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Rare-Earth and Transuranic Elements*

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The possible existence of a second rare-earth-like group of elements beginning with uranium and extending to the transuranic elements, is discussed by a calculation of the atomic eigenfunctions of the $4f$ and $5f$ electrons. Energy and spatial extension of the $4f$ eigenfunctions drop suddenly at the beginning of the rare-earth group; the binding energy is calculated to be 0.95 ev in lanthanum, $Z=57$, and 5 ev in neodymium, $Z=60$. The $5f$ eigenfunctions undergo the same type of change around $Z=92$. The binding energies were calculated to be 1.35 ev for $Z=86$, 8.5 ev for $Z=91$ and 14 ev for $Z=93$.

Introduction

The chemical behavior of element 93, recently discovered by McMillan and Abelson[1] is strikingly similar to that of uranium and has led these authors to the assumption that a second rare-earth group might start at uranium. In this paper this possibility is discussed from the theoretical point of view.

The first rare-earth group is due to a sudden decrease in energy and size of the $4f$ electronic orbits. A second rare-earth group could occur due to a similar change in the $5f$ eigenfunctions. For this reason, a calculation was made of the shape and energy of the $5f$ eigenfunctions in the neighborhood of $Z=92$. To get a clearer insight into the question, the $4f$ eigenfunctions at the beginning of the first rare-earth group, around $Z=58$, were also studied.

This same problem has been discussed by Sugiura and Urey[2] on the basis of the old quantum theory.

The Potential Energy

The potential energy used for the computation of the eigenfunctions is the statistical, or Thomas-Fermi[3] potential, of the form

$$-\frac{e^2}{r}[1+(Z-1)\varphi(r/\mu)],\qquad \mu=\frac{3^{2/3}h^2}{2^{13/3}\pi^{4/3}me^2}\frac{1}{Z^{1/3}}, \tag{1}$$

where $\varphi(x)$ is a universal function, the same for all atoms, decreasing from 1 at $x=0$ to 0 at $x=\infty$. $\varphi(x)$ has been computed numerically by Fermi.[3] The scale of x, that is the value μ, depends on the atomic number Z.

The differential equation for the determination of the radial part v of $r\cdot\psi$ for an f function, with $l=3$, is

$$v''=\frac{8\pi^2m}{h^2}[E-V(r)]v, \tag{2}$$

with

$$V=-\frac{e^2}{r}[1+(Z-1)\varphi(r/\mu)]+\frac{h^2}{8\pi^2m}\cdot\frac{12}{r^2}. \tag{3}$$

The effective potential V, potential energy plus potential of the centrifugal force, is plotted in Figs. 1a, 1b, for the two extreme cases that were treated, $Z=57$ and $Z=93$. Figure 1b, which pictures V for small r, is drawn in a scale of energies one hundred times that of Fig. 1a.

It is seen that V is negative in two different regions. The valley for large r is very broad and shallow. In this region, $(Z-1)\varphi(r/\mu)$ is already small compared to 1 in all cases, so that position and depth of the minimum scarcely change with Z, and are, indeed, practically the same as for hydrogen. For hydrogen, $Z=1$, there exists only this one minimum of V.

As Z increases, a second minimum of the effective potential V develops at small values of r. Its position shifts to the inside with increasing Z—from $r=0.22$A for $Z=57$ to $r=0.09$ for $Z=93$. The depth increases very rapidly, from 101 electron volts at $Z=57$ to 1335 electron volts at $Z=93$. At the same time, the valley

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[1] E. McMillan and P. H. Abelson, Phys. Rev. **57**, 1185 (1940).

[2] Y. Sugiura and H. C. Urey, Kgl. Danske Vid. Sels. Math.-fys. Medd. **7**, 3 (1926).

[3] E. Fermi, Leipziger Vorträge, 95–111, 1928.

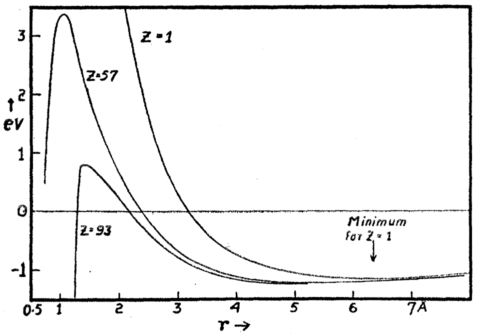

FIG. 1a. Effective potential energy $V(r)$, Eq. (3), for large values of r.

becomes narrower and the curvature at the minimum increases.

The positions of the two minima and their values for different atomic numbers are given in Table I.

QUALITATIVE DISCUSSION

The qualitative behavior of the $4f$ and $5f$ eigenfunctions can now be readily deduced. Perhaps this can be done most clearly by speaking of the potential barrier between the two valleys as if it were infinitely high. In that case, the two valleys would have independent sets of levels. Since the first valley is very much narrower, its levels are much more widely spaced than those of the second one. For small Z, the first level of the inner valley will be positive (above ionization). In that case, the lowest level of the total system is that of the outer valley. Since here the potential is practically that of hydrogen, and hardly varies with Z, the binding energy of the $4f$ electrons will be approximately constant and about the same as for hydrogen, 0.85 ev. Actually, the lowest eigenfunction will have two maxima, at the place of the two valleys, but the value of v at the outer maximum will be much larger than at the inner one.

There comes a value of Z when the inner valley is so deep that its first electron level sinks below the first level of the outer valley. At that point the shape of the $4f$ eigenfunction changes abruptly to one corresponding to an internal orbit. As Z increases, the bottom of the inner valley sinks rapidly, carrying down the $4f$ level. Since, however, the valley becomes not only deeper but also narrower, the decrease of the level is not as rapid as that of the bottom.

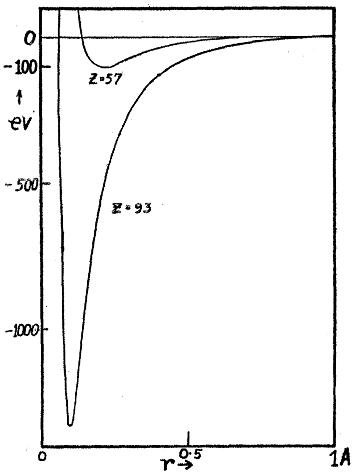

FIG. 1b. Effective potential energy $V(r)$, Eq. (3), for small values of r.

Experimentally, we know that just this occurs at the rare-earth group, around $Z=58$. The sudden spatial shrinkage of the $4f$ orbit agrees with the experimental fact that these functions, although containing the most loosely bound electrons, do not influence the valence properties of the atoms.

At the place in the periodic system where the $4f$ function changes its character, the $5f$ function also undergoes some changes. For lower values of Z, the $5f$ level is simply the second level of the outer valley; the $5f$ function is hydrogen-like in shape and energy (about 0.52 ev), with one node somewhere in the outer valley. After the lowest level of the inner valley has sunk below that of the outer one, that is after the rare-earth group, the second level of the total system is the lowest level of the outer valley. The $5f$ function will consequently behave in that region like a $4f$ hydrogen function; its node occurs somewhere

TABLE I. *Positions and depth of minimum values of V.*

Z	Position of 1st Minimum A	Depth of 1st Minimum ev	Position of 2nd Minimum A	Depth of 2nd Minimum ev
1	—	—	6.35	1.13
57	0.22	101	5.7	1.18
60	0.17	147	5.6	1.21
86	0.11	984	5.5	1.23
91	0.094	1218	5.5	1.23
93	0.092	1335	5.5	1.23

in the region of the inner valley. As Z increases, the energy of the level will remain practically constant around 0.85 ev.

But then a Z value is reached at which the inner potential trough becomes so deep that even the second level of the inner valley drops below the lowest level of the outer valley. One will predict that at that point a second rare-earth group sets in, with all the characteristics of the first one; the energy of the $5f$ level starts to drop, and from then on keeps decreasing with increasing atomic number; the orbits shrink suddenly and become inner eigenfunctions, therefore do not influence the valence character of the atoms.

In order to determine where the shrinkage of the $4f$ and $5f$ eigenfunctions occurs, some numerical integrations of Eq. (2) were undertaken.

THE $4f$ EIGENFUNCTIONS

Lanthanum, $Z=57$, is the first of the rare earths, the one which does not yet have a filled $4f$ orbit. Calculation shows that the binding energy is 0.92 ev, not much changed from that of hydrogen (0.85 ev). The eigenfunction is still located essentially outside the atom. It has two maxima, at $r=0.54$A and $r=7.3$A (the maximum of the $4f$ function of hydrogen occurs at 8.47A), but the value of v, the radial part of $r\psi$, at the second maximum is about six times the value of the first maximum.

At $Z=60$, neodymium, the eigenfunction has undergone the expected radical change. The binding energy has dropped to 5 electron volts, considerably below the value of the potential energy in the outer valley. The first maximum of the eigenfunction occurs at 0.36A, but the second one has entirely disappeared; at $r=2$A the function has already dropped to one-tenth of its value at the maximum. The $4f$ function is now entirely an inner function.

TABLE II. *Binding energies.*

	$4f$			$5f$	
Z	SUBSTANCE	BINDING ENERGY IN EV	Z	SUBSTANCE	BINDING ENERGY IN EV
1	Hydrogen	0.85	1	Hydrogen	0.54
57	Lanthanum	0.95	86	Radon	1.35
60	Neodymium	5	91	Protactinium	8.5
86	Radon	250	93	Neptunium	14

For $Z=86$, radon, the binding energy of the $4f$ function lies between 200 and 300 electron volts.

THE $5f$ EIGENFUNCTIONS

The $5f$ eigenfunction of hydrogen crosses the x axis at about 10.5A. In lanthanum, $Z=57$, this node occurs somewhere around 8A. At $Z=60$, the node has come down suddenly to about one-tenth of that value, namely to $r=0.75$A. For subsequent values of Z, up to about $Z=85$, the node moves still further inside. Beyond this node, the eigenfunction has two maxima of absolute value, the first one still located in the inner potential valley, the second one, higher and wider, in the outer potential valley, at about 6A. It is the neighborhood of this outermost maximum of absolute value of v which gives the essential contribution to $|\psi|^2$; the effective potential energy in this range determines the energy. The eigenfunction is here essentially an outer eigenfunction and, according to the qualitative discussion above, we shall expect the energy to be about constant and of the order of that of the $4f$ function of hydrogen, 0.85 electron volt.

The first actual determination of energy was made for radon, $Z=86$. Here, however, the second shrinkage of the $5f$ eigenfunction has already just set in. The energy has fallen to 1.35 electron volts, just below the minimum of the outer potential valley. The function $v=r\psi$ has a maximum at 0.14A, a node at 0.27A, and a minimum (maximum of absolute value) at 0.7A. The outer minimum has just disappeared, but the function does not fall off very rapidly with distance. In short, the ψ function is just on the verge of becoming an inner eigenfunction.

At $Z=91$, protactinium, the shrinkage is more complete. The energy has dropped to 8.5 electron volts. For $Z=93$, neptunium, it is 14 electron volts.

The energies obtained are tabulated in Table II.

COMPARISON WITH d ORBITS

The sudden change in character and energy of the eigenfunction with a change in the atomic number is typical for the f orbits only, and does not occur in the same manner for any other angular quantum number. Only for $l=3$ does the effective potential energy V possess two ranges of negative values, separated by a region of positive V.

This is seen most easily by considering, instead of V, a function proportional to r^2V, namely

$$[\mu e^2(Z-1)]^{-1}r^2V(r) = -(r/\mu)\varphi(r/\mu) + l(l+1)(4/3\pi)^{\frac{2}{3}}Z^{\frac{1}{3}}/(Z-1) - r/\mu(Z-1). \quad (4)$$

$x\varphi(x)$ is plotted against $x=r/\mu$ in Fig. 2. The straight lines

$$l(l+1)(4/3\pi)^{\frac{2}{3}}Z^{\frac{1}{3}}/(Z-1) - x/(Z-1) \quad (5)$$

are also plotted for some values of Z, and for $l=2$ and $l=3$. Wherever $x\varphi(x)$ is larger than this straight line for a given Z, the effective potential energy is negative. Figure 2 shows that for Z less than about 47 the solid straight lines (5) with $l=3$ intersect the curve only once. For these values of Z there exists only one range of negative potential. For $Z=50$, and also for all larger values of Z, the straight lines with $l=3$ intersect the curve three times, which shows that there exist two separate ranges of negative potential energy.

For the d electrons, $l=2$, the function (4) differs from that for the f electrons only in that 12 in the second term has to be replaced by 6. The corresponding straight lines are parallel to the lines with $l=3$ for the same value of Z, and their intersection with the y axis is half as high. These lines are dotted in Fig. 2 for various values of Z. It is seen that for all values of Z the lines for $l=2$ intersect the curve once only. The effective potential energy for the d electrons has, therefore, only one range of negative values.

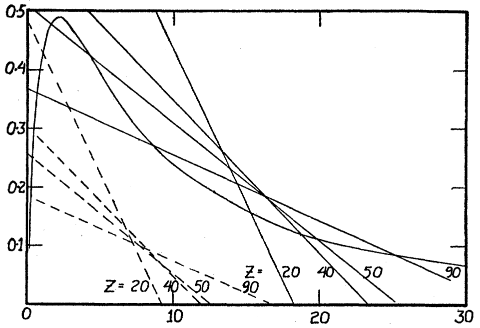

FIG. 2. Curved line represents $x\varphi(x)$ (see Eq. (4)). Solid straight lines represent Eq. (5) for $l=3$, dotted lines for $l=2$.

CONCLUSION

The calculations for the rare-earth group agree moderately well with the experimental facts. The theory would predict that the 4f orbits start to be filled at $Z=61$ or $Z=60$, at the earliest. Actually, the first 4f electron occurs at $Z=58$.

In the neighborhood of $Z=92$, the theory predicts occurrence of a second rare-earth group; the first filled 5f level should occur at $Z=91$ or 92. Experimentally it appears that uranium does not yet possess a 5f electron. Inaccuracies of a few units in Z are to be expected in a calculation based on the statistical model.

Sincere thanks are due to E. Fermi, who suggested the problem and took a great deal of interest in it.