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Optimization of auxiliary basis sets for RI-MP2 and RI-CC2 calculations: Core–valence and quintuple-ζ basis sets for H to Ar and QZVPP basis sets for Li to Kr†

Christof Hättig

Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

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An implementation of analytic basis set gradients is reported for the optimization of auxiliary basis sets in resolution-of-the-identity second-order Møller–Plesset perturbation theory (RI-MP2) and approximate coupled-cluster singles-and-doubles (RI-CC2) calculations. The analytic basis set gradients are applied in the optimization of auxiliary basis sets for a number of large one-electron orbital basis sets which provide correlation energies close to the basis set limit: the core–valence basis sets cc-pwCVXZ (B–Ne, Al–Ar) with X = D, T, Q, 5, the quintuple-ζ basis sets cc-pV5Z (H–Ar) and cc-pV(5 + d)Z (Al–Ar) and the doubly-polarized valence quadruple-ζ basis sets QZVPP for Li–Kr. The quality of the optimized auxiliary basis sets is evaluated for several test sets with small and medium sized molecules.

1. Introduction

In 1998 Weigend *et al.*[1] demonstrated that with optimized auxiliary basis sets the resolution-of-the-identity (RI) approximation for four-index electron repulsion integrals[2–4] (ERIs) leads to large savings in the computational costs for second order Møller–Plesset perturbation theory (MP2) calculations while the errors introduced by this approximation can be kept small compared to the one-electron basis set error. The RI approximation reduces the CPU time for MP2 calculations typically by about an order of magnitude or more and the scaling of the core memory and disk space requirements is decreased so that they are no longer bottlenecks for large scale MP2 calculations.[5]

Since then the RI approximation for ERIs has been successfully applied to several correlated *ab initio* methods as *e.g.* the approximate coupled-cluster singles-and-doubles model CC2,[6] multi-reference CI and perturbation theory,[7,8] local MP2 [9] and coupled-cluster methods[10] and the explicitly correlated MP2-R12 [11] approach. Today the RI approximation for ERIs is implemented in several programm packages and has become a standard tool for large scale calculations with correlated *ab initio* methods. (For the usage of the RI approximation in the framework of density functional and Hartree–Fock theory the reader is referred to refs. 4, 12–15)

As mentioned above, optimized auxiliary basis sets are a prerequisite for the efficiency and accuracy of the resolution-of-the-identity approximation for ERIs. The optimization of auxiliary basis sets is, however, usually considered to be a tedious task, in particular for correlated *ab initio* methods. For RI-MP2 and RI-CC2 (for which the same basis sets can be used) optimized auxiliary basis sets have been reported in refs. 1 and 16 for the basis sets SVP,[17] TZVP[18] and TZVPP[1] and the correlation-consistent basis sets[19–21] cc-pVXZ, cc-pV(X + d)Z, aug-cc-pVXZ, and aug-cc-pV(X + d)Z for X = D, T and Q. These optimizations were carried out with a special version of the RI-MP2 program of Weigend and Häser,[5] which was modified to calculate the weighted error functional for the approximated ERIs, eqn. (5) below. The derivatives of the functional with respect to the exponents and contraction coefficients were evaluated numerically by finite differences. Such an approach is limited in its applicability by an unfavourable scaling of the computational costs and the limited accuracy of the numerical gradients.

The aim of the present work is to resolve this bottleneck with an implementation of analytic gradients and to provide an efficient tool for the optimization of such auxiliary basis sets.

In Section II the weighted error functional which is used for the optimization of the auxiliary basis sets for RI-MP2 and RI-CC2 calculations is briefly reviewed and the expressions for the first derivatives with respect to parameters of the auxiliary basis are derived. By relating the result to the expressions for RI-MP2 energy gradients[5,22,23] it is shown how these derivatives can be implemented by simple modifications of an RI-MP2 gradient program. In Section III the implementation of the analytic basis set gradient is applied for the optimization of auxiliary basis sets for a number of large one-electron basis sets, which in Section IV are assessed by comparing for several test sets with in total 193 molecules the error introduced by the resolution-of-the-identity approximation with the one-electron basis set error. In Section V a short summary and some conclusions are given.

II. Gradients for the optimization of auxiliary basis sets

In a spin orbital basis the MP2 correlation energy is

$$E_{\mathrm{MP2}} = -\frac{1}{4}\sum_{aibj}\frac{\langle ab||ij\rangle^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}, \qquad (1)$$

where $\langle ab\|ij\rangle = (ai|bj) - (aj|bi)$. The indices i, j denote here occupied and a, b virtual (unoccupied) canonical SCF spin orbitals and ε_{p} are the SCF orbital energies. In the RI

† The optimized auxiliary basis sets reported in the present work are available together with those of refs. 1 and 16 by ftp[27] or on request from the author. The implemented analytic basis set gradient for the functional δ_{RI} is available as part of the TURBOMOLE program package. For details the reader is refered to the TURBOMOLE web page.[25]

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approximation the four-index ERIs are approximated as

$$(ai|bj) \approx (ai|bj)_{\mathrm{RI}} = \sum_{PQ} (ai|P) V^{-1}_{PQ} (Q|bj) \quad \text{with} \quad V_{PQ} = (P|Q), \tag{2}$$

where P and Q are auxiliary basis functions and $(ai|P)$ and $(P|Q)$ are three- and two-index ERIs.

The resolution-of-the-identity error in the MP2 correlation energy, which is defined as the difference between the result obtained in a RI-MP2 calculation and that of a conventional calculation, can be split into two contributions:

$$\Delta_{\mathrm{RI}} = E_{\mathrm{RI-MP2}} - E_{\mathrm{MP2}} \tag{3}$$

$$= -\frac{1}{2} \sum_{aibj} \frac{\langle ab||ij\rangle (\langle ab||ij\rangle_{\mathrm{RI}} - \langle ab||ij\rangle)}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j} - \frac{1}{4} \sum_{aibj} \frac{(\langle ab||ij\rangle_{\mathrm{RI}} - \langle ab||ij\rangle)^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j} \tag{4}$$

The errors in the individual four-index electron repulsion integrals (ERIs) can be positive or negative, therefore the first term, which is linear in the error of the ERIs, can not be used as a functional for a variational optimization of the auxiliary basis sets. Only the second term, which is quadratic in the error of the ERIs, is negative semi-definite and suitable for a variational optimization. The negative of the latter term, *i.e.* the functional

$$\delta_{\mathrm{RI}} = \frac{1}{4} \sum_{aibj} \frac{(\langle ab||ij\rangle_{\mathrm{RI}} - \langle ab||ij\rangle)^2}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}, \tag{5}$$

is minimized to determine optimized auxiliary basis sets for the resolution-of-the-identity in RI-MP2 and RI-CC2 calculations.[1,16] In δ_{RI} the SCF orbital energies appear as in the MP2 energy linear in the denominators. Compared to other choices for the denominators and in particular to a minimization of just the average squared errors in the ERIs, this leads to an optimal convergence for correlation energies with the size of the thereby optimized auxiliary basis sets.

Previous optimizations of auxiliary basis sets for RI-MP2 calculations[1,16] employed for the minimization of δ_{RI} numerical gradients evaluated by finite differences. This technique required the evaluation of δ_{RI} at least once for each basis set parameter that had to be varied. This lead to a rapid increase in the computational costs with the basis set size for fully optimized auxiliary basis sets. Futhermore, the numerical errors of the finite difference procedure hinder a tight convergence of the optimization procedure. For the optimization accurate auxiliary basis sets for large one-electron orbital basis sets analytic basis set gradients are thus an important prerequisite.

The gradient of δ_{RI} with respect to a parameter λ of the auxiliary basis set $\{P\}$ can be expressed in a form which is very similar to that of some contributions to the gradient for the RI-MP2 correlation energy:

$$\frac{\mathrm{d}\delta_{\mathrm{RI}}}{\mathrm{d}\lambda} = -\frac{1}{2} \sum_{aibj} \frac{\langle ab||ij\rangle_{\mathrm{RI}} - \langle ab||ij\rangle}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j} \frac{\mathrm{d}\langle ab||ij\rangle_{\mathrm{RI}}}{\mathrm{d}\lambda} \tag{6}$$

$$= \sum_{\mu\nu P} \tilde{\Delta}^{ao}_{\mu\nu P} \left(\mu\nu \middle| \frac{\mathrm{d}P}{\mathrm{d}\lambda}\right) - 2 \sum_{PQ} \tilde{\gamma}^{ao}_{PQ} \left(\frac{\mathrm{d}P}{\mathrm{d}\lambda} \middle| Q\right) \tag{7}$$

The intermediates $\tilde{\Delta}^{ao}_{\mu\nu \mathrm{P}}$ and $\tilde{\gamma}^{ao}_{PQ}$ are three- and two-index two-electron densities which differ from corresponding intermediates in the calculation of RI-MP2 energy gradients[5,22] only in that the amplitudes calculated in the RI approximation,

$${}^{\mathrm{RI}}t^{ab}_{ij} = -\frac{\langle ab||ij\rangle_{\mathrm{RI}}}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}, \tag{8}$$

are replaced by the difference amplitudes

$$\tilde{t}^{ab}_{ij} = {}^{\mathrm{RI}}t^{ab}_{ij} - t^{ab}_{ij} = -\frac{\langle ab||ij\rangle_{\mathrm{RI}} - \langle ab||ij\rangle}{\varepsilon_a - \varepsilon_i + \varepsilon_b - \varepsilon_j}. \tag{9}$$

The three-index two-electron density matrix $\tilde{\Delta}^{ao}$ is defined as:[5,22]

$$\tilde{\Delta}^{ao}_{\mu\nu P} = \sum_i C_{\nu i} \sum_a C_{\mu a} \sum_{bj} \tilde{t}^{ab}_{ij} \sum_Q (bj|Q) V^{-1}_{QP}, \tag{10}$$

and the two-index two-electron density density matrix $\tilde{\gamma}^{ao}$ is obtained as:[5,22]

$$\tilde{\gamma}_{PQ} = \sum_{\alpha\beta} \tilde{\Delta}^{ao,P}_{\alpha\beta} \sum_R (\alpha\beta|R) V^{-1}_{RQ}. \tag{11}$$

Based on the above equations, the derivatives of δ_{RI} with respect to the exponents and contraction coefficients of the auxiliary basis can be obtained by relatively simple modifications of an RI-MP2 energy gradient code. This has been exploited to implement these basis set gradients in the RICC2 module[6,22] of the TURBOMOLE package.[24] In combination with the optimization module RELAX and a small script which controls the iterative optimization this results in an efficient (almost) black box procedure for the optimization of auxiliary basis sets, which is made available with the current version[25] of the TURBOMOLE package. Since the canonical orbitals and the non-approximated four-index ERIs do not depend on the auxiliary basis, these need to be evaluated only once. This reduces the costs for a gradient calculation for δ_{RI} to about 2–3 times the costs of a RI-MP2 energy calculation. For atoms a single gradient calculation for δ_{RI} lasts even for large one-electron basis sets on modern PCs typically some seconds, so that these optimization can easily be carried out interactively.

III. Optimization of auxiliary basis sets

In ref. 16 optimized auxiliary basis sets were reported for the correlation consistent basis set series cc-pVXZ and aug-cc-pVXZ (X = D, T, Q) for the elements H, He, B–Ne, Al–Ar and Ga–Kr as well as for the cc-pV(X + d)Z and aug-cc-pV(X + d)Z basis set series for the atoms Al–Ar. As pointed out above, these and the auxiliary basis sets reported in ref. 1 for the basis sets SVP, TZVP and TZVPP were obtained using numerical gradients obtained by a finite difference technique.

In the present work the analytic gradient implementation described in Section II has been employed to complement these auxiliary basis sets by those for the highly accurate one-electron basis sets cc-pV5Z[19] and aug-cc-pV5Z[20] for the atoms H, He and B–Ne and cc-pV(5 + d)Z and aug-cc-pV(5 + d)Z[21,20] for the atoms Al–Ar as well as by those for the weighted core–valence basis set series[26] cc-pwCVXZ for the atoms B–Ne and Al–Ar with cardinal numbers X = D, T, Q, 5.

In the course of optimizing the wCX auxiliary sets it was found that a few of the valence auxiliary basis sets (cc-pVDZ for C–F, cc-pVTZ and cc-pVQZ for Ne, and the diffuse functions for the respective aug-cc-pVXZ basis sets) reported in ref. 16 were not completly converged. Since this caused problems for the optimization of the core–valence wCX auxiliary functions, these basis sets have been reoptimized. The new auxiliary cc-pVDZ (C–F), cc-pVTZ (Ne) and cc-pVQZ (Ne) basis sets lead only to slight improvements for the RI approximation, but are more consistent (in the range of exponents covered) with the other cc-pVXZ auxiliary basis sets and are now made available *via* ftp[27] as default auxiliary basis sets.

In ref. 16 no auxiliary basis sets were reported for the cc-pVXZ sets[28] for the (earth) alkali atoms Li, Be, Na and Mg. These have now been included in the present work. Furthermore, optimized auxiliary basis set are reported for

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the doubly-polarized valence quadruple-ζ basis QZVPP published recently by Weigend *et al.*[29] for the atoms H–Kr. The latter basis is a valuable alternative to the cc-pVQZ basis, in particular for the third-row elements Ga–Kr, since in difference to the latter basis it allows to correlate the 3d shell. Since in the work described in ref. 1 no auxiliary basis sets were optimized for the rare gas atoms He, Ne, Ar and Kr, for these atoms also auxiliary SVP, TZVP and TZVPP basis sets have been constructed in the course of the present work. All auxiliary basis sets reported here are available together with those from refs. 1 and 16 by ftp[27] (see below).

A. Auxiliary quintuple-ζ basis sets

To keep the auxiliary quintuple-ζ basis sets consistent with those for the lower cardinal numbers (X = D, T, Q), these basis sets were constructed using a similar scheme as that described in ref. 16. For He–Ar the optimizations of the cc-pV5Z (cc-pV(5 + d)Z) auxiliary sets were carried out for the atoms in there electronic ground state based on a spin-unrestricted Hartree–Fock (UHF-SCF) wavefunction, while for hydrogen the optimization was done for the H_2 molecule ($R_{HH} = 1.39\ a_0$). Even though the cc-pV5Z basis sets have only been designed to correlate the valence electrons, they are often used without applying a frozen core approximation. Therefore all occupied (and virtual) orbitals have been included in the calculation of the error functional δ_{RI}. This is done to guarantee a high accuracy for the RI approximation irrespective of the use of the frozen core approximation. For the second-row atoms Al–Ar the same auxiliary sets are used for cc-pV5Z and cc-pV(5 + d)Z and the optimizations have been carried with the slightly larger cc-pV(5 + d)Z orbital basis.

As is apparent for the atoms, the auxiliary basis sets should include at least functions with angular momenta up to $l_{occ} + l_{bas}$, where l_{occ} is the highest angular momentum occupied in the SCF wavefunction and l_{bas} the highest angular momentum included in the orbital basis, to obtain an accurate resolution of the identity for products of one occupied and one virtual orbital. For the hydrogen atom, which in covalent bonds is often strongly polarized, it turned however out that also functions with $l_{aux} = l_{occ} + l_{bas} + 1$ should be included.[1,16] For consistency and to use the same number of auxiliary basis functions for atoms of the same row and orbital basis sets of the same size, also for He, Li and Be functions with l_{aux} up to $l_{occ} + l_{bas} + 1$ are included. As for the lower cardinal numbers, the auxiliary basis sets are not contracted and the same number of primitive functions is used for atoms in the same row of the periodic table and same orbital basis set size. The number of GTOs included for each angular momentum are given in Table 1.

For the atoms He, Li and Be the auxiliary functions with the highest angular momentum (*h* for He and *i* for Li and Be) could not be optimized at the atoms, since they do not contribute to the correlation energy of the (unpolarized) atoms. These functions were determined as follows: the exponent for the *h* function for He was interpolated as $\alpha_{h_1} = \sqrt{\alpha_{g_1}\alpha_{g_2}}$ and for Li and Be the exponents of the *i* functions were taken from the second *h* function, because for B–Ne the (optimized) exponents for *i* where close to those of the second *h* function.

The additional diffuse functions for the aug-cc-pV5Z (aug-cc-pV(5 + d)Z) auxiliary sets were optimized for the respective anions. As for the lower cardinal numbers, it was found that the addition of one diffuse auxiliary function for each angular momentum is sufficient to obtain for the aug-cc-pV5Z (aug-cc-pV(5 + d)Z) basis sets a similar accuracy as for the non-augmented sets. For He the exponent of the diffuse *h* function was again interpolated from the *g* functions as $\alpha_{h_2} = \sqrt{\alpha_{g_2}\alpha_{g_3}}$.

B. Auxiliary core–valence basis sets

In analogy to the cc-pwCV*X*Z and cc-pwCV(*X* + d)Z orbital basis sets the respective auxiliary basis sets are build up in a modular way by adding to the cc-pV*X*Z auxiliary basis a set of functions (“wC*X*”) with tight exponents to expand the additional four-index integrals $\langle ai \| bj \rangle$ which are obtained when the core–valence correlation functions are included in the orbital basis. Their role is to expand orbital products $\phi_\alpha(\vec{r})\phi_i(\vec{r})$ where either ϕ_i is a core orbital or ϕ_α one of the additional correlation and polarization functions of the (orbital) core–valence set. Thus, for the atoms B–Ne, for which the core consists of the 1s orbital and the orbital core–valence set includes functions with angular momenta up to $l_{wC} = l_{bas} - 1 = X - 1$, it is sufficient to include in the wC*X* auxiliary set functions with angular momenta up to $l_{occ} + l_{bas} - 1$. For the second-row atoms Al–Ar, however, the most important core orbitals are those of the 2s2p shell and therefore the wC*X* auxiliary sets include, as the orbital core–valence set, functions with the same maximum angular momentum as the cc-pV*X*Z sets. Table 1 lists the number of GTOs added in each angular momentum for the cc-pwCVXZ auxiliary basis sets.

The exponents of the auxiliary core–valence functions were mostly optimized as described above for the cc-pV*X*Z auxliary basis sets. For some functions, however, minimization of δ_{RI} led to exponents which were close to an exponent of one of the tight functions already contained in the cc-pV*X*Z auxiliary set. In these cases the respective exponents were replaced by the geometric mean of the two closest exponents in the cc-pV*X*Z auxiliary basis. For the optimization of the wC*X* auxiliary sets all occupied orbitals have been included in the calculation of δ_{RI} and its gradients; only for the cc-pwCVDZ and cc-pwCVTZ sets for Al–Ar the 1s orbitals have been excluded (frozen).

C. Auxiliary QZVPP basis sets for Li to Kr

For the doubly-polarized valence quadruple-ζ basis sets from Weigend *et al.*[29] several groups of atoms have to be distinguished which differ in how the orbital basis sets have been constructed. The optimization schemes for the orbital basis sets are reflected and, for some of the atoms, are also exploited in

Table 1 Number of primitive GTOs for the auxiliary basis sets cc-pV*X*Z and cc-pwCV*X*Z. For the atoms Al–Ar the same auxiliary basis sets are used for the cc-pV*X*Z and the cc-pV(*X* + d)Z orbital basis sets. In parentheses are the ratios of the number of basis functions in the auxiliary and the orbital basis given

	cc-pVDZ cc-pV(D + d)Z	cc-pVTZ cc-pV(T + d)Z	cc-pVQZ cc-pV(Q + d)Z	cc-pV5Z cc-pV(5 + d)Z
H, He	3s2p1d (2.8)	4s3p2d1f (2.1)	5s4p3d2f1g (1.8)	6s5p4d3f2g1h (1.7)
Li–Ne	7s5p4d2f (4.0)	8s6p5d3f1g (2.7)	8s7p6d5f3g1h (2.4)	10s8p7d6f4g3h1i (2.1)
Na–Ar	9s7p5d3f (3.3)	10s8p7d5f2g (3.1)	11s9p8d6f3g1h (2.5)	12s11p9d7f5g3h1i (2.3)
	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ	cc-pwCV5Z
B–Ne	+3s2p1d (3.9)	+4s3p2d1f (2.6)	+4s4p3d2f1g (2.2)	+4s4p4d3f2g1h (1.9)
Al–Ar	+3s3p3d2f (4.3)	+4s4p3d2f1g (3.0)	+4s4p3d3f3g2h (2.4)	+4s4p4d3f3g2h2i (2.0)

Table 2 Number of GTOs in the orbital and auxiliary QZVPP basis sets

	Orbital basis	Auxiliary basis	N_{aux}/N_{orb}
H, He	[4s3p2d1f]	(5s4p3d2f1g)	1.8
Li	[6s4p2d1f]	(9s6p3d2f)	1.6
Be	[7s4p2d1f]	(9s7p4d2f)	1.8
B–Ne	[7s4p3d2f1g]	(8s7p6d5f3g1h)	2.3
Na	[9s5p4d2f]	(12s11p9d7f3g)	2.9
Mg	[9s5p5d2f]	(12s11p8d6f3g)	2.4
Al–Ar	[9s6p4d2f1g]	(11s9p8d6f3g1h)	2.3
K	[11s6p4d3f]	(14s13p9d8f5g)	2.8
Ca	[11s6p4d3f]	(14s12p9d8f5g)	2.8
Sc–Ni	[11s6p5d3f2g]	(15s13p11d8f7g5h2i)	3.3
Cu–Zn	[11s6p5d3f2g]	(15s13p11d9f7g5h2i)	3.4
Ga–Kr	[11s7p4d4f1g]	(13s12p11d9f7g5h1i)	3.3

the construction of the auxiliary basis sets. The size of the resulting auxiliary basis sets are given in Table 2 together with the size of the QZVPP orbital basis sets and the ratios of the number of functions in the two basis sets N_{aux}/N_{orb}.

a. H, He, B–Ne and Al–Ar. For these atoms the QZVPP (orbital) basis is made up of the segmented contracted QZV kernel of s and p functions (for H and He only s functions) and a primitive set of polarization functions taken for H, He and B–Ne from the cc-pVQZ and for Al–Ar from the cc-pV(Q + d)Z basis. One could thus expect that the auxiliary basis sets for the cc-pVQZ basis would provide an accurate resolution of the identity also for the QZVPP orbital basis. Test calculations with the molecules used for evaluating the performance of the auxiliary basis sets (see below) showed, however, that this gives RI errors which are larger than what one would like to have for a quadruple-ζ basis set. Therefore, an QZVPP auxiliary basis has been constructed for these atoms from the f, g and h (for H and He the p, d and f) functions of the cc-pVQZ (cc-pV(Q + d)Z) auxiliary basis and a new spd set (for H and He an s set) which has been optimized by minimizing δ_{RI} for the atoms. Only for hydrogen the optimization was done at the H_2 molecule. For Al–Ar the 1s orbital was through this optimization excluded from the calculation of the δ_{RI} functional and its gradient.

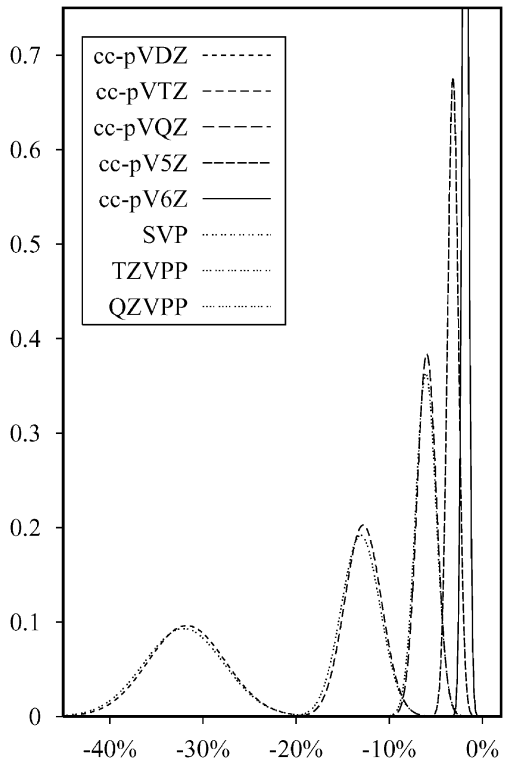


Fig. 1 One-electron basis set errors in the MP2 valence correlation energy (in % of the estimated limiting value) shown as normalized Gaussian distributions determined from $\bar{\Delta}$ and Δ_{std} for the tests with row 1 (B–Ne) and row 2 (Al–Ar) atoms.

b. Ga–Kr. The QZVPP orbital basis for the third row atoms Ga–Kr is constructed in a similar way as those for B–Ne and Al–Ar, but since Ga–Kr have an occupied 3d shell the QZV kernel includes also d functions and only the f and g polarization functions of the cc-pVQZ sets are included in the QZVPP basis. The most important difference, however, is that

Table 3 The test sets used to evaluate the performance of the optimized auxiliary basis sets. The first set consists of 42 molecules that contain only H, He and the elements B–Ne, while the second set comprises of 30 molecules which contain also at least one of the second row elements Al–Ar. Since the aug-cc-pVXZ and cc-pwCVXZ basis set series are not available for the (earth) alkali atoms Li, Be, Na and Mg, the molecules containing these atoms are grouped into two separate sets (19 molecules containing Li or Be and 12 molecules with Na or Mg) and the last set comprises 90 molecules containg the third row elements K–Kr

Row 1 (B–Ne)	Row 2 (Al–Ar)
B_2H_6, B_4H_4, BF_3, BH_3, BH_3CO, BH_3NH_3, $B_3N_3H_6$	H_2S, H_2S_2, P_2, CS_2, S_2, S_5, SF_2
C_2H_2, C_2H_3N, C_2H_4, C_2H_6, C_4H_4, C_6H_6, CF_4, CO	SF_4, Cl_2, ClF, ClF_3, Al_2O_3, Al_2S_3
CH_2O, CH_2O_2, CH_3N, CH_3OH, CH_4,CO_2, F_2, H_2, Ne_2	$AlCl_3$, AlF_3, AlH_3, HCl, PF_3, PF_5
H_2CO_3, H_2O, H_2O_2, HCN, HF, HNC, HNO, NH_3, NH_4F	PH_3, Ar_2, H_2SO_4, H_3PO_4, HCP
HNO_2, HNO_3, He_2, N_2, N_2H_2, N_2H_4, N_4, NF_3, OF_2	SF_6, $SiCl_4$, SiF_4, SiH_4, SiO_2, SiS_2

Row 1 (Li, Be)	Row 2 (Na, Mg)
Li_2, Li_2O, $Li_4(CH_3)_4$, Li_4Cl_4, Li_4H_4, Li_8, $LiBH_4$, $LiCl$	Na_2O, Na_2S, Na_3N, Na_3P
LiF, LiH, Li_2S, PLi_3, Be_2F_4, Be_2H_4	$NaCl$, NaF, NaH, Na_2
Be_4, $Be(CH_3)_2$, $BeF_2(OH_2)_2$, BeH_2, BeS	$MgCl_2$, MgF_2, MgH_2, Mg_4

Row 3 (K–Kr)
K_2, K_2S, K_3P, KBr, KCl, KF, KH, Ca_4, $CaCl_2$, CaF_2, CaH_2, $ScCl_3$, ScF, ScF_3, ScH_3, ScO
$TiCl_4$, $Ti(CO)_4$, TiF_3,TiF_4, TiH_4, TiO, TiO_2, TiS_2, VH_5, VO, VOF_3, $CrCl_3$, $Cr(CO)_6$, CrF_3, CrH, CrO_3
MnF_2, MnO, MnO_2, MnO_3F, MnO_4^-, MnS, $Fe(CO)_5$, FeF_2, FeF_3, FeO, $Fe(C5H5)_2$, $CoCl_2$, $CoCl_3$, CoF_2, CoF_3, CoO
$NiCl_2$, $Ni(CO)_4$, NiF_2, NiF_3, NiO, NiS, Cu_2O, Cu_2S, $CuCl$, $CuCl_2$, $CuCN$, CuF, CuH, $ZnCl_2$, ZnF_2, $ZnH2$, $Zn(CH_3)_2$
$GaCl$, $GaCl_3$, GaF, GaH_3, $GeCl_4$, GeF_4, GeH_4, GeO, GeO_2, As_4, $AsCl_3$, $AsCl_6^-$, AsH_3, Se_8, SeH_2, SeO_2
Br_2, $BrCl$, BrO^-, BrO_2^-, BrO_3^-, BrO_4^-, HBr, $HCBr_3$, Kr_2

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Table 4 Relative errors in the MP2 valence correlation energies obtained with the cc-pVXZ (H, He, B–Ne) and cc-pV(X + d)Z (Al–Ar) series and for the basis sets SVP, TZVPP and QZVPP. Listed are the mean error $\bar{\Delta} = (1/n)\sum_{i=1}^{n}\Delta_i$, the standard deviation $\Delta_{\mathrm{std}} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(\Delta_i - \bar{\Delta})^2}$, and the maximum absolute error, $|\Delta|_{\mathrm{max}} = \max_i |\Delta_i|$ with $\Delta_i = (E_{\mathrm{X}}^{\mathrm{corr}} - E_{\mathrm{lim}}^{\mathrm{corr}})/E_{\mathrm{lim}}^{\mathrm{corr}} \times 100\%$. For the row 2 (Al–Ar) test set the results for the cc-pVXZ basis sets are given in parentheses. The basis set limits $E_{\mathrm{lim}}^{\mathrm{corr}}$ have been extrapolated from the results for cc-pV5Z (cc-pV(5 + d)Z) and cc-pV6Z (cc-pV(6 + d)Z)

Row 1 (B–Ne)	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	−29.66	−11.66	−5.28	−2.72	−1.57	−29.76	−11.98	−5.52
Δ_{std}	3.93	1.93	0.99	0.50	0.29	4.18	2.06	1.11
$\lvert\Delta\rvert_{\mathrm{max}}$	41.95	17.28	8.13	4.19	2.42	42.56	18.13	9.39

Row 2 (Al–Ar)	cc-pV(D + d)Z	cc-pV(T + d)Z	cc-pV(Q + d)Z	cc-pV(5 + d)Z	cc-pV(6 + d)Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	−34.18	−14.30	−6.83	−3.65	−2.11	−35.28	−14.59	−6.83
	(−34.67)	(−14.42)	(−6.97)	(−3.78)	(−2.19)			
Δ_{std}	4.19	1.93	1.03	0.64	0.37	4.36	2.08	1.05
	(4.52)	(2.06)	(1.12)	(0.72)	(0.42)			
$\lvert\Delta\rvert_{\mathrm{max}}$	43.13 (44.90)	18.61 (19.10)	9.24 (9.70)	5.44 (5.83)	3.15 (3.37)	44.61	19.02	9.08

in addition Weigend *et al.* added two tight f functions to account for the polarization and correlation of the 3d shell. Since the correlation of the 3d shell has a strong effect on the optimized auxiliary functions of all included angular momenta, all functions of the QZVPP auxiliary basis were determined by minimizing for the neutral atoms (in their electronic ground state) δ_{RI} for the occupied orbitals of the shells 3s3p3d and 4s4p.

c. Li, Be, Na, Mg, K and Ca. For the (earth) alkali atoms Weigend *et al.* determined the polarization functions for the QZVPP basis by maximization of the MP2 correlation energy. They differ in the number of functions and in the maximum angular momentum by those for the respective cc-pVQZ basis sets and, most importantly, account to a much larger extent for core and core–valence correlation effects to ensure a balanced treatment of neutral atoms and cations. To carry these features over to the auxiliary basis, first a set of relatively tight functions was optimized for the cations which has then been augmented by some more diffuse functions optimized for Li, Na and K for the metal dimers and for Be, Mg and Ca for the tetramers. The calculation of δ_{RI} included for all six atoms the occupied orbitals of the valence and the next lower shell.

d. Sc–Zn. A similar procedure was applied for the optimization of the auxiliary basis sets for the transition metal atoms. The innermost tight functions were optimized for the cations with the highest oxidation number usually found in chemical compounds, while the outermost diffuse functions were optimized for the neutral atoms. For Ti–Co also cations with intermediate oxidation numbers (Ti^{2+}, V^{3+}, Cr^{3+}, Mn^{2+}, Mn^{4+}, Fe^{2+}, Co^{2+}) were included in the optimization to determine auxiliary functions with intermediate exponents. As for Ga–Ar, the occupied orbitals from the 1s2s2p core shells were for the optimization excluded from the calculation of the error functional δ_{RI}.

IV. Evaluation of the auxiliary basis sets

The auxiliary basis sets described above have mostly been optimized for atoms (or atomic cations and anions). To evaluate the accuracy obtained with these basis sets in calculations on molecules, we investigated the RI error, eqn. (3), for a

Table 5 Relative errors in the MP2 valence correlation energies obtained with the aug-cc-pVXZ (aug-cc-pV(X + d)Z) basis sets and the MP2 core plus valence correlation energies calculated with the cc-pwCVXZ basis sets. Listed are the mean error $\bar{\Delta} = (1/n)\sum_{i=1}^{n}\Delta_i$, the standard deviation $\Delta_{\mathrm{std}} = \Delta_{\mathrm{std}} = \sqrt{[1/(n-1)]\sum_{i=1}^{n}(\Delta_i - \bar{\Delta})^2}$, and the maximum absolute error, $|\Delta|_{\mathrm{max}} = \max_i|\Delta_i|$ with $\Delta_i = (E_X^{\mathrm{corr}} - E_{\mathrm{lim}}^{\mathrm{corr}})/E_{\mathrm{lim}}^{\mathrm{corr}} \times 100\%$. The values for $E_{\mathrm{lim}}^{\mathrm{corr}}$ have been estimated from the results for X = Q and 5. Note that for the cc-pwCVXZ basis sets a frozen core approximation was applied to the 1s inner core orbitals of the second row elements Al–Ar

Row 1 (B–Ne)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
$\bar{\Delta}$	−25.89	−10.01	−4.48	−2.29
Δ_{std}	2.86	1.55	0.80	0.41
$\lvert\Delta\rvert_{\mathrm{max}}$	35.19	14.63	6.88	3.52

Row 2 (Al–Ar)	aug-cc-pV(D + d)Z	aug-cc-pV(T + d)Z	aug-cc-pV(Q + d)Z	aug-cc-pV(5 + d)Z
$\bar{\Delta}$	−29.24	−12.19	−5.72	−2.93
Δ_{std}	3.21	1.59	0.79	0.41
$\lvert\Delta\rvert_{\mathrm{max}}$	36.48	15.63	7.20	3.69

Row 1 (B–Ne)	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ	cc-pwCV5Z
$\bar{\Delta}$	−32.42	−11.57	−4.98	−2.55
Δ_{std}	2.55	1.00	0.52	0.27
$\lvert\Delta\rvert_{\mathrm{max}}$	41.03	14.76	6.57	3.37

Row 2 (Al–Ar)	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ	cc-pwCV5Z
$\bar{\Delta}$	−46.07	−18.53	−8.39	−4.29
Δ_{std}	4.99	2.62	1.24	0.63
Δ_{max}	54.19	21.96	10.02	5.13

Table 6 Relative RI error in the MP2 valence correlation energy obtained with the cc-pVXZ (cc-pV(X + d)Z), SVP, TZVPP and QZVPP basis sets for molecules with the main group elements B–Ne and Al–Ar. The relative RI error was calculated as $\Delta_i^{RI} = (E_{corr} - E^{corr,RI})/E_{lim}^{corr} \times 100\%$ with E_{lim}^{corr} extrapolated from the correlation energies in the cc-pV5Z (cc-pV(5 + d)Z) and cc-pV6Z (cc-pV(6 + d)Z) basis sets

Row 1 (B–Ne)	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	0.0013	0.0078	0.0058	0.0026	0.0202	0.0076	0.0046
Δ_{std}	0.0164	0.0067	0.0034	0.0015	0.0219	0.0074	0.0033
$\lvert\bar{\Delta}\rvert$	0.0132	0.0081	0.0058	0.0026	0.0232	0.0084	0.0046
$\lvert\Delta\rvert_{max}$	0.0339	0.0268	0.0134	0.0069	0.0781	0.0247	0.0125

Row 2 (Al–Ar)	cc-pV(D + d)Z	cc-pV(T + d)Z	cc-pV(Q + d)Z	cc-pV(5 + d)Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	−0.0061	−0.0011	0.0033	0.0021	0.0014	0.0003	0.0032
Δ_{std}	0.0353	0.0124	0.0070	0.0028	0.0436	0.0181	0.0068
$\lvert\bar{\Delta}\rvert$	0.0256	0.0087	0.0041	0.0023	0.0270	0.0118	0.0042
Δ_{max}	0.1202	0.0419	0.0254	0.0095	0.1496	0.0620	0.0239

set of 193 small and medium sized compounds. Depending on the availability of the basis sets this test set is divided into five subsets as shown in Table 3.

All basis sets included in the present work are available for the atoms H, He, B–Ne and Al–Ar and for these the most comprehensive comparison is possible. The hierarchical structure of the correlation consistent basis sets from Dunning and coworkers for these atoms allows to obtain accurate estimates for the basis set limit of the MP2 correlation energy. In the present work the limits have been extrapolated with the formula

$$E_X = E_\infty + A/X^3 \qquad (12)$$

from the results for $X = 5$ and 6 or 4 and 5 (see Tables 4 and 5 and Fig. 1). The results for the valence basis sets (shown in Table 4) reflect the well-known convergence behaviour of the correlation consistent basis sets cc-pVXZ (cc-pV(X + d)Z). The results for the SVP, TZVPP and QZVPP basis sets, which are shown for comparison, are quite similar to those for the cc-pVXZ (cc-pV(X + d)Z) basis sets with, respectively, X = D, T and Q. This is not surprising since for these atoms the TZVPP and QZVPP basis sets include the polarization functions from the basis sets of Dunning and coworkers. The diffuse functions included in the aug-cc-pVXZ and aug-cc-pV(X + d)Z sets have only a minor effect on the convergence of the correlation energy, as is seen from the results in Table 5, and also for the core–valence basis sets the relative errors in the (core plus valence) correlation energy are very similar to those of the valence correlation energy in the standard basis sets.

The estimates for the one-electron basis set errors given in Tables 4 and 5 can be compared with the auxiliary basis set error (*i.e.* the RI error). The latter should be smaller by at least an order of magnitude to ensure that the overall accuracy of a quantum chemical calculation is not affected by the RI approximation. In ref. 16 it was demonstrated for the cc-pVXZ (cc-pV(X + d)Z) basis sets with X = D, T, Q that with the optimization strategy and the number of GTOs chosen for the auxiliary basis sets, the RI errors are more than two orders of magnitude smaller than the one-electron basis set errors. The present results for the elements H, He, B–Ne and Al–Ar, which are based on improved estimates for the basis set limit of the MP2 valence correlation energy and now include the new auxiliary basis sets for $X = 5$ and for the QZVPP basis are shown in Table 6 and Fig. 2. The results for the aug-cc-pVXZ (aug-cc-pV(X + d)Z) and the core–valence basis sets cc-pwCVXZ are collected in Table 7. These numbers show that with the new optimized auxiliary basis sets for the QZVPP, cc-pV5Z (cc-pV(5 + d)Z), aug-cc-pV5Z (aug-cc-pV(5 + d)Z) and the core–valence basis sets cc-pwCVXZ similar relative accuracies (*i.e.* ratios of the RI and the one-electron basis set errors) are obtained as for the basis sets reported in refs. 1 and 16. For all these basis sets the RI errors are more than two orders of magnitude smaller than the one-electron basis set errors.

For alkali and alkali earth atoms and, in particular, for transition metal atoms the basis set convergence is less regular than for elements of the main groups III–VIII and it depends much more on the oxidation state. Therefore, it has not been tried to extrapolate the basis set limit of the MP2 correlation energies for the molecules that contain the elements Li, Be, Na, Mg and K–Kr. The results for the RI errors are listed in Tables 8 and 9. Since the basis set convergence for these compounds is slower than for the molecules which contain only the atoms H, He, B–Ne and Al–Ar, it is expected that for the (earth) alkali and transition metal atoms the RI errors are in most cases also more than two orders of magnitude smaller than the one-electron basis set errors. Somewhat larger RI errors are only observed for the small SVP and cc-pVDZ basis

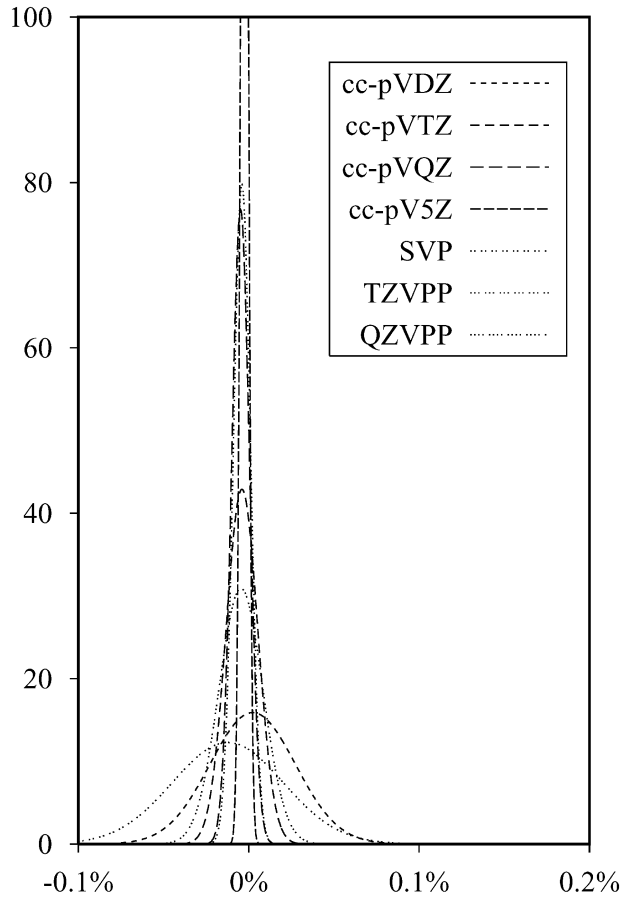


Fig. 2 RI auxiliary basis set errors in the MP2 valence correlation energy (in % of the estimated one-electron basis limit for the latter) shown as normalized Gaussian distributions determined from $\bar{\Delta}$ and Δ_{std} for the tests with row 1 (B–Ne) and row 2 (Al–Ar) atoms.

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Table 7 Relative RI error in the MP2 valence correlation energy obtained with the aug-cc-pVXZ (aug-cc-pV(X + d)Z) basis sets and the MP2 all electron correlation energies calculated with the cc-pwCVXZ basis sets for X = D, T, Q, 5. The relative RI error was calculated as $\Delta_i^{\mathrm{RI}} = (E^{\mathrm{corr}} - E^{\mathrm{corr,RI}})/E_{\mathrm{lim}}^{\mathrm{corr}} \times 100\%$ where $E_{\mathrm{lim}}^{\mathrm{corr}}$ was obtained as described in the caption of Table 5

Row 1 (B–Ne)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
$\bar{\Delta}$	−0.0013	0.0063	0.0047	0.0022
Δ_{std}	0.0143	0.0047	0.0022	0.0009
$\lvert\bar{\Delta}\rvert$	0.0118	0.0064	0.0047	0.0022
Δ_{max}	0.0293	0.0205	0.0101	0.0051
Row 2 (Al–Ar)	aug-cc-pV(D + d)Z	aug-cc-pV(T + d)Z	aug-cc-pV(Q + d)Z	aug-cc-pV(5 + d)Z
$\bar{\Delta}$	−0.0150	−0.0009	0.0034	0.0023
Δ_{std}	0.0260	0.0137	0.0040	0.0015
$\lvert\bar{\Delta}\rvert$	0.0242	0.0078	0.0035	0.0023
Δ_{max}	0.0691	0.0539	0.0154	0.0056
Row 1 (B–Ne)	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ	cc-pwCV5Z
$\bar{\Delta}$	0.0001	0.0038	0.0035	0.0020
Δ_{std}	0.0122	0.0053	0.0024	0.0010
$\lvert\bar{\Delta}\rvert$	0.0099	0.0049	0.0035	0.0020
Δ_{max}	0.0274	0.0182	0.0092	0.0046
Row 2 (Al–Ar)	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ	cc-pwCV5Z
$\bar{\Delta}$	−0.0048	−0.0009	0.0017	0.0011
Δ_{std}	0.0112	0.0054	0.0024	0.0009
$\lvert\bar{\Delta}\rvert$	0.0101	0.0045	0.0020	0.0011
Δ_{max}	0.0271	0.0142	0.0082	0.0034

Table 8 Relative RI error in the MP2 valence correlation energy for molecules containing Li, Be, Na or Mg. The relative RI error was calculated as $\Delta_i^{\mathrm{RI}} = (E^{\mathrm{corr}} - E^{\mathrm{corr,RI}})/E^{\mathrm{corr}} \times 100\%$. The following orbitals have not been considered in the calculation of the correlation energy: 1s for B–F, 1s2s2p for P, S, Cl and 1s for Na, Mg

Row 1 (Li, Be)	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	0.0473	0.0120	0.0097	0.0046	0.0556	0.0353	0.0062
Δ_{std}	0.1101	0.0155	0.0111	0.0038	0.0816	0.0536	0.0059
$\lvert\bar{\Delta}\rvert$	0.0701	0.0143	0.0097	0.0046	0.0665	0.0365	0.0062
Δ_{max}	0.3478	0.0392	0.0479	0.0134	0.2211	0.2224	0.0212
Row 2 (Na, Mg)	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	SVP	TZVPP	QZVPP
$\bar{\Delta}$	0.0565	0.0188	0.0159	0.0026	0.1934	0.0096	0.0008
Δ_{std}	0.1531	0.0457	0.0284	0.0027	0.6396	0.0388	0.0025
$\lvert\bar{\Delta}\rvert$	0.0889	0.0280	0.0175	0.0027	0.2906	0.0259	0.0018
Δ_{max}	0.4722	0.1311	0.0913	0.0091	2.1438	0.0795	0.0056

Table 9 Relative RI error in the MP2 valence correlation energy for molecules containing the atoms K–Kr. The relative RI error was calculated as $\Delta_i^{\mathrm{RI}} = (E^{\mathrm{corr}} - E^{\mathrm{corr,RI}})/E^{\mathrm{corr}} \times 100\%$. The following orbitals have not been considered in the calculation of the correlation energy: 1s for C–F, 1s2s2p for P, S, Cl and K–Zn and 1s2s2p3s3p for Ga–Kr

	SVP	TZVP	TZVPP	QZVPP
$\bar{\Delta}$	0.0181	−0.0049	−0.0018	0.0000
Δ_{std}	0.2619	0.0590	0.0177	0.0015
$\lvert\bar{\Delta}\rvert$	0.0593	0.0227	0.0087	0.0011
Δ_{max}	2.1917	0.3632	0.1034	0.0042

sets for the alkali and earth alkali dimers and tetramers (Li_2, Li_8, Be_4, Na_2, Mg_4, K_2, Ca_4) and to a smaller extend for their hydrids. If these molecules are taken out of the test sets the average and in particular the maximum RI errors are considerably smaller (*e.g.* for the SVP basis set the maximum RI errors decrease to 0.0632% for Li and Be, 0.1778% for Na and Mg and 0.0733% for K–Kr). However, for these cases also the convergence with respect to the one-electron basis set is rather poor since the small standard basis sets do not contain the diffuse polarization functions required for an accurate description of these compounds.

V. Summary and conclusions

The present communication reports an implementation of analytic gradients for the weighted error functional used in the optimization of auxiliary basis sets for RI-MP2 and RI-CC2 calculations. Combined with standard optimization techniques the analytic (auxiliary) basis set gradients provide an efficient tool for the optimization of auxiliary basis sets.

This has been applied in Section III to construct auxiliary basis sets for the correlation-consistent quintuple-ζ basis sets cc-pV5Z (cc-pV(5 + d)Z) and aug-cc-pV5Z (aug-cc-pV(5 +

d)Z), and for the core–valence basis sets cc-pwCVXZ with $X =$ D, T, Q, 5 from Dunning and coworkers[19,20,26,30] as well as for the QZVPP basis sets from Weigend *et al.*[29] In the course of this work a few auxiliary basis sets reported in ref. 16 (cc-pVDZ for C–F, cc-pVTZ and cc-pVQZ for Ne, and the diffuse functions for the respective aug-cc-pVXZ basis sets) have been reoptimized and new auxiliary basis sets have been constructed for the cc-pVXZ series with $X =$ D, T, Q, 5 for the (earth) alkali atoms Li, Be, Na, and Mg and for the SVP, TZVP and TZVPP basis sets for Ne, Ar and Kr.

The accuracy of the auxiliary basis sets has been tested for MP2 correlation energies for several test sets with in total 193 molecules. Similar as for the auxiliary basis sets for SVP, TZVP, TZVPP and the correlation consistent basis sets with $X =$ D, T, Q also for the new auxiliary basis sets developed in the present work, the errors introduced by the resolution-of-the-identity approximation are about two orders of magnitude smaller then the one-electron basis set errors. Thus, the RI errors do not affect the accuracy of the final results of RI-MP2 and RI-CC2 calculations compared to experiment or to other correlation methods or calculations performed with other one-electron basis sets. In particular for the correlation consistent basis set series the RI errors will therefore also not affect the results of basis set extrapolations *e.g.* using eqn. (12) above.

Somewhat larger RI errors, for the small SVP and cc-pVDZ basis sets in the order of a few percent of the correlation energy, are found for metal dimers and small clusters and for metal hydrids, *i.e.* for unusual oxidation states and/or binding situations. However, in all those cases also the one-electron basis set errors are larger than usual. This is a consequence of the strategy used for the construction of the auxiliary basis sets in the present and in previous work. It followed as much as possible the schemes used for the construction of the respective one-electron basis sets. In particular, the optimization of the exponents of the auxiliary basis has (apart from a few exceptions) been done for the (isolated) atoms or atomic ions. The auxiliary basis sets should thus provide an accurate approximation for the resolution of the identity basically in about the same cases in which the corresponding one-electron basis sets are able to describe accurately the correlated wavefunction.

References

1 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143–152.
2 J. L. Whitten, *J. Chem. Phys.*, 1973, **58**, 4496–4501.
3 B. I. Dunlap, J. W. D. Connolly and J. R. Sabin, *J. Chem. Phys.*, 1979, **71**, 3396–3402.
4 O. Vahtras, J. E. Almlöf and M. W. Feyereisen, *Chem. Phys. Lett.*, 1993, **213**, 514–518.
5 F. Weigend and M. Häser, *Theor. Chim. Acta*, 1997, **97**, 331–340.
6 C. Hättig and F. Weigend, *J. Chem. Phys.*, 2000, **113**, 5154–5162.
7 S. Grimme and M. Waletzke, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2075–2081.
8 S. Grimme and M. Waletzke, *J. Chem. Phys.*, 1999, **111**, 5645–5655.
9 H.-J. Werner, F. R. Manby and P. J. Knowles, *J. Chem. Phys.*, 2003, **118**, 8149.
10 M. Schütz and F. R. Manby, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3349–3358.
11 A. J. May and F. R. Manby, *J. Chem. Phys.*, 2004, **121**, 4479–4485.
12 C. van Alsenoy, *J. Comput. Chem.*, 1988, **9**, 620.
13 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–289.
14 M. Sierka, A. Hogekamp and R. Ahlrichs, *J. Chem. Phys.*, 2003, **118**, 9136–9148.
15 F. Weigend, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4285–4291.
16 F. Weigend, A. Köhn and C. Hättig, *J. Chem. Phys.*, 2002, **116**, 3175–3183.
17 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
18 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.
19 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
20 D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1994, **100**, 2975–2988.
21 T. H. Dunning, K. A. Peterson and A. K. Wilson, *J. Chem. Phys.*, 2001, **114**, 9244–9253.
22 C. Hättig, *J. Chem. Phys.*, 2003, **118**, 7751–7761.
23 M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, *J. Chem. Phys.*, 2004, **121**, 737–750.
24 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
25 TURBOMOLE V5.7, http://www.turbomole.com.
26 K. A. Peterson and T. H. Dunning, *J. Chem. Phys.*, 2002, **117**, 10548–10560.
27 The Turbomole basis set library is available by FTP from ftp://ftp.chemie.uni-karlsruhe.de/pub/basen auxiliary basis sets for RI-MP2 and RI-CC2 calculations are available from ftp://ftp.chemie.uni-karlsruhe.de/pub/cbasen.
28 The basis sets were obtained from: Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. PNL is a multiprogram laboratory operated by Batelle Memorial Institute for the US Department of Energy under contract DE-AC06-76RLO 1830.
29 F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2003, **119**, 12753–12762.
30 D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358–1371.

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