Statistical method to determine some properties of atoms

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Abstract

The present work aims at showing some results over the distribution of electrons in a heavy atom that can be obtained treating such electrons, given their considerable number, via a statistical method: *i.e.* in other words, by regarding them as a gas of electrons surrounding the nucleus.

The electron gas is, naturally, in a completely degenerate condition, so that classical statistics cannot be applied to it; we must instead make use of the kind of statistics proposed by the Author[1] and founded upon the application to gas theory of Pauli's exclusion principle. A consequence is that the electrons kinetic energy results effectively much larger than what it should be according to the principle of energy equipartition and practically independent of temperature, at least as long as it does not increase beyond certain limits.

In this Note we shall show, first, how it is possible to compute the statistical distribution of the electrons around the nucleus; and from it we shall compute the energy necessary to a complete ionization of the atom, *i.e.* to strip it of all its electrons. The computation of the electrons distribution around the nucleus allows us, furthermore, to determine the behavior of the potential at various distances away from the nucleus and, therefore, to know the electric field in which the electrons of the atom are found. I hope to be able to show, in a forthcoming work the application of the above to the approximate calculation of the binding energies of the individual electrons

[*]Read at the 4 December 1927 session by the member O.M. Corbino.

[1]E. Fermi, ≪Zs. f. Phys.≫, **36**, 902, (1926).

and to some questions about the structure of periodic classification of the elements.

To determine the electrons distribution we must first look for the relationship between their density and the electric potential at each point. If V is the potential, the energy of an electron will be $-e\,V$, hence, according to the classical statistics, the electrons density should be proportional to $\mathrm{e}^{e\,V/kT}$. Instead, according to the new statistics, the relation between density and temperature is the following:

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

were α is a global constant for the gas; the function F in our case (complete degeneracy) has the asymptotic expression [2]

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

Hence in our case it is

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

where

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

represents, up to an additive constant, the potential. Remark that, since we deal with a gas of electrons, we must take into account[3] that the statistical weight of the electrons is 2 (corresponding to the two possible orientations of

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[2]**Translator's note**: The computation is

$$n = \int \frac{\mathrm{e}^{-\beta(\frac{p^2}{2m}-\mu)}}{1+\mathrm{e}^{-\beta(\frac{p^2}{2m}-\mu)}} \frac{d^3p}{h^3}$$

with $A = \mathrm{e}^{\beta\mu}$ and $\beta\mu = (\log\alpha + \beta eV)$ hence $A = \alpha\,\mathrm{e}^{\beta eV} \equiv \mathrm{e}^{\beta ev}$ with $v = V + \frac{kT}{e}\log\alpha$. Notice that in modern notations $\log\alpha = \beta\frac{p_F^2}{2m}$ with p_F the Fermi momentum, *i.e.* the radius of the Fermi sphere. The formulae for $F(A), G(A)$ were introduced and derived in: E.Fermi, *Zur quantelung des idealen einatomigen gases*, ≪Zs. f. Physik≫, **36**, 902-912, 1926" [see Eq.(22),(23) and, for degenerate gases, (27)].

[3]W. Pauli, ≪Zs. f. Phys.≫, **41**, 81 (1927).

the rotating electron); hence for the density of the electrons we must actually take twice the value in Eq.(3); *i.e.* we get

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

If in our case the classical statistics held, we would have an average electrons kinetic energy $= \frac{3}{2}kT$. Instead according to the new statistics it is given by

$$L = \frac{3}{2} kT \, \frac{G(\alpha \mathrm{e}^{\frac{eV}{kT}})}{F(\alpha \mathrm{e}^{\frac{eV}{kT}})}$$

where G denotes a function which, at complete degeneracy, assumes the asymptotic expression

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

hence in our case we find

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

Remark then that the electric density at a point is, evidently, given by $-ne$ and, therefore, the potential v satisfies the equation

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

In our case it will evidently be a function of the distance r to the nucleus, only; Eq.(7) can therefore be written as

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

If by Z we denote the atomic number of our atom it will the clearly be

$$\lim_{r=0} rv = Ze, \qquad \int n d\tau = 4\pi \int_0^\infty r^2 n \, dr = Z \quad (d\tau = \text{ volume element}). \tag{9}$$

The last equation, taking into account Eq.(5), can be written as:

$$\frac{2^{\frac{13}{2}}\pi^2 m^{\frac{3}{2}} e^{\frac{5}{2}}}{3h^3}\int_0^\infty v^{\frac{3}{2}}\, r^2\, dr = Z\, e \tag{10}$$

The potential v will therefore be obtained by looking for a function satisfying Eq.(8) with the two conditions Eq.(9) and (10).

To simplify the search for v change the variables r, v into x, ψ setting

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

where it is

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

Then Eq.(8),(9) and (10) become

$$\begin{cases} \psi'' + \frac{2}{x} = \psi^{\frac{3}{2}} \\ \lim_{x=0} x\psi = 1 \\ \int_0^\infty \psi^{\frac{3}{2}} x^2 dx = 1 \end{cases} \tag{13}$$

Such equations further simplify setting

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

They become, indeed,

$$\begin{cases} \varphi'' = \frac{\varphi^{\frac{3}{2}}}{\sqrt{x}} \\ \varphi(0) = 1 \\ \int_0^\infty \varphi^{\frac{3}{2}}\sqrt{x}\, dx = 1 \end{cases} \tag{15}$$

It is easy to see that the last condition is certainly satisfied if φ vanishes at $x = \infty$. Thus it remains to look for a solution of the first of Eq.(15) with the boundary conditions $\varphi(0) = 1$, $\varphi(\infty) = 0$.

Having failed to find the general integral of the first of Eq.(15) I solved it numerically. The graph in Fig.1 represents $\varphi(x)$; for x near 0 it is

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

In this way is solved the problem of determining the electric potential of the atom at a given distance from the nucleus. It is given by

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

It is therefore possible to say that the potential at each point equals that of an effective charge

$$Ze\varphi(\frac{r}{\mu})$$

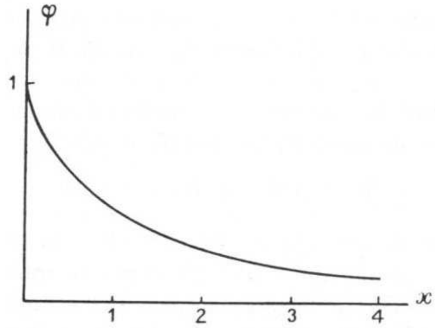

Fig. 1.

We now compute the total energy of the atom: it should be computed as the sum of the kinetic energy of all electrons and of the potential energy of the nucleus and of all electrons. But it is simpler to keep in mind that in an atom the total energy equals, aside from the sign, the kinetic energy (in any event, this can be checked in our case via an easy computation). Thus it is

$$W = -\int Ln\, d\tau$$

and by Eq.(5) (6) (11) (12) (14) we get

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

The last integral can be evaluated keeping in mind that φ satisfies Eq.(15) and (16); one finds

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

hence it is

$$W = -1.58 \frac{2^{\frac{13}{3}} 3^{\frac{1}{3}} \pi^{\frac{4}{3}} m e^4 Z^{\frac{7}{3}}}{7h^2} = -1.58 \frac{2^{\frac{1}{3}} 3^{\frac{1}{3}}}{7\pi^{\frac{2}{3}}} R h Z^{\frac{7}{3}}$$

i.e.

$$W = -1.54\, R\, h Z^{\frac{7}{3}} \tag{18}$$

where R denotes Rydberg's number, so that $-Rh$ is the ground state energy of hydrogen.

Eq.(18) gives the energy necessary to strip an atom of all its electrons. Of course, by the statistical criteria from which it has been derived, it begins to be valid only for considerable values of Z; in fact we find that for hydrogen Eq.(18) gives $W = -1.54Rh$, while in reality it is $W = -Rh$; a discrepancy of 54%. For helium the energy to obtain a complete ionization equals evidently the sum of the ionization of He and of He^+; *i.e.* it is

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

while from the theory it results $1.54 \cdot 2^{\frac{7}{3}} Rh$; hence the discrepancy is reduced to 35% in this case. For the elements immediately following helium (Li,Be,B,C) the atomic energy is almost entirely due only to the two K-electrons (in carbon about 86%) and, therefore, the statistical method will have to yield still considerable discrepancies, For C a discrepancy is still found close to 34%.

It has to be expected, instead, that for elements of considerable atomic weight discrepancies between the statistical theory and the empirical data should be much reduced; unfortunately data for a precise check are missing and we can only rely on a rough evaluation of the screening numbers for the various orbits; nevertheless such an evaluation indicates a much better agreement.

Translated by Giovanni Gallavotti**,** May 2011

NdT: The applications of the theory, called *Thomas-Fermi theory*, developed independently by L.H. Thomas and, one year later, by E. Fermi (this translation) are very numerous: see the collected works of E. Fermi, *Note e memorie*, vol I, Accademia dei Lincei and U. of Chicago Press, 1962, p.77, where historical remarks can be found. The strength and modernity of the method can perhaps be best appreciated by the key role that it plays in understanding the "stability of matter". In this respect chief references are the books: E. Lieb, *The stability of matter: from atoms to stars*, Springer, 2005

and E.Lieb, R.Seiringer. *The Stability of Matter in Quantum Mechanics*, Cambridge University Press, 2010.