Onset of Atomic-Subshell Filling in Ordinary and Superheavy Elements

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Energy considerations in the central-field approximation to the one-electron problem are used to derive a theoretical expression, namely, $Z_1(l) \geq (\frac{1}{6})\ (2l+1)^3$, for the atomic number $Z_1(l)$ at which a given atomic l subshell first begins to become occupied. The lowest integral values of $Z_1(l)$ satisfying this relation for $l=0$, 1, 2, and 3 are found to be in exact agreement with the corresponding empirical values, i.e., $Z_1=1$, 5, 21, and 58, respectively. In the domain of the superheavy elements ($100 \lesssim Z \lesssim 200$) and beyond, this relation gives $Z_1(l)=122$, 222, and 367 for $l=4$, 5, and 6, respectively. The first member of this latter triad is in close accord with a recent estimate of $Z_1(4)=125$, cited by Seaborg. Comparison is made with the work of others in this field. To the writer's knowledge, this is the first calculation, without arbitrary introduction or adjustment of parameters, to yield results in complete accord with experiment.

I. INTRODUCTION

One of the earliest and most striking applications of the Thomas-Fermi (TF) statistical model of the atom was a calculation,[1] likewise due to Fermi, aimed at theoretically predicting the empirically observed[1] first occurrence of atomic-subshell occupation in the building-up sequence of the Periodic Table of the elements. That is, it was desired to show, on the basis of TF theory, that the filling of atomic subshells with orbital angular momentum quantum numbers $l=0$, 1, 2, and 3, corresponding to the appearance of s, p, d, and f electrons, respectively, occurred for the first time in the elements having atomic numbers $Z_1=1$ (hydrogen), 5 (boron), 21 (scandium), and 58 (cerium).

Fermi's original results[1] came strikingly close to, but did not agree completely with, the empirical values. Moreover, it was subsequently shown by Jensen and Luttinger[2] that if an accurate, instead of a drastically approximate, numerical evaluation of Fermi's analytic result is performed, the errors in the predicted first appearance of p, d, and f electrons become quite large. Several other workers[3-6] have since approached this problem in a variety of ways, obtaining fair agreement with experiment. As far as the writer is aware, however, none of these agrees completely with the observed data.

We further note that the very approach basic to many of the above calculations has been criticized by some authors[2] for introducing quantization of angular momentum into the TF model. In the latter, it is objected, angular momentum possesses a continuous distribution of possible values.

It is the purpose of this paper, therefore, to present a calculation both free from the above objection and giving, for the first time, results in complete accord with experiment. In addition, this calculation is used to determine where, in the group of the so-called superheavy elements and beyond, the filling of g, h, and i subshells ($l=4$, 5, and 6, respectively) may be expected to commence.

II. FORMULATION AND SOLUTION OF PROBLEM

In place of nearly all the past formulations[1,3-5] of the problem, wherein quantization of angular momentum was arbitrarily introduced as something intrinsically foreign to the TF model, let us adopt an approach based upon the energetics of the one-electron problem in the central-field approximation. The radial part of the wave equation in this case is[7]

$$\frac{d^2R}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{L^2\hbar^2}{2mr^2}\right) R = 0, \tag{2.1}$$

where $R(r)$ is the radial component of the wave function, r is the radial distance from the center of the atom, $\hbar$ is Planck's constant divided by 2π, and m, E, V, and L denote, respectively, the electron's mass, total (negative) energy, potential energy, and magnitude of angular momentum. We note that Eq. (2.1) is the same as that for an electron moving, in one dimension, with an effective potential energy[7]

$$V_{\text{eff}} = V(r) + \frac{(l+\frac{1}{2})^2}{2r^2}\ e^2a_0, \tag{2.2}$$

where we have used the relation $\hbar^2/me^2 = a_0$, in which a_0 is the first Bohr radius in hydrogen, e is the magnitude of the electronic charge, and L has been replaced by its WKB equivalent[8] of $l+\frac{1}{2}$, as is customary and appropriate in this semiclassical type of argument.[9] This is the usual compromise[1,3-5,10-13] between the exact quantum-mechanical $[l(l+1)]^{1/2}$ and the old quantum number k.

Now, in order that the electron be bound to its parent atom, it is clearly necessary that there exist a region in which V_{eff} is negative. In view of Eq.

(2.2) and the fact that for all r finite, r^{-2} is always positive whereas $V(r)$ is always negative, the requirement that $V_{eff} < 0$ may therefore also be expressed by demanding that

$$-(r^2V)_{max} \geq \tfrac{1}{2}e^2a_0(l+\tfrac{1}{2})^2 , \qquad (2.3)$$

with the equality sign holding for the limiting case where binding just begins to become possible. Relation (2.3) thus determines, within the present approximation, the first appearance of an electron with given orbital angular momentum quantum number l, i.e., the onset of atomic-subshell filling.

Having completed the formulation of our problem, we now proceed to solve it by means of a rather accurate analytic approximation[14] to the exact numerical solution of the dimensionless TF equation, namely,

$$\varphi(r) = (1 + a_1x)^{-2}; \qquad (2.4)$$

where φ is the well-known TF screening function, [10,11] and

$$a_1 = \tfrac{1}{4}\pi^{2/3}, \quad x = r/\mu, \quad \mu = \tfrac{1}{4}(9\pi^2/2Z)^{1/3}a_0 . \qquad (2.5)$$

In terms of φ, one has from TF theory[10,11] that, in the case of neutral atoms,

$$V(r) = -(Ze^2/r)\varphi . \qquad (2.6)$$

Using Eqs. (2.4)–(2.6) in extremalizing the left-hand member M (say) of relation (2.3), one finds that setting $\partial M/\partial r = 0$ gives

$$r_m = \mu/a_1 = (\tfrac{9}{2})^{1/3}Z^{-1/3}a_0 . \qquad (2.7)$$

Here r_m is that value of r for which M is maximized. Substitution of this result into relations (2.6) and (2.3) finally yields

$$Z_1 \geq \tfrac{1}{6}(2l+1)^3 . \qquad (2.8)$$

This constitutes our solution of the problem: For any specified orbital quantum number l, it is the lowest integral value Z_1 satisfying relation (2.8) that designates the particular element at which the corresponding subshell first begins to be occupied.

III. RESULTS AND DISCUSSION

The atomic numbers Z_1 marking the onset of atomic-subshell filling, as predicted by relation (2.8), are given in Table I. Also listed there, for comparison, are theoretical results obtained by other methods, [1–6] as are the respective empirical data. [1] First among the former are Fermi's original values, [1] agreeing perfectly with experiment, except for the case of $l = 3$. It has been pointed out by Jensen and Luttinger, [2] however, that this agreement depends crucially upon an approximation which Fermi made in the evaluation of an integral —say, N— appearing in his analytic result. That is, he replaced N by the product of the integrand evaluated at the center of the interval times the length of the interval. Upon performing an exact evaluation of N, on the other hand, these authors found that Fermi's expression gave the results shown in the second row of Table I. These are seen to differ markedly from the corresponding empirical values, the errors for $l = 1$, 2, and 3 being, respectively, 20, 19, and 24%.

The next set of values for Z_1, due to Sommerfeld, [3] rests essentially upon Fermi's work. The same holds with respect to Tietz's more recent results, [4,5] derived from two methods of solution differing from each other but slightly.

Formulating the problem in a manner quite different from Fermi's, Jensen and Luttinger[2] find the values for Z_1 shown in the fourth row of our table. In this case, the discrepancies from the empirical data for p, d, and f electrons amount to 40, 29, and 26%, respectively.

Though taking an approach unlike that of any of the above authors and using, furthermore, the Thomas-Fermi-Dirac (TFD) rather than the TF model of the atom, Iwanenko and Larin[6] obtained results numerically identical with those of Sommerfeld's, and thus in disagreement with the empirical data for d and f

TABLE I. Atomic numbers Z_1 marking onset of atomic-subshell filling.

Subshell designation — l =	s 0	p 1	d 2	f 3	g 4	h 5	i 6	Ref.[a]
	1	5	21	55	···	···	···	Fermi[b] (approximate integration)
	···	4	17[c]	44	···	···	···	Fermi[d] (exact integration)
	1	5	20	54	···	···	···	Sommerfeld[e]
	···	3[c]	15[c]	43	···	···	···	Jensen and Luttinger[d]
	1	5	22	59	···	···	···	Tietz[f]
	1	6	22	60	···	···	···	Tietz[g]
	1	5	20	54	···	···	···	Iwanenko and Larin[h]
	···	···	···	···	125	···	···	Seaborg[i]
	1	5	21	58	122	222	367	This work
	1	5	21	58	···	···	···	Empirical[j]

[a] An empirical formula, namely, $Z_1 = 1 + \frac{1}{6}(2l+2)(2l+1) \times (2l)$, was brought to the author's attention by E. R. Davidson. It gives Z_1 correctly for s, p, and d electrons, but yields too small a value ($Z_1 = 57$) in the case of $l = 3$.

[b] References 1 and 2.

[c] Rounded up to nearest integer.

[d] Reference 2.

[e] Reference 3.

[f] Reference 4.

[g] Reference 5.

[h] Reference 6.

[i] Reference 16.

[j] Reference 1; see Ref. 7, p. 332.

electrons, respectively.

Turning to the present work, one sees from the corresponding entries in Table I, readily verified by means of our result (2.8), that the latter yields values for Z_1 in complete agreement with the empirical data for each of the four values of l, 0–3.

In view of the considerable efforts[15–19] currently being made in connection with the search, synthesis, and theoretical study of the so-called superheavy elements ($100 \lesssim Z \lesssim 200$), it was thought to be of interest to apply our analytic result (2.8) also in this novel and exciting domain of the expanded Periodic Table of the elements. On this basis, the first appearance of a g electron ($l = 4$) is expected to occur in element 122, in reasonable accord with a tentative estimate of $Z_1 = 125$, cited by Seaborg.[16] Similarly, for the (presently hypothetical) elements beyond the superheavy group, ground-state h and i electrons should, according to our result (2.8), appear first in those elements having $Z_1 = 222$ and 367, respectively.

To the extent that our method for determining $Z_1(l)$ involves a number of approximations, it is of course difficult to assess the accuracy of those calculated values for which comparison with experiment is currently not feasible. Nevertheless, the fact that accord with experiment is complete for the four cases $l = 0–3$ would make it appear plausible that our result for $Z_1(4)$, e.g., is not far off the mark. In any event, such estimates, aside from their theoretical interest, may be of aid in the experimental verification of $Z_1(4)$.

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