STATISTICAL EQUATION WITH PURELY VOLUME EFFECT OF EXCHANGE

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The note presents a statistical equation with exchange, where only one aspect of exchange correlations equal to the volume correction produced by the exchange holes in the electron gas of the statistical model is considered and the energy correction due to the exchange is neglected. The situation is the inverse of that represented by the Thomas-Fermi-Dirac equation where only the energetical aspect of exchange is taken into account.

Introduction of a purely volume effect of exchange yields a further expansion of the electron gas of the statistical atom in comparison with the atom with both exchange corrections included.

§ 1

In the Thomas-Fermi-Dirac (TFD) statistical equation, only the energetical aspect of the exchange effect is taken into account. This gives a contraction of the Thomas-Fermi (TF) statistical atom, since the energy of the gas is everywhere lowered by the exchange term. If the volume aspect of the exchange due to the existence of the empty space produced by the exchange holes in the electron gas is introduced simultaneously with the energetical aspect (Olszewski 1963, henceforth denoted by [I]), the gas tends to expand and the electron density of the statistical atom in the region of high densities becomes lower than in the Thomas-Fermi-Dirac and in Thomas-Fermi atoms (see [I]). The decrease in density near the nucleus is compensated by an increase of the density in the outer atomic regions.

The situation concerning the electron density at the atomic boundary provides still another distinction between the statistical atom with only one, *i.e.* energetical, aspect of the exchange effect introduced in the model (TFD atom), and the atom where both aspects — that of exchange energy and that of exchange volume — are considered simultaneously. The TFD model has only one admissible boundary electron density value corresponding to abruption of the density at the boundary. This situation is the inverse of the continuous distribution of atomic electron density predicted by wave mechanics. However, if both aspects of exchange are introduced in the model, two different density distributions are possible (see [I]). The one decreases continuously to zero and the atomic dimensions are thus spread to infinity, so that we have qualitative agreement with the wave

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mechanical electron distribution of a free atom. The second distribution — of lower energy than the first one and with density abruption analogous to that of the TFD model — is considered as representing an atom in a crystal lattice.

§ 2

The purpose of the present note is to investigate briefly the form of the solution (of the density distribution) of the statistical atom in the case when the energetical aspect of exchange is neglected and only the volume correction due to exchange correlations is considered. Thus the assumptions concerning exchange are here exactly the opposite of those which lie at the foundation of the TFD model (see Sec. 1).

By variation of the energy we have the relation

$$\frac{5}{3}\,\varkappa_k\,\varrho^{\frac{2}{3}} - e[V_e^k + V_e^e - V_0] = 0 \tag{1}$$

known from the TF model (the exchange energy term is excluded). V_e^k, V_e^e are respectively the electrons-nucleus and electrons-electrons potentials, V_0 is the Lagrangian multiplier, ϱ denotes the density, $\varkappa_k$ is equal to $0.3\,(3\pi^2)^{\frac{2}{3}}\,e^2a_0$ and a_0 is the radius of the Bohr orbital (Gombás 1949).

We now introduce into the density a correction due to the exchange potential V_e^a. Thus, the expression for $\varDelta V_e^a$ has now to be taken into account in the statistical equation (cf. [I]). In order to have everywhere in (1) the total potential with V_e^a, where

$$V_e^a = \frac{3}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} e\varrho^{\frac{1}{3}} \tag{2}$$

(Slater 1951, Gombás 1956), we add to (1) Eq. (2) multiplied by the charge $-e$. We have then instead of (1)

$$\frac{5}{3}\,\varkappa_k\,\varrho^{\frac{2}{3}} - [V - V_0]e + 2\varkappa_a\,\varrho^{\frac{1}{3}} = 0, \tag{3}$$

where V is the total potential

$$V = V_e^k + V_e^e + V_e^a, \tag{4}$$

and $\varkappa_a$ is equal to $\dfrac{3}{4}\left(\dfrac{3}{\pi}\right)^{\frac{1}{3}} e^2$. In this way we arrive at the density

$$\varrho = \left(\frac{2}{ea_0}\right)^{\frac{3}{2}} \frac{1}{3\pi^2}\left[\left(V - V_0 + \frac{9e}{8\pi^2a_0}\right)^{\frac{1}{2}} - \left(\frac{9e}{8\pi^2a_0}\right)^{\frac{1}{2}}\right]^3. \tag{5}$$

Substituting (5) in Poisson equation, we obtain a statistical equation analogous to that of [I], or to Eq. (16) of the preceding article of this issue. (This article will be denoted henceforth by [II].) The reduced form of the present statistical equation is

$$\psi''(x) = x\left[\left\{\frac{\psi(x)}{x}\right\}^{\frac{1}{2}} - \gamma'\right]^3, \tag{6}$$

where

$$\gamma' = 3\gamma \tag{7}$$

$$\psi = \frac{r}{Ze}\left[V - V_0 + \frac{9e}{8\pi^2 a_0}\right] \tag{8}$$

$$r = \mu x, \tag{9}$$

μ, γ, Z, r have meanings identical to those of [I, II].

The condition for vanishing of the pressure at the atomic boundary $(dE/dr_0 = 0, r_0$ being the atomic radius) gives in the case of the energy density function of the Thomas-
-Fermi model only one boundary electron density

$$\varrho(r_0) = 0. \tag{10}$$

Thus we have for ψ a set of boundary conditions fully identical to that of [I], or of [II], for the case of φ for the free atom (or ion) (Eqs (20)—(22) of [II]), if γ' replaces γ in Eq. (21) of [II[. Following the reasoning applied in [I] we obtain once more for the neutral atom an electron density distribution extending to infinity. Now, however, $\gamma' > \gamma$. This imposes the conclusion — in analogy to the behaviour of the solution of the statistical equation of [I, II] in respect to the solutions of the TF and TFD equations — that the absolute value of the initial slope, $\psi_0'(0)$, for the atom of Eq. (6) will be smaller (for a given Z) than $\varphi_0'(0)$ for the free atom of [II][1]. Following up this analogy we can expect a still slower decrease of the density in the outer regions of the atom of (6) than in the case of the free atom of [I, II] (a stronger decrease of the density in the internal regions in the atom of the present note); the total energy of the free atom of (6), as well as the density at the boundary for a given r_0 (in the case of the compressed atom), will now be raised in comparison with the analogous quantities of [I and II].

A similar situations can be predicted in the case of positive ions. In particular, the radius of the positive ion of the present model should be greater than that of the same free ion in [I, II].

The above discussion leads to the general conclusion that neglection of the energetical correction of exchange, with preservation of the volume correction, yields a further expansion of the electron gas of the statistical model, *i.e.* the result that should have been expected.

No numerical calculations on the atom of the present note have been performed.

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Gombás, P., *Encyclopedia of Physics*, **36**, Springer-Verlag, Berlin 1956.
Olszewski, S., *Phys. Status solidi*, **3**, 2221 (1963) [I]; *Acta phys. Polon.* (1964) (preceding article) [II].
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[1] A comparison of the initial slopes of the reduced solutions in the various statistical models gives (for the case of the neutral Kr atom): -1.6178552 in the TFD model (Gombás 1949); -1.5880464 in the TF model (Gombás 1949) and -1.5730975 in the model of [I] and [II].