n + *l* Filling Rule in the Periodic System and Focusing Potentials

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The Klechkovskiĭ rule of filling of one-electron states in the periodic table is considered; according to this rule, levels with lowest values of $N = n + l$ (sum of principal and orbital quantum numbers) are consecutively filled up, and for equal values of N the levels with smallest values of n are filled up. It is shown that for the potential $U(r) \sim r^{-1}(r+R)^{-2}$ which possesses special focusing properties and which closely resembles the Thomas-Fermi potential, additional degeneracy occurs for levels with identical values of N and an energy $E = 0$. The degeneracy is lifted at $E < 0$ and the sequence of split levels corresponds to the second part of the rule. Good agreement is observed between values $Z = Z_N$ for which levels with a given N appear in the model potential, and values of Z for which electrons with the same N values first appear in atoms in the periodic system.

THE focusing potentials considered in the earlier articles[1,2] can be used in a somewhat unexpected manner, by applying the results to the problem of the order of filling of levels in the periodic system of elements.

There is a well known rule, investigated in particular detail by Klechkovskiĭ[3], according to which the filling of the single-electron states in neutral atoms occurs with increasing charge of the nucleus Z in accordance with the law (n + *l*, n), i.e., the electron occupies free states with the smallest value of the sum $N = n + l$ of the principal quantum number n and of the azimuthal quantum number *l*, and in the presence of several states with identical N, the state with the smallest n is filled (and hence with the largest *l*). The rule (n, *l*), which is valid for a slightly screened Coulomb potential and which is satisfied for deep levels of the atom (x-ray terms), is not very useful at a low electron binding energy, and therefore is not satisfied upon successive filling of the levels in the periodic table. A comparison of the two rules is shown in Figs. 1 and 2. Ideal satisfaction of each rule would correspond to a strictly triangular diagram. We see that the exceptions to the (n + *l*, n) rule are few (to be sure, not all the ground-state configurations have been determined at present uniquely; we have used the data given in[4]). Deviations from the rule by one electron are found in 16 cases, and by two electrons in two cases, but usually the atom has an excited state satisfying the rule near the ground state. It is perfectly possible that some of the ground states of the atoms are not described at all by the single-configuration approximation, but, be it as it may, it is seen from the figure that the (n + *l*, n) rule reflects objectively the properties of the effective field of the atom in which an electron moves. Thus, the single-electron potential gives at low energies groups of almost degenerate levels with the same value of N, and the splitting within such a group should increase with increasing binding energy.

The family of potentials

$$U_\mu(r) = -\frac{2v}{r^2 R^2 [(r/R)^\mu + (R/r)^\mu]^2} \tag{1}$$

(μ, v, R are certain constants), which have an exact focusing action in classical mechanics for zero-energy particles, was considered in[2]. In the corresponding
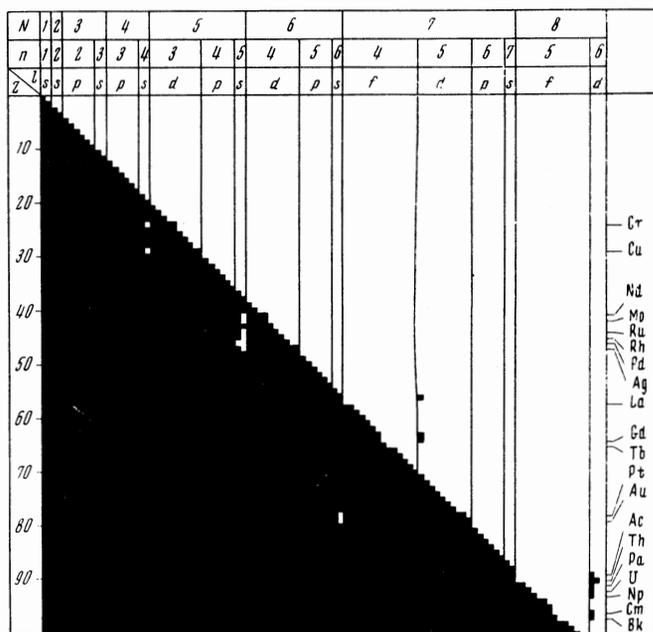

FIG. 1. Empirical data on the filling of single-electron states with increasing number of the element Z in the periodic table. The dark squares correspond to occupied states. The grouping is carried out in accordance with the rule (n + *l*, n). In the right-hand column are indicated the elements for which exceptions from the rule are observed.

wave problem, the values of v at which there are levels with energy E = 0 depend only on the sum $n + (\mu^{-1} - 1)l$. Thus, with increasing v, the potential well becomes deeper and new levels appear in groups with identical value of the indicated linear combination of the quantum numbers. In particular, putting $\mu = 1/2$, we obtain the potential

$$U_{1/2}(r) = -\frac{2v}{rR(r+R)^2}, \tag{2}$$

in which states with identical n + *l* appear simultaneously at the value $v = v_N$,

$$v_N = \frac{1}{4} R^2 N(N+1). \tag{3}$$

If we choose the single-electron potential in the atom in such a form, then the splitting of the levels inside a group with given N will be due to the difference between
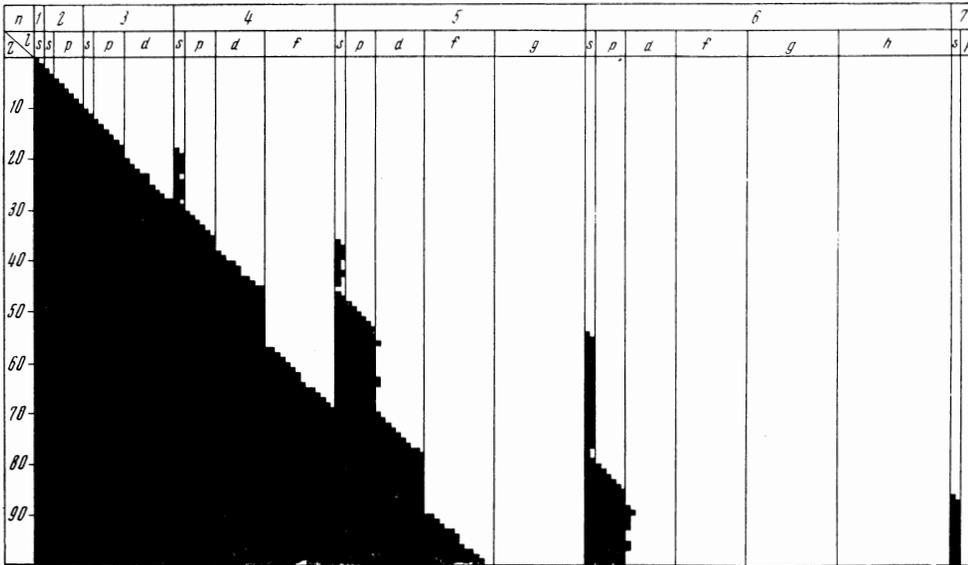
FIG. 2. The same as Fig. 1, but grouping in accordance with the (n, *l*) rule.

their energy and zero. As shown in the Appendix, the larger n at fixed N, the deeper the given level. Thus, the second part of the (n + *l*, n) rule is satisfied also for the potential (2).

What is remarkable is that merely the specification of the character of the level degeneracy produces at the point r = 0 a Coulomb singularity connected in the single-electron potential with attraction to the nucleus (none of the other potentials $U_\mu(r)$ has such a singularity). To obtain $U_{1/2}(r) \approx -Z/r$ as r → 0 it is necessary to stipulate the equality

$$2v/R^3 = Z. \tag{4}$$

At large r, the single-electron potential in a neutral atom behaves like $-1/r$, leading to a Rydberg condensation of the levels, whereas the potential (2) decreases more rapidly. Some improvement (with decrease in simplicity and clarity) could be obtained by taking a potential $U_{1/2}(r) - 1/r$ by simultaneously replacing Z by $Z - 1$ in (4), but we shall not do so, assuming that our potential is suitable for energies that are not too close to the boundary of the continuous spectrum. In the statistical theory of the atom, the single-electron potential is given by $-Z\chi(x)/r$, where $\chi(x)$ s the well known Thomas-Fermi function, $x = b^{-1}Z^{1/3}r$ and $b = (1/2)(3\pi/4)^{2/3} \approx 0.8853$. It is natural to compare this potential with our potential (2), which can be represented, taking (4) into account, in the form $U_{1/2}(r) = -Z\chi(x)/r$, where

$$\widetilde{\chi}(x) = (1 + \alpha x)^{-2}, \tag{5}$$

$$\alpha = bZ^{-1/3}R^{-1}, \tag{6}$$

(α and x are dimensionless). It turns out that if we choose $\alpha = 1/2$, then the functions $\chi(x)$ and $\widetilde{\chi}(x)$ will be quite close to each other in the region of medium values of x, which is vital for the determination of the energy levels. In the interval $3 < x < 6$, the absolute error is approximately 0.003. At smaller x, the absolute error reaches 0.034, but the relative error is still small (less than 4%). As x → ∞ we have $\chi(x) \sim x^{-3}$, whereas $\chi(x) \sim x^{-2}$. It is well known, however, that in the region of

large x, just as close to the nucleus, the conditions for the applicability of the statistical approximation no longer hold, and the Thomas-Fermi function itself is insufficiently accurate here.

In classical mechanics, the potential $U_{1/2}(r)$ is focusing for electrons with zero energy (Fig. 3). In this case all the trajectories with E = 0 close after two turns around the origin, i.e., the period of the initial oscillations is twice as large as the period of revolution ($T_r = 2T_\varphi$), corresponding to a dependence of v on only the linear combination $N - 1 = n_r + 2l$, where $n_r = n - l - 1$ is the radial quantum number. At $E < 0$, an additional precession of the orbits appears, and the additional degeneracy is lifted.

An approximate expression of the type (5), among various other analytic approximations, is proposed also by Tietz[5,6], who started from entirely different considerations. Tietz sought an approximate solution of the linear Thomas-Fermi equation for the atom. The constant α was chosen by him in two ways: from the normalization of the electron momentum distribution[5]
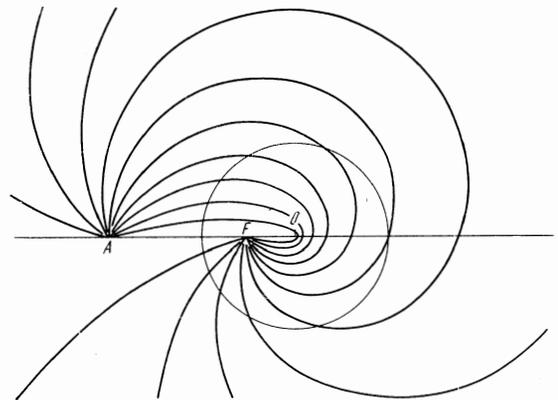
FIG. 3. Focusing properties of potential (2) for particles with zero energy. Only half of each trajectory is shown. All the particles that are emitted simultaneously from the source A fall in the focus F at the same instant of time.

$(\alpha = (\pi/8)^{2/3} \approx 0.569)$ and a variational principle[6] $(\alpha = 2^{-4}(35\pi/4)^{2/3} \approx 0.538)$, but this leads to a larger deviation of $\tilde{\chi}(x)$ from the exact function $\chi(x)$, in the region of medium values of x, than obtained by us. Tietz then substituted this function into the Fermi formula, which describes, within the framework of the statistical theory, the construction of groups in the periodic system[7]. The Schrödinger equation with a potential of the form (2) was solved approximately for deep levels using the fact that in this case the potential can be regarded as being almost of the Coulomb type[8]. An exact solution of the equation at zero energy was obtained by Tietz only in the case $l = 0$[9] (Tietz used an analytic potential of a somewhat more general form, which did not admit of exact solution at other values of l). The focusing properties of the potential (2), and also the presence of additional degeneracy at E = 0, was not considered by Tietz.

The values $Z = Z_N$ at which levels with a given N appear, is determined from the formula

$$Z_N = \left[\frac{\alpha}{2b} N(N+1)\right]^{3/2}, \qquad (7)$$

which follows from (3), (4), and (6). It is curious that, as seen from the table, the values of Z_N calculated with this formula at $\alpha = 1/2$, agree well with the values $Z^{(N)}$ at which electrons with the same N first appear[1]. Generally speaking, the filling of a given level could begin also at values of Z considerably larger than Z_N. The proximity of these numbers shows that levels with a given N, which appear with increasing Z, are almost immediately filled by electrons, so that the binding energy of the last electron never turns out to be too large. This is exactly why the (n + l, n) rule, which is strictly valid at small binding energies, is so well satisfied for realistic atoms.

N	Z_N	$Z^{(N)}$	N	Z_N	$Z^{(N)}$
1	0.44	1	5	24.7	21
2	2.2	3	6	40.8	39
3	6.2	5	7	62.9	57
4	13.4	13	8	91.7	88

We see thus that the considered model potential makes it possible to explain important properties of neutral atoms, although it does not take into account certain essential properties of the effective fields in which the atomic electrons move. The main inaccuracy consists in neglecting the Coulomb potential $-1/r$, which acts on the electron at large values of r. However, if the binding energy for the electron is larger than several electron volts, then in the region where the wave function differs noticeably from zero the Coulomb potential $-1/r$ is small compared with the main part of the atomic potential, and it can be neglected (or regarded as a perturbation). Only for very low energies (Rydberg

condensation levels) does the Coulomb potential play the principal role, but these states of the electron correspond to highly excited atoms and are not connected directly with the configuration of the ground and first-excited terms.

In principle one might use the formulas obtained in the Appendix to determine the ionization potential of different atoms, but such a calculation without allowance for the Coulomb term can claim to yield only qualitative results.

The relation between the considered model and the real problem of electron motion in an atom is unique. At E = 0, when the equation for the model potential can be solved exactly, this equation cannot be used, owing to the incorrect behavior of the potential as $r \to \infty$, and at large negative values of E the model yields nothing new compared with the usual problem of a screened Coulomb field. Only in a certain relatively narrow region, starting with a binding energy of several electron volts, can one expect reasonable results, but it is precisely this region which is the fundamental one for the solution of the problem of the order of the filling of the levels.

From among other applications of the model, notice should be taken of the possibility of describing the scattering of slow electrons by atoms, including resonances resulting from the transition of states that are bound at $Z > Z_N$ into quasistationary and virtual states when $Z < Z_N$. Here, again, the scattering of very slow electrons will be described by the model incorrectly, since the model does not take into account the real polarization forces between the electron and the atom. However, starting with an energy on the order of 0.5—1 eV, the polarization forces make a small contribution to the scattering, and at high energies, up to the start of the inelastic processes there should be a reasonable agreement between scattering by real atoms and by our model potential. Thus, for atoms with $Z \lesssim Z_N$ we can expect the immediate appearance of an entire aggregate of resonances in the electron scattering for different values of l.

The approximate properties of the atomic potential considered here, namely the focusing of classical trajectories and the additional degeneracy at E = 0, should apparently have also other physical consequences.

APPENDIX

To ascertain the order of the energy levels with identical N in a potential $U_{1/2}(r)$ at E < 0, let us determine the course of the terms $E_{nl}(Z)$ near the point $Z = Z_N$ (the potential (2) depends on Z via the relations (3) and (6)). The wave functions (non-renormalized) corresponding to these points are expressed in terms of the Gegenbauer polynomials C_n^{λ}[2]:

$$\psi_{nlm}(\mathbf{r}) = \left(\frac{r}{R}\right)^l \left(\frac{r}{R}+1\right)^{-(2l+1)} C_{n_r}^{2l+3/2}\left(\frac{R-r}{R+r}\right) Y_{lm}(\vartheta, \varphi). \qquad (A.1)$$

We have used perturbation theory, taking the functions (A.1) and the zeroth approximation and regarding the difference between the potential with the given value of Z and with the value $Z = Z_N$ as a perturbation. As a result, the slope of the terms determined by the well

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[1]After this article was sent to press, an article by Abrahamson was published[13], in which a single-electron potential of the same type as ours is used. The Schrödinger equation is not solved in[13], and it is assumed that the first level with a given l appears for those values of Z at which the effective potential (with allowance for the centrifugal term) begins to take on negative values. It is well known, however, that this is not true in the three-dimensional problem. Therefore the good agreement between the results of[13] and the empirical data should be regarded as accidental.

known theorem of Gell-Mann and Feynman:

$$\frac{\partial E_{nl}}{\partial Z}\bigg|_{Z=Z_N} = \frac{1}{M_{nl}}\left(\frac{\partial U_{1/2}}{\partial Z}\right)_{nl}, \qquad (A.2)$$

where $M_{nl} = \langle \psi_{nlm} | \psi_{nlm} \rangle$,

$$\left(\frac{\partial U_{1/2}}{\partial Z}\right)_{nl} = \left\langle \psi_{nlm} \left| \frac{\partial U_{1/2}}{\partial Z}\right|_{Z=Z_N} \right| \psi_{nlm} \right\rangle.$$

However, the question of applying perturbation theory to a discrete level with zero energy is not quite true. It is discussed in greater detail in[10]. We indicate here only that for a given value of the orbital momentum l the correction of $(l + 1)$-st order to the energy, calculated in accordance with the usual perturbation theory, becomes infinite. In this case, we are interested in first order, so that the indicated circumstance makes the formula (A.2) inapplicable only for the s-states. The general expression for the correction to the s-state energy

$$\sqrt{-2E_{n0}} = -\frac{2\langle\psi_{n00}|V^{(1)}|\psi_{n00}\rangle}{c_{n0}^2}, \quad c_{n0} = \lim_{r\to\infty} r\psi_{n00}(r), \qquad (A.3)$$

where $V^{(1)}$ is a perturbation, can be obtained with the aid of arguments analogous to those used in the theory of the effective scattering radius (see also[10]). It follows from (A.3), in particular, that on the E(Z) diagram the s-terms touch the boundaries of the continuous spectrum[11], and consequently lie higher than all the remaining terms with given N.

The matrix elements $(\partial U_{1/2}/\partial Z)_{nl}$ reduce to normalization integrals for the Gegenbauer polynomials, as a result of which we obtain

$$\left(\frac{\partial U_{1/2}}{\partial Z}\right)_{nl} = -\frac{b^2}{3\alpha^2 Z_N^{2/3}}\frac{\pi 2^{-4(2l+1)}\Gamma(4l+n_r+3)}{n_r!(n_r+2l+3/2)[\Gamma(2l+3/2)]^2}. \qquad (A.4)$$

The calculation of M_{nl} is more cumbersome, but can still be considered analytically by using the recurrence relations for C_n^λ and formula (16.316) from[12]:

$$M_{nl} = \frac{b^3}{\alpha^3 Z_N}\frac{2l+3/2}{n_r+2l+3/2}\{f(n_r+1)-f(n_r-1)\} \qquad (A.5)$$
$$(l \neq 0),$$

where

$$f(\nu) = \frac{\Gamma(2l-1)\Gamma(2l+3)\Gamma(\nu-1)\Gamma(4l+n_r+3)\Gamma(4l+\nu+4)}{n_r!(\nu-1)!\Gamma(4l+n_r+1)(\Gamma(4l+3)\Gamma(4l+5)}$$
$$\times {_4F_3}(-n_r,4l+n_r+3,2l-1,-3; 2l+2,4l+\nu+1,-\nu-2; 1).$$

The series for the generalized hypergeometric function $_4F_3$ reduces here to a finite sum.

A comparison of the values $\partial E/\partial Z|_{Z=Z_N}$ shows that the second part of the (n + l, n) rule is satisfied.

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