BSSE-Correction Scheme for Consistent Gaussian Basis Sets of Double- and Triple-Zeta Valence with Polarization Quality for Solid-State Calculations

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Revised versions of our published pob-TZVP [Peintinger, M. F.; Oliveira, D. V. and Bredow, T., J. Comput. Chem., 2013, 34 (6), 451–459.] and unpublished pob-DZVP basis sets, denoted as pob-TZVP-rev2 and pob-DZVP-rev2, have been derived for the elements H—Br. It was observed that the pob basis sets suffer from the basis set superposition error (BSSE). In order to reduce this effect, we took into account the counterpoise energy of hydride dimers as an additional parameter in the basis set optimization. The overall performance, portability, and SCF stability of the resulting rev2 basis sets are significantly improved compared to the original pob basis sets. © 2019 Wiley Periodicals, Inc.

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Introduction

Quantum-chemical calculations in general strongly depend on the chosen set of basis functions. Standard methods employ either plane waves or atom-centered contracted Gaussian-type basis functions (CGFs). While a plane wave basis is suitable for all compounds, CGFs are not universal and have to be generated explicitly for each element in the periodic table. For molecular systems, there exists a large variety of standard basis sets for almost all elements of the periodic table.[1] The situation is different for solids since molecular basis sets cannot be used without modification due to linear-dependence issues. This lead to the development of individual basis sets for specific solids, which could not be easily transferred to other compounds. In our previous works, we developed consistent basis sets of triple-zeta quality for the elements H—Br, as well as double- and triple-zeta basis sets for Rb—I (with the exception of *Tc*) for solid-state calculations with the widely used crystalline-orbital code CRYSTAL,[2,3] which we denoted as pob-TZVP[4,5] and pob-DZVP,[5] respectively. The aim was to create a set of consistent Gaussian basis sets that are generally applicable for a wide range of solids. We started with the well-known Ahlrichs Def2-TZVP[6] basis sets and removed primitive Gaussians with small exponents that caused linear dependency in the SCF procedure. In a second step, we reoptimized the exponents of the remaining Gaussians. We were able to show that these basis sets provided not only stable and robust SCF convergence, but also on average better results for structural optimizations in the given test set of ionic insulators and semiconducting solids than the available CRYSTAL standard basis sets. Small atom-centered basis sets strongly suffer from basis set incompleteness error (BSIE), especially the basis set superposition error (BSSE). Effective correction methods, for example, the periodic geometrical correction scheme for the intermolecular and intramolecular BSSE by Brandenburg et al.,[7] compensate this inherent deficiency of finite basis sets to a certain degree. However, the effectiveness of these methods also depends on how well balanced the basis set is. Because some of our pob basis sets showed unreasonably high BSSE, we developed a modified optimization method to overcome this issue. Based on our experience with the original pob-TZVP basis set, we also modified certain optimization parameters, such as the threshold for the smallest value of orbital exponents, to achieve higher accuracy and better overall performance.

In this work, we hereby present a BSSE correction scheme and a revised version of our pob-TZVP basis sets for H—Br, which we denote as pob-TZVP-rev2. We also present basis sets of double zeta quality denoted as pob-DZVP-rev2 for H—Br, which are the revisions of our unpublished pob-DZVP basis sets.

Basis Set Optimization

Our new pob-TZVP-rev2-basis sets are based on the pob-TZVP[4] basis sets obtained in previous work. The pob-DZVP-rev2 basis sets are based on the def2-SVP[8,9] basis sets developed by the group of Ahlrichs. These consist of highly contracted Gaussians for core shells and three less contracted or primitive CGFs per valence shell. For every valence shell, there is at least one primitive or contracted polarization function of higher angular momentum.

The variational optimization procedure of the basis sets follows as described in our previous work. We first removed primitive functions with orbital exponents lower than 0.1. We then augmented the truncated basis sets until the number of

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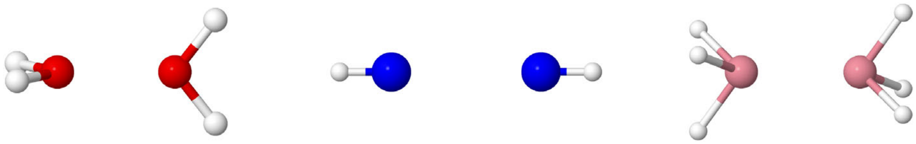

Figure 1. Molecular dimers for BSSE estimation: $(H_2O)_2$, $(NaH)_2$, and $(CoH_3)_2$ modeled using monomer reference structures by the group of Grimme.[10] Images were generated with Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org. [Color figure can be viewed at wileyonlinelibrary.com]

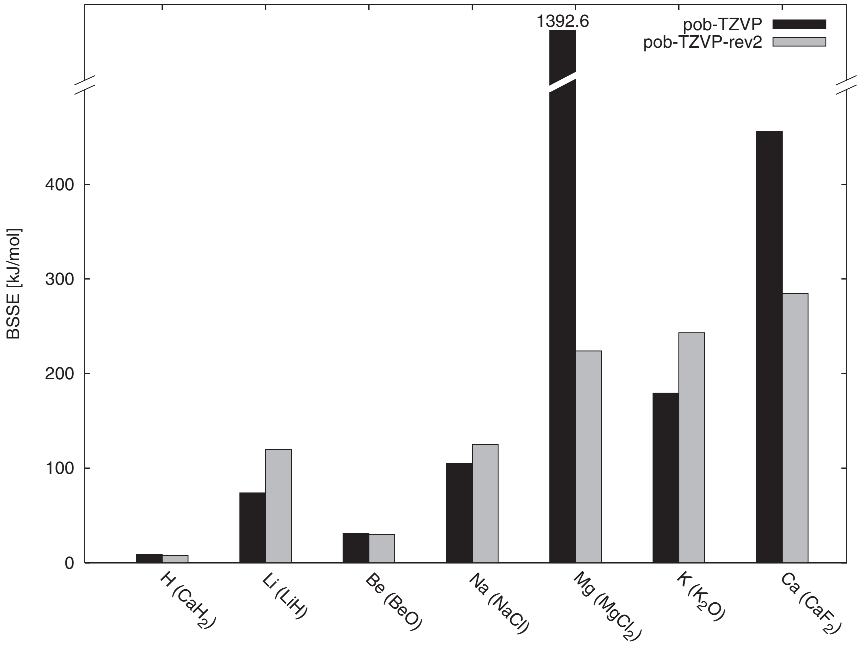

Figure 2. BSSE for the pob-TZVP and pob-TZVP-rev2 basis sets of *s*-block elements in selected systems.

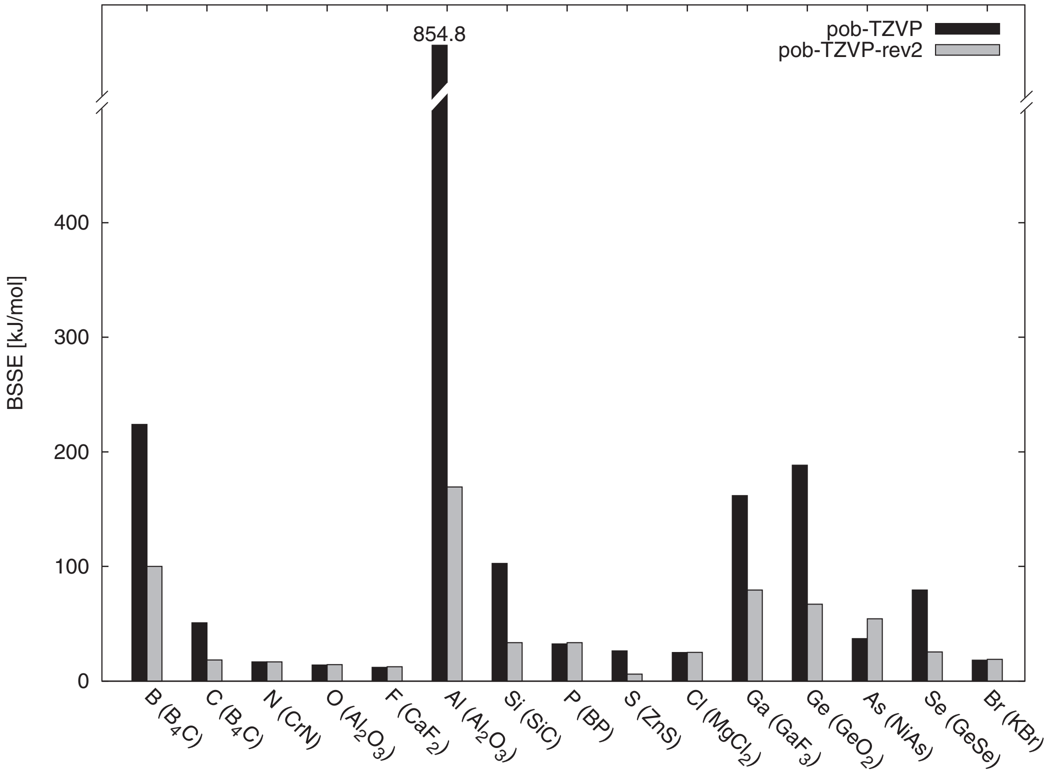

Figure 3. BSSE for the pob-TZVP and pob-TZVP-rev2 basis sets of *p*-block elements in selected systems.

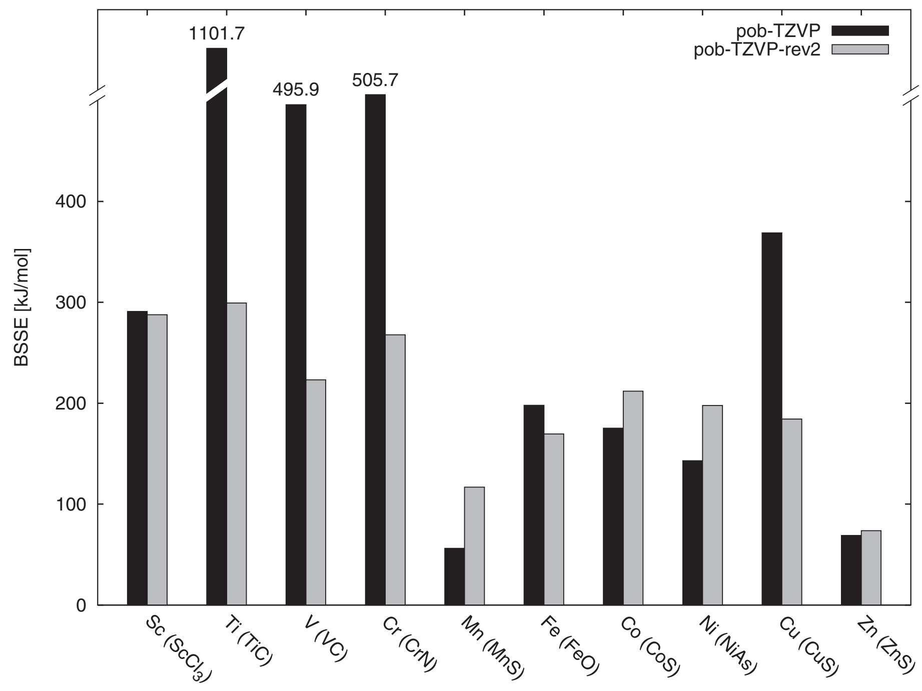

Figure 4. BSSE for the pob-TZVP and pob-TZVP-rev2 basis sets of *d*-block elements in selected systems.

basis functions matched the desired quality level. The starting values of the orbital exponents were chosen to be $\frac{1}{2}$ to $\frac{1}{3}$ of the orbital exponent of the next inner function. We observed that a lower limit of 0.15 for the orbital exponents assures numerical stability and provides good results at reasonable computational timings. Only in some cases, a lower threshold of 0.12 was chosen in order to improve results, while maintaining stability and performance.

In order to take BSSE effects into account, a set of artificial molecular hydride dimer structures (H_nA–AH_n) was calculated for A = Li—Br with the new basis sets using reference structures by the group of Grimme.[10] n was chosen according to the valence of element A. In the dimer structures, the hydrogen atoms from both AH_n monomers are at maximum distance in order to minimize contribution of the H-basis to the BSSE. Three examples are shown in Figure 1.

As both monomers are identical, a simplified counterpoise energy $E_{cp} = 2E(A)_{aa'} - 2E(A)_a$ was then calculated at different A–A distances between 1.4 Å and 5 Å fixing all angles, with $E(A)$ being the total energy, a the basis set at the position of A, and a' the ghost orbitals. The dimer structures and potential curves

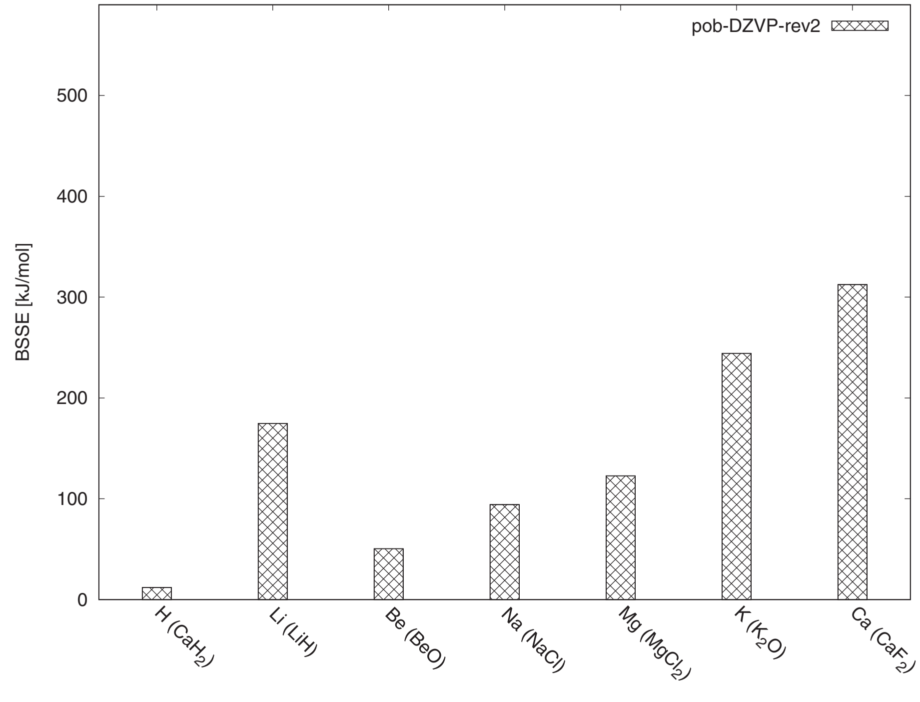

Figure 5. BSSE for the pob-DZVP-rev2 basis sets of *s*-block elements in selected systems.

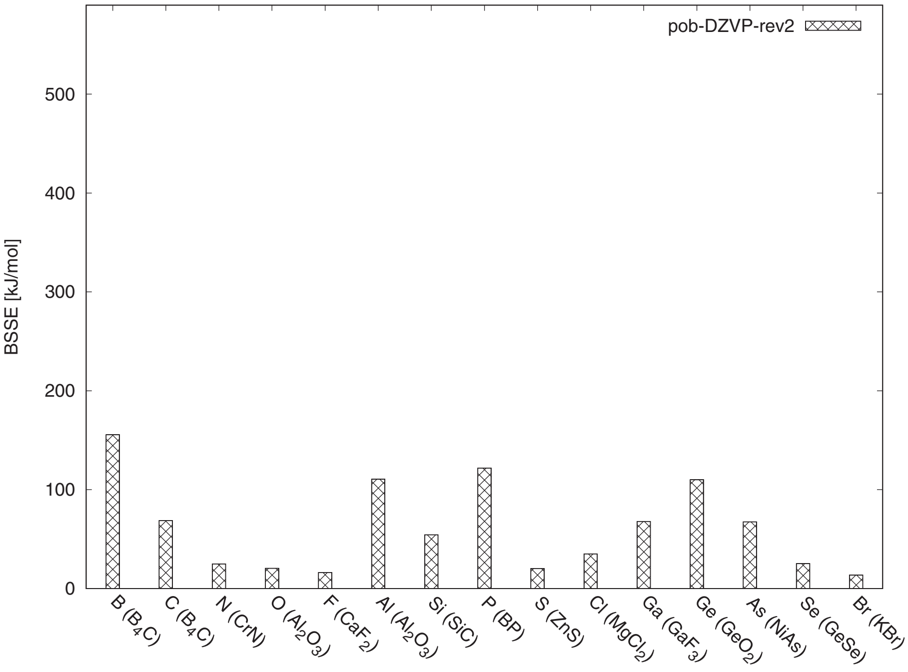

Figure 6. BSSE for the pob-DZVP-rev2 basis sets of *p*-block elements in selected systems.

are given in the Supporting Information to this article. If necessary, the basis set of the heavy atom was then reoptimized in order to minimize E_{cp}.

In a third step, we performed test calculations for other solids, which were not included in the original test set[4] and made further small adjustments if necessary to improve the SCF stability. Both the BSSE correction and the exponent readjustment for additional systems result in final basis sets, which are not fully variational for all reference systems but perform well in the considered range of binding situations at reasonable computational cost and with good SCF stability.

Computational Details

All quantum-chemical calculations of the crystalline systems were performed with the crystalline orbital program CRYSTAL17.[2] Basis set and structure optimizations were performed using the hybrid DFT functional PW1PW,[11] which has been shown to provide good structural results for ionic solid compounds. The correlation functional is PWGGA, whereas the exchange functional is a mixture of 20% Fock and 80% PWGGA exchange. The basis set optimizations were accomplished with a python-script, which runs single point calculations

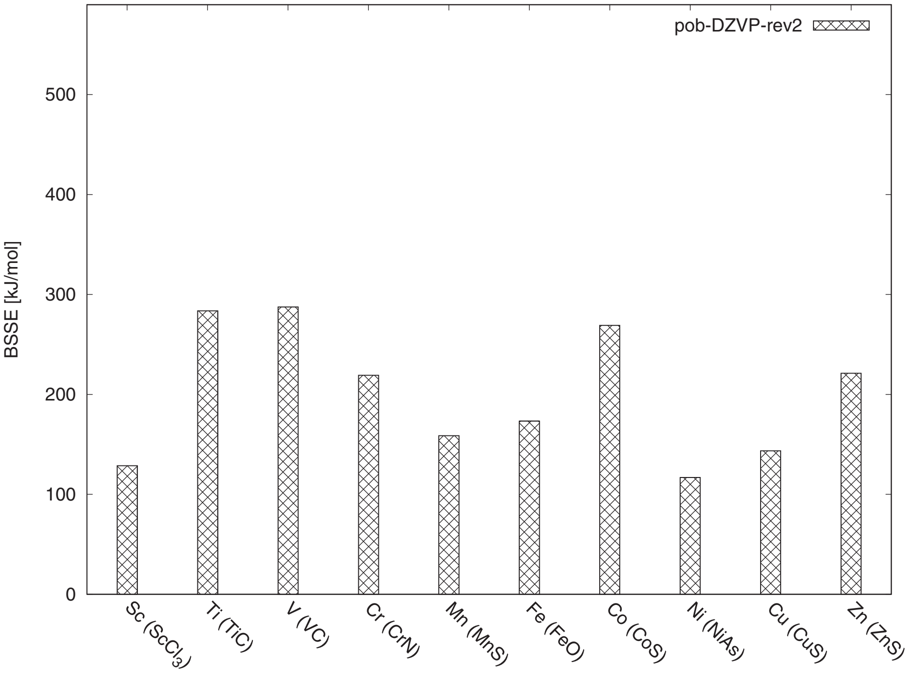

Figure 7. BSSE for the pob-DZVP-rev2 basis sets of *d*-block elements in selected systems.

Table 1. Mean and standard deviation of counterpoise energies of pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets in selected crystalline systems in kJ/mol.

		pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Mean	*s*-block	321.0	147.8	144.4
	p-block	130.4	46.9	64.2
	d-block	340.4	203.3	200.1
Standard deviation	*s*-block	495.9	106.8	106.8
	p-block	219.8	45.0	44.8
	d-block	311.9	72.1	64.9

Table 2. Experimental and calculated lattice parameters (Å) of selected ionic cubic solid compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	a			
Compound	Experiment	pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
LiF	4.027[17]	4.027	4.045	3.999
NaF	4.632 [18]	4.627	4.642	4.631
KF	5.347 [19]	5.364	5.367	5.303
CaF_2	5.463[20]	5.476	5.495	5.465
SiF_4	5.410[21]	5.587	5.361	5.248
LiCl	5.130 [22]	5.132	5.130	5.087
NaCl	5.640 [23]	5.662	5.616	5.612
KBr	6.570[24]	6.618	6.588	6.552
K_2O	6.436[25]	6.434	6.456	6.310
MgO	4.217[19]	4.204	4.209	4.186
CaO	4.811[26]	4.770	4.806	4.822
LiH	4.083[27]	4.037	4.044	4.043
NaH	4.890[28]	4.800	4.803	4.781
KH	5.704[29]	5.633	5.639	5.479
K_2S	7.407[30]	7.333	7.433	7.323

with CRYSTAL17 and uses the numerical minimization library MINUIT2, which is a part of the ROOT[12] project widely used in particle physics. The counterpoise energies for the molecular hydride dimers were obtained via MP2 calculations with ORCA 3.0.[13]

Results and Discussion

As in our previous works, we performed structural optimizations on binary and selected ternary ionic solids in order to test the stability, portability, and quality of our pob-TZVP-rev2 and pob-DZVP-rev2 basis sets. The evaluation of the results was carried out by comparison to experimental lattice parameters and results obtained with our previous basis set version, the pob-TZVP basis sets, which were already proven to perform on average better than the standard basis sets provided by the CRYSTAL basis set database[14] in the given test set. One has to keep in mind that the basis set limit can only give an account of the accuracy of the underlying theoretical approach, here the hybrid method PW1PW. This method has repeatedly demonstrated high accuracy for solid-state calculations.[15,16] Thus, we chose this procedure as reference and regard deviations from experiment as a quality measure of the basis sets.

BSSE in crystalline systems

In order to examine whether lowering the BSSE in artificial dimer systems at varying distances had a positive effect on the BSSE in the crystalline structure, we calculated the counterpoise energy for every basis set in a selected system using CRYSTAL's

Table 3. Experimental and calculated lattice parameters (Å) of selected ionic hexagonal solid compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	Experiment		pob-TZVP		pob-TZVP-rev2		pob-DZVP-rev2	
Compound	*a*	*c*	*a*	*c*	*a*	*c*	*a*	*c*
BeF_2	4.739	5.188[31]	4.748	5.165	4.769	5.221	4.748	5.217
$ScCl_3$	6.378	17.790[32]	6.387	17.874	6.370	17.889	6.348	17.476
$MgBr_2$	3.810	6.260[33]	3.832	6.616	3.823	6.460	3.838	6.467
$MgCl_2$	3.636	17.666[34]	3.598	17.530	3.632	17.699	3.643	16.989
BeO	2.697	4.378[35]	2.709	4.392	2.714	4.387	2.704	4.360
α-SiO_2	4.916	5.409[36]	5.004	5.484	4.968	5.468	4.920	5.439
B_2O_3	4.336	8.340[37]	4.375	8.713	4.363	8.591	4.329	8.183
Al_2O_3	4.754	12.990[19]	4.783	12.994	4.764	12.931	4.813	13.069
$NaNO_3$	5.070	16.822[38]	5.117	16.756	5.105	16.845	5.099	16.297
$MgCO_3$	4.633	15.018[39]	4.655	14.891	4.655	15.029	4.641	14.909
$FePO_4$	5.031	11.247[40]	5.188	11.437	5.124	11.384	4.802	10.990

Table 4. Experimental and calculated lattice parameters (Å) of selected ionic orthorhombic compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	Experiment			pob-TZVP			pob-TZVP-rev2			pob-DZVP-rev2		
Compound	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*B*	*c*
$NaNO_2$	3.565	5.385	5.573[41]	3.531	5.426	5.518	3.561	5.404	5.492	3.513	5.407	5.482
CaH_2	5.960	3.601	6.817[28]	5.869	3.569	6.704	5.869	3.585	6.684	5.906	3.575	6.790
$CrCl_2$	5.985	6.644	3.488[42]	5.877	6.373	3.516	5.991	6.570	3.528	5.838	6.373	3.519
GeSe	10.770	3.825	4.389[43]	10.894	3.848	4.397	10.849	3.839	4.456	10.775	3.862	4.392

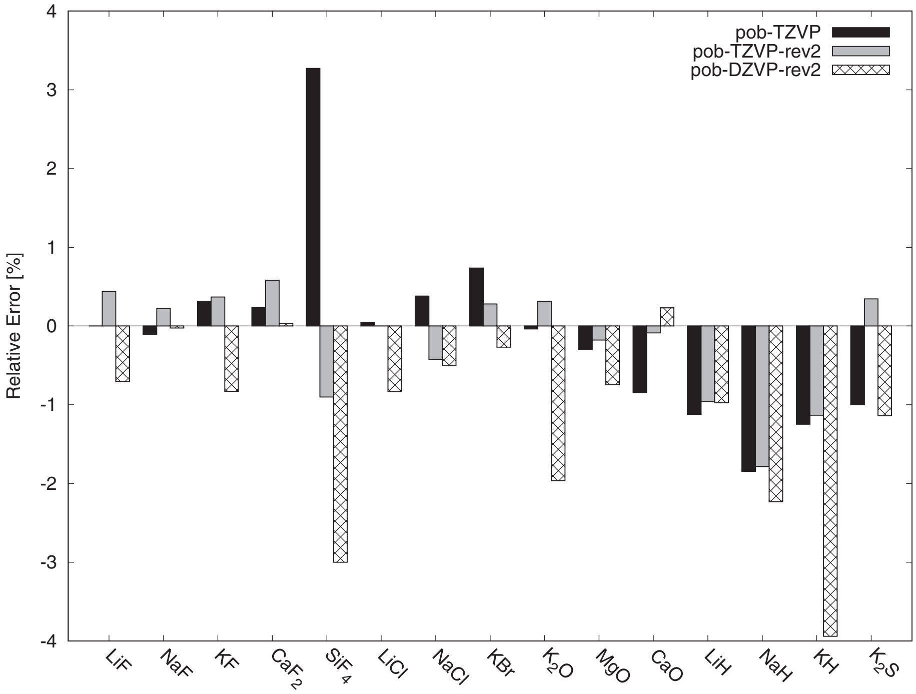

Figure 8. Relative error in the lattice constants of ionic cubic compounds with respect to experimental values.

ATOMBSSE method. The results can be seen in the Figures 2–7. In some cases, such as the K, As, Co, and Ni TZVP basis sets, the BSSE slightly increased from pob-TZVP to pob-TZVP-rev2 due to the new lower threshold for the orbital exponent. However, considerable reductions were obtained for all other elements, so that the pob-TZVP-rev2 basis sets lead to similar BSSEs for all parameterized elements, and therefore to a higher degree of consistency. The BSSEs obtained for both pob-TZVP-rev2 and pob-DZVP-rev2 basis sets have a much lower standard deviation than the pob-TZVP basis sets, as can be seen in Table 1.

Ionic systems

To test our basis sets for ionic compounds, we optimized the lattice constants and atomic positions of selected oxides and halides. The results are given in Table 2 for cubic, in Table 3 for hexagonal, and in Table 4 for orthorhombic systems. The relative errors with respect to experiment are given in Figure 8 for cubic, in Figure 9 for hexagonal, and in Figure 10 for orthorhombic systems. The mean deviation of calculated lattice parameters with respect to the experiment is 0.77% for pob-TZVP and 0.53% for pob-TZVP-rev2 for cubic systems. The pob-

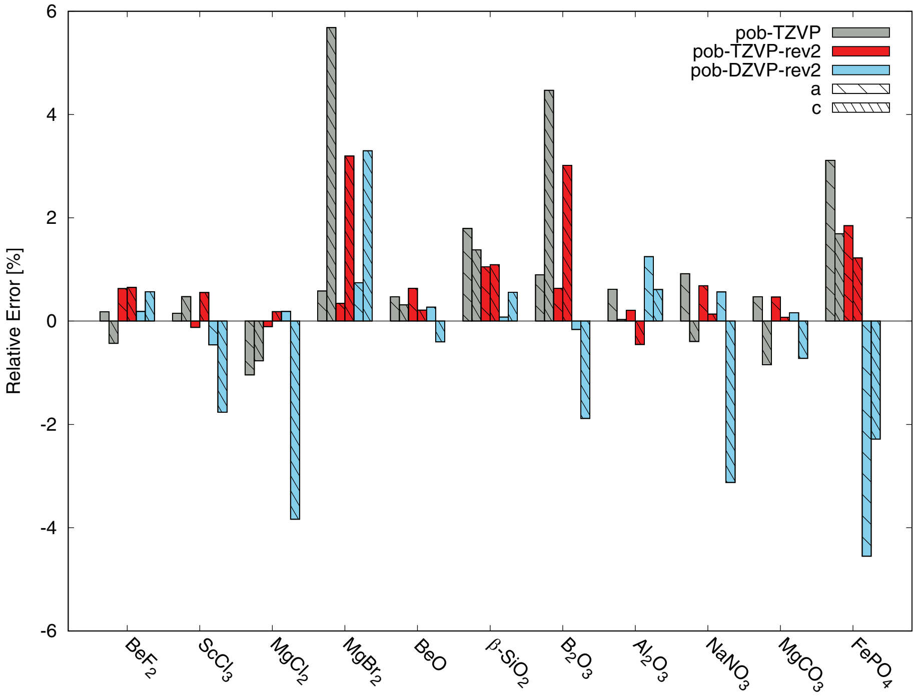

Figure 9. Relative error in the lattice constants of hexagonal ionic compounds with respect to experimental values. [Color figure can be viewed at wileyonlinelibrary.com]

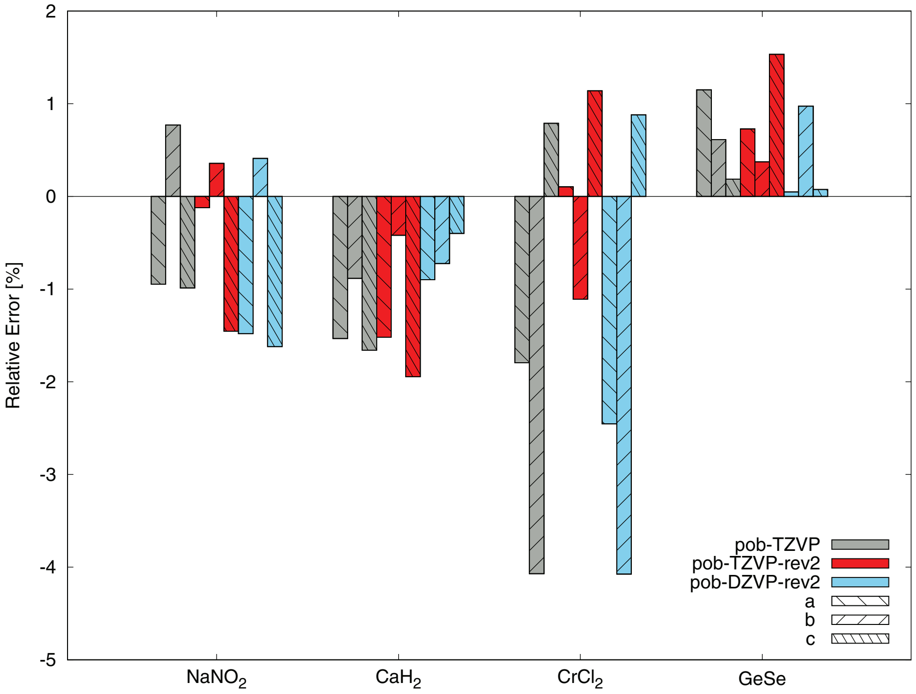

Figure 10. Relative error in the lattice constants of orthorhombic compounds with respect to experimental values. [Color figure can be viewed at wileyonlinelibrary.com]

DZVP-rev2 deviate slightly more with 1.16%. RMSD, maximum error, and the standard deviation of the calculated lattice constants for the pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets can be seen in Table 5. By revising the pob-TZVP basis sets, the mean error was reduced significantly. The pob-DZVP-rev2 basis sets provide reasonable accuracy; in the case of hexagonal and orthorhombic test systems, it is comparable or even better than with pob-TZVP. Most importantly the portability was improved significantly. The pob-TZVP-rev2 basis sets show both a smaller maximum error and smaller standard deviation than pob-TZVP.

Semiconductors

The calculated lattice constants of a variety of semiconductors and covalent compounds are given in Table 6 for cubic and Table 7 for hexagonal crystal systems where they are compared with experimental data and results obtained with the pob-TZVP basis sets. The pob-TZVP-rev2 mean error of the calculated lattice constants compared to the experiment is 0.49% for cubic and 1.27% for hexagonal systems, which is an improvement compared to the pob-TZVP results, 0.81% for cubic and 1.99% for hexagonal systems. Although slightly worse than pob-TZVP-rev2, the pob-DZVP-rev2 basis sets performed on average better than pob-TZVP, with mean deviations of 0.79% for cubic and 1.75% for hexagonal structures. The relative errors with respect to experimental data are shown in Figure 11 for cubic

Table 5. RMSD, maximum error, and standard deviation of lattice constants with respect to the experiment of selected ionic solid compounds obtained with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets in percentage.

		pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Cubic ionic	RMSD	0.77	0.53	1.16
	Maximum error	3.27	1.78	3.94
	Standard deviation	0.88	0.47	1.14
Hexagonal ionic	RMSD	1.95	1.28	2.09
	Maximum error	5.71	3.22	5.09
	Standard deviation	1.84	1.08	1.56
Orthorhombic ionic	RMSD	2.46	1.83	2.32
	Maximum error	4.52	2.50	4.84
	Standard deviation	1.45	0.46	1.77

Table 6. Experimental and calculated lattice parameters (Å) of selected cubic semiconductors and covalent compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	a			
Compound	Experiment	pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
C (diamond)	3.567[44]	3.547	3.550	3.554
AlP	5.421[45]	5.392	5.450	5.503
AlN	4.365[45]	4.373	4.367	4.406
Na_2Se	6.825[46]	6.695	6.761	6.742
GaAs	5.653[47]	5.690	5.671	5.701
GaP	5.448[48]	5.476	5.465	5.469
α-ZnS	5.400[49]	5.391	5.413	5.468
MnSe	5.460[50]	5.500	5.462	5.482
ZnSe	5.674[48]	5.646	5.675	5.677
β-BN	3.625[51]	3.606	3.605	3.597
β-SiC	4.358[52]	4.344	4.388	4.372
TiC	4.328[19]	4.214	4.294	4.297
Cu_3N	3.817[53]	3.730	3.781	3.760
VC	4.163[54]	4.152	4.163	4.164
VN	4.137[55]	4.150	4.081	4.066
TiN	4.235[56]	4.205	4.216	4.214
CrN	4.135[56]	4.187	4.180	4.164
MnS	5.220[57]	5.196	5.227	5.278

Table 7. Experimental and calculated lattice parameters (Å) of selected hexagonal semiconductors with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	Experiment		pob-TZVP		pob-TZVP-rev2		pob-DZVP-rev2	
Compound	*a*	*c*	*a*	*c*	*a*	*c*	*a*	*c*
NiAs	3.618	5.034[58]	3.613	5.066	3.587	4.990	3.541	4.985
α-SiC	3.081	15.125 [59]	3.070	15.061	3.101	15.215	3.090	15.162
α-BN	2.536	4.199 [60]	2.542	4.198	2.541	4.198	2.535	4.191
B_4C	5.610	12.140[61]	5.585	11.910	5.611	12.025	5.593	11.954
ScB_2	3.148	3.515[62]	3.128	3.493	3.130	3.499	3.128	3.487
CoS	3.440	5.790[63]	3.510	5.787	3.525	5.792	3.513	5.765
CuS	3.788	16.333[64]	3.760	15.500	3.883	16.545	3.944	16.967
β-ZnS	3.817	6.256[65]	3.750	6.050	3.832	6.246	3.878	6.284
GaF_3	5.012	12.990[66]	5.112	13.126	5.035	13.135	5.050	13.170
GeO_2	4.985	5.645[67]	5.090	5.716	5.057	5.707	4.983	5.696

and Figure 12 for hexagonal systems. RMSD, maximum error, and standard deviation are summarized in Table 8. The lower maximum error and standard deviation indicate a better portability of the basis sets also to systems they were not optimized for. This can also be seen by examining different phases of the same compound. For ZnS, we calculated both the α- (zinc blende) and the β-phase (wurtzite). The pob-TZVP basis set performs well in the cubic α-ZnS (−0.17%) but gives a fairly high error in β-ZnS (+2.52%). The pob-TZVP-rev2 basis, however, provides good results in both structures (deviations of 0.40% and 0.24%, respectively).

Transition metal oxides

Calculated lattice constants are given in Table 9 for cubic and in Table 10 for hexagonal and tetragonal transition metal oxides. The relative errors with respect to experimental values are given in Figure 13 for cubic and Figure 14 for hexagonal systems. For cubic and hexagonal transition metal oxides, the mean deviation is 1.03% and 1.40% for pob-TZVP and only 0.59% and 0.94% for the pob-TZVP-rev2 basis sets. The corresponding pob-DZVP-rev2 mean deviation is 1.00% and 1.58%, respectively. RMSD, maximum error, and standard deviation are summarized in Table 11.

HF calculations

The pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets were optimized with a hybrid DFT method. To explore to which extend the developed basis sets are transferable to other methods, we also calculated the lattice constants for a few selected cases at HF level. The results are given in Table 12. The relative errors with respect to experiment are given in Figure 15. Generally, the HF results for lattice constants are slightly worse than for PW1PW. It is observed that the errors obtained with the rev2 basis sets are almost identical to those of pob-TZVP. On

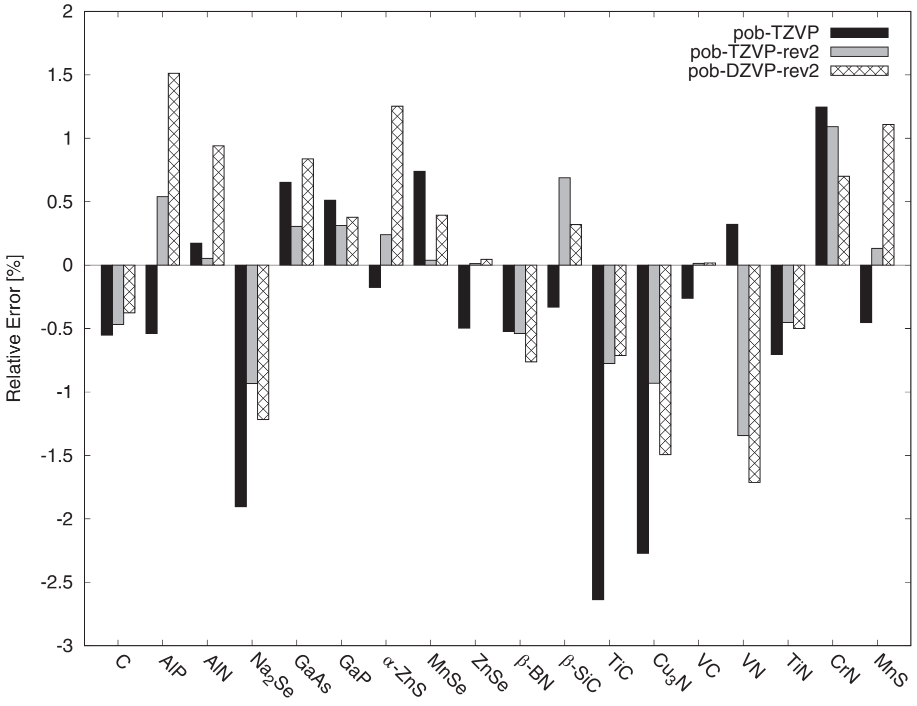

Figure 11. Relative error in the lattice constants of cubic semiconductors with respect to experimental values.

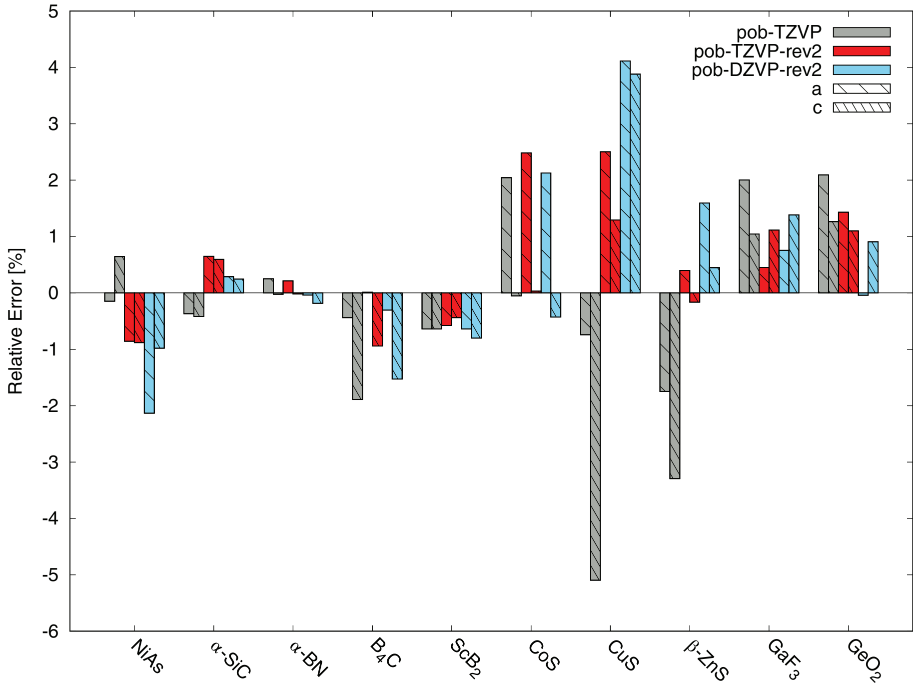

Figure 12. Relative error in the lattice constants of hexagonal semiconductors with respect to experimental values. [Color figure can be viewed at wileyonlinelibrary.com]

Table 8. RMSD, maximum error, and standard deviation of lattice constants with respect to the experiment of selected semiconductors obtained with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets in percentage.

		pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Cubic semiconductors	RMSD	0.81	0.49	0.79
	Maximum error	2.64	1.34	1.71
	Standard deviation	0.73	0.40	0.51
Hexagonal semiconductors	RMSD	1.99	1.27	1.75
	Maximum error	5.15	2.82	5.66
	Standard deviation	1.54	0.85	1.54

Table 9. Experimental and calculated lattice parameters (Å) of selected cubic transition metal oxides with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	a			
Compound	Experiment	pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Sc_2O_3	9.846[19]	9.832	9.836	9.818
MnO	4.445[19]	4.400	4.387	4.375
FeO	4.326 [19]	4.242	4.347	4.348
CoO	4.250[19]	4.256	4.236	4.175
NiO	4.195[19]	4.177	4.165	4.137
Cu_2O	4.269[68]	4.126	4.221	4.214
$ZnCr_2O_4$	8.329[69]	8.347	8.336	8.312

Table 10. Experimental and calculated lattice parameters (Å) of selected hexagonal and tetragonal transition metal oxides with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	Experiment		pob-TZVP		pob-TZVP-rev2		pob-DZVP-rev2	
Compound	*a*	*c*	*a*	*c*	*a*	*C*	*a*	*c*
V_2O_3	4.952	14.002[19]	5.038	13.835	5.039	13.836	5.023	13.742
Cr_2O_3	4.961	13.599[19]	4.993	13.535	4.999	13.510	4.992	13.459
ZnO	3.249	5.204[19]	3.270	5.123	3.254	5.156	3.270	5.007
TiO_2 (rutile)	4.587	2.954[70]	4.587	2.952	4.587	2.951	4.572	2.953
TiO_2 (anatase)	3.782	9.502[70]	3.751	9.710	3.774	9.548	3.776	9.503

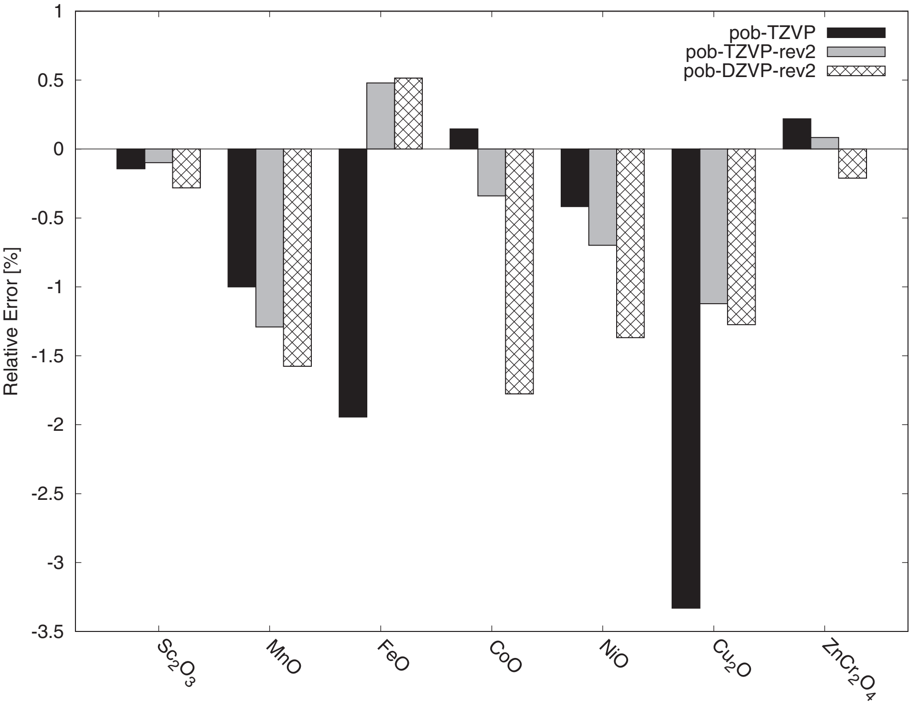

Figure 13. Relative error in the lattice constants of cubic transition metal oxides with respect to experimental values.

average using pob-TZVP basis sets, the mean deviation is 1.00%, with pob-TZVP-rev2 1.01% with pob-DZVP-rev2 0.97%, however, the maximum error and the standard deviation decreases using the new basis sets. RMSD, maximum error, and standard deviation can be found in Table 13.

Molecular crystals

For molecular crystals, the BSSE can have a large influence on the structure. Therefore nine selected structures of the X23 benchmark set of organic crystals[71] have been optimized where dispersion interaction or hydrogen bonds dominate or both occur simultaneously. The mean deviation is 5.22% for pob-TZVP and 3.63% for the pob-TZVP-rev2 basis sets. The corresponding pob-DZVP-rev2 mean deviation is 3.72%. Since dispersion corrections lead to a significant improvement of the structure parameters of molecular systems, the D3 correction by Grimme et al.[10] was applied. This reduces the errors to 2.87% for pob-TZVP and 1.66% for pob-TZVP-rev2 and 3.60%

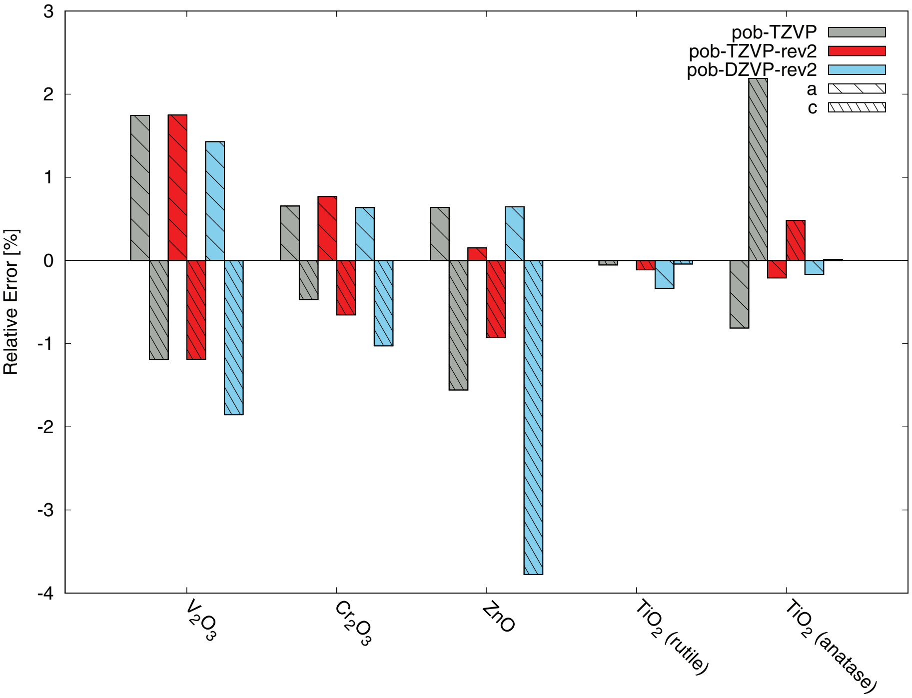

Figure 14. Relative error in the lattice constants of hexagonal and tetragonal transition metal oxides with respect to experimental values. [Color figure can be viewed at wileyonlinelibrary.com]

Table 11. RMSD, maximum error, and standard deviation of lattice constants with respect to the experiment of selected transition metal oxides obtained with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets in percentage.

		pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Cubic TM oxides	RMSD	1.03	0.59	1.00
	Maximum error	3.33	1.29	1.78
	Standard deviation	1.21	0.48	0.65
Hexagonal TM oxides	RMSD	1.40	0.94	1.58
	Maximum error	2.33	2.11	3.83
	Standard deviation	0.95	0.75	1.53

Table 12. Experimental and calculated HF lattice parameters (Å) of selected ionic cubic compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets.

	a			
Compound	Experiment	pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
LiF	4.027[17]	4.027	4.007	3.983
NaF	4.632[18]	4.606	4.609	4.593
KF	5.347[19]	5.409	5.438	5.382
CaF_2	5.463[20]	5.512	5.533	5.520
LiCl	5.130[22]	5.271	5.235	5.173
NaCl	5.640[23]	5.702	5.709	5.670
K_2O	6.436[25]	6.469	6.458	6.360
MgO	4.217[19]	4.189	4.198	4.184
CaO	4.811[26]	4.859	4.854	4.858
LiH	4.083[27]	4.155	4.158	4.146
NaH	4.890[28]	4.880	4.879	4.880
KH	5.704[29]	5.784	5.767	5.589

Table 13. RMSD, maximum error, and standard deviation of HF lattice constants with respect to the experiment of selected ionic compounds with pob-TZVP, pob-TZVP-rev2, and pob-DZVP-rev2 basis sets in percentage.

		pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2
Cubic ionic	RMSD	1.00	1.01	0.97
	Maximum error	2.75	2.05	2.02
	Standard deviation	0.74	0.62	0.47

for pob-DZVP-rev2. Both with and without dispersion correction, the pob-TZVP-rev2 basis set show the smallest standard deviation. RMSD, maximum error, and standard deviation can be found in Table 14. The structural parameters are given in the Supporting Information.

Thermochemistry

We calculated thermochemical properties for the cubic ionic solids as shown in Table 15. The zero-point energy was calculated according to Pascale et al.[73,74] The difference in atomization enthalpies obtained using pob-TZVP and pob-TZVP-rev2 basis sets is between 1 and 6 kJ/mol. This is most likely due to the cancellation effects between the solid and the atomic references. Therefore, the absolute mean errors of the two types of basis sets are quite similar around 7%.

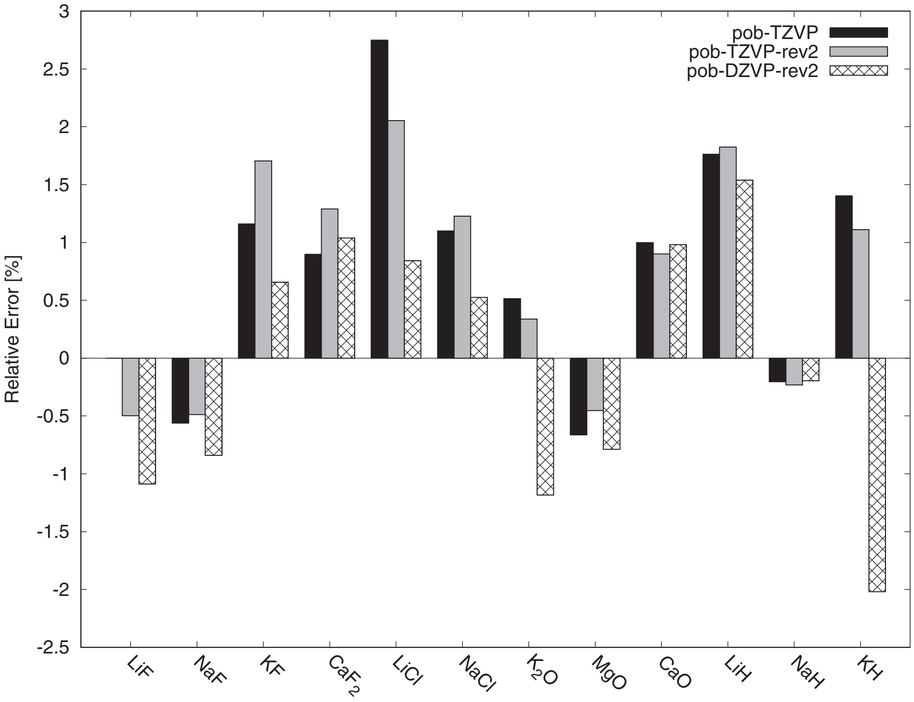

Figure 15. Relative error in the HF lattice constants of ionic cubic compounds with respect to experimental values.

Table 14. RMSD, maximum error and standard deviation of lattice constants with respect to the experiment of selected molecular crystals of the X23 benachmark set obtained with pob-TZVP, pob-TZVP-rev2 and pob-DZVP-rev2 basis sets in %.

	pob-TZVP	pob-TZVP-rev2	pob-DZVP-rev2	pob-TZVP/D3	pob-TZVP-rev2/D3	pob-DZVP-rev2/D3
RMSD	5.22	3.63	3.72	2.87	1.66	3.60
Max. error	13.45	7.30	12.31	5.38	2.39	11.57
Std. dev.	4.17	1.91	4.35	1.91	0.62	3.09

Table 15. Experimental and calculated atomization enthalpies of selected ionic solid cubic compounds with pob-TZVP, pob-TZVP-rev2 and pob-DZVP-rev2 basis sets. Energies are given in kJ/mol.

Compound	Experiment[72]	pob-TZVP	pob-TZVP-rev2
LiCl	685	659	654
NaCl	640	617	616
LiF	849	816	812
NaF	762	734	730
KF	737	699	694
K_2O	790	683	682
MgO	994	957	953
LiH	518	438	437
NaH	382	361	361
KH	365	329	329

Conclusions

We have presented a revised method for optimizing basis sets for periodic quantum-chemical solid state calculations resulting in well-balanced, generally applicable, consistent both TZV and DZV with polarization quality basis denoted by pob-TZVP-rev2 and pob-DZVP-rev2. They provide robust and stable SCF convergence for a wide range of different compounds. This holds for the DFT method for which the pob-TZVP basis sets were optimized and also for the HF method that may serve as a starting point for electron-correlation calculations. We have shown that the computed lattice constants are improved over results obtained with the previously developed pob basis sets. Maximum errors and standard deviations decreased significantly in the tests sets, which indicate that the new basis sets are better transferable to other systems.

For convenient use, all basis sets are available for download as separate files and as one single file with neutral atomic configurations from our website (https://www.chemie.uni-bonn.de/pctc/mulliken-center) and also as Supporting Information to this article.

Keywords: CRYSTAL · basis sets · pob-DZVP-rev2 · pob-TZVP-rev2 · solid-state

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Additional Supporting Information may be found in the online version of this article.

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