

Minimum atomic parameter basis sets for elements 1–54 in a Hartree–Fock setting

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Abstract

Basis sets featuring single-exponent radial functions for each of the $n\ell$ subshells and orthogonality of the radial parts for different values of n within the same ℓ have been generated for elements 1–54 of the periodic table, by minimizing the total energy for different spectroscopic states. The derived basis sets can be fairly dubbed as MAP (minimal atomic parameter/Moscow–Aachen–Paris) basis sets. We show that fundamental properties (total energy, radial expectation values, node positions, etc.) of the generated MAP orbital sets are astonishingly close to those obtained with much larger basis sets known in the literature, without numerical inconsistencies. The obtained exponents follow simple relations with respect to the nuclear charge Z .

KEYWORDS

atoms, Slater-type basis sets, minimal parametrization, Hartree–Fock

1 | INTRODUCTION. WHY A NEW SET OF SLATER-LIKE FUNCTIONS TO DESCRIBE ATOMS?

Quantum chemical modeling starts from finite sets of basis functions so that quality and efficiency of electronic-structure calculations depend on the properties of the latter. This is emphasized in almost every handbook of quantum chemistry (see, e.g., Helgaker et al. [1]) and manifests itself in a wide variety of basis sets used for different objects and their properties [2–4]. Currently, the dominating motivation of quantum-chemical modeling is the accurate numerical reproduction of different properties by using heavy computations. This approach answers questions like “What numerical value has a quantity of interest?” However, a purely numerical approach cannot provide any explanation. A rarely recognized deficiency of this approach is that the experimental data to be numerically reproduced are not available with sufficient accuracy or even definition [5]. An alternative to this numerical approach—which almost disappeared from the literature—aims at a conceptual explanation of experimental trends by using semi-quantitative models. Although this second way sacrifices the numerical accuracy to some extent, these approaches are to be considered as complementary to the former. They, however, need as well basis sets as a starting point, although the requirements differ, as formulated for instance in Nagy and Jensen [6]. In fact, only the following seems to be mandatory for the qualitative or at best semi-quantitative approach: “Each basis function should reflect the nature of the problem, such that a good representation of the orbitals can be achieved by a limited (small) number of functions.” [6] If this requirement is satisfied in a consistent way, that is, by a physically substantiated set of parameters defining a small number of functions, then one can hope to meet another desideratum underlined in Nagy and Jensen [6]: providing basis sets for a good fraction of the periodic table depending on the only true parameter—the atomic number, that is, the nuclear charge Z [7, 8], and this through a regular and sensible dependence of the parameters and basis orbitals. We would like to achieve in the present contribution to consider atomic basis sets as semi-observable entities [9].

The paper is organized as follows. In Section 2 we provide the theoretical scheme of constructing minimally parameterized sets of atomic orbitals with one single exponent for each $n\ell$ subshell while keeping the correct nodal structure. Next, in Section 3, we describe the results of solving the energy-optimization problem for atoms up to $Z = 54$ (Xe) in a restricted-open-shell Hartree–Fock setting, and discuss the obtained results, in order to draw conclusions (Section 4). A compilation of the data can be found in the accompanying Supporting Information, and all purely technical details are collected in the Appendix.

2 | THE CONSTRUCTION PROCEDURE

Minimally parameterized basis sets of the form

$$\varphi_{n\ell m}(\vec{r}) = N_{n\ell} P_{n\ell}(2\xi_{n\ell}r) e^{-\xi_{n\ell}r} \times Y_{\ell m}(\theta, \phi) \quad (1)$$

are defined so that the correct nodal structure of the orbitals (orthogonality between different functions of same ℓ) is maintained by the radial polynomial $P_{n\ell}(2\xi_{n\ell}r)$ —the form originally used by Fock and coworkers [10] for the Be atom and for closed $2s^2 2p^6$ shell ions (like Na^+) and then independently rediscovered and employed for the entire 2nd period [11]—leaving the exponents $\xi_{n\ell}$ to be the only free parameters of the basis, as many as subshells. Writing the normalized radial functions as:

$$\begin{aligned} R_{1s}(r) &= N_{1s} e^{-\xi_{1s}r} \\ R_{2s}(r) &= N_{2s} (1 + a_{2s}(2\xi_{2s}r)) e^{-\xi_{2s}r} \\ R_{3s}(r) &= N_{3s} (1 + a_{3s}(2\xi_{3s}r) + b_{3s}(2\xi_{3s}r)^2) e^{-\xi_{3s}r} \\ R_{4s}(r) &= N_{4s} (1 + a_{4s}(2\xi_{4s}r) + b_{4s}(2\xi_{4s}r)^2 + c_{4s}(2\xi_{4s}r)^3) e^{-\xi_{4s}r} \dots \end{aligned} \quad (2)$$

(and similarly for higher values of the angular momentum) and evaluating the general overlap integral

$$\int_0^\infty r^n e^{-\xi_1 r} e^{-\xi_2 r} r^2 dr = \frac{(n+2)!}{(\xi_1 + \xi_2)^{n+3}} \quad (3)$$

we arrive at an iterative scheme as a 2s orbital should be orthogonal to 1s, 3s orthogonal to both 2s and 1s and so forth, leading together with the normalization to $n - \ell$ conditions for the $n - \ell$ coefficients of the polynomial $P_{n\ell}(2\xi_{n\ell}r)$. So constructed MAP functions are linear combinations of Slater monomials of the form:

$$r^n \exp(-\xi r) \quad (4)$$

with the coefficients depending parametrically on the ensemble of ξ 's of the functions of lower n . For instance for the 4s orbital we obtain three equations for the three coefficients a_{4s} , b_{4s} and c_{4s} , in a systematic and generalizable manner. The corresponding equations can be found in Supporting Information. We can thus determine the orbitals from the exponents $\xi_{n\ell}$ without ambiguity, and optimize the total energy with respect to them. Technically, the total energy for an (open-shell) atom is written, using a non-relativistic Hamiltonian for the atomic system with one or several open shells [12–14]. As no orbital expansion coefficients have to be determined by minimization (they come immediately from the orthonormality condition), one single evaluation of $E_\Psi = \langle \Psi | \hat{H} | \Psi \rangle$ is needed for each set of exponents. The determination of the exponents through the minimization of the total energy is then left to a simplex procedure [15] since the gradients used originally [11] become too cumbersome for the elements beyond the 2nd period. Note that the present procedure is indeed a Hartree–Fock scheme, optimizing the total energy with respect to the parameters of a single-determinant wavefunction, however without the construction and diagonalization of a Fock matrix of the commonly employed Roothaan–Hall procedure.

3 | RESULTS AND DISCUSSION

3.1 | Energy minimization and orbital exponents

For the elements $Z = 1\text{--}54$ (H–Xe) we optimized the exponents for atomic ground states as given by the Aufbau principle, without paying attention to exceptions like Cr, Cu, and most of the 4d transition elements. For the same elements we have from the literature the highly optimized multi-exponent Bunge basis sets [16], which, in terms of total energy, are very close to numerical Hartree–Fock energies [17]. Our basis sets yield total energies slightly higher than the Hartree–Fock limit, about 0.3%–0.7%, which is an amazingly small difference, given the number of free parameters in our calculations. Set aside the proposition of Fock et al. [10], closest to our approach and covering a large part of the periodic table, are the single-zeta basis sets of Clementi and Raimondi [18], with the same number of exponents as ours, but constructed as optimized linear combinations of nodeless Slater functions. The number of free parameters is thus about twice as large as ours (exponents and expansion

coefficients with orthonormality constraints), and the difference to total energies obtained with Bunge's basis sets about a factor two reduced with respect to ours (see Figure 1).

Overlap integrals between core orbitals in the Bunge sets and respective MAP orbitals are found to be larger than 0.99 (>0.999 for the 1s shell), and still larger than 0.90 for valence orbitals (for more details see below). One exception is the Pd atom for which the Bunge basis set [16] had been determined using the physical $4d^{10}5s^0$ ground state without the need to describe a 5s orbital.

Remarkably, in most cases the exponents of valence s -, p - and d -orbitals, determined from the energy minimization procedure, follow, as functions of the atomic number, roughly linear trends as shown in Figure 2, corroborating the semi-empirical argument given in the Introduction.

A closer look reveals that despite almost perfect linear trends particularly for smaller n the deviations from the trends of Figure 2 are not statistical, but systematic. The dependency of orbital exponents with given $n\ell$ on the nuclear charge is piecewise linear, clearly visible for instance for the 4s exponents in the three groups 19–20 (K and Ca, 4s as valence), 21–30 (Sc–Zn, filling of the 3d inner shell) and 31–54 (4s being outside

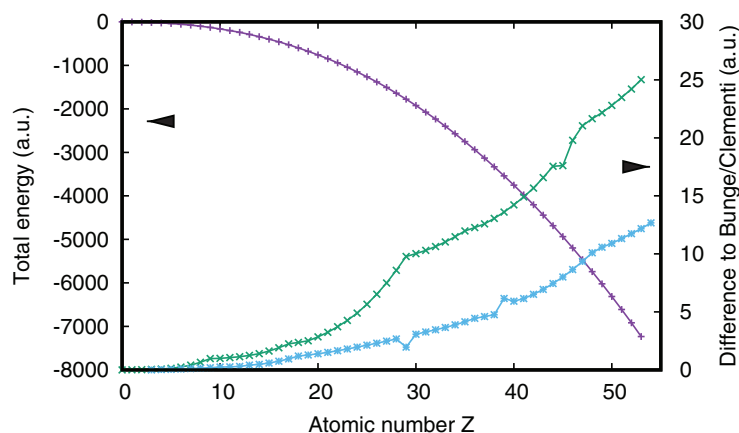


FIGURE 1 Total energies (left scale) and difference to Bunge's large basis sets in green and Clementi and Raimondi's [18] single- ζ basis sets in light blue (right scale)

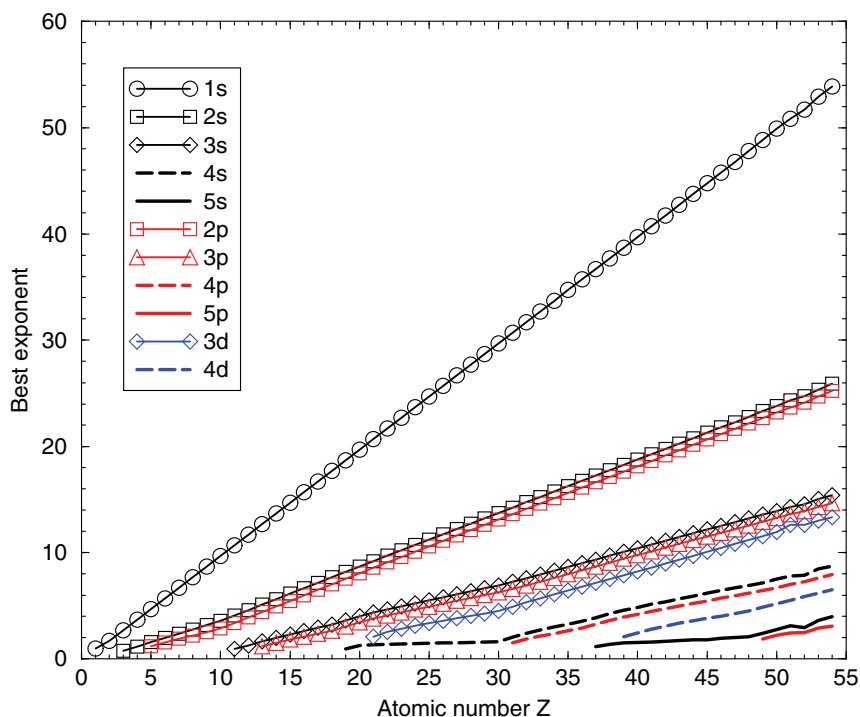


FIGURE 2 The optimal exponents as functions of the atomic number Z . The visually almost straight lines coming up to surface up to 3d are in fact misleading: see the text for details

TABLE 1 Piecewise linear fits $\xi(Z) = aZ + b$ for s , p , and d MAP exponents together with R^2 values

Orbital	Character	Z-range	a	b	R^2	n_{MAP}^*	n_{Slater}^*	σ_{MAP}	$S_{\text{MAP}}^{(\text{ref})}$	$S_{\text{Slater}}^{(\text{ref})}$	
1s	Core	3–54	0.9999	−0.28	1.0000	1.000	1				[He]
2s	Valence	3–4	0.3928	−0.34	—	1.989	2	0.218	1.3481	1.7	[He]
2s	“Valence”	5–10	0.3990	−0.41	.9999			0.206	1.8555		[He]
2s	Core	11–54	0.5026	−1.36	.9999				2.7185	4.15	[Ne]
2p	Valence	5–10	0.3319	−0.45	.9993	1.982		0.341	2.6057	1.7	[He]
2p	Core	11–54	0.5042	−2.05	.9999				4.0731	4.15	[Ne]
3s	Valence	11–12	0.3479	−2.89	—	3.012	3	−0.048	8.1782	8.8	[Ne]
3s	“Valence”	13–18	0.3137	−2.39	.9995			0.054	7.9385		[Ne]
3s	Core	19–54	0.3319	−2.82	.9987				8.5170	11.25	[Ar]
3p	Valence	13–18	0.2878	−2.51	.9986	3.015		0.132	9.3091	8.8	[Ne]
3p	Core	19–54	0.3316	−3.44	.9981				10.3791	11.25	[Ar]
3d	Valence	21–30	0.2558	−3.09	.9902	2.739		0.299	14.7677	18	[Ar]
3d	Core	31–54	0.3650	−6.35	.9999				17.3947	21.15	[Ar]3d ¹⁰
4s	Valence	19–20	0.3135	−5.01	—	3.841	3.7	−0.204	15.3673	16.8	[Ar]
4s	Transition	21–30	0.0294	+0.72	.9963			0.886	15.8198	17.15	[Ar]
4s	“Valence”	31–36	0.2993	−7.19	.9960			−0.150	22.9818	25.3	[Ar]3d ¹⁰
4s	Core	37–54	0.2602	−5.65	.9982				21.7150	27.75	[Kr]
4p	Valence	31–36	0.2718	−6.85	.9947	3.870		−0.052	24.9061	25.3	[Ar]3d ¹⁰
4p	Core	37–54	0.2583	−6.18	.9978				23.9585	27.75	[Kr]
4d	Valence	39–48	0.2672	−8.24	.9897	3.076		0.177	32.3038	30	[Kr]
4d	Core		0.3250	−11.04	.9994				33.9833	39.15	[Kr]4d ¹⁰
5s	Valence	37–38	0.3206	−10.84	—		4			34.8	[Kr]
5s	Transition	39–48	0.0206	+0.67	.9989					35.15	[Kr]
5s	“Valence”	49–54	0.2687	−11.05	.9972					43.3	[Kr]4d ¹⁰
5p	Valence	49–54	0.2581	−10.97	.9952					43.3	[Kr]4d ¹⁰

Note: For the ns orbitals the character in quotes means that the same orbital is still a valence orbital in the corresponding transition-element series and beyond in the respective p -blocks. The interpretation of the fitting parameters in terms of effective principal quantum numbers n^* and screening increments σ is given in respective columns of the table. For more explanation see the text. Similarly, the constant core contributions to screening $S^{(\text{ref})}$ as derived from the slopes and intercepts of the linear fits (b) and from the Slater rules are given. The last column comprises the configurations of the cores used to calculate the constant contributions to the screening.

of completely filled shells). In Table 1 we fit the different regions identified for all orbitals to the linear expression $\xi(Z) = aZ + b$. As examples the corresponding linear trends are shown in Figure 3 for 4s and 5s-exponents.

3.2 | Linear trends for the exponents and comparison with Slater rules

The linear trends for the exponents obtained in Section 3.1 can be interpreted in terms of Slater rules [19]. According to the latter, the orbital exponents in the monomials Equation (4) pertaining to the $n\ell$ -th subshell are to be set according to:

$$\xi_{n\ell}^{(s)} = \frac{(Z - S_{n\ell}(Z))}{n^*}, \quad (5)$$

where $S_{n\ell}(Z)$ is a screening of the nuclear charge Z characteristic for the given subshell; n^* is some effective principal quantum number. According to the well-known Slater [19] rules, $S_{n\ell}(Z)$ has two contributions. One is constant induced by the electrons from the subshells inner relative to the $n\ell$ -th one. It is roughly equal to the number of electrons in the inner subshells, but this amount is slightly reduced due to the respective reduction of the screening produced by the subshell immediately underlying one at hand, whereas the electrons of even lower subshells each reduce the nuclear charge felt by an electron in the given shell by unity. Another contribution comes from electrons of the same (sub)shell.

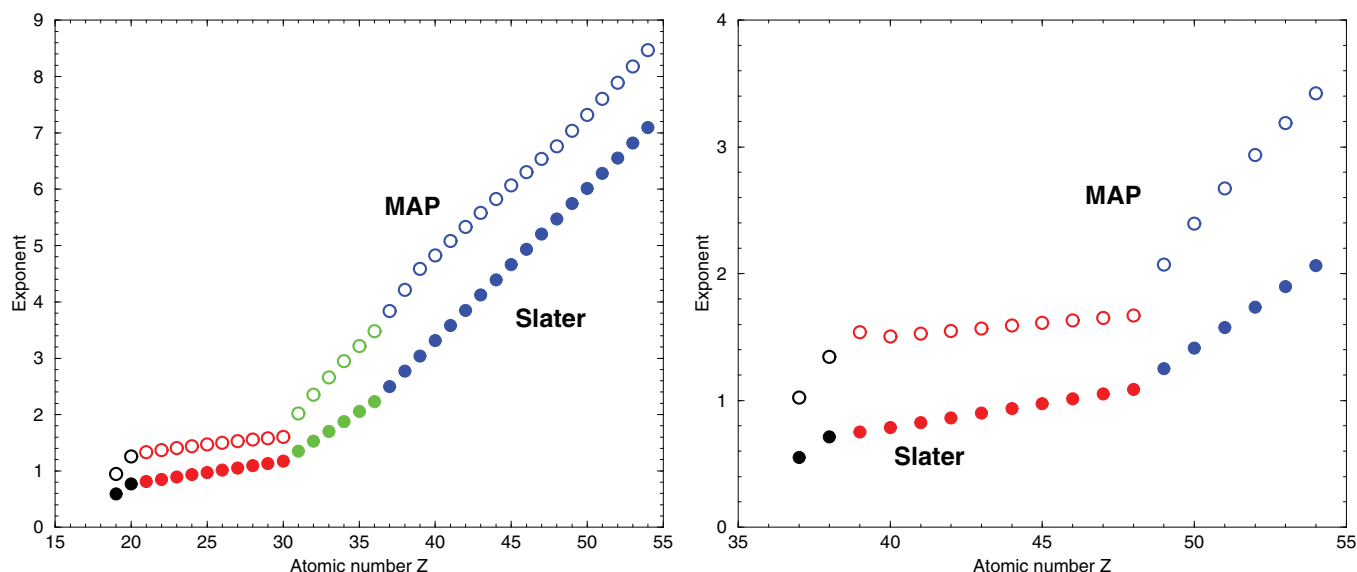


FIGURE 3 Piecewise linear trends for 4s (left) and 5s (right) orbital exponents. Yttrium ($Z = 39$) is an outlier, for so far unknown reason. Parameters of all linear fits are assembled in Table 1

Slater's recipe is that it is remarkably smaller than unity by a constant amount $\sigma_s = 0.35$ for all subshells. For the ranges of Z corresponding to the filling of an $n\ell$ subshell, which then qualifies as a valence (incomplete) subshell, each step in Z yields an increase of the number of electrons by one. The screening constant $S_{n\ell}(Z)$ is then augmented by σ until it reaches a maximum screening at the value of Z when the subshell turns filled. When this happens, further steps in Z add electrons outer to it with no augment of its screening. This all results in piecewise linear relations of the exponents ξ and the atomic number Z , which can be used for comparison. Specifically, the slopes of the linear relations of ξ versus Z in the valence ranges of Z 's are equal to $\frac{(1-\sigma)}{n^*}$ whereas in the core ranges they are simply $\frac{1}{n^*}$.

The results on the MAP exponents assembled in Table 1 fairly fit into the general picture outlined by the Slater rules. Indeed, the slopes (the a constants) for the “core” (filled) and “valence” subshells are fairly different. This allows us to estimate the quantities n_{MAP}^* and σ_{MAP} according to the above expressions. The obtained values are assembled in the respective columns of Table 1. Remarkably, the values n_{MAP}^* derived from the linear fits of the MAP exponents (actually, in the “core” ranges of the nuclear charges) deviate very little from the n_s^* values prescribed by the Slater rules. The slopes in the valence ranges allow to determine the contributions of electrons in the partially filled subshells to the screening. They are in a somewhat worse agreement with the Slater rules. The latter are best of all satisfied for $n = 2$, where σ_{MAP} almost coincides with the Slater value of 0.35 (which exactly shows up for $2p$ valence orbitals). For the MAP orbitals with $n = 3$ the screening increment σ_{MAP} is remarkably smaller than the Slater prescription with the largest deviation observed for the $3s$ subshell. For the subshells $n = 4$ the situation undergoes some qualitative dissimilarity with the prescriptions of the Slater rules. On one hand, the increment of the screening σ_{MAP} induced by an electron in the partially filled $3d$ -shell of a transition element on the $4s$ electrons is fairly close to that prescribed by Slater (0.85). On the other hand, the qualitative feature of a *weaker* screening by electrons of the same shell than by those in the inner shells is reversed. This manifests in the negative values of the σ_{MAP} parameters for $4s$ and $4p$. The absolute values of these constants are not that large that is the slopes in “core” and “valence” ranges almost coincide for $4s$ orbitals.

Similarly to using slopes, we used the intercepts b of the linear fits of the exponents and the boundary Z -values $Z_{n\ell}$ of the respective ranges to estimate the constant screening contributions $S_{\text{MAP}}^{(\text{ref})} = S_{n\ell}(Z_{n\ell})$ which are, respectively, given by expressions $\sigma_{\text{MAP}}Z_{n\ell} - n_{\text{MAP}}^*b$ and $-n_{\text{MAP}}^*b$ for the valence and core ranges and assembled in the respective columns of Table 1. We see that in all cases the constant screening estimated from the fits of the MAP exponents follow the trends similar to those prescribed by the Slater rules and have close numerical values. A deeper analysis of the trends described by the quantities n_{MAP}^* , σ_{MAP} and $S_{\text{MAP}}^{(\text{ref})}$ ultimately reduces to that of the electron–electron interactions as described in the MAP basis. It will be performed elsewhere. Notice, however, that the determination of these quantities was not currently possible for the orbitals with $n = 5$ since for these latter no information about the behavior of the corresponding exponents in the core regime is available.

3.3 | Atomic radii

As we mentioned in Section 1, the proposed MAP setting [11] for the atomic orbital basis in its primitive form dating back to 1930s [10] has the advantage that its parameters—orbital exponents—have a direct physical significance. Thus, one can hope to relate them more or less directly to

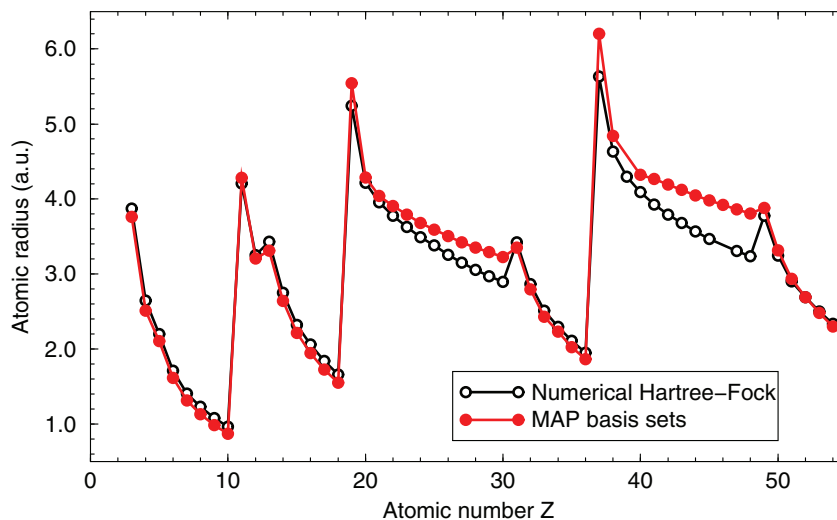


FIGURE 4 Atomic radii obtained from Bunge's (black open circles) and the MAP orbitals (red full circles), defined as the expectation value $\langle r \rangle$ of the outermost (partially) filled orbital or subshell. The respective interpolating lines are eyeguides

some observable characteristics of atoms and eventually those of molecules and crystals/materials. For instance atomic radii may be extracted. Experimentally, these are generally derived by fitting some data on interatomic separations observed in various contexts.

The MAP exponents provide already the size of an atom due to the asymptotically exponential decay of the electron density [20]. A simple measure for an atomic radius is the average radial position $\langle r \rangle$ of the most diffuse orbital. This quantity can be evaluated in any basis set, and we can compare directly orbitals of the Hartree-Fock limit to the MAP orbitals characterized by one single exponent. Figure 4 gives these data for all elements up to Xenon.

The coincidence is again quite striking, atomic radii obtained with the two orbital sets are nearly superposable, but for the 3d and 4d transition elements.

3.4 | Nodes of the radial MAP functions

Further investigation of the orbitals coming from the MAP setting, Equation (1), led us to an observation depicted in Figure 5 at the hand of the s orbitals of an Iodine atom. More generally, see Figure 6, it can be seen that for a given atom and given value of the azimuthal quantum number ℓ the positions of the nodes of the radial functions $R_{n\ell}(r)$ —the roots of the polynomials $P_{n\ell}(2\xi_{n\ell} r)$ —almost coincide for smaller values of n and for all nodes $k < n - \ell - 1$, counted from the origin, $r = 0$.

This behavior had already been conjectured in the literature [21] in a slightly different context, and, more recently, in a numerical study [22] of the outer spinors in a relativistic setting. It also comes up in the studies on ab initio Gaussian atomic basis sets [2, 6, 23] and may be a general property of all basis-set-expanded atomic orbitals representing, more or less realistic, the atomic one-electron states.

Additionally, we see that the positions of the nodes with the same number, as counted from the nucleus as functions of Z , follow fairly smooth curves, at least for 2s to 4s. They appear in groups, almost coinciding for the respective nodes, starting at the Z values at which further nodes for same ℓ and different n appear.

We observe an evident cusp for the third root of the 4s polynomial between $Z = 30$ and $Z = 31$, at the end of the first transition series. The 4s-exponent is almost constant in this range, but orthogonality has to be achieved with evolving 1s, 2s, and 3s exponents. Beyond $Z = 31$ the 4s exponent varies as well, which adds a different component to the orthogonality constraint, without successive fillings of inner shells. The same is observed for the 5s at $Z = 39$ (Y) and $Z = 48$ (Cd) for the filling of the 4d shell.

These results may be eventually understood by looking more in detail at the polynomials $P_{n\ell}(2\xi_{n\ell} r)$ which maintain the orthogonality between different functions of the same ℓ . Indeed, inspecting Table 1 closely, we see that at least for the core shells the slopes a of the linear relations $\xi_{n,\ell}(Z) \approx aZ + b$ are fairly close to inverse integers $1/n_{\text{MAP}}^*$. The higher Z , the smaller the effect of b , and the ratios $\xi_{n,\ell}(Z)/\xi_{n',\ell}(Z)$ are close to the ratios of the corresponding integers, that is, the exponents themselves can be represented as $\xi_{n,\ell} = Z_\ell^*/n$ through some effective Z_ℓ^* . It is, however, known from our previous work [11] that for the exponents inversely proportional to integers the recurrent relations between the coefficients $a_{n\ell}$, $b_{n\ell}$, $c_{n\ell}$, ... Equation (2) of the polynomials $P_{n\ell}$ Equation (1) transform to those of the Laguerre polynomials, that is, the MAP polynomials approach the Laguerre ones in the limit of large Z . As a consequence, the nodes of the MAP polynomials flow to the corresponding nodes of the (associated) Laguerre polynomials. For small values of the argument the Laguerre polynomials can be (asymptotically) approximated through Bessel functions of the first kind [24, 25], which we summarize in

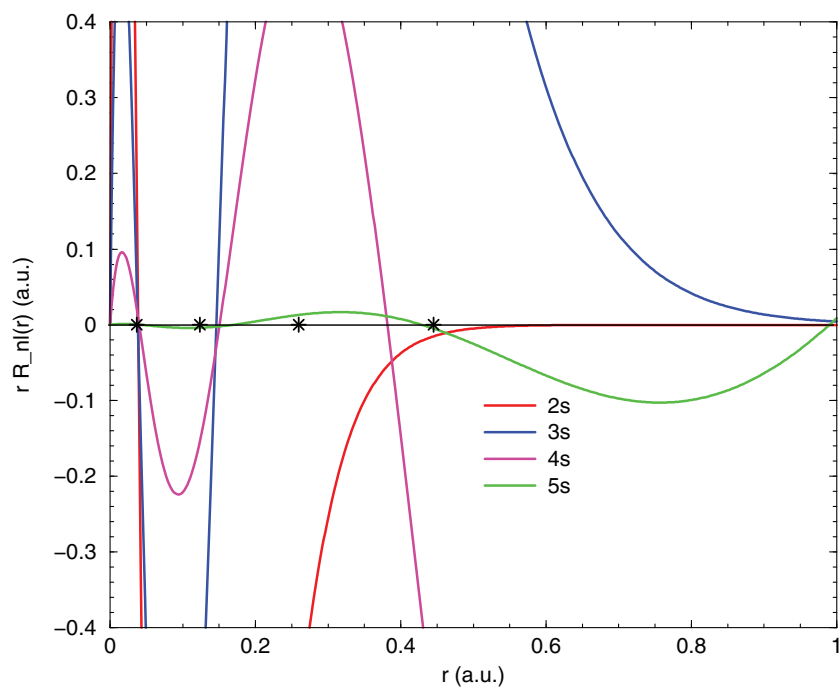


FIGURE 5 Plot of the different radial functions of s symmetry for a Iodine atom ($Z = 53$). We clearly see the close coincidence of the first and the second orbital node. Black stars correspond to the estimates described by Equation (7), see Section 3.4

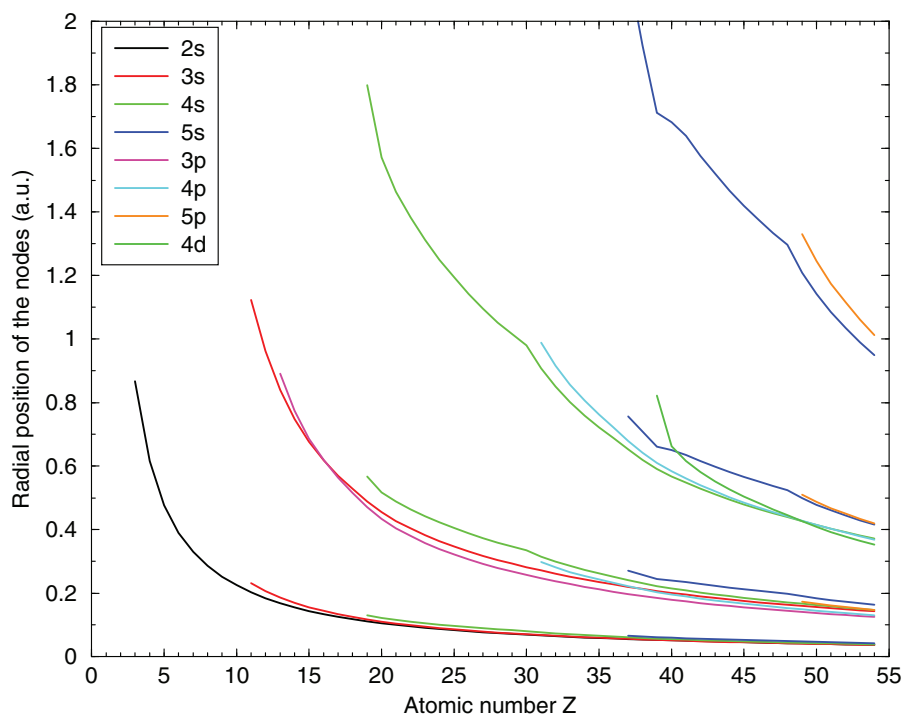


FIGURE 6 Position of the nodes of the radial functions 2s to 5p. Multiple lines of the same color refer to the subsequent nodes counted from the origin, $r = 0$, of the same orbital

$$P_{n\ell}(2\xi_{n\ell}r) \xrightarrow[Z \rightarrow \infty]{} L_{n-\ell-1}^{2\ell+1}\left(\frac{2Z_\ell^*r}{n}\right) \xrightarrow[\text{small } r]{} \frac{J_{2\ell+1}(2\sqrt{2Z_\ell^*r})}{(2Z_\ell^*r)^{\frac{2\ell+1}{2}}} \quad (6)$$

From this we can immediately read an estimate for the positions of the roots of the MAP polynomials:

$$r_{n\ell}(k) \approx \frac{j_{2\ell+1,k}^2}{8Z_\ell^*}, \quad (7)$$

where $j_{2\ell+1,k}$ is k -th root of the Bessel function $J_{2\ell+1}$ of the first kind, independent of n and inversely proportional to the (effective) nuclear charge, corroborating the graphs of Figure 6.

The above estimate basically repeats the old observation based on the WKB treatment of the hydrogen atom (see Condon and Shortley [26]). For an iodine atom ($Z = 53$) we have the s exponents ξ_{1s} to ξ_{5s} as 52.6862, 25.2486, 14.8828, 8.1798, and 3.1897, respectively, fairly resembling the hydrogenic Z/n series 53, 26.5, 17.666, 13.25, 10.6, ultimately yielding the Laguerre polynomials. On the other hand, minimizing the quadratic deviation of the MAP exponents from Z_ℓ^*/n for a common Z_ℓ^* leads to a value of $Z_\ell^* = 49.845$.

The roots of the Bessel functions are tabulated and the expected positions of the nodes derived from them are: 0.036818, 0.123428, 0.259552, and 0.445178 Bohr from the origin, respectively. We find 0.0431757, 0.168321, 0.429621, 0.989825 Bohr as nodes of the $5s$ orbital which is fairly close for the first node, but more and more off for the subsequent ones. The expected positions are reported in Figure 5.

Of course, the reason for this result is that for the inner shells the screening is fairly correct, and as well the approximation of the Laguerre polynomial via a Bessel function. For the outer nodes, screening via the chosen Z_ℓ^* becomes quite wrong and the approximation through the Bessel function less reliable.

4 | CONCLUSIONS

Minimally parameterized exponential basis sets of the form Equation (1) originating yet from 1930s [10] are defined so that the correct nodal structure (the orthonormality) of the orbitals is maintained through a polynomial depending only on the exponential parameters. Within this setting each (sub)shell can be described by only one single parameter—its orbital exponent. Assuming this we recently explored [11] atoms of the second row of the periodic table, and extended the approach up to ($Z = 54$), that is, including the fifth period.

The (sub)shell-specific orbital exponents $\xi_{\text{MAP}}^{(n\ell)}$ are derived through optimizing the total energy written in the Hartree–Fock approximation. Overlaps of the obtained orbitals with the corresponding ones from purely numerical approaches or much longer expansions [16] are quite large ($>90\%$) and may serve as basis for atomic projection and subsequent analysis of the results of PAW/DFT calculations [27]. The details of the spatial structure of atomic states, like position of the nodes close to the nucleus or the asymptotic behavior for large r are fairly well reproduced.

Despite the restricted number of free parameters the proposed basis sets result in good total energies, and exponents follow simple piecewise linear relations as functions of the nuclear charge Z . The switches between different linear trends occur either at the end of rows of the periodic system or when within a row a new (sub)shell starts being filled. Our minimally parameterized basis sets are not intended to replace the modern ones designed for molecular applications with numerical precision. They, however, may serve as a set of physical parameters for more qualitative or semi-quantitative studies aimed at establishing and explaining trends in the chemical behavior.

5 | IMPLEMENTATION

From a given set of exponents, the linear equations to obtain the coefficients of the polynomials are solved, and a corresponding input for Clementi's atomic Hartree–Fock program [28] is produced. The procedure is easily embedded into a simplex algorithm, as described in standard textbooks of numerical optimization problems [15]. Alternatively to Clementi's program, a local implementation in Moscow (I. Popov) was used [11], and another specific implementation in Paris of the equations presented in Roothaan and Bagus [13], the latter coupled to the CADNA numerical verification package [29], for assuring numerical accuracy of the results during the simple optimization procedure, leaving only numerically significant digits in the results. Either of the programs [13, 28] runs smoothly for the atoms up to $Z = 54$ (Xe, $5s^25p^6$) giving (exactly) the same result as the gradient optimization procedure [11] when it goes about the second period thus confirming the mutual consistency of either protocol.

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AUTHOR CONTRIBUTIONS

Peter Reinhardt: Software; writing manuscript; data production. **Ilya Popov:** Data curation; formal analysis; methodology; software. **Andrei Tchougréeff:** Conceptualization; formal analysis; methodology; project administration; software; writing-original draft.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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