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The electron binding energy analysis proposed before for atoms is applied to positive free ions. As a result the binding energy self-similar dependence on atomic number and ionization degree of ions is shown up. The revealed scaling enables to compare electron binding energies in a large number of atoms and ions, manifests the relativistic spin-orbit interaction effect in heavy atoms and can be used for the new data verification. One can represent the orbital energies in filled shells of arbitrary many-electron atom or ion through two independent of the atomic number functions. The polynomial fit approximation of the last ones is constructed to estimate the binding energies in ions. The estimation can be used as initial value in more perfect computation and for rough calculation of the ionization cross section of many-electron atoms and ions by other particles.

Key words: many-electron atom, free ion, ionization degree, electron binding energy, atomic number self-similarity, ionization cross-section, relativistic effects

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Зависимость от степени ионизации и релятивистские эффекты в энергиях связи электронов в свободных атомах и ионах

Анализ энергий связи электронов, предложенный ранее для атомов, применяется к свободным положительным ионам. В результате обнаружено свойство подобия энергий связи по атомному номеру и степени ионизации ионов. Найденный скейлинг позволяет сравнивать энергии связи в большом числе атомов и ионов, наглядно показывает влияние релятивистского спин-орбитального взаимодействия в тяжелых атомах и может быть использован для проверки новых данных по орбитальным энергиям связи. Энергии связи в заполненных оболочках могут быть выражены через две не зависящие от атомного номера функции. Для последних построены полиномиальные аппроксимации с целью аналитической оценки энергий связи в произвольном многоэлектронном ионе. Эти оценки могут быть использованы, например, как начальные значения в более точных расчетах или для приближенного вычисления сечения ионизации многоэлектронных атомов и ионов другими частицами.

Ключевые слова: многоэлектронный атом, свободный ион, степень ионизации, энергия связи электрона, подобие по атомному номеру, сечение ионизации, релятивистские эффекты

Introduction

The calculation and experimental measurement of the electron binding energies in the free atoms and ions are still an actual problem [1, 2]. These values are necessary for spectroscopic research method, astrophysical applications, computation of the ionization cross section of atoms and ions by other particles and so on.

Large experimental material on the energy levels of electrons in atoms and ions is contained in the tables [3]. The subsequent refinement of data for the neutral atoms is presented in [4]-[6]. Experimental data on binding energies in the neutral atoms from hydrogen to uranium are summarized in the report [2]. Inaccuracies in the measured energy levels of inner electron shells in atoms and ions are discussed, e.g., in [1], [7].

Two main theoretical approaches are used to calculate the binding energies of electrons in atoms and ions: the density functional method [8]-[10] and the self-consistent field approximation [11]-[17]. In spite of great success in the theory and computational capabilities, the problems remain, especially for intermediate and heavy atoms. The discrepancies between theoretical and experimental data in this region are discussed in the review [1], where detailed tables of experimental and theoretical X-ray K and L terms are presented for all neutral atoms from neon to fermium.

The spectroscopic accuracy forces to take into account relativistic effects, the effects of size and strain of a nucleus, and quantum electrodynamic effects. A separate problem is that theoretical calculations are performed for an isolated atom, whereas the experimental data are obtained for elements in their natural state [4]-[6] or in their compounds [18].

The non-relativistic quantum-mechanical calculation of the energy levels of electrons in an atom is reduced to the search for the eigenvalues of the Schroedinger equation. It is a difficult problem, which should be solved individually for each atom. The corresponding equations are usually solved by an iterative process with a reasonable initial approximation, e.g., the semi-classical one, where Thomas-Fermi (TF) statistical model [19]-[22] is used for the atomic potential and values, obtained from the Bohr-Sommerfield quantization condition are applied for the electronic spectrum. However, this spectrum should be also calculated individually for each atom. It is yet known that the characteristics of a free atom within the TF model are similar in atomic number Z. In particular, the self-consistent TF atomic potential can be represented in terms of a single function universal for all elements.

It has been shown in [23], [24] that the electron energy levels in filled shells of atoms also have an atomic-number similarity within both the TF model, and moreover in more accurate quantum mechanical ones. The revealed properties have been also confirmed for experimental binding energies.

1. Semi-classical approach

The varied models such as LDA (local density approximation) and relativistic RLDA [10], Dirac-Fock (DF) [15] and many-configuration Dirac-Fock (MCDF) [16] are applied to calculate the orbital energies in atoms and ions. In [23, 24] the analysis of the experimental [2] and calculated [10] electron binding energies has been done for all the free atoms from neon (atomic number Z = 10) to uranium (Z = 92). The analysis was based on the semi-classical approach.

If one uses the semi-classical Thomas-Fermi (TF) atom model [22], Bohr-Zommerfeld quantization condition

$$S_{E_{nl}}(\lambda) = \int_{R_{E\lambda}{'}}^{R_{E\lambda}} p_{E\lambda}(r) dr = \pi\left(n - l - \frac{1}{2}\right) = \pi(n - \lambda), \tag{1}$$

$$l > 0,$$
$$S_{E_{n0}}(0) = \pi n, \quad l = 0, \tag{2}$$

and assumption of the orbital energy E_{nl} square-law dependence on the orbital quantum number l [25], n being a principal one,

$$E_{nl} = E_{n0} - \frac{S_{E_{n0}}{''}(0)}{2T_{E_{n0}}} \lambda^2, \tag{3}$$

the Z-scaling of the semi-classical orbital energy data is revealed:

$$\tag{4}$$

$$E_{nl} = Z^{4/3} e(\sigma_n) + Z^{2/3} d(\sigma_n) \lambda^2, \quad \sigma_n = \pi n Z^{-1/3}.$$

Here $S_E(\lambda)$ and $p_{E\lambda}(r) = \sqrt{p_E^2(r) - \lambda^2/r^2}$ are the radial action and momentum of an electron with the energy E and orbital momentum $\lambda = l + 1/2$, $p_E^2(r) = 2[E - U(r)]$, $U(r)$ is the TF self-consistent potential, $T_E = \partial S_E/\partial E$ is a classical time, $S_{E_{n0}}{''}(0)$ is a second derivation of a radial action $S_E(\lambda)$ in λ at the point $\lambda = 0$, a value E_{n0} is computed from Eq. (2), the integration region is restricted by turning points $R_{E\lambda}{'}$, $R_{E\lambda}$. The two unique functions $e(\sigma_n)$ and $d(\sigma_n)$ in Eq. (4) are calculated through the TF atomic potential.

The inverse problem is to construct the dependences $e(\sigma_n)$ and $d(\sigma_n)$ from the known theoretic or experimental values $E_{nl}(Z)$. This procedure has been done in [23, 24] and also showed a Z-scaling (but not precise, and approximate one) of electron binding energies in filled shells of many-electron atoms. The scaling may be used to estimate analytically the orbital energies. Besides the allocation of the functions $e(\sigma_n)$ and $d(\sigma_n)$ has allowed to represent the orbital energy data for all the free atoms from neon to uranium in two figures. It is very convenient to analyze and compare a large array of the orbital energies of many atoms, and also test new calculated or experimental data.

Below the similar approach is extended to the positive many-electron ions.

2. Electron binding energies in free ions by the TF-model and calculated from the MCDF-model

First the ion TF model is used and the type of the corresponding scaling is searched. Then we use the electron binding energy tables [15], [16] to build the dependencies $e(\sigma_n)$ and $d(\sigma_n)$.

The TF equation for a free ion with a charge z differs from one for an atom by the boundary condition only [26]:

$$U_{TF}(r) = -Z\varphi(x)/r, \; r = c\,xZ^{-1/3}, \; c = 0.88534,$$

$$\sqrt{x}\varphi'' = \varphi^{3/2}, \;\; \varphi(0) = 1, \; x_0\varphi'(x_0) = -\alpha = z/Z.$$

Therefore a new dependence of the function $\varphi(x, \alpha)$ on the ionization degree α as on the parameter appears. It means that all the functions in the equations (1)-(4) depend on α too.

The functions $\lg|e(\sigma, \alpha)|$ and $\lg d(\sigma, \alpha)$ from the TF-model for different α are shown in figure 1. The TF calculation is produced for $Z = 1$ and so $\alpha = z$ here. One can see a monotone decreasing functions $\lg|e(\sigma, \alpha)|$ with overall parts for different values α. The right figure 1 shows that a function $\lg d(\sigma, \alpha)$ by the TF-model weakly depends on the ionization degree α, especially for filled shells ($\sigma < 3$).
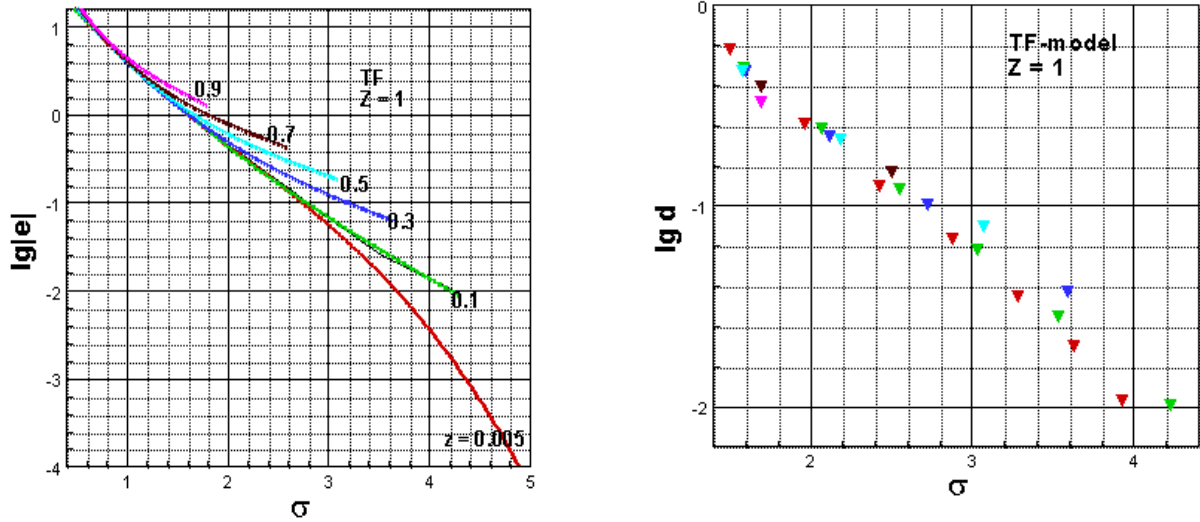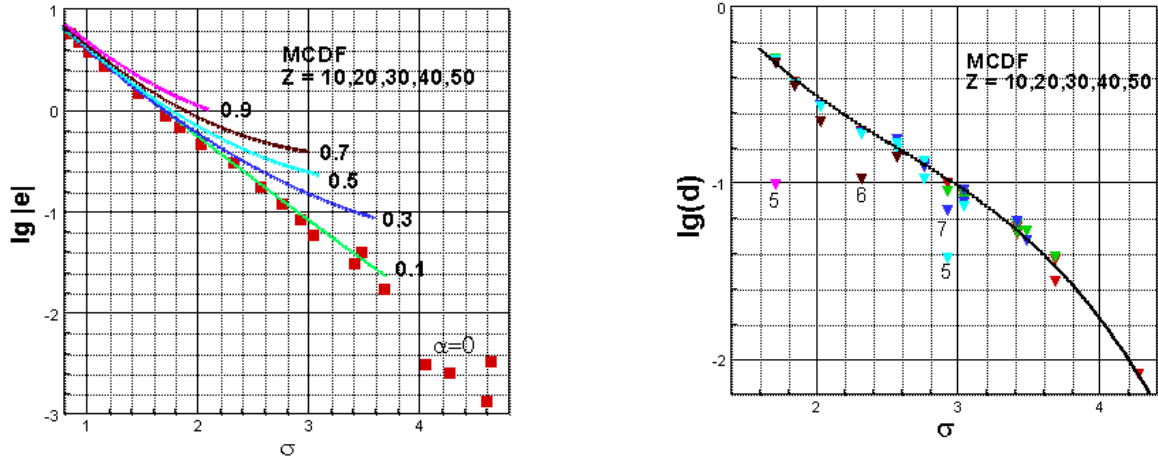

Fig. 1 Functions $\lg|e(\sigma, \alpha)|$ (left) and $\lg d(\sigma, \alpha)$ (right) calculated from the TF model. Different colors of lines and symbols signify the different degree ionization: see ciphers nearby lines on the left figure.

Below these regularities are verified in the orbital energies of free ions calculated from a more accurate MCDF-model [16]. We suppose the equation (4) to be true for all the MCDF data $\{E_{nl}\}$ and find the couples of values:

$$e_n(\alpha) = \frac{E_{n0}(\alpha)}{Z^{4/3}} \quad \text{and} \quad \sigma_n = \frac{\pi n}{Z^{1/3}}; \tag{5}$$

$$d_n(\alpha) = \frac{E_{nl}(\alpha) - E_{n0}(\alpha)}{Z^{2/3}\lambda^2} \quad \text{and} \quad \sigma_n. \tag{6}$$

The results obtained thus from the binding energies $\{E_{nl}\}$ for the elements with atomic number $Z = 10, 20, 30, 40, 50$ and $\alpha = 0, 0.1, 0.3, 0.5, 0.7, 0.9$ are shown in figure 2, the relativistic spin-orbital level splitting being replaced by its average. One can see the similar dependence with the TF one (see figure 1) except some points with cipher nearby symbol on the right figure 2. The cipher signifies the number of electrons N_e in the ion. It means that the approach is true only for the many-electron ions ($N_e \geq 10$) that corresponds to the TF-model area of application.

Fig.2 Functions $\lg|e(\sigma, \alpha)|$ (left) and $\lg d(\sigma, \alpha)$ (right), reconstructed from the spectra E_{nl} by the MCDF-model [16]. The different colors of lines and symbols signify the different ionization degrees: see the corresponding ciphers nearby the lines — square interpolations (7) — on the left figure. The line on the right figure is the cubic interpolation (10) and the cipher nearby the symbol denotes the number of electrons N_e in the ion.

The curves on the left figure 2 are the square polynomial fit

$$\lg|e(\sigma, \alpha)| = \sum_{k=0}^{2} a_k \sigma^k, \tag{7}$$

approximating the correspondent dependence at different values α. The coefficients of the square polynomial are presented in table 1. One can see a smoothed dependence of the coefficients a_k on α which may be interpolated by square polynomials too:

$$a_k(\alpha) = \sum_{m=0}^{2} c_m^k \, \alpha^m. \tag{8}$$

Table 1

Polynomial fit data a_k for the function $\lg |e(\sigma, \alpha)| = \sum_{k=0}^{2} a_k \, \sigma^k$ calculated from electron binding energies by MCDF-model [16] for certain values α in ions with atomic number $Z = 10, 20, 30, 40, 50$.

α	a_0	a_1	a_2
0.0	1.531368987532	-0.9508725990119	0.01988458441012
0.1	1.600703744393	-1.054499781604	0.05720449135094
0.3	1.690055054397	-1.198845561051	0.1204050430195
0.5	1.732599828495	-1.269972650337	0.1630655789157
0.7	1.724625214300	-1.261886757311	0.1838766051511
0.9	1.709164710003	-1.222005721042	0.1967462630893

Combining into one Eqs. (7) and (8) one can obtain

$$\lg |e(\sigma, \alpha)| = \sum_{k=0}^{2} \sum_{m=0}^{2} c_m^k \, \alpha^m \sigma^k. \tag{9}$$

The coefficients c_m^k are presented in table 2.

Table 2

Coefficients c_m^k, b_k in Eqs. (9), (10)

	c_m^k			k	b_k
$m \setminus k$	0	1	2	0	2.1117
0	1.5372	-0.9557	0.0204	1	-2.4106
1	0.6420	-1.0414	0.3944	2	0.7424
2	-0.5089	0.8363	-0.2225	3	-0.0956

The curve on the right figure 2 is the cubic polynomial fit:

$$\lg d(\sigma, \alpha) = \sum_{k=0}^{3} b_k \sigma^k. \tag{10}$$

The corresponding coefficients b_k are also presented in table 2. So all the regularities are described with 13 coefficients c_m^k, b_k.

The theoretical area of the approach application are

1. the atomic number $Z \geq 10$;
2. the number of electrons in the ion $N_e \geq 10$;
3. the filled shells.

3. Analytical estimation of electron binding energies in many-electron free ions

The functions $e(\sigma, \alpha)$ and $d(\sigma, \alpha)$ were constructed from the definite ions MCDF data. Here we examine their validity for some other many-electron ions ($10 \leq Z \leq 56$) by means of comparison with available MCDF-results [16]. To estimate analytically the electron orbital levels in a free ion it is enough to assign an atomic number Z, charge z and use Eq. (4) with the functions $e(\sigma, \alpha)$ and $d(\sigma, \alpha)$ by Eqs. (9), (10) and table 2.

Table 3

Electron binding energies (in eV) in Xe ions by the MCDF-model and its estimation by the equation (4) with functions (9), (10).

Ions		Xe^{+2}		Xe^{+12}		Xe^{+22}	
n	l	MCDF	Eq. (4)	MCDF	Eq. (4)	MCDF	Eq. (4)
1	0	34588	31869	34816	32657	35246	33636
2	0	5482	5620	5708	5790	6127	6221
2	1	5131, 4810	5165	5359, 5035	5334	5780, 5456	5766
3	0	1174	1107	1393	1398	1781	1820
3	1	1028, 966	957	1248, 1184	1248	1638, 1571	1670
3	2	712, 699	689	932, 916	980	1324, 1310	1403
4	0	245	243	441	460	752	842
4	1	192, 179	189	390, 366	406	699	788
4	2	91, 89	93	284, 283	309		
5	0	43	60				
5	1	31, 31	50				
Ions		Xe^{+32}		Xe^{+12}		Xe^{+52}	
1	0	36097	34823	37370	36237	40270	37903
2	0	6946	6972	8082	8149		
2	1	6615, 6276	6516	7763, 7430	7693		
3	0	2430	2443	3243	3381		
3	1	2305, 2212	2293				
3	2	2023	2026				

The estimation results are compared with MCDF data in some ions of xenon in

table 3 and in six different ions of the various elements in table 4. Two values E_{nl} at $l > 0$ by MCDF-model [16] are the relativistic level splitting. It is not great for $Z <$ 60, the maximal one being for the energies E_{nl} at $n = 2, l = 1$. The relational estimation inaccuracy does not exceed 10% for filled shells. Other levels are properly estimated by order of magnitude only.

Table 4

Electron binding energies $-E_{nl}$ (in eV) in some ions by the MCDF-model [16] and their estimation by the equation (4) with functions (9), (10)

Ions		$Al^{+2}(Z = 13)$		$K^{+8}(Z = 19)$		$Cu^{+15}(Z = 29)$	
n	l	MCDF	Eq. (4)	MCDF	Eq. (4)	MCDF	Eq. (4)
1	0	1592	1639	3799	3925	9541	9790
2	0	150	143	556	547	1644	1617
2	1	104, 103	96	475, 472	460	1501, 1476	1446
3	0	28	23	175	195	556	590
3	1					514	540
Ions		$Rb^{+13}(Z = 37)$		$Cs^{+19}(Z = 55)$		$Ba^{+3}(Z = 56)$	
1	0	15582	15624	36513	34511	37476	34254
2	0	2447	2487	6248	6309	6032	6148
2	1	2247, 2179	2375	5889, 5540	5840	5661, 5284	5665
3	0	653	683	1722	1736	1332	1252
3	1	585, 560	598	1572, 1503	1581	1176, 1102	1094
3	2	446, 450	456	1243, 1229	1306	832, 817	810
4	0			677	719	299	290
4	1			614, 597	662	240, 224	231
4	2					127, 124	126
5	0					64	76
5	1					48, 46	64

4. Account for relativistic effects in many-electron atoms

In this section the LDA- and RLDA-results [10] for the electron binding energies in free atoms are compared. Non-relativistic LDA function $e(\sigma)$ is calculated for all the atoms with $10 \leq Z \leq 92$ and shown on figure 3 to the left. Here (and below on the left figure 4) the big symbols ∇ correspond to rare gases data. The pairs of numbers $e_n - \sigma_n$ according (5) by RLDA for the rare gases and uranium are shown on figure 3 to the right. One can see the relativistic effects little affect the dependence, without changing its single-valued monotonically diminishing nature.
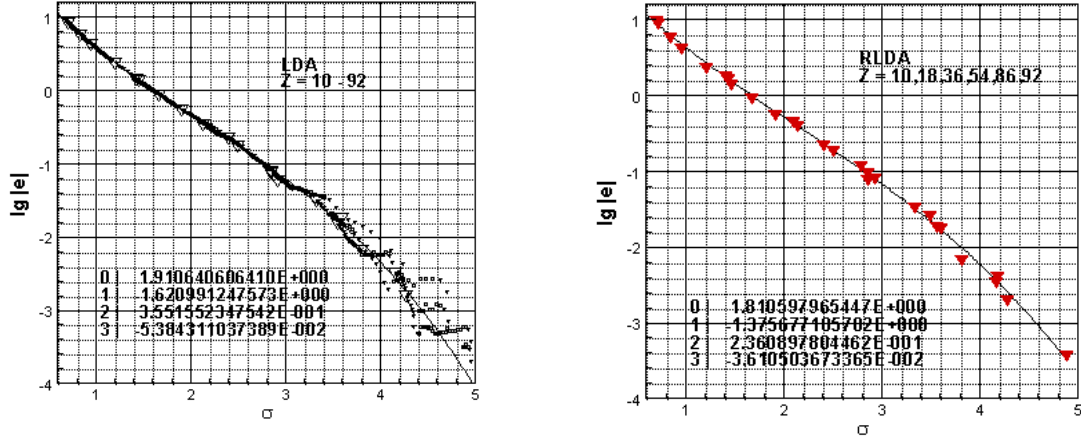
Fig.3 Function $\lg|e(\sigma,\alpha)|$ by Local Density Approximation [10]: non-relativistic (LDA) model (left) and relativistic LDA (RLDA) model (right). Lines are cubic interpolations, which coefficients are printed on the figures.

If the relativistic effects are small, i.e. for elements $Z \leq 40$ the function $d(\sigma)$ behaves similarly as it has been shown in [23], [24]. However, in the heavy atoms the single-valued nature of function $d(\sigma)$ is lost. One can see on the right figure 4 the visible $d_{nl}(\sigma)$ branching for the different values l, and in addition, a bifurcation due to the spin-orbit interaction for each l. Here an increase in the relativistic effects with an increase in the atomic number is visually manifested, all the dependence on σ preserving smooth nature and fitting the corresponding dependence for the rare gases.
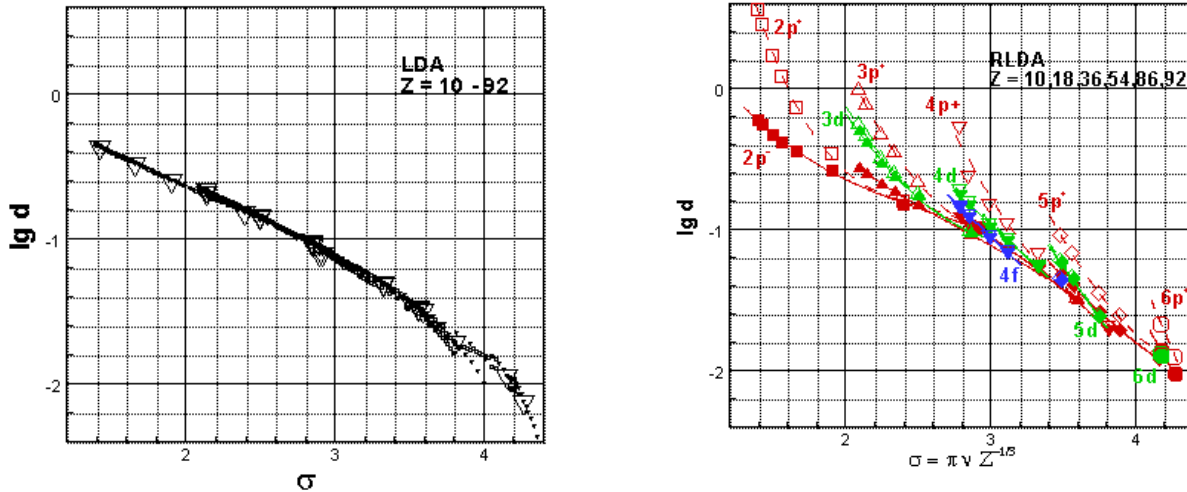

Fig. 4 Function $\lg d(\sigma,\alpha)$ by Local Density Approximation [10]: non-relativistic (LDA) model (left) and relativistic LDA (RLDA) model (right). Here red symbols is for $l = 1$, green and blue ones are for $l = 2$ and 3 correspondingly. Filled and non-filled symbols correspond to levels with $j = l - 1/2$ and $j = l + 1/2$.

Conclusions

In the paper the electron binding energies in atoms and ions were studied. Atomic number and ionization degree similarity (scaling) are shown in filled shells of free ions and relativistic effects visualization are demonstrated for many-electron atoms. The discovered scaling enables to estimate electron binding energies in ions by means of two independent on atomic-number functions $e_n(\sigma)$ and $d_{nlj}(\sigma)$. The estimation inaccuracy for filled shells of free ions is less than 10% and reasonably describes other levels. Therefore the proposed approach can be used as initial value in more accurate computation and for rough calculation of the ionization cross section of many-electron atoms and ions by other particles.

The revealed continuous $e_n(\sigma)$ and $d_{nlj}(\sigma)$ dependences can be also used for the new data verification and for the recovery of the missing information about the binding energies in the neighboring atoms.

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