ON THE MOMENTUM DISTRIBUTION OF ELECTRONS IN THE STATISTICAL THEORY OF THE ATOM

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Beside the spatial distribution $\varrho(r)$ of the electrons in an atom in some cases it is needed to know also $\omega(p)$, the distribution of electrons in the momentum space [$\omega(p)\,dv_p = \omega(p)\,dp_x\,dp_y\,dp_z$ gives us the number of electrons in the atomic system with momentum components between the values p_x and $p_x + dp_x$, p_y and $p_y + dp_y$, p_z and $p_z + dp_z$ respectively; p denotes the absolute value of the momentum, dv_p the volume element of the three dimensional momentum space].

In the framework of the statistical theory of the atom BURKHARDT [1], KÓNYA [2], as well as COULSON and MARCH [3] discussed the determination of the radial momentum distribution $\Omega(p) = 4\pi p^2\,\omega(p)$. In a later paper the author has proved [4], that the two density distributions $\varrho(r)$ and $\omega(p)$ are approximate solutions of the same order of the wave mechanical many-body problem and that the relation between the two density functions corresponds to the wave mechanical transformation theory. These relations can be expressed as follows:

$$\varrho(r) = \frac{1}{\hbar^3}\,\frac{1}{3\pi^2}\,P^3(r)\,, \tag{1}$$

$$\omega(p) = \frac{1}{\hbar^3}\,\frac{1}{3\pi^3}\,R^3(p)\,, \tag{2}$$

where $\hbar = \dfrac{h}{2\pi}$, h being Planck's constant. In equation (1) $P(r)$ is the maximal value of the momentum, which the electrons — considered to bee free — in a spatial volume element at the distance r from the nucleus can posses. In equation (2) $R(p)$ denotes the maximal value of the radiusvektor, which the electrons in a volume element of the momentum space lying at the distance p from the origo of the momentum space can posses.

With the help of these formulas we can unically derive the two density functions from one another. If $\varrho(r)$ is a known and monotonically decreasing function of r, so we get from equation (1) the momentum value

$$p = P(r) = (3\pi^2)^{1/3}\,\hbar\varrho^{1/3}(r)\,, \tag{3}$$

where the momentum distribution function $\omega(p)$ is given by eq. (2), $R(p)$ being the inverse function of $P(r)$.

In the case of the reversed problem if $\omega(p)$ is a known and monotonically decreasing function of p, we obtain from eq. (2) the value

$$r = R(p) = (3\pi^2)^{1/3}\,\hbar\,\omega^{1/3}(p) \tag{4}$$

of the radius-vektor, where the spatial distribution function $\varrho(r)$ is given by eq. (1), $P(r)$ being now the inverse of the function $R(p)$.

Our goal is here to give a simple deduction of eq. (1) and (2) in § 1 and to examine the function $\omega(p)$ qualitatively in § 2.

§ 1.

a) *Determination of $\omega(p)$ from $\varrho(r)$*. Let us consider the spatial density of electrons as given. We suppose that it is a monotonically decreasing function of r. In the volume element dv_r at the distance r from the nucleus there are ϱdv_r electrons which can be regarded as free. These electrons are distributed in the momentum space in such a way, that their total energy will be minimal. By the given value of r the potential energy is fixed, so their kinetic energy will be as small as possible. This means that they fill the states around the origo of the momentum space. In consequence of the Pauli-principle the maximal number of electrons in one state can be two. So these electrons must fulfil all states [5] from zero up to the maximal momentum $P(r)$ given by eq. (3). This means, that the electrons present in the spatial volume element dv_r are distributed with the constant density

$$\varrho(r)\,dv_r \Big/ \frac{4\pi}{3}\,P^3(r) = \frac{1}{\hbar^3}\,\frac{dv_r}{4\pi^3} \tag{5}$$

in the sphere with the radius $P(r)$ around the origo of the momentum space.

Let us now consider the volume element dv_p of the momentum space belonging to the momentum p, where the momentum distribution has the value $\omega(p)$. From all the spatial volume elements which fulfil the condition $P(r) \geq p$, a contribution according to eq. (5) is given to the momentum distribution $\omega(p)$.

Since the function $P(r)$ is also a monotonically decreasing one these spatial volume elements forme a sphere with the radius $R(p)$ around the nucleus. The radius $R(p)$ is determined by the condition, that on the surface of this sphere

$$p = P(r)\,,$$

p being the given value of the momentum. We can see that $R(p)$ is the inverse of the function $P(r)$ defined by eq. (3).

Following from these we obtain

$$\omega(p) = \int\limits_{P(r)\geq p} \frac{1}{\hbar^3} \frac{dv_r}{4\pi^3} = \frac{1}{\hbar^3} \frac{1}{\pi^2} \int\limits_0^{R(p)} r^2\, dr = \frac{1}{\hbar^3} \frac{1}{3\pi^2} R^3(p)\,,$$

which is the result in eq. (2).

b) *Determination of $\varrho(r)$ from $\omega(p)$.* Let be $\omega(p)$ the electron density in the momentum space a given and monotonically decreasing function of p.

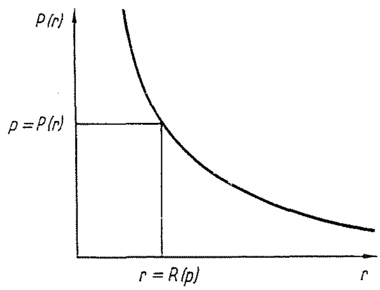

Fig. 1

Now we take a volume element of the momentum space dv_p belonging to the momentum p, where the electron density has the value $\omega(p)$. By choosing the momentum value p we have fixed also the kinetic energy of the $\omega(p)\, dv_p$ electrons in dv_p. The distribution of these electrons in the coordinate space will be again such that the total energy will be minimal and this means that the potential energy must be minimal. Thus these electrons take place around the origo of the coordinate space, as near to the origo as allowed by the Pauli-principle. From all these it follows [4], that these electrons are distributed in the coordinate space with the constant density

$$\omega(p)\, dv_p \Big/ \frac{4\pi}{3} R^3(p) = \frac{1}{\hbar^3} \frac{dv_p}{4\pi^3} \tag{6}$$

in the sphere with the radius $R(p)$ determined by eq. (4).

To the value of the density function $\varrho(r)$ on a place at the distance r from the origo of the coordinate space all the volume elements of the momentum space dv_p give the contribution (6) for wich $R(p) \geq r$. Now the function $R(p)$ is monotonically decreasing and so these volume elements of the momentum space forme a sphere with the radius $p = P(r)$ around the origo of the momentum space. On the surface of this sphere the condition

$$r = R(p)$$

is fulfilled. From this it follows, that $P(r)$ is the inverse function of $R(p)$ defined by eq. (4).

From the proceedings we get at once:

$$\varrho(r) = \int\limits_{R(p)\geqq r} \frac{1}{\hbar^3}\frac{dv_p}{4\pi^3} = \frac{1}{\hbar^3}\frac{1}{\pi^2}\int\limits_0^{P(r)} p^2\,dp = \frac{1}{\hbar^3}\frac{1}{3\pi^2}P^3(r)\,,$$

which is the result in eq. (1).

The simple deductions given here show clearly the close symmetry between the two treatments (the descriptions of the electron distribution in the coordinate and momentum space respectively). This is a consequence of the supposition, that we can regard the electrons inside the spatial volume elements as a free electron gas.

§ 2.

The behaviour of the spatial distribution $\varrho(r)$ is well known as well for the T—F model as for the Thomas—Fermi-Dirac model involving the exchange interaction and for the development of this model involving the correlation correction also [5], [6]. The detailed examination of the momentum distribution function $\omega(p)$ has not yet been carried out, only the papers [2] and [3] discuss some characteristics of the radial distribution function $\Omega(p)$.

The derived general relations make it possible to look over the behaviour of $\omega(p)$.

a) The momentum distribution in the T—F model. The spatial distribution $\varrho(r)$ in the T—F model can be determined from the solution $\varphi = \varphi_0(x)$ of the T—F differential equation

$$\varphi'' = \frac{\varphi^{3/2}}{x^{1/2}} \tag{7}$$

satisfying the boundary conditions

$$\varphi_0(0) = 1\,, \quad \varphi_0(x_0) = 0\,, \quad x_0\varphi_0'(x_0) = -\frac{Z-N}{Z} \tag{8}$$

for free atoms and ions, or

$$\varphi_0(0) = 1, \qquad x_0\varphi_0'(x_0) = \varphi_0(x_0) \tag{9}$$

for compressed neutral atoms.

With the help of this function $\varphi_0(x)$ one obtain

$$\varrho(x) = \frac{Z}{4\pi\,\mu^3}\left(\frac{\varphi_0}{x}\right)^{3/2},$$

$$r = \mu x,\ \mu = \frac{1}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3} a_0\,,$$

where Z is the atomic number, N the number of the electrons, $r_0 = \mu x_0$ is the boundary radius of the atom and a_0 the first Bohr radius of the H-atom.

In the T—F model it is characteristic for the density function $\varrho(r)$ [5], that in all cases

$$\varrho(r) \sim \frac{1}{r^{3/2}}, \quad if\ r \to 0 . \tag{10}$$

For great values of r

1. in the case of free neutral atoms r_0 is infinite and

$$\varrho(r) \sim \frac{1}{r^6}, \quad if\ r \to \infty ; \tag{11}$$

2. in the case of free positive ions r_0 is finite and according to eq. (8) $\varrho(r_0) = 0$;

3. in the case of compressed neutral atoms according to eq. (9) r_0 is finite and $\varrho(r_0) \neq 0$.

From these facts we can establish to the electron density $\omega(p)$ in the momentum space the followings. According to eq. (3) and (10)

$$P(r) \sim \varrho^{1/3}(r) \sim \frac{1}{r^{1/2}}, \quad if\ r \to 0 .$$

The inverse function of $P(r)$ is thus

$$R(p) \sim \frac{1}{p^2}, \ if\ p \to \infty$$

and so according to eq. (2), both for free atoms and ions and for compressed atoms

$$\omega(p) \sim \frac{1}{p^6}, \ if\ \ p \to \infty \tag{12}$$

Thus now we find the same behaviour for $\omega(p)$ in the case of large p values (as well for free atoms, ions and for compressed atoms), as for $\varrho(r)$ in the case of large r values (for free neutral atoms only).

Examining $\omega(p)$ in the case of small values of p, it follows for free neutral atoms, that

$$P(r) \sim \frac{1}{r^2} \quad , \quad if \quad r \to \infty ,$$

so

$$R(p) \sim \frac{1}{p^{1/2}} \quad , \quad if \quad p \to 0,$$

hence

$$\omega(p) \sim \frac{1}{p^{3/2}} \quad , \quad if \quad p \to 0 . \tag{13}$$

Comparing the eq. (10) and (13) moreover the eq. (11) and (12) one can see, that for free neutral atoms the functions $\varrho(r)$ and $\omega(p)$ show an identical behaviour.

In the case of positive ions and compressed neutral atoms when in the coordinate space a finite boundary radius r_0 exists, the density $\omega(p)$ does not break off in the momentum space, but tends to zero in order according to eq. (12) and disappears only in the infinity. However tending with p to zero, the value of $\omega(p)$ does not tend to infinity, but takes up the finite value

$$\omega(0) = \frac{1}{\hbar^3} \frac{1}{3\pi^2} r_0^3 . \tag{14}$$

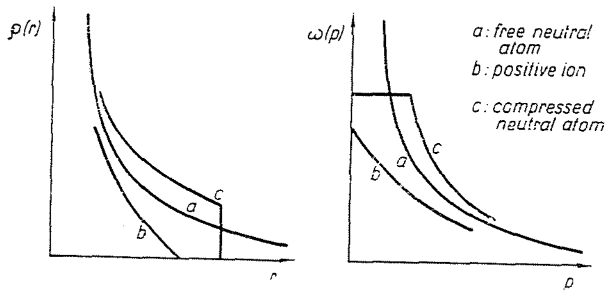

Fig. 2

In the case of compressed atoms $\omega(p)$ reaches this value already at

$$p_0 = P(r_0) = (3\pi^2)^{1/3} \hbar \varrho^{1/3} (r_0) . \tag{15}$$

Therefore the value of $\omega(p)$ is constant in the interval $0 \leq p \leq p_0$ (Fig. 2, curve c).

b) *The momentum distribution in the T—F—D models*

For these models instead of eq. (7) $\varrho(r)$ can be obtained from the solution $\psi = \psi_0(x)$ of the T—F—D differential equation

$$\psi'' = x \left[\left(\frac{\psi}{x} \right)^{1/2} + \beta_0 \right]^3 \tag{16}$$

satisfying the boundary conditions

$$\psi_0(0) = 1 , \quad \psi_0(x_0) = \frac{\beta_0^2}{16} x_0 , \quad x_0 \psi_0'(x_0) - \psi_0(x_0) = - \frac{Z - N}{Z} . \tag{17}$$

The density function $\varrho(r)$ is given by the formula

$$\varrho(x) = \frac{Z}{4\pi \mu^3} \left[\left| \frac{\psi_0}{x} \right|^{1/2} + \beta_0 \right]^3 \tag{18}$$

where e is the elementary charge,

$$\beta_0 = \frac{2(\varkappa_a + \lambda_0)}{3(4\pi)^{1/3} e^2 Z^{2/3}} \, .$$

$$\varkappa_a = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} e^2 ,$$

$$\lambda_0 = \begin{cases} 0 & \text{taking only the exchange interaction into account,} \\ 0{,}1582\, e^2 & \text{regarding the correlation correction too [6].} \end{cases}$$

We can see from eq. (18) and from the first eq. of (17) that the function $\varrho(r)$ tends again to infinity at $r = 0$ according to eq. (10). Thus our establishment for $\omega(p)$ in eq. (12) is valid also in these models.

It is characteristic for all cases (examining now only free atoms and ions), that we have a finite boundary radius r_0 in the coordinate space and that the value of the density at this boundary radius is the same for all atoms and ions

$$\varrho(r_0) = \begin{cases} 0{,}002127 \text{ a. u. in the case of the T—F—D model,} \\ 0{,}003862 \text{ a. u. in the case involving the correlation too.} \end{cases}$$

In consequence of these characteristics in these models the electron density $\omega(p)$ in the momentum space has an analogue shape as the curve c in Fig. 2. The value p_0 corresponding to eq. (15) is the same for all atoms and ions:

$$p_0' = \begin{cases} 0{,}3979 \text{ a. u. in the case of the T—F—D model,} \\ 0{,}4854 \text{ a. u. in the case involving the correlation too.} \end{cases}$$

Now the function $\omega(p)$ has the constant value corresponding to eq. (14) in the interval $0 \leq p \leq p_0'$.

Summary

In this paper we have presented a very simple deduction of the relation between the distribution of electrons in the coordinate and momentum space in the framework of the statistical theory of the atom. We examined further qualitatively the behaviour of the two density function, by which we have found a symmetry of very high degree especially in the case of the T—F model for free neutral atoms.

Literature

1. BURKHARDT, G.: Ann. d. Phys. (5), **26**, 567 (1936).
2. KÓNYA, A.: Hung. Acta Phys. **1**, 12 (1949).
3. COULSON, C. A., MARCH, N. H.: Proc. Phys. Soc., **LXIII**, 367 (1950).
4. KÓNYA, A.: Acta Phys. Hung., in print.
5. GOMBÁS, P.: Hb. d. Phys. Bd. **XXXVI**, Springer-Verlag, Berlin—Göttingen—Heidelberg.
6. GOMBÁS, P.: Ann. d. Phys (7), **7**, 1 (1961).

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