Angular Momentum Distributions in the Thomas-Fermi-Dirac Model of the Atom

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According to the Thomas-Fermi and the Thomas-Fermi-Dirac models of the atom, the electrons in an atom of a given Z have a given continuous distribution in angular momentum. Therefore, the question of how many s, p, d, or f electrons are to be found in an atom of a given Z cannot be answered by the statistical model as it stands. However, this question can be answered by assigning all the electrons which have values of angular momentum within a certain interval to a definite angular momentum quantum number l. There is, of course, some arbitrariness involved in selecting the method of angular momentum assignment. Fermi first calculated a set of curves for the numbers $\nu(l,Z)$ of s, p, d, and f electrons in an atom as a function of Z on the basis of a particular angular momentum assignment, and using the Thomas-Fermi statistical theory. Since the completion of Fermi's work, Dirac has modified the Thomas-Fermi theory to include the exchange effects of the electrons. In the present work, curves for $\nu(l,Z)$ have been calculated on the basis of the Thomas-Fermi-Dirac theory in order to investigate the effect on such curves of the exchange interaction between the electrons. Complete sets of curves have been found using the angular momentum assignment proposed by Fermi, and also using an angular momentum assignment proposed later by Jensen and Luttinger. Some isolated points on the $\nu(l,Z)$ curve have been plotted using a third angular momentum assignment. On the basis of the analysis of the graphs so obtained and their comparison with the empirical data, it is concluded that the exchange effects are not negligible for this calculation, that no simple angular momentum assignment such as the ones proposed by Fermi and by Jensen and Luttinger agrees well with the theory, and that it is probably possible by sufficient juggling to find an angular momentum assignment which would fit the empirical data reasonably well.

I. INTRODUCTION

A PROBLEM which is of interest in atomic physics is the determination of the number of electrons with a given orbital angular momentum quantum number l which are present in an atom of a given atomic number Z. This problem was first treated by Fermi[1] and later treated by Jensen and Luttinger[2] on the basis of the Thomas[3]-Fermi[1] statistical model of the atom. The question of the number of electrons with a given l in the atom is not subject to treatment by the statistical model as it stands because in this model the electrons are distributed continuously in angular momentum over a given range of values. However, this question can be answered by assigning all the electrons with angular momenta within a certain interval to a given angular momentum quantum number l. Since there is some arbitrariness involved in selecting the method by which this is done, the question set forth is not well defined. Various methods of angular momentum assignment are discussed in Secs. II and III below.

Jensen and Luttinger discussed the angular momentum assignment which Fermi used and proposed another one. They mentioned the fact that Fermi used, in his treatment, an approximate integration which was not sufficiently accurate to give a reliable representation of the model. However, they did not extend their treatment as far as Fermi did. Fermi obtained the complete curves for the number $\nu(l,Z)$ of electrons with quantum number l per atom as a function of Z over the whole range of values of Z for s, p, d, and f electrons. Jensen and Luttinger determined only the values of Z for which the p, d, and f electrons make their first appearances in the atom. They used the value of Z for which the appropriate curve for $\nu(l,Z)$ cuts the line, $\nu(l,Z)=1$ as the value of Z for which the electron of the corresponding angular momentum makes its first appearance.

Since there is arbitrariness involved in selecting the method of angular momentum assignment, the question of which method best fits the experimental data should be investigated. The following argument indicates that the first-appearance problem is not a good one for this application. The general types of curves for $\nu(l,Z)$ which are obtained using the statistical model with an angular momentum assignment of the type mentioned above are qualitatively like the curves which Fermi obtained. These curves are found in Fermi's original paper[1] and are reproduced in Condon and Shortley.[4] The general form of the empirical curves is restricted greatly by the fact that the number $\nu(l,Z)$ of electrons present must be an integer for any integral value of Z. These curves have abrupt jumps in them and their slopes only change discontinuously. On the other hand, the theoretical curves vary smoothly and have only continuous changes in slope. Therefore, the theoretical curves cannot be expected to agree with the empirical curves at all points. It seems most reasonable then to observe how well the theoretical curves agree on the average with the empirical curves. Since the theoretical curves which fit the empirical ones the best on the average do not agree with them for all values of Z, it does not seem reasonable to expect a particular theoretical curve necessarily to be the one which best agrees with the corresponding empirical curve at some previously selected, individual value of Z. The first-appearance problem for a given quantum number consists of comparing the theoretical

[1] E. Fermi, Z. Physik 48, 73 (1928).
[2] J. H. D. Jensen and J. M. Luttinger, Phys. Rev. 86, 907 (1952).
[3] J. H. Thomas, Proc. Cambridge Phil. Soc. 23, 542 (1927).
[4] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (University Press, Cambridge, 1935).

TABLE I. Forms of the function $L(l)$ which are to be used in Eq. (1) for each type of angular momentum assignment.

l assignment	$L(l)$
Jensen and Luttinger	$\frac{1}{2}\{[l(l-1)]^{\frac{1}{2}}+[l(l+1)]^{\frac{1}{2}}\}$
Fermi	l
Text	$[l(l+1)]^{\frac{1}{2}}$

and experimental results at a particular value of Z. Therefore, the use of the agreement between the theoretical and experimental results in the first-appearance problem as a criterion for choosing the best angular momentum modification might give misleading results.

The treatments mentioned above are based on the Thomas-Fermi statistical model of the atom. This model neglects the exchange interaction between electrons which is not really negligible. The model was modified by Dirac[5] to account for the exchange interaction. The Thomas-Fermi-Dirac model should therefore be used in preference to the Thomas-Fermi model in testing the statistical theory of the atom. The angular momentum considerations are of exactly the same nature in both models. Therefore, the theoretical adjustments which must be made in accounting for exchange effects in the angular momentum problem are slight. The purpose of the present work was to investigate the forms of the curves for $\nu(l,Z)$ which result from various angular momentum assignments using the Thomas-Fermi-Dirac model, and to see which ones best agree on the average with the empirical curves. In the process of this investigation it was found that the exchange effects are not negligible.

An interesting approach to the first-appearance problem which does not make use of an angular momentum assignment of the type discussed in the present work was given by Ivanenko and Larin.[6] Their method involves retaining the continuous distribution of the electrons in angular momentum. Because of the marked difference between their viewpoint and that of the present work, it was found instructive to determine which (if any) special case of the treatment used here corresponds to the result of the latter viewpoint. This is done in Sec. IV.

II. SUMMARY OF THE RESULTS

Jensen and Luttinger[2] have discussed in detail the general method of angular momentum assignment which accounts for the fact that orbital angular momentum is quantized. The expression which they obtained for the number $\nu(l,Z)$ of electrons which are present in an atom of atomic number Z is

$$\nu(l)=N\{L(l)\}-N\{L(l+1)\}, \qquad (1)$$

where

$$N(L)=\frac{4}{3\pi}\int\frac{dx}{x}\left[\left(\frac{3\pi Z}{4}\right)^{\frac{2}{3}}x\varphi-L^2\right]^{\frac{3}{2}}, \qquad (2)$$

where

$$x=\frac{r}{\mu},\quad \mu=\frac{1}{(4\pi\sigma_0)^{\frac{1}{3}}eZ^{\frac{1}{3}}}=\tfrac{1}{4}\left(\frac{9\pi^2}{2Z}\right)^{\frac{1}{3}}a_0,$$

and $\varphi(x)$ is the solution to the Thomas-Fermi-Dirac equation for the particular value of Z involved. The integration is carried out over values of x for which $(3\pi Z/4)^{\frac{1}{3}}x\varphi-L^2$ is positive. The form of the function $L(l)$ determines the particular angular momentum assignment. The most straightforward angular momentum assignment is the one proposed by Jensen and Luttinger. The form of the function $L(l)$ is tabulated in Table I for this angular momentum assignment, the one originally used by Fermi and a third one which is discussed below.

A summary of the curves obtained in the present calculations and those obtained from previous calculations is given in Table II.

The solution to the Thomas-Fermi-Dirac equations which were used came from two sources, Metropolis and Reitz[7] and Jensen *et al.*[8] The Metropolis and Reitz tables do not contain solutions for the neutral uncompressed atom. Therefore, it was necessary to make approximations to these solutions using the solutions which they do contain. The thesis[9] upon which this discussion is based contains an account of these approximations and the method of numerical integration which was used. The spreads involved in some of the curves in Figs. 1 and 2 are results of these approximations.

TABLE II. Summary of the results which have been plotted in Figs. (1) and (2), with indications as to the statistical theory which is used, the type of angular momentum assignment which is used, the figures in which the given results are plotted, and the values of l for which the given results are plotted. In the last column, all entries without the superscript c or d indicate the results which were calculated in the present investigation.[a]

Theory	Angular momentum assignment	Figure containing curves	Values of l considered
T-F-D	J and L	1	1, 2, 3, 4
T-F-D	F	2	1, 2, 3, 4
T-F-D[b]	Text	2	1, 2, 3
T-F	F(approx)	2	(1)[c]
T-F[b]	F(exact)	2	1
T-F[b]	F(exact)	2	(2, 3, 4)[d]
Empirical		1, 2	(1, 2, 3, 4)[c]

[a] Key: T-F-D—Thomas-Fermi-Dirac; T-F—Thomas-Fermi; J and L—Jensen and Luttinger; F—Fermi; F(approx)—Fermi assignment with approximate integration; F(exact)—Fermi assignment with exact integration.
[b] Indicates that only isolated points have been plotted.
[c] Curves obtained from Fermi's original graph which is illustrated in Condon and Shortley.[4]
[d] Points obtained from the first appearance calculations of Jensen and Luttinger.[2]

[5] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).
[6] D. Ivanenko and S. Larin, Doklady Akad. Nauk (S.S.S.R.), **88**, 45 (1953).
[7] N. Metropolis and J. R. Reitz, J. Chem. Phys. **29**, 555 (1951).
[8] Jensen, Meyer-Gossler, and Rohde, Z. Physik **110**, 277 (1938).
[9] T. A. Oliphant, thesis, M. S., Cornell, 1956 (unpublished).

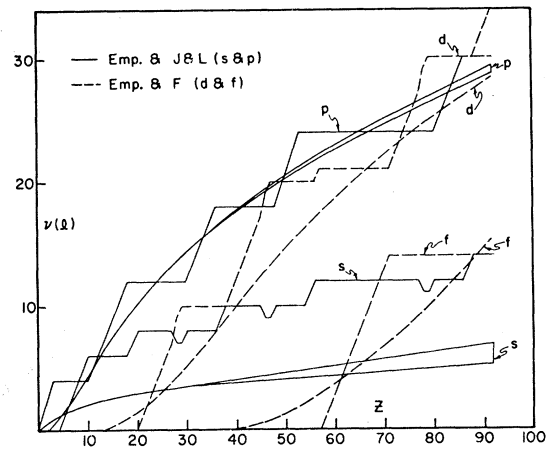

FIG. 1. Number $\nu(l)$ of electrons per atom with angular momentum quantum number l, as a function of Z. The curves consisting of broken lines represent the empirical data and the smoothly varying curves represent results of the T-F-D theory using the Jensen and Luttinger angular momentum assignment (see Table II).

III. DISCUSSION

The first of the present calculations was done for the Thomas-Fermi-Dirac theory using the Jensen and Luttinger angular momentum assignment (see Fig. 1). The fact that was first noticed was that the s electron curve is much too low, the p electron curve is about right, the d electron curve is a bit too low and it is not possible to tell much about the f electron curve. In order to discuss the meaning of these features, a brief digression is necessary. In the process of deriving Eqs. (1) and (2) the following expression is obtained for the number of electrons which have an angular momentum lying between $\hbar L$ and $\hbar(L+dL)$ in the unmodified statistical model.

$$n(L)dL=\frac{4L}{\pi}\int\frac{dx}{x}\left[\left(\frac{3\pi Z}{4}\right)^{\frac{2}{3}}x\varphi-L^2\right]^{\frac{1}{2}}dL. \qquad (3)$$

This integration is carried out over values of x for which $(3\pi Z/4)^{\frac{2}{3}}x\varphi-L^2$ is positive. The number $\nu(l)$ of electrons with quantum number l is calculated in the following way:

$$\nu(l)=\int_{L(l)}^{L(l+1)}n(L)dL$$

$$=\int_{L(l)}^{L(l+1)}\frac{4L}{\pi}\int\frac{dx}{x}\left[\left(\frac{3\pi Z}{4}\right)^{\frac{2}{3}}x\varphi-L^2\right]^{\frac{1}{2}}dL. \qquad (4)$$

This integration can be visualized by the graphs contained in Fig. 3. These curves are schematic plots of the x integrands in the expression (3) for $n(L)$ as functions of L for the various angular momentum assignments. Integration of one of these curves gives the x integrand of Eq. (4). Equation (4) is exactly equivalent to Eqs. (1) and (2). It is evident, according to Fig. 3(a), that there is a correlation between the relative widths of the L intervals and the heights of the theoretical curves relative to the empirical curves. If it is assumed that the height of the theoretical curve for d electrons is correct insofar as angular momentum subdivision is concerned, then the s-electron curve is too low and the p-electron curve is too high. Also the width of the s-electron region in Fig. 3(a) is smaller and the width of the p-electron region larger than that of the d-electron region.

The foregoing correlation suggested that the various numbers l should have intervals of equal length on the diagram in order to give theoretical curves with heights roughly proportional to the heights of the empirical curves. This leads to the postulate that $\int dL=1$ for each angular momentum interval. The simplest way of setting up an angular momentum assignment under this requirement is to set up the assignment illustrated in Fig. 3(b), which turns out to be identical with the Fermi assignment. Therefore, it is not necessary to regard the Fermi angular momentum assignment as an approximation to that of Jensen and Luttinger.

The above observations lead to another calculation using the Thomas-Fermi-Dirac theory, but this time using the Fermi angular momentum assignment. The theoretical curves lie below the empirical curves to about the same extent for each value of l. This justifies the conclusion that the constancy of the width of the angular momentum interval should give heights to the $\nu(l)$ curves which are roughly proportional to the heights of the empirical curves. There is, however, still the difficulty that the theoretical curves all fall below the empirical ones.

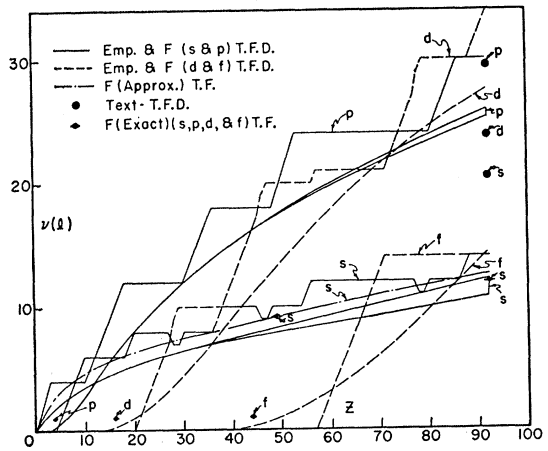

FIG. 2. Number $\nu(l)$ of electrons per atom with angular momentum quantum number l, as a function of Z. The curves consisting of broken lines represent the empirical data. Four of the smoothly varying curves represent the results of the T-F-D theory using the Fermi angular momentum assignment and a fifth one consists of an earlier calculation of Fermi[1] using the T-F theory. The round points are for the T-F-D theory using a third type of angular momentum assignment and the diamond-shaped points are for the T-F theory as calculated by Jensen and Luttinger[2] using their angular momentum assignment (see Table II).

No further straightforward ways were found to set up the angular momentum assignment which would bring the theoretical curves closer to fitting the empirical ones. The method of setting up the angular momentum assignment is, however, somewhat arbitrary. The question which remains is then whether it is possible to set up an angular momentum assignment, with less previous justification, which will bring the theoretical curves closer to fitting the empirical ones. In order to determine whether or not this could be done, the most extreme angular momentum assigned which seemed at all reasonable was set up. It is illustrated in Fig. 3(c). In this assignment all electrons with angular momentum below $\hbar[l(l+1)]^{\frac{1}{2}}$ are assigned to the quantum number $l-1$. This is the most extreme modification that still seems reasonable because it does not seem reasonable to assign an electron of angular momentum greater than $[l(l+1)]^{\frac{1}{2}}$ to the quantum number $l-1$. It must be kept in mind that the relative angular momentum interval lengths are not equal although they do decrease monotonically. Points at $Z=92$ have been calculated for s, p, and d electrons. The s point lies very much above the corresponding point on the empirical $\nu(l)$ curve, the p point lies above it, and the d point lies below it. Therefore, it seems possible that some method of assignment of angular momentum intermediate between this method and the Fermi method would give good average agreement with the empirical curves. Because of the arbitrariness involved in the angular momentum assignment, the determination of the exact method of angular momentum subdivision which gives the best agreement with the experimental data would probably not be of too much significance.

It is interesting to see whether the theoretical curves given in Fig. 2 would fit the empirical curves better if the exchange correction were removed. The individual points in Fig. 2 which were obtained from the first-appearance calculations of Jensen and Luttinger are points on the theoretical curves which would be obtained by removing the exchange correction from the theoretical curves which are plotted in Fig. 2. The fact that these points lie above the corresponding Thomas-Fermi-Dirac curves suggests that there is a good possibility that the removal of the exchange correction would improve the agreement between the theoretical and empirical curves. In a brief investigation of this question, two points on the s curve were calculated and plotted in Fig. 2. The positions of these two points verify the expectation for the s curve. The curves which would be obtained by extending these calculations can be regarded as the old Fermi curves corrected for the error in the approximate integration which he used. The two points calculated suggest the possibility that such curves would agree with the empirical curves as well as or better than the original Fermi curves. The analysis might have proceeded in the following way if the exchange effects had been neglected at the beginning. The angular momentum interval length problem would have come up in the Jensen and Luttinger method of angular momentum assignment and would have been settled by examining the figure corresponding to Fig. 3(a). Then the Fermi angular momentum assignment would have been used and, if the rest of the curves fitted as well as the brief portion which was actually calculated, there would have been a tendency to be satisfied with the results and to say that perhaps the exchange effects are negligible.

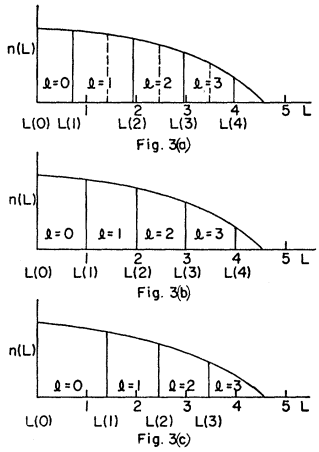

FIG. 3. Schematic plots of the x integrand in the expression (3) for $n(L)$ as functions of L for the various angular momentum assignments. The regions in L assigned to each value of l are indicated therein. Figure 3(a) is for the Jensen and Luttinger angular momentum assignment, Fig. 3(b) is for the Fermi, and Fig. 3(c) for the additional angular momentum assignment [see Table I for the forms of the function $L(l)$].

The results which have been obtained, however, indicate that the exchange effects are not negligible. The individual points plotted in Fig. 2 for the Thomas-Fermi theory would lie on the corresponding curves in Fig. 2 which were plotted for the Thomas-Fermi-Dirac theory if the exchange effects were negligible, since the only difference in the two cases lies in the fact that one of them contains the exchange effects and the other one does not. The disagreement between the results with and without exchange effects is apparent. Since electrons are known to have the exchange interaction, we must accept the Thomas-Fermi-Dirac theory in preference to the Thomas-Fermi model. Therefore, the above-mentioned investigation in the Thomas-Fermi theory was not carried out. At this point it should be reemphasized that the angular momentum assignment is somewhat arbitrary and that by changing it sufficiently it is probably possible to get good average agreement between the theory corrected for exchange effects and the experimental data, even though not with the most straightforward type of angular momentum assignment.

IV. THEORY WITHOUT ANGULAR MOMENTUM ASSIGNMENT

An approach to the problem which accounts for the exchange forces between the electrons but does not make explicit use of an angular momentum assignment was used by Ivanenko and Larin[6] in the first-appearance problem. It is instructive to discuss this viewpoint and

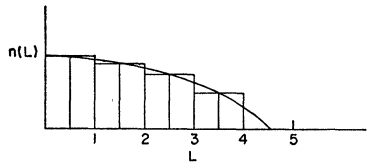

FIG. 4. Same curve as in Fig. 3(b). The rectangular blocks illustrate the approximate method of integration of this curve used by Fermi.[1]

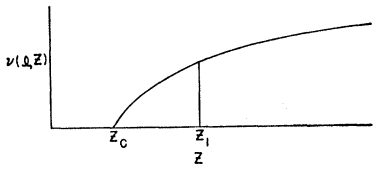

FIG. 5. Schematic plot of $\nu(l,Z)$ as a function of Z, obtained without the explicit use of an angular momentum assignment of the type discussed in Sec. II.

to see how it corresponds to a slightly modified special case of the present viewpoint.

The assumption made by Ivanenko and Larin is equivalent to requiring that if in the expression (3) for $n(L)$ there is a range of values of x over which the integrand is positive then the electron with angular momentum L has made its appearance. The value of Z for which an electron with quantum number l makes its first appearance is then found by requiring that L have the value $(l+\frac{1}{2})\hbar$ and determining the value of Z at which the x integrand in (3) first begins to have a region in x over which it is positive.

The following treatment gives the same results as the Ivanenko and Larin treatment. The Fermi angular momentum assignment is used and it is assumed that the curve can be replaced by the blocked-in curve in Fig. 4. This is exactly what Fermi did in his approximate integration. Therefore, Eq. (4) becomes

$$\nu(l)=\int_{L(l)}^{L(l+1)} n(L)dL=n(L)\int_{L(l)}^{L(l+1)} dL.$$

In the Fermi method,

$$\int_{L(l)}^{L(l+1)} dL=1.$$

Therefore,

$$\nu(l,Z)=n(l+\tfrac{1}{2},Z).$$

This results in the relation

$$\nu(l,Z)=\frac{4L}{\pi}\int\frac{dx}{x}\left[\left(\frac{3\pi Z}{4}\right)^{\frac{2}{3}}x\varphi-(l+\tfrac{1}{2})^2\right]^{\frac{1}{2}}. \quad (5)$$

The graphs for this $\nu(l,Z)$ for the Thomas-Fermi theory are the ones originally given by Fermi.[1] One of the curves is reproduced schematically in Fig. 5. Now for a value Z_1 of Z which is greater than Z_c, $\nu(l,Z)$ has a finite range of integration in x. This value Z_c of Z is therefore the value of Z at which the electron with quantum number l makes its first appearance in the Ivanenko and Larin theory. This is equivalent to the value of Z at which the curve given by Eq. (5) intersects the line $\nu(l)=0$. This is slightly different from the discrete angular momentum approach because in the latter approach the first appearance occurs at the Z for which $\nu(l,Z)$ in Eq. (5) intersects the line $\nu(l)=1$ instead of $\nu(l)=0$.

In conclusion it should be pointed out that Ivanenko and Larin have compared the critical Z for first appearance of an electron of a given angular momentum with the experimental data. In view of the arguments which were advanced in Sec. I in favor of comparing the curve $\nu(l,Z)$ with the data on the average over the whole range of values of Z, their excellent agreement with experiment seems somewhat fortuitous.

V. ACKNOWLEDGMENTS

I would like to thank Professor Philip Morrison for suggesting this problem and for his help and encouragement throughout its progress, and Mr. N. Baker for providing a translation of the Russian paper.

Note added in proof.—In a Letter to the Editor[10] Larin pointed out the difference between the treatment by Ivanenko and Larin[6] of the first-appearance problem, which maintained the continuous distribution of angular momenta, and the treatment of Jensen and Luttinger,[2] which considered the quantized nature of the angular momentum.

[10] S. I. Larin, J. Exptl. Theoret. Phys. (U.S.S.R.) **28**, 498–501 (1955).