Moseley Law for Atomic Orbital Exponents

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The piecewise linear dependence of orbital exponents ξ characterizing either nonorthogonal Slater or orthogonal minimum atomic parameters/Moscow-Aachen-Paris (MAP) radial parts of atomic orbitals is theoretically derived from a plausible model of electronic subshell energy and compared with their values derived from a pragmatic Koga basis set covering the elements from H to Lr ($Z = 103$). So derived values of exponents as well follow piecewise linear laws as functions of the nuclear charge Z. The linear branches of the ξ vs Z fairly follow the structure of the Periodic Table being specific for the segments of the Z values corresponding to p-, d- and f-elements, respectively. In details, however, the parameters of the theoretical linear dependencies of orbital exponents ξ on Z and those derived from the pragmatic basis set (referred to as experimental) differ from each other which will be addressed elswhere.

1. INTRODUCTION AND THEORY

In the years 1913-1914 Moseley [1, 2] had experimentally established that the square roots of atomic ionization potentials are linearly dependent on nuclear charges Z which not long before that has been identified with the atom's ordinal numbers in the Periodic Table [3] – the single parameter ultimately characterizing a chemical element. The ionization potentials of atomic one-electron states (atomic orbitals – AO's) are related with the parameter of their spatial decay – the orbital exponent – through:

$$\xi_{n\ell} \approx \sqrt{2\mathrm{IP}_{n\ell}}, \tag{1}$$

($\mathrm{IP}_{n\ell}$ is the average ionization potential – the sum of all ionization potentials of the subshell, characterized by the principal n and azimutal ℓ quantum numbers, divided by the number of electrons in it) [4, 5], provided these states have an asymptotic form

$$\propto r^{(n-1)} e^{-\xi_{n\ell} r} \tag{2}$$

for the electronic subshell.

This form of the atomic radial function is known as the Slater-type orbital (STO) where the dependence of the orbital exponents $\xi_{n\ell}$ on Z was formulated as a set of *Slater rules* [6]. Later [7, 8] some improvements to the Slater rules have been proposed, which theoretically could be extended to the entire available and practically sensible range of the Z values ($= 1 \div 118$). All these schemes represent orbital exponents in the form:

$$\xi_{n\ell}(Z) = \frac{Z - S_{n\ell}(Z)}{n^*(n)},$$

where $n^*(n)$ is the effective principal qunatum number, and $S_{n\ell}(Z)$ is a screening function of the Coulomb field of the atomic nucleus specific for each $n\ell$-subshell.

The screening functions $S_{n\ell}(Z)$ [6–8] are sums of contributions from all electrons in the atom with electronic configuration $\prod_{n\ell} (n\ell)^{p_{n\ell}}$:

$$S_{n\ell}(Z) = \sum_{n'\ell'} \left(p_{n'\ell'}(Z) - \delta_{n'\ell',n\ell}\right) \sigma_{n'\ell',n\ell}(Z),$$

where the subshell occupation numbers $p_{n\ell}(Z)$ can be taken as prescribed by the Madelung-Klechkowskij rules [9, 10] or set according to experiment. The quantities $\sigma_{n'\ell',n\ell},(Z)$ as well characteristic for the Z-th element are parameters of the mutual screening of the subshells, and the Kronecker delta-symbol $\delta_{n'\ell',n\ell}$ serves to exclude the screening of an electron in the $n\ell$-subshell by itself.

The structure of the Periodic Table reflects the sequence of the subshells' filling in that sense that the quantities $p_{n\ell}(Z)$ in each segment of the Z values, corresponding to the filling of the $n\ell$-subshell are equal to $Z - Z_{n\ell}$, where $Z_{n\ell}$ is the atomic number, immediately preceding the filling of it. (At $Z = Z_{n\ell}$ the $n\ell$-subshell does not contain electrons).[1] For the numbers $Z_{n\ell}$ one can take the values preceding the atomic number $Z_{n+\ell}$, at which an electron with a given value of $n + \ell$ appears for the first time according to [9] i.e. $Z_{n\ell} = Z_{n+\ell} - 1$. Respectively, the dependencies $\xi_{n\ell}(Z)$ separate in branches, referring to the filling of different subshells. Obviously, the

[1] The segment of transition elements is an example: for their $3d$-subshell $Z_{3d} = 20$, since Ca is the element immediately preceding this segment.

length of a segment of the Z values, where the subshell $n\ell$ is being filled, equals to $2\,(2\ell+1)$.[2]

The rules [6–8] suggest the linear dependence of exponents on Z:

$$\xi_{n\ell}\,(Z) = a_{n\ell}Z + b_{n\ell} \tag{3}$$

conforming with the Moseley law [1, 2] only if the screening functions $S_{n\ell}\,(Z)$ are also linear in Z. The rules [6–8] suggest that the slopes $a_{n\ell}$ and intercepts $b_{n\ell}$ (with ordinate) in the segments of the Z values, where the $n\ell$-subshell is being filled (i.e. it is open) or, where it is already filled, and, thus, can be ascribed to the core, significanly differ.

Since the times whan the rules [6–8] have been proposed, numerous basis sets have been developed (see e.g. [11] and references therein) to be used in quantum chemistry calculations. The orbitals in these sets (hereinafter referred to as pragmatic), however, lack whatever single characteristic. A method of comparing the formal rules of ascribing exponents' with the pragmatic basis sets has been proposed in Ref [12]. Namely, following an early suggestion dating back to V.A. Fock [13], we proposed a minimal atomic parameter (MAP) form [14] of the radial function:

$$R_{n\ell}(r) \propto (2\xi_{n\ell}r)^{\ell}\, P_{n\ell}(2\xi_{n\ell}r)\exp\left(-\xi_{n\ell}\,r\right),$$

which permits to construct sets of AOs which like the STOs are characterized by the unique subshell specific parameter $\xi_{n\ell}$ – orbital exponent, but through its construction assure the orthogonality of the radial parts for the different values of n at the same value of ℓ thanks to the polynomial multipliers $P_{n\ell}$.

Further, in paper [15] it has been shown that the MAP exponents extracted from whatever pragmatic basis (see [16, 17] by maximizing the overlap between the subspaces spanned by the respective basis sets against the MAP exponents as well follow the linear trends of the form eq. (3). This result can be considered as experimental evidence for the linear relations for orbital exponents coming from *in silico* side, rather than postulated.

In order to obtain some more theoretical view of the postulated and observed linear trends we consider partially filled $n\ell$-subshell. For an atom with nuclear charge Z it contains $Z - Z_{n\ell}$ electrons. Denoting the exponent $\xi_{n\ell}$ by ξ for brevity, we rewrite the subshell energy as:

$$\left[\frac{\xi^2}{2\mu_{n\ell}} - \frac{Z\xi}{n}\alpha_{n\ell} + \frac{\xi}{n}\sum_{n'\ell'\neq n\ell} p_{n'\ell'}\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right) + \frac{1}{2}\frac{\xi}{n}\gamma_{n\ell}\,(Z - Z_{n\ell} - 1)\right](Z - Z_{n\ell}),$$

where we abbreviated $\xi_{n'\ell'}$ by ξ'. Correction coefficients $\alpha_{n\ell}$, $\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right)$, $\gamma_{n\ell}$ describe deviations of the matrix elements of, respectively, core attractions, interactions of electrons in subshells $n'\ell'$ and $n\ell$, and within the $n\ell$-subshell from the value $\frac{\xi}{n}$; $\mu_{n\ell}$ is an effective mass of electron in the $n\ell$-subshell. It, apparently, describes the deviation of electron kinetic energy in it from the value of $\frac{\xi^2}{2}$ characteristic for H-like orbitals featuring $\mu_{n\ell} = 1$.

For the filled $n\ell$-subshell, when some other (most frequently a lower-lying) subshell $n^s\ell^s$ is being filled (e.g. the filled ns-subshell of a transition element atom with the $(n-1)d$ subshell being filled) the formula changes to:

$$\left[\frac{\xi^2}{2\mu_{n\ell}} - \frac{Z\xi}{n}\alpha_{n\ell} + \frac{\xi}{n}\sum_{n'\ell'<n\ell} p_{n'\ell'}\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right) + \right.$$
$$\left. + \frac{\xi}{n}\,(Z - Z_{n^s\ell^s})\,\beta_{n^s\ell^s,n\ell}\left(\frac{\xi}{\xi^s}\right) + \frac{1}{2}\frac{\xi}{n}\gamma_{n\ell}\,(4\ell+1)\right](2\,(2\ell+1)).$$

Minimizing the subshell energy with respect to ξ we arrive to piecewise linear dependence of the orbital exponents on Z:[3]

$$\xi_{n\ell} = \frac{\mu_{n\ell}}{n}\begin{cases} \alpha_{n\ell}Z - \frac{\gamma_{n\ell}}{2}\,(Z - Z_{n\ell} - 1) - {\sum_{n'\ell'}}'\, 2\,(2\ell'+1)\,\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right) & , \\ \alpha_{n\ell}Z - \beta_{n^s\ell^s,n\ell}\left(\frac{\xi}{\xi^s}\right)(Z - Z_{n^s\ell^s}) - {\sum_{n'\ell'}}''\, \sum 2\,(2\ell'+1)\,\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right) + \frac{\gamma_{n\ell}}{2}\,(4\ell+1) & , \\ \alpha_{n\ell}Z - \sum_{n'\ell'<n\ell} 2\,(2\ell'+1)\,\beta_{n'\ell',n\ell}\left(\frac{\xi}{\xi'}\right) + \frac{\gamma_{n\ell}}{2}\,(4\ell+1) & \end{cases} \tag{4}$$

(here $\sum_{n'\ell'}{}'$ refers to the summation over $n'\ell' < n\ell$ and $\sum_{n'\ell'}{}''$ over $n'\ell' < n\ell, n'\ell' \neq n^s\ell^s$). The first row refers to the exponent for the $n\ell$-subshell being filled, the second row to a lower-lying $n^s\ell^s$-one being filled and the bottom row to the filled $n\ell$-subshell in the core.

For further estimates we conditionally accept $\mu_{n\ell} \times \alpha_{n\ell} = 1$, as for H-like orbitals which may be easily rectified later. Then the parameters of the linear branches eq. (3) come from estimates of the integrals of the electron-electron interaction. It has been shown [12] that the MAP orbitals, although provide necessary number of radial nodes to assure the orthogonality condition, have much weaker oscillation amplitudes of the wave function in the range of smaller r's than those of the H-like functions with the same exponent so that the MAP functions are pretty close (up to small oscillations in the core region) to the nodeless STO's. Thus, semi-quantitative treatment may be based on STO's.

In the simplest approximation the interaction between electrons in the subshells reduces to the Slater-Condon parameter F^0 (SCP) [18]. For a pair of STO's with exponents ξ, ξ' and principal quantum numbers n, n' they are given by:

$$\frac{\xi'}{n'} + \frac{\xi}{n} - \frac{(2n'+2n)!}{n'n(2n')!(2n)!}\frac{\xi'^{2n'+1}\xi^{2n+1}}{(\xi'+\xi)^{2n'+2n+1}}\left[n\,{}_2F_1\left(1, 2n'+2n+1; 2n'+1; \frac{\xi'}{\xi'+\xi}\right)\right.$$
$$\left. + n'\,{}_2F_1\left(1, 2n'+2n+1; 2n+1; \frac{\xi}{\xi'+\xi}\right)\right],$$

where ${}_2F_1\left(a, b; c; z\right)$ is the Euler hypergeometric function [19]. For the intrashell SCP we get after some algebra:

$$F^0 = \frac{\xi}{n}\left(1 - \frac{(4n-1)!!}{4^n(2n)!}\right) \approx \frac{\xi}{n}\left(1 - \frac{1}{\sqrt{2\pi n}}\right),$$

which immediatey yields:

$$\gamma_{n\ell} = 1 - \frac{(4n-1)!!}{4^n(2n)!} \approx 1 - \frac{1}{\sqrt{2\pi n}}. \qquad (5)$$

In order to study qualitative behavior of $\beta_{n'\ell',n\ell}$'s we, first, consider two limits: $n' < n$; $\frac{\xi}{\xi'} \ll 1$ and $n < n'; \frac{\xi'}{\xi} \ll 1$. Then in the lowest order with respect to the small parameters we get

$$F^0 \approx \begin{cases} \frac{\xi}{n}\left[1 - \frac{(2n'+2n)!}{(2n')!(2n)!}\left(\frac{\xi}{\xi'}\right)^{2n}\right] & n' < n; \frac{\xi}{\xi'} \ll 1, \\ \frac{\xi'}{n'}\left[1 - \frac{(2n'+2n)!}{(2n')!(2n)!}\left(\frac{\xi'}{\xi}\right)^{2n'}\right] & n < n'; \frac{\xi'}{\xi} \ll 1, \end{cases}$$

where the upper row refers to the interaction of electrons in the current subshell with parameters $n\xi$ with a lower-lying subshell with parameters $n'\xi'$, and the lower row to that with a subshell $n'\xi'$, lying above the current one.[4] It can be seen that the interactions with the more contracted lower lying subshells rapidly flow to the magnitude of the interaction with a point charge in the center of atom, whereas the integral of interaction of an electron in the current subshell with electrons in outer subshells only weakly depend on the exponent of the current subshell. Furthemore, setting as in the case of H-like orbitals $\xi'/\xi = n/n'$, we arrive to the following estimate for the quantities $\beta_{n'\ell',n\ell}$:

$$1 + \frac{n'^2}{n^2} - \frac{2n'}{n}\frac{(2n'+2n)!}{(2n')!(2n)!}\left[n' B_{\frac{n'}{n'+n}}(2n, 2n'+1) + n B_{\frac{n}{n'+n}}(2n', 2n+1)\right], \qquad (6)$$

Table 1. Contributions of the n'-shells to the screening of electrons in the n-shell.†

n'/n	1	2	3	4	5	6	7
1	0.625	0.971	0.999	1.	1.	1.	1.
2	0.243	0.727	0.957	0.997	1.	1.	1.
3	0.111	0.425	0.774	0.950	0.994	0.999	1.
4	0.062	0.249	0.535	0.804	0.947	0.991	0.999
5	0.040	0.160	0.358	0.606	0.824	0.945	0.988
6	0.028	0.111	0.250	0.440	0.656	0.839	0.945
7	0.020	0.082	0.184	0.326	0.504	0.694	0.851

† The principal quantum number of the *screened* shell (n) is listed in the uppermost row, the principal quantum number of the *screening* shell (n') in the leftmost column. E.g. the amount of screening of the shell with principal quantum number $n = 2$ by the shell with $n' = 1$ equals to 0.971 (1-st row, 2-nd column); similarly, the screening of the shell with $n = 1$ (1^{st} column) by the shell with $n' = 7$ (7^{th} row) equals to 0.020.

which, although involves approximations, covers both limiting cases (here $B_z(a, b)$ is the Euler incomplete beta-function [19]).

2. RESULTS AND DISCUSSION

Following the analysis of the previous Section we calculated values of $\beta_{n',n}$ (in the accepted setting they are ℓ, ℓ' independent) for $n, n' = 1 \div 7$ which are assembled in Table 1 (the γ_n values stand on the diagonal). We see that higher-lying shells are almost 100% screened by the lower lying – upper triangle of Table 1 where the principal quantum numbers of the higher-lying number the columns of the Table. Inversely, the higher-lying shells produce only a minor contribution to the screening of the lower ones whose principal quantum numbers refer to the rows – the lower triangle of the Table.

With use of these values we estimated the slopes $a_{n\ell}$ of the piecewise linear dependencies eq. (3) of the exponents on Z within the segments referring to the filling of the $n\ell$-subshells. They are assembled in Table 2 together with the estimates of the same slopes derived from the Slater [6] and Burns [7] rules and the analytic estimate of the screening [8]. Additionally, we provide the parameters of the Z-dependencies of the orbital exponents [15] by the method [12], namely, by minimizing the Frobenius angle between the subspaces spanned, respectively, by the Koga basis AO's [17], covering the Z values upto 103, and the MAP AO's against the MAP exponents $\xi_{n\ell}$. The values of the MAP exponents derived from the pragmatic Koga basis set can be considered as experimental. The difference with Ref. [15] is that the segments of the Z values where the fitting to the linear model has been performed in the present

Table 2. Theoretical estimates of the slopes $a_{n\ell}$ in eq. (3) for the (sub)shells being filled compared with the corresponding values derived from the rules [6–8]. The values printed in the same font refer to the same value of ℓ.

n	Slater [6]	Burns [7]	Bessis [8]	Present work		
				eq. (4)	MAP [15]	
2	0.325	0.325	0.324	0.318	*0.367*	s
					0.294	p
3	0.217	0.217	0.216	0.204	*0.290*	s
					0.262	p
					0.213	d
4	0.176	0.163	0.162	0.150	*0.260*	s
					0.255	p
					0.230	d
					0.169	f
5	0.163	0.130	0.129	0.118	*0.235*	s
					0.239	p
					0.217	d
					0.162	f
6	0.155	0.108	0.108	0.097	*0.231*	s
					0.242	p
7	–	0.093	0.092	0.082	–	

paper are strictly limited to the segments where the $n\ell$-subshells are being filled according to prescription of the formal Madelung-Klechkowskij $(n + \ell, n)$ rules [9, 10] reproducing the standard construction of the Periodic Table, whereas in Ref. [15] the ranges where the fits had been performed were selected by visual arbitration of the linear branches of the ξ vs Z dependencies.

The dependencies of the MAP exponents [15] together with the theoretical values obtained by eqs. (4), (6) as functions of the efficient core charges $Z - Z_{n\ell}$ are depicted in Figs. 1 – 4.

The obtained results may be described as follows. In all cases either the theoretical or experimental exponents are almost ideally linear as functions of $Z - Z_{n\ell}$. In this repect experiment agrees with theory. Minor deviations of the points from lines in Figs. 1, 2 are due to irregularities of the subshell filling patterns in the d- and f-series: neither d- nor f-elements follow any unque filling pattern like s^2d^g or, respectively, s^2f^g with $g = Z - Z_{n\ell}$. The simplest picture occurs for Lanthanoid and Actinoid (f-element) series. The slopes of the dependencies for the $4f$ and $5f$ exponents (Fig. 1) almost coincide as do the values of the $6s$ and $7s$ exponents themselves.

For the transition series (d-elements, Fig. 2) we observe the behavior of exponents generally recembling that of the f- and s-exponents of the f-elements. Namely, the d- and s-exponents grow linearly with $Z - Z_{n\ell}$ the former ones with noticeable slopes which are almost the same for different values of n in case of the experimental exponents. As for the s-exponenets either experimental or theoretical values increase with $Z - Z_{n\ell}$ much slower than the d-exponents.

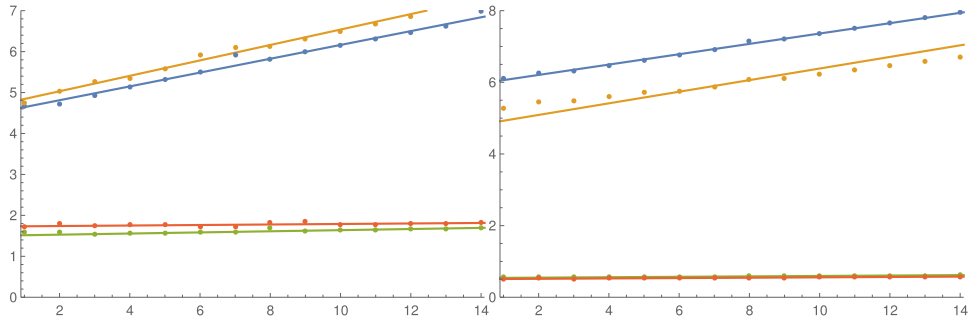

Figure 1. Graphs of dependencies of $4f$ (blue), $5f$ (orange), $6s$ (green), $7s$ (red) exponents on the effective nuclear charge $Z - Z_{n\ell}$ and their linear fits. Left: exponent values extracted in Ref. [15] from Koga basis [17]. Right: the similar dependencies derived according to eq. (4).

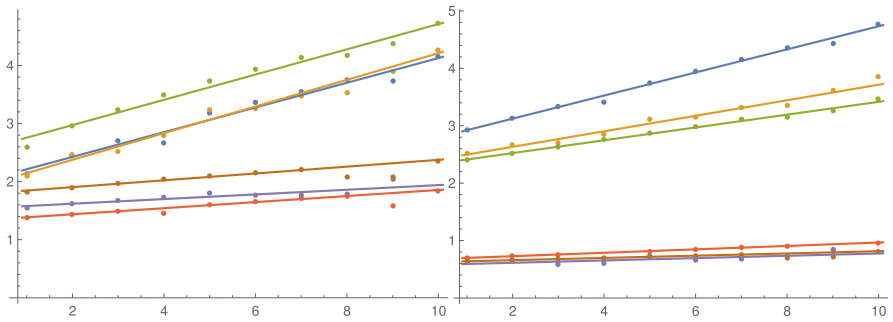

Figure 2. Graphs of dependencies of $3d$ (blue), $4d$ (orange), $5d$ (green), $4s$ (red), $5s$ (violet), $6s$ (light brown) exponents on the effective nuclear charge $Z - Z_{n\ell}$ and their linear fits. Left: exponent values extracted in Ref. [15] from Koga basis [17]. Right: the similar dependencies derived according to eq. (4).

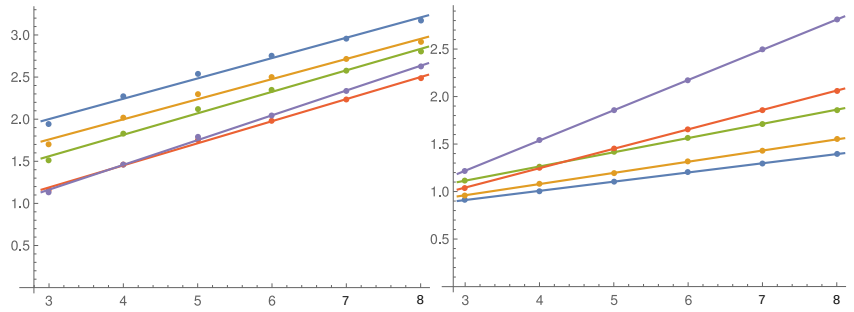

Figure 3. Graphs of dependencies of $6p$ (blue), $5p$ (orange), $4p$ (green), $3p$ (red), $2p$ (violet) exponents on the effective nuclear charge $Z - Z_{n\ell}$ and their linear fits. Left: exponent values extracted in Ref. [15] from Koga basis [17]. Right: the similar dependencies derived according to eq. (4).

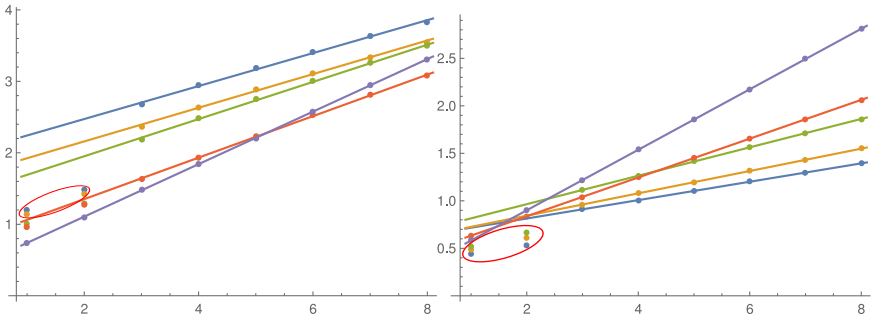

Figure 4. Graphs of dependencies of $6s$ (blue), $5s$ (orange), $4s$ (green), $3s$ (red), $2s$ (violet) exponents on the effective nuclear charge $Z - Z_{n\ell}$ and their linear fits. Left: exponent values extracted in Ref. [15] from Koga basis [17]. Right: the similar dependencies derived according to eq. (4).

The dependencies of the p- and s-exponents on $Z - Z_{n\ell}$ depicted in Figs. 3, 4 are represented in a way that simplifies the verification of the hypothesis of single sp-shells as formulated in Refs. [20, 21]. Having this in mind, we set $Z - Z_{n\ell}$ – the value of the effective core charge for each first p-element in a period – to be equal to three. With this caveat we notice that the p-exponents follow the same $Z - Z_{n\ell}$ dependence patterns as do other $n\ell$-exponents.

When it comes to s-exponents (Fig. 4), the features characteristic for the $Z - Z_{n\ell}$ dependencies of other types of orbitals manifest themselves as in the cases of other ℓ-values. Specific of the s-orbitals can be described as follows: for the smaller principal quantum numbers ($n = 2, 3$) the hypothesis of a single sp-shells may be substantiated by the single linear dependencies of the s-exponents along the entire periods. This, however, changes for larger vaues of the the principal quantum number ($n \geq 4$). The intrusion of d- and f-elements in the sequence of subshells' filling between s- and p-ones breaks a uniform slope of s- and p-exponents so that those in the beginning of the periods (alkali and alkaline earth elements) elapse from the otherwise ideally linear dependence of these exponents extracted from the subsequent p-elements. It can be also noticed that for larger n's the slope of the s- and p-exponents turn to be very close to each other which was not the case for the smaller n's. Fairly remarkably, however, the degenerate *slopes* for the s-exponents of the s-elements (alkali and alkaline earths) extracted from the Koga basis by minimizing the Frobenius angles are only slightly larger than the slopes extracted by the same method from the basis sets for p-elements (respectively, 0.280, 0.284, and 0.281 for 4s, 5s and 6s vs. 0.260, 0.235, and 0.231), so that the difference cannot be seen of the graphs Fig. 4. It is also remarkable that the slopes of the Koga-MAP exponents of ns-orbitals are very close to those of the (n – 1)p-orbitals as it can be seen from Table 2. This eventually might be interpreted as a hint towards an alternative grouping of the sp-shells, namely, that implied by the Janet's Left-Step [22] Periodic Table (see also [20, 21]).

Although the piecewise linear dependence of orbital exponents on Z or $Z - Z_{n\ell}$ as derived from model eq. (4) is fairly confirmed by experiments the slopes of these linear trends are underestimated by the theory eqs. (4) – (6) as compared to experiment for all n's. (Also observe different scale of the ordinate of the left and right panels of Figs. 3 – 4). Also the cut-offs of the linear dependencies (the constant screening accumulated by the atom with $Z = Z_{n\ell}$ – the atomic core – produced by the already filled subshells) are quite different for the theoretical and experimental values so that the order of the graphs depicting the dependencies of ξ's on $Z - Z_{n\ell}$ for different values of n is opposite for the experimental and theoretical values. Specifically, theoretical 4f-exponents are systematically larger than the 5f ones whereas for the experimental values this order is inverted. Similar discord between the experimental and theoretical values is as well observed for other subshells and segments of the Periodic Table.

3. CONCLUSION

In the present work on the basis of the model eq. (4) we managed to establish theoretically generally known linear dependencies of the AOs' exponents on the nuclear charges Z (atomic numbers) similar to the fundamental Moseley law and to derive expressions for the parameters of these trends. With use of an approximate form of the AO's the estimates of the interaction parameters for electrons belonging to different subshells and abiding within the same subshell have been derived. With help of these estimates the parameters of the linear trends of orbital exponents vs Z have been obtained and compared with the analogous parameters describing similar dependencies extracted from the pragmatic Koga basis sets available for the elements with $Z = 1 \div 103$. Although the numerical agreement between theoretical estimates of the parameters of the $\xi_{n\ell}(Z)$ dependencies and analogous experimental ones is quite poor their general linear character is reproduced. The observed discrepancies between theory and experiment will be addressed elsewhere.

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