Accurate Coulomb-fitting basis sets for H to Rn†

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A series of auxiliary basis sets to fit Coulomb potentials for the elements H to Rn (except lanthanides) is presented. For each element only one auxiliary basis set is needed to approximate Coulomb energies in conjunction with orbital basis sets of split valence, triple zeta valence and quadruple zeta valence quality with errors of typically below *ca.* 0.15 kJ mol^{-1} per atom; this was demonstrated in conjunction with the recently developed orbital basis sets of types def2-SV(P), def2-TZVP and def2-QZVPP for a large set of small molecules representing (nearly) each element in all of its common oxidation states. These auxiliary bases are slightly more than three times larger than orbital bases of split valence quality. Compared to non-approximated treatments, computation times for the Coulomb part are reduced by a factor of *ca.* 8 for def2-SV(P) orbital bases, *ca.* 25 for def2-TZVP and *ca.* 100 for def2-QZVPP orbital bases.

Introduction

Resolution of identity (RI) methods are an efficient tool to reduce computational effort in calculations of two-electron four-center integrals. For these methods, either the products of orbital basis functions or the total electron density are approximated in terms of so-called auxiliary basis functions, which leads to expressions looking formally like inserting the resolution of identity.[1–3] Various implementations have been worked out applying these methods to MP2[4–7] and coupled cluster[8,9] treatments, as well as to the Hartree–Fock exchange part, RI-K,[10–12] and to the Coulomb part, RI-J,[13–17] of the Fock matrix. RI-J turned out to be very successful in conjunction with density functional methods, where the exchange–correlation part can be calculated quite efficiently, which makes the calculation of Coulomb integrals the time-consuming part of the calculation. With the use of RI methods the formal scaling behavior of computation times is reduced from N^4 to N^3, as four-center integrals are replaced by two- and three-center integrals that can be calculated with high efficiency, according to recent reports.[18,19] As the number of auxiliary basis functions needed for an accurate fit is rather small, for typical applications (molecules containing a few atoms to some hundred; basis sets of split valence or triple zeta valence quality) RI-approximated calculations of the Coulomb part are usually *ca.* one order of magnitude faster than non-RI treatments, and thus of similar computational costs as the evaluation of the exchange–correlation part.[14]

An obstacle to RI methods might be that different auxiliary basis sets are needed for different orbital basis sets for the same element. This is true for RI-MP2/CC2 and RI-K, where the products of individual orbitals are fitted by auxiliary basis set expansions, but for RI-J it seems to be avoidable, as the quantity fitted here is the total density, which depends comparatively weakly on the chosen orbital basis set. Indeed, the RI-J auxiliary basis sets presented previously[13,14] for orbital basis sets of split valence and triple zeta valence quality, def-SV(P)[20] and def-TZVP,[21] are quite similar for a given element and in many cases even identical for the two different orbital basis sets. Also, RI errors in bond energies for these auxiliary bases are similar when used with different orbital basis sets, and are typically 0.3–0.6 kJ mol^{-1} per atom (for alkali and alkali earth metal compounds they are often significantly larger). These errors are more than one order of magnitude smaller than errors arising from the incompleteness of the orbital bases for which they were designed: for atomization energies, differences to the basis set limit in DFT calculations are typically 10–30 kJ mol^{-1} (per atom) for def-SV(P)[20] orbital bases and slightly smaller for def-TZVP[21] orbital bases; compounds containing (earth) alkali metals often show larger errors.

Recently improved orbital basis sets[22] termed def2-SV(P), def2-SVP and def2-TZVP/PP as well as an improved def2-QZVP/PP for H to Rn were developed (the sub-types "(P)", "P" and "PP" differ in number and type of polarization functions). These orbital bases represent the full spectrum of basis set qualities reasonable for DFT treatments. For atomization energies typical errors (per atom) to the DFT orbital basis set limit are at *ca.* 5 kJ mol^{-1} for def2-TZVP orbital bases and *ca.* 1 kJ mol^{-1} (or slightly more) for def2-QZVPP. For SV(P) orbital bases the quality was only improved for alkali (earth) metals, so the errors amount to 10–30 kJ mol^{-1} throughout. If one requires auxiliary basis set errors to be one order of magnitude smaller than orbital basis set errors, it is obvious that the accuracy of previously presented auxiliary basis sets[13,14] (called "previous" auxiliary bases in the following sections) is sufficient for use in conjunction with def2-SV(P)/P orbital bases[22] (at least for compounds not containing

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s-elements), but with def2-TZVP/PP[22] it might be risky, and with def2-QZVP/PP bases[22] it is not reasonable to use the RI approximation with previous auxiliary bases.[13,14] An improved series of Coulomb fitting auxiliary bases, (termed "improved" auxiliary bases), was developed whilst considering the following goals. First, the accuracy of the improved auxiliary bases had to be sufficient for all orbital bases up to at least def2-QZVP, which was previously recommended as the orbital basis set to use for reference quality DFT calculations.[22] Second, only *one* auxiliary basis set per element should be sufficient for use in conjunction with *all* types of def2-bases (and other orbital bases of similar qualities). Due to the above-mentioned rather weak dependence of the total density on the orbital basis, this second goal seemed within reach. Third, the size of auxiliary bases had to be kept as small as possible, so that the calculation times when using the improved auxiliary bases instead of the previous auxiliary bases would not increase too much, which was of particular importance when using the improved auxiliary basis sets in conjunction with small orbital bases.

In section 1 a short review of Coulomb-fitting methods and several possible ways of constructing auxiliary bases are presented. Section 2 reports a thorough test of previous auxiliary bases. Section 3 outlines optimization goals and strategy and improved auxiliary basis sets are specified. Test results for the improved auxiliary basis sets are presented in section 4, and a summary and recommendations for use are given in section 5.

1. Theoretical background

The electron density $\rho(\mathbf{r})$ can be expressed by an expansion in terms of auxiliary functions $P(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_{\nu\mu} D_{\nu\mu}\nu(\mathbf{r})\mu(\mathbf{r}) \approx \rho_{RI}(\mathbf{r}) = \sum_{P} c_P P(\mathbf{r}) \qquad (1)$$

$D_{\nu\mu}$ is the density matrix and $\nu(\mathbf{r})$ and $\mu(\mathbf{r})$ are basis functions. Here we consider only atom centered Gaussian functions, which are used for most quantum chemical program systems; the auxiliary functions $P(\mathbf{r})$ are also Gaussian functions. In order to determine the expansion coefficients, we require the (Coulomb) self-interaction of the error of the above expansion to be minimal[13]

$$(\rho - \rho_{RI} \mid \rho - \rho_{RI}) = \min, \qquad (2)$$

which leads to

$$c_P = \sum_{Q,\nu,\mu} (P|Q)^{-1}(Q|\nu\mu)D_{\nu\mu}, \qquad (3)$$

and to

$$\Delta RI = E^J - E^J_{RI} = 1/2\,(\rho \mid \rho) - 1/2\,(\rho_{RI} \mid \rho_{RI}) \geq 0 \quad (4)$$

ΔRI is always positive (zero for a complete auxiliary basis) and it depends on P, so exponents of Coulomb-fitting auxiliary basis sets can be optimized by minimizing this quantity. For contracted auxiliary basis sets the expansion coefficients c_P (eqn (3)) can be used as contraction coefficients. We note, that for spherically symmetric charge distributions, *e.g.* atoms with completely or half-filled shells, only auxiliary basis functions

with $l = 0$ (s-type auxiliary functions) yield a contribution to E^J_{RI} and generally *ca.* 99% of E^J_{RI} arises from s-type auxiliary functions, higher *l*-types are necessary to describe anisotropy resulting from bonding atoms or for atoms with partially filled shells.

One might think of several different types of sets $\{\eta\}$ of N optimized exponents. The simplest is an "even tempered" auxiliary basis set

$$\eta_i = f\eta_{i-1} \ i = 2, \dots N, \qquad (5)$$

containing only two parameters, f and η_1, to be optimized. With this rigid prescription a rather large amount of functions is needed to obtain the desired accuracy, as relatively small values for f are necessary for exponents describing the valence shell, whereas larger values are usually sufficient for inner shells. Therefore, a modification to the recursive prescription given in eqn (5) was proposed previously[13]

$$\eta_i = f_1\eta_{i-1}\left(1 + f_2\left(\frac{i-2}{N+1}\right)^2\right) i = 2, \dots, N. \qquad (6)$$

For the previous auxiliary basis sets this prescription was used to optimize exponents of s-functions for all elements, as well as the d- (and g-) exponents for main group elements (and transition metals) with partially filled valence shells. Auxiliary bases constructed this way might still be improved, if exponents are individually optimized by

$$\frac{\partial E_J(\eta_i)}{\partial \eta_i} = 0, \qquad (7)$$

i.e. by repeated calculation of gradients of the Coulomb energy with respect to auxiliary basis set exponents and subsequent relaxation procedures, until convergence is reached. This route was pursued previously for the optimization of fitting bases for MP2 methods[23,24] and for the HF exchange part of the Fock matrix.[11] For reasons discussed below, we used this procedure for the optimization of s-type RI-J auxiliary functions only, while the sets of higher auxiliary functions were of the form given by eqn (6).

2. Accuracy of previously presented auxiliary basis sets

In the first step, we tested the quality of the previous RI-J auxiliary basis sets,[13,14] used in conjunction with recently developed[22] def2- (orbital-) basis sets. We used the same large test set of molecules specified in conjunction with the def2-bases,[25] which includes more than 300 molecules representing (nearly) each element in all its common oxidation states. For each molecule in this set, we calculated the (non-RI) Coulomb energy for def2-SV(P), def2-TZVP and def2-QZVPP bases at the DFT(BP86)[26,27] level and compared it with the Coulomb energy obtained within the RI-approximation for the same set of MOs. In all cases we used the auxiliary bases specified at the right hand side of Table 1 (column label "Previous"), which are the largest among the previous auxiliary basis sets (as mentioned above, the differences between sets optimized for different orbital bases are small). The test set was divided into three groups: "p-compounds", containing only main group

Group	Improved Primitives/contracted	Contraction pattern	*N*	Previous[a] Contracted	*N*
H	(5s2p1d) /[3s1p1d]	{311/2/1}	11	[3s2p1d]	14[b]
2s	(12s5p4d2f1g)/[6s4p3d1f1g]	{711111/2111/211/2/1}	49	[7s2p2d1f]	29[c]
3s	(14s5p5d2f1g)/[8s4p4d1f1g]	{71111111/2111/2111/2/1}	56	[5s2p2d1f]	28
4s	(19s5p5d3f1g)/[8s4p4d1f1g]	{(12)1111111/2111/2111/3/1}	56	[6s2p2d1f]	29
5s	(11s5p5d3f1g)/[8s4p4d1f1g]	{41111111/2111/2111/3/1}	56	[5s2p2d]	21
6s	(11s5p5d3f1g)/[8s4p4d1f1g]	{41111111/2111/2111/3/1}	56	[5s2p2d]	21
2p	(12s5p4d2f1g)/[6s4p3d1f1g]	{711111/2111/211/2/1}	49	[7s3p3d1f]	38[cd]
3p	(14s5p5d2f1g)/[8s4p3d1f1g]	{71111111/2111/311/2/1}	51	[5s3p2d1f1g]	40
4p	(19s5p5d3f1g)/[8s4p3d2f1g]	{(12)1111111/2111/311/21/1}	51	[6s4p2d1f1g]	44
5p	(11s5p5d3f1g)/[8s4p3d2f1g]	{41111111/2111/311/21/1}	51	—[e]	—[e]
6p	(11s5p5d3f1g)/[8s4p3d2f1g]	{41111111/2111/311/21/1}	51	—[e]	—[e]
3d	(19s5p5d3f3g)/[8s5p5d2f3g]	{(12)1111111/11111/11111/21/111}	89	[6s4p2d3f2g]	68
4d	(11s5p5d3f3g)/[8s5p5d2f3g]	{41111111/11111/11111/21/111}	89	[7s4p3d3f2g]	73
5d	(11s5p5d3f3g)/[8s5p5d2f3g]	{41111111/11111/11111/21/111}	89	[8s4p3d3f2g]	74

[a] Previous auxiliary bases may slightly differ in the number of primitives and contracted functions within a group of elements.[13,14] Typical representatives of a group are given here. [b] Data refer to the previous auxiliary basis used for the def-TZVPP orbital basis. Auxiliary bases to be used in conjunction with def-SV(P)/def-SVP/def-TZVP orbital bases contain only 5/8/9 contracted functions. [c] Data refer to the previous auxiliary bases used for the def-TZVPP orbital bases. Auxiliary bases to be used in conjunction with smaller bases are smaller by one s-function. [d] The previous auxiliary basis set for F contains an additional d-function. [e] Previous auxiliary bases were not designed to be used in conjunction with orbital bases for small core ECPs.

elements (and hydrogen), "d-compounds", which also contain transition metals, and "s-compounds", which also contain alkali or alkali earth metals.

In Fig. 1 the errors in the Coulomb energy per atom, ΔRI (eqn (4)), obtained with the previous auxiliary bases in conjunction with the large def2-QZVPP orbital bases are plotted *vs.* those obtained when combining the same previous auxiliary bases with relatively small def2-SV(P) bases. Rectangular boxes representing the mean values ± the standard deviation
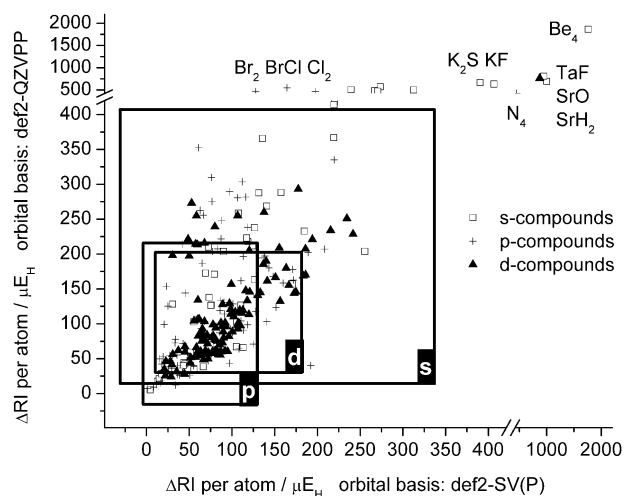

Fig. 1 RI errors per atom in Coulomb energies, in μE_H, for previous auxiliary basis sets in conjunction with def2-SV(P) and def2-QZVPP orbital basis sets[22] for a set of more than 300 molecules[25] containing hydrogen and main group elements only (p-compounds), transition metals (d-compounds), or alkali (earth) metals (s-compounds). The rectangular boxes represent the mean value ± the standard deviation for each of the three groups of compounds.

are also shown in Fig. 1. The explicit statistical data are given in Table 2 (also given for the def2-TZVP orbital bases). The implementation of orbital bases of different qualities and the use of a large test set show that the errors for the RI-J approximation depend on the specific molecule rather than on the size of the orbital basis: mean values and standard deviations are not much larger for the def2-QZVPP orbital bases than for the def2-SV(P), whereas even for the small bases one observes several cases with atypically large errors. For p- and d-compounds typical errors per atom—estimated by adding mean value and standard deviation—are below *ca.* 200 μE_H, as stated previously,[13,14] but for s-compounds they are *ca.* twice as large; for the latter several molecules with non-typically large errors of more than 500 μE_H are found.

The RI errors in the atomization energies per atom are expected to be similar to the RI errors in the total energies, as error cancellations caused by the RI errors for the atoms are small (*ca.* 10–20 μE_H), so typical RI errors for atomization energies amount to up to *ca.* 0.5 kJ mol^{-1} (*ca.* 200 μE_H). For critical cases errors of more than 1 kJ mol^{-1} are expected, and even larger errors are expected for some compounds containing s elements. If we require the RI errors to be *ca.* one order of magnitude smaller than errors from the incompleteness of the basis set, the previous auxiliary bases are usually sufficient for orbital bases of split valence quality but not for the recently presented triple and quadruple zeta valence bases, for which the orbital basis set errors are much smaller than for split valence bases.[22]

It is thus necessary to develop improved auxiliary basis sets for reasons of accuracy, and in any case for the 5p and 6p elements, as the "old" orbital bases (def-SVP *etc.*)[14] and corresponding auxiliary bases were optimized for large core ECPs, whereas the recently presented orbital bases (def2-SVP *etc.*)[22] are designed for small core ECPs covering only the inner 28 (46) electrons.

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Table 2 Errors in total energies per atom for auxiliary bases presented previously,[13,14] "previous", and the auxiliary bases presented here, when used in conjunction with different orbital bases.[22] The column label "improved, primitives" refers to the improved primitive auxiliary basis sets, the column label "improved" to the final contracted auxiliary bases (see also Table 1 and text). Mean values, $\varnothing$, standard deviations, σ, and maximum values, max., are given in μE_H and refer to a large test set containing more than 300 molecules.[25] See text for further details

Aux. basis	Previous			Improved, primitives			Improved		
Orbital basis	def2-QZVPP	def2-TZVP	def2-SV(P)	def2-QZVPP	def2-TZVP	def2-SV(P)	def2-QZVPP	def2-TZVP	def2-SV(P)
s-compounds									
$\varnothing$	252.4	226.5	184.1	6.8	7.0	20.4	21.2	15.7	32.5
σ	292.5	295.8	280.3	6.9	7.0	15.2	14.3	11.3	20.7
Max.	1867	2012	1762	34.9	39.6	43.8	79.0	62.9	84.4
At.	Be_4	Be_4	Be_4	BaO	BaO	BaO	BaH_2	BaO	$CaCl_2$
p-compounds									
$\varnothing$	—[a]	—[a]	—[a]	21.7	22.9	37.3	43.7	38.5	56.9
σ	—[a]	—[a]	—[a]	15.5	16.3	22.3	19.3	18.9	28.4
Max.	—[a]	—[a]	—[a]	82.7	88.4	93.4	113.3	101.8	123.2
At.	—[a]	—[a]	—[a]	As_4S_4	As_4S_4	Cl_2	Se_8	As_4S_4	P_4
2p- to 4p-compounds									
$\varnothing$	138.4	117.0	87.9	19.1	20.4	35.7	42.2	35.7	53.7
σ	112.6	90.5	61.7	15.8	16.7	23.9	20.4	19.1	29.0
Max.	548.6	457.0	449.7	82.7	88.4	93.4	113.3	101.8	123.2
At.	Cl_2	Cl_2	N_4	As_4S_4	As_4S_4	Cl_2	Se_8	As_4S_4	P_4
d-compounds									
$\varnothing$	118.4	112.3	97.8	17.9	19.7	28.8	31.2	29.6	43.1
σ	87.6	92.1	84.9	11.7	12.6	14.4	15.0	16.1	18.3
Max	763.6	893.5	874.6	51.5	54.5	68.8	87.6	78.8	90.9
At	TaF	TaF	TaF	NiO	NiO	NiO	ScH_3	CrO_3	CrF_3

[a] Previous auxiliary bases were not designed to be used in conjunction with orbital bases for small core ECPs, so results can only be given for 2p–4p element compounds.

3. Optimization of improved auxiliary basis sets and tests

Optimization goals

(1) Due to the above results it seems to be both reasonable and possible to provide only one auxiliary basis set per atom suited for all orbital basis sets from split valence to quadruple zeta valence quality. For each atom this set has to be large enough to properly describe all critical cases in the test set.

(2) As in previous studies,[11,13,23] we require the RI errors to be at least one order of magnitude smaller than those arising from the incompleteness of the basis set, which means that for total energies, typical RI errors for auxiliary bases used in conjunction with def2-QZVP/PP basis sets should be *ca.* 0.1 kJ mol^{-1} (or slightly above), *i.e. ca.* 50 μE_H.

(3) The size has to be kept as small as possible for reasons of efficiency, in particular because of the desired use in conjunction with small orbital bases.

(4) Identical contraction patterns, at least within a group of elements, are desirable.

Optimization strategy

The improved auxiliary basis sets presented here were optimized for the def2-QZVPP orbital bases throughout. These are the most accurate among our consistent series of orbital basis sets, so for these the RI errors have to be the smallest, which is best achieved for auxiliary basis sets that have been optimized for the respective orbital basis. Despite the fact that the RI-J auxiliary bases are mainly used in DFT calculations, they were optimized for densities calculated at the Hartree–Fock level, as due to the great variety of DFT functionals the choice of a certain one is not clear; nevertheless differences are not expected to be large.

The s-type auxiliary functions that fit the dominating spherically symmetric part of the electron density in the vicinity of an atom were optimized at the respective atom by repeated calculation of gradients followed by a relaxation step. Functions of higher *l*-types, which are needed for the description of anisotropies arising from bonding atoms (and also from partially filled atomic shells), were optimized at a representative type of compounds, namely the (mono-) hydride of each element; in case of hydrogen H_2 was used. This restriction to a special type of compounds might lead to smaller errors for bonds of this type compared to others if the exponents are optimized individually (eqn (7)). Thus, for non-s functions the form given by eqn (6) was chosen, and after extensive test calculations a few manual corrections were also made (see below). This route was followed in all cases except for rare gases, for which the non-s functions were extrapolated from the preceding element, as the asymmetry of the charge density due to the presence of a hydrogen atom is too small to get reliable values for the exponents of non-s functions. Note that in contrast to the previously presented sets, for atoms with partly (non-half) filled p or d shells leading to atomic contributions from d- and g-type auxiliary functions the respective exponents were also optimized at the hydrides in this work. This may lead to slightly larger errors for the atoms (compared to atom-optimized d- or g-auxiliary functions), but improves accuracy for molecules and also the error compensation when calculating bond energies.

Optimization of primitive sets and tests

Exponents of each *l*-quantum number are optimized separately in the sequence of increasing *l*-types, functions of a particular *l*-type are optimized in presence of that of lower

l-types. In order to select relevant from less relevant exponents, we started from an even-tempered set of auxiliary functions (small factor *f*, see eqn (5)), that is (approximately) complete with respect to the respective *l*-quantum type, $\{\eta^C\}$, consisting of N^C auxiliary functions. η_1 was optimized so that $E_J(\{\eta^C\})$ = max. Next, each single function was removed separately (and added again) resulting in N^C values of E_J for N^C sets with $N^C - 1$ functions. The exponent corresponding to the smallest Coulomb energy difference to $E_J(\{\eta^C\})$ was removed. This was repeated as long as the energy difference to $E_J(\{\eta^C\})$ was smaller than a given threshold, which was decided to be 10 μE_H. The resulting *N* exponents ranging from η^R_{min} to η^R_{max} were rearranged as described by eqn (6). The parameters η_1, f_1 and f_2 were optimized starting from

$$\eta_1 = \eta^R_{min}, f_1 = 0.9 \times \sqrt[N-1]{\frac{\eta^R_{max}}{\eta^R_{min}}}, f_2 = 0.1.$$

For the s-type functions the resulting set was further optimized by repeatedly calculating gradients followed by relaxation steps.

This procedure was carried out for all elements, leading to auxiliary basis sets of similar sizes (*i.e.* numbers of primitives per *l*-quantum type) within a group of elements. Next, for each group a typical size was chosen (close to the maximum size of the respective group), and the above procedure was repeated, but now in the second step the number of exponents was reduced until the desired number of primitives was reached (and not a desired accuracy). This led to the sets of primitive functions shown in the second column of Table 1.

The resulting sets of primitive auxiliary functions were tested in the same way as the previous auxiliary basis sets. The above requirements of accuracy were fulfilled in most cases. A typical example of the required accuracy not being reached can be seen for Cl_2, where the error with the optimized auxiliary basis set amounted to 122 μE_H for the def2-TZVP orbital basis set (errors in conjunction with the other orbital bases are similar). These larger errors were traced back to the values for the exponents of f- and g-type auxiliary functions, which describe anisotropic features of the p shell. For Cl_2 these are different from those for ClH, for which these exponents were optimized. When replacing the relatively steep set optimized for ClH, $\eta_{f1}^{ClH} = 3.082$, $\eta_{f2}^{ClH} = 1.203$, $\eta_g^{ClH} = 1.665$, by a less steep set, $\eta_{f1} = \eta_{f2}^{ClH} = 1.203$, $\eta_{f2} = (\eta_{f2}^{ClH})^2/\eta_{f1}^{ClH} = 0.4700$, $\eta_g = (\eta_{f1}\eta_{f2})^{1/2} = 0.7521$, the error is reduced to 37 μE_H. Similarly, the f-functions were modified for P and Si and for all 4p–6p elements, and the g-functions were modified for all 2p and 3p elements.

The final sets of primitives were tested as described above, and the results are shown in Fig. 2. Relevant statistical data can be found in the middle column of Table 2 (column label "improved primitives"). Average errors per atom amount to *ca.* 10–40 μE_H, depending on the type of compound and the orbital basis set used. The largest error is still smaller than 100 μE_H. So, with these auxiliary basis sets the errors introduced by the RI approximation are more than one order of magnitude smaller than those resulting from the incompleteness of the orbital basis set, even for the def2-QZVPP orbital bases. As intended, the smallest errors occur for def2-QZVPP basis sets (adding the largest mean value and standard deviation one
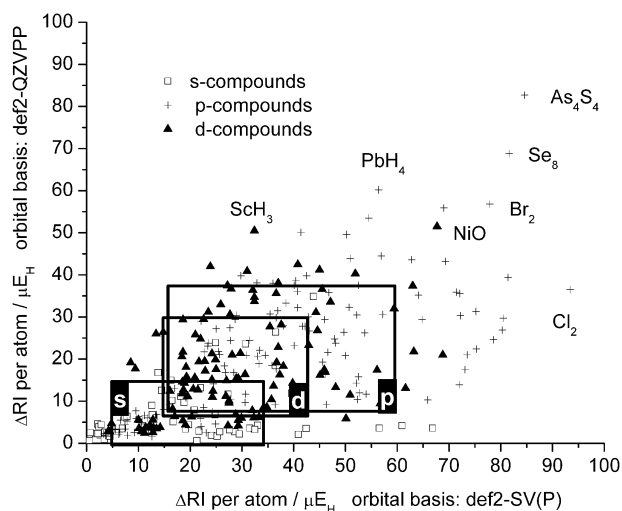

Fig. 2 RI errors per atom in Coulomb energies, in μE_H, for primitive sets of improved auxiliary basis functions in conjunction with def2-SV(P) and def2-QZVPP orbital basis sets[22] for a set of more than 300 molecules.[25] See also Fig. 1.

gets less than 40 μE_H) Those for def2-TZVP are in the same range, and for def2-SV(P) bases they are somewhat larger, below *ca.* 60 μE_H.

Contracted auxiliary basis sets

The sets of primitives indeed fulfil the requirements of accuracy defined in the previous section, but they are of a much larger size than the previously optimized sets,[13,14] *e.g. ca.* twice as large for the p elements. Computational effort for the time-determining steps increases linearly with the number of auxiliary basis functions, so contracting auxiliary functions with the expansion coefficients given in eqn (3) will lead to savings in computation time. These coefficients were calculated for the hydrides of the elements. The contraction length for each *l*-quantum number was determined by testing the contracted bases in conjunction with the def2-QZVPP bases at the above-mentioned test set, making sure that the accuracy is kept within the limits given above.

Finally, a few manual corrections were made, as coefficients determined from hydrides are not always the best choice. As an example, the contraction coefficients evaluated for the two f-functions at F calculated for HF are not appropriate for F_2, as for HF the steeper f-function makes the dominant contribution, while for F_2 the contributions from both f-functions are equal. Setting the two contraction coefficients to the same value improved the result very much for F_2 and did not cause much harm in the other cases. The same was done for the similar cases S, Cl and O and for the two p-functions at H (due to unusually large errors for *e.g.* SrH_2), as well as for the two p-functions at Ga, Ge, In, Sn, Tl, Pb (due to comparably large errors for the oxides).

The contraction patterns of the final auxiliary bases are given in Table 1 (column label "improved"). They are always identical for a group of elements (*e.g.* Sc–Zn), and moreover very similar for groups across the periods. For p and d
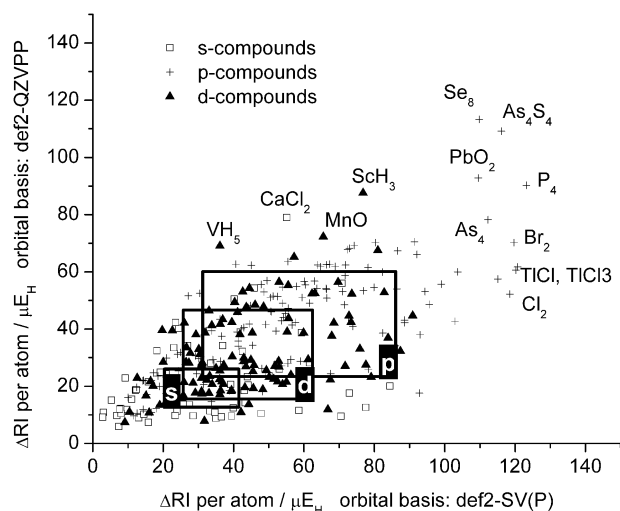
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Fig. 3 RI errors per atom in Coulomb energies, in μE_H, for contracted improved auxiliary basis sets in conjunction with def2-SV(P) and def2-QZVPP orbital basis sets[22] for a set of more than 300 molecules.[25] See also Fig. 1.

elements these auxiliary bases are larger than the previous sets by a factor of *ca.* 1.25–1.3. For s elements improved auxiliary bases are *ca.* twice as large as the previous ones.

4. Test of improved auxiliary basis sets

Total energies

For the final improved auxiliary basis sets the same tests were carried out as for the previous auxiliary bases. The results are given in Fig. 3 and at the right hand side of Table 2 (column label "improved"). In conjunction with def2-TZVP and def2-QZVPP bases typical errors (average plus standard deviation) are below *ca.* 60 μH, and even for the worst case below 120 μE_H, which reflects the robustness of the auxiliary basis sets. For the uncontracted auxiliary basis sets in conjunction with def2-SV(P) bases, errors are *ca.* 1.5 times larger. These numbers can be understood as upper limits, as the test set contains mainly small molecules, for which RI fitting is known to be more problematic than for larger systems, as for the latter

auxiliary basis functions from neighbor atoms "help" to describe anisotropies of the density at a particular atom. Moreover, for atomization energies error compensation in the range of the RI errors for the atoms (*ca.* 10 μE_H) is expected. Thus, these auxiliary basis sets are sufficient for split valence and triple zeta valence orbital bases and also suffice for quadruple zeta valence orbital bases.

Molecular properties

For selected systems that previously turned out to be critical, RI errors in atomization energies (per atom), structure parameters, dipole moments and vibration frequencies were investigated and compared with errors resulting from the incompleteness of the orbital basis set. Optimization of structure parameters and subsequent calculations of atomization energies were carried out for the three orbital basis sets def2-SV(P), def2-TZVP and def2-QZVPP.[22] The calculations were done both with and without the RI approximation using the improved and previous auxiliary basis sets. The results for atomization energies are displayed in Table 3 and those for further properties are given in Table 4. For practical reasons all data are given in SI units from this point on. As expected, errors in atomization energies reveal a picture similar to the RI errors in total energies; they do not show a significant dependence on the orbital basis used, but rather depend on the complexity of the electron distribution of the particular system. For the critical cases presented in Table 3 this means errors of *ca.* 0.2 kJ mol^{-1} at the most for the improved auxiliary bases and *ca.* 1.5 kJ mol^{-1} for the previous bases (note that for Be$_4$ an atypically large error of more than 5 kJ mol^{-1} is observed). Like for the total energies, typical errors are expected to be two to three times smaller. Comparing these results with errors arising from the incompleteness of the orbital basis and requiring *ca.* one order of magnitude between these errors, we state that the improved auxiliary basis sets provide an accurate fit for all of the basis sets presented, where "all" refers to both all types of orbital bases def2-SV(P) up to def2-QZVP/PP and all elements H to Rn.

For equilibrium structure parameters, the RI errors obtained with improved auxiliary bases are typically below 0.1 pm and thus sufficiently small to be used in conjunction with all def2-orbital basis sets. In most cases this is also true for the previous auxiliary bases, at least for p- and d-

Table 3 Errors ΔRI in atomization energies per atom (kJ mol^{-1}) for critical cases selected from the large molecular test set,[25] for orbital bases of types def2-SV(P), def2-TZVP and def2-QZVPP[22] in conjunction with improved ("imp.") and previous ("prev.") auxiliary basis sets. In column "no RI" the atomization energies per atom obtained without the RI approximation are given

	def2-SV(P)			def2-TZVP			def2-QZVPP		
	no RI	ΔRI imp.	ΔRI, prev.	no RI	ΔRI imp.	ΔRI, prev.	no RI	ΔRI imp.	ΔRI, prev.
Se$_8$	241.66	0.09	0.08	242.61	0.20	0.51	243.35	0.23	0.68
As$_4$S$_4$	257.42	0.13	0.33	262.69	0.23	0.82	261.55	0.23	1.00
Cl$_2$	121.28	−0.02	0.10	131.26	0.02	1.15	131.77	0.03	1.40
Br$_2$	112.43	0.00	−0.01	115.30	−0.09	0.69	116.57	0.07	1.03
N$_4$	330.76	0.12	1.15	330.98	0.05	1.11	331.51	0.06	1.15
ReH	113.67	0.06	0.17	120.55	0.07	0.21	121.92	0.07	0.22
BaS	215.53	0.02	0.28	217.70	0.07	0.71	222.0	0.06	0.76
KH	87.65	0.04	0.67	90.58	0.01	1.29	92.75	0.04	1.70
Be$_4$	116.96	0.06	5.11	114.81	0.09	5.92	118.27	0.05	5.47

Table 4 Errors ΔRI in bond distances (d/pm), angles (γ/°), dipole moments (μ/D) and selected frequencies (ν/cm^{-1}) for several types of orbital bases,[22] previous ("prev.") and improved ("imp.") auxiliary bases. See also Table 3

		def2-SV(P)			def2-TZVP			def2-QZVPP		
		no RI	ΔRI, imp.	ΔRI, prev.	no RI	ΔRI, imp.	ΔRI, prev.	no RI	ΔRI, imp.	ΔRI, prev.
Se$_8$	d	237.09	−0.02	−0.05	236.31	+0.04	+0.02	236.15	+0.01	+0.01
	γ	108.12	−0.03	−0.03	108.14	−0.00	−0.01	108.23	−0.02	−0.03
	ν	194.52	+0.31	+0.50	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
As$_4$S$_4$	d_{S-S}	210.98	−0.01	−0.03	207.59	+0.01	+0.08	207.34	+0.03	+0.13
	d_{S-As}	266.94	−0.00	−0.02	264.40	−0.01	−0.01	264.42	+0.05	+0.07
	d_{As-As}	247.11	−0.05	+0.01	245.55	−0.03	+0.04	245.46	−0.00	+0.09
	ν	456.75	+0.13	+0.12	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
Cl$_2$	d	206.20	0.00	−0.09	201.57	+0.02	−0.01	201.21	+0.02	−0.02
	ν	483.94	−0.04	+0.55	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
Br$_2$	d	233.06	+0.03	−0.04	231.51	+0.03	−0.03	231.17	+0.04	−0.00
	ν	298.85	−0.31	+0.38	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
N$_4$	d	145.66	0.00	−0.01	146.60	0.01	0.03	146.45	+0.08	+0.09
	ν	764.89	−0.38	+0.49	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
ReH	d	165.62	0.01	0.02	164.17	0.00	0.02	163.94	0.02	0.02
	μ	1.162	−0.009	−0.108	1.113	−0.002	−0.002	1.100	−0.002	0.001
	ν	2070.6	−0.82	−1.17	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
BaS	d	259.37	−0.03	−0.07	255.09	−0.03	−0.11	254.11	0.00	−0.07
	μ	9.237	0.004	0.002	9.777	−0.004	0.013	9.831	0.001	0.026
	ν	371.81	−0.30	−0.38	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}	—^{a}
KH	d	228.91	0.05	−0.06	226.68	0.03	−0.73	224.93	0.04	−1.07
	μ	7.468	0.006	0.008	7.384	0.002	−0.007	7.400	−0.000	−0.050
	ν	946.79	−0.85	8.56	945.78	−0.53	15.7	—^{a}	—^{a}	—^{a}
Be$_4$	d	208.98	0.01	0.51	206.18	0.02	0.71	204.42	0.02	0.79
	ν	684.36	−0.16	−10.36	677.40	−0.28	−38.69	—^{a}	—^{a}	—^{a}

^{a} Analytical second derivatives for f-functions in the orbital basis are not yet implemented.

compounds; obviously, the positions of minima of the potential surface depend less on the quality of the auxiliary bases than their depths.

For dipole moments, the RI errors are very small for the improved auxiliary bases, and for the systems tested are always below 0.01 D, which again is small compared to typical errors in dipole moments for def2-SV(P) orbital bases (*ca.* 0.5 D) or def2-TZVP bases (*ca.* 0.2 D).[22]

In order to investigate the accuracy of auxiliary bases for the curvature of the energy potential surface, vibration frequencies were calculated using analytical second derivatives.[16] Considerations of these are restricted to def2-SV(P) basis sets in most cases, as currently only up to d-type orbital basis functions can be used with the respective module. For molecules consisting of more than two atoms only the frequency that shows the largest RI error with the improved auxiliary basis sets is given in Table 5. For the improved auxiliary basis sets the RI errors are always below 1 cm^{-1}. The largest error (0.85 cm^{-1}) occurs for KH with the def2-SV(P) orbital basis. Orbital basis set dependencies are much larger, *e.g.* −7 cm^{-1} for Be$_4$, when exchanging def2-SV(P) with def2-TZVP, or (numerically evaluated) +44 cm^{-1} for Cl$_2$. We note in passing that errors of numerical differentiation are in the same range as RI errors, which was the reason for discussing only results for analytical second derivatives. For the previous auxiliary bases similar accuracy is obtained for the p and d element compounds, but for KH and Be$_4$ one gets comparably large errors of *ca.* 10 cm^{-1}. Obviously in these cases the curvature at minima on the potential surface is more sensitive to deficits of the auxiliary basis than the minimum positions and depths, so the much more reliable improved auxiliary bases are recommended to be used for this purpose.

Computation times

RI-J methods are mainly used to accelerate the Coulomb part in DFT calculations, so that CPU times for the latter are in the same range as those for the exchange–correlation part. Within the RI approximation the most demanding step—the calculation of the three-center integrals ($\nu\mu|P$)—depends linearly on the size of the auxiliary basis; thus one expects a roughly 1.3 times larger computational effort for the Coulomb part when using the improved instead of the previous auxiliary basis set. CPU times for a representative case, Co$_7$Se$_7$(CO)$_4$(C$_5$H$_5$)$_3$,[28] calculated at an Intel Xeon CPU (2.4 GHz) using the modules "ridft" and "dscf" of the program system TURBOMOLE[29] with orbital bases of types def2-SV(P), def2-TZVP and def2-QZVPP together with the improved and previous auxiliary basis sets are given in Table 4. In the case of the previous auxiliary bases the (slightly differing) optimized sets for the corresponding previous orbital basis sets def-SV(P) and def-TZVP were taken for the def2-SV(P) and def2-TZVP orbital bases. For the def2-QZVPP orbital bases the largest available among the previous auxiliary basis sets were taken (in the same manner as for the tests described in section 2). As expected, the ratio of CPU times necessary for the evaluation of the Coulomb part with improved and previous auxiliary basis sets is close to that of the ratio of size of improved and previous sets, and it amounts to *ca.* 1.4 for SV(P) and TZVP. For the whole SCF procedure (ten iterations were performed) the increase of computational effort is less significant, as *ca.* half of the time is spent in the evaluation of the exchange–correlation part, even if the coarsest grid is chosen; for the present example CPU times become larger by *ca.* 25% when using the improved auxiliary basis sets. Computational

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Table 5 Computation times (in minutes), obtained with TURBOMOLE[29] at an Intel Xeon CPU with 2.4 GHz for $Co_7Se_7(CO)_4(C_5H_5)_3$,[28] with several orbital basis sets[22] in conjunction with previous and improved auxiliary basis sets; $t(J)$ is the time taken for the Coulomb part, the total time refers to the entire SCF procedure, *i.e.* Coulomb and exchange–correlation part (the coarsest grid was used) in each of the 10 iterations and additionally the time for the setup of the $(P|Q)$ matrix before the iterations. The three-center integrals were recalculated in each iteration (fully direct RI-J)

		def2-SV(P)	def2-TZVP	def-QZVPP
Number of basis functions[a]		744	1454	3084
Number of auxiliary basis functions[a]	Improved auxbasis	2321	2321	2321
	Previous auxbasis	1738	1821	1896
	Improved/previous	1.34	1.27	1.22
$t(J)$ per iteration	Improved	1.57	4.68	16.17
	Previous	1.10	3.38	12.26
	Improved/previous	1.43	1.38	1.32
Total time (10 iterations)	Improved	21.5	70.1	292
	Previous	16.8	57.6	247
	Improved/previous	1.28	1.22	1.18
	No RI	178	1846	30 000[b]
	No RI/improved	8.28	26.3	103

[a] Spherical harmonic basis functions. [b] Estimated from the time for one iteration using MOs from partly converged RI-DFT.

savings compared to non-RI treatments are very pronounced; for the present example, in the case of the def2-SV(P) orbital basis set total costs are reduced by a factor of 8. For def2-TZVP bases, which were previously recommended for accurate DFT treatments, the total costs were reduced by a factor of *ca.* 25, and for def2-QZVPP bases these were reduced by a factor of *ca.* 100.

5. Summary and recommendations

We presented optimized Coulomb fitting basis sets for H–Rn; only one auxiliary basis set per element is needed to fit Coulomb contributions for orbital basis sets of split valence, triple zeta valence and quadruple zeta valence quality. Typical RI errors are at least one order of magnitude smaller than typical errors due to the incompleteness of the bases, even for the very accurate def2-QZVP/PP bases. This was demonstrated for the total energies of a large set of molecules,[25] and for atomization energies, dipole moments, equilibrium distances and vibration frequencies in a subset containing selected critical cases of the large test set. Results were compared to those calculated with auxiliary basis sets obtained previously; for p and d elements the latter are smaller by *ca.* 25% and *ca.* half as large for s elements. Despite their larger size, the use of the improved (def2-) auxiliary basis sets instead of the previous ones is recommended for the following reasons. For d and 2p–4p elements RI errors in total energies (and also in bond energies) are roughly four times smaller than those calculated using the previous basis sets, and for 5p and 6p elements only the improved auxiliary basis sets match the small core ECPs used for the def2-orbital bases. For s elements the reliability of the improved auxiliary basis sets is much higher than that of the previous basis sets, which in some cases showed unexpected large errors. Thus, to be always on the safe side, the improved auxiliary bases are recommended as default fitting bases for the recently presented def2-bases and are consequently named def2-auxiliary bases. Finally, we note that for geometry optimizations of compounds containing only 2p–4p and/or d elements the previous auxiliary basis sets are of sufficient accuracy to be used in conjunction with orbital basis sets of split valence quality and usually also in conjunction with those of triple zeta valence quality; so, for these purposes one also may use the previous auxiliary bases to save *ca.* 25% of computation time.

Availability

Improved auxiliary bases are available as ESI,† together with the (Cartesian) coordinates of the molecules of the test set and all data used for the statistical evaluations in the present work. Previous auxiliary bases are available on the internet,[30] and the improved basis sets will be available at this site in the near future.

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