

Optimized Slater-Type Basis Sets for the Elements 1–118

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Received 3 July 2002; Accepted 2 December 2002

Abstract: Seven different types of Slater type basis sets for the elements H ($Z = 1$) up to E118 ($Z = 118$), ranging from a double zeta valence quality up to a quadruple zeta valence quality, are tested in their performance in neutral atomic and diatomic oxide calculations. The exponents of the Slater type functions are optimized for the use in (scalar relativistic) zeroth-order regular approximated (ZORA) equations. Atomic tests reveal that, on average, the absolute basis set error of 0.03 kcal/mol in the density functional calculation of the valence spinor energies of the neutral atoms with the largest all electron basis set of quadruple zeta quality is lower than the average absolute difference of 0.16 kcal/mol in these valence spinor energies if one compares the results of ZORA equation with those of the fully relativistic Dirac equation. This average absolute basis set error increases to about 1 kcal/mol for the all electron basis sets of triple zeta valence quality, and to approximately 4 kcal/mol for the all electron basis sets of double zeta quality. The molecular tests reveal that, on average, the calculated atomization energies of 118 neutral diatomic oxides MO, where the nuclear charge Z of M ranges from $Z = 1$ –118, with the all electron basis sets of triple zeta quality with two polarization functions added are within 1–2 kcal/mol of the benchmark results with the much larger all electron basis sets, which are of quadruple zeta valence quality with four polarization functions added. The accuracy is reduced to about 4–5 kcal/mol if only one polarization function is used in the triple zeta basis sets, and further reduced to approximately 20 kcal/mol if the all electron basis sets of double zeta quality are used. The inclusion of g-type STOs to the large benchmark basis sets had an effect of less than 1 kcal/mol in the calculation of the atomization energies of the group 2 and group 14 diatomic oxides. The basis sets that are optimized for calculations using the frozen core approximation (frozen core basis sets) have a restricted basis set in the core region compared to the all electron basis sets. On average, the use of these frozen core basis sets give atomic basis set errors that are approximately twice as large as the corresponding all electron basis set errors and molecular atomization energies that are close to the corresponding all electron results. Only if spin-orbit coupling is included in the frozen core calculations larger errors are found, especially for the heavier elements, due to the additional approximation that is made that the basis functions are orthogonalized on scalar relativistic core orbitals.

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Key words: Slater type basis sets; Zeta quality; ZORA equation

Introduction

In many quantum chemical calculations one would like to use the largest basis sets possible, but often one can only afford to use basis sets of limited quality. In any case, one would like to know the accuracy of the basis set used. In this article an attempt is made to judge a number of Slater-type basis sets (STO) of different quality. One of the advantages to have several basis sets is that one can have a better idea of how the results of calculations of a certain property converge with respect to the basis set size.

In this article, double zeta, triple zeta, and quadruple zeta STO basis sets are developed and tested for all the elements ranging from H ($Z = 1$) up to E118 ($Z = 118$). Nonrelativistically optimized STO basis sets of double zeta quality are already avail-

able for most elements; see, for example, refs. 1–3. As is well known, however, relativistic effects are important for the heavier elements. Therefore, the basis sets in this article are optimized for the use in the zeroth-order regular approximated (ZORA) relativistic equation,^{4–7} which is an excellent approximation to the fully relativistic Dirac equation, especially in the valence region, which is important in quantum chemical calculations.

There are different ways of including relativistic effects in quantum chemical calculations. The best would be to use the full four-component Dirac equation, but this is still relatively expensive. Another possibility is to use one of the possible one- or

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two-component approximate relativistic equations, like the equations based on the Douglas–Kroll transformation,^{8,9} or the ZORA equation, which is used in this article. One can also use the more approximate relativistic effective core potential method, where the relativistic effects are included in the effective potential.

In quantum chemical calculations one often needs a smaller number of Slater-type functions than Gaussian-type functions (GTOs), to obtain the same accuracy. However, especially the evaluation of the two-electron integrals with GTOs can be implemented more efficiently than with STOs. Also in the literature one can find more Gaussian basis sets than Slater-type basis sets. For example, recently accurate relativistic Gaussian basis sets were developed for the elements ranging from H ($Z = 1$) to Lr ($Z=103$) in ref. 10. The systematically derived STO basis sets described in this article will make it easier to use STO basis sets of the desired quality. STOs are also sometimes used in calculations where one includes numerically calculated atomic orbitals in the basis set. The use of only a minimal basis set of numerically calculated atomic orbitals is often not enough for an accurate description of molecular orbitals. The inclusion of extra STOs in the basis set can then be used for a better description of these molecular orbitals.

To reduce the number of basis functions one can use methods in which only the valence electrons are treated explicitly, like the frozen core approximation, which is used in this article, or the more approximate effective core potential method, mentioned before. Note that these approximations do not necessarily mean that one has to use nonrelativistic kinematics for the valence electrons. For example, in this article, both the all-electron calculations as well as the frozen core calculations use the (scalar relativistic) ZORA equation. For computational efficiency the basis sets that are used in the frozen core calculations (frozen core basis sets) only have a limited basis set in the core region.

Seven different types of basis sets will be discussed in this article ranging from a frozen core double-zeta quality up to an all-electron quadruple-zeta quality with polarization functions added. All STO basis sets for all the elements ranging from H ($Z = 1$) up to E118 ($Z = 118$) will be tested on their performance in neutral atomic and diatomic oxide density functional calculations. The calculations will be performed both at the scalar relativistic (SR) level and with the inclusion of spin-orbit coupling. The ADF (Amsterdam Density Functional) program^{11–13} is used for electronic structure calculations on the atomic and molecular systems. For a subset of the diatomics, namely the group 2 and group 14 diatomic oxides, the band-structure program BAND,^{14,15} which is part of the ADF package, is used to calculate the influence of adding g-type STOs in the basis set and h- and i-type STOs in the fit set. Especially for the lighter elements more STO basis sets are available in the data bases of the ADF program. One of the main new developments in this respect are the even tempered basis sets generated by Chong,¹⁶ which will not be discussed in this article.

Slater-Type Basis Sets

Several Slater type basis sets of different quality were made for the elements H–E118 (nuclear charge $Z = 1–118$). The exponents of the STOs were fitted to numerical scalar relativistic ZORA orbitals. These numerical orbitals were calculated using the simple

spin-restricted $X\alpha$ version¹⁷ of density functional theory ($\alpha = 0.7$), with a point electric charge for the nucleus. We could have chosen a different density functional in our calculations, but from experience we know that this does influence the results much, because the shape of the orbitals does not depend a lot on the precise density functional used. The procedure for finding the exponents is the same as was described in detail in ref. 3, except here numerical SR ZORA orbitals are used instead of nonrelativistic ones. For the lighter elements H–Kr ($Z = 1–36$) still some of the nonrelativistically optimized basis sets are used in the SR ZORA calculations, as will be described below.

Four different types of all-electron basis sets were made, with acronyms DZ, TZP, TZ2P, and QZ4P. In the database of the molecular ADF program¹³ these basis sets are better known as basis sets II, IV, V, and QZ, respectively. The idea is (and was) that basis sets of similar quality are grouped together. The basis sets that will be discussed in this article are part of the adf2002 release of the ADF program (see Web site <http://www.scm.com>, where the described basis sets are freely available). In comparison with the adf2000 release of the ADF program the QZ4P basis set is new, and new basis sets are available for the elements with $Z = 104–118$. Some of the other basis sets are also modified, partly as a result of the test calculations that are presented in this article.

Due to the current limitations of the molecular ADF program, only s-, p-, d-, and f-type STOs are included in these basis sets. The all-electron DZ, TZP, and TZ2P basis sets all are double zeta in the core, whereas the all-electron QZ4P basis sets are triple zeta in the core. In the valence region the DZ basis sets are double zeta, the TZP and TZ2P basis sets are triple zeta, and the QZ4P basis set are quadruple zeta. Table 1 shows under the header “valence orbitals” the occupied orbitals that are considered to be in the valence region and which are fitted with two (DZ), three (TZ), or four (QZ) STOs. This list of valence orbitals is not meant to be a definition of valence orbitals, the detonation is used here only for convenience. Table 1 also shows under the header of the name of the basis sets the number of extra functions of s-, p-, d-, or f-type STOs that are included in the basis sets. These functions can be either polarization functions or (somewhat) diffuse functions, which are included mostly for a better description of molecular orbitals. These extra functions include functions that are unoccupied in the atom but have the same principal quantum number as an occupied atomic orbital, such as 2p for Li and Be, 4p for the first row transition metals, etc. In general, these basis sets are not adequate for an accurate calculation of (highly) excited states, for which one needs to include extra diffuse basis functions. For the lighter elements H–Kr ($Z = 1–36$) the nonrelativistically optimized exponents³ were used in the DZ, TZP, and TZ2P basis sets, because these basis sets are already flexible enough to represent the scalar relativistic ZORA orbitals reasonably accurately. For the elements Rb–E118 ($Z = 37–118$) the difference between the nonrelativistic and scalar relativistic ZORA orbitals is so large that a separate optimization is necessary, especially for an accurate description of the core orbitals. To describe these core orbitals more accurately, an extra tight 1s STO function was added to the all-electron DZ, TZP, and TZ2P basis sets for the elements Rb–E118 ($Z = 37–118$), and an extra tight 2p STO function for the elements In–E118 ($Z = 49–118$). For the same reason, the large QZ4P basis sets also contain extra 1s and 2p STO functions,

Table 1. Comparison of the Sizes of the All Electron Basis Sets (See Also the Text).

Elements		Valence orbitals	Extra functions			
			DZ	TZP	TZ2P	QZ4P
H—He	Z = 1–2	1s		p	pd	s2p2d
Li	Z = 3	2s	p	2pd	2pdf	3p2d2f
Be	Z = 4	2s	p	3pd	3pdf	3p2d2f
B—Ne	Z = 5–10	2s 2p		d	df	2d2f
Na	Z = 11	2p 3s	p	pd	pdf	p2d2f
Mg	Z = 12	2p 3s	p	pd	2pdf	p2d2f
Al—Ar	Z = 13–18	3s 3p		d	df	3d2f
K	Z = 19	3p 4s	pd	p2d	p2df	p4d3f
Ca	Z = 20	3p 4s	pd	p2d	p3df	p4d3f
Sc—Zn	Z = 21–30	3d 4s	pd	p	pf	2pd3f
Ga—Kr	Z = 31–36	3d 4s 4p		d	df	2d3f
Rb—Sr	Z = 37–38	3d 4p 5s	pd	p2d	p2df	p2d3f
Y—Cd	Z = 39–48	4d 5s	p	p	pf	p3f
In—Xe	Z = 49–54	4d 5s 5p		d	df	d3f
Cs—Ba	Z = 55–56	4d 5p 6s	pd	p2df	p2d2f	p2d4f
La—Gd	Z = 57–64	4f 5d 6s	pf	p	p	2p2f
Tb—Yb	Z = 65–70	4f 5d 6s	pf	p	pf	2p2f
Lu—Hg	Z = 71–80	4f 5d 6s	p	p	pf	2p2f
Tl—Rn	Z = 81–86	4f 5d 6s 6p		d	df	d2f
Fr—Ra	Z = 87–88	7s	pdf	p2df	p2d2f	pd3f
Ac—Lr	Z = 89–103	5f 6d 7s	pf	p ^a	2p	2p
Rf—E112	Z = 104–112	5f 6d 7s	p	p	pf	2pf
E113—E118	Z = 113–118	5f 6d 7s 7p			f	sd2f

^aIn the case of the actinide frozen core basis set there are two extra p functions.

especially for the heavier elements. The extra tight functions are added on top of the extra functions that were already described in Table 1. Especially the s-type electrons do not behave like Slater-type functions near the nucleus, but like Dirac-type functions that are of the form:

$$r^{\eta-1}e^{-\zeta r} \quad (1)$$

where η does not have to be an integer value. For STO's η is an integer.

The frozen core approximation is important to reduce the sizes of the basis sets and therefore for saving computer time. Three different types of frozen core basis sets were made, with acronyms DZ, TZP, and TZ2P. In the valence region these basis sets are the same as the corresponding all-electron basis sets. However, in the core region these optimized frozen core basis sets have a single-zeta quality, whereas the corresponding all electron ones all have a double-zeta quality in this region. The basis functions in the frozen core calculations are orthogonalized on the accurately calculated core orbitals, coming from atomic calculations. In the (SR) ZORA case, one needs extra core-like basis functions, to get high accuracy for the heavier systems. Again, this is due to the fact that the core wiggles of especially the s-type valence electrons do not behave like Slater-type orbitals near the nucleus. For this reason an extra 1s-type STO with large exponent is included in all the frozen core TZP and TZ2P basis sets starting from Cs-E118 ($Z = 55$ –118). Again, for the lighter elements H-Kr ($Z = 1$ –36) the non-

relativistic optimized exponents³ were not changed in the DZ, TZP, and TZ2P basis sets, only the description of the frozen core orbitals were changed from nonrelativistic to scalar relativistic ZORA. We refer to ref. 18 for a more detailed discussion of the frozen core approximation in the relativistic case, including the core orthogonalization procedure and (core) basis set requirements in that case.

In Table 2, the frozen cores are given for the frozen core basis sets that are tested in this article. For most elements there are also basis sets available that correspond to larger frozen cores than given in this table. These are not tested in this article. In the molecular ADF program the frozen core approximation in the

Table 2. Definition of the Frozen Cores That Are Used in the Calculations.

Elements			Frozen orbitals
Li–Mg	Z = 3–12	1s	
Al–Zn	Z = 13–30	1s 2s 2p	
Ga–Sr	Z = 31–38	1s 2s 2p 3s 3p	
Y–Cd	Z = 39–48	1s 2s 2p 3s 3p 3d	
In–Ba	Z = 49–56	1s 2s 2p 3s 3p 3d 4s 4p	
La–Rn	Z = 57–86	1s 2s 2p 3s 3p 3d 4s 4p 4d	
Fr–Ra	Z = 87–88	1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p	
Ac–E118	Z = 89–118	1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d	

ZORA case (including spin-orbit) is not implemented. Nevertheless, results will be reported of frozen core ZORA calculations, where the basis functions are orthogonalized on SR ZORA core orbitals. This is theoretically not fully justified;¹⁸ see also the discussion in the next section.

Table 1 gives details on the sizes of the basis set, but an example may help to clarify the differences in the sizes of the basis sets. We will use here the same notation that is often used for the sizes of contracted Gaussian type basis sets, because it is relatively short. If we take, for example, radon ($Z = 86$), the frozen core DZ basis set size is [8s7p4d3f]/(4s4p2d3f), the frozen core TZ2P basis set size is [10s8p6d4f]/(6s5p4d4f), the all-electron TZ2P basis set size is (14s12p8d4f), and the all electron QZ4P basis set size is (23s19p12d7f). The sizes of these basis sets show a typical behavior that one can find in the basis set sizes of the heavier atoms described in this article, namely that the all electron basis set size is much larger than the corresponding frozen core one, and that the all electron QZ4P basis set is again much larger than all the other all electron basis sets.

The ADF program uses a fit of the density in STOs to be able to calculate the Coulomb potential accurately. For this fit an extensive auxiliary STO basis set, also called fit set, is used. Due to the current limitations of the molecular ADF program, only s-, p-, d-, f-, and g-type STOs are included in the fit sets. This fit set is included in the database file for a given element. The number of fit functions in the fit set in the QZ4P basis sets is much larger than in the other basis sets. Also, the fit set differs whether one has an all electron or a frozen core basis set. The errors that are introduced by the use of a fit of the electron density will be discussed in the section on the test calculations.

The results with the QZ4P basis set are further tested against the results using the band-structure program BAND.¹⁴ This program uses as basis set both numerically calculated atomic orbitals (spinors) and STOs. The details how the (SR) ZORA method is implemented in this BAND program can be found in ref. 15, where details can also be found on the atomic potential approximation (APA) and the frozen core approximation, which are used in our calculations. In the ADF program and in the BAND program the frozen core approximation is implemented correctly in the SR ZORA case. If spin-orbit coupling is included, however, only the BAND program correctly orthogonalizes the basis functions on the ZORA core spinors. In this case, the ADF program orthogonalizes the basis functions on the SR ZORA core orbitals, which is not correct, see the discussion before. In the BAND calculations the same frozen cores are used as described in Table 2. Because the BAND program has the numerically calculated valence orbitals (spinors) in the basis, one usually does not need extra core-like basis functions for a high accuracy. In the (sub-) valence region the STOs in the basis sets for the BAND program that are tested in this article are the same as in the QZ4P basis sets. Only each numerically calculated (sub-) valence orbital (spinor) replaces the STO, which has the largest overlap with this orbital (spinor). The BAND program also uses a fit of the density in STOs to be able to calculate the Coulomb potential accurately. In the calculations the fit set used was taken from the large QZ4P fit set. Additional calculations are performed using the BAND program to study the effect of adding g-type STOs in the basis set and h- and i-type STOs in the fit set.

Atoms

In this section results of atomic basis set calculations are systematically compared with those of numerical calculations. For the exchange correlation potential the spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. The electron configurations used in the calculations are given in Table 3. It should be noted that these electron configurations are not always the experimental ground-state configurations, especially not in the case of the lanthanides and actinides. The electron configurations for these atoms are chosen such that all lanthanides have a partially filled 5d shell, and all actinides have a partially filled 6d shell. One of the advantages is that one then can get numerically converged valence d orbitals, which one may fit with STOs, as described in the previous section. Another advantage is that one then also gets numerically calculated (and converged) valence d ($d_{3/2}$ or $d_{5/2}$) orbital (spinor) energies, which one may compare with basis set calculated values.

If spin-orbit coupling is included in the calculation the same Table 3 can be used for the electron configuration, except that (if $l > 0$) now first the spinors with $j = l - 1/2$ are filled and next the spinors with $j = l + 1/2$. Thus, for example, a d^5 configuration in Table 3 will be a $(d_{3/2})^4(d_{5/2})^1$ configuration in the ZORA case. In the calculations we will later also use spin-orbit averaged configurations. In these calculations the electrons are divided in a spin-orbit averaged way over the different open shell irreps. If we again take the example of the d^5 configuration in Table 3, this leads to a $(d_{3/2})^2(d_{5/2})^3$ configuration in the spin-orbit averaged ZORA case. For other configurations the spin-orbit averaging can lead to fractional occupation numbers.

In Figures 1 and 2 a comparison is made between (SR) ZORA valence spinor (orbital) energies of the neutral atoms ($Z = 1$ –118) calculated numerically and those energies calculated using a basis set. The results of the all electron QZ4P basis set can also be viewed in more detail in Figure 3. The average basis set errors are given in Table 4. For convenience, here the definition is used that if the absolute value of the numerically calculated energy of a spinor (orbital) is lower than 1 a.u. (≈ 627.5 kcal/mol) this spinor (orbital) is considered to be a valence spinor (orbital). If this definition is used for the neutral atoms with $Z = 1$ up to 118, there are in total 289 difference orbitals in the SR ZORA case and 459 different spinors in the ZORA case that are considered to be valence.

Figures 1 and 2 show what can be expected, namely that if the all electron basis set is increased the basis set errors are reduced. The results with the all electron TZP basis set, which are not shown in these figures, are almost identical to the results with the all electron TZ2P basis set. This is not surprising, because the only difference between these basis sets is an extra polarization function in the TZ2P basis set, which in most cases will not affect the occupied atomic orbitals. Table 4 shows that on the average the results with the all electron TZP or TZ2P basis sets (average absolute error ≈ 1 kcal/mol) are about three times more accurate than the results with the all electron DZ basis set (average absolute error ≈ 3 –4 kcal/mol). The results with the large QZ4P basis set (average absolute error ≈ 0.03 kcal/mol) are more than an order of magnitude better than the results with the all electron TZP or TZ2P basis sets. This is also often true if one looks at the basis set errors

Table 3. Atomic Electron Configurations Used in the Calculations.

H	1s ¹	Ga	3d ¹⁰ 4s ² 4p ¹	Pm	4f ⁴ 5d ¹ 6s ²	Pa	5f ¹ 6d ² 7s ²
He	1s ²	Ge	3d ¹⁰ 4s ² 4p ²	Sm	4f ⁶ 5d ¹ 6s ²	U	5f ³ 6d ¹ 7s ²
Li	2s ¹	As	3d ¹⁰ 4s ² 4p ³	Eu	4f ⁶ 5d ¹ 6s ²	Np	5f ⁴ 6d ¹ 7s ²
Be	2s ²	Se	3d ¹⁰ 4s ² 4p ⁴	Gd	4f ⁷ 5d ¹ 6s ²	Pu	5f ⁵ 6d ¹ 7s ²
B	2s ² 2p ¹	Br	3d ¹⁰ 4s ² 4p ⁵	Tb	4f ⁸ 5d ¹ 6s ²	Am	5f ⁶ 6d ¹ 7s ²
C	2s ² 2p ²	Kr	3d ¹⁰ 4s ² 4p ⁶	Dy	4f ⁹ 5d ¹ 6s ²	Cm	5f ⁷ 6d ¹ 7s ²
N	2s ² 2p ³	Rb	5s ¹	Ho	4f ¹⁰ 5d ¹ 6s ²	Bk	5f ⁸ 6d ¹ 7s ²
O	2s ² 2p ⁴	Sr	5s ²	Er	4f ¹¹ 5d ¹ 6s ²	Cf	5f ⁹ 6d ¹ 7s ²
F	2s ² 2p ⁵	Y	4d ¹ 5s ²	Tm	4f ¹² 5d ¹ 6s ²	Es	5f ¹⁰ 6d ¹ 7s ²
Ne	2s ² 2p ⁶	Zr	4d ² 5s ²	Yb	4f ¹³ 5d ¹ 6s ²	Fm	5f ¹¹ 6d ¹ 7s ²
Na	3s ¹	Nb	4d ⁴ 5s ¹	Lu	4f ¹⁴ 5d ¹ 6s ²	Md	5f ¹² 6d ¹ 7s ²
Mg	3s ²	Mo	4d ⁵ 5s ¹	Hf	4f ¹⁴ 5d ² 6s ²	No	5f ¹³ 6d ¹ 7s ²
Al	3s ² 3p ¹	Tc	4d ⁶ 5s ¹	Ta	4f ¹⁴ 5d ³ 6s ²	Lr	5f ¹⁴ 6d ¹ 7s ²
Si	3s ² 3p ²	Ru	4d ⁷ 5s ¹	W	4f ¹⁴ 5d ⁴ 6s ²	Rf	5f ¹⁴ 6d ² 7s ²
P	3s ² 3p ³	Rh	4d ⁸ 5s ¹	Re	4f ¹⁴ 5d ⁵ 6s ²	Db	5f ¹⁴ 6d ³ 7s ²
S	3s ² 3p ⁴	Pd	4d ¹⁰	Os	4f ¹⁴ 5d ⁶ 6s ²	Sg	5f ¹⁴ 6d ⁴ 7s ²
Cl	3s ² 3p ⁵	Ag	4d ¹⁰ 5s ¹	Ir	4f ¹⁴ 5d ⁷ 6s ²	Bh	5f ¹⁴ 6d ⁵ 7s ²
Ar	3s ² 3p ⁶	Cd	4d ¹⁰ 5s ²	Pt	4f ¹⁴ 5d ⁸ 6s ²	Hs	5f ¹⁴ 6d ⁶ 7s ²
K	4s ¹	In	4d ¹⁰ 5s ² 4p ¹	Au	4f ¹⁴ 5d ¹⁰ 6s ¹	Mt	5f ¹⁴ 6d ⁷ 7s ²
Ca	4s ²	Sn	4d ¹⁰ 5s ² 4p ²	Hg	4f ¹⁴ 5d ¹⁰ 6s ²	E110	5f ¹⁴ 6d ⁸ 7s ²
Sc	3d ¹ 4s ²	Sb	4d ¹⁰ 5s ² 4p ³	Tl	4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	E111	5f ¹⁴ 6d ⁹ 7s ²
Ti	3d ² 4s ²	Te	4d ¹⁰ 5s ² 4p ⁴	Pb	4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	E112	5f ¹⁴ 6d ¹⁰ 7s ²
V	3d ³ 4s ²	I	4d ¹⁰ 5s ² 4p ⁵	Bi	4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	E113	5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹
Cr	3d ⁴ 4s ²	Xe	4d ¹⁰ 5s ² 4p ⁶	Po	4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	E114	5f ¹⁴ 6d ¹⁰ 7s ² 7p ²
Mn	3d ⁵ 4s ²	Cs	6s ¹	At	4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	E115	5f ¹⁴ 6d ¹⁰ 7s ² 7p ³
Fe	3d ⁶ 4s ²	Ba	6s ²	Rn	4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶	E116	5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴
Co	3d ⁷ 4s ²	La	5d ¹ 6s ²	Ra	7s ¹	E117	5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵
Ni	3d ⁸ 4s ²	Ce	4f ¹ 5d ¹ 6s ²	Fr	7s ²	E118	5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶
Cu	3d ¹⁰ 4s ¹	Pr	4f ² 5d ¹ 6s ²	Ac	6d ¹ 7s ²		
Zn	3d ¹⁰ 4s ²	Nd	4f ³ 5d ¹ 6s ²	Th	6d ² 7s ²		

in individual orbital (spinor) energies. The largest basis set errors with the all electron TZP or TZ2P basis sets can be found in the energies of the lanthanide 4F (4f_{5/2} and 4f_{7/2}) and the transactinide

7s (7s_{1/2}) orbitals (spinors). In the case of ZORA, thus with inclusion of spin-orbit coupling, there are also relatively large errors in the calculated energies of the transactinide 7p_{1/2} spinors.

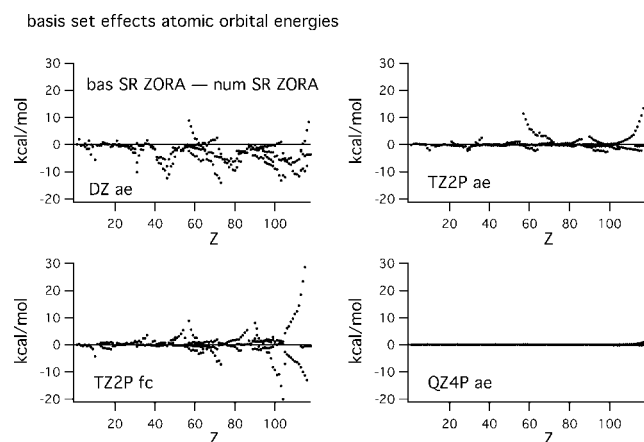


Figure 1. Differences (in kcal/mol) between basis set calculated SR ZORA valence atomic orbital energies and numerically calculated ones. Z is the nuclear charge of the atom. The spherical spin restricted X α ($\alpha = 0.7$) approximation is used. See Table 4 for average differences and the text for more details.

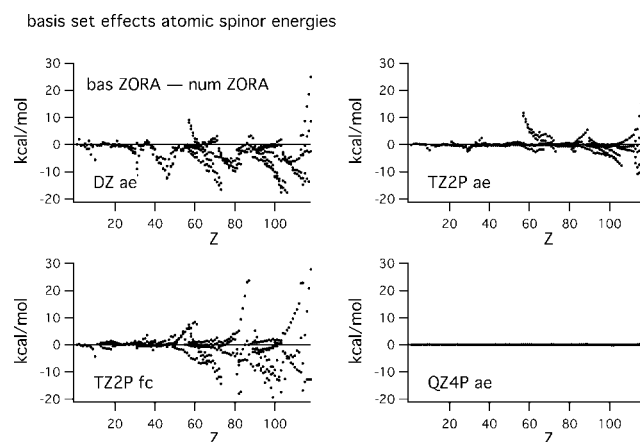


Figure 2. Differences (in kcal/mol) between basis set calculated ZORA valence atomic spinor energies and numerically calculated ones. Z is the nuclear charge of the atom. The spherical spin restricted X α ($\alpha = 0.7$) approximation is used. See Table 4 for average differences and the text for more details.

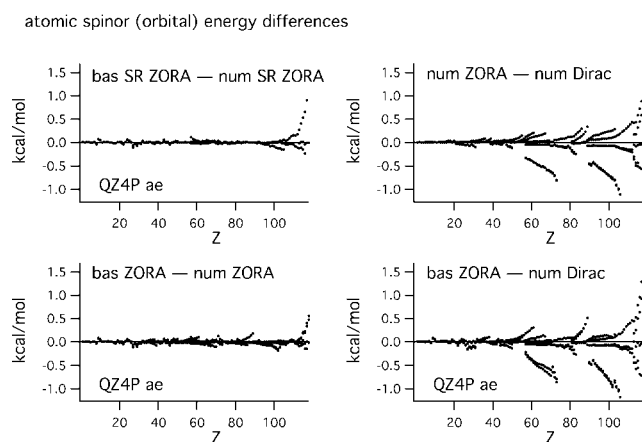


Figure 3. Differences (in kcal/mol) between basis set calculated (SR) ZORA valence atomic spinor (orbital) energies and numerically calculated ones and between calculated ZORA valence atomic spinor energies and numerically calculated Dirac spinor energies. The ZORA calculations were performed both numerically and in a basis set (QZ4P ae). Z is the nuclear charge of the atom. The spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. See Tables 4 and 5 for average differences and the text for more details.

The largest errors with the all electron QZ4P basis set can be found in the energies of the tansactinide $7s$ ($7s_{1/2}$) orbitals (spinors), and in the case of ZORA, also in the energies of the transactinide $7p_{1/2}$ spinors. The maximum error with the TZP or TZ2P basis set is in the SR ZORA case approximately 13 kcal/mol, and in the ZORA case approximately 26 kcal/mol. For comparison, the maximum errors with the QZ4P basis set are below 1 kcal/mol.

Figure 3 and Table 5 show the accuracy of the ZORA method in comparison with the fully relativistic Dirac equation. The average absolute difference between the numerically calculated occupied ZORA valence spinor energies and numerically calculated Dirac ones is only 0.16 kcal/mol. The average absolute basis set error in the calculation of these occupied ZORA valence spinor energies with the large QZ4P basis set is even smaller than this, namely only 0.03 kcal/mol. This means that for the calculation of

Table 5. Average Differences (in kcal/mol) between Calculated ZORA Valence Spinor Energies of the Neutral Atoms ($Z = 1$ –118) and Numerically Calculated Dirac Spinor Energies.

	num ZORA — num Dirac	bas ZORA — num Dirac
Average error	−0.07	−0.07
Av. abs. error	0.16	0.17
Max. error	−1.11	1.61
Worst Case	Sg $5f_{7/2}$	E118 $7s_{1/2}$

The ZORA calculations were performed both numerically and in a basis set (QZ4P ae). The spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. See Figure 3 and the text for more details.

occupied valence spinor energies there is not much reason to further increase the QZ4P basis set, because one then runs into the limitations of the ZORA method itself. Of course, there are many other properties than the spinor energies, like (hyper-) polarizabilities and excitation energies, which can be calculated more accurately if the basis set is increased.

As was described in the previous section, the core wiggles of the valence orbitals in the frozen core basis sets are described in a single zeta expansion. This is important because this will reduce the basis set size and thus save computer time in the calculations. Only the frozen core TZP and TZ2P basis sets for the elements Cs–E118 ($Z = 55$ –118) have an extra $1s$ -type STO with large exponent to make an effective double zeta description of the core wiggles in the $1s$ region. On the other hand, the all electron DZ, TZP, and TZ2P are all at least of double zeta quality in the whole core region. This means that the results with the frozen core basis sets are not the same as those with the corresponding all-electron basis sets, not even in the atomic calculations, where the use of the frozen core approximation is not an approximation by itself. Figures 1 and 2 show that the largest differences appear for elements with $Z > 80$. In the SR ZORA case, especially the valence energies of the actinide $5f$ orbitals and the transactinide $6d$ and $7s$ orbitals calculated with the frozen core basis sets are not described as accurately as in the all-electron case. In the ZORA case, which includes spin-orbit coupling, besides the valence energies of the

Table 4. Average Differences (in kcal/mol) between Basis Set Calculated (SR) ZORA Valence Spinor (Orbital) Energies of the Neutral Atoms ($Z = 1$ –118) and Numerically Calculated Ones.

	DZ fc	DZ ae	TZP fc	TZP ae	TZ2P fc	TZ2P ae	QZ4P ae
SR ZORA							
Average error	−3.9	−3.0	0.4	0.2	0.4	0.2	0.01
Av. abs. error	8.3	3.4	2.4	0.9	2.4	1.0	0.03
Max. error	92.1	−14.0	42.3	13.4	42.2	13.4	0.91
Worst case	E117 7s	Ta 4f	E117 7s	E117 7s	E117 7s	E117 7s	E117 7s
ZORA							
Av. error	−8.0	−3.2	−1.6	−0.2	−1.5	−0.1	0.00
Av. abs. error	12.8	4.0	5.5	1.4	5.4	1.4	0.03
Max. error	−104.1	24.9	105.0	26.0	105.0	26.0	0.56
Worst case	Lr $5f_{7/2}$	E118 $7p_{1/2}$	E118 $7p_{1/2}$	E118 $7p_{1/2}$	E118 $7p_{1/2}$	E118 $7p_{1/2}$	E118 $7s_{1/2}$

The spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. See Figures 1 to 3 and the text for more details.

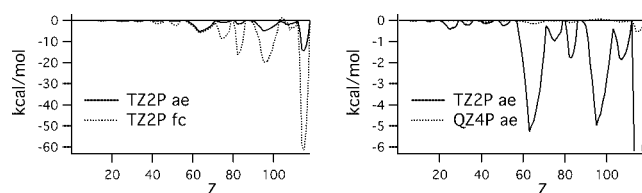


Figure 4. Differences (in kcal/mol) between basis set calculated and numerically calculated ZORA effects in the total energy of the neutral atoms ($Z = 1-118$) due to the spin-orbit averaging of the electron configuration. The spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. See Table 6 and the text for more details.

actinide $5f_{5/2}$ and $5f_{7/2}$ spinors and the transactinide $6d_{3/2}$, $6d_{5/2}$, and $7s_{1/2}$ spinors also the valence spinor energies of the $6p_{1/2}$ and $7p_{1/2}$ spinors calculated with the frozen core basis sets are not described as accurately as in the all-electron case. Some of the results with the TZ2P frozen core basis sets do not even fit in the figure. These are in the SR ZORA case the results for the $7s$ orbitals of E116 ($Z = 116$) and E117 ($Z = 117$), and in the ZORA case the results for the $6p_{1/2}$ spinors of Ra ($Z = 88$) and Ac ($Z = 89$) and 20 other spinors, all with $Z \geq 100$, see also the maximum errors in Table 4. The errors can be reduced in the SR ZORA case by adding more core-like basis functions. However, this will make calculations more expensive, and one may wonder why not to use the all-electron basis set in the first place. In the ZORA case (thus including spin-orbit) the frozen core basis sets are not really suited because the basis functions are orthogonalized on SR ZORA core orbitals. In this case, it is dangerous to include core-like basis functions (other than s functions), especially for the heavier atoms, because this can lead to variational collapse, as has been explained in more detail in ref. 18. In the spherical case for light atoms, the spin-orbit split (ZORA) eigenfunctions [$j = l + 1/2$ and $j = l - 1/2$] have almost the same radial behavior as the SR ZORA orbitals, the difference is then only in the spin and angular part. For closed-shell cores then there is no difference whether one uses full ZORA or SR ZORA orbitals, because they span the same space. For heavier atoms, where spin-orbit coupling is important, this is no longer true. The radial behavior of the eigenfunctions in a Coulomb potential near the origin can be quite different for SR ZORA or ZORA orbitals. Especially, the ZORA $p_{1/2}$ -orbital differs from the SR ZORA p -orbital, because it has a mild singularity near the origin. This means that one needs more core-like basis functions in the ZORA case than in the SR ZORA case, for the

same accuracy in the description of the core wiggles of the valence spinors (orbitals). This would not have been a problem in the ZORA case if one would correctly orthogonalize on ZORA core spinors, see again ref. 18.

The effect in the energy of the spin-orbit averaging of the atomic electron configuration can be calculated both numerically and with a basis set. The differences between the basis set results, and the numerical results are shown in Figure 4 and Table 6. These differences give an idea about the accuracy of the basis sets in the calculation of spin-orbit splittings. It should be noted that there is only an effect of spin-orbit averaging if there is at least one partially filled shell with $l > 0$ in the electron configuration. For all basis sets the maximum basis set error is reached for the element E115 (see Table 6). For this element E115 the $7p^3$ electron configuration in Table 3 means a $(7p_{1/2})^2(7p_{3/2})^1$ electron configuration in the ZORA case without spin-orbit averaging, and a $(7p_{1/2})^1(7p_{3/2})^2$ electron configuration after spin-orbit averaging. The basis set errors given in Table 6 are in the order of magnitude of the basis set errors given in Table 4. Thus, the accuracy of the calculation of individual spinor (orbital) energies can give an idea about the accuracy of the calculation of the difference in the energy between different electron configurations.

Figure 4 also shows that the results of the calculation of the spin-orbit effect with the all-electron TZ2P basis sets are quite close to the results with the corresponding frozen core basis sets, except for the atoms with nuclear charge $Z > 70$, in which case the results with frozen core are not so accurate any more. For an accurate description of the calculated spin-orbit effects, which are shown in Figure 4, one needs an accurate description of the core wiggles of the valence spinors, especially for atoms with nuclear charge $Z > 70$. An accurate description of these core wiggles is possible if the all electron basis sets are used, but it is not really possible if the frozen core basis sets are used, because the basis functions are orthogonalized on SR ZORA core orbitals. As was explained before, this is especially a problem for the heavier atoms. Note that the frozen core results for the $6d$ transactinide atoms are relatively accurate. We believe that this is fortuitous.

Because the BAND program has the numerically calculated valence orbitals (spinors) in the basis, there are no basis set errors in the BAND calculations for the atoms. Furthermore, one is free in the choice of the electron configuration of the reference atoms. Note that in the BAND program the frozen core approximation is implemented correctly also if spin-orbit coupling is included in the calculations.

Table 6. Average Differences (in kcal/mol) between Basis Set Calculated and Numerically Calculated ZORA Effects in the Total Energy of the Neutral Atoms ($Z = 1-118$) Due to the Spin-Orbit Averaging of the Electron Configuration.

	DZ fc	DZ ae	TZP fc	TZP ae	TZ2P fc	TZ2P ae	QZ4P ae
Av. abs. error	5.6	1.4	4.9	1.4	4.9	1.4	0.05
Max. error	-59.6	-12.4	-61.3	-14.2	-61.3	-14.2	-0.54
Worst case	E115	E115	E115	E115	E115	E115	E115

The spherical spin restricted $X\alpha$ ($\alpha = 0.7$) approximation is used. See Figure 4 and the text for more details.

Diatomic Oxides

The basis sets are further tested in the calculations of the bond energies of the oxides of all elements with nuclear charge Z ranging from $Z = 1$ –118, which means that the basis sets for all these elements are tested. Another advantage of using these test molecules is that many of the bond distances are known experimentally. Some preliminary calculations showed that basis set effects on the calculated bond energies are usually larger for the oxides than, for example, for the hydrides or halides if they are calculated at the experimental bond distance. This means that the diatomic oxides form a relatively stringent test for the calculation of basis set effects in atomization energies.

The diatomic oxides are calculated using the (nonrelativistic) LDA approximation for the exchange-correlation energy. If reported, the experimental bond lengths of ref. 19 are used. If not reported in this reference, a bond length of 1.6 Å is used for the 3d metal oxides, a bond length of 1.7 Å is used for the 4d and 5d metal oxides, a bond length of 1.8 Å is used for the lanthanide oxides, and a bond length of 1.9 Å is used for the actinide and transactinide oxides. The used bond lengths are given in Table 7. The molecular bond energy is calculated with respect to the spherical spin-restricted (and spin-orbit averaged) reference atoms. By doing this, we want to avoid the important but also complicated problem of how to calculate the reference energies of the open-shell atoms in density functional calculations (see for example ref. 20). The electron configurations used for the reference atoms are again the ones given in Table 3 (see also previous section). The basis set effects are evaluated with respect to the bond energy calculated with the large all electron QZ4P basis set as the reference. For a few molecules the results of the all electron QZ4P basis set are compared with the results of calculations with the band-structure program BAND, which is part of the ADF package. In the SR ZORA case the spin-polarized LDA approximation is used, whereas in the ZORA case the spin-restricted LDA approximation is used. In the calculated diatomics the (spin-) density is always cylindrically averaged. In the open-shell molecules the same occupation numbers are used in the calculations with the different basis sets. The used all-electron molecular configurations are given in Table 7. The aufbau principle is not always satisfied in the calculations, especially not in the calculations of the lanthanide and actinide oxides. Due to the approximations mentioned above, the calculated molecules will not always have the lowest energy and the most optimal bond distance. However, the purpose here is not to obtain the best possible bond energy that could be compared with experiment, but the purpose here is to obtain an estimate for the basis set effects in such calculations of bond energies. To do this meaningfully, it is important that the same electron configuration, bond distance, and exchange-correlation functional are used in the calculations with the different basis sets, which is the case in the present calculations.

The calculated (SR) ZORA bond energies with the all electron QZ4P basis set are presented in Table 8. Note that the ZORA results cannot be compared directly with the SR ZORA results, due to the different density functional methods used (spin-restricted vs. spin-unrestricted). Figure 5 shows the differences between the (SR) ZORA bond energies of the 118 neutral diatomic oxides that are calculated with several different basis sets and those energies

that are calculated with the large all-electron QZ4P basis set. The average absolute differences are given in Table 9. For the all-electron DZ basis set this difference is approximately 22 kcal/mol. The difference is reduced to about 4–5 kcal/mol if the all-electron TZP basis set is used, and further reduced to approximately 1–2 kcal/mol if the all-electron TZ2P basis set is used. Thus, to reduce the basis set effects, it is important to go from a double-zeta to a triple-zeta description in the valence region, but it is even more important to include polarization functions in the basis sets. One can think of a DZP basis set, which is a double zeta valence basis set plus one polarization function added (in the ADF program available for the lighter elements), as a compromise basis set, which is relatively small, but still gives rather accurate results. Some test calculations revealed that, indeed, such a basis set is capable of reducing the errors that were found with the DZ basis set considerably. It should be noted that the polarization functions are not important for an accurate calculation of the occupied atomic valence orbital (spinor) energies. This means that the accuracy of the basis sets in the calculation of atomic occupied valence orbital (spinor) energies is not directly transferable to the accuracy of the basis sets in the calculation of molecular bond energies.

In the SR ZORA case the bond energies calculated with the frozen core basis sets are quite close to those calculated with the corresponding all-electron basis sets, except for some of the oxides MO, with nuclear charge Z of M close to 100. The difference in the frozen core and all-electron results is largest for MdO, where it is approximately 10 kcal/mol if the TZ2P basis set is used. We will now discuss some of the reasons for this difference in the case of MdO, because these are illustrative also for the other oxides MO, with nuclear charge Z of M close to 100. The reason is not that the chosen core is too large. The main reason is that one needs extra basis functions in the core region. One especially needs extra p STOs in the core region to be able to describe the core wiggles of the valence $6p$ orbital better. As was described in the previous section, the core wiggles of the valence orbitals in the frozen core basis sets are described in a single zeta expansion, whereas this is at least a double-zeta expansion in the corresponding all-electron basis sets. The improved description of the $6p$ orbital due to extra p STOs in the core region also indirectly improves the accuracy of the calculated $5f$ orbitals, and gives an improved result for the bond energy. One could say that another reason for the difference of the all-electron and frozen core results lies in the chosen atomic electron configuration for Md. If one would have chosen a $5f^{13}7s^2$ electron configuration instead of the used $5f^{12}6d^17s^2$ electron configuration of Table 3, the frozen core and all-electron results would be much closer in energy. This is mainly due to the fact that also in the molecule MdO, if the molecular electron configuration of Table 7 is used, the electron configuration is close to 13 electrons in the $5f$ shell of Md (obtained from a Mulliken population analysis). This means that there can be an effective cancellation of errors in the calculation of the molecule with respect to its constituent atoms, such that the calculated bond energy is relatively accurate. The basis set effects in the calculated bond energy of MdO and the basis set effect in the difference in total energy of the $5f^{13}7s^2$ electron configuration and the $5f^{12}6d^17s^2$ electron configuration for Md are in the same order of magnitude if the frozen core TZ2P basis set is used. The size of this effect can be

Table 7. Molecular Bond Distances and Electron Configurations Used in the Calculations.

	Bond distance	SR ZORA								ZORA			
		σ		π		δ		ϕ		$j_z =$			
		α	β	α	β	α	β	α	β	1/2	3/2	5/2	7/2
OH	0.970	3	3	2	1					8	1		
HeO	1.2	3	3	2	2					8	2		
LiO	1.7	4	4	2	1					10	1		
BeO	1.331	4	4	2	2					10	2		
BO	1.204	5	4	2	2					11	2		
CO	1.1283	5	5	2	2					12	2		
NO	1.1508	5	5	3	2					13	2		
O ₂	1.208	5	5	4	2					14	2		
FO	1.15	5	5	4	3					14	3		
NeO	1.3	5	5	4	4					14	4		
NaO	1.4	6	5	4	4					15	4		
MgO	1.749	6	6	4	4					16	4		
AlO	1.618	7	6	4	4					17	4		
SiO	1.510	7	7	4	4					18	4		
PO	1.476	7	7	5	4					19	4		
SO	1.481	7	7	6	4					20	4		
ClO	1.570	7	7	6	5					20	5		
ArO	1.7	7	7	6	6					20	6		
KO	1.7	8	7	6	6					21	6		
CaO	1.822	8	8	6	6					22	6		
ScO	1.668	9	8	6	6					23	6		
TiO	1.620	9	8	6	6	1				24	6		
VO	1.589	9	8	6	6	2				22	8	1	
CrO	1.61	9	8	7	6	2				24	8		
MnO	1.77	9	8	8	6	2				23	8	2	
FeO	1.6	10	8	8	6	2				24	8	2	
CoO	1.6	10	8	8	6	2	1			24	9	2	
NiO	1.6	9	9	8	6	2	2			26	8	2	
CuO	1.6	9	9	8	7	2	2			26	9	2	
ZnO	1.6	9	9	8	8	2	2			26	10	2	
GaO	1.6	10	9	8	8	2	2			27	10	2	
GeO	1.625	10	10	8	8	2	2			28	10	2	
AsO	1.624	10	10	9	8	2	2			29	10	2	
SeO	1.648	10	10	10	8	2	2			30	10	2	
BrO	1.717	10	10	10	9	2	2			30	11	2	
KrO	1.717	10	10	10	10	2	2			30	12	2	
RbO	1.8	11	10	10	10	2	2			31	12	2	
SrO	1.920	11	11	10	10	2	2			32	12	2	
YO	1.788	12	11	10	10	2	2			33	12	2	
ZrO	1.712	12	12	10	10	2	2			34	12	2	
NbO	1.691	12	11	10	10	4	2			34	13	2	
MoO	1.7	12	11	11	10	4	2			34	14	2	
TcO	1.7	12	11	12	10	4	2			33	14	4	
RuO	1.7	12	11	12	10	4	3			34	14	4	
RhO	1.7	12	11	12	10	4	4			34	15	4	
PdO	1.7	12	12	12	10	4	4			36	14	4	
AgO	2.003	12	12	12	11	4	4			35	16	4	
CdO	1.9	12	12	12	12	4	4			36	16	4	
InO	1.9	13	12	12	12	4	4			37	16	4	
SnO	1.832	13	13	12	12	4	4			38	16	4	
SbO	1.826	13	13	13	12	4	4			39	16	4	
TeO	1.825	13	13	14	12	4	4			40	16	4	
IO	1.868	13	13	14	13	4	4			40	17	4	

(continued)

Table 7. (Continued)

	Bond distance	SR ZORA								ZORA			
		σ		π		δ		ϕ		$j_z =$			
		α	β	α	β	α	β	α	β	1/2	3/2	5/2	7/2
XeO	1.9	13	13	14	14	4	4			40	18	4	
CsO	1.9	14	13	14	14	4	4			41	18	4	
BaO	1.9397	14	14	14	14	4	4			42	18	4	
LaO	1.826	15	14	14	14	4	4			43	18	4	
CeO	1.8	15	14	14	14	5	4			43	18	5	
PrO	1.8	15	14	14	14	5	4	1		43	19	5	
NdO	1.8	15	14	15	14	5	4	1		44	19	5	
PmO	1.8	15	14	15	14	6	4	1		44	19	5	1
SmO	1.8	15	14	15	14	6	4	2		44	19	6	1
EuO	1.8	15	14	16	14	6	4	2		44	20	6	1
GdO	1.8	15	15	16	14	6	4	2		45	20	6	1
TbO	1.8	15	15	16	14	6	5	2		45	20	7	1
DyO	1.8	15	15	16	14	6	5	2	1	45	21	7	1
HoO	1.8	15	15	16	15	6	5	2	1	45	21	7	2
ErO	1.8	15	15	16	15	6	6	2	1	46	21	7	2
TmO	1.8	15	15	16	15	6	6	2	2	46	21	8	2
YbO	1.8	15	15	16	16	6	6	2	2	46	22	8	2
LuO	1.790	16	15	16	16	6	6	2	2	47	22	8	2
HfO	1.723	16	16	16	16	6	6	2	2	48	22	8	2
TaO	1.687	16	16	16	16	7	6	2	2	48	23	8	2
WO	1.7	16	16	16	16	8	6	2	2	48	24	8	2
ReO	1.7	16	16	17	16	8	6	2	2	48	24	9	2
OsO	1.7	16	16	17	16	8	7	2	2	48	24	10	2
IrO	1.7	16	16	18	16	8	7	2	2	48	26	9	2
PtO	1.727	16	16	18	16	8	8	2	2	50	24	10	2
AuO	1.7	16	16	18	17	8	8	2	2	50	25	10	2
HgO	1.7	16	16	18	18	8	8	2	2	50	26	10	2
TlO	1.8	17	16	18	18	8	8	2	2	51	26	10	2
PbO	1.922	17	17	18	18	8	8	2	2	52	26	10	2
BiO	1.9	17	17	19	18	8	8	2	2	53	26	10	2
PoO	1.9	17	17	20	18	8	8	2	2	54	26	10	2
AtO	1.9	17	17	20	19	8	8	2	2	54	27	10	2
RnO	1.9	17	17	20	20	8	8	2	2	54	28	10	2
FrO	1.9	18	17	20	20	8	8	2	2	55	28	10	2
RaO	1.9	18	18	20	20	8	8	2	2	56	28	10	2
AcO	1.9	19	18	20	20	8	8	2	2	57	28	10	2
ThO	1.840	19	19	20	20	8	8	2	2	58	28	10	2
PaO	1.9	19	18	20	20	9	8	3	2	58	28	11	2
UO	1.9	19	18	21	20	9	8	3	2	58	29	11	2
NpO	1.9	19	18	21	20	10	8	3	2	58	29	12	2
PuO	1.9	19	18	21	20	10	8	4	2	58	30	12	2
AmO	1.9	19	18	22	20	10	8	4	2	58	30	12	3
CmO	1.9	19	19	22	20	10	8	4	2	58	30	12	4
BkO	1.9	19	19	22	20	10	9	4	2	59	30	12	4
CfO	1.9	19	19	22	20	10	9	4	3	60	30	12	4
EsO	1.9	19	19	22	21	10	9	4	3	60	30	13	4
FmO	1.9	19	19	22	21	10	10	4	3	60	30	14	4
MdO	1.9	19	19	22	21	10	10	4	4	60	31	14	4
NoO	1.9	19	19	22	22	10	10	4	4	60	32	14	4
LrO	1.9	20	19	22	22	10	10	4	4	61	32	14	4
RfO	1.9	20	20	22	22	10	10	4	4	62	32	14	4
DbO	1.9	20	20	22	22	11	10	4	4	62	33	14	4
SgO	1.9	20	20	22	22	12	10	4	4	62	34	14	4

(continued)

Table 7. (Continued)

	Bond distance	SR ZORA								ZORA			
		σ		π		δ		ϕ		$j_z =$			
		α	β	α	β	α	β	α	β	1/2	3/2	5/2	7/2
BhO	1.9	20	20	23	22	12	10	4	4	63	34	14	4
HsO	1.9	20	20	24	22	12	10	4	4	64	34	14	4
MtO	1.9	20	20	24	22	12	11	4	4	64	34	15	4
E110O	1.9	21	20	24	22	12	11	4	4	64	34	16	4
E111O	1.9	21	20	24	22	12	12	4	4	64	35	16	4
E112O	1.9	20	20	24	24	12	12	4	4	64	36	16	4
E113O	1.9	21	20	24	24	12	12	4	4	65	36	16	4
E114O	1.9	21	21	24	24	12	12	4	4	66	36	16	4
E115O	1.9	21	21	25	24	12	12	4	4	67	36	16	4
E116O	1.9	21	21	26	24	12	12	4	4	68	36	16	4
E117O	1.9	21	21	26	25	12	12	4	4	68	37	16	4
E118O	1.9	21	21	26	26	12	12	4	4	68	38	16	4

explained largely by the basis set error in the 5f orbital of Md, which is about 11 kcal/mol if the frozen core TZ2P basis set is used. Again, this serves as an example that the accuracy of the calculation of individual orbital (spinor) energies can give an idea about the accuracy of the calculation of the difference in the energy between different electron configurations.

In the ZORA case, the results with the all-electron basis sets are quite close to the results with the corresponding frozen core basis sets, except for the diatomic oxides MO with nuclear charge Z of M larger than 70. In the previous section a similar situation was found in the calculation of the effect of the spin-orbit averaging in neutral atomic ZORA calculations. There also the frozen core calculations for the elements with nuclear charge Z of M larger than 70 were not so accurate as the corresponding all-electron ones. As discussed in the atomic section, the main reason for these inaccuracies is that the frozen core basis functions are orthogonalized on SR ZORA core orbitals, which is not correct if one performs a ZORA calculation. This is not such a problem for the lighter elements, but it is a problem for the heavier elements.

Table 10 shows the average and maximum first-order errors in the bond energy due to the use of an approximated fitted electron density in the calculation of the Coulomb potential. For a few basis sets Figure 6 shows the results in more detail. The first-order fit corrections are included in the evaluated molecular bond energies. On average, the calculated first-order fit corrections for all the basis sets are well below 1 kcal/mol. One may expect the higher order fit corrections to be even smaller, which means that the fit set is accurate enough not to influence the conclusions made for the accuracy of the basis sets. The fit set used in the all-electron QZ4P basis set is even an order of magnitude better than those of the other basis sets described in Table 10. For this QZ4P basis set relatively the largest errors in the first-order fit correction can be found in the lanthanide and actinide oxides (see also Fig. 6). In these cases one needs to include fit function with quantum number $l \geq 5$ if one wants to reduce the fit error, because they are not included in the used fit sets. On the other hand, also for these molecules the first-order fit corrections are already so small that for

an accuracy of a few tenths of a kcal/mol one does not need to go beyond the used fit sets.

The basis set super position errors (BSSE) might influence the accuracy of the calculations more. Table 11 shows the average and maximum BSSEs calculated with the tested basis sets for the diatomic oxides. For a few basis sets Figure 6 shows the SR ZORA results for the BSSEs in more detail. The BSSE in the case of the all-electron QZ4P basis set is always below 0.1 kcal/mol. The average absolute BSSEs calculated with the all electron DZ basis set and the all-electron and frozen core TZ basis sets are approximately 0.5 kcal/mol. Only the BSSEs calculated with the smallest basis set, namely the frozen core DZ basis set, can be as large as 10 kcal/mol for some of the actinide oxides. The average errors in this case are approximately 2 kcal/mol. It should be noted that the results in Tables 8 and 9 for the bond energies are calculated without the inclusion of the BSSE. Up to an accuracy of 0.1 kcal/mol this is certainly correct for the all electron QZ4P basis set. If one would include the BSSEs in the results of Table 9 one obtains slightly less accurate results for calculations with the DZ and TZ basis sets. This means that the basis set errors in these calculations of the bond energies are partly compensated by the BSSEs, thus a partly cancellation of errors.

For a few molecules the results of the molecular ADF program with the all-electron QZ4P basis set are tested against the results of the band-structure program BAND with frozen core basis sets. The 12 tested molecules are the group 2 oxides BeO, MgO, CaO, SrO, BaO, and RaO, and the group 14 oxides CO, SiO, GeO, SnO, PbO, and E114O, which are all closed-shell molecules in the ground state. First, the same restrictions are used as in the molecular ADF program, namely that the STOs in the basis sets have to be of s, p, d, or f type. As described before in the (sub-) valence region the basis sets used are of similar quality as the QZ4P basis sets. In this case, the calculated bond energies using the BAND program are in very close agreement with those energies calculated with the ADF program using the large QZ4P basis set (see Table 12). Both at the SR ZORA and at the ZORA level the calculated bond energies with the two programs are within 0.5 kcal/mol of each other, except for E114O at the ZORA level where the difference is 1.0

Table 8. Calculated (SR) ZORA Bond Energies (in kcal/mol) of 118 Neutral Diatomic Oxides Calculated with the All Electron QZ4P Basis Set.

	SR ZORA	ZORA		SR ZORA	ZORA		SR ZORA	ZORA		SR ZORA	ZORA
OH	−180.3	−171.1	GaO	−169.6	−163.5	PmO	−363.3	−300.1	PaO	−312.7	−311.2
HeO	−4.6	−4.6	GeO	−245.6	−245.7	SmO	−404.1	−296.9	UO	−303.6	−303.5
LiO	−140.9	−132.6	AsO	−223.7	−221.8	EuO	−458.4	−296.2	NpO	−325.3	−319.7
BeO	−181.0	−181.0	SeO	−197.3	−187.0	GdO	−465.8	−278.6	PuO	−353.6	−345.9
BO	−277.0	−263.6	BrO	−135.1	−132.6	TbO	−417.6	−316.0	AmO	−394.3	−340.7
CO	−362.9	−362.9	KrO	−38.2	−38.3	DyO	−375.3	−330.7	CmO	−401.0	−329.5
NO	−305.0	−299.2	RbO	−103.5	−93.5	HoO	−340.6	−314.9	BkO	−370.6	−352.3
O ₂	−247.4	−224.2	SrO	−172.2	−172.2	ErO	−315.0	−312.9	CfO	−350.3	−356.0
FO	−118.3	−111.9	YO	−248.7	−244.5	TmO	−292.8	−301.1	EsO	−327.7	−353.1
NeO	44.4	44.4	ZrO	−277.9	−278.0	YbO	−288.1	−290.5	FmO	−321.4	−346.7
NaO	−30.2	−16.5	NbO	−317.8	−293.8	LuO	−237.9	−234.4	MdO	−325.3	−337.7
MgO	−122.6	−122.6	MoO	−297.7	−275.4	HfO	−290.2	−291.1	NoO	−319.1	−318.4
AlO	−194.4	−188.4	TcO	−274.0	−252.2	TaO	−295.8	−298.7	LrO	−216.9	−218.0
SiO	−275.3	−275.3	RuO	−240.6	−228.7	WO	−302.2	−301.9	RfO	−279.8	−284.4
PO	−254.8	−250.9	RhO	−213.7	−196.8	ReO	−277.3	−284.7	DbO	−280.1	−294.1
SO	−221.6	−206.4	PdO	−132.6	−119.9	OsO	−250.6	−261.1	SgO	−280.5	−303.7
ClO	−144.7	−140.4	AgO	−109.7	−101.3	IrO	−227.6	−211.0	BhO	−258.3	−295.8
ArO	−27.7	−27.7	CdO	−86.0	−86.3	PtO	−209.7	−213.2	HsO	−234.8	−279.4
KO	−99.7	−88.5	InO	−153.4	−147.3	AuO	−119.0	−123.2	MtO	−205.0	−255.3
CaO	−180.1	−180.1	SnO	−215.5	−215.9	HgO	−60.0	−65.1	E110O	−137.3	−220.0
ScO	−250.0	−245.1	SbO	−200.6	−201.5	TlO	−134.2	−131.4	E111O	−116.7	−162.3
TiO	−270.8	−252.3	TeO	−182.6	−179.3	PbO	−201.0	−204.8	E112O	−55.2	−82.6
VO	−296.1	−230.0	IO	−133.6	−134.8	BiO	−187.2	−200.4	E113O	−122.8	−139.2
CrO	−300.6	−255.3	XeO	−59.1	−59.7	PoO	−171.8	−190.5	E114O	−179.0	−209.6
MnO	−295.2	−220.2	CsO	−124.2	−116.6	AtO	−127.7	−142.3	E115O	−168.4	−224.9
FeO	−250.5	−236.0	BaO	−204.9	−204.9	RnO	−60.7	−64.4	E116O	−156.4	−229.9
CoO	−218.2	−223.4	LaO	−278.9	−275.3	FrO	−110.5	−105.0	E117O	−117.2	−168.2
NiO	−226.6	−210.5	CeO	−290.2	−284.5	RaO	−170.7	−171.0	E118O	−60.1	−70.9
CuO	−140.0	−135.5	PrO	−304.0	−294.3	AcO	−247.5	−244.5			
ZnO	−100.0	−100.1	NdO	−328.7	−301.9	ThO	−310.9	−310.7			

The nuclear charge Z of M of the diatomics MO ranges from $Z = 1$ –118. The molecular bond energy was calculated with respect to the spherical spin-restricted reference atoms, within the LDA approximation for the exchange-correlation energy. For ZORA, the results are shown in the case the atoms are calculated in a spin-orbit averaged way. These are artificial bond energies due to the used electronic configurations of the molecules and the atoms.

kcal/mol. This means that one can get accurate results using the frozen core approximation for bond energies also at the ZORA level, thus including spin-orbit coupling, if it is correctly implemented. The advantage of the BAND program is that it can calculate the core wiggles of the atomic valence orbitals (spinors) with numerical precision. The close agreement of the results of the all-electron QZ4P basis set with the results of the BAND program suggests that one does not need to include extra core-like basis functions in the all electron QZ4P basis set for an accuracy of about 1 kcal/mol in the bond energy.

The question still remains if the results are close to the basis set limit. Because the basis sets used in the BAND program are of similar quality in the (sub-) valence region as the QZ4P basis sets, a comparison of the results with these basis sets will not tell the influence of extra diffuse functions and/or extra polarization functions to the large QZ4P basis set. One question is, for example, the influence of adding extra g-type STOs. This is tested with the BAND program, where for each element the basis set used is

increased with two g-type STOs. For each element the same two g-type STOs are chosen, always with exponents equal to 2 and 5. At the same time h- and i-type STOs were added in the fit set. Due to the inclusion of these g-type STOs, the absolute value of the calculated bond energies increased with almost 1.0 kcal/mol for RaO and E114O, but with less than 0.5 kcal/mol for the other 10 tested molecules (see Table 12). The inclusion of the h- and i-type STOs in the fit caused the already very small first-order fit correction to be even smaller.

Conclusions

Seven different types of relativistic Slater-type basis sets for the elements H ($Z = 1$) up to E118 ($Z = 118$), ranging from a frozen core basis set with double zeta quality up to an all-electron basis set with quadruple-zeta valence quality, were tested in their performance in atomic and diatomic calculations. The frozen core

basis set effects bond energy diatomic oxides

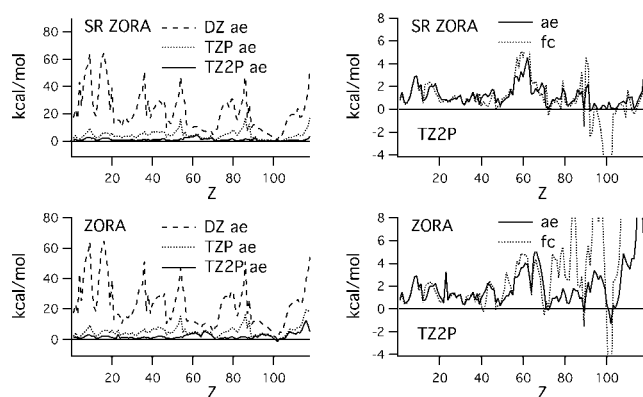


Figure 5. Differences (in kcal/mol) between the (SR) ZORA bond energies of 118 neutral diatomic oxides calculated with the mentioned basis set and those energies calculated with the large all-electron QZ4P basis set. The nuclear charge Z of M of the diatomics MO ranges from $Z = 1$ –118. The molecular bond energy was calculated with respect to the spherical spin-restricted reference atoms, within the LDA approximation for the exchange-correlation energy. In the case of ZORA, the atoms are calculated in a spin-orbit averaged way. See Table 9 for average values and the text for more details.

basis sets, which have a restricted basis set in the core region compared to the all-electron basis sets, are optimized basis sets to be used in calculations using the frozen core approximation. On average, the absolute basis set error of 0.03 kcal/mol in the density

BSSE and fit error diatomic oxides SR ZORA

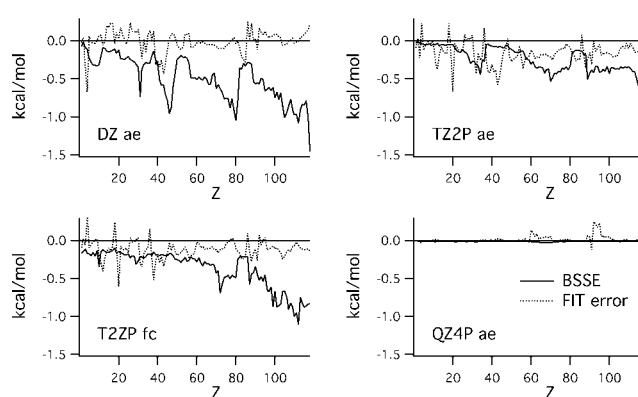


Figure 6. Calculated first-order fit corrections (fit error, dotted line) and basis set superposition errors (BSSE, solid line) in the SR ZORA bond energy (in kcal/mol) of 118 neutral diatomic oxides MO, where the nuclear charge Z or M ranges from $Z = 1$ –118. See Tables 10 and 11 for average values and the text for more details.

functional calculation of the valence spinor energies of the neutral atoms with the largest all-electron basis set of quadruple zeta quality is lower than the average absolute difference of 0.16 kcal/mol in these valence spinor energies if one compares the results with the ZORA equation to those of the fully relativistic Dirac equation. This average absolute basis set error in the calculation of valence orbital and spinor energies increases to about 1 kcal/mol for the all electron basis sets of triple-zeta valence qual-

Table 9. Average Differences (in kcal/mol) between the (SR) ZORA Bond Energies of 118 Neutral Diatomic Oxides Calculated with the Mentioned Basis Set and Those Energies Calculated with the Large All Electron QZ4P Basis Set.

	DZ fc	DZ ae	TZP fc	TZP ae	TZ2P fc	TZ2P ae
SR ZORA						
Average error	15.5	22.0	4.1	4.5	0.9	1.2
Av. abs. error	22.5	22.0	4.8	4.5	1.6	1.2
Max. error	65.3	64.6	16.7	16.8	−9.0	4.5
Worst case	SO	SO	XeO	RnO	MdO	SmO
ZORA: atoms SO averaged^a						
Average error	19.3	22.9	7.6	5.3	4.3	2.0
Av. abs. error	25.7	22.9	7.9	5.3	4.7	2.0
Max. error	75.1	64.6	55.5	19.5	47.6	12.3
Worst case	E116O	SO	E116O	E116O	E116O	E116O
ZORA: atoms not SO averaged^b						
Average error	13.6	21.4	2.7	4.0	−0.6	0.7
Av. abs. error	23.4	21.5	5.8	4.3	3.6	1.4
Max. error	−72.9	64.4	−34.4	18.0	−38.3	−7.7
Worst case	MdO	SO	E114O	E118O	E114O	E114O

The nuclear charge Z of M of the diatomics MO ranges from $Z = 1$ –118. The molecular bond energy was calculated with respect to the spherical spin-restricted reference atoms, within the LDA approximation for the exchange-correlation energy. For ZORA, the results are shown both in the case the atoms are calculated in a spin-orbit averaged way and if the atoms are not calculated in a spin-orbit averaged way. See Figure 5 and the text for more details.

^aReference atoms are spin-orbit averaged.

^bReference atoms are not spin-orbit averaged.

Table 10. Average Calculated First-Order Fit Corrections in the Bond Energy (in kcal/mol) of 118 Neutral Diatomic Oxides MO, Where the Nuclear Charge Z of M Ranges from Z = 1–118.

	DZ fc	DZ ae	TZP fc	TZP ae	TZ2P fc	TZ2P ae	QZ4P ae
SR ZORA							
Average error	0.4	0.0	−0.1	−0.1	−0.1	−0.2	0.02
Av. abs. error	0.4	0.1	0.1	0.2	0.1	0.2	0.02
Max. error	1.2	−0.7	−0.5	−0.6	−0.6	−0.7	0.24
Worst case	SrO	BeO	MgO	CaO	CaO	CaO	UO
ZORA							
Average error	0.4	−0.0	−0.1	−0.2	−0.1	−0.2	0.01
Av. abs. error	0.4	0.1	0.1	0.2	0.1	0.2	0.02
Max. error	1.2	−0.7	−0.5	−0.6	−0.6	−0.7	0.16
Worst case	SrO	BeO	MgO	CaO	CaO	CaO	PuO

This first-order fit correction is included in the evaluated molecular bond energy. See Figure 6 and the text for more details.

ity, to approximately 2–5 kcal/mol for the frozen core basis sets of triple-zeta valence quality and the all-electron basis sets of double-zeta quality, and to approximately 10 kcal/mol for the frozen core basis sets of double-zeta quality. The basis sets were further tested by the calculation of the atomization energy of 118 neutral diatomic oxides MO, where the nuclear charge Z of M ranges from Z = 1–118. On average, the results with the all-electron basis sets of triple-zeta quality with two polarization functions added are within 1–2 kcal/mol of the much larger all-electron basis sets, which are of quadruple-zeta valence quality with four polarization functions added. The accuracy is reduced to about 4–5 kcal/mol if only one polarization function is used, and further reduced to approximately 20 kcal/mol if the all electron basis sets of double-zeta quality are used. The accuracy of the results with the frozen core basis sets are close to the corresponding all-electron ones, except for the heavy oxides if spin-orbit coupling is included in the calculations, which is caused by the fact that the basis functions in the ADF program are not orthogonalized on ZORA core spinors as they should be, but they are orthogonalized on scalar relativistic ZORA core orbitals.

The errors that are made because the electron density is fitted to calculate the Coulomb potential are estimated to be smaller than a few tenths of a kcal/mol. The BSSEs for the all-electron QZ4P basis set are less than 0.1 kcal/mol for the calculated bond energies of the diatomic oxides. The average absolute BSSEs calculated with the all-electron DZ basis set and the all-electron and frozen core TZ basis sets are approximately 0.5 kcal/mol. The average absolute BSSE in the case of the smallest basis set, namely the frozen core DZ basis set, is approximately 2 kcal/mol.

Compared to the ADF program, the advantage of performing frozen core calculations with the BAND program is that its numerical atomic basis functions already have accurate core wiggles. With the ADF program, on the other hand, one needs to include extra core-like basis functions in the frozen core basis sets to obtain the same accuracy in these core wiggles. Therefore, the BAND program has been used to test the frozen core approximation in SR ZORA calculations against benchmark all-electron QZ4P calculations. It appears that one can get an accuracy of better than 1 kcal/mol in the calculation of the atomization energy of the group 2 and group 14 diatomic oxides, if one uses large basis sets

Table 11. Average Calculated Basis Set Superposition Errors (BSSE) in the Bond Energy (in kcal/mol) of 118 Neutral Diatomic Oxides MO, Where the Nuclear Charge Z of M Ranges from Z = 1–118.

	DZ fc	DZ ae	TZP fc	TZP ae	TZ2P fc	TZ2P ae	QZ4P ae
SR ZORA							
Average error	−2.1	−0.5	−0.3	−0.2	−0.4	−0.3	−0.01
Av. abs. error	2.1	0.5	0.3	0.2	0.4	0.3	0.01
Max. error	−9.9	−1.5	−0.7	−0.8	−1.1	−1.1	−0.03
Worst case	MdO	E118O	MdO	E118O	E112O	E118O	YbO
ZORA							
Average error	−2.3	−0.6	−0.5	−0.4	−0.5	−0.5	−0.02
Av. abs. error	2.3	0.6	0.5	0.4	0.5	0.5	0.02
Max. error	−10.8	−1.7	−1.7	−1.3	−1.9	−1.6	−0.04
Worst case	MdO	E118O	BhO	HsO	E112O	E118O	TcO

The BSSE is not included in the evaluated molecular bond energy. See Figure 6 and the text for more details.

Table 12. Differences (in kcal/mol) Between the (SR) ZORA Bond Energies of 12 Closed Shell Neutral Diatomic Oxides Calculated with the Mentioned Basis Set and Those Energies Calculated with the Large All-Electron QZ4P Basis Set.

		BeO	MgO	CaO	SrO	BaO	RaO	CO	SiO	GeO	SnO	PbO	E114O
SR ZORA													
DZ	fc	41.1	15.6	36.2	26.5	28.3	22.3	41.7	44.4	21.5	15.7	12.9	14.7
DZ	ae	43.2	18.3	39.2	29.5	28.2	26.9	42.3	47.2	22.5	17.3	15.2	18.3
TZP	fc	1.5	2.0	5.5	3.8	7.1	13.1	4.1	4.4	2.4	4.5	4.0	3.3
TZP	ae	1.5	2.3	6.2	4.4	6.9	12.8	4.1	3.4	2.4	4.4	4.3	3.8
TZ2P	fc	0.4	0.5	0.6	0.9	2.9	3.3	1.1	2.2	0.5	0.9	0.2	-0.1
TZ2P	ae	0.5	0.7	1.1	1.4	2.8	1.6	1.2	1.2	0.4	0.6	0.4	0.3
BAND ^a	fc	0.5	0.3	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.2
+ g ^b	fc	0.3	0.2	0.3	0.3	0.0	-0.4	-0.2	0.1	-0.1	-0.2	-0.3	-0.8
ZORA													
DZ	fc	41.1	15.6	36.3	26.5	28.1	21.4	41.7	44.4	21.5	15.8	15.1	37.4
DZ	ae	43.2	18.3	39.2	29.5	28.1	26.2	42.3	47.2	22.5	17.3	15.2	23.7
TZP	fc	1.5	2.0	5.6	3.8	6.9	12.1	4.1	4.4	2.4	4.5	6.3	26.5
TZP	ae	1.5	2.3	6.2	4.4	6.8	12.1	4.1	3.4	2.4	4.4	4.5	10.1
TZ2P	fc	0.4	0.5	0.6	0.9	2.7	2.9	1.1	2.2	0.5	1.0	2.5	22.5
TZ2P	ae	0.5	0.7	1.1	1.4	2.7	1.0	1.2	1.2	0.4	0.6	0.5	6.0
BAND ^a	fc	0.4	0.1	0.4	0.4	0.3	0.5	0.1	0.3	0.2	0.2	0.2	1.0
+ g ^b	fc	0.3	0.0	0.3	0.3	0.0	-0.3	-0.3	0.0	-0.1	-0.2	-0.3	0.1

The molecular bond energy was calculated with respect to the spherical spin-restricted reference atoms, within the LDA approximation for the exchange-correlation energy. In the case of ZORA, the atoms are calculated in a spin-orbit averaged way.

^aBAND basis sets of QZ4P quality in the (sub-) valence region, without g-type STOs, see text.

^bBAND basis sets include g-type STOs, see text.

that are of similar quality in the (sub-) valence region as in the benchmark calculations. Calculations with the BAND program also show that one can get the same kind of accuracy in the results using the frozen core approximation at the ZORA level, which is correctly implemented in the BAND program, when these results are compared to benchmark all-electron ZORA ADF calculations. Adding g-type STOs to the large basis sets had an effect of less than 1 kcal/mol on the atomization energies.

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