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Atomic orbital bases of Bunge and Koga studied by Frobenius products with Moscow-Aachen-Paris (MAP) orbitals

Dedicated to Prof. Dr. W.H. Eugen Schwarz on occasion of his 85-th birthday

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The minimization of Frobenius angles between functional subspaces spanned by different sets of atomic functions is employed to determine the values of orbital exponents ξ characterizing minimum atomic parameters/Moscow-Aachen-Paris (MAP) basis sets providing the best representation of two Hartree-Fock based atomic basis sets: that of Bunge et al. available for elements H–Xe and that of Koga and Thakkar spanning H to Lr ($Z = 103$). So-extracted values of exponents follow piecewise linear laws as functions of the nuclear charge Z resembling the prescriptions set by Slater's rules for the orbital exponents. In details, however, the rules proposed by Slater are not precisely followed, neither for effective principal quantum numbers n^* nor screening increments σ. Nevertheless, the linear pieces of the ξ vs Z follow the structure of the Periodic Table being specific for the segments corresponding to p-, d- (transition) and f- (Lanthanides and Actinides) elements, respectively.

I. INTRODUCTION AND THEORY

Today we dispose of many different basis sets to describe orbitals and electron densities in atoms, molecules and solids[1,2]. For numerical efficiency, most are of Gaussian type, even if the parameters, exponents and expansion coefficients individually do not have any physical meaning. In 1993, Bunge et al published[3] sets of linear combinations of Slater monomials of the form

$$r^{(k-1)}e^{-\xi r} \qquad (1)$$

with different powers $(k-1)$ and orbital exponents ξ. These orbitals hereinafter called "Bunge" are very close to numerical orbitals,[4,5] and are the simplest ones in terms of the number of employed parameters. Still, the individual parameters of these orbitals are physically not meaningful. In previous articles[6,7] we reconsidered therefore an original idea proposed by Fock[8] of representing atomic orbitals using only *one* single exponent $\xi_{n\ell}$ per each atomic subshell $n\ell$, multiplied with a polynomial to ensure orthogonality between different shells of same angular momentum. The physical meaning of this parameter can be linked to the ionization potential $\mathrm{PI}_{n\ell}$ according to Refs. 9,10 as

$$\xi_{n\ell} \approx \sqrt{2\mathrm{PI}_{n\ell}}. \qquad (2)$$

For each atomic orbital we write the radial function $R_{n\ell}(r)$ as

$$R_{n\ell}(r) \propto (2\xi_{n\ell}r)^{\ell} P_{n\ell}(2\xi_{n\ell}r) \exp\left(-\xi_{n\ell}\, r\right) \qquad (3)$$

where $P_{n\ell}(x)$ is a polynomial of degree $n-\ell-1$. Starting with $P_{\ell+1,\ell} \equiv 1$, the successive polynomials, as para-

metric functions of the exponents, ensure orthogonality for a common ℓ. The orthonormality conditions result in a system of linear equations to determine unambiguously all coefficients of the polynomials. This scheme is called MAP as Moscow–Aachen–Paris, or Minimal Atomic Parameters.[6]

The exponents are determined by minimizing the total Hartree-Fock energy of the atomic ground state configurations following the Aufbau principle[11]. For the orbital exponents of the elements H – Xe (i.e. $Z = 1 \ldots 54$) we found[7] piece-wise linear relations of the form

$$\xi_{n\ell}(Z) = a_{n\ell}\, Z + b_{n\ell}. \qquad (4)$$

Slopes $a_{n\ell}$ and cutoffs $b_{n\ell}$ are specific for the segments of the Periodic Table where subshells with quantum numbers $n\ell$ are respectively being filled (open) or are closed (belong to the core).

Energy minimization leads to stable values for the exponents, however in a long and tedious simplex procedure, loosing about 3% of the total energy with respect to Bunge or numerical orbitals.

Much easier seems to maximize the overlap of MAP orbitals with Bunge (or any other) orbitals with respect to exponents. A convenient numerical instrument for this is provided by the Frobenius angle between the spaces spanned by corresponding orbital sets.

Let $\{|\beta\rangle\}$ and $\{|\mu\rangle\}$ be two orbital sets. We define then operators (respectively, matrices) acting in the L^2 Hilbert space as

$$\mathbf{M} = \sum_{\mu=1}^{m} |\mu\rangle\langle\mu|; \qquad \mathbf{B} = \sum_{\beta=1}^{b} |\beta\rangle\langle\beta|. \qquad (5)$$

Linear operators form a linear spapce since their sum and product with (complex) numbers are themselves op-

erators. The trace of the product $\text{tr}(\mathbf{C}^\dagger \mathbf{D})$ of the matrix representations of any pair of linear operators $\mathbf{C}$ and $\mathbf{D}$ defines a scalar product of operators. This *Frobenius* product has all qualities of a scalar product – it is bilinear, positive definite for $\mathbf{C} = \mathbf{D}$, and zero in this case if and only if $\mathbf{C} (= \mathbf{D})$ is the zero operator.

Applying the definition of the Frobenius product to matrices $\mathbf{M}_{\lambda\kappa} = \langle \lambda | \mathbf{M} | \kappa \rangle$ and similarly to $\mathbf{B}$ we get

$$
\begin{aligned}
\text{tr}\left(\mathbf{M}^\dagger \mathbf{B}\right) &= \sum_{\kappa\lambda} \sum_{\mu} \sum_{\beta} \langle \kappa | \mu \rangle \langle \mu | \lambda \rangle \langle \lambda | \beta \rangle \langle \beta | \kappa \rangle \\
&= \sum_{\mu} \sum_{\beta} \langle \beta \underbrace{\sum_{\kappa} | \kappa \rangle \langle \kappa |}_{=\mathbf{I}} \mu \rangle \langle \mu \underbrace{\sum_{\lambda} | \lambda \rangle \langle \lambda |}_{=\mathbf{I}} \beta \rangle \\
&= \sum_{\mu} \sum_{\beta} |\langle \beta | \mu \rangle|^2 \qquad (6)
\end{aligned}
$$

where we used an expansion:

$$
\mathbf{I} = \sum_\kappa | \kappa \rangle \langle \kappa | = \sum_\lambda | \lambda \rangle \langle \lambda |
$$

of identity operator $\mathbf{I}$ over a complete basis of the Hilbert space and the definition of the Frobenius operator norm as the square root of the product of a matrix with itself $|\mathbf{C}| = \sqrt{\text{tr}(\mathbf{C}^\dagger \mathbf{C})}$ we may define a Frobenius angle between the two subspaces spanned by the sets $\{|\beta\rangle\}$ and $\{|\mu\rangle\}$ as

$$
\begin{aligned}
\cos\varphi_{\mathbf{MB}} &= \frac{\text{tr}\left(\mathbf{M}^\dagger \mathbf{B}\right)}{|\mathbf{M}|\,|\mathbf{B}|} \\
&= \frac{\sum_{\mu\beta} |\langle \beta | \mu \rangle|^2}{\sqrt{\sum_{\mu\mu'} |\langle \mu | \mu' \rangle|^2}\sqrt{\sum_{\beta\beta'} |\langle \beta | \beta' \rangle|^2}} \\
&= \frac{\sum_{\mu=1}^{m} \sum_{\beta=1}^{b} |\langle \beta | \mu \rangle|^2}{\sqrt{m}\sqrt{b}} \qquad (7)
\end{aligned}
$$

We see that this cosine is always positive (angles between 0 and $\frac{\pi}{2}$ only) which we can interpret as a probability — the probability of an electron, described by an orbital expanded in set M, to be found in the space spanned by the set B and vice versa.

MAP orbitals are fully defined through the set of exponents. These parameters can now be used to optimize not the total energy, but the Frobenius angle (or maximize its cosine) between Bunge and MAP orbital sets.

We re-determined in this way all MAP exponents for atoms $Z = 1 \div 54$ i.e. H–Xe (see Ref. 12), finding cosines > 0.96 for all values of Z. In the present contribution we will extend the approach to elements Cs – Lr, with Z ranging from 55 to 103 taking the Koga orbitals[13] for given and optimizing the Frobenius angles between them the MAP orbitals with respect to exponents. We will try to derive again simple rules between exponents and the nuclear charge Z.

Table I: Parameters of the fits of the exponents as functions of Z for variable intervals, found from the condition of the minimum Frobenius angle with the Bunge orbitals according to eq. (7) with their errors δ and values of the R^2 criterium and Slater parameters $n^*_{n\ell}$, $\sigma_{n\ell}$.

$n\ell$	Z		$a_{n\ell}$	$b_{n\ell}$	$\delta(a_{n\ell})$	$\delta(b_{n\ell})$	R^2	$n^*_{n\ell}$	$\sigma_{n\ell}$
1s	2:	He-Xe	1.0143	−0.45	0.0010	0.03	0.999951	0.986	
2s	3:10	Li-Ne	0.3674	−0.36	0.0009	0.01	0.999967	1.973	0.275
	10:	Ne-Xe	0.5069	−1.64	0.0008	0.03	0.999909		
3s	11:18	Na-Ar	0.3034	−2.34	0.0048	0.07	0.998491	3.083	0.064
	19:	K-Xe	0.3243	−2.81	0.0023	0.09	0.998235		
4s	20:30	Ca-Zn	0.05414	0.24	0.0013	0.03	0.994975	3.733	0.798
	30:	Zn-Xe*	0.2679	−6.03	0.0032	0.14	0.996895		
5s	38:48	Sr-Cd*	0.0591	−0.76	0.0032	0.14	0.976638	4.038	0.761
	48:	Cd-Xe	0.2477	−9.78	0.0078	0.40	0.995013		
2p	5:10	B-Ne	0.2943	−0.31	0.0053	0.04	0.998712	1.960	0.423
	10:	Ne-Xe	0.5102	−2.30	0.0006	0.02	0.999938		
3p	13:18	Al-Ar	0.2622	−2.22	0.0064	0.10	0.997603	3.022	0.208
	19:	K-Xe	0.3309	−3.70	0.0027	0.10	0.99766		
4p	31:36	Ga-Kr	0.2550	−6.35	0.0102	0.34	0.993685	3.814	0.027
	37:	Rb-Xe	0.2622	−6.51	0.0049	0.22	0.994449		
5p	49:	In-Xe	0.2390	−9.95	0.0107	0.55	0.992118	4.185	
3d	21:30	Sc-Zn	0.2171	−2.32	0.0058	0.15	0.994392	2.641	0.427
	30:	Zn-Xe	0.3787	−7.13	0.0029	0.12	0.998638		
4d	39:45	Y-Rh	0.2535	−7.70	0.0108	0.46	0.990943	3.247	0.177
	46:	Pd-Xe	0.3080	−10.47	0.0039	0.19	0.998893		

* without Palladium ($Z = 46$).

II. RESULTS AND DISCUSSION

First we consider as in Ref. 12 exponents obtained from the comparison with Bunge orbitals for elements $Z = 1 \div 54$. Their dependence upon Z, shown in Fig. 1, is resumed in form of parameters in Table I. Either guided by the eye or by calculating R^2, the exponents seem to follow perfectly linear relations. The only exception is the palladium atom (Pd, $Z = 46$), for which the ground state configuration does not contain the 5s orbital – and thus the dimensions of the projector spaces between Bunge and MAP differ.

The R^2 values in Table I as validity criterion confirm the linear rules. In this way the numbers $a_{n\ell}$ and $b_{n\ell}$, although similar to the energy-optimized ones in Ref. 7, differ beyond confidence intervals $(a_{n\ell} \pm 3\delta(a_{n\ell}))$ and similarly for $b_{n\ell}$. This is not further surprising as quite different methods are employed for their determination.

As in Ref. 7, we may borrow some help from Slater's second rule:[14]

$$
a_{n\ell} = \frac{1}{n^*_{n\ell}} \times \begin{cases} 1 - \sigma_{n\ell} & \text{open shell (incomplete)} \\ 1 & \text{closed shell (complete)} \end{cases}
$$

where $n^*_{n\ell}$ represents an effective principal quantum number, and $\sigma_{n\ell}$ a screening of the nucleus for each electron due to the presence of the other electrons on the same or inner subshells. As seen from Table I, values $n^*_{n\ell}$ coincide with n for $n = 1 \div 3$ as prescribed by Slater's rules. For $n > 3$ the effective principal numbers $n^*_{n\ell}$ are less than n, their values are as well close to those proposed by Slater. We see thus that MAP exponents from orbital fits are following the same trends as those from Hartree-Fock energy optimizations.

This success encouraged us to maximize the overlap $\cos\varphi_{\mathbf{MK}}$ between the atomic orbitals proposed by Koga et al. and our MAP construction, for all atoms with $Z = 1 \div 103$. Figure 2 shows the *defect* – the quantity $(1 - \cos\varphi_{\mathbf{MK}})$ – as a function of Z. Clearly, in all cases, the
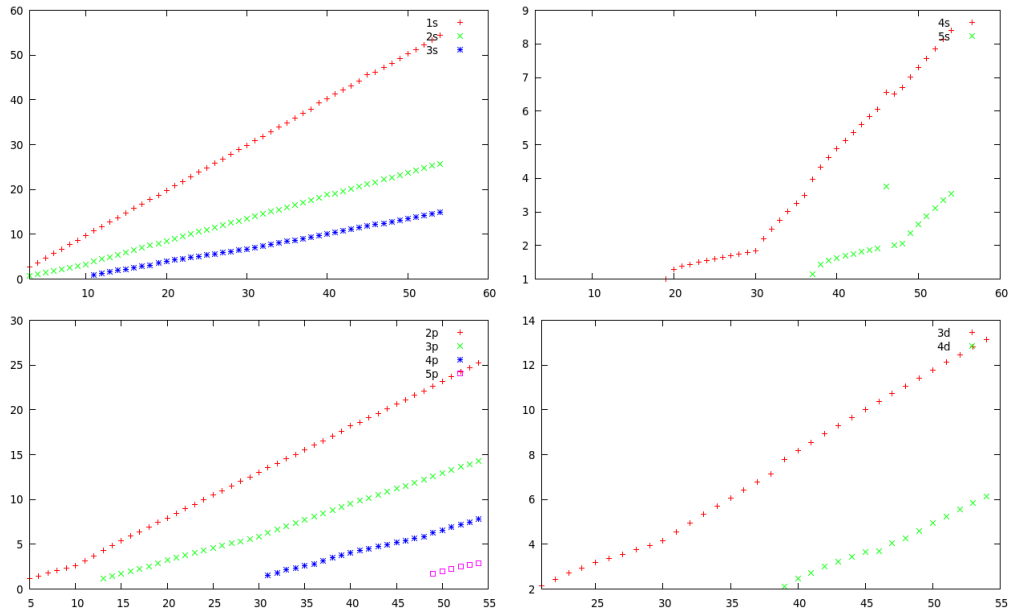
Figure 1: The dependence of the exponents of the Bunge orbitals on the nuclear charge Z (atomic number) determined for the subshells $n\ell$ Top line: $1s$-$3s$ - left; $4s$-$5s$ - right; bottom line: $2p$-$5p$ - left; $3d$-$4d$ - right.
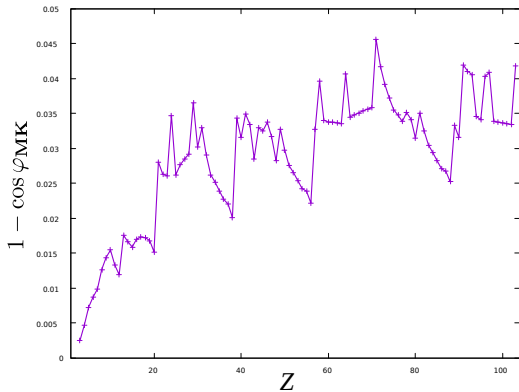

Figure 2: Defect, that is the quantity $1 - \cos\varphi_{\mathbf{MK}}$ as a function of Z for the Koga orbitals in the range $Z = 1 \div 103$.

defect does not exceed 0.05 and is mainly around 0.03 or between 0.25 and 0.35. In Ref. 12 we observed similar trends comparing MAP and Bunge orbitals for elements with $Z = 1 \div 54$. Thus with use of the MAP orbitals we could verify the similarity of Bunge and Koga orbital spaces.

The dependence of the exponents on the nuclear charge Z, obtained here from the optimization of the Frobenius angle with the Koga orbital sets, is shown in Figure 3. Their coefficients – eq. (4) – are collected in Table II. For determining the quantities $a_{n\ell}$ and $b_{n\ell}$, the points which deviate from the linear branches have been excluded. This refers to the outer ns shells where only two points are available, and similarly the outlyers like $Z = 46$ (Pd) and $Z = 57, 58, 64$ (La, Ce, Gd), are ex-

cluded from the fit.

In Figure 3 we clearly see that the exponents follow the generalized Slater rules: slopes $a_{n\ell}$ are smaller for the subshells being filled (open ones), and larger for the already filled (closed core) shells. Also, for transition metals and Lanthanoides/Actinoides the exponents of outer ns ($n = 4 \div 7$) shells change only little with Z (rows 6, 8, 10, 13, 14, 16, 17, 25 of Table II). This is as well in agreement with generalized Slater rules since electrons of these subshells in the respective segments of Z are strongly screened from the nuclei by the lower lying d or f subshells.

In general, it should be noted that shell structures are easily seen from the dependence of the exponents with Z: two linear branches meet with one single change in slope, going from an open-shell situation to a closed-shell one. There are two exceptions from this rule: one concerns n_{sp} shells ($n = 5, 6$) which exhibit not two, but several distinct slopes due to the presence of the transition elements as well as Lanthanoides and the Actinoides. The other is the $4p$ shell where we see only one single branch (Fig. 3, middle-left panel). The numerical values of the two expected slopes are identical with respect to the interval of confidence (rows 22 and 23 of Tab. II).

Parameters $n^*_{n\ell}$ of the Slater rules determined from the data of Table II show to remain very close to the principal number n for shells with $n \leq 4$ (in all cases differences are less than 0.05, see Table II). Slater's suggestion proposing an effective principal number of 3.7 for $n = 4$ cannot be confirmed from the exponents extracted from Koga orbitals. In contrast to this Slater's effective principal number of 3.7 seems to be confirmed by the data extracted from Bunge orbitals (remarkably, the differences

Table II: Parameters for the fits of the exponents as functions of Z for different intervals Z as extracted from the minimum of the Frobenius angles of with the Kogae orbitals, according to eq. (7) with their errors δ and the values of the R^2 criterion and the Slater parameters $n^*_{n\ell}$ and $\sigma_{n\ell}$. Column "sup" contains a "+" if the confidential interval for $a_{n\ell}, b_{n\ell}$ determined from the Bunge orbitals (Table I) and from the Koga ones (this Table) overlap and "−" if not. This cell remains empty if the necessary information is missing in Table I.

| $n\ell$	row	Z		$a_{n\ell}$	$b_{n\ell}$	$\delta(a_{n\ell})$	$\delta(b_{n\ell})$	R^2	sup	$n^*_{n\ell}$	$\sigma_{n\ell}$
1s	1	2:	He-Lr	1.0070	−0.32	0.0002	0.01	0.999995	−	0.9931	
2s	2	3:10	Li-Ne	0.3674	−0.36	0.0009	0.01	0.999967	+	1.9821	0.2718
	3	10:	Ne-Lr	0.5045	−1.60	0.0003	0.02	0.999975	+		0
3s	4	11:18	Na-Ar	0.3034	−2.34	0.0048	0.07	0.998491	+	2.9833	0.0948
	5	19:	K-Lr	0.3352	−3.19	0.0006	0.04	0.999782	−		0
4s	6	20:28	Ca-Ni	0.0562	0.18	0.0040	0.10	0.965494	+	4.0297	0.7734
	7	31:	Ga-Lr	0.2481	−5.20	0.0008	0.06	0.999222	−		0
5s	8	39:48	Y-Cd	0.0372	0.15	0.0100	0.44	0.696613	+	3.8993	0.8245
	9	49:57	In-La	0.2766	−11.25	0.0164	0.87	0.982779			−0.3038
	10	59:68	Pr-Er	0.0812	−0.16	0.0004	0.03	0.999832			0.6173
	11	72:80	Hf-Hg	0.1889	−7.64	0.0038	0.29	0.997136			0.1096
	12	81:	Tl-Lr	0.2121	−9.21	0.0036	0.33	0.993951			0
6s	13	56:70	Ba-Yb	0.0143	0.69	0.0003	0.02	0.996536		3.6659	0.9474
	14	72:77	Hf-Ir	0.0614	−2.51	0.0013	0.10	0.998132			0.7748
	15	80:90	Hg-Th	0.2728	−19.47	0.0069	0.59	0.99426			0
	16	91:	Pa-Lr	0.0731	−1.58	0.0044	0.42	0.962348			0.7320
7s	17	89:102	Ac-No	0.0062	1.18	0.0024	0.23	0.385791	−	−	−
2p	18	5:10	B-Ne	0.2943	−0.31	0.0053	0.04	0.998712	+	1.9728	0.4193
	19	11:	Na-Lr	0.5069	−2.21	0.0001	0.0	0.999994	−		0
3p	20	13:18	Al-Ar	0.2622	−2.22	0.0064	0.10	0.997603	+	2.9574	0.2246
	21	19:	K-Lr	0.3381	−3.96	0.0005	0.04	0.999788	+		0
4p	22	31:36	Ga-Kr	0.2550	−6.35	0.0102	0.34	0.993701		4.0152	0.0233
	23	37:	Rb-Lr	0.2491	−5.91	0.0009	0.07	0.999065	+		0
5p	24	49:57	In-La	0.2578	−10.91	0.0065	0.34	0.995587	+	3.7190	0.0412
	25	59:70	Pr-Yb	0.0642	0.04	0.0005	0.03	0.999503			0.7614
	26	71:80	Lu-Hg	0.1914	−8.83	0.0021	0.16	0.999009			0.2882
	27	81:89	Tl-Ac	0.2689	−14.81	0.0012	0.11	0.99985			0
	28	89:	Ac-Lr	0.1870	−7.48	0.0014	0.13	0.999316			0.3045
6p	29	81:89	Tl-Ac	0.2565	−18.81	0.0063	0.53	0.995854		3.6659†	0.0596
	30	89:	Ac-Lr	0.0597	−1.20	0.0039	0.37	0.94795			0.7811
3d	31	21:28	Sc-Ni	0.2291	−2.64	0.0147	0.36	0.975764	+	2.8579	0.3452
	32	29:	Cu-Lr	0.3499	−5.92	0.0009	0.06	0.999523	−		0
4d	33	39:45	Y-Rh	0.2296	−6.81	0.0194	0.82	0.965571	+	3.7350	0.1426
	34	46:56	Pd-Ba	0.3175	−11.00	0.0048	0.25	0.997912			-0.1860
	35	57:71	La-Lu	0.2080	−4.93	0.0068	0.45	0.989369			0.2229
	36	71:	Lu-Lr	0.2677	−8.87	0.0009	0.09	0.999621			0
5d	37	71:77	Lu-Ir	0.2528	−15.27	0.0128	0.94	0.987415		3.4821	0.1197
	38	78:88	Pt-Ra	0.2872	−18.24	0.0039	0.32	0.998335			0
	39	89:	Ac-Lr	0.1582	−6.41	0.0113	1.09	0.937314			0.4490
6d	40	89:	Ac-Lr	0.0153	1.46	0.0154	0.42	0.705118	−	−	−
4f	41	58:70	Ce-Yb	0.1760	-5.63	0.0038	0.25	0.995303		3.2224	0.4328
	42	71:90	Lu-Th	0.2868	-13.27	0.0020	0.17	0.999131			0.0757
	43	91:	Pa-Lr	0.2785	-11.91	0.0010	0.10	0.999852			0.1025
	44	71:	Lu-Lr	0.3103	-15.09	0.0030	0.26	0.997181			0
5f	45	91:	Pa-Lr	0.1885	-12.31	0.0057	0.55	0.990095	−	−	−
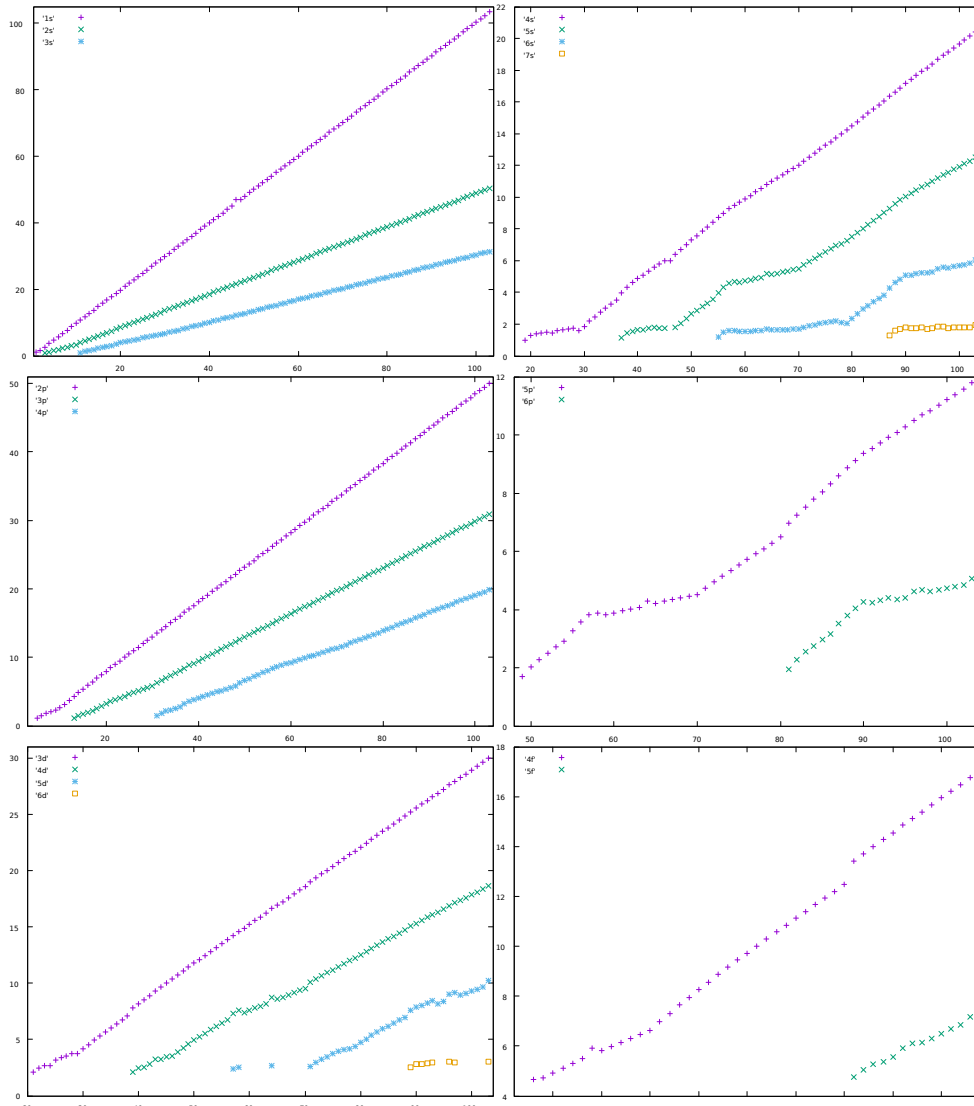
Figure 3: Dependencies of exponents $\xi_{n\ell}$ extracted from Koga orbitals on nuclear charge Z (atomic number) for subshells $n\ell$. Upper line: $1s$-$3s$ – left; $4s$-$7s$ – right; middle line: $2p$-$4p$ – left; $5p$-$6p$ – right; bottom line: $3d$-$6d$ - left; $4f$-$5f$ – right.

between the Bunge and Koga sets appear in the rows of Table II containing "–" and these latter appear only in the rows referring to the core subshells). We explain this discrepancy by the larger number of data points available for Koga orbitals.

For principal quantum numbers $n \geq 5$ the linear dependencies of $\xi_{n\ell}$ from Z are seen in the respective segments. However, the values cannot be explained as simply as for $n \leq 4$. The $5s$ subshell has the most complicated, but still understandable form of dependence of ξ_{5s} on Z. Although, formally, starting with $Z = 55$ (Cs – the first element of the 6-th period) it is a core shell, dependence of its orbital exponent has a complex structure.

Indeed, for $Z \geq 55$ the segments of Z referring to Lanthanoids, $5d$ transition elements, $6p$-elements and, finally, Actinoids. It is difficult to select the segment where $5s$ orbital truely belongs to the core. For the subshells

with smaller $n (\leq 4)$ the core orbital is always one with the maximal slope $a_{n\ell}$. For the $5s$ orbital two segments with similar slopes: for elements $5p$ (row 9 Tab. II) and elements $6p$ (row 12 Tab. II) which, respectively, yield the values of n_{5s}^* of 3.6163 and 3.8993 can be found. The first option is not perfectly good, since e.g. the segments of p-elements for $n \leq 4$ are not ascribed to the core. Taking the last segment for the true core one, we obtain a set of values σ_{5s} given in Tab. II (rows 8–12). Of these values ony that for $5p$ elements is negative. Purely theoretically, it is not impossibile to have negative $\sigma_{n\ell}$: this simply means that the interaction of electron with others within the subshell (being filled) is stronger than that with others in the lower lying subshells (already filled).

As for $5p$ shell, for it the unique possibility to select the segment, where it belongs to the core, is to accept for that the segment of $6p$ elements (row 27 Tab. II). Under

this assumption we obtain the value of n_{5p}^* close to n_{5s}^* and the entire set of positive values of σ_{5p}, although, with a very small value for the $5p$ elementis themselves (row 24 Tab. II).

For the $6s$ subshell no segment can be safely selected, where it would belong to the core. Making notice that for the $5s$ subshell the slopes in the segments of Z for elements $5p$ and $6p$ are similar, we assume the $6s$ subshell to belong to the core in the segment of $6p$ elements. Under this assumption we obtain the value of n_{6s}^* which is much smaller than 6, and the whole set of positive values of σ_{6s} (in the segments of Lanthanoids, $5d$ transition elements and Actinoids).

As for subshell $6p$, there is no sufficient datae to determine the value of n_{6p}^* reliably. As we have already seen n_{5p}^* to be close to n_{5s}^*, we set n_{6p}^* equal to n_{6s}^* and this way find the values σ_{6p} for the $6p$ elements and equalliy for Actinoids (row 29, 30 Tab. II).

As for nd subshells ($n = 3 \div 5$), the dependencies of their exponents on Z look out fully regular (Fig. 3 bottom line, left). It is to be noted that efficient quantum numbers n_{nd}^* are always smaller that respective n's and most of all for $n = 5$, which are even much smaller than 4. The reason for this is not clear for the moment.

The slopes a_{4f} in the segments Lu–Th and Ac–Lr are close. Even their confidential intervals marginally intersect. Thus we determine the common value of the slope for the both intervals and used it to determine the efficient number n_{4f}^* (row 44 Tab. II).

Meanwhile, the general observation deduced from datae of Tables I, II relative to the subshells $5s$, $5p$, $6s$, (and eventually $6p$) is that the efficient principal quantum numbers are not only smaller, but much smaller than principal quantum numbers n's, that is, $n_{n\ell}^*$ are smaller than 4. This requires some explanation, but we postpone it for future publications.

Above, we have considered the dependencies of $\xi_{n\ell}$ and Z in general; the structure of the Periodic Table is reflected in these dependencies. Of course, it should be noted that there is a similarity between the dependencies of $\xi_{n\ell}$ on Z in Fig. 3 of the present article and Figure 9 of Ref. 15 showing $\sqrt{\mathrm{PI}_{n\ell}}$ as a function of Z. Periodicity, however, as understood chemically, manifests itself differently (see for example Ref. 15,16).

In order to study this we reorder the linear dependencies $\xi_{n\ell}$ on Z to make clear the periodic structure of open subshells. Actualy, in each segment corresponding to filling of some subshell with quantum numbers $n\ell$, it contains $Z - Z_{n\ell}$ electrons,[1] where $Z_{n\ell}$ is the atomic number immediately precedent to the beginning of the filling of the $n\ell$ subshell (at $Z = Z_{n\ell}$ the subshell $n\ell$ contains yet no electrons[2]). In the Periodic Table of the longest form

Table III: Characteristic values of atomic numbers $Z_{n+\ell}$; Z_n of the first appearence of electron with the given values $(n + l)$ or n with the help of Klechkowski's function to calculate and symbols of elements and the respective configurations.

$n+\ell; n$	$\dfrac{Z_{n+\ell}}{Z_n}$		
1	1	H	$1s^1$
2	3	Li	[He]$2s^1$
3	5	B	[Be]$2p^1$
	11	Na	[Ne]$3s^1$
4	13	Al	[Mg]$3p^1$
	19	K	[Ar]$4s^1$
5	21	Sc	[Ca]$3d^1$
	37	Rb	[Kr]$5s^1$
6	39	Y	[Cd]$4d^1$
	55	Cs	[Xe]$6s^1$
7	57	La	[Ba]$5d^1$
	87	Fr	[Rn]$7s^1$
8	89	Ac	[Ra]$6d^1$

(that with 32 columns, see e.g. Ref. 15,16) the elements with equal values $Z - Z_{n\ell}$ belong to the same group: formaly stand in the same column. The definition of the $Z_{n\ell}$ numbers through the numbers of columns in Periodic Table looks out to be overly formal. It, however, is not such. Curiousely, it is possible to take for $Z_{n\ell}$'s the numbers immediately, preceeding the numbers $Z_{n+\ell}$, at with an electron with a given value $n + \ell$ first appears according to the $(n + \ell, n)$-rule[18] i.e. $Z_{n\ell} = Z_{n+\ell} - 1$. Although in Ref. 15 it is repeatedely stressed that the $(n + \ell, n)$-rule[18] is only valid in the books written for students, and that even some chemist enjoy the idea that this rule cannot be derived from laws of physics, both statements are not completely true. As for the $(n + \ell)$-part of this rule, Klechkowskij has strictly shown,[19] calculating the number of states referring to the given value of $(n + \ell)$, the number $Z_{n+\ell}$ can be represented by simplisic (Kletchkowskij) function:

$$\mathrm{K}(y) = \frac{y^3}{6} \begin{cases} -\frac{y}{6} & \text{for } y \text{ odd} \\ +\frac{y}{3} & \text{for } y \text{ even} \end{cases} \qquad (8)$$

namely, $Z_{n+\ell} = \mathrm{K}(n + \ell) + 1$ and the sought number $Z_{n\ell}$ simply equals to $\mathrm{K}(n + \ell)$, where one has to chose a suitable combination of n and ℓ. Similarly, the function K gives the values $Z_n = \mathrm{K}(n + 1) - 1$ at which electron with quantum number n (and thus $\ell = 0$) appears for the first time, correctly in all cases, by this indicating the boundaries of the periods of the Table of Elements. Both numbers are collected in Table III which shows that neutral atoms perfectly follow the $(n + \ell)$-rule.

Exceptions from the $(n + \ell, n)$-rule touch only its n-pars. Those occurring in rows $(n + \ell) = 7, 8$ refer only

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[1] Previously, the dependency on $Z - Z_{n\ell}$ had been used in Ref. 17 for analyzis of the properties of Lanthanoids and Actinoids.
[2] An example is the segment of transition elements: for the sub-

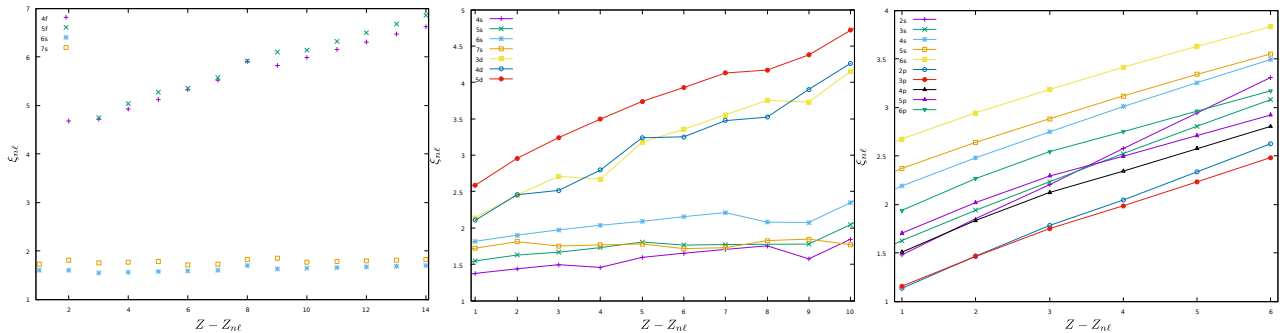shell $3d$ $Z_{3d} = 20$ since Ca is the last element preceeding this segment.

Figure 4: Dependence of selected orbital exponents in MAP setting f- (to the left), d- (middle) and p-elements (to the right) on the reduced nuclear charge which makes $Z - Z_{n\ell}$.

to the order in which $4f$ and $5d$ ($5f$ and $6d$) orbitals are being filled, not the value $Z_{n+\ell}$ where electrons with $(n + \ell) = 7, 8$ appear for the first time.

These exceptions do not seem to be relevant. Indeed, deviations from the n-(sub)rule of the general $(n + \ell, n)$-rule, as observed in experiments, can depend on interactions (correlations) of electrons or be a manifestation of relativism. Neither can be reproduced by computing numbers of states with those or others quantum numbers (as Kletchkowskij did it). On the other hand, Koga orbitals determined for Lanthanoids and Actinoids implicitly contain some information related to correlations or/and relativism. This happens since the ground states of the atoms for which the orbitals are determined, are "manū propriā" of the authors[13] selected in agreement with experiments. Thus in Fig. 4 we present dependencies $\xi_{n\ell}$ on $Z - Z_{n\ell}$ in the segments corresponding to f-, d- ans p-elementis (where f-, d- and p-subshells are open ones). The result shows perfectly that which one could expect.

Namely, the data related to f-elements (Lanthanoids and Actinoids – Fig. 4 left) are the simplest to interpret. As it is seen from Figure 4, the values of the exponents ξ_{4f} and ξ_{5f} and similarly to ξ_{6s} and ξ_{7s}, respectively, almost coincide for Lanthanoids and Actinoids. Even more, the exponents ξ_{ns}, $n = 6, 7$ almost do not depend on $Z - Z_{n\ell}$. By contrast, although the exponents ξ_{4f} and ξ_{5f} for equal $Z - Z_{n\ell}$ almost coincide, their values notably increase quasi-linearly with the efficient core charge. A simplest physically or chemically relevant conclusion from that is: *atomic* radii of Lanthanoids and Actinoids (i.e., true radii of atoms which are determined by the outermost subshells) coincide (following the datae condensed in Koga bases of these atoms) and, moreover, on $Z - Z_{n\ell}$ do not depend. By contrast, *ionic* radii of the 3+ ions of these elements, whose outermost subshells are nf, decrease with increase of efficient core charge $Z - Z_{n\ell}$, since they are inversely proprtional to increasing ξ_{nf} by this showing Lanthanoid (and eventually Actinoid) *contraction*. To add, we note that since exponents for quantum numbers $n = 6, 7$ for s-orbitals and those with quantum numbers $n = 4, 5$ for f-orbitals, respectively coincident, the unique possibility to reproduce whatever difference between Lan-

tanoids and Actinoids remains in the difference of the numbers of nodes they, respectively, have. This conclusion as well derives from the data condensated in Koga bases.

The picture completely changes when we consider nsp subshells (Fig. 4 right). There the exponents ns or np grow almost linearly with $Z - Z_{n\ell}$. Most remarkably, the slopes for s- and p-orbitals almost coincide with only two exceptions. One is the intersection dependencies of exponents of $Z - Z_{n\ell}$ for $2p$ and $3p$ subshells (two lower lines in Fig. 4 right), which are too much close to provide whatever interpretation to their intersection. Another one is the relatively strong dependence of the ξ_{2s} (!) exponents which grow with $Z - Z_{n\ell}$ much faster and intersect respective lines, depicting the dependencies of the exponents $5p$, $4p$ et $3s$. Beyond the mentioned exceptions the orbital exponents ξ_{ns} and ξ_{np} increase in parallel with increaing $Z - Z_{n\ell}$, but show a noticeable dependency on n which absent in the segments of Lanthanoids and Actinoids.

Transition elements, as Fig. 4 (middle) shows, takes an intermediate position between nf and nsp. In respective segments the orbital exponents for ns slightly grow remaining in a narrow corridor with, meanwhile, a visible increment between $n = 4$ and $n = 6$ whereas those for $n = 5, 7$ almost not differ. Orbital exponents nd ($n = 3 \div 5$) grow almost linearly, but their spread around a hypothetical strait line remains noticeable. A minimal difference between the exponents' values for $3d$ and $4d$ subshells against a notable increment to them for $5d$ also is to be noted.

Generally the dependences of $\xi_{n\ell}$ on $Z - Z_{n\ell}$ extracted from the data condensed in the Koga basis sets confirm the observations of Refs. 15,16 opposing the orbitals (subshells) sp and df. As well, the way of variation of the MAP-exponents with $Z - Z_{n\ell}$ is clearly seen to coincide with the quasi-linear Pearson's electroneganvity dependencies shown in Fig. 22 of Ref. 15.

The data extracted from the Koga orbitals extend to the principal quantum number $n = 7$ which is the number of periods in the Mendelejew Table covered by the Koga orbital basis sets. One may expect periodicity in a chemical sense to manifest itself in the that abundant

information. That's what it looks like this in the data shown in Fig. 4. According to them the periodicity in the case of f-elements is perfect, since the exponents for atoms with equal values $Z - Z_{n\ell}$ simply coincide: the formal characteristic of periodic functions. Similarly, ns exponents for atoms of transitive elements with equal $Z - Z_{n\ell}$ are closest and so do the nd exponents.

For the p-elements chemical periodicity condensed in Koga basis sets seems to appear differently. The exponents of the orbitals 2 and $3p$ nearly coincide and similarly 4 and 5 p which acquire a few growth with respect to $n = 2, 3$. The exponents for the orbitals $6p$ through a constant increase they differ from those for $5p$.

With regard to the energy gap observed in Ref. 15,16 between the subshells np and $(n + 1)s$, we do not see it in the data drawn from the Koga basis sets. Indeed, $\xi_{2p} (Z - Z_{2p} = 6)$ (end of the 2-nd period) is larger rather than smaller than $\xi_{3s} (Z - Z_{3p} = 1)$ which in turn should be larger than $\xi_{3s} (Z - Z_{3s} = 1)$ (beginning of the 3-rd period). Under the hypothesis eq. (2) this means that the gap $2p$–$3s$ is negative. The same holds for the pair of subshells $3p$–$4s$. Only for the pairs $4p$–$5s$ and $5p$–$6s$ we can expect for a positive gap if we rely on information derived from the Koga basis sets.

One also could expect to find signs of the *double periodicity*[20] for that extended data set. This hope, however, does not seem to be justifiable. According to the previous discussion, the exponents for the p-orbitals are grouped in the dyads with sequential values of $n, n+1 = 2k, 2k+1$ in such a way that a kind of double periodicity appears. It should be noted, however, that the aggregation proposed in Ref. 20 applies not to the sequential (even *with* odd) but for alternate (even *versus* odd) periods. Therefore, although, there is certain aggregation of elements with respect to n, additional to the common one, which arises from the dependencies of the exponents $\xi_{n\ell}$ on $Z - Z_{n\ell}$, it does not conform with the original hypothesis Ref. 20. Curiously, aggregation of subsequent periods in dyads (even and odd) is as well explained through the Klechkowski function which differently behaves for even and odd values of argument. All this requires a deeper investigation, which we will postpone for the future.

III. CONCLUSIONS

1. Frobenius products eq. (6) of the matrices of the form eq. (5) built of vectors of sets $\{|\beta\rangle\}$ and $\{|\mu\rangle\}$ or Frobenius angle eq. (7) between respective orbital subspaces show these to be useful to compare different vector sets.

2. The MAP form of the orbitals eq. (3) is one which needs a minimum number of parameters while keeping the correct number of orbital nodes.

3. With use of Frobenius products we derived the MAP orbital exponents optimally representing the Bunge orbitals for elements H – Xe ($Z = 1...54$) and Koga orbitals for H – Lr ($Z = 1...103$).

4. This way one can analyze properties of all atomic orbital sets. Indeed, Frobenius angles between Bunge/Koga and optimal MAP orbital sets are of the order of 15 degrees which corresponds to a loss of 3 – 5 % of the number of electrons upon projection from one orbital set to the other.

5. Generally, both orbital sets i.e. Bunge and Koga ones show regular dependencies on Z of the MAP orbital exponents derived from them. By this we show that the idea to represent atomic orbitals in the MAP form was not useless since by this we could study (in)consistency of various orbital sets.

6. The orbital exponents of the MAP functions extracted by the minimization of the Frobenius angles show to a high precision linear relations with the atomic number Z as Slater's rules predict, and reproduce the general structure of the Periodic Table. The most notable differences are (i) for $n \leq 4$ effective principal numbers n^* are closest to n itself (Slater proposes however $n^* = 3.7$ instead of $n = 4$); (ii) for $n \geq 5$ the generated n^* values are much smaller than n, and in fact even less than 4.

7. Tracing MAP exponents $\xi_{n\ell}$ against respective effective core charges (or chemical group numbers) $Z - Z_{n\ell}$, where the $Z_{n\ell}$ are determined by the reduced $(n + \ell, n)$-rule or the Klechkowski function, prove the perfect periodicity of the sequential arrangement of the chemical elements suggested first by Mendelejew.

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