Consistent Gaussian Basis Sets of Triple-Zeta Valence with Polarization Quality for Solid-State Calculations

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Consistent basis sets of triple-zeta valence with polarization quality for main group elements and transition metals from row one to three have been derived for periodic quantum-chemical solid-state calculations with the crystalline-orbital program CRYSTAL. They are based on the def2-TZVP basis sets developed for molecules by the Ahlrichs group. Orbital exponents and contraction coefficients have been modified and reoptimized, to provide robust and stable self-consistant field (SCF) convergence for a wide range of different compounds. We compare results on crystal structures, cohesive energies, and solid-state reaction enthalpies with the modified basis sets, denoted as pob-TZVP, with selected standard basis sets available from the CRYSTAL basis set database. The average deviation of calculated lattice parameters obtained with a selected density functional, the hybrid method PW1PW, from experimental reference is smaller with pob-TZVP than with standard basis sets, in particular for metallic systems. The effects of basis set expansion by diffuse and polarization functions were investigated for selected systems. © 2012 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.23153

Introduction

At almost every level of theory, the accuracy of a quantum-chemical calculation strongly depends on the quality of the basis functions used for the expansion of the molecular or crystalline orbitals. In most implementations either plane waves or atom-centered contracted Gaussian basis functions (CGFs) are used, whereas Slater-type orbitals and numerical basis sets are less common. In contrast to a plane wave basis, CGFs are not universal and an individual basis set has to be developed for each element in the periodic table.

For molecular calculations, there is a vast variety of standard Gaussian basis sets of different quality levels available.[1,2] Popular basis sets for molecular calculations, for example, those developed by the Ahlrichs group, are implemented in most molecular quantum-chemical codes for convenient use. They are available in split valence,[3,4] triple-zeta valence (TZV),[3,5,6] and quadruple-zeta valence[7] quality augmented by one or two sets of polarization functions (P, PP). These basis sets in general contain small orbital exponents (<0.1). In periodic calculations, two problems arise that will be discussed in terms of the widely used crystalline-orbital program CRYSTAL09[8,9] in this article. In CRYSTAL09, the crystalline orbitals are expanded in Bloch functions that are obtained by a linear combination of CGFs multiplied with a **k**-vector dependent phase factor. The overlap integrals between Bloch functions are larger in absolute value compared with their atomic counterparts in molecules. If the basis functions are too diffuse, the overlap matrix has small eigenvalues and may even be indefinite so that the basis set becomes linearly dependent. A similar problem with numerical stability exists in the density fitting procedure used to accelerate density-functional theory (DFT) calculations and has been successfully overcome by a modified singular value decomposition.[10] As such a procedure is not available for the self-consistent field (SCF) procedure in CRYSTAL09, the only viable way is to modify molecular basis sets for the particular requirements of solid-state calculations.

The molecular basis sets can in practice only be used in solid-state calculations, if the functions with small orbital exponents (<0.1 as a rule of thumb) are removed. However, these pruned basis sets may no longer be of a consistent quality level. For this reason, the available basis sets for solid-state calculations[11] were often optimized for a particular system. This may lead to a lack of portability as will be discussed later.

To our knowledge, there is no consistent standard all-electron CGF basis set of a defined quality for all elements of the periodic table for periodic calculations available.

TZVP basis sets offer a good balance between accuracy and performance for molecules. We selected the def2-TZVP standard as starting point for the construction of a consistent and portable basis set of a defined quality level for solid-state calculations, which can be used for different compounds, methods, and crystal systems. The basis sets obtained after restructuring the contraction scheme, and reoptimization of the orbital exponents and contraction coefficients will be denoted as pob-TZVP in the following. The basis sets are tested by calculating lattice constants and atomization enthalpies of selected solid compounds. We compare pob-TZVP results with results that were obtained using CRYSTAL standard basis sets.

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Contract/grant sponsor: Deutsche Forschungsgemeinschaft (DFG); Contract/grant numbers: SFB813 (Chemistry at Spin Centers—Concepts, Mechanisms, Functions).

Table 1. Number of contracted basis functions (s/p/d/f) for the pob-TZVP, def2-TZVP,[3,5] and selected CRYSTAL standard basis sets for the group 1 and 2 elements.

	Number of functions (s/p/d/f)		
Element	pob-TZVP	def2-TZVP	CRYSTAL
H	311/1	311/1	511/1[15]
Li	6211/1	62111/111	5/11/1[16]
Na	73211/511/1	73211/5111/111	85111/5111[17]
K	842111/6311/1	842111/6311/111	86511/6511/3[17]
Be	6211/1	62111/121/1	5111/11[18]
Mg	73211/511/1	73211/5111/111	8511/511/1[19]
Ca	842111/6311/1	842111/63111/211	86511/6511/21[20]

Basis Set Optimization

The basis sets for elements from H–Br presented in this work are based on the def2-TZVP basis sets developed by the group of Ahlrichs.[3,5] These consist of highly contracted Gaussians for core shells and three less contracted or primitive GGFs per valence shell. For every valence shell, there is at least one primitive or even contracted polarization function of higher angular momentum. This means, for example, that one of the four p-functions in the Mg basis set is a polarization function for the s-valence.

These basis sets could in principle be used in solid-state calculations, if functions with orbital exponents smaller than 0.1 were removed. As a different number of functions per element are cut off depending on the threshold, they are then no longer of a consistent quality level.

Table 2. Number of contracted basis functions (s/p/d/f) for the pob-TZVP, def2-TZVP, and a selected CRYSTAL standard basis for the elements of groups 13–17.

	Number of functions (s/p/d/f)		
Element	pob-TZVP	def2-TZVP	CRYSTAL
B	6211/411/1	62111/411/11/1	621/21/1[21]
Al	73211/5111/1	73211/51111/21/1	8511/511/1[22]
Ga	842111/63111/5111	842111/63111/5111/1	864111/64111/41[23]
C	6211/411/1	62111/411/11/1	6311/311/11[20] 621/21/1[24]
Si	73211/5111/1	73211/51111/21/1	86311/6311/1[25]
Ge	842111/63111/5111	842111/63111/5111/1	97631/7631/63[26]
N	6211/411/1	62111/411/11/1	621/21/3[27]
P	73211/5111/1	73211/51111/21/1	8521/521/1[28]
As	842111/64111/5111	842111/64111/5111/1	*
O	6211/411/1	62111/411/11/1	8411/411/1[29]0 8411/411/11[20]
S	73211/5111/1	73211/51111/21/1	863111/63111/11[30]
Se	842111/64111/5111	842111/64111/5111/1	97631/7631/51[31]
F	6211/411/1	62111/411/11/1	7311/311[32]
Cl	73211/5111/1	73211/51111/21/1	86311/6311[33]
Br	842111/64111/5111	842111/64111/5111/1	*

An asterisk indicates that there is no all-electron basis set available.

Our pob-TZVP basis sets inherit the highly contracted core-shell Gaussians and three (contracted or primitive) basis functions per valence shell of the def2-TZVP basis sets, but only one primitive polarization function of higher angular momentum is added as polarization for the complete shell. This scheme results in smaller numbers of contracted and primitive Gaussians than in the original def2-TZVP basis sets.

We, therefore, augmented the truncated basis sets until the number of basis functions matched the TZVP quality level. The starting values of the orbital exponents were chosen to be $\frac{1}{2}$ to $\frac{1}{3}$ of the next inner orbital exponent, which is a standard procedure recommended by the CRYSTAL09 developers.[9] The orbital exponents and contraction coefficients of the valence shells were variationally optimized for selected solids using the hybrid DFT functional PW1PW.[12] This functional has been shown to provide good agreement with experiment for lattice parameters and cohesive energies.[12–14]

We then performed test calculations for other solids and made further adjustments when necessary. The obtained final basis sets, denoted as pob-TZVP, are therefore not fully variational for all reference systems. The final values of orbital exponents and contraction coefficients depend on the selected systems and on the DFT method that has been used. However, as the changes necessary in the adjustments were relatively small, we hope that the basis sets are portable to other systems. Later on we will apply the pob-TZVP basis sets also to Hartree–Fock (HF) calculations ('HF calculations' section).

As a boundary condition for the orbital exponents, we kept a predefined lower threshold of 0.1 for the exponents for stability and portability reasons. This will also allow the addition of diffuse basis functions for special cases, e.g., metals, as will be discussed later.

The number of functions in the presented pob-TZVP, the original def2-TZVP and the CRYSTAL standard basis sets are listed in Table 1 for group 1 and 2 elements, Table 2 for the elements from group 13–17 and Table 3 for third-row transition metals.

Table 3. Number of contracted basis functions (s/p/d/f) for the pob-TZVP, def2-TZVP and selected CRYSTAL standard basis sets for third-row transition metals..

	Number of functions (s/p/d/f)		
Element	pob-TZVP	def2-TZVP	CRYSTAL
Sc	842111/6311/411/1	842111/6311/4111/1	86411/6411/3[a]
Ti	842111/6311/411/1	842111/6311/4111/1	86411/6411/31[34]
V	842111/6311/411/1	842111/6311/4111/1	86411/6411/31[35]
Cr	842111/6311/411/1	842111/6311/4111/1	86411/6411/41[36]
Mn	842111/6311/411/1	842111/6311/4111/1	86411/6411/41[37]
Fe	842111/6311/411/1	842111/6311/4111/1	86411/6411/41[38]
Co	842111/6311/411/1	842111/6311/4111/1	86411/6411/41[26]
Ni	842111/6311/411/1	842111/6311/4111/1	86411/6411/41[37]
Cu	842111/6311/411/1	842111/6311/4111/1	632111/33111/311[26]
Zn	842111/6311/411/1	842111/6311/4111/1	86411/64111/41[39]

[a] Harrison et al. (unpublished).

Table 4. Experimental and calculated lattice parameters of selected ionic solid cubic compounds with CRYSTAL standard and pob-TZVP basis sets..

	a		
Compound	Experiment	CRYSTAL	pob-TZVP
LiCl	5.130[48]	5.134[16,33]	5.132
NaCl	5.640[49]	5.609[17,33]	5.609
LiF	4.027[50]	3.971[16,32]	4.027
NaF	4.632[51]	4.636[17,32]	4.627
KF	5.347[52]	5.320[17,32]	5.364
CaF_2	5.463[53]	5.477[20,32]	5.476
K_2O	6.436[54]	6.289[17,29]	6.434
MgO	4.217[52]	4.207[20,29]	4.204
CaO	4.811[55]	4.752[20,29]	4.770
LiH	4.083[56]	3.965[15,16]	4.037
NaH	4.890[57]	4.758[15,17]	4.800
KH	5.704[58]	5.554[15,17]	5.633

Lengths are given in Å.

Computational Details

All quantum-chemical calculations were performed with the crystalline orbital program CRYSTAL09.[8,9,40,41]

Preliminary basis set optimizations were performed using the generalized gradient approximation density functional presented by Wu and Cohen (WC).[42,43] This method was chosen, because it has been shown to provide reasonable results for a variety of solids.[44]

The final optimizations of the basis sets and structure optimizations were performed using the hybrid DFT functional PW1PW,[12] which has been shown to deliver very good structural and thermochemistry results for oxides and other compounds.[12–14] The correlation functional is PW91,[45] whereas the exchange functional is a mixture of 20% HF and 80% PW91 exchange. The optimizations were executed with a python script, which runs single point calculations with the CRYSTAL09 program and uses the numerical minimization library MINUIT2 that is part of the ROOT[46] project and that is widely used in particle physics.

Structure optimizations and the calculation of the cohesive energies were carried out using the PW1PW[12] hybrid functional for all compounds except for metals. The structure optimizations of metallic compounds were performed using the WC functional.

Results and Discussion

To test the stability, portability, and quality of our pob-TZVP basis sets, we calculated various properties of homoatomic and binary ionic solids, semiconductors, and metals. We compared the results obtained with the pob-TZVP basis sets to results obtained with standard basis sets taken from the CRYSTAL basis set database.[11] The total energy per unit cell is a measure of the variational quality of the basis sets and is therefore given in the supporting information for both basis sets.

Test set

Our test set is based on that used by the group of Kresse evaluating a plane wave implementation of hybrid functionals to extended systems.[47] It consists of archetypical metallic, semiconducting, and ionic systems, including transition metal oxides. As we present a basis set for row one to three, we excluded systems that contain elements of the fourth row from the test set. The test set of metallic systems was extended to include all cubic main group metals (Li, Na, K, Ca, and Al) and all cubic transition metals (Sc, V, Cr, Fe, Ni, and Cu) and an intermetallic alloy (Ni_3Al). The test set of semiconductors was also extended to cover all elements of the groups 13–17.

To cover all transition metals, we also enlarged the original test set of transition metal monoxides to include cuprite, some transition metal dioxides, and sesquioxides. Results for systems were only included in the statistics, if there was a CRYSTAL standard basis set available. The calculated maximum error is the sum of errors for each lattice parameter per system. For example, for orthorhombic systems, it is the sum of errors for *a*, *b*, and *c*.

Ionic systems

We optimized lattice constants and atomic positions of selected oxides, halides, hydrides, carbonates, nitrides, and phosphates. The results are given in Table 4 for cubic, Table 5 for hexagonal, and Table 6 for orthorhombic systems and are compared with experimental data and results obtained with a CRYSTAL standard basis.

Of course one has to keep in mind that the basis set limit can only give an account of the accuracy of the underlying theoretical approach, in this case the hybrid method PW1PW,[12] on the other hand, this method has repeatedly demonstrated high accuracy for solid-state structure parameters.[13,14] Therefore, we use this method as reference and regard deviations from the experiment as a quality measure of the basis sets.

The relative errors with respect to experiment are shown in Figure 1 for cubic, Figure 2 for hexagonal, and Figure 3 for orthorhombic systems.

Table 5. Experimental and calculated lattice parameters of selected ionic hexagonal solid compounds.

	Experiment		CRYSTAL		pob-TZVP	
Compound	*a*	*c*	*a*	*c*	*a*	*c*
BeF_3	4.688	5.185[52]	4.892	5.397[18,32]	4.748	5.165
$ScCl_3$	6.378	17.790[59]	6.729	16.555[a],[33]	6.387	17.874
$MgBr_2$	3.887	7.108[60]	*	*	3.832	6.616
BeO	2.697	4.378[61]	2.702	4.377[18,29]	2.709	4.392
a-SiO_2	4.916	5.409[62]	4.959	5.459[25,29]	5.004	5.484
B_2O_3	4.336	8.340[63]	–	–[21,29]	4.375	8.713
Al_2O_3	4.754	12.990[52]	4.778	12.991[22,29]	4.783	12.994
$NaNO_3$	5.070	16.822[64]	5.085	17.222[17,27,29]	5.117	16.756
$MgCO_3$	4.633	15.018[65]	4.658	14.986[20,29]	4.655	14.891
$FePO_3$	5.031	11.247[66]	4.897	11.003[29,38,67]	4.946	10.995

A N-dash indicates that the SCF did not converge or the structure optimization failed. An asterisk indicates that there is no all-electron basis set available for this element. Lengths are given in Å.
[a] Harrison et al. (unpublished).

Table 6. Experimental and calculated lattice parameters of selected ionic orthorhombic solid compounds.

	Experiment			CRYSTAL			pob-TZVP		
Compound	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
$BeBr_2$	5.569	10.405	5.543[68]		*		5.784	11.431	5.636
$NaNO_2$	3.565	5.385	5.573[69]	3.567	5.343	5.536[17,27,29]	3.544	5.357	5.572
CaH_2	5.960	3.601	6.817[57]	5.887	3.572	6.761[15,20]	5.869	3.569	6.704
$CrCl_2$	6.644	5.985	3.488[70]	6.266	6.246	3.688[33,36]	6.373	5.877	3.516
GeSe	10.770	3.825	4.389[71]	10.654	3.827	4.653[26,31]	10.894	3.848	4.397

An asterisk indicates that there is no all-electron basis set available for this element. Lengths are given in Å.

As most of the standard basis sets were optimized for these systems, the overall performance of the standard basis sets is good. But, it is even better with the pob-TZVP basis sets. The maximum error in the lattice constants calculated with the CRYSTAL basis sets is 2.9 and 1.8% with the pob-TZVP basis. The mean error in the lattice constant is 1.3% for the CRYSTAL and 0.7% for the pob-TZVP basis sets.

For hexagonal systems, the maximum error in the calculated lattice constants is 12.5% ($ScCl_3$) for the CRYSTAL and 3.9% ($FePO_4$) for the pob-TZVP basis sets. The mean error is 2.0% for the CRYSTAL and 0.8% for the pob-TZVP basis sets.

For orthorhombic systems, the maximum error is 15.8% for the CRYSTAL and 6.7% for the pob-TZVP basis sets. The mean error is 2.3% for the CRYSTAL and 1.2% for the pob-TZVP basis sets.

In summary, our basis sets show a better overall performance than the CRYSTAL standard basis sets. The mean error is significantly reduced compared with the standard basis sets. The pob-TZVP basis shows a good portability, because there are no outliers and the maximum error is much lower than for the standard basis sets.

Additional Polarization Functions The presented pob-TZVP basis sets are, with respect to polarization, more similar to def-TZVP[6] than to def2-TZVP. In Ref. [3], it is demonstrated that def-TZVP basis sets[6] are suffering from the lack of polarization functions even at HF and DFT level. To our experience, additional polarization functions are essential for the treatment of ionic alkaline and alkaline earth metal compounds. To study the influence of polarization functions in more detail, we therefore augmented the previously described pob-TZVP basis sets with an additional polarization function and reoptimized the exponents of both polarization functions for these compounds for selected cases. These exponents are given in the supporting information. In the case of hydrogen and lithium also, valence functions were modified. These basis sets are denoted as "pob-TZVPP." The additional polarization functions lead to an improvement of the calculated lattice constants (Table 7). For the selected cubic compounds, the maximum error is 2.7% for the CRYSTAL, 1.4% for the pob-TZVP, and 0.6% for the pob-TZVPP basis sets. The mean error of the lattice constants is 1.6% for the CRYSTAL, 1.1% for the pob-TZVP, and 0.2% for the pob-TZVPP basis sets. It is, therefore, planned to develop a consistent pob-TZVPP basis set with fully optimized orbital exponents for all elements in forthcoming work.

Semiconductors

The calculated lattice constants of a variety of semiconductors and covalent compounds are given in Table 8 for cubic and Table 9 for hexagonal crystal systems where they are compared with experimental data and results obtained with CRYSTAL standard basis sets. The relative errors with respect to experimental data are shown in Figure 4 for cubic and Figure 5 for hexagonal systems.

The maximum error for cubic semiconductors is 4.4% for CRYSTAL basis sets and 3.1% for pob-TZVP. The mean error is 1.0% for the CRYSTAL standard basis sets and 0.8% the pob-TZVP basis sets. For hexagonal semiconducting systems, the maximum error is rather large, 30.6% for CRYSTAL, and 9.8% for the pob-TZVP basis sets. The mean error is 3.1% for CRYSTAL and 1.0% for the pob-TZVP basis sets.

Some standard basis sets cannot be used to all different systems. For example, one of the standard basis sets for carbon, which gives satisfactory results for ionic compounds,[20] suffers from severe SCF convergence problems, when applied to diamond. We found this behavior in several cases for the CRYSTAL standard basis sets but never for our present basis sets.

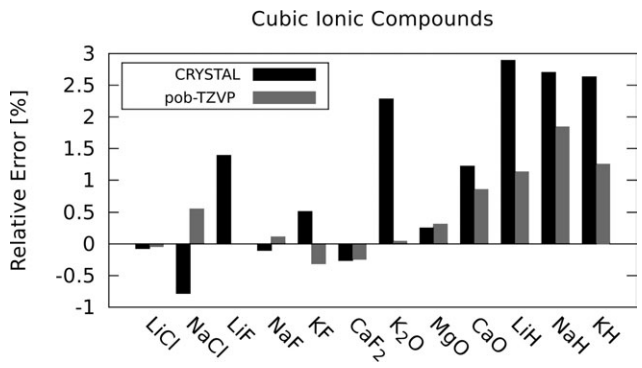

Figure 1. Relative error in the lattice constants of cubic compounds with respect to experimental values.

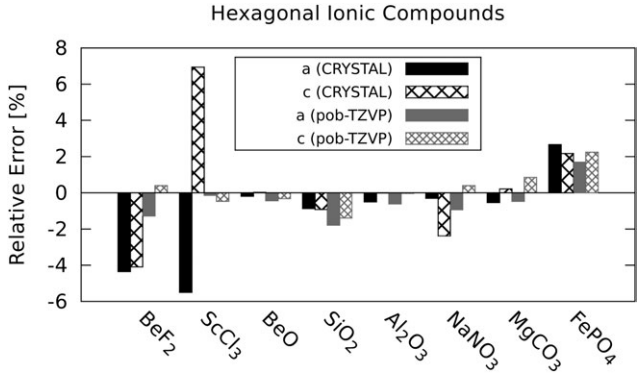

Figure 2. Relative error in the lattice constants of hexagonal compounds with respect to experimental values.

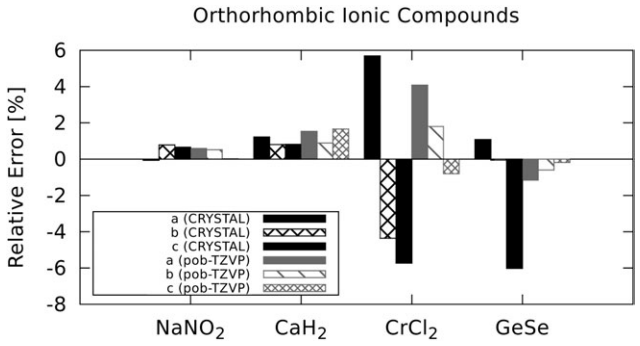

Figure 3. Relative error in the lattice constants of orthorhombic compounds with respect to experimental values.

Transition metal oxides

The calculated lattice constants are given in Table 10 for cubic and Table 11 for hexagonal transition metal oxides. The relative errors with respect to experimental values are given in Figure 6 for cubic and Figure 7 for hexagonal and tetragonal systems.

For cubic transition metal oxides, the maximum error is 1.1% for the standard and only 0.3% for the pob-TZVP basis sets. The mean error is 0.6% for the standard and 0.3% for the pob-TZVP basis sets. The maximum errors for both lattice constants are 4.6% for the standard and 4.0% for the pob-TZVP basis sets. The sum of mean errors is 1.3% for the standard and 1.1% for the pob-TZVP basis sets. Also for transition metal oxides the pob-TZVP basis set provide an improvement over the standard basis sets at PW1PW level.

Metals

In the case of metallic systems, the choice of the basis set is more delicate than for insulators or semiconductors. Diffuse and polarization functions are generally important, and the resulting basis set is often close to linear dependency. To test if our presented basis set is applicable to metals, we optimized the lattice constants and atomic positions of several cubic metals, for example, Li, Na, and K representing alkali metals, Ca representing alkaline earth metals, Sc, V, Cr, Fe, Ni, and Cu representing transition metals and Al. Ni_3Al was included as an example for an alloy.

Table 7. Experimental and calculated lattice parameters of selected ionic solid cubic compounds with CRYSTAL standard, pob-TZVP, and pob-TZVPP basis sets.

	a			
Compound	Experiment	CRYSTAL	pob-TZVP	pob-TZVPP
NaCl	5.640[49]	5.684[17,33]	5.609	5.640
CaO	4.811[55]	4.752[20,29]	4.770	4.773
NaH	4.890[57]	4.758[15,17]	4.800	4.812
KH	5.704[58]	5.554[15,17]	5.633	5.642
K_2S	7.407[72]	7.407[17,30]	7.350	7.370

Lengths are given in Å.

Table 8. Experimental and calculated lattice parameters of selected cubic semiconductors and covalent compounds.

	a		
Compound	Experiment	CRYSTAL	pob-TZVP
C (diamond)	3.567[73]	3.567[24]	3.547
Si	5.431[74]	5.428[25]	5.391
Ge	5.621[75]	5.680[26]	5.667
AlP	5.421[76]	5.385[22,28]	5.392
AlN	4.365[76]	4.258[22,27]	4.373
Na_2Se	6.825[77]	6.536[17,31]	6.695
GaAs	5.653[78]	*	5.690
GaP	5.448[79]	5.477[23,67]	5.476
ZnS	5.400[80]	5.440[30,39]	5.391
MnSe	5.460[81]	5.351[31,37]	5.500
ZnSe	5.674[79]	5.692[31,39]	5.646
b-BN	3.625[82]	3.622[21,27]	3.606
b-SiC	4.358[83]	4.364[20,25]	4.344
TiC	4.328[52]	4.443[20,34]	4.321
Cu_3N	3.817[84]	3.786[26,27]	3.730
VC	4.163[85]	4.166[27,35]	4.152
VN	4.137[86]	4.008[27,35]	4.078
TiN	4.235[87]	4.163[27,34]	4.205
CrN	4.135[87]	3.970[27,36]	4.187
K_2S	7.407[72]	7.407[17,30]	7.350
MnS	5.220[88]	5.263[30,37]	5.196

An asterisk indicates that there is no all-electron CRYSTAL standard basis set available from the CRYSTAL basis set database. Lengths are given in Å.

Although most of the optimization runs failed or gave bad results with the CRYSTAL standard basis sets, the presented pob-TZVP basis sets gave satisfactory results without further modifications, showing the portability of the presented basis sets. The results can be easily improved by adding diffuse valence functions with very small orbital exponents. As the lower limit for orbital exponents in pob-TZVP is 0.1, we suggest adding a diffuse s-function (and if necessary a diffuse p-function) with an orbital exponent of 0.050 or 0.033 to the basis set. This is in accordance with the recommended procedure that the ratio of orbital exponents should be between $\frac{1}{3}$ and $\frac{1}{2}$.[9] Examples are given for metals of the s- and p-block in Table 12. While this is a standard working procedure for metallic

Table 9. Experimental and calculated lattice parameters of selected hexagonal semiconductors.

	Experiment		CRYSTAL		pob-TZVP	
Compound	*a*	*c*	*a*	*c*	*a*	*c*
NiAs	3.618	5.034[89]	*	*	3.613	5.066
a-SiC	3.081	15.125[90]	3.084	15.131[20,25]	3.070	15.061
a-BN	2.536	4.199[91]	2.554	4.220[21,27]	2.542	4.198
B_4C	5.610	12.140[92]	–	—[20,22]	5.585	11.910
ScB_2	3.148	3.515[93]	–	Ref. [21], Harrison et al. (unpublished)	3.128	3.493
CoS	3.440	5.790[94]	3.524	5.966[26,30]	3.510	5.787
CuS	3.788	16.333[95]	–	Refs. [26,30]	3.802	16.077
GaF_3	5.012	12.990[96]	5.216	13.129[23,32]	5.112	13.126
GeO_2	4.985	5.645[97]	5.055	5.696[26,29]	5.090	5.716

An asterisk indicates that there is no all-electron basis set available from the CRYSTAL basis set database. An N-dash indicates that the structure optimization failed. Lengths are given in Å.

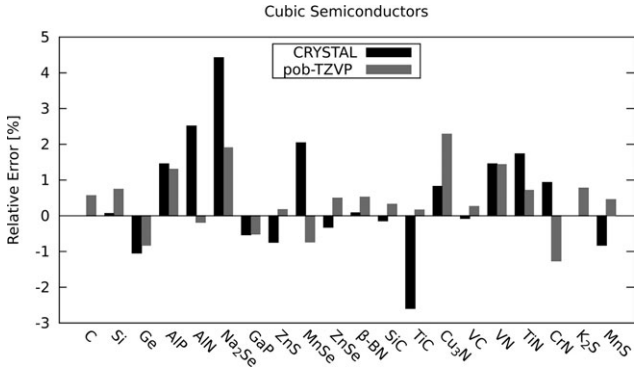

Figure 4. Relative error in the lattice constants of cubic semiconductors with respect to experiment.

Table 10. Experimental and calculated lattice parameters of selected cubic transition metal oxides.

	a		
Compound	Experiment	CRYSTAL	pob-TZVP
Sc_2O_3	9.846[52]	9.867[a],[29]	9.832
MnO	4.445[52]	4.396[29,37]	4.400
FeO	4.300[52]	4.25[29,38]	4.242
CoO	4.250[52]	4.249[26,29]	4.256
NiO	4.195[52]	4.169[29,37]	4.177
Cu_2O	4.269[98]	4.234[26,29]	4.126
$ZnCr_2O_4$	8.329[99]	8.369[29,36,39]	8.347

Lengths are given in Å.
[a] Harrison et al. (unpublished).

systems, this might again lead to linear dependency of the basis in other systems. To maintain basis set stability and portability, we therefore do not include these functions in our presented basis set and suggest adding these functions when needed for bulk or surface calculations of metals. We will refer to the basis sets including diffuse functions for metals as pob-TZVP+s, if an s-function was added.

The results of the structure optimizations with our pob-TZVP and pob-TZVP+s basis sets are given and compared with results obtained using standard basis sets in Table 12.

In general, the pob-TZVP+s results for the calculated lattice parameters are improved compared with pob-TZVP. In particular for K and Ca, the errors were significantly reduced, from −0.68 to −0.10 Å(K) and from −0.45 to −0.11 Å(Ca). For Li, the results obtained with pob-TZVP were not further improved by augmenting with a diffuse s-function.

Thermochemistry

We calculated thermochemical properties for the cubic ionic solids shown in Table 13. The zero-point energy was calculated according to Pascale et al.[40,41]

The calculated atomic reference energies are lower for the pob-TZVP than for the CRYSTAL standard basis sets in the range of 3.5×10^{-4} to 3.4×10^{-2} Hartree (1–90 kJ/mol), showing that the presented basis sets are closer to the variational limit. But in general, the quality of the basis set has a much smaller effect on the thermodynamic properties compared with the lattice parameters. The difference in atomization enthalpies between pob-TZVP and CRYSTAL standard basis sets is between 0 and 18 kJ/mol. This is most likely due to cancellation effects between the solid and the atomic references. Therefore, the absolute mean errors of the two types of basis sets are quite similar, 6 and 7%, respectively.

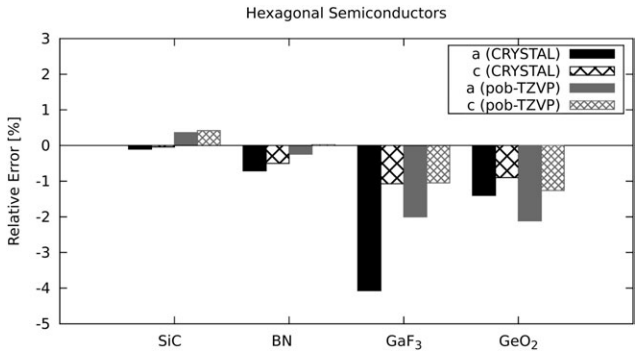

Figure 5. Relative error in the lattice constants of hexagonal compounds with respect to experiment.

HF calculations

The pob-TZVP basis sets were optimized with DFT methods. 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 14. As a first result, the pob-TZVP basis sets can be applied also to HF calculations of solids. They require, however, special care for the integral truncation thresholds (parameters TOLINTEG in CRYSTAL09). Rapid SCF convergence was only obtained for systems like MgO, NaF, LiF, and LiH, when the parameter ITOL5[9] was significantly increased with respect to the recommended value. We used ITOL1–ITOL4 = 8 and ITOL5 = 27 in our calculations.

Generally, the HF results for lattice constants are slightly worse than for PW1PW for pob-TZVP basis sets. For the CRYSTAL basis sets, the errors are similar. Thus, there is some projection of the obtained orbital exponents and contraction coefficients on the method used for their optimization. However, this effect is not very pronounced as can be seen by the

Table 11. Experimental and calculated lattice parameters of selected hexagonal and tetragonal transition metal oxides.

	Experiment		CRYSTAL		pob-TZVP	
Compound	*a*	*c*	*a*	*c*	*a*	*c*
V_2O_3	4.952	14.002[52]	5.058	13.844[29,35]	5.038	13.835
Cr_2O_3	4.961	13.599[52]	5.010	13.552[29,36]	4.993	13.535
ZnO	3.249	5.204[52]	3.263	5.224[29,39]	3.270	5.123
TiO_2 (rutile)	4.587	2.954[100]	4.600	2.956[29,34]	4.587	2.952

Lengths are given in Å.

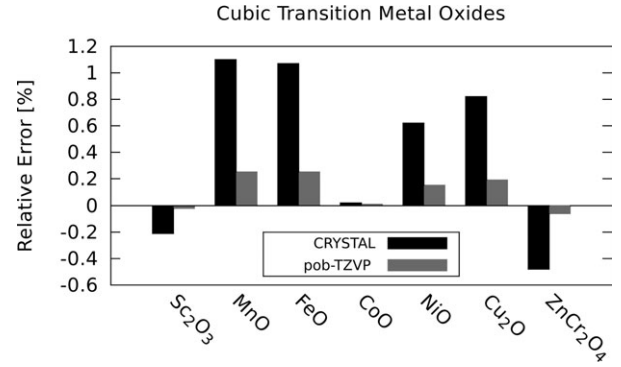

Figure 6. Relative error in the lattice constants of cubic transition metal oxides with respect to experiment.

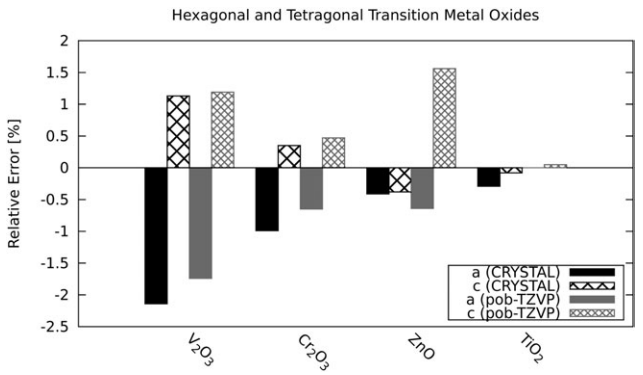

Figure 7. Relative error in the lattice constants of hexagonal and tetragonal transition metal oxides with respect to experiment.

error statistics. The maximum error in the lattice constants calculated with the CRYSTAL basis sets is 3.0 and 2.8% with the pob-TZVP basis. The mean error in the lattice constants is 1.2% for the CRYSTAL standard basis sets and 1.0% for the pob-TZVP basis sets. The total energies per unit cell are given in the Supporting Information.

Table 12. Experimental and calculated lattice constants of selected cubic metals.

Metal	Experiment[52]	CRYSTAL	pob-TZVP	pob-TZVP+s	Shell (exponent)
Li	4.404	3.871[101]	4.390	4.444	s (0.050)
Na	4.291	–[17]	4.269		
K	5.247	–[17]	4.570	5.141	s (0.033)
Ca	4.486	–[20]	4.035	4.324	s (0.067)
Sc	4.541	–[a]	4.428		
V	3.024	2.637[26]	2.946		
Cr	3.680	3.233[36]	3.473		
Fe	2.867	–[102]	2.746		
Ni	3.524	3.171[37]	3.423		
Cu	3.615	3.363[26]	3.506		
Al	4.050	3.494[22]	3.731	4.092	p (0.05)
Ni_3Al	3.550[103]	3.105[22,37]	3.434		

An N-dash indicates that the optimization of the lattice constant failed. The value in brackets is the orbital exponent of the added function. Lengths are given in Å.
[a] Harrison et al. (unpublished).

Table 13. Experimental and calculated atomization enthalpies of selected ionic solid cubic compounds with CRYSTAL standard and pob-TZVP basis sets.

Compound	Experiment[104]	CRYSTAL	pob-TZVP
LiCl	685	663[16,33]	654
NaCl	640	614[17,33]	614
LiF	849	834[16,32]	823
NaF	762	733[17,32]	738
KF	737	705[17,32]	692
CaF_2	1562	1531[20,32]	1540
K_2O	790	701[17,29]	683
MgO	994	971[20,29]	970
CaO	1062	1030[20,29]	1034
LiH	518	471[15,16]	457
NaH	382	374[15,17]	379
KH	365	349[15,17]	333

Energies are given in kJ/mol.

Summary

We have presented a well-balanced, generally applicable, consistent TZV with polarization quality basis set for periodic quantum-chemical solid-state calculations, denoted by pob-TZVP. It provides robust and stable SCF convergence for a wide range of different compounds, and it is variationally better than the standard basis sets provided by the CRYSTAL basis set database. 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 starting point for electron correlation calculations. For example, our presented Li basis performs well in metallic Li, ionic Li and LiCl, in which Li is positively charged, as well in LiH in which Li is negatively charged. We have shown that the computed lattice constants are an improvement over the standard basis sets for both DFT and HF methods. 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 (http://www.thch.uni-bonn.de/tc/) and also as Supporting Information to this article.

Table 14. Experimental and calculated HF lattice parameters of selected compounds with CRYSTAL standard and pob-TZVP basis sets.

	a		
Compound	Experiment	CRYSTAL	pob-TZVP
LiCl	5.130[48]	5.284[16,33]	5.271
NaCl	5.640[49]	5.788[17,33]	5.702
LiF	4.027[50]	4.007[16,32]	4.027
NaF	4.632[51]	–[17,32]	4.606
KF	5.347[52]	5.400[17,32]	5.409
CaF_2	5.463[53]	5.533[20,32]	5.512
K_2O	6.436[54]	6.407[17,29]	6.469
MgO	4.217[52]	4.191[20,29]	4.189
CaO	4.811[55]	4.860[20,29]	4.859
LiH	4.083[56]	4.105[15,16]	4.155
NaH	4.890[57]	4.884[15,17]	4.880
KH	5.704[58]	5.758[15,17]	5.784

An N-dash indicates that the structure optimization failed. Lengths are given in Å.

Acknowledgments

The authors thank Friederike Eberhagen for preliminary test calculations and Christoph Reimann for his help with python scripting.

Keywords: CRYSTAL · basis sets · TZVP · solid-state calculations

How to cite this article: M. F. Peintinger, D. V. Oliveira, T. Bredow, *J. Comput. Chem.* **2012,** *0000,* 00–00. DOI: 10.1002/jcc.23153

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

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Received: 27 June 2012
Revised: 14 September 2012
Accepted: 17 September 2012
Published online on