43) A statistical method for the determination of some properties of the atom (*)

"Un metodo statistico per la determinazione di alcune proprietà dell'atomo,"
*Rend. Lincei **6**, 602–607 (1927).*

The purpose of this work is to show some results about the distribution of electrons in a heavy atom which can be obtained dealing with these electrons, given their great number, using a statistical method; or in other words, considering them as a gas formed by electrons surrounding the nucleus.

Naturally this gas of electrons comes to find itself in a state of complete degeneracy, so much so that we cannot deal with it using classical statistics; on the contrary we must use the form of statistics proposed by the author ([†]) and based on the application of Pauli's exclusion principle to the theory of gas. This has the effect that the kinetic energy of the electrons, in the conditions in which they come to find themselves inside the atom, actually turns out to be bigger than it would have been according to the principle of equipartition of energy and practically independent of the temperature, at least as long as it does not go beyond certain limits.

In this Note we shall show first of all how the distribution of electrons around the nucleus can be calculated statistically; and based on this we shall then calculate the necessary energy to ionize completely the atom, that is to tear off all the electrons from it. The calculation of the distribution of electrons around the nucleus also allows the determination of the behavior of the potential at various distances from the nucleus and therefore to know the electric field in which the electrons of the atom come to find themselves. I hope to be able to show in a future work the application of this to the approximate calculation of the binding energies of single electrons and to some questions about the structure of the periodic system of elements.

To determine the distribution of electrons, we must first of all search for the relation between their density and the electric potential at every point. If V is the potential, the energy of an electron will be $-eV$ and therefore according to classical statistics, the density of electrons would have to then be proportional to $e^{eV/kT}$. But, according to the new statistics, the relation between density and temperature is the following one:

$$n = \frac{(2\pi mkT)^{3/2}}{h^3} F(\alpha e^{eV/kT}) \tag{1}$$

where α is constant for the whole gas; the function F in our case (complete degeneracy), has the asymptotic expression

$$F(A) = \frac{4}{3\sqrt{\pi}}(\log A)^{3/2}. \tag{2}$$

Then in our case we find

$$n = \frac{2^{7/2}\,\pi m^{3/2}\,e^{3/2}}{3h^3} v^{3/2} \tag{3}$$

where

$$v = V + \frac{kT}{e} \log \alpha \tag{4}$$

represents the potential, apart from an additional constant. Now we observe that since in our case we are dealing with a gas of electrons, we must take into account the fact ($\ddagger$) that the statistical weight of the electron is 2 (corresponding to the two possibilities for the orientation of the spinning electron); and so for the density of electrons we must actually take a value equal to twice the value (3); namely we have:

$$n = \frac{2^{9/2}\,\pi m^{3/2}\,e^{3/2}}{3h^3}v^{3/2}\;. \tag{5}$$

If in our case classical statistics were valid, we would have the average kinetic energy of the electrons $= \frac{3}{2}kT$. On the contrary according to the new statistics it turns out to be

$$L = \frac{3}{2}kTG(\alpha e^{eV/kT})/F(\alpha e^{eV/kT})$$

where G represents a function that, in the case of complete degeneracy, takes the asymptotic expression

$$F(A) = \frac{8}{15\sqrt{\pi}}(\log A)^{5/2}.$$

Therefore we find for our case

$$L = \frac{3}{5}\,ev\;. \tag{6}$$

Now we observe that the electric density at a point is evidently given by $-ne$ so the potential v satisfies the equation

$$\Delta v = 4\,\pi\,ne = \frac{2^{13/2}\,\pi^2 m^{3/2}\,e^{5/2}}{3h^3}v^{3/2}\;. \tag{7}$$

Since in our case it will then evidently be only a function of the distance r from the nucleus; then (7) can be written

$$\frac{d^2v}{dr^2} + \frac{2}{r}\frac{dv}{dr} = \frac{2^{13/2}\,\pi^2 m^{3/2}\,e^{5/2}}{3h^3}v^{3/2}\;. \tag{8}$$

If we indicate by Z the atomic number of our atom we shall evidently have

$$\lim_{r=0} rv = Ze \tag{9}$$

$$\int nd\tau = 4\pi\int_0^\infty r^2\,ndr = Z \qquad (d\tau = \text{volume element})\;.$$

$\ddagger$W. Pauli, *Zs. f. Phys.* **41**, 81 (1927).

This last equation, taking into account (5) can be written:

$$\frac{2^{13/2}\pi^2 m^{3/2} e^{5/2}}{3h^3} \int_0^\infty v^{3/2} r^2 dr \; = \; Ze \; . \tag{10}$$

So the potential v will be obtained searching for a function which satisfies Eq. (8) with the two conditions (9) and (10).

To simplify the search for v we change the variables r, v into two others x, ψ proportional to them, setting

$$r = \mu x \qquad , \qquad v = \gamma \psi \tag{11}$$

where we have

$$\mu = \frac{3^{2/3} h^2}{2^{13/3} \pi^{4/3} m e^2 Z^{1/3}} \qquad , \qquad \gamma = \frac{2^{13/3} \pi^{4/3} m Z^{4/3} e^3}{3^{2/3} h^2} \; . \tag{12}$$

Equations (8), (9) and (10) thus become

$$\begin{cases} \psi'' + \frac{2}{x}\,\psi' = \psi^{3/2} \\[2ex] \lim_{x=0} x\psi = 1 \\[2ex] \int_0^\infty \psi^{3/2} x^2 dx = 1 \; . \end{cases} \tag{13}$$

These equations simplify further by setting

$$\varphi = x\psi \; . \tag{14}$$

Indeed they become

$$\begin{cases} \varphi'' = \varphi^{3/2}/\sqrt{x} \\[2ex] \varphi(0) = 1 \\[2ex] \int_0^\infty \varphi^{3/2} \sqrt{x}\,dx = 1 \; . \end{cases} \tag{15}$$

It is easy to see that the last condition is certainly satisfied if φ goes to zero for $x = \infty$. So it remains only to search for a solution to the first of (15), with the conditions at its limits $\varphi(0) = 1$, $\varphi(\infty) = 0$.

Since I did not succeed in finding the general integral of the first of (15), I have solved it numerically. The graph in Figure 1 represents $\varphi(x)$; for x close to zero we have

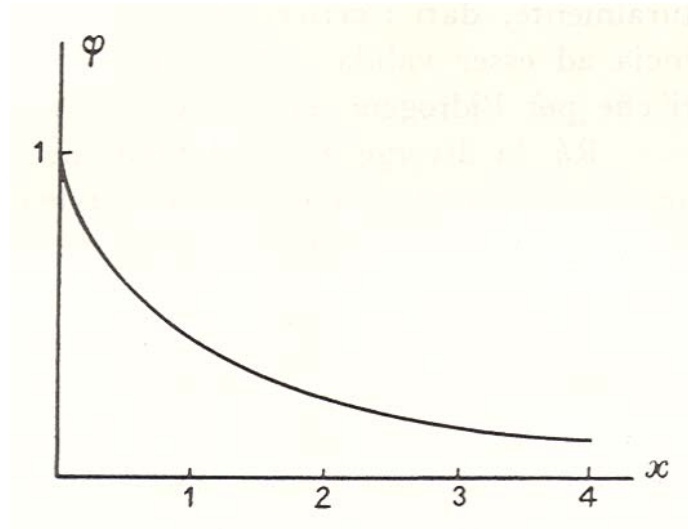$$\varphi(x) = 1 - 1.58\,x + \frac{4}{3}\,x^{3/2} + ... \tag{16}$$

Fig. 1

Thus the problem of the determination of the electric potential of the atom at a fixed distance from the nucleus is solved. Its result is given by

$$v = \gamma \frac{\varphi(x)}{x} = \frac{\gamma\mu}{r}\varphi(x) = \frac{Ze}{r}\varphi\left(\frac{r}{\mu}\right) \ . \tag{17}$$

So we can therefore say that the potential at every point is equal to that produced by an effective charge

$$Ze\,\varphi\left(\frac{r}{\mu}\right) \ .$$

Now we move on to calculate the total energy of the atom; this should be calculated as the sum of the kinetic energy of all the electrons and the potential energy of the nucleus and electrons. However, it is easier taking into account the fact that in an atom the total energy is equal, except for the sign, to the kinetic energy (which anyway in our case can be verified with an easy calculation). Thus we have

$$W = -\int L\,n d\tau$$

and taking into account (5), (6), (11), (12), (14) we find

$$W = -\frac{3}{5}\int_0^\infty r^2\,nv\,dr = -\frac{2^{13/3}3^{1/3}\pi^{4/3}me^4Z^{7/3}}{5h^2}\int_0^\infty \frac{\varphi^{5/2}}{\sqrt{x}}\,dx \ .$$

The last integral can be evaluated taking into account that φ satisfies (15) and (16); one finds

$$\int_0^\infty \frac{\varphi^{5/2}}{\sqrt{x}}\,dx = -\frac{5}{7}\left(\frac{d\varphi}{dx}\right)_{x=0} = \frac{5}{7}\,1.58$$

and therefore we have

$$W = -1.58 \,\frac{2^{13/3}3^{1/3}\pi^{4/3}me^4Z^{7/3}}{7h^2} = -1.58 \,\frac{2^{1/3}3^{1/3}}{7\pi^{2/3}} Rh\,Z^{7/3}$$

that is

$$W = -1.54 \, RhZ^{7/3} \tag{18}$$

where by R we indicate Rydberg's number, so that $-Rh$ is the energy of the fundamental state of hydrogen.

(18) gives us the necessary energy to tear off from an atom all its electrons. Naturally given the statistical criteria which it has been deduced from, it begins to be valid only for considerable values of Z; in fact we find that for hydrogen (18) gives $W = -1.54 \, Rh$, while we actually have $W = -Rh$; the discrepancy is thus 54%. For helium the energy to produce complete ionization is obviously equal to the sum of the ionization energies of He and He^+; so we have

$$-W = (1.8 + 4) \, Rh = 5.8 \, Rh$$

but from the theory we obtain $1.54 \cdot 2^{7/3} = 7.8 \, Rh$; therefore the discrepancy in this case comes down to 35%. For the elements immediately following helium (Li, Be, B, C), nearly all of the atomic energy is due only to the two K electrons (for carbon about 86%) so the statistical method of course must still certainly give considerable discrepancies. For C in fact we still find a discrepancy close to 34%.

But we must expect that for elements of considerable atomic weight, the discrepancies between the statistical theory and empirical data are very much reduced; unfortunately the data is lacking for a precise comparison and we can base ourselves only on a rough valuation of the shield numbers for various orbits; such an evaluation, however, shows much better agreement.