

The integrability and the structure of atom

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Received November 28, 2001
Communicated by E.Ya. Khruslov

The paper contains the proof and generalization of the Madelung hypothesis which is widely used in the quantum theory of atom for explanation of the structure of periodic system of elements. The justification and many-well generalization of the Tietz atomic potential are also presented in the paper.

1. Introduction

The self-consistent potential in the atom with Z electrons at $Z \rightarrow \infty$ is known to be the Thomas–Fermi potential. We have proved that at $Z \rightarrow 1$ the atomic potential is the Tietz potential $V(r) = -(Z/r)(1 + (Z/r))^{-2}$, with R as a parameter, or its deformation. Eigenstates of this potential at an energy $E = 0$ are degenerate and form the Mendeleev electron shell. In terms of these electron shells we explain the structure of the periodic system of elements. In particular, we have proved for the periodic system of elements the empirical rule $(n + l, n)$, according to which electrons in atom fill at first the states with the least quantum number $n + l$ and for the given value of the number $n + l$ fill the states with the least possible quantum number n . Here n and l are the principal and orbital quantum numbers. For the Schrödinger operator with the Tietz potential the radial part of the one-electron wave function is shown to satisfy the Heun equation. Among deformations of the Tietz potential there are many-well potentials which can explain the deviations from the $(n + l, n)$ rule and the existence of the d -, f - and g -electron transition series in the periodic system of elements.

Further we use the atomic units $e = \hbar = m = 1$.

Mathematics Subject Classification 2000: 81-XX.

2. The Hartree–Fock electron ground state of atom and the resonance equation

Let us consider the Hamiltonian of neutral atom with Z electrons,

$$H = - \sum_{k=1}^Z \left(\frac{1}{2} \Delta_k + \frac{Z}{r_k} \right) + \frac{1}{2} \sum_{i,k=1, i \neq k}^Z \frac{1}{r_{ik}},$$

where r_k is the distance from the k -th electron to the nucleus and r_{ik} is the distance between i -th and k -th electrons. In the Hartree–Fock approximation the ground state energy of atom is

$$E(Z) = \sum_{l=0}^{l^{max}} \sum_{n_r=0}^{n_r^{max}(l)} E(n_r, l),$$

where summing goes over the domain $E(n_r, l) \leq 0$. The summands are

$$E(n_r, l) = - \int \psi_{n_r, l}^*(\mathbf{r}) \left(\frac{1}{2} \Delta + \frac{Z}{r} \right) \psi_{n_r, l}(\mathbf{r}) dv + \frac{1}{2} \sum_{l', n_r'} \int \int \frac{\rho_{l', n_r'}(\mathbf{r}, \mathbf{r}) \rho_{l', n_r'}(\mathbf{r}', \mathbf{r}') - |\rho_{l', n_r'}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} dv dv',$$

$$\rho_{l, n_r}(\mathbf{r}, \mathbf{r}') = \psi_{n_r, l}^*(\mathbf{r}) \psi_{n_r, l}(\mathbf{r}'),$$

where $\psi_{n_r, l}(\mathbf{r})$ is the one-electron wave function with the radial quantum number n_r and the orbital quantum number l .

Further we study a dependence of the ground state energy of atom $E(Z)$ on the charge Z assuming it a continuous variable.

When $Z \rightarrow \infty$ and the difference of summands for adjacent values of quantum numbers is small enough we can present the ground state energy of atom $E(Z)$ by means of the Euler–McLauren formula as a sum

$$E(Z) = c_7 Z^{7/3} + c_6 Z^{6/3} + c_5 Z^{5/3} + \dots,$$

with some constants c_k , $k = 1, 2, \dots$, where the first term is the Thomas–Fermi energy, the second term is the Scott correction and so on (see e.g. [1, 2]).

When $Z \rightarrow 1$ and the difference of summands for adjacent values of quantum numbers becomes large we must use the Poisson summation formula and hence we can present the ground state energy of atom as

$$E(Z) = \bar{E} + \tilde{E}, \quad \bar{E} = \int_{-a'}^{l^{max}+a} dl \int_{-b'}^{n_r^{max}(l)+b} dn_r E(n_r, l),$$

$$\tilde{E} = \sum_{(k,s) \neq (0,0)} \int_{-a'}^{l^{max}+a} n_r^{max}(l)+b \int_{-b'} dn_r E(n_r, l) \cos(2\pi(kn_r + sl)),$$

where the term \bar{E} is the Thomas–Fermi energy and the term \tilde{E} is the shell part of the energy of atom which is the sum of integrals with the fast oscillating integrands. The phase of these oscillations

$$\phi(l) = k(n_r^{max}(l) + b) + sl$$

has the stationary point and the value of every integral is largest possible if this stationary point is infinitely degenerate, i.e., if the resonance equation $qn_r^{max}(l) + pl = const.$, $q, p \in \mathbb{N}$, $0 < l < l^{max}$, holds. Thus, we come to

Theorem 2.1. *If the charge $Z \rightarrow 1$ then the ground state electron configuration satisfies the resonance equation*

$$qn_r^{max}(l) + pl = const., \quad q, p \in \mathbb{N}, \quad 0 < l < l^{max}.$$

In terms of quantum mechanics this equation states that the atomic energy $E = 0$ is degenerate. In terms of classical mechanics this equation means that the electron orbit with the energy $E = 0$ is closed, since frequencies ω_r and ω_ϕ of radial and orbital oscillations are in resonance,

$$\left(\frac{\partial n_r}{\partial l}\right)_{E=0} = \left(\frac{\partial I_r}{\partial I_\phi}\right)_{E=0} = -\frac{(\partial E / \partial I_\phi)_{I_r}}{(\partial E / \partial I_r)_{I_\phi}} = -\frac{\omega_\phi}{\omega_r} \Big|_{E=0} = -\frac{p}{q}.$$

Here $I_r = 2\pi n_r$, $I_\phi = 2\pi l$ are the adiabatic invariants. The Coulomb potential, which is the atomic potential at $Z = 1$, satisfies the resonance equation for any value of the $E < 0$.

3. The Tietz potential

Now we discuss properties of atom with the resonance atomic potential. Using the Bohr–Sommerfeld semiclassical formula [3]

$$\frac{1}{\pi} \int_{r_-}^{r_+} (2(E - V(r) - l(l+1)/2r^2))^{1/2} dr = n_r(E, l) + \gamma,$$

at $E = 0$ and a new variable $x = \ln(r/R)$, where R is parameter, we can present the resonance equation in the form

$$\frac{1}{\pi} \int_{x_-}^{x_+} (2(E_l - W(x)))^{1/2} dx = \frac{1}{q}(const - pl) + \gamma,$$

$$E_l = -l(l + 1)/2, \quad W(x) = r^2 V(r)|_{r=Re^x}.$$

We can interpret the last equation as the Bohr–Sommerfeld semiclassical formula for the spectrum $E_l = -l(l + 1)/2$ in the one-dimensional potential $W(x)$. We call solutions $W(x)$ (or $V(r)$) the resonance potentials. It turns out that they are soliton potentials or their isospectral (or isoresonance) deformations. We can easily prove the following statements.

Proposition 3.1. *The potential*

$$\begin{aligned} U_{\alpha,\beta,R}(r) &= r^2 W_{\alpha,\beta}(x)|_{x=\ln(r/R)} = -\frac{\beta}{r^2 \cosh^2(x/\alpha)} \Big|_{x=\ln(r/R)} \\ &= -\frac{\beta}{r^2((r/R)^{1/\alpha} + (R/r)^{1/\alpha})^2}, \quad \alpha = \frac{p}{q}, \end{aligned}$$

is the one-well resonance potential.

Proposition 3.2. *If the potential*

$$U_{\alpha,\beta,R}(r) = -\frac{\beta}{r^2((r/R)^{1/\alpha} + (R/r)^{1/\alpha})^2}$$

coincides at small r with the Coulomb potential, $U_{\alpha,\beta,R}(r) = -Z/r, r \rightarrow 0$, then $\alpha = 2$, and $\beta = ZR$, and thus we get the Tietz potential

$$V(r) = U_{2,ZR,R}(r) = -\frac{Z}{r(1 + (r/R))^2}.$$

At $R \rightarrow \infty$ the Tietz potential coincides with the Coulomb potential.

Proposition 3.3. *If in the Tietz potential the total number of states is equal to the charge Z of the nucleus, then*

$$R = (9/2)^{1/3} Z^{-1/3} = 1,651 Z^{-1/3}.$$

Proposition 3.4. *The orbit in the Tietz potential at $E = 0$ is closed and described with an equation*

$$(r/R) + (R/r) = 2(1 + 2a \sin^2 \phi), \quad \text{where } a = (Z/2M^2 R) - 1.$$

T. Tietz [4] has introduced his potential in atomic physics in 1960 and used it with success for calculations of different atomic characteristics and explanation of the periodic system of elements, although he considered it always only just as a good rational approximation to the Thomas–Fermi potential. Later on Yu.N. Demkov and V.N. Ostrovsky [5, 6] pointed out that the Tietz potential is a particular case of potentials which were considered in some problems of optics by J. Maxwell [7] and V. Lenz [8] and which are solutions of the resonance equation but did not elucidate the origin of this equation.

4. The Schrödinger operator with the Tietz potential — semiclassical approximation

In the semiclassical approximation it is useful to replace the energy E , the radial quantum number n_r and the orbital quantum number l by the scaled quantities

$$\epsilon = \frac{ER}{Z}, \quad \nu = \frac{n_r + \gamma}{(2ZR)^{1/2}}, \quad \lambda = \left(\frac{l(l+1)}{2ZR} \right)^{1/2}.$$

Proposition 4.1. *The Bohr–Sommerfeld quantization rule for the Tietz potential can be presented in the form*

$$\nu = \frac{1}{\pi} \int_a^b \sqrt{P_4(x)} \frac{dx}{x(1+x)},$$

$$P_4(x) = \epsilon x^2(1+x)^2 + x - \lambda^2(1+x)^2,$$

where a, b , are real zeros of the polynomial $P_4(x)$. It means that the scaled radial quantum number ν is a period of the elliptic integral of the third type. It means also that the spectrum of atom is defined in the semiclassical approximation by the universal equation $\epsilon = f(\nu, \lambda)$ which does not depend explicitly on the charge Z and the parameter R .

Using this theorem we can obtain approximate formulae for the spectrum in different special cases, for example we have

Proposition 4.2. *If $\lambda \neq 0$ and $\epsilon \rightarrow -0$, then the spectrum of the Schrödinger operator with the Tietz potential in the semiclassical approximation is of the following form:*

$$\epsilon \simeq -(1 - \nu - 2\lambda) \frac{16\lambda^5}{3 - 8\lambda^2}.$$

Accurate study of the turning points allows one to calculate the constant γ in the Bohr–Sommerfeld quantization rule.

Proposition 4.3. *For the Tietz potential at the energy $E = 0$ we have*

$$\gamma = (3/2) + 2\{l - [l(l+1)]^{1/2}\} \simeq (1/2) + \delta_{l,0}.$$

By means of this result we can resent the resonance equation as follows.

Proposition 4.4. *Let for the Tietz potential the parameter ζ be of the form*

$$\zeta = 2ZR = (M + 3/2)^2, \quad M \in \mathbb{N},$$

then in the semiclassical approximation the states with the quantum numbers n, l , satisfying the equation

$$n + l = M + 1 - \delta_{l,0},$$

are degenerate at the energy $E = 0$.

5. The Schrödinger operator with Tietz potential — exact results

Let us assume a solution of the Schrödinger equation with the Tietz potential in the form

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi), \quad R_{nl}(r) = u_{nl}(r)/r.$$

Proposition 5.1. *For the Schrödinger operator with Tietz potential the radial part $u(z)$ of the eigenfunction satisfies the linear ordinary differential equation with rational coefficients, which has two regular and one irregular singular points (the confluent Heun equation),*

$$\frac{d^2u}{dz^2} + \left(2ER^2 + \frac{2ZR}{z(1+z)^2} - \frac{l(l+1)}{z^2} \right) u = 0, \quad z = \frac{r}{R}.$$

The Heun equation and its properties are described in the book [9].

Now let us change the variable z and the function $u(z)$ in such a way:

$$z \rightarrow 2z + 1, \quad u(z) \rightarrow (z - 1)^{\mu_1} (z + 1)^{\mu_2} e^{-p(z-1)} v(z).$$

Then by means of the parameters p, m, s ,

$$p = \frac{1}{2}(-2ER^2)^{1/2}, \quad \begin{pmatrix} m \\ s \end{pmatrix} = l + \frac{1}{2} \pm \left(\frac{1}{4} + 2ZR \right)^{1/2},$$

we can express the function $v(z)$ in terms of the Laguerre polynomials $L_k^{m+s}(x)$,

$$v_{n,m,s}(z) = \sum_{k=0}^{\infty} g_k(n, m, s) L_k^{m+s}(2p(z-1)).$$

Here the coefficients $g_k(n, m, s)$ satisfy the three-term recurrence relation

$$\begin{aligned} & A_k^L g_{k+1} + B_k^L g_k + C_k^L g_{k-1} = 0, \quad g_{-1} = 0, \\ \text{where } & A_k^L = (k + m + s + 1)(k + s + 1), \quad C_k^L = k(k + m), \\ & B_k^L = 2p^2 - \frac{1}{2}(2(k + p) + m + s + 1)^2 + \frac{1}{4}((m - s)^2 - 1). \end{aligned}$$

By means of the rational functions

$$w_k(z) = (z - 1)^k (z + 1)^{-k},$$

we can express the function $v(z)$ in terms of the expansion

$$v_{n,m,s}(z) = \sum_{k=0}^{\infty} f_k(n, m, s) w_k(z).$$

Here the coefficients $f_k(n, m, s)$ satisfy the three-term recurrence relation

$$\begin{aligned} & A_k^J f_{k+1} + B_k^J f_k + C_k^J f_{k-1} = 0, \quad f_{-1} = 0, \\ \text{where } & A_k^J = (k + m + s + 1)(k + 1), \quad C_k^J = (k + s)(k + m), \\ & B_k^J = 2p^2 - \frac{1}{2}(2(k + p) + m + s + 1)^2 + \frac{1}{4}((m - s)^2 - 1). \end{aligned}$$

The eigenvalues in both cases are defined by the equation

$$\det \begin{pmatrix} B_0 & A_0 & 0 & 0 & \dots \\ C_1 & B_1 & A_1 & 0 & \dots \\ 0 & C_2 & B_2 & A_2 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix} = 0.$$

We can see that the spectrum of the Schrödinger operator with the Tietz potential loses its universality in comparison to the semiclassical approximation.

Proposition 5.2. *Let for the Tietz potential the parameter ζ be of the form*

$$\zeta = 2ZR = (M + 1)(M + 2), \quad M \in \mathbb{N},$$

then the states with the quantum numbers n, l , satisfying the equation

$$n + l = M + 1 - \delta_{l,0}$$

are degenerate at the energy $E = 0$.

**6. The ordering of subshells (n, l) in the periodic system
of elements and the Madelung rule $(n + l, n)$.
The Mendeleev electron shell and values of periods**

The following statements are simple consequences of the resonance equation.

Proposition 6.1. *For the atom with the resonance potential the following rule $(n + l)$ is valid: with the growth of charge Z the electrons fill consecutively the states with the least possible value of the quantum number $n + l$.*

The rule $n + l$ is valid absolutely for the whole system of elements.

Proposition 6.2. *For the atom with the Tietz potential the following rule $(n + l, n)$ is valid: with the growth of charge Z the electrons fill consecutively the states with the least possible value of the quantum number $n + l$, and at given number $n + l$ fill the states with the least possible quantum number n .*

The rule $(n + l, n)$ as an empirical one was formulated for the first time by E. Madelung [10] in 1936 and later on was rediscovered repeatedly many times (see V.M. Klechkovsky [11]). Since we have proved the $(n + l, n)$ rule only for the Tietz potential, the domain of its validity might be less than that for the $(n + l)$ rule which is valid for all resonance potentials.

The rule $(n + l, n)$ gives a principle for consecutive appearance of the subshells (n, l) with $2(2l + 1)$ degenerate states in atoms with the growth of the charge Z . According to this rule the (n, l) -subshells in atom form the following linearly ordered sequence:

$$\{(n, l)\} = \{(1, 0), (2, 0), (2, 1), (3, 0), (3, 1), (4, 0), \\ (3, 2), (4, 1), (5, 0), (4, 2), (5, 1), (6, 0), \\ (4, 3), (5, 2), (6, 1), (7, 0), (5, 3), (6, 2)etc.\}$$

The rule $(n + l, n)$ describes correctly the real electron configurations of all elements of periodic system with small number of exclusions [11]. There exist 17 elements (Cr, Cu, Nb, Mo, Ru, Rh, Ag, La, Ce, Gd, Pt, Au, Ac, Pa, U, Np, Cm), whose electron configurations differ by 1 electron, and there exist 3 elements (Pd, Ir, Th), whose electron configurations differ by 2 electrons from the configurations predicted with the rule $(n + l, n)$.

The rule $(n + l, n)$ enables us to calculate quantitative characteristics of the periodic system of elements with algebraic means.

Let Z_l designate the charge of atom at which the electron with the orbital quantum number l appears for the first time, Z_n designate the charge of atom at which the electron with the principal quantum number n appears for the first time, Z_{n+l} designate the charge of atom at which the electron with the given sum

of the principal and orbital quantum numbers $n+l$ appears for the first time, and $Z_{n,l}$ designate the charge of atom at which the electron with the given values of the principal quantum number n and the orbital quantum number l appears for the first time. Using the well known formulas

$$\sum_{k=1}^{k=n} k = \frac{1}{2}n(n+1), \quad \sum_{k=1}^{k=n} k^2 = \frac{1}{6}n(n+1)(2n+1),$$

we can calculate these numbers easily:

$$\begin{aligned} Z_l &= (1/6)(2l+1)^3 + (1/6)(5-2l), \\ Z_n &= (1/6)(n+l)^3 + (1/2)(n+l)[\sin^2(\pi/2)n - (1/3)] - 1, \\ Z_{n+l} &= (1/6)(n+l)^3 + (1/2)(n+l)[\sin^2(\pi/2)(n+l) - (1/3)] + 1, \\ Z_{n,l} &= (1/6)(n+l+1)^3 + (1/2)(n+l+1)[\sin^2(\pi/2)(n+l) - (1/3)] \\ &\quad - 2(l+1)^2 + 1. \end{aligned}$$

Now let us introduce the definition of the Mendeleev electron shell.

Definition 1. *The M -th Mendeleev electron shell is the set of states with quantum numbers n, l , which satisfy the equality*

$$n+l = M+1 - \delta_{l,0}$$

and are degenerate at the energy $E = 0$.

In order to find subshells (n, l) , which correspond to the M -th Mendeleev period, we must solve at a fixed number M the equation $n+l = M+1 - \delta_{l,0}$ with respect to the quantum numbers n , $n = 1, 2, \dots$, and l , $l = 0, 1, \dots, n-1$. It enables us to prove the following statements.

Proposition 6.3. *The number of elements in the Mendeleev M -th period is equal to*

$$N_M = \sum_{l=0}^{[M/2]} 2(2l+1) = 2[(M+2)/2]^2,$$

where $[x]$ means the integral part of the real number x . Numbers N_M , $M = 1, 2, \dots$, form the sequence 2, 8, 8, 18, 18, 32, 32, etc., which coincides with empirical lengths of the periods of the system of elements.

Proposition 6.4. *The atomic charge ${}_M Z$ of the initial element of the Mendeleev M -th period is equal to*

$${}_M Z = Z(M) - 1,$$

and the atomic charge Z_M of the final element of the Mendeleev M -th period is equal to

$$Z_M = Z(M + 1) - 2,$$

where

$$Z(M) = \frac{2}{3} \left[\frac{M}{2} \right] \left(\left[\frac{M}{2} \right] + 1 \right) \left(2 \left[\frac{M}{2} \right] + 1 \right) + \delta 2 \left(\left[\frac{M}{2} \right] + 1 \right)^2, \\ \delta = M \pmod{2},$$

and $[x]$ is the integral part of the real number x .

The sequence $\{Z_M\} = \{1, 3, 11, 19, 37, 55, 87, \text{etc.}\}$ corresponds to alkaline metals and the sequence $\{Z_M\} = \{2, 10, 18, 36, 54, 86, \text{etc.}\}$ corresponds to noble gases.

Below in the table we have presented the ordered sequence of subshells $\{(n, l)\}$ for the every M -th Mendeleev period which is built in accordance with our theory. This table represents a quantum mechanical construction of the periodic system of elements.

M	$\{(n, l)\}$
1	(1, 0)
2	(2, 0), (2, 1)
3	(3, 0), (3, 1)
4	(4, 0), (3, 2), (4, 1)
5	(5, 0), (4, 2), (5, 1)
6	(6, 0), (4, 3), (5, 2), (6, 1)
7	(7, 0), (5, 3), (6, 2), (7, 1).

The deviation of the structure of the real periodic system from that predicted by the $(n + l, n)$ rule may be a result of the deviation of the atomic potential from the Tietz one. Hence it is reasonable to consider a complete set of resonance potentials.

7. Isoresonance deformations of the Tietz potential and many-well atomic potentials. The transition and rare-earth series of elements

According to previous considerations we can present the resonance equation in the form of Abelian integral equation with respect to $W(x)$,

$$\frac{1}{\pi} \int_{x_-}^{x_+} (2(E_l - W(x)))^{1/2} dx = \frac{1}{q}(\text{const} - pl) + \gamma,$$

$$E_l = -l(l+1)/2, \quad W(x) = r^2 V(r)|_{r=Re^x}.$$

Solutions of this equation define resonance potentials by means of the formula

$$V(r) = r^{-2} W(x)|_{x=\ln(r/R)}.$$

In particular, the Tietz potential $V(r) = U_{2,ZR,R}(r)$ corresponds at $ZR = (1/2)(M+1)(M+2)$ to the $(M+1)$ -soliton potential $W_{2,ZR,R}(x) = (ZR/2) \cosh^{-2}(x/2)$.

The general resonance potential is the isoresonance deformation of the Tietz one-well potential and in generic case has many wells. We can give an exact formulation of this statement.

Proposition 7.1. *All resonance potentials $V_{\alpha,\beta,R}(r)$ are deformations of the Tietz potential and can be presented in the form*

$$V_{\alpha,\beta,R}(r,t) = r^{-2} W_{\alpha,\beta}(x,t)|_{x=\ln(r/R)} = -r^{-2} \frac{d^2}{dx^2} \ln \det A(x,t) \Big|_{x=\ln(r/R)},$$

$$A(x,t) = \left\| \delta_{j,k} + \frac{\alpha \gamma_j}{j+k} \exp\left(-\frac{1}{\alpha}(j+k)x + \frac{8}{\alpha^3} j^3 t\right) \right\|_0^N,$$

where $N = \alpha\beta^{1/2}$, γ_j are some constants and t is the deformation parameter.

As a consequence we have an important statement.

Proposition 7.2. *In the M -th Mendeleev period of the periodic system of elements the effective atomic potential*

$$U_{eff}(r) = U_T^{def}(r) + \frac{l(l+1)}{2r^2},$$

where $U_T^{def}(r)$ is some isoresonance deformation of the Tietz potential, may have no more than $[M/2] + 1$ wells, where $[x]$ means the integer part of number x . In other words, the effective atomic potential in the M -th period of the periodic system may have as much wells as much subshells (n, l) are contained in the M -th period.

In physics of atom the many-well potentials have been used to explain a collapse of electron states and the existence of the d -, f -, and g -electron transition series in the periodic system of elements [12, 13]. E. Fermi[14], M. Göppert–Mayer [15] and R. Latter [16] studied two-well potentials, G.J. Wendin and A.F. Starace [17] considered also three-well potentials. V.N. Ostrovsky built two-well potentials of the Tietz potentials [18]. In the frame of our approach the atomic potential in the M -th Mendeleev period may have no more than $([M/2] + 1)$ wells.

If we know eigenvalues and eigenstates for the Schrödinger operator with the Tietz potential we can obtain effectively these quantities for the deformed Tietz potential by means of the deformation transformation described by the Korteweg–de Vries equation and their higher analogs [19].

8. Conclusion

For the Mendeleev periodic system of elements the rule $(n + l, n)$ is proved, according to which electrons in atom fill at first the states with the least quantum number $n + l$ and for the given value of the numbers $n + l$ they fill the states with the least quantum number n . The definition of the Mendeleev electron shell is given which is used for the construction of the periodic system of elements. The atomic potential appears to be the Tietz potential $V(r) = -(Z/r)(1 + (r/R))^2$, with R as a parameter, or its deformations. In the semiclassical approximation for the Tietz potential the universal one-electron energy spectrum is found. For the Schrödinger operator with the Tietz potential the radial part of the one-electron wave function is proved to satisfy to the Heun equation. Among deformations of the Tietz potential there are many-well potentials which we can describe effectively by appropriate eigenvalues and eigenfunctions. These many-well potentials can explain the existence of the d -, f -, and g -electron transition series in the periodic system of elements.

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$$\frac{d^2 y}{dz^2} + \left(\frac{\gamma}{z} + \frac{\delta}{z-1} + \frac{\varepsilon}{z-a} \right) \frac{dy}{dz} + \frac{\alpha\beta z - q}{z(z-1)(z-a)} y = 0.$$

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