

All-electron scalar relativistic basis sets for the 6p elements

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Received: 28 August 2012 / Accepted: 5 October 2012
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Abstract New segmented all-electron relativistically contracted (SARC) basis sets have been developed for the elements $_{81}\text{Ti}$ – $_{86}\text{Rn}$, thus extending the SARC family of all-electron basis sets to include the 6p block. The SARC basis sets are separately contracted for the second-order Douglas–Kroll–Hess and the zeroth-order regular approximation scalar relativistic Hamiltonians. Their compact size and segmented construction are best suited to the requirements of routine density functional theory (DFT) applications. Evaluation of the basis sets is performed in terms of incompleteness and contraction errors, orbital properties, ionization energies, electron affinities, and atomic polarizabilities. From these atomic metrics and from computed basis set superposition errors for a series of homonuclear dimers, it is shown that the SARC basis sets achieve a good balance between accuracy and size for efficient all-electron scalar relativistic DFT applications.

Keywords All-electron basis sets · Scalar relativistic calculations · DKH · ZORA · SARC

1 Introduction

The wide availability of scalar relativistic Hamiltonians in general-purpose quantum chemistry software, in combination

with algorithmic advances related to the efficient use of density functional theory (DFT), has increased the potential for scalar relativistic all-electron DFT calculations of heavy element systems. Scalar relativistic effects lead to contraction of orbitals with small angular momenta and expansion of orbitals with large angular momenta. These effects can be treated adequately with one of the widely available scalar relativistic Hamiltonians, the Douglas–Kroll–Hess (DKH) [1–5] and the zeroth-order regular approximation (ZORA) [6–8].

The relativistic contraction of the inner shells implies that the use of non-relativistic atomic basis sets is inappropriate owing to the absence of functions that can properly describe this effect. Hence, the development of all-electron basis sets adapted to the potential described by the scalar relativistic Hamiltonians is necessary. It should be noted that scalar relativistic calculations, even when significant spin–orbit coupling effects are expected, can serve as an attractive starting point for more elaborate treatments, especially given the negligible overhead of methods such as ZORA and DKH2 compared to standard non-relativistic calculations.

Even though effective core potentials have earned their well-deserved place in the quantum chemistry arsenal [9, 10], all-electron calculations are required in several cases. These include, for example, applications where inner-shell spectroscopic properties are being probed [11] and where topological analysis of electron densities [12, 13] is performed. In the latter case, the replacement of the core electrons by an effective potential may create topological inconsistencies and artifacts that extend into the bonding region [14]. All-electron calculations are also desirable in general as a confirmation that a particular ECP converges correctly to the all-electron limit for all spin states involved [15].

Electronic supplementary material The online version of this article (doi:10.1007/s00214-012-1292-x) contains supplementary material, which is available to authorized users.

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A family of segmented all-electron relativistically contracted (SARC) basis sets adapted to the two most popular scalar relativistic Hamiltonians has been developed in the recent years for the third-row transition metals [16], the lanthanides [17] and the actinides [18]. In the present paper, we propose an extension of the SARC basis set family to the 6*p* elements, $_{81}\text{Ti}$ – $_{86}\text{Rn}$.

Among the existing all-electron basis sets for 6*p* elements, it is worth mentioning the basis sets of Dyll [19–22], which can be used in spin-dependent relativistic treatments. Several basis sets that include the 6*p* block are available for four-component calculations [23–28]. Although they are adapted to an altogether different theoretical approach, it is worth noting that such basis sets can in principle be used in scalar relativistic calculations if they have been constructed with the same exponents for each spin–orbit component (“*l*-optimized” basis sets).

Following the atomic natural orbital approach, whereby a guiding factor in the construction of the basis set is the natural orbital occupation numbers, Roos et al. [29] have constructed ANO basis sets with relativistic core correlation (ANO-RCC) based on DKH atomic densities. The Sapporo basis sets [30, 31] follow the correlation-consistent approach instead, whereas Laikov has proposed an alternative family of basis sets [32, 33] using a method based on a spin-free four-component one-electron scalar relativistic approximation to the Dirac Hamiltonian [34]. Most of the above-mentioned basis sets have a generally contracted form, which can be a drawback for most general-purpose quantum chemistry programs as it amplifies the cost of two-electron integral generation. At the same time, such basis sets are geared toward correlated post-Hartree–Fock calculations, which require fairly extensive high angular momentum spaces in order to recover a sufficient part of the correlation energy. Neither of these characteristics is beneficial for routine DFT calculations.

In this work, we target the “middle-ground” of scalar relativistic DFT and construct SARC basis sets for the 6*p* elements. The SARC basis sets have a computationally favorable segmented contraction and a compact set of polarization functions that serve the requirements of relatively fast-convergent DFT and do not have to double as correlation functions for post-Hartree–Fock approaches. Exponents of the Gaussian primitives are derived from the same simple rules that were introduced in previous reports [16–18]. Contraction coefficients are determined separately for the ZORA and DKH2 schemes, since these two approximations produce different potentials close to the nucleus and hence differently shaped core orbitals [16]. The quality of construction of the new basis sets is evaluated for a range of atomic and molecular properties and

shown to fulfill the twin goal of accuracy and efficiency. All SARC basis sets are incorporated in the basis set library of the freely available ORCA program package [35].

2 Methodology

The starting point for the construction of the SARC basis sets is a set of radial expectation values for the innermost atomic orbital per angular momentum quantum number. These values are obtained from atomic ground-state restricted open-shell Hartree–Fock (ROHF) calculations with Zerner’s spin-averaged (SA) formalism [36, 37]. SA-ROHF averages over all states of a given spin for a given configuration and therefore produces degenerate orbitals that are more appropriate for our purposes than the configuration-averaged (CA) variant, which averages over all states regardless of spin [37]. The basis set used for these calculations was the universal Gaussian basis set (UGBS) of de Castro and Jorge [38, 39]. Exponents from the UGBS were employed in a completely uncontracted (33*s*27*p*19*d*15*f*) form corresponding to 314 basis functions per atom, which is a sufficiently large basis set to be used as reference for benchmarking purposes. The $6s^26p^n$ ($n = 1$ –6) Hund configurations were assumed for Ti – Rn .

In line with the procedure described in detail elsewhere [16, 17], SA-ROHF/UGBS radial expectation values $\langle r_l \rangle$ of the radially most contracted *s*, *p*, *d*, and *f* orbitals were employed in deriving the exponents α_l of the tightest *s*, *p*, *d*, and *f* functions according to Eq. 1:

$$\alpha_l = k_l \frac{2f_l^2}{\pi \langle r_l \rangle^2} \quad (1)$$

where $f_l = 1, 4/3, 8/5$, and $64/35$ ($l = s, p, d, f$) and k_l is a scaling factor that adjusts the steepness of the generator exponent for each angular momentum. Calibration calculations led to the scaling factors of 25,000, 5,000, 250, and 250 for *s*, *p*, *d*, and *f* functions, respectively. These factors produce exponents that are tight enough to capture the essential effects of the ZORA and DKH2 scalar relativistic Hamiltonians near the core, without introducing numerical instabilities [40]. Nevertheless, we have observed that the use of a finite nucleus model in certain cases facilitates SCF convergence. Gaussian primitives were subsequently obtained in an even-tempered manner from the series $\alpha_l x_l^{-i}$ ($i = 1, 2, \dots$), where the adjustable parameter x_l dictates the spacing and, depending on the cutoff, the number of primitive functions. The coefficients for the final contraction were determined separately for the DKH2 and ZORA scalar relativistic Hamiltonians.

3 Results and discussion

3.1 Basis set parameters

The SA-ROHF/UGBS radial expectation values of the first s , p , d , and f orbitals for each atom are listed in Table 1. A regular and smooth contraction is observed as the series is traversed from thallium to radon. According to Eq. 1, these values lead to the generating primitive exponents listed in Table 2, which likewise become progressively steeper from the lighter to the heavier element.

With the goal of achieving a balance between efficiency and accuracy, the primitive spacing parameter x_l was separately adjusted to 2.20, 2.40, 2.50, and 2.70 for angular momentum $l = s, p, d$ and f , respectively. These values were found to represent a reasonable compromise between a small enough number of primitives and a reasonably accurate description of all angular spaces to minimize errors with respect to the UGBS reference. Calibration calculations showed that it is adequate to terminate the series with one additional function after the limit of 0.02 for s , 0.04 for p , 0.06 for d , and 0.2 for f functions. These cutoffs ensure that the outer primitives are sufficiently diffuse to be useful in the description of the anionic states of the $6p$ elements, without being so small as to create convergence instabilities due to linear dependencies in actual calculations. If a given application requires more diffuse functions, these can be easily added by, for example, extending the primitive series using the aforementioned generating parameters or an empirically adjusted scaling factor.

With the above cutoff values, 244 primitive functions were obtained in total, constituting a $(29s21p15d11f)$ uncontracted set. For generality, this set is common to both scalar relativistic Hamiltonians. Adaptation to the DKH and ZORA Hamiltonians is achieved at the contraction stage. This involved creating contracted Gaussian-type functions (CGTFs) from the innermost eight s , eight p , seven d , and eight f primitives to create the final basis sets with a $[22s14p9d4f]$ contracted pattern and 137 basis functions. The final basis sets can be considered of triple- ζ

Table 1 Radial expectation values of innermost orbitals (in Bohr) determined from spin-averaged ROHF calculations

	$\langle r_s \rangle$	$\langle r_p \rangle$	$\langle r_d \rangle$	$\langle r_f \rangle$
Tl	0.018687	0.066456	0.164479	0.455385
Pb	0.018457	0.065592	0.162018	0.442489
Bi	0.018233	0.064751	0.159629	0.430420
Po	0.018014	0.063930	0.157309	0.419089
At	0.017800	0.063130	0.155054	0.408427
Rn	0.017592	0.062350	0.152862	0.398370

Table 2 Maximum exponents per angular momentum (in Bohr⁻²) used in the SARC basis sets

	α_s	α_p	α_d	α_f
Tl	45,576,498.90053	1,281,324.72218	15,060.49281	2,566.17665
Pb	46,719,469.98286	1,315,303.13035	15,521.49550	2,717.93479
Bi	47,874,457.72036	1,349,691.89716	15,989.55992	2,872.49383
Po	49,045,573.23256	1,384,580.43880	16,464.66719	3,029.92213
At	50,231,960.32442	1,419,894.31995	16,947.05146	3,190.17937
Rn	51,426,823.38371	1,455,642.35861	17,436.56857	3,353.28711

quality in the valence space, with the outer ($2df$) primitives acting as polarization functions.

The importance of separate adaptations for DKH2 and ZORA in terms of contraction coefficients is clearly revealed when the ZORA-contracted basis sets are used with the DKH2 Hamiltonian and vice versa. A DKH2 calculation for bismuth using the SARC–ZORA basis set results in atomic ground-state energy that is $1.56 E_h$ higher than obtained with the appropriate DKH-contracted basis set. The inverse situation is even more pronounced, since a ZORA calculation for Bi using the SARC–DKH basis sets results in an energy difference exceeding $2.35 E_h$.

To balance the present basis sets in molecular calculations, the corresponding SARC basis sets are recommended for elements heavier than Xe [16–18], while the all-electron DKH2 or ZORA reconstructions of the def2-TZVP basis sets [41] should be sufficient for lighter elements [16]. All basis sets are available as part of the ORCA basis set library [35].

3.2 Truncation errors

In the following evaluations, we focus on comparisons between SARC and UGBS results in order to verify that the significant truncation of the one-particle basis set does not introduce significant errors in the SARC basis sets with respect to the large UGBS reference. First of all, in Table 3 spin-averaged ROHF–DKH2 and ROHF–ZORA total electronic energies obtained with the uncontracted UGBS and the SARC basis sets are compared, the former taken as a close-to-basis-set-limit reference. The energy difference, which is interpreted as a numerical estimate of the incompleteness error, rises for both Hamiltonians from Tl to Rn. In both cases, the energy differences span a narrow range between 0.5 and $0.7 E_h$. These values are particularly encouraging because they confirm that the size reduction in the SARC basis sets for the $6p$ elements does not introduce any significant or unsystematic errors. To put these numbers in perspective, it is noted that the corresponding incompleteness error ranges for the lanthanide and actinide SARC basis sets compared to the UGBS reference were 1.07 – $3.98 E_h$ and 1.01 – $2.26 E_h$, respectively [17, 18].

Table 3 Estimated incompleteness and contraction errors (in E_h) from comparison of the UGBS (314 functions) and SARC basis sets (137 functions), obtained from spin-averaged ROHF calculations

	UGBS	SARC	ΔE_{inc}	ΔE_{contr}
<i>DKH2</i>				
Tl	−20,226.36054	−20,225.80788	0.553	0.016
Pb	−20,861.64861	−20,861.06725	0.581	0.018
Bi	−21,509.82175	−21,509.21147	0.610	0.020
Po	−22,170.96133	−22,170.32210	0.639	0.021
At	−22,845.34781	−22,844.67987	0.668	0.023
Rn	−23,533.17975	−23,532.48361	0.696	0.025
<i>ZORA</i>				
Tl	−21,002.93783	−21,002.37621	0.562	0.012
Pb	−21,686.18488	−21,685.60684	0.578	0.013
Bi	−22,384.23670	−22,383.64504	0.592	0.014
Po	−23,097.88356	−23,097.28190	0.602	0.015
At	−23,827.52369	−23,826.91657	0.607	0.017
Rn	−24,573.49273	−24,572.88565	0.607	0.018

A part of the incompleteness error arises from the contraction of the innermost primitive Gaussian-type functions in the SARC basis sets. To quantify this contraction error, additional calculations were performed with the fully uncontracted (29s21p15d11f) SARC basis sets. The energy difference between contracted and uncontracted forms ranges from 0.016 to 0.025 E_h for the DKH2 contraction and from 0.012 to 0.018 E_h for the ZORA contraction. These values again compare favorably with the corresponding contraction errors of previously reported SARC basis sets, which were up to five times greater than those of the present 6p basis sets [17, 18]. Given that the contraction error constitutes only 2.1–3.6 % of the total incompleteness error, the proposed contraction pattern is expected to retain sufficient flexibility despite the significant reduction in size compared to the uncontracted basis. An even more aggressive contraction might be possible, but the present scheme already appears to be a good compromise between cost and accuracy.

3.3 Orbital properties

As an additional evaluation metric, the energies and the radial expectation values for atomic orbitals are compared between the UGBS and SARC basis sets. Being in the middle of the series, bismuth serves as a representative example of the overall agreement between the UGBS and SARC basis sets in terms of orbital energies and radial extents (Table 4). As a consequence of the reduction of primitives and of the contraction, and as anticipated based on our previous experience with the SARC basis sets,

Table 4 Orbital energies (E_h) and radial expectation values (Bohr) for bismuth: comparison between UGBS and SARC basis sets from spin-averaged ROHF calculations

	UGBS		SARC		ΔE	$\Delta \langle r \rangle$
	E	$\langle r \rangle$	E	$\langle r \rangle$		
1s	−3,336.8298	0.0149	−3,336.9143	0.0149	−0.0845	0.0000
2s	−606.0118	0.0656	−606.0825	0.0656	−0.0707	0.0000
2p	−521.8633	0.0599	−521.9311	0.0599	−0.0678	0.0000
3s	−149.0181	0.1708	−149.0634	0.1708	−0.0453	0.0000
3p	−124.4357	0.1726	−124.4709	0.1726	−0.0352	0.0000
3d	−98.1761	0.1575	−98.2147	0.1575	−0.0386	0.0000
4s	−35.6649	0.3771	−35.6898	0.3771	−0.0249	0.0000
4p	−27.4213	0.4004	−27.4360	0.4006	−0.0147	−0.0002
4d	−17.4755	0.4214	−17.4850	0.4216	−0.0095	−0.0002
5s	−6.6647	0.8417	−6.6701	0.8414	−0.0054	0.0003
4f	−6.5895	0.4396	−6.5993	0.4398	−0.0098	−0.0002
5p	−4.2425	0.9525	−4.2437	0.9526	−0.0012	−0.0001
5d	−1.3103	1.2260	−1.3096	1.2265	0.0007	−0.0005
6s	−0.6762	2.2519	−0.6768	2.2508	−0.0006	0.0011
6p	−0.3174	2.9974	−0.3174	2.9975	0.0000	−0.0001

[16–18], energy differences are most pronounced for the chemically inert core orbitals. Nevertheless, they are well controlled and less than 0.1 E_h even for the innermost s orbitals. It is unlikely that such errors are chemically relevant for molecular calculations [42, 43]. Agreement with the UGBS reference improves fast toward the semi-core region, and the energies for the valence shells predicted by the two basis sets are essentially the same. Importantly, radial expectation values practically coincide for all orbitals, showing that the reduced size of the SARC basis affects neither the reproduction of scalar relativistic effects nor the description of the chemically important valence space.

3.4 Atomic properties

The first ionization energy (IE) and the electron affinity (EA) are crucial indicators of the quality of a basis set because they are sensitive to basis set incompleteness in the valence region. Thus, comparison between values computed with the SARC basis sets and those computed with the UGBS reference basis set serve to highlight potential deficiencies in the former. For this purpose, IE and EA values were computed with both basis sets using the mainstream B3LYP functional with the DKH2 Hamiltonian, a representative example of a scalar relativistic DFT setup. Table 5 summarizes the results obtained with the two basis sets for the first ionization energies of Tl–Rn and the electron affinities of Tl–At. Almost perfect coincidence between the UGBS and SARC values is witnessed for the ionization energies, while the electron affinities computed with the SARC basis sets tend to be slightly greater in

Table 5 B3LYP-DKH2 results with the SARC and UGBS basis sets for the first ionization energy and electron affinity (eV) of the 6*p* elements

	B3LYP/ UGBS		B3LYP/ SARC		CASPT2/ANO- RCC ^a		Expt. ^b	
	IE	EA	IE	EA	IE	EA	IE	EA
Tl	5.41	0.16	5.41	0.21	5.47	0.34	6.11	0.20
Pb	6.94	1.13	6.94	1.16	7.12	1.40	7.42	0.36
Bi	8.49	0.91	8.49	0.92	8.87	0.66	7.29	0.95
Po	8.41	1.94	8.41	1.95	8.21	1.81	8.43	1.9?
At	10.00	3.05	10.00	3.05	9.92	3.04	9.54	2.82
Rn	11.63		11.64		11.69		10.75	

CASPT2/ANO-RCC and experimental values are provided for comparison

^a From Ref. [29], without inclusion of spin–orbit coupling

^b Reproduced from Ref. [29]

magnitude than the UGBS values. Still, the EA differences between the two basis sets are only 0.02 eV on average and therefore too small to be considered of consequence.

These comparisons serve as an internal benchmark to confirm that UGBS values are accurately reproduced by the SARC basis sets and that no defects have been inadvertently introduced in the construction of the latter. B3LYP-DKH2 results are not, in principle, expected to compare favorably with experiment for these properties, not only because of the intrinsic limitations of the method but also because the ionization energies and electron affinities of the 6*p* elements are severely affected by spin–orbit coupling. Thus, comparison of the B3LYP values with the experimental ones in Table 5 yields a mean absolute deviation (MAD) of 0.62 eV for the ionization energies, with individual deviations ranging from underestimation of the IE of Tl by 0.70 eV to overestimation of the IE of Bi by 1.20 eV. For electron affinities, the MAD of B3LYP is 0.22 eV, with the largest difference observed for Pb.

It is illuminating, however, to compare these results with the corresponding CASPT2 values by Roos et al. [29], obtained with the generally contracted all-electron ANO-RCC basis sets. The two methods, B3LYP and CASPT2, turn out to be surprisingly similar for absolute IE and EA values, while they also mirror each other in terms of the individual trends for each quantity and each atom. As shown by Roos et al. [29], deviations from experiment can be attributed largely—but not exclusively—to spin–orbit coupling, since a treatment of spin–orbit coupling by the restricted active space state interaction approach (RASSI-SO) [44] reduced the MAD values of CASPT2 for ionization energies and electron affinities from 0.68 and 0.36 eV, respectively, to 0.16 and 0.30 eV.

In conclusion, the SARC basis sets are sufficiently flexible to reproduce the results of the much larger UGBS basis

set for the atomic properties of the 6*p* series considered here. Comparison of the B3LYP with the CASPT2 calculations demonstrates that the accuracy of predicted properties is unlikely to be affected by the basis set, but rather that other considerations such as non-scalar relativistic effects and the treatment of electron correlation may become dominant. B3LYP-ZORA produces similar behavior to the results discussed above. It is stressed, however, that DFT calculations with ZORA appeared to be more sensitive to the integration accuracy compared with the DKH2 Hamiltonian. Hence, if ZORA is employed instead of DKH2, it is advisable to use larger radial integration grids and to verify that a particular setting ensures convergence of the computed energy to the desired precision.

3.5 Electric properties

As a measure of the tendency of the atomic charge distribution to distort in response to an external electric field, atomic polarizabilities are indicative of the ability of the basis set to model the response to an external perturbation such as, for example, an approaching ion. To test how the SARC basis sets perform in this respect, two closed-shell species were selected from the opposite ends of the series, Tl⁺ and Rn. The polarizabilities were computed by solving the coupled-perturbed SCF equations analytically at the B3LYP-DKH2 level. The SARC values are 20.36 and 34.89 a.u. for Tl⁺ and Rn, respectively. These deviate negligibly from the UGBS values of 20.39 and 34.70 a.u., showing that the SARC basis sets are sufficiently flexible for such properties. It is noted that considering the simplicity of the present theoretical approach, the computed atomic polarizability of Rn is also in good agreement with the previously recommended values of 34.60 a.u. [45] and 33.18 a.u. [46] for this atom.

3.6 Basis set superposition errors

Incompleteness of a given basis set in the valence region is the source of the well-known basis set superposition error (BSSE). This is observed as a spurious energetic stabilization in a system composed of two subunits and is caused by the compensation of the basis set incompleteness of each subunit by valence basis functions of the other. A typical approach to mitigate the BSSE effects is the counterpoise correction method (CPC) of Boys and Bernardi [47]. Here we employ the CPC method in studying the 6*p* homonuclear diatomic molecules, with the purpose of quantifying the BSSE that might be expected to arise from valence incompleteness in the SARC basis sets. Scans of the potential energy surface for each diatomics were performed using the PBE0 hybrid functional [48, 49] with the DKH2 Hamiltonian and a Gaussian finite nucleus model [50].

Table 6 Bond lengths r (Å) and dissociation energies D_e (eV) of homonuclear diatomics computed with the PBE0 density functional and the DKH2 Hamiltonian using a finite nucleus model, without and with BSSE counterpoise corrections (CPC)

	PBE0/SARC		PBE0/SARC + CPC		Δr	ΔD_e
	r	D_e	r	D_e		
Tl ₂	3.116	1.19	3.118	1.19	0.002	0.00
Pb ₂	2.890	1.56	2.891	1.56	0.001	0.00
Bi ₂	2.605	2.27	2.606	2.27	0.001	0.00
Po ₂	2.710	2.68	2.711	2.68	0.001	0.00
At ₂	2.835	1.85	2.835	1.85	0.000	0.00

The electronic states were assumed to be the same as those of lighter p -block dimers, that is, $^3\Pi_u$ for Tl₂, $^1\Sigma_g^+$ for Pb₂, $^1\Sigma_g^+$ for Bi₂, $^3\Sigma_g^-$ for Po₂, and $^1\Sigma_g^+$ for At₂.

The optimized bond lengths and the dissociation energies for all dimers are summarized in Table 6. The trend in computed bond lengths is the same as for the diatomics of the lighter p elements [29]. Starting from the longest bond that is always observed for the group 13 diatomic, the bond lengths become shorter moving to the heavier diatomics until the minimum of the block is reached in group 15. Beyond this point, the homonuclear bond lengths increase slightly. In terms of the construction of the SARC basis sets, the most important observation is that the average BSSE for bond lengths is only 0.001 Å, while the error in computed dissociation energies is essentially zero (<0.01 eV). The neglect of spin–orbit coupling is again expected to be the largest source of error in terms of comparisons with experiment, but this issue will not be pursued here. For the present purposes, the comparison of uncorrected and counterpoise-corrected values is sufficient to conclude that no serious BSSE effects are expected to arise from the valence space of the SARC basis sets in molecular DFT applications.

4 Conclusions

Segmented all-electron relativistically contracted basis sets have been constructed for the $6p$ elements, $_{81}\text{Tl}$ – $_{86}\text{Rn}$, to enable efficient all-electron scalar relativistic DFT calculations with the DKH and ZORA Hamiltonians. These basis sets extend the recently reported SARC basis set family for the $5d$, $4f$, and $5f$ series [16–18]. The $6p$ basis sets follow a $(29s21p15d11f)/[22s14p9d4f]$ contraction that was found to adequately address the need for moderate size and polarization. The exponents are common for the DKH and ZORA Hamiltonians, but the coefficients are separately optimized so that they best reflect the differences of each Hamiltonian.

Compared with the reference UGBS basis sets, the SARC basis sets showed total incompleteness errors smaller than $0.7 E_h$, while the contraction errors for either Hamiltonian were very well controlled and smaller than $0.025 E_h$. The orbital energies and radial expectation values for the semi-core and valence orbitals essentially coincided with the reference UGBS values, indicating that a high degree of flexibility is retained by the SARC basis sets in this region. The good performance of the basis sets in DFT calculations is also confirmed in calculations of ionization energies, electron affinities, and atomic polarizabilities. Finally, evaluation of basis set superposition errors in a series of $6p$ diatomic molecules demonstrated that the errors in computed equilibrium bond lengths and in dissociation energies are practically negligible.

Acknowledgments We gratefully acknowledge financial support from the Max Planck Society.

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