A historical note on the maximum atomic number of chemical elements

H. Kragh and B. Carazza

Steno Museum, University Park 100
8000 Aarhus C, Denmark
Dipartimenta di Fisica,
Università di Parma, 43100 Parma, Italy

ABSTRACT. We discuss various early attempts to deduce the highest chemical element of the periodic system by means of quantum-theoretical considerations, an area still of interest to some physicists. The first attempts in this tradition employed the Bohr-Sommerfeld atomic model, the criterion for Z_{max} being that the velocity of a K-electron must not exceed the velocity of light. Other attempts, from the 1920s and 1930s, utilized the idea of a fundamental constant of time duration which, if it exists, must be smaller than the minimum period of revolution of an atomic electron. Finally we mention some speculative ideas of applying Eddingtonian theory for the same purpose.

RÉSUMÉ. Nous discutons quelques lointaines tentatives de déduire quel est le dernier possible élément chimique de la table périodique sur la base de considérations théoriques quantiques, un sujet encore intéressant pour quelques physiciens. Les premières tentatives dans cette tradition utilisèrent le modèle atomique de Bohr-Sommerfeld, le critère pour individualiser Z_{max}, étant donné que la vitesse d'un électron K ne peut pas exéder celle de la lumière. D'autres tentatives des anneés 20 aux années 30 se basèrent sur l'idée d'une unité fondamentale d'intervalle de temps qui, au cas où il existerait, devrait être plus petit que la moindre période de révolution d'un électron dans l'atome. Finalement nous citons quelques spéculations sur l'application de la théorie d'Eddington dans le même but.

Two articles in this journal recently discussed the limit of the periodic table due to the electrodynamic instability of atoms with a large number of electrons. P.Kundu [1] argued that Z_{max} is given by the inverse fine structure constant ($\alpha^{-1} = ca\ 137$) and found it significant that the atomic mass number of the first forbidden element ($Z = 138$)

happens to be exactly 3/2 of the mass number of uranium. Similarly, N.I.Nijegodorov [2] discussed the speed of a K-electron in multi-electron atoms and argued by means of the Dirac eqation that the last (hypothetical) hydrogen-like atom in the periodic table must have atomic number $Z = 136$. The author mentioned several other physicists who, since the 1960s, have discussed the question of the final element in the periodic system.

It is the purpose of the present note to point out that neither is this question new at all, nor are the methods discussed by Kundu and Nijegodorov. In fact, the problem was discussed in a quantum theoretical perspective since the early 1920s. Apart from serving as a historical reminder of this fact, we believe that a brief discussion of some of the early attempts may have interest in its own right. We end the paper by briefly pointing out the present interest in the so-called electrodynamic instability of super-heavy elements, a feature that can only be treated by means of relativistic quantum mechanics.

1. Methods based on ordinary quantum theory

Speculative attempts to determine the maximum number of chemical elements predate quantum atomic theory. The early attempts, which date back to 1884, were mostly based on numerological reasoning concerning the periodic system [3]. Being scarcely more than guesswork, they need not concern us here. Yet it is of interest to note that detailed calculations of the maximum number of electrons were also carried out for pre-quantum atomic models. Thus, in J.J. Thomson's atomic model no more than 471 electrons can be in equilibrium [25].

The first quantum theoretical treatment of the problem may have been due to the Norwegian astrophysicist Svein Rosseland [4], working at Bohr's institute in Copenhagen, who responded to a suggestion [5] that radioactivity might be caused by the perturbations of orbital electrons coming very close to the nucleus. Within the framework of the so-called old quantum theory, Rosseland pointed out in 1923 that according to Sommerfeld's relativistic theory the shortest distance from the nucleus to an elliptically moving electron will be attained for electrons with azimuthal quantum number $k = 1$ and be approximately given by

$$r = \frac{a_0}{2Z}\left(1 - \alpha^2 Z^2\right)$$

Here a_0 is the Bohr radius ($= \hbar^2/me^2$) and α is the fine structure constant, $\alpha = e^2/\hbar c$. In conformity with the notation of the 1920s, the orbit of an electron is characterized as n_k with n the principal quantum number and k the azimuthal quantum number ($k = \ell + 1$). Since r will diminish with increasing Z, and the nuclear size will increase, Rosseland concluded that there would exist an upper limit for Z. Although he did not calculate this limit, he found it unlikely that there would exist elements with atomic numbers much larger than 92. Rosseland stressed the tentative nature of his suggestion by adding that "our knowledge of nuclear structure is probably far too scanty to permit of any definite conclusions concerning these questions at present." Writing in 1923, before quantum mechanics and the discovery of the neutron, his cautious attitude was wise.

Inspired by Rosseland's argument, Niels Bohr stated the same year without proof that an electron in an n_k orbit would fall into the nucleus if $Z/k \geq 1/\alpha = 137$, which he saw as indicating "an understanding of the limitation of the atomic number of existing elements" [6]. For $k = 1$, this means that $Z < 137$. Whether Bohr considered super-heavy elements a possibility is doubtful, but in 1922, in his Nobel address, he wrote down the complete electron configuration (in terms of n_k) of the hypothetical inert gas with $Z = 118$ [7]. Bohr's remark can be understood by following the elaboration by Arnold Sommerfeld [8], who used the relativistic energy expression he had derived for a hydrogen-like atom in 1915. Introducing the radial quantum number $n_r = n - k$, the energy E depends on the quantum numbers by

$$1 + \frac{E}{mc^2} = \left\{ 1 + \frac{\alpha^2 Z^2}{\left[n_r + \sqrt{k^2 - \alpha^2 Z^2} \right]^2} \right\}^{-1/2}$$

For a circular orbit ($n = k,\ n_r = 0$)

$$1 + \frac{E}{mc^2} = \sqrt{1 - \alpha^2 (Z/k)^2}$$

In order that the energy shall remain real, and hence could be ascribed a physical meaning, one must have that

$$1 - \alpha^2 (Z/k)^2 \geq 0 \quad \text{or, for } k = 1,\ Z \leq 1/\alpha = 137$$

For $k > \alpha Z$, electrons of momentum p move in rotating elliptic orbits with a perihelion motion given by the real quantity

$$\gamma^2 = 1 - (Ze^2/c^2)/p^2 = 1 - (k/\alpha Z)^2$$

Sommerfeld proved that if $k < \alpha Z$ the motion would not be elliptical, but the electron would instead perform a spiral motion around the nucleus, approaching it with almost the speed of light. For $k = 1, Z = 137$ would therefor be the limit between allowed, elliptical orbits and forbidden, spiralling orbits. In 1924 (before the introduction of spin), half integral azimuthal quantum numbers were assumed to exist in higher atoms. If $k = 1/2$, the limit will be about 68, which obviously poses a problem. However, Sommerfeld suggested that if the perturbations of the other electrons were taken into account the limit might possibly be raised to 92.

Of course Sommerfeld's treatment is highly schematic, leaving out, as it does, screening effects due to the other electrons and the modification of the inverse-square law of force expected at very small distances from the nucleus. This was pointed out by Walter Kossel, among others, in 1928 [9]. Kossel suggested that the attractive magnetic forces between the K-electrons squeezed together near the nucleus might determine the highest value of Z. The question of what constitutes, in principle, the last element of the periodic system was well known and often discussed in the old quantum theory [10].

When Sommerfeld's relativistic extension of Bohr's theory was replaced by the Dirac equation, the first solutions for a one-electron system showed that the energy expression for the lowest bound state remained unchanged, although the permitted values and the meaning of the quantum numbers were now somewhat different [11,12]. The first physicist to provide an exact solution for the Dirac equation applied to one-electron atoms, Walter Gordon, commented on the problem of a highest Z [13; see also 14]. As a purely mathematical requirement in order to solve the Dirac equation for a nuclear charge Ze, he found that $1 - \alpha^2 Z^2 \geq 1/4$, meaning that the maximum Z is $\sqrt{3}/2\alpha$ or about 119. In Gordon's treatment, screening corrections due to the presence of other electrons were not taken into account. In general, also within the Dirac theory the lowest permitted energy goes towards zero when Z approaches 137 from below, and it becomes imaginary when $Z > 137$. A point nucleus with $Z > 137$ cannot support the lowest bound electron.

Within the framework of the relativistic wave equation also the effect of a finite nuclear size has been considered, but with a result opposite to

that obtained by Rosseland in 1923. In fact, if the central charge distribution is not point-like, the attractive potential deviates from and is less singular than a pure Coulomb potential, with the result that the critical value for Z becomes larger. We refer to the detailed treatment of Popov [15]. It is worth pointing out that in ordinary, non-relativistic quantum mechanics there is no "collapse to the centre". This phenomenon is a consequence of introducing, in one way or another, the special theory of relativity.

2. Methods based on minimum-time hypothesis

In the late 1920s, there appeared several ideas of a smallest time interval, i.e., a fixed minimum duration ΔT below which time measuring would have no meaning. This general idea, of wich is given a detailed account in [16], was developed by many physicists, including de Broglie in a study of 1932 [17]. If durations are limited by ΔT, so is the period of revolution for a K-electron and then its velocity. And since the velocity is determined by the nuclear charge, this implies a maximum atomic number. In the simple (non-relativistic) Bohr theory we have :

$$v = Zc\alpha \qquad \text{and} \qquad r = \hbar/mv$$

Assuming $\Delta T = h/mc^2$ the condition is

$$2\pi r/v > h/mc^2$$

which, with the expressions for v and r substituted, leads to the old result $Z < 137$. In a even simpler way, it follows from $v = Zc\alpha$ and $v < c$.

According to Henry Flint and Owen Richardson [18, 19], h/m_0c^2 should be understood as a minimum proper time, which led them to a smaller value of Z_{max}. Their argument, based on the Bohr atomic theory mixed in a somewhat obscure manner with elements of special relativity, was as follows. The period of revolution, measured in the electron's proper time, must be larger than the postulated minimum time interval :

$$\frac{2\pi r}{v}\sqrt{1-\frac{v^2}{c^2}} > \frac{h}{m_0c^2}$$

Introducing in this inequality $r = \hbar/mv$ with m expressed relativistically by m_0 leads to :

$$1 - \frac{v^2}{c^2} > \frac{v^2}{c^2} \qquad \text{or} \qquad v < \frac{c}{\sqrt{2}}$$

That is, Flint and Richardson claimed that the velocity of orbital electrons could not exceed 71% of the velocity of light. Accepting this result, it follows immediately from $v = Zc\alpha$ that $Z < (\alpha\sqrt{2})^{-1}$ or $Z < 97$.

This was a result that seemed reasonable at the time, but of course it built on the then obsolete Bohr-Sommerfeld model. In 1934, Walter Glaser and Kurt Sitte reconsidered it in the light of Dirac's quantum mechanical theory of the electron, but keeping to the hypothesis of a minimum time interval [20]. In Dirac's theory there is no definite distance or velocity of the electron (a fact which Nijegodorov [2] seems to ignore), but it is possible to find the quantum mechanical analogies. Using the standard formulae for the average values of r^{-2} and dx_i/dt, Glasser and Sitte found that

$$v = Zc\alpha \qquad \text{(as in the Bohr theory)}$$

and

$$r = \left[\frac{a_0}{Z\sqrt{2}}\right] \sqrt{2(1 - Z^2\alpha^2) - \sqrt{1 - Z^2\alpha^2}}$$

Using the criterion that the period of revolution $2\pi r/v$ has to exceed h/mc^2, they found the maximum atomic number to be $Z = 90.5 \pm 0.5$. Given the existence of uranium this number is too small, of course, but Glaser and Sitte argued that the effects of the second K- electron would result in a correction that would increase the number, probably to 92.

As mentioned by Glaser and Sitte, Flint and Richardson's condition that $v < c/\sqrt{2}$ can be obtained also by requiring that the de Broglie wavelength for a bound electron must always exceed de Compton wavelength. I.e.

$$\frac{h}{m_0 v}\sqrt{1 - \frac{v^2}{c^2}} > \frac{h}{m_0 c}$$

Glaser and Sitte, and also Flint and Richardson, considered their results to constitute support of the hypothesis of a minimum time interval [16].

3. Eddingtonian attempts

The mentioned examples show that it is possible to obtain reasonable values for the maximum atomic number in very different ways, using atomic models that are more or less adequate and special hypotheses that are more or less justified. Given the popularity in some quarters of Arthur Eddington's ambitious attempt to bridge cosmology and quantum mechanics it is not surprising that also this theory [21] may be used to yield a result.

For example, in 1932 V.V. Narlikar applied Eddington's unorthodox theory to argue that the highest possible number of electrons in an atom is 92 [22]. According to Eddington's E-algebra, the magic number 137 (or 136 +1) represented the number of degrees of freedom of a two-particle system. Assuming a one-to-one correspondence between degrees of freedom and independent wave-functions this may (by means of the Pauli exclusion principle) be interpreted as meaning that the maximum number of electrons is 137. Narlikar may have felt that 137 was an unrealistically large atomic number. At any rate, he modified Eddington's analysis so that the number 137 was reduced to 92, and from this he concluded that "there can be no element beyond uranium".

After the war - and after the discovery of the first transuranium elements - a spanish physicist, D. M. Masriera, used the same theory to obtain the number of [23]. Masriera, who had advanced the hypothesis in Spanish four years earlier, concluded that 96 was the number of possible single wave equations of nuclear particles. We shall not be further concerned with these ideas, far away from mainstream physics as they were and are.

4. Conclusion

It has been shown that attempts to deduce the highest element in the periodic system by means of considerations from quantum theory go far back in time and were discussed as early as the 1920s. The examples we have mentioned are far from exhaustive. The general ideas underlying the work of Nijegodorov [2] and the authors he discusses are essentially the same as those found in, e.g., Bohr and Sommerfeld. Given the many papers on this subject, and the fact that one may arrive at reasonable results for Z_{max} in so many different ways, it seems doubtful if the upper limit of the periodic table can be deduced in a justified manner from atomic physics. Presently there is good reason to believe that, whatever

the value of Z_{max}, it is not a question of the electronic structure but of the instability of the nucleus for super-heavy elements. If this is the case, calculations of the electron configuration for hypothetical super-heavy atoms, such as $Z = 137$, lose much of their relevance.

All the same, calculations of the mentioned kind and of the "electrodynamic limit" for artificially produced unstable super-heavy atoms, including $Z > 137$, are still of considerable interest, namely, in the area of strong fields in quantum electrodynamics. In fact, in "quasi-atoms" formed in heavy ion collisions objects with $Z\alpha > 1$ have been studied, albeit with a lifetime of only 10^{-20} second [24].

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