Present State of the Statistical Theory of Atoms

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THE fundamental problem of the statistical theory of atoms is the determination of the electron and potential distributions in atoms. We give here a brief account of the achievements in solving this problem and of the most important problems yet to be solved.[1]

Much of the recent work deals with the foundations of the statistical model starting mostly from very general, and partly from field theoretical, considerations. This tendency is very welcome since, in our opinion, the possibilities of progress based on elementary methods have practically been exhausted, and further progress seems to be possible only in this direction. Up to the present, these general methods have given only a few new results; rather, they threw some light on the connection between the statistical theory and wave mechanics which, of course, is also very important.

In the further development one must not lose sight of the requirement that the fundamental equations of the statistical model of atoms, including different correction terms, should not be too complicated and, in any case, not more complicated than the basic equations of the wave-mechanical many-body problem to be approximated. One must always bear in mind that the statistical model is a rather rough approximation of the wave-mechanical atom, and its advantage is its extreme simplicity both in structure and application. We first briefly summarize its foundations and development.

The original Thomas–Fermi model is based on the assumption that the electrons of a heavy atom can be treated as a free-electron gas, and, accordingly, the kinetic energy of the atoms can be identified with the Fermi energy of the electron gas. In calculating the electrostatic energy of the electron gas, one makes the assumption that the electron gas is distributed continuously and that the electrons are present in this negatively charged gas in a "smeared out" state. In this way, in the original Thomas–Fermi model, the potential energy of the electrons also contains the electrostatic self-energy of the electrons.

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[1] Literature, up to 1956, can be found in the article by P. Gombás, "Statistische Behandlung des Atoms," in *Handbuch der Physik*, edited by S. Flügge (Julius Springer-Verlag, Berlin, 1956), Vol. 36, Sec. 2, p. 108.

One of the most important relations is deduced from the assumption that the electrons occupy cells of the lowest energy in phase space; that is, they fill all the momentum-space cells up to a certain maximum momentum of absolute value p_μ. From this it follows that the relation

$$p_\mu = \tfrac{1}{2}(3/\pi)^{\frac{1}{3}} h \rho^{\frac{1}{3}} \tag{1}$$

exists between p_μ and the electron density ρ, where h is the Planck constant.

For the electron of the highest energy of the atom the following energy relation holds

$$p_\mu^2/2m - Ve = -V_0 e , \tag{2}$$

where m is the mass of the electron, e the positive elementary charge, V the potential of the atom, and V_0 is a constant, which is equal to the maximum value of the potential. Obviously, the first term on the left-hand side of the above equation represents the kinetic energy of the electron of maximum energy, and the second term (taken with its sign) is the potential energy of this electron. According to Eq. (2) the sum of these two energies is the constant $-V_0 e$, that is, the total energy of the electron in the highest energy state.

From (1) and (2) immediately follows

$$c_k \rho^{\frac{2}{3}} = (V - V_0)e \tag{3}$$

or

$$\rho = \sigma(V - V_0)^{\frac{3}{2}} , \tag{4}$$

where c_k and σ are given by

$$c_k = \tfrac{1}{2}(3\pi^2)^{\frac{2}{3}} e^2 a_0 , \quad \sigma = (e/c_k)^{\frac{3}{2}} , \tag{5}$$

and a_0 is the first Bohr radius of hydrogen.

With the aid of (4) one gets from Poisson's equation the Thomas–Fermi equation

$$\Delta(V - V_0) = 4\pi\sigma e(V - V_0)^{\frac{3}{2}} \tag{6}$$

with the following boundary conditions:

$$V \to Ze/r \quad \text{for} \quad r \to 0$$

and

$$V \to 0 \quad \text{for} \quad r \to \infty ,$$

where r is the distance from the nucleus and Z the

atomic number. V_0 is obtained from the normalization condition

$$\int \rho dv = N , \qquad (7)$$

where dv is the volume element and N the number of electrons. If V_0 is defined as above, the normalization condition is automatically satisfied.

This model has the following defects. First, the electron density becomes infinite like $1/r^{\frac{3}{2}}$ at the nucleus. Secondly, the electron density vanishes as $1/r^6$ at large distances from the nucleus. This is in contradiction with the behavior of the wave-mechanical electron density which is constant at the nucleus and vanishes exponentially at large distances from the nucleus.

The energies of the Thomas–Fermi atoms are also not satisfactory. Namely, they are about 10% lower for heavy, and about 30% lower for light atoms than the corresponding empirical and semiempirical energies.

Many improvements have been made on the original Thomas–Fermi model, which take into account more exactly both the potential energy and the kinetic energy of the electrons. Let us first consider the potential-energy corrections.

In the original model only the electrostatic Coulomb interaction between electrons has been taken into account; further, it has been assumed that the electrons are "smeared out" in the electron gas surrounding the nucleus. Consequently, the electrostatic Coulomb interaction includes the electrostatic self-interaction of the electrons. This defect has been eliminated by Fermi and Amaldi by subtracting from the potential of the atom the mean potential, V_e/N, of one electron, where V_e is the potential of the complete electron cloud. This correction gives a good approximation at the border of the atom and improves the electron and potential distributions in this region.

A further correction, by Dirac, of the potential energy takes into account the exchange interaction between electrons. This correction gives in the Thomas–Fermi relation (3) an extra term, $-c_a \rho^{\frac{1}{3}}$, on the left-hand side. Here, c_a is the constant $c_a = (3/\pi)^{\frac{1}{3}} e^2$.

This correction changes the electron distribution at the border of the atom in a fundamental way since, with this correction, the radii of atoms and positive ions (negative ions are not stable) become finite, and the electron density drops discontinuously from a finite value to zero on the border. From this fact many authors concluded that, with this cor-

rection, the statistical atoms and ions do not exist in the free state, because the discontinuity of the electron density cannot be reconciled with the results of wave mechanics. Other authors are of the opinion that, in the statistical model, the electron gas should be considered as a semiclassical one, in the density distribution of which discontinuities are allowed. According to this, in spite of the discontinuity of the electron density, free Thomas–Fermi–Dirac atoms and ions may represent a useful semiclassical approximation of the wave-mechanical atoms and ions. We adopt this latter conception.

Another correction is the correlation correction, which results from the correlation interaction of the electrons which, one should note, is the last essential correction contributing to the potential energy.[2] This is smaller than the above mentioned two corrections and plays an important role only on the border of the atom; namely, the atom and ion radii are, in comparison with the Thomas–Fermi–Dirac atom and ion, slightly reduced and the electron density on the border is increased by about 50%.

These are about all the most important corrections contributing to the potential energy. Moreover, one should note, all these corrections are well founded and very satisfactory. The situation is quite different with corrections to the kinetic energy which arise from the fact that the electron gas in an atom, especially in the neighborhood of the nucleus, cannot be regarded as free. The potential, even in a small volume of the atom, cannot be regarded as constant. Various corrections to the kinetic energy have been considered but, unfortunately, none of these can be accepted as satisfactory and final. In our opinion one of the most important present tasks of the statistical theory of atoms is the systematic and completely satisfactory deduction of the corrections to the kinetic energy.

We now review the kinetic-energy corrections made by others. First, is the so-called Weizsäcker correction. As a result of this correction the above-mentioned defects of the statistical model, i.e., the singularity of the electron density at the nucleus, and the discontinuity of the electron density on the border, or the $1/r^6$ falling off of it at infinity, disappear. In particular, the electron density at the nucleus is constant and falls off exponentially at infinity. Both these results for the electron density are in good agreement with the corresponding results of wave mechanics. However, the agreement of energies

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[2] P. Gombás, Acta Phys. Hung. **13**, 233, 1961; **14**, 83 (1962); Z. Physik. **121**, 523 (1943); H. W. Lewis, Phys. Rev. **111**, 1554 (1958).

with empirical data is not so good; the energies of the model, including the Weizsäcker correction, are 20–25% higher than the empirical or semiempirical ones.

Unfortunately, the Weizsacker correction has the defect that it cannot be deduced in a completely satisfactory manner. It can be made plausible by supposing that all the n electrons in an elementary volume dv occupy the same state of the lowest energy described by the real eigenfunction ψ. This means that, for the moment, the Pauli principle is disregarded. In this case the electron density in dv takes the form

$$\rho = n\psi^2 . \qquad (8)$$

The Schrödinger kinetic energy density is given by

$$W = \tfrac{1}{2} e^2 a_0 n (\text{grad } \psi)^2 . \qquad (9)$$

From (8) and (9) we get for W

$$W = \tfrac{1}{8} e^2 a_0 (\text{grad } \rho)^2 / \rho , \qquad (10)$$

which is usually called the Weizsäcker correction of the kinetic energy. From this form of W the Weizsäcker correction of Eq. (3) can be obtained. The Pauli principle is then usually taken into account by adding to (10) the Fermi energy of the electrons, of which the major part (but not all) is the consequence of the Pauli principle. The addition of these two energies results in an error because the two expressions partly overlap and, consequently, a part of the kinetic energy is taken into account twice. This is the reason for the too high energies mentioned above.

An essential part of this discrepancy can be eliminated by putting $(p_r - \tfrac{1}{2} h/2\pi r)^2/(2m)$ in place of the radial part $p_r^2/(2m)$ of the Fermi kinetic energy, where p_r is the radial momentum of the electron and m is its mass.[3] This correction improves the electron distribution, because it approximates better the wave-mechanical Hartree–Fock distribution than the original Weizsäcker distribution, and it behaves exactly like the wave-mechanical distribution at the nucleus and at large distances from the nucleus. The atomic energies, with the above correction, show a very good agreement with experiment. Moreover, with small modification the new energy expression, for the values $N = 1$ and $N = 2$, goes over into the exact wave-mechanical expression. The energies calculated with this new expression show, from the lightest to the heaviest atoms, a deviation smaller than 2% from the empirical or semiempirical values. Considering that these energies

are distributed in a range of 5 orders of magnitude, the agreement is excellent.

A correction of the kinetic energy which is the most self-contained, is due to Plaskett.[4] Plaskett starts from the Schrödinger equation for one electron, which is of the following form:

$$f'' + (8\pi^2 m/h^2)(E - U)f = 0 , \qquad (11)$$

where $f = r\psi$ is r times the radial eigenfunction ψ, E the energy parameter, f'' the second derivative of f with respect to r, and U is the effective potential energy of the electron

$$U = -Ve + (h^2/8\pi^2 m)l(l+1)/r^2 . \qquad (12)$$

If we write f in the form

$$f = R(r)e^{(2\pi i/h)S(r)} , \qquad (13)$$

then Eq. (11) splits, as is well known, into two equations, one of which, for S, is given by

$$S'^{\frac{1}{2}} \frac{d^2}{dr^2}\left(\frac{1}{S'^{\frac{1}{2}}}\right) - \frac{4\pi^2}{h^2} S'^2 + \frac{8\pi^2 m}{h^2}(E - U) = 0 , \qquad (14)$$

where S' is the first derivative of S with respect to r. Keeping in mind that the relation

$$S = \int_0^r p_r dr , \qquad \text{i.e.,} \qquad S' = p_r \qquad (15)$$

holds between S and the radial momentum p_r of the electron, we get the equation for p_r

$$p_r^{\frac{1}{2}} \frac{d^2}{dr^2}\left(\frac{1}{p_r^{\frac{1}{2}}}\right) - \frac{4\pi^2}{h^2} p_r^2 + \frac{8\pi^2 m}{h^2}(E - U) = 0 . \qquad (16)$$

This equation holds for all values of the radial momentum, in particular for its maximum value $p_{r\mu}$; in this case, we have $E = E_\mu$, where E_μ is the maximum energy of the electron. If we take into account the fact that the relation

$$p_{r\mu} = [h/4(2l+1)]D_l \qquad (17)$$

exists between $p_{r\mu}$ and the radial density D_l of the electrons of angular momentum quantum number l, then we get for D_l the equation

$$D_l^{\frac{1}{2}} \frac{d^2}{dr^2}\left(\frac{1}{D_l^{\frac{1}{2}}}\right) - \frac{\pi^2}{4(2l+1)^2} D_l^2$$
$$+ \frac{8\pi^2 m}{h^2}(E_\mu - U) = 0 . \qquad (18)$$

The total radial density D of the electrons is ob-

[3] P. Gombás, Acta Phys. Hung. 3, 105 (1953); 3, 127 (1953); 5, 483 (1956); Ann. Phys. 18, 1 (1956).

[4] J. S. Plaskett, Proc. Phys. Soc. (London) A66, 178 (1953).

tained by summation over l, i.e.,

$$D = \sum_l D_l . \qquad (19)$$

The first term on the left side of Eq. (18) corresponds to the kinetic-energy correction and the second term results from the Fermi kinetic energy.

Relation (17) is valid only in the classical ($p_{r_\mu} \geq 0$) region of the electron orbit and, correspondingly, the same is true for Eq. (18). In the non-classical region, where p_{r_μ} is imaginary, the relation between p_{r_μ} and D_l is different and the equation for D_l differs from (18), but this equation has not yet been subject to detailed investigation.

By applying Eq. (18) to the harmonic oscillator, it turns out that there is an infinite number of equivalent solutions, but it has not yet been possible to select the actual solution from these.[5] Thus, the kinetic-energy correction, calculated with this very promising method, has not given satisfactory results either.

It appears that one of the most important present day problems of the statistical theory of the atom is the completely satisfactory deduction of the kinetic-energy correction. A further task would be the deduction from wave mechanics of a general relation between electron density and potential which would include the kinetic-energy correction in a natural way, and would hold even for the lightest atoms. Strictly speaking, this would not simply mean a further development of the statistical theory itself but, rather, the deduction of this general wave-mechanical relation in an adequate approximation. The point is just the "adequate approximation." The exact relation is extremely involved; the point would really be to deduce a useful approximation from the general exact relation, which would satisfy these conditions.

A few words may be said about the more exact structure of the electron distribution—the so-called $K-$, $L-$, $M-$, $\cdots$ shell structure—of which the maxima are so characteristic of the wave-mechanical radial electron distributions. The deduction of these maxima with purely statistical methods would be a beautiful and surprising result of the statistical theory. But this deduction, attempted by some authors, would seem to be an impossible task. The grouping of electrons into shells is caused by quantum-mechanical effects, and it is hard to see how the electrons would form spatially well-separated groups of 2, 8, 18, 32, $\cdots$ electrons when treated globally, i.e., statistically, with neglect of their individual quantum-mechanical properties.

The reason for the failure of some works attempting this problem might be in this fact. There have been some calculations in which the deduction of the maxima, corresponding to the shells, of the radial electron density has been attempted by grouping the electrons according to their angular momentum quantum number. These works have, as was to be expected, been unsuccessful. Though in such calculations there might occur maxima, these do not correspond to the $K-$, $L-$, $M-$, $\cdots$ shells, since these result from the grouping of electrons according to their principal and not the angular momentum quantum number.

Though the deduction of the maxima, corresponding to the $K-$, $L-$, $M-$, $\cdots$ shells, on purely statistical grounds seems to be a hopeless task, the problem of the incorporation, but not deduction, of the maxima into the statistical theory has been successfully solved.[6] For this purpose the electrons of the shells are treated separately right from the outset. The consequence of the Pauli exclusion principle, that closed shells cannot take up more electrons, is taken into account by means of a statistical repulsive potential developed by the author.[7] In this way it has been possible to incorporate these density maxima into the statistical theory, not only in the case of light, but also of the heaviest atoms. These statistical electron distributions, which include maxima corresponding to the shells, are obtained easily and show a very good agreement with the results of wave mechanics. The results are shown on Figs. 1, 2, and 3 for the Ar atom, the Rb^+ and Hg^{++} ions, respectively. On each of these figures the total statistical radial electron density D is plotted against r and compared with the wave-mechanical radial density calculated by the self-consistent field method. The statistical radial-electron densities approximate very well the wave-mechanical ones. In particular, the maxima of the statistical distributions and those of the wave-mechanical ones are practically at the same distances from the nucleus. Further, since in this statistical model the electron densities, both at the nucleus and at great distances from it, are identical with the wave-mechanical results, this model might perhaps form the basis of further development in the statistical model of atoms.

[5] R. A. Ballinger and N. H. March, Proc. Phys. Soc. (London) A67, 378 (1954).

[6] P. Gombás and K. Ladányi, Acta Phys. Hung. 5, 313 (1955); 7, 255 (1957); 7, 263(1957); 8, 301 (1958); Z. Phys. 158, 261 (1960); P. Gombás and T. Szondy, Acta Phys. Hung. 14, 335 (1962).

[7] P. Gombás, Z. Physik 118, 164 (1941); Acta Phys. Hung. 1, 285 (1952); in Handbuch der Physik, edited by S. Flügge (Julius Springer-Verlag, Berlin, 1956), Vol. 36, Sec. 2, pp. 168–171.
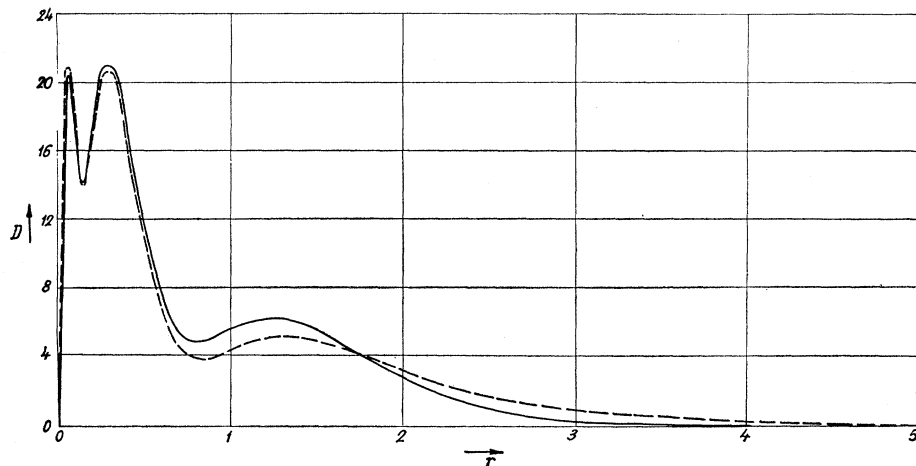
Fig. 1. Radial electron density D as a function of r for the Ar atom. The solid curve represents the statistical radial electron density and the dashed curve the wave mechanical one. r is in units of a_0 and D in units of $1/a_0$.
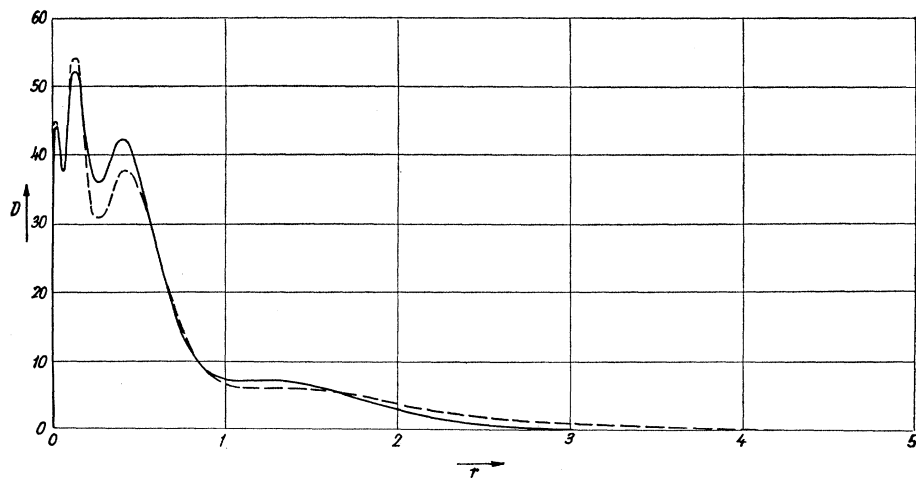

Fig. 2. Radial electron density D as a function of r for the Rb$^+$ ion. The solid curve represents the statistical radial electron density and the dashed curve, the wave-mechanical one. r is in units of a_0 and D in units of $1/a_0$.
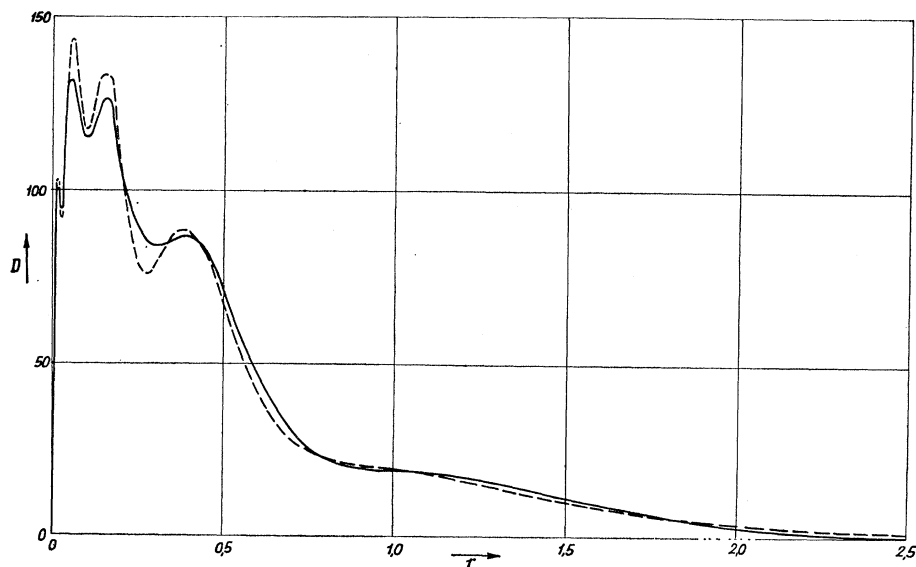

Fig. 3. Radial electron density D as a function of r for the Hg^{++} ion. The solid curve represents the statistical radial electron density and the dashed curve, the wave-mechanical one. r is in units of a_0 and D in units of $1/a_0$.