central orbits on the basis of the relations (1), suggests that an insight in the origin of these levels may be obtained by a mechanical analysis of orbits in a

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[1] Heisenberg and Jordan, Zs. für Phys. l. c.

central field of force. Instead, however, of identifying the subordinate quantum number k with the azimutal quantum number n_φ, we may from the researches of WENTZEL[1] on X-ray spectra, and of BORN and HEISENBERG[2] on optical spectra infer that a more suitable basis for the analysis is obtained if n_φ is taken equal to $k - \frac{1}{2}$, and accordingly is given the values $\frac{1}{2}, \frac{3}{2} \ldots n - \frac{1}{2}$.

In order now for a given atom to find a central field which is suitable for representing the X-ray levels, we proceed in a manner analogous to that followed by Fues and Hartree. Calling the potential of the electron in the field V, the energy equation may be written in the form

$$\frac{1}{2m}\left(p_r^2 + \frac{p_\varphi^2}{r^2}\right) + V = -W$$

where W is the work necessary to remove the electron from the field. Denoting the reduced spectroscopic levels by $\nu_{n,k}$, we may write

$$W = \frac{\nu_{n,k}}{R} W_0, \qquad W_0 = \frac{2\pi^2 e^4 m}{h^2}.$$

Introducing the variable ϱ by

$$r = a_0 \varrho, \qquad a_0 = \frac{h^2}{4\pi^2 e^2 m},$$

we now get from the quantum conditions, eliminating p_φ

$$n - \left(k - \frac{1}{2}\right) = \frac{1}{\pi} \int_{\varrho_{min}}^{\varrho_{max}} \frac{d\varrho}{\varrho} \sqrt{Q(\varrho) - P(\varrho)} \qquad (2)$$

where

[1] G. WENTZEL, Ann. der Phys. 76, 803, 1925.
[2] M. BORN and W. HEISENBERG, Zs. für Phys. **23**, 388, 1924.

$$P(\varrho) = \frac{\nu_{n,k}}{R} \varrho^2 + k(k-1), \qquad Q(\varrho) = -\varrho^2 \frac{V}{W_0} - \frac{1}{4}.$$

In order to determine the function V for a given element the procedure is now to draw a set of parabolas, one for each level, representing the functions $P(\varrho)$, and then by trial in the diagram to draw a Q-curve intersecting these parabolæ in such a way that the condition (2) is satisfied with as high an accuracy as possible.

The use of fractional values for the radial and azimuthal quantum numbers implies that in our case the P-curves always cut the Q-curve in two points, in contrast to the treatment of Fues and Hartree where the use of integral quantum numbers in (1) implies that the Q-curve will be tangent to those P-curves for which $n = k$. In drawing the Q-curve we start from small values of ϱ, and construct the Q-curve so as to satisfy condition (2) for the K- and L-levels. Having thus obtained the Q-curve for the inner part of the atom near the nucleus we proceed outwards by trial, taking the M- and L-levels into account.

It is of interest to note that it is possible to obtain a check on the field of force calculated in this way from the reduced levels by a consideration of the screening constants entering into the representation of the relativity doublets. These constants are defined by the Sommerfeld formula

$$\frac{\Delta \nu}{R} = \frac{(N-s)^4 \alpha^2}{n^3 k(k-1)}.$$

From the theory of the origin of these doublets as due to the electronic spin, it follows that s can be obtained from the equation

$$\overline{\left(\frac{N_{\text{eff}}}{r^3}\right)} = (N-s)\overline{\left(\frac{1}{n^3}\right)}_{N-s}$$

where N_{eff} is defined by equating the electric force in the atom at a distance r from the nucleus to $\dfrac{e\,N_{eff}}{r^2}$, and where the right side of the equation refers to an electron which is bound in the Coulomb field surrounding a nucleus of charge $(N-s)$ in a state corresponding to the same values of n and k. The lines above the symbols in the formula indicate time-mean values which strictly speaking are to be taken in the sense of the quantum mechanics. It is, however, to be expected that a high degree of approximation may be obtained by taking the mean values over orbits defined by the relation (1). For the calculation of s, we obtain in this way the formula

$$(N-s)^4 = n^3 \left(k - \frac{1}{2}\right)^3 \left(\overline{\frac{N_{eff}}{\varrho^3}}\right), \qquad (3)$$

where ϱ is defined as above.

§ 2. Application to elements in the 6th period.

In the calculation of the central field we have used the X-ray terms obtained by Bohr and Coster[1], Hjalmar[2] Dolejsek[3] and Nishina.[4] The results are given in Table I for the atoms of caesium, lanthanum and neodymium, and the curves of Q for Cs and Nd are shown in figs. 2 and 3. As shown in the table it has been possible to construct the Q-curves so as to fit condition (2) with a very close approximation for almost all levels. In fig. 4 a representation is given of the variation of N_{eff} with ϱ for caesium. While the field used by Fues is represented by the broken line, the full curve corresponds to our calculations. It is

[1] N. Bohr and D. Coster, l. c.

[2] E. Hjalmar, Zs. für Phys. 15, 65, 1923.

[3] V. Dolejsek, Zs. für Phys. 21, 111, 1924.

[4] Y. Nishina, Phil. Mag. 49, 521, 1925.

Table I.

Level	$\frac{\nu}{R}$ observed			$\frac{\nu}{R}$ reduced			n_k	$(n-k)$ calc.		
	Cs (55)	La (57)	Nd (60)	Cs	La	Nd		Cs	La	Nd
K_I ...	2646.0	2864.2	3214.2	2533.0	2733.5	3088.1	1_1	0.00	0.00	0.00
L_I ...	421.8	462.9	526.2	390.4	426.3	480.0	2_1	1.00	1.01	1.01
L_{II} ...	394.9	434.2	495.5	363.5	397.6	449.3	2_2	0.00	0.00	0.00
L_{III} ..	369.3	404.4	457.8							
M_I ...	89.8	100.7	116.5	83.4	92.9	106.0	3_1	1.99	2.00	2.00
M_{II} ..	79.3	90.0	104.8	72.9	82.2	94.3	3_2	0.99	1.00	0.99
M_{III} ..	74.4	84.0	96.8							
M_{IV} ..	54.6	62.9	74.2	53.1	61.1	71.7	3_3	0.00	0.00	0.00
M_V ...	53.6	61.7	72.5							
N_I ...	17.1	20.5	23.7	15.9	19.4	22.3	4_1	2.99	3.00	3.00
N_{II} ...	13.6	16.5	19.2	12.4	15.4	17.8	4_2	2.00	1.99	2.00
N_{III} ..	12.6	15.4	17.8							
N_{IV} ..	5.9	7.8	9.2	5.7	7.8	9.2	4_3	1.00	1.00	1.01
N_V ...	5.7	7.8	9.2							
O_I ...	1.9	3.0	3.1	1.9	3.0	3.1	5_1	3.96	3.93	3.90
O_{II} ...	1.7	2.3	2.7	1.7	2.3	2.7	5_2	2.80	2.90	2.80

seen, that our procedure gives a more smooth variation of
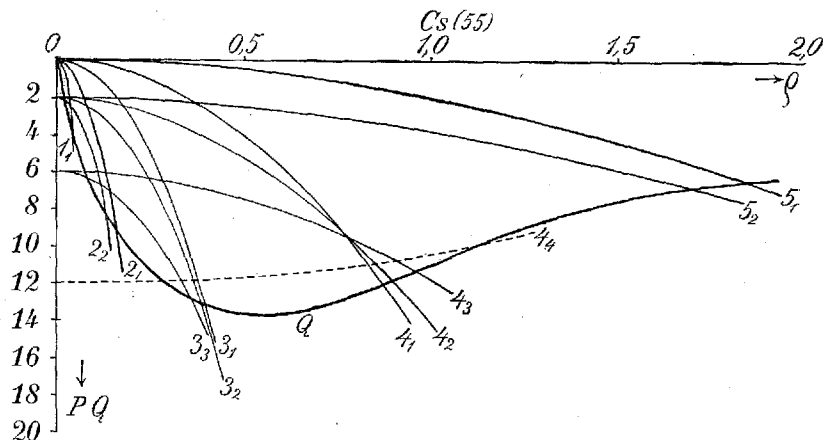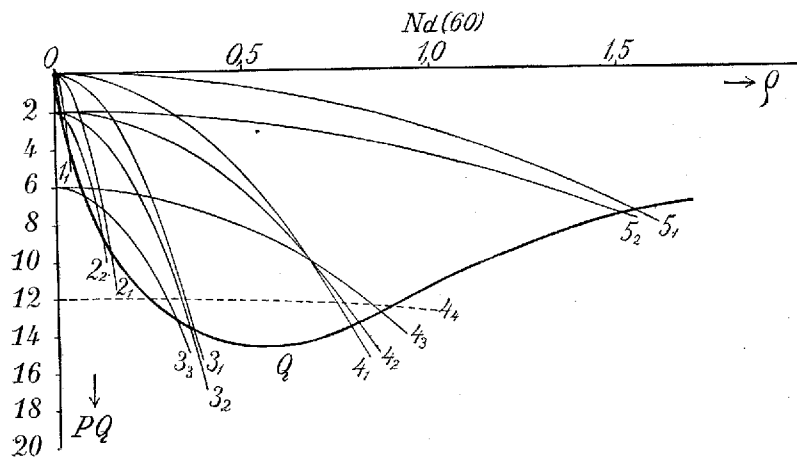the field, at the same time as it allows a closer agreement

Fig. 2.

Fig. 3.

with the quantumtheoretical expectation. For caesium we find by formula (3) for the screening constants appearing
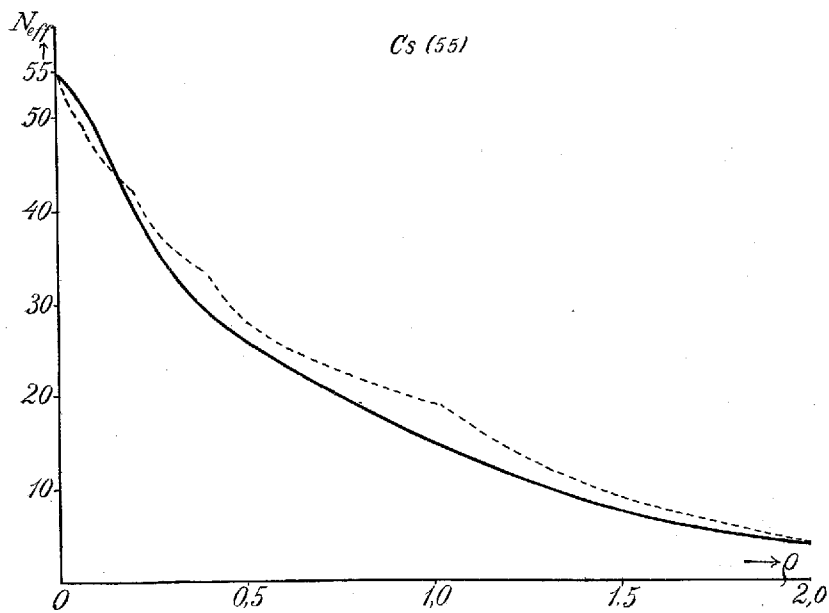

Fig. 4.

in the relativity doublets L_{II}, L_{III} and M_{II}, M_{III} and M_{IV}, M_V, 2,8, 12,4 and 9,2 respectively in close agreement with empirical values 3,5, 13,0 and 8,4.[1] The accuracy with which the screening constants of the N-doublets are known is so small that such a comparison would have only little interest. As regards the O-levels the empirical values for $\frac{\nu}{R}$ are so uncertain that no weight can be attached to the deviations of the $(n-k)$ values in the table from integers. Moreover, these levels depend essentially on the field in the outer region of the atom, which is only of secondary interest for the present investigation. Our main object is, in fact, to examine the conditions for the appearance in the interior of the atoms of electrons which are bound in 4_4 states. As a result of this examination it was found, that it was possible for all three elements to draw a P-parabola which corresponds to $n=4$ and $k=4$. While, for Nd this parabola corresponds to the positive $\frac{\nu}{R}$ value 0,70, it was found that negative values for $\frac{\nu}{R}$ had to be used in the case of Cs and La. Thus for Cs we obtained $\frac{\nu}{R} = -1{,}71$ and for $La\,\frac{\nu}{R} = -0{,}25$. This means that in the two latter elements an electron cannot be bound in the interior of the atom in a 4_4 state. In order to judge where such electrons may appear for the first time, we have on fig. 5 given a diagram which represents the calculated value of $\frac{\nu}{R}$ as a function of the atomic number. From the curve drawn through the three points we are led to expect that the first element in which the 4_4 levels appear will be Cerium which is actually the first member of the family of the rare earths.

[1] This agreement would remove the apparent difficulty in the theory of the spinning electron pointed out by Wentzel (Zs. für Phys. 37, 911, 1926) in connection with a theoretical computation of the screening constants in X-ray dublets.

Notwithstanding the limitation inherent in the method applied, this agreement with the theoretical considerations of Bohr as regards the origin of the rare earths, gives
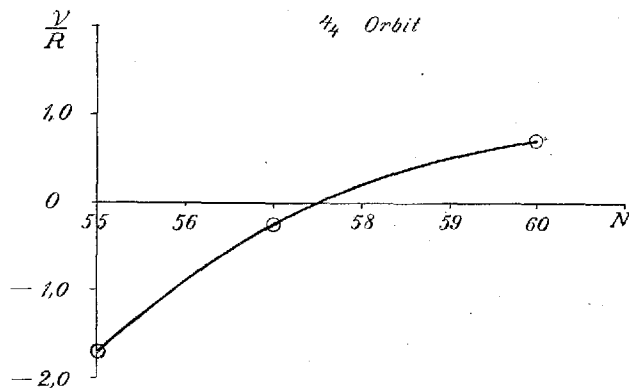

Fig. 5.

undoubtedly strong support for the applicability of this method for our present purpose.

§ 3.   Application to elements in the 7th period.

Table II contains in a similar way as Table I the results of our calculations regarding the elements Th and Ur. For Ur the Q curve is given in fig. 6. The question as regards the appearance of electrons in 5_4 states is also discussed in the same way as the appearance of 4_4 states in the previous paragraph. It was found that for both elements a P-parabola could be drawn corresponding to $n = 5$ and $k = 4$, but for both the values of the corresponding level were found to be negative. For thorium $\frac{\nu}{R} = -2,0$ and for Uranium $\frac{\nu}{R} = -1,1$. Extrapolating, as shown in fig. 7, by

means of a straight line we are led to the expectation that
levels corresponding to interior 5_4 electrons should not

Table II.

Level	$\frac{\nu}{R}$ observed		$\frac{\nu}{R}$ reduced		n_k	$(n-k)$ calc.	
	Th (90)	U (92)	Th	U		Th	U
K_I	8073.5	8477	7239.7	7565.7	1_1	0.00	0.00
L_I	1509.7	1603.0	1212.3	1275.5	2_1	1.00	1.00
L_{II}	1451.5	1539.8 ⎫	1154.1	1212.3	2_2	0.00	0.00
L_{III}	1200.6	1263.2 ⎬					
M_I	381.6	408.9	307.7	324.6	3_1	2.01	2.00
M_{II}	354.4	382.1 ⎫	280.5	297.8	3_2	1.00	0.99
M_{III}	298.0	317.2 ⎬					
M_{IV}	256.6	274.0 ⎫	239.1	254.6	3_3	0.00	0.00
M_V	244.9	261.0 ⎬					
N_I	98.6	106.6	76.5	83.9	4_1	3.01	3.00
N_{II}	90.2	95.7 ⎫	68.1	73.0	4_2	1.98	2.00
N_{III}	71.2	77.1 ⎬					
N_{IV}	50.6	56.3 ⎫	47.5	52.2	4_3	1.00	1.00
N_V	48.8	53.6 ⎬					
N_{VI}	24.8	28.4 ⎫	23.5	27.0	4_4	0.00	0.01
N_{VII}	24.0	27.6 ⎬					
O_I	19.8	23.9	10.6	15.5	5_1	4.02	4.02
O_{II}	16.2	18.2 ⎫	7.0	9.8	5_2	3.01	3.01
O_{III}	7.6	12.4 ⎬					
O_{IV}	5.5	8.6 ⎫	4.9	6.0	5_3	2.00	2.00
O_V	4.9	6.0 ⎬					

appear before an element with atomic number 95. Just as
our calculations in the former paragraph were in close
agreement with the observed appearance of the rare earth
elements, we have in this obtained an explanation of the
apparent anomaly in the periodic table that no analogy to
the rare earth family has been detected in the known
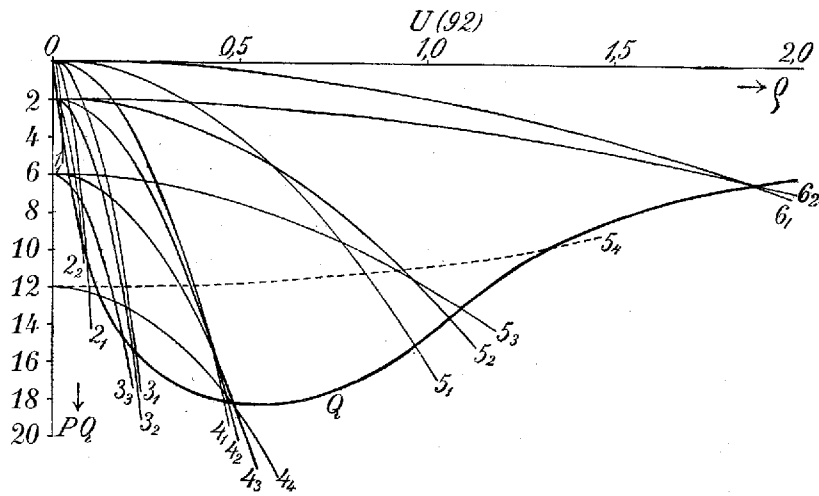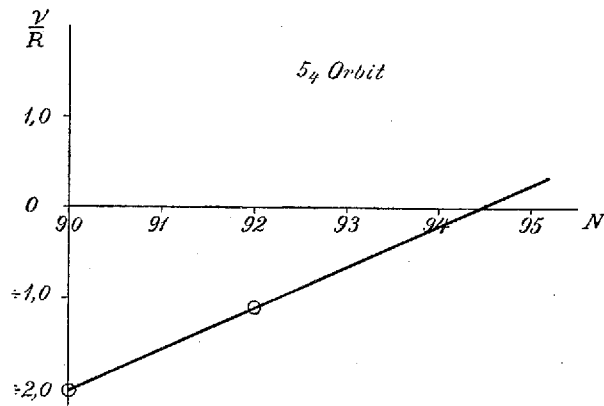elements within the 7th period.

Fig. 6.

Fig. 7.

Concluding remarks.

Through an examination of the field of force in the interior of the atom it is shown that a satisfactory explanation can be given of the apparent anomalies in the 6th and 7th period of the system of the elements. Although the method applied, in making use of orbital pictures, does not quite correspond to the present state of the quantum theory, arguments are developed for the reliability of the conclusions reached as regards the present purpose.

The authors wish to thank Professor N. Bohr, who suggested this research, for the interest he has taken and for his advice given during the progress of the work.