from the regression line, are also increased, and become 0.24 and 0.20. The ratio of $L:S:M$, therefore, is changed little: 24:15:20 for a control and 24:60:20 for a treated leaf which differ little from the published ratios 7:5:5 and 7:20:5. The conclusions thus remain unchanged.

Owing to temporary mechanical difficulty during the press run of the April issue of these PROCEEDINGS (vol. 51, no. 4), the equation at the bottom of page 666 was incompletely printed in some copies. The complete form of this equation, which is equation (5) in the article entitled "The Order of Electron Shells in Ionized Atoms," by S. A. Goudsmit and Paul I. Richards, is correctly as follows:

$$C_l + l + {}^1\!/_2 = \frac{A}{\alpha^{1/2}}\left[(1 + \alpha)^{1/2} - \left(1 + \alpha\frac{(l + {}^1\!/_2)^2}{A^2}\right)^{1/2}\right] \tag{5}$$

* This work was supported by grant G-9078 from the National Science Foundation to B. D. Davis.

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THE ORDER OF ELECTRON SHELLS IN IONIZED ATOMS*

By S. A. Goudsmit and Paul I. Richards

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Madelung's Rule and Its Generalization.—The order in which electron shells are filled in the periodic system of the elements has been studied in detail in the early years of development of the Bohr atom. It is not always appreciated that for ionized atoms the electron shells are filled in a different order from that of neutral atoms. Madelung[1] discovered a simple empirical rule for neutral atoms. It consists of two parts.

(A) When considering consecutive neutral atoms the electron shells fill up in the order of the quantum number sum $(n + l)$.

(B) For electrons in states of equal $(n + l)$ the order of filling goes with increasing n.

This rule is remarkably well obeyed throughout the periodic table. It gives, for example, correctly that 4s-electrons $(n + l = 4)$ appear before 3d-electrons $(n + l = 5)$, that 4f-electrons will appear after $Z = 56$ and 5f-electrons after $Z = 88$.

Many of the minor deviations from the Madelung Rule can be ascribed to the large spread of multiplet levels in complex electron configurations. While the center of gravity of the multiplet levels may obey the Madelung Rule, one of the levels of a higher state may have been pushed down below the lower state by large exchange interactions. The simple array of the periodic table of the elements as given, for example, in Bacher and Goudsmit[2] is based on Madelung's Rule. The Catalan periodic table[3] reflects this rule in even more detail.

Fermi[4] has shown by numerical computation that the statistical Thomas-Fermi atom gives approximately the correct place in the periodic system for the first appearance of a shell with given angular momentum $l\hbar$. More recently part (A) of Madelung's Rule has been derived[5] directly from approximate solutions for the statistical electron distribution in the Thomas-Fermi atom.

In this paper we wish to extend these considerations to ionized atoms, since the results may be of interest in connection with recent observations of spectra of highly ionized atoms.[6] For very highly ionized atoms the energies are almost hydrogenic. Very elementary considerations lead in this case directly to the following rule.

(A) For highly ionized atoms the electron shells fill up in the order of the quantum number n.

(B) For electrons in states with equal n the order of filling goes with increasing l.

This rule gives the order in which electron states are usually enumerated, namely, $1s$ $2s$ $2p$ $3s$ $3p$ $3d$ $4s$ $4p$ $4d$ $4f$ ... and so on. Figure 1 represents

f^{14}	d^{10}	p^6	s^2	s^2	p^6	d^{10}	f^{14}	g^{18}
			1 2	1 2				
			3 4	3 4	5··10			
		5··10	11 12	11 12	13··18	19···28		
		13··18	19 20	29 30	31··36	37···46	47····60	
	21···30	31··36	37 38	61 62	63··68	69···78	79····92	93·····110
	39···48	49··54	55 56	111 112	etc.			
57····70	71···80	81··86	87 88					
89····102	etc.							

a. NEUTRAL ATOMS   b. HIGHLY IONIZED ATOMS

FIG. 1.—The "Periodic System" for (a) neutral and (b) highly ionized atoms.

schematically the electron shell structure of neutral and highly ionized atoms. The former (Fig. 1a) is merely the skeleton of the Periodic Table representations mentioned above.

Since the Thomas-Fermi atom can be used to derive part (A) of Madelung's Rule, it should be considered as valid in the limit of neutral atoms with a very large number of electrons. In this limit states with the same $(n + l)$ are expected to coincide as far as the filling order is concerned. Similarly part (A) for the highly ionized atoms can be considered as a limiting case for which states with the same value of n coincide. If we make the self-evident assumption that there is a gradual transition between these two limits, part (B) of the rules follows at once. This is most easily seen in Figure 2. At the top of this diagram we have arranged the states in the order in which they are filled in the limiting case of neutral atoms; at the bottom we have done the same for extreme ions. The lines connecting the states separate those coinciding, and near the two limits the order in each group is just that given by part (B) of both rules.

The diagram shows that up to the $3p$-shell the order is the same for neutral atoms and ions. The first crossover in order occurs between $4s$ and $3d$; for neutrals the
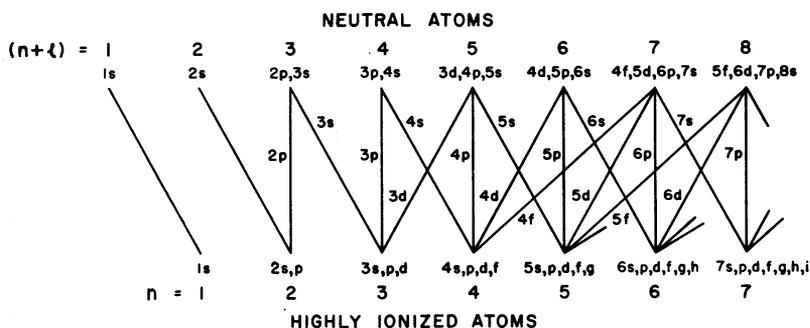
NEUTRAL ATOMS

Fig. 2—The order in which electron shells are filled and the transition between neutral and highly ionized atoms.

order is $4s$ $3d$, for ions it is $3d$ $4s$.   The remaining problem is to determine at which ion this and other crossovers occur.

The rules can be expressed in formulas.   By inspection of Figure 1 one can derive the following expressions.

For neutral atoms, part (A):   A given $(n + l)$-value occurs for the first time with the $(N + 1)$st electron, N is given by

$$N = 1/6[(n + l)^3 - (n + l)] + {}^1\!/_2(n + l). \tag{1}$$

The last term occurs only for $(n + l)$ even.

For highly ionized atoms, part (A):   A given n-value begins with the $(N + 1)$st electron,

$$N = 1/12[(2n - 1)^3 - (2n - 1)]. \tag{2}$$

These equations should be considered as limiting formulas.   It is also possible to express the complete rule, both parts (A) and (B) in a formula, namely, for neutrals, a $(n + l)$-shell begins at the $(N + 1)$st electron,

$$N = {}^1\!/_6[(n + l)^3 - (n + l)] + {}^1\!/_2(n + l)^2 + {}^3\!/_4(n + l) - 2l(l + 2)$$
$$- {}^7\!/_4 \pm {}^1\!/_4(n + l + 1). \tag{3}$$

The plus sign is for $(n + l)$ odd, the minus sign for $(n + l)$ even.   For $n = l + 1$, this formula reduces to equation (1).

Similarly for highly ionized atoms, a $(n + l)$-shell begins with the $(N + 1)$st electron.

$$N = {}^1\!/_{12}[(2n - 1)^3 - (2n - 1)] + 2l^2. \tag{4}$$

Approximations similar to those used for neutral atoms in the papers cited above can also be applied to the Thomas-Fermi distribution for ions.   The result, which shall be derived in a later section, is as follows.

The number C_l of filled shells with an angular momentum $l\hbar$ in a positive ion of N electrons and nuclear charge Z is approximately given by the following equations

$$C_l + l + {}^1\!/_2 = \qquad (1 + \alpha)^{1/2} - \left(1 + \alpha\frac{(l + {}^1\!/_2)^2}{A^2}\right)^{1/2}\Bigg] \tag{5}$$

$$\frac{N-1}{Z} = \left(\frac{\alpha}{1+\alpha}\right)^{3/2} \frac{(1+\alpha)^{3/2} + 3(1+\alpha)}{[(1+\alpha)^{1/2} + 1]^3}. \tag{6}$$

In these equations A stands for $(6Z)^{1/3}$, and α is a parameter determined by the degree of ionization. For total ionization $\alpha = 0$, for neutral atoms and large Z the parameter α approaches infinity.

In a statistical treatment the number of particles is supposed to be large, and C_l is considered to be a continuous variable. In our case, however, the number of electrons is not large, and the filling of shells is not a continuous process but occurs in steps. We must therefore give a special interpretation to equation (5). We shall assume that that value of the pair N, Z for which $C_l = 0$ indicates where the first l-shell begins to fill up, when $C_l = 1$ the second l-shell starts, and so on. Thus, when $l = 2$ and $C_2 = 0$, the $3d$ shell begins, at $C_2 = 1$ we start the $4d$ shell, and so on. This interpretation is chosen so that the results of equations (5) and (6) approach equations (1) and (2). However, for the limiting cases $\alpha \to \infty$ and $\alpha \to 0 (Z \to \infty$, N finite) these equations (5) and (6) give only the cubic term of equations (1) and (2).

There is a simple relation between n and C_l based on the convention that $n \geq l + 1$, namely,

$$n = C_l + l + 1. \tag{7}$$

In order to determine at which ion the $3d$ and $4s$ shells cross over, we note that the beginning of the $3d$ shell is given by equations (5) and (6) when $l = 2$ and $C_2 = 0$, and the $4s$-shell starts when $l = 0$ and $C_0 = 3$. These two conditions determine a value for Z and N, in this example $Z = 27.4$, $N = 17.6$. Thus, in the neighborhood of ten times ionized cobalt or nickel, the $3d$- and $4s$-shell represent approximately equal binding energies for the last added electron.

The numerical results obtained in this way should of course not be taken literally. The nature of the problem is such that one can only hope to determine the vicinity in which the crossover occurs. Irregularities and reversals of order can be expected between the start and finish of filling a shell. It is thus not reasonable to attempt a more precise determination of the crossover by using better approximations of the Thomas-Fermi distribution or by performing elaborate machine computations. More exact results can eventually only be achieved by high-precision calculations of the ground states of each individual ion, though the answer is more likely to come first from new experimental data.

Table 1 shows the computed cross-over points which fall within the range of existing elements.

Figure 3 gives a schematic representation of the results we have obtained. The number of electrons N is plotted against the nuclear charge Z. The lines represent

TABLE 1

VALUES OF Z, N NEAR WHICH THE ORDER OF ELECTRON SHELLS REVERSES

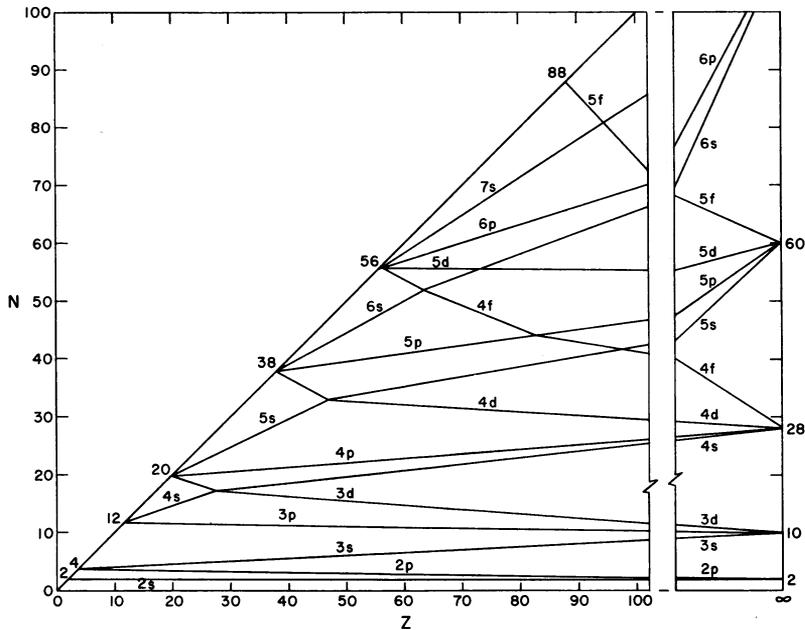|			
$4s$	$3d$	$Z = 27.4$	$N = 17.6$
$5s$	$4d$	47.0	33.2
$6s$	$4f$	63.3	52.1
$6s$	$5d$	73.7	55.7
$5p$	$4f$	83.3	44.2
$7s$	$5f$	94.5	80.8
$5s$	$4f$	97.7	41.8

FIG. 3.—The order of electron shells as a function of the nuclear charge Z and the number of electrons N.

the beginning of the various shells. However, only the order in which these shells occur is significant in this graph, not their precise position. For example, if we consider the neutral atoms we follow the graph along the 45° line $N = Z - 1$. (The -1 arises from the $N-1$ in equation (6), which is explained later in this paper.) In this way we meet the lines indicating the shells in just the order in which they are filled. If, on the other hand, we consider all twelvefold ions, we must follow the graph along the line $N = Z - 13$. We now find in two places a different order of the shells. We can also take a bare nucleus of charge Z and ask in which order shells will be filled if we add electrons. This is given by a vertical line at the chosen Z. In principle it should be possible to replace the line segments drawn in this diagram by appropriate steps and read off the electron configuration of the ground state for any ion. However, the computations are not good enough for this refinement which eventually may be obtained from experimental data on spectra of ions.

Approximate Solutions of the Thomas-Fermi Distribution for Ions.—The Thomas-Fermi statistical model for atoms and ions expresses the electron density, ρ, as a function of radial position, r, in terms of a dimensionless function, $\phi\ (x)$, of a dimensionless variable, x:

$$\rho = (Z/4\pi\mu^3)\,[\phi(x)/x]^{3/2}$$

with

$$x = r/\mu$$

$$\mu = (a_0/4)\,(9\pi^2/2Z)^{1/3}$$

where a_0 is the Bohr radius $(\hbar^2/me^2)$ and Ze is the nuclear charge of the atom or ion.

The function $x^{-1}\phi(x)$ is essentially the electrostatic potential, and ϕ itself is determined by the Thomas-Fermi equation,

$$d^2\phi/dx^2 = \phi^{3/2}/x^{1/2} \tag{8}$$

with $$\phi(0) = 1.$$

The remaining boundary condition on ϕ can be expressed in a number of ways; for our purposes, the following form is the most convenient one:

$$\int x^{1/2}\phi^{3/2}dx = N/Z \tag{9}$$

where N is the total number of electrons in the ion or atom and the integral extends over the region where ϕ is positive.

In terms of these quantities, the Thomas-Fermi theory then yields[7] the following semiclassical expression for the number of electrons having angular momentum $l\hbar$,

$$N_l = 2(l + 1/2)(6Z/\pi^2)^{1/3} \int [x\phi - \beta^2]^{1/2}dx \tag{10}$$

where $$\beta = 2(l + 1/2)(6\pi Z)^{-1/3}$$

and the integral extends over the region where the square root is real.

These relations pertain to the original, simple Thomas-Fermi theory, which we shall use in the following derivations. A correction noted by Fermi and Amaldi,[8] however, can easily be applied to our final results; namely, they observed that the electrostatic potential, ϕ/x, should represent the potential seen by a single electron, and in consequence, ϕ itself should refer to only $N - 1$ electrons. This correction merely amounts to replacing N by $N - 1$ in equation (9), but we shall postpone it to simplify the intervening manipulations.

For neutral atoms, Fermi[9] calculated $\phi(x)$ and the integral in equation (10) numerically, obtaining good over-all agreement with the experimental values of N_l and explaining for the first time the delayed appearance of f-shell electrons and the complete lack of g-electrons in the atoms of the periodic table. Later, Tietz[10] observed that the function

$$\phi_T(x) = (1 + ax)^{-2}; \qquad a = (\pi/8)^{2/3} \tag{11}$$

is a surprisingly good approximation to the solution, ϕ_0, for a neutral atom. (With the quoted value of a, the condition equation (9) is satisfied exactly.) With this approximation, Tietz obtained from equation (10) the simple result,

$$N_l = 4(l + 1/2)[(6Z)^{1/3} - 2(l + 1/2)]. \tag{12}$$

With $l = 0, 1, 2, 3$ for s, p, d, f electrons, this agrees closely with Fermi's numerical results.

To obtain analytic results for ionized atoms, we must choose an approximation to the ionic solutions, $\phi(x)$ with $N \neq Z$, and evaluate the integral in equation (10). Examination of numerically computed ionic solutions[11] indicates that for very small N/Z the graph of $\phi(x)$ is nearly a straight line descending from $\phi(0) = 1$, while for N/Z close to unity, $\phi(x)$ follows the solution for the neutral atom near $x = 0$ and

transfers to an approximately straight line crossing the ϕ-axis at rather large x. These observations suggest the approximation,

$$\phi(x) = \frac{1 - (x/b)}{(1 + ax)^2}, \tag{13}$$

that is, Tietz's function equation (11) multiplied by $1 - (x/b)$. We expect this approximation to become quite accurate for small N/Z, and Tietz has shown that it is very good for $N/Z = 1(b = \infty)$. We shall investigate the intermediate region later.

The parameter b should be chosen to satisfy equation (9); in this way, we ensure that $\int N_l \, dl = N$. When equation (13) is substituted in equation (9) and the integration is performed, one finds

$$\frac{N}{Z} = \frac{\alpha^{3/2}}{(\alpha + 1)^{1/2}} \times \frac{[(\alpha + 1)^{1/2} + 3]}{[(\alpha + 1)^{1/2} + 1]^3} \tag{14}$$

where

$$\alpha = ab = (\pi/8)^{2/3}b.$$

This relation determines b for a given value of N/Z. Equation (6) is the same as equation (14), except that N has been replaced by $(N - 1)$.

An exact solution for $N/Z = 0.48$ has been tabulated in an appendix by Gombás.[12] This exact solution can be compared with our approximation, equation (13) by setting $b = 5.57$, which corresponds to $N/Z = 0.48$ according to equation (14). Since we propose to use equation (13) in the integral equation (10), it is appropriate to compare the functions $x\phi$. It is then found that, where $x\phi$ has appreciable magnitude, the maximum difference between the exact and approximate functions amounts to about 12 per cent. Since $x\phi$ occurs under a square root and since this expression is then integrated, the final approximation to N_l will be much closer than 12 per cent. Note also that we have ensured that $\int N_l \, dl$ will be exactly N.

With these justifications, we proceed to substitute equation (13) into equation (10). When the resulting integral is carried out, one finds the following result after considerable manipulation:

$$N_l = [4\gamma(6Z)^{2/3}/\alpha^{1/2}] \times [(1 + \alpha)^{1/2} - (1 + \alpha\gamma^2)^{1/2} - \gamma\alpha^{1/2}] \tag{15}$$

where

$$\gamma = (l + 1/2)/(6Z)^{1/3}.$$

For $\alpha \to \infty$, corresponding to $N \to Z$, this reduces to Tietz's result equation (12), as it must. Since a filled l-shell contains $2(2l + 1)$ electrons, the number of filled shells is given by

$$C_l = N_l/2(2l + 1). \tag{16}$$

This substitution transforms equation (15) into equation (5). Using $(6Z)^{2/3}$ and $(6Z)^{2/3}/\alpha$ as variables, this equation simplifies and the cross-over points can be obtained by elementary algebra.

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[7] See Gombás, P., *loc. cit.*, p. 169.

[8] *Ibid.*, p. 66 ff.

[9] *Ibid.*, p. 168.

[10] Tietz, T., *Ann. Physik*, **15**, 186 (1955), and **5**, 237 (1960).

[11] Gombás, P., *loc. cit.*, p. 42.

[12] Miranda, C., see Gombás, P., *loc. cit.*, Appendix, Table 55.

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*IN SITU DETECTION AND ESTIMATION OF CHLOROPHYLL AND OTHER PIGMENTS—PRELIMINARY RESULTS**

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Communicated by Roger Revelle, February 26, 1964

In an earlier publication[1] it was shown that spectroradiometric measurements of the spacelight within a scattering-absorbing medium contained information about the absorption spectra of the components of the medium. The instrument used for the early experimental work was a small spectrograph with which we were unable to explore the region of the spectrum beyond 650 mμ. We were, therefore, unable to show the important chlorophyll band in this region. This difficulty has now been overcome, and experimental measurements have been made on fresh-water plants found in ordinary pond water in southern California and in Pacific coastal water.

Instrument.—The data reported here were taken with a new instrument, shown in Figure 1, which was specially built for the work by W. G. Fastie. The instrument is a double monochromator of the Ebert type.[2] The entrance slit, D, of the first monochromator can be alternately irradiated by flux from the light field by means of objectives A or B and the rotating sector disk C. In normal operation the detector gives a reading of the flux from objective A, followed by a reading of the flux from objective B, followed by a zero reading. During this cycle, which requires 2 sec, the wavelength cams remain stationary. The wavelength setting of the instrument is controlled by means of two cams (one of which is shown at E) which rotate the gratings in stepwise fashion to change the wavelength position in 5-mμ increments over the wavelength range of the instrument from 300 mμ to 750 mμ. The bandwidth of measurement can be adjusted by varying the slit width. The measurements reported here were all made with a bandwidth of about 10 mμ of spectrum. The wavelength resolution and accuracy at this setting are illustrated