ARTICLES

Efficient use of the correlation consistent basis sets in resolution of the identity MP2 calculations

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

Andreas Köhn
Universität Karlsruhe (TH), Institut für Physikalische Chemie, Lehrstuhl für Theoretische Chemie, Kaiserstraße 12, D-76128 Karlsruhe, Germany

Christof Hättig[a)]
Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

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The convergence of the second-order Møller–Plesset perturbation theory (MP2) correlation energy with the cardinal number X is investigated for the correlation consistent basis-set series cc-pVXZ and cc-pV$(X+d)$Z. For the aug-cc-pVXZ and aug-cc-pV$(X+d)$Z series the convergence of the MP2 correlation contribution to the dipole moment is studied. It is found that, when d-shell electrons cannot be frozen, the cc-pVXZ and aug-cc-pVXZ basis sets converge much slower for third-row elements then they do for first- and second-row elements. Based on the results of these studies criteria are deduced for the accuracy of auxiliary basis sets used in the resolution of the identity (RI) approximation for electron repulsion integrals. Optimized auxiliary basis sets for RI-MP2 calculations fulfilling these criteria are reported for the sets cc-pVXZ, cc-pV$(X+d)$Z, aug-cc-pVXZ, and aug-cc-pV$(X+d)$Z with $X=$D, T, and Q. For all basis sets the RI error in the MP2 correlation energy is more than two orders of magnitude smaller than the usual basis-set error. For the auxiliary aug-cc-pVXZ and aug-cc-pV$(X+d)$Z sets the RI error in the MP2 correlation contribution to the dipole moment is one order of magnitude smaller than the usual basis set error. Therefore extrapolations towards the basis-set limit are possible within the RI approximation for both energies and properties. The reduction in CPU time obtained with the RI approximation increases rapidly with basis set size. For the cc-pVQZ basis an acceleration by a factor of up to 170 is observed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1445115]

I. INTRODUCTION

During the last decade the series of correlation consistent basis sets[1–5] cc-pVXZ with $X=$D, T, Q, 5,...have become the most popular basis sets in correlated *ab initio* calculations. Because of the correlation consistent contruction scheme applied over several ζ levels, i.e., cardinal numbers X, they provide an invaluable basis for systematic calculations. Especially the hierachical structure, which allows application of extrapolation schemes to estimate the complete basis-set limit, makes these basis sets to a powerful tool for highly accurate calculations. In particular for second-order Møller–Plesset perturbation theory (MP2) and approximated coupled cluster singles and doubles (CC2) calculations, a drawback of these basis sets is their size for higher ζ levels, increasing as $O(\zeta^3)$, which leads to huge computational expenses for the calculation of electron repulsion integrals (ERIs), increasing with $O(\zeta^{12})$. Together with the costs for atomic orbital (AO) to molecular orbital (MO) transformation of the ERIs, the latter dominate the total costs of MP2 and CC2 calculations.

An approximation, which efficiently reduces the computational demands for MP2 and CC2 without affecting significantly the accuracy, is the resolution of the identity (RI) approximation[6,7] of four-index electron repulsion integrals:

$$(ai|bj)=\sum_{PQ}(ai|P)V^{-1}_{PQ}(Q|bj), \tag{1}$$

with the Coulomb metric

$$V_{PQ}=(P|Q). \tag{2}$$

In the latter equations $(ai|P)$ and $(P|Q)$ are, respectively, three- and two-index ERIs, a,b denote virtual molecular orbitals, i,j occupied molecular orbitals, and P,Q auxiliary basis functions. With this approximation, the computational costs for RI-MP2 (Refs. 8 and 9) and RI-CC2 (Ref. 10) calculations increase only as $\approx O(\zeta^9)$ if the basis set size, i.e., the ζ level, is increased. The RI approximation is thus a very appealing approach for benchmark calculations with highly ac-

a)Author to whom correspondence should be addressed: Electronic address: christof.haettig@int.fzk.de

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TABLE I. Test set of 95 sample molecules. The set is divided into three groups. The first group consists of 42 molecules that contain only hydrogen and first-row elements. The second group consists of 30 molecules that contain at least one second-row element, and the last group consists of 23 molecules that also contain third-row elements. The 44 molecules used for the study on dipole moments are printed in bold letters.

Row 1	Row 2	Row 3
B_2H_6, B_4H_4, BF_3, BH_3	**H_2S**, **H_2S_2**, P_2, CS_2	As_4, **$AsCl_3$**, $AlCl_6^-$, **AsH_3**
BH_3CO, **BH_3NH_3**, $B_3N_3H_6$	Cl_2, **ClF**, ClF_3, Al_2O_3	Br_2, **BrCl**, BrO^-, BrO_2^-
C_2H_2, **C_2H_3N**, C_2H_4, C_2H_6	**Al_2S_3**, $AlCl_3$, AlF_3, AlH_3	BrO_3^-, BrO_4^-, **GaCl**
C_4H_4, C_6H_6, CF_4, **CH_2O**	Ar_2, **H_2SO_4**, **H_3PO_4**, **HCP**	$GaCl_3$, **GaF**, GaH_3, $GeCl_4$
CH_2O_2, **CH_3N**, **CH_3OH**, CH_4	**HCl**, **PF_3**, PF_5, **PH_3**	GeF_4, GeH_4, **GeO**, GeO_2
CO, CO_2, F_2, H_2	S_2, **S_5**, **SF_2**, **SF_4**	Kr_2, Se_8, **SeH_2**, SeO_2
H_2CO_3, **H_2O**, **H_2O_2**, **HCN**	SF_6, $SiCl_4$, SiF_4, SiH_4	
HF, **HNC**, **HNO**, **HNO_2**	SiO_2, SiS_2	
HNO_3, He_2, N_2, **N_2H_2**		
N_2H_4, N_4, **NF_3**, **NH_3**		
NH_4F, Ne_2, **OF_2**		

curate basis sets, provided that auxiliary basis sets can be constructed, such that the error introduced by the resolution of the identity (RI error) is negligible compared to the error caused by the incompleteness of the one-electron basis set.

In Sec. II of this paper we investigate the convergence of the MP2 correlation energy and the MP2 correlation contribution to the dipole moment for the cc-pVXZ, cc-pV($X+d$)Z, aug-cc-pVXZ, and aug-cc-pV($X+d$)Z series. We apply extrapolation schemes to estimate complete basis-set limits and remaining basis set errors obtained with the individual basis sets. From the results of this study we can deduce requirements for the auxiliary basis sets, such that the accuracy of RI-MP2 and RI-CC2 calculations with these basis sets are not affected by RI errors.

Optimized auxiliary basis sets for the series cc-pVXZ, cc-pV($X+d$)Z, aug-cc-pVXZ, and aux-cc-pV($X+d$)Z with $X=$D, T, and Q are reported in Sec. III for all elements for which the one-electron basis sets are available. It is demonstrated that the constructed basis sets meet the requirements devised in Sec. II and that the factor by which the RI approximation reduces the computational expenses rapidly increases with basis-set size. A summary of the results and the conclusions that can be drawn from the present investigation is given in Sec. IV.

TABLE II. Relative errors in the MP2 valence correlation energies obtained with the cc-pVXZ basis sets for $X=$D, T, Q, 5 and for the TURBOMOLE basis sets SVP, TZVP, and TZVPP. For row 2 the results for the cc-pV($X+d$)Z basis sets are given in parentheses. Listed are the mean error $\overline{\Delta}=(1/n)\Sigma_{i=1}^{n}\Delta_i$, the standard deviation $\Delta_{\mathrm{std}}=\sqrt{[1/(n-1)]\Sigma_{i=1}^{n}(\Delta_i-\overline{\Delta})^2}$, and the maximum absolute error, $\Delta_{\mathrm{max}}=\max_i|\Delta_i|$ with $\Delta_i=(E_X^{\mathrm{corr}}-E_{\mathrm{lim}}^{\mathrm{corr}})/E_{\mathrm{lim}}^{\mathrm{corr}}\times 100\%$. For the MP2 valence correlation energies the mean absolute error $\overline{|\Delta|}=(1/n)\Sigma_{i=1}^{n}|\Delta_i|$ is for all basis sets used identical to the absolute value of $\overline{\Delta}$ and is therefore not listed.

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	SVP	TZVP	TZVPP
				Row 1			
$\overline{\Delta}$	−29.41	−11.34	−4.93	−2.36	−29.11	−24.16	−11.54
Δ_{std}	3.84	1.80	0.84	0.34	3.65	2.76	1.75
Δ_{max}	41.45	16.57	7.34	3.37	37.29	29.90	14.90
				Row 2			
$\overline{\Delta}$	−33.99	−13.50	−5.97	−2.75	−34.30	−30.42	−13.56
	(−33.44)	(−13.51)	(−5.96)	(−2.76)			
Δ_{std}	4.38	1.82	0.81	0.37	3.96	3.77	1.79
	(4.05)	(1.72)	(0.76)	(0.35)			
Δ_{max}	43.56	17.13	7.50	3.54	40.41	37.66	15.64
	(41.97)	(16.95)	(7.39)	(3.51)			
				Row 3			
$\overline{\Delta}$	−56.70	−34.86	−20.27	−4.12	−39.61	−39.07	−25.30
Δ_{std}	10.15	9.79	6.64	0.61	3.41	4.78	5.93
Δ_{max}	73.75	51.90	31.67	5.22	46.21	47.33	33.76
				All			
$\overline{\Delta}$	−37.46	−17.72	−8.97	−2.91	−33.56	−30.00	−15.83
Δ_{std}	6.04	4.99	3.29	0.42	3.98	3.89	4.24
Δ_{max}	73.75	51.90	31.67	5.22	46.21	47.35	33.76

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II. BASIS-SET CONVERGENCE OF THE MP2 CORRELATION ENERGY AND THE MP2 DIPOLE MOMENT

A. Correlation energy

To assess the typical error in the MP2 correlation energy obtained with the correlation consistent basis sets, we have set up a test set of 95, mostly polyatomic, sample molecules. This test set, which is listed in Table I, was chosen such that each element of the main groups III–VII and rows 1–3, i.e., B–F, Al–Cl, and Ga–Br, is represented by at least three molecules. Because the basis-set demands depend upon to which row of the periodic system an atom belongs, we divided the sample molecules into three groups: the first group includes all molecules that contain only hydrogen and first-row elements, the second group consists of all molecules that also contain second-row elements, and the third group consists of the molecules that also contain third-row elements.

For all 95 molecules we computed the MP2 valence correlation energies for the four correlation consistent basis sets[1,3,4] cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z. For molecules containing second-row elements also the values for the cc-pV$(X+d)$Z basis sets have been computed for $X=$D, T, Q, and 5. We calculated only the valence correlation energies since these basis sets do not include core-correlation functions. Thus, we kept the core electrons—for first-row elements $1s^2$ and for second-row elements $1s^2 2s^2 2p^6$—frozen. For third-row elements a problem arises: generally, only $4s$ and $4p$ are considered valence shells, and the correlation consistent basis sets have thus been designed for frozen $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ cores.[5] For various examples in our test set, however, it turns out that the separation between the $3d$ and $4s$ shells is small (especially for Ga and Ge) and the $3d$ orbitals have energies comparable to those of the fluorine and oxygen $2s$ orbitals (and the $3s$ orbitals of chlorine, respectively), which have to be included in the correlation treatment. This difficulty has already been noticed by the authors of Ref. 5. We decided therefore to include the $3d$ electrons for all third-row elements in the correlation treatment, though slower basis-set convergence has to be expected for these molecules.

All calculations were done at the self-consistent field (SCF) equilibrium geometries for the polarized split valence (SVP) basis with the MPGRAD[11] module of the TURBOMOLE program package,[12] and the resolution of the identity approximation was not employed to avoid contamination of the results for the one-particle basis-set error with RI errors.

Since accurate numerical or explicitly correlated MP2 calculations are not easily accessible for such a large set of polyatomic molecules, we extrapolated the basis-set limit for the MP2 valence correlation energies from results of the before-mentioned calculations. For each molecule we fitted the correlation energies (E_X^{corr}) obtained with the cc-pVXZ basis sets with $X=$T, Q, and 5 to the two-parameter power form proposed by Helgaker *et al.*[13]:

$$E_X^{\mathrm{corr}} = E_{\mathrm{lim}}^{\mathrm{corr}} + AX^{-3}. \tag{3}$$

The extrapolated basis set limits for the MP2 correlation energies $E_{\mathrm{lim}}^{\mathrm{corr}}$ obtained by this formula have been found[14,15] to be superior to cc-pV6Z results, with a remaining uncertainty of only a few millihartree per atom. They thus provide a reliable basis for estimating the error in the MP2 valence correlation energies obtained with the basis sets cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z. A similar extrapolation was done for the cc-pV$(X+d)$Z basis sets[16] for the row 2 subset of the test sample. For comparison also the results for the SVP (Ref. 17), TZVP (Ref. 18) and TZVPP (Refs. 19 and 9) basis sets from the TURBOMOLE basis-set library[19] are included. For these basis sets we used the $E_{\mathrm{lim}}^{\mathrm{corr}}$ obtained from the cc-pVXZ series as reference.

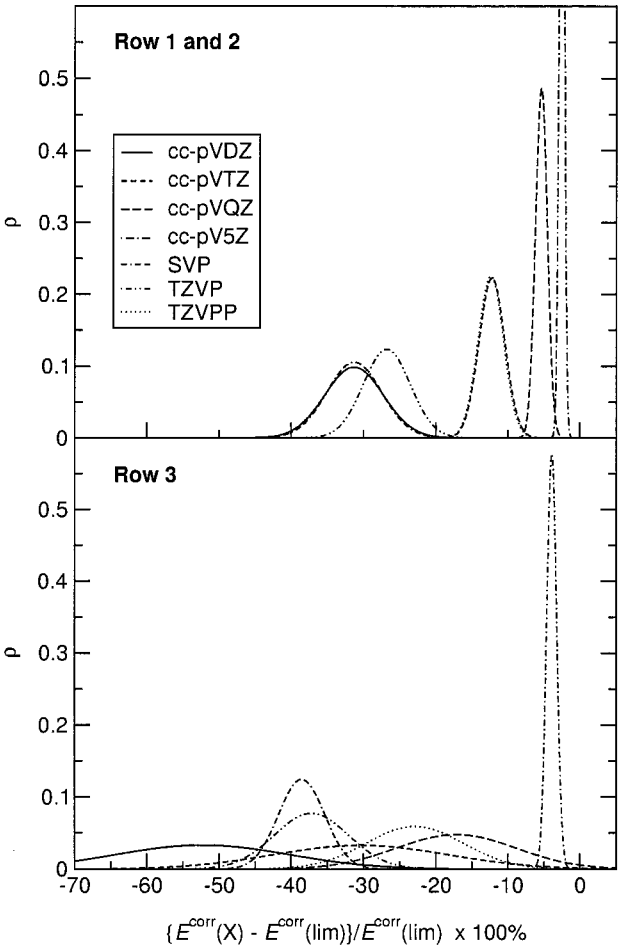


FIG. 1. Distribution of the one-electron basis set error in the MP2 correlation energy (in %) for the test set listed in Table I.

In Table II we listed for each basis set the mean error, the standard deviation, and the maximum error for the three groups of our test set and for the complete test set. The results are shown in graphical form in Fig. 1. As expected, we observe for all three groups of molecules a smooth decrease of the errors for the cc-pVXZ basis sets with increasing cardinal number X. Only little difference is found between the cc-pV$(X+d)$Z and the cc-pVXZ results. The TURBOMOLE SVP and TZVPP basis sets perform for first- and second-row elements very similar to, respectively, cc-pVDZ and cc-pVTZ. For third-row elements, however, the SVP and TZVPP sets give significantly better results than their correlation consistent counterparts cc-pVDZ and cc-pVTZ, which is due to the more flexible contraction used for the d functions. The TZVP basis, which was optimized solely

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for Hartree-Fock calculations[18] is not suitable for correlated calculations, because it does not contain the semidiffuse higher angular momentum functions needed for an accurate description of the Coulomb cusp.

For all six basis sets the errors for first- and second-row elements are of very similar magnitude. For these elements and basis sets there is little difference between the maximum absolute error $\Delta_{\max}$ and the absolute value of the mean error $|\overline{\Delta}|$. Also the standard deviations are small, meaning that for these cases most of the error is systematic. For the correlation consistent basis set series cc-pVXZ we find that for the molecules with third-row elements the mean and maximum absolute errors and in particular the standard deviations are much larger than those for the first- and second-row elements. This effect is much less pronounced for the SVP and the TZVPP basis sets. Thus, with the cc-pVXZ basis sets one does not get the same accuracy for third-row elements as is obtained for first- and second-row elements if the $3d$ shell is correlated. The results are almost shifted by one cardinal number, meaning that with a cc-pVXZ basis one obtains for third-row elements only about the accuracy which for first- and second-row elements is already obtained with the cc-pV$(X-1)Z$ basis. This effect is probably due to an insufficient number of polarization functions for the d electrons in the basis sets for the third-row elements.

From the results of this study we can deduce some criteria for the auxiliary basis sets used in the resolution of the identity. What one would like to have is that the additional error introduced by the resolution of the identity approximation does not significantly change the distribution of errors one already has without this approximation. The maximum absolute error, the mean error, and the standard deviation due to the RI approximation should therefore be small compared to the corresponding values in Table II. Since the RI errors are mainly statistically distributed, the strongest conditions are those for the standard deviation and the maximum absolute error. Using the results for the first- and second-row elements and an average MP2 correlation energy of approximately 140 millihartree/atom, we thus obtain for the cc-pVDZ basis the requirements $\Delta_{\max}^{\mathrm{RI}} \ll 30\%$ of the correlation energy or 45 millihartree/atom and $\Delta_{\mathrm{std}}^{\mathrm{RI}} \ll 4\%$ or 6 millihartree/atom. The auxiliary basis for cc-pVTZ should fulfill $\Delta_{\max}^{\mathrm{RI}} \ll 10\%$ or 17 millihartree/atom and $\Delta_{\mathrm{std}}^{\mathrm{RI}} \ll 2\%$ or 2 millihartree/atom, and for the cc-pVQZ basis $\Delta_{\max}^{\mathrm{RI}} \ll 5\%$ or 7 millihartree/atom and $\Delta_{\mathrm{std}}^{\mathrm{RI}} \ll 1\%$ or 1 millihartree/atom.

B. Dipole moment

The calculation of first-order response properties such as the dipole moment requires the augmentation of the standard basis sets with diffuse functions. Halkier *et al.*[20] have calculated for the molecules HF and BH the basis-set limits of the dipole moment for MP2, coupled cluster singles and doubles (CCSD), and CCSD with a perturbation correction for connected triple excitations (CCSD(T)) using both extrapolation and R12 methods. They showed for these two molecules that the basis-set limit of the correlation contribution can be obtained from a two-point extrapolation of an aug-cc-pVXZ series. The suggested expression has the same form as Eq. (3):

$$\mu_X^{\mathrm{corr}} = \mu_{\mathrm{lim}}^{\mathrm{corr}} + AX^{-3}. \tag{4}$$

We chose from the test sample the subset of 44 molecules possessing a nonvanishing dipole moment (printed in

TABLE III. Relative basis set error $\Delta_i = (\mu_X^{\mathrm{corr}} - \mu_{\mathrm{lim}}^{\mathrm{corr}})/\mu_{\mathrm{lim}}^{\mathrm{corr}} \times 100\%$ in the correlation contribution to the MP2 dipole moment (see text) obtained with the aug-cc-pVXZ basis sets for $X=$T, Q, 5 and a T/Q extrapolation. The basis-set limit was estimated from a $Q/5$ extrapolation. The test set consisted of CO, H_2O, HCN, HF, HNC, NH_3, and ClF (row 1), HCP, HCl, H_2S, and PH_3 (row 2), AsH_3, BrCl, GaCl, GaF, GeO, and SeH_2 (row 3).

	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	aug-cc-pVTZ/ aug-cc-pVQZ
		Row 1 ($n=6$)		
$\overline{\Delta}$	7.03	3.09	1.58	0.22
Δ_{std}	5.19	2.29	1.17	0.38
$\overline{\lvert\Delta\rvert}$	7.23	3.26	1.67	0.37
$\Delta_{\max}$	12.57	5.56	2.85	0.66
		Row 2 ($n=5$)		
$\overline{\Delta}$	23.10	10.48	5.36	1.27
Δ_{std}	29.69	15.28	7.83	4.86
$\overline{\lvert\Delta\rvert}$	30.34	15.25	7.81	4.24
$\Delta_{\max}$	47.19	23.04	11.80	5.88
		Row 3 ($n=6$)		
$\overline{\Delta}$	−58.03	−21.65	−11.08	4.90
Δ_{std}	255.10	169.79	86.93	126.58
$\overline{\lvert\Delta\rvert}$	188.75	108.61	55.61	84.41
$\Delta_{\max}$	392.08	270.19	138.34	217.66

TABLE IV. Relative basis set error $\Delta_i = (\mu_x^{\mathrm{corr}} - \mu_{\mathrm{lim}}^{\mathrm{corr}})/\mu_{\mathrm{lim}}^{\mathrm{corr}} \times 100\%$ in the correlation contribution to the MP2 dipole moment (see text) obtained with the aug-cc-pVXZ basis sets for $X=$D, T, Q compared to the basis set limit estimated from a T/Q extrapolation. For row 2 the results for the cc-pV$(X+d)$Z basis sets are given in parentheses.

	aug-cc-pVDZ [aug-cc-pV$(D+d)$Z]	aug-cc-pVTZ [aug-cc-pV$(T+d)$Z]	aug-cc-pVQZ [aug-cc-pV$(Q+d)$Z]
		Row 1 ($n=23$)	
$\overline{\Delta}$	7.78	7.42	3.13
Δ_{std}	13.13	6.35	2.68
$\overline{\lvert\Delta\rvert}$	11.99	7.99	3.37
$\Delta_{\max}$	34.26	19.38	8.18
		Row 2 ($n=14$)	
$\overline{\Delta}$	13.13	9.19	3.88
	(13.51)	(9.39)	(3.96)
Δ_{std}	48.32	22.99	9.70
	(42.14)	(23.01)	(9.71)
$\overline{\lvert\Delta\rvert}$	29.54	18.06	7.62
	(24.66)	(17.38)	(7.33)
$\Delta_{\max}$	151.30	39.62	16.71
	(134.71)	(45.13)	(19.04)
		Row 3 ($n=7$)	
$\overline{\Delta}$	0.72	−9.74	−4.11
Δ_{std}	149.73	110.57	46.65
$\overline{\lvert\Delta\rvert}$	104.90	81.93	34.56
$\Delta_{\max}$	256.43	182.61	77.04

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TABLE V. Specification of auxiliary basis sets. The auxiliary basis sets for (aug-)cc-pVXZ and (aug-)cc-pV($X+d$)Z are identical.

	cc-pVDZ cc-pV(D+d)Z	cc-pVTZ cc-pV(T+d)Z	cc-p-VQZ cc-pV(Q+d)Z
H	3s2p1d	4s3p2d1f	5s4p3d2 f1g
B–Ne	7s5p4d2 f	8s6p5d3f1g	8s7p6d5f3g1h
Al–Ar	9s7p5d3f	10s8p7d5f2g	11s9p8d6f3g1h
Ga–Kr	9s8p7d4f2g	10s9p8d6f4g1h	11s10p9d7f5g3h1i
	aug-cc-pVDZ aug-cc-pV(D+d)Z	aug-cc-pVTZ aug-cc-pV(T+d)Z	aug-cc-pVQZ aug-cc-pV(Q+d)Z
H	+1s1p1d	+1s1p1d1f	+1s1p1d1f1g
B–Ne	+1s1p1d1f	+1s1p1d1f1g	+1s1p1d1f1g1h
Al–Ar	+1s1p1d1f	+1s1p1d1f1g	+1s1p1d1f1g1h
Ga–Kr	+1s1p1d1f	+1s1p1d1f1g	+1s1p1d1f1g1h

bold letters in Table I). Again, only the valence electrons (including the 3d electrons of Ga–Kr, cf. above) were correlated. The calculations with exact two-electron integrals were carried out with the DALTON program,[21] since frozen-core relaxed properties are not implemented in the MPGRAD[11] module of TURBOMOLE.

The basis set limit was obtained from an extrapolation employing aug-cc-pVXZ (X=T, Q, called the T/Q extrapolation hereafter), since pentuple-ζ calculations with DALTON were prohibitive for molecules with more than two nonhydrogen atoms. The reliability of the estimated basis-set limit was tested for 17 small molecules for which aug-cc-pV5Z calculations could be carried out, such that a Q/5 extrapolation was possible. Table III displays the results. For first- and second-row compounds the extrapolation scheme works well: The T/Q extrapolation leads to a better result (i.e., smaller standard deviation and smaller maximum error compared to the Q/5 limit) than a single 5Z calculation. However, more pronounced than for the correlation energies, the uncertainties for second-row molecules are larger, the standard deviation and the maximum error being nearly one order of magnitude larger. No reliable extrapolation seems possible for the third-row compounds. Large changes in the dipole moment are observed; for GaF and GaCl even the sign of the correlation contribution changes. The T/Q extrapolation hardly improves the deviations of the QZ calculations, and it is even doubtful if the Q/5 extrapolation is a useful estimate of the basis-set limit at all. Again, the problem is due to correlation of d electrons for which the aug-cc-pVXZ basis sets are not designed.

The deviations of aug-cc-pVXZ/aug-cc-pV($X+d$)Z from the estimated basis-set limit for the 44 molecules are given in Table IV. Again, for first- and second-row molecules, a nice convergence towards the limit is observed though, as stated abvove, for second-row molecules larger uncertainties are found and convergence is not as smooth as for those of the first row. The basis-set limits obtained from the aug-cc-pVXZ and the aug-cc-pV($X+d$)Z basis-set series are quite similar, within a standard deviation of 1.8% and a maximum deviation of 4.2% (for ClF_3). For the latter case

TABLE VI. Relative RI error $\Delta_i^{\mathrm{RI}}=(E_X^{\mathrm{corr,RI}}-E_X^{\mathrm{corr}})/E_{\mathrm{lim}}^{\mathrm{corr}}\times 100\%$ in the RI-MP2 correlation energy obtained with the cc-pVXZ (X=D,T,Q), SVP, TZVP, and TZVPP basis sets and the corresponding auxiliary basis sets. For row 2 the results for the cc-pV ($X+d$)Z basis sets are given in parentheses.

	cc-pVDZ [cc-pV(D+d)Z]	cc-pVTZ [cc-pV(T+d)Z]	cc-pVQZ [cc-pV(Q+d)Z]	SVP	TZVP	TZVPP
			Row 1			
$\overline{\Delta^{\mathrm{RI}}}$	0.0019	0.0077	0.0058	0.0190	0.0067	0.0077
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	0.0169	0.0068	0.0034	0.0204	0.0198	0.0075
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.0140	0.0080	0.0058	0.0222	0.0169	0.0086
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	0.0336	0.0269	0.0135	0.0714	0.0559	0.0248
			Row 2			
$\overline{\Delta^{\mathrm{RI}}}$	−0.0063 (−0.0059)	−0.0013 (−0.0014)	0.0033 (0.0034)	0.0009	−0.0119	0.0002
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	0.0340 (0.0356)	0.0125 (0.0124)	0.0071 (0.0071)	0.0446	0.0416	0.0185
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.0249 (0.0261)	0.0089 (0.0088)	0.0040 (0.0041)	0.0277	0.0323	0.0122
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	0.1147 (0.1205)	0.0420 (0.0411)	0.0255 (0.0255)	0.1501	0.1315	0.0622
			Row 3			
$\overline{\Delta^{\mathrm{RI}}}$	−0.0058	−0.0031	−0.0012	−0.0063	−0.0096	−0.0068
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	0.0094	0.0044	0.0015	0.0079	0.0073	0.0045
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.0092	0.0047	0.0018	0.0079	0.0098	0.0073
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	0.0207	0.0116	0.0028	0.0205	0.0235	0.0138
			All			
$\overline{\Delta^{\mathrm{RI}}}$	−0.0026	0.0023	0.0033	0.0071	−0.0032	0.0018
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	0.0227	0.0099	0.0054	0.0306	0.0283	0.0130
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.0163	0.0075	0.0043	0.0205	0.0201	0.0094
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	0.1147	0.0420	0.0255	0.1501	0.1315	0.0622

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TABLE VII. Relative RI error $\Delta_i^{\mathrm{RI}}=(\mu_X^{\mathrm{corr,RI}}-\mu_X^{\mathrm{corr}})/\mu_{\mathrm{lim}}^{\mathrm{corr}}\times 100\%$ in the MP2 dipole moment obtained with the aug-cc-pVXZ basis sets for $X=$D, T, Q and the corresponding auxiliary basis sets. For row 2 the results for the aug-cc-pV$(X+d)$Z basis sets are given in parentheses.

	aug-cc-pVDZ [aug-cc-pV(D+d)Z]	aug-cc-pVTZ [aug-cc-pV(T+d)Z]	aug-cc-pVQZ [aug-cc-pV(Q+d)Z]
		Row 1 ($n=23$)	
$\overline{\Delta^{\mathrm{RI}}}$	−0.26	−0.09	−0.03
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	0.31	0.10	0.04
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.31	0.10	0.04
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	1.09	0.36	0.14
		Row 2 ($n=14$)	
$\overline{\Delta^{\mathrm{RI}}}$	−0.84	−0.19	−0.04
	(−0.90)	(−0.19)	(−0.05)
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	1.09	0.39	0.14
	(1.16)	(0.39)	(0.14)
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	0.86	0.28	0.10
	(0.93)	(0.28)	(0.11)
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	2.80	0.93	0.35
	(2.98)	(0.94)	(0.36)
		Row 3 ($n=7$)	
$\overline{\Delta^{\mathrm{RI}}}$	−1.57	−0.51	−0.07
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	1.67	0.86	0.28
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	1.57	0.53	0.17
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	5.04	2.28	0.65

also an improved convergence of the aug-cc-pV$(X+d)$ series is apparent, i.e., the errors of the aug-cc-pVXZ ($X=$D,T,Q) results with respect to the basis-set limit are halved.

Taking again the typical basis set errors found for first- and second-row compounds, we set up the following criteria for the auxiliary basis sets: $\Delta_{\mathrm{max}}^{\mathrm{RI}}\ll 34\%$ of $\Delta\mu$ and $\Delta_{\mathrm{std}}^{\mathrm{RI}}\ll 13\%$ for aug-cc-pVDZ, $\Delta_{\mathrm{max}}^{\mathrm{RI}}\ll 19\%$ and $\Delta_{\mathrm{std}}^{\mathrm{RI}}\ll 6\%$ for aug-cc-pVTZ, and $\Delta_{\mathrm{max}}^{\mathrm{RI}}\ll 8\%$ and $\Delta_{\mathrm{std}}^{\mathrm{RI}}\ll 2.5\%$ for aug-cc-pVQZ.

III. OPTIMIZATION OF AUXILIARY BASIS SETS

A. Optimization strategy and specification of auxiliary basis sets

Auxiliary basis sets for RI-MP2 and RI-CC2 calculations have been optimized for the cc-pVXZ and aug-cc-pVXZ ($X=$D,T,Q) basis sets (elements H–He, B–Ne, and Ga–Kr) and for the cc-pV$(X+d)$Z and aug-cc-pV $(X+d)$Z basis sets (elements Al–Ar). We followed the procedure outlined in a previous work.[9] The optimizations of the cc-pVXZ/cc-pV$(X+d)$Z auxiliary basis sets were done at the atoms, except for hydrogen, which was optimized at H_2.

TABLE VIII. RI error per atom $\Delta_i^{\mathrm{RI}}=(E_X^{\mathrm{corr,RI}}-E_X^{\mathrm{corr}})/N^{\mathrm{atoms}}$ in the RI-MP2 correlation energy in microhartrees obtained with the cc-pVXZ ($X=$D,T,Q), SVP, TZVP, and TZVPP basis sets and the corresponding auxiliary basis sets. For row 2 the results for the cc-pV$(X+d)$Z basis sets are given in parentheses.

	cc-pVDZ [cc-pV(D+d)Z]	cc-pVTZ	cc-pVQZ [cc-pV(T+d)Z]	SVP	TZVP [cc-pV(Q+d)Z]	TZVPP
			Row 1			
$\overline{\Delta^{\mathrm{RI}}}$	−6.32	5.81	5.41	13.67	−2.68	5.15
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	22.70	4.57	2.12	18.58	23.82	6.21
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	16.38	6.43	5.41	20.45	18.13	7.17
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	75.18	14.21	11.36	43.83	73.28	14.26
			Row 2			
$\overline{\Delta^{\mathrm{RI}}}$	−24.91	−8.70	1.67	−18.72	−41.05	−10.10
	(−24.53)	(−8.42)	(1.85)			
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	34.76	11.57	4.27	36.35	38.94	14.94
	(36.97)	(11.70)	(4.34)			
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	35.23	12.28	3.60	32.77	48.23	15.68
	(37.15)	(12.14)	(3.78)			
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	98.43	32.95	10.02	99.82	113.32	34.36
	(101.74)	(33.11)	(9.85)			
			Row 3			
$\overline{\Delta^{\mathrm{RI}}}$	−20.37	−11.54	−4.67	−19.21	−28.31	−22.41
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	23.14	10.99	3.98	22.06	18.91	14.95
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	24.47	13.11	5.22	22.83	28.48	22.87
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	64.19	35.97	11.33	53.13	58.60	51.79
			All			
$\overline{\Delta^{\mathrm{RI}}}$	−15.59	−2.97	1.79	−4.60	−21.11	−6.37
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	28.19	11.90	5.23	30.65	33.06	16.27
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	24.29	9.89	4.79	24.95	30.22	13.68
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	98.43	35.97	11.36	99.82	113.32	51.79

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TABLE IX. RI error per atom $\Delta_i^{\mathrm{RI}}=(E_X^{\mathrm{corr,RI}}-E_X^{\mathrm{corr}})/N^{\mathrm{atoms}}$ in the RI-MP2 correlation energy in microhartrees obtained with the aug-cc-pVXZ (X = D,T,Q) basis sets and the corresponding auxiliary basis sets. For row 2 the results for the cc-pV($X+d$)Z basis sets are given in parentheses.

	aug-cc-pVDZ [aug-cc-pV(D+d)Z]	aug-cc-pVTZ [aug-cc-pV(T+d)Z]	aug-cc-pVQZ [aug-cc-pV(Q+d)Z]
		Row 1	
$\overline{\Delta^{\mathrm{RI}}}$	−11.98	5.31	4.76
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	22.16	3.49	1.80
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	16.94	5.70	4.76
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	67.46	11.15	10.51
		Row 2	
$\overline{\Delta^{\mathrm{RI}}}$	−38.18	−2.07	3.76
	(−38.70)	(−1.86)	(3.97)
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	32.57	9.39	2.23
	(33.75)	(9.50)	(2.34)
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	41.55	7.49	3.99
	(42.51)	(7.54)	(4.18)
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	105.38	26.87	7.24
	(109.23)	(27.10)	(7.54)
		Row 3	
$\overline{\Delta^{\mathrm{RI}}}$	−33.13	−6.04	−2.02
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	25.62	8.51	3.57
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	34.20	8.08	3.13
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	89.65	24.52	8.48
		All	
$\overline{\Delta^{\mathrm{RI}}}$	−25.37	0.23	2.80
$\Delta_{\mathrm{std}}^{\mathrm{RI}}$	29.02	8.51	3.69
$\overline{\lvert\Delta^{\mathrm{RI}}\rvert}$	28.89	6.84	4.12
$\Delta_{\mathrm{max}}^{\mathrm{RI}}$	105.38	26.87	10.51

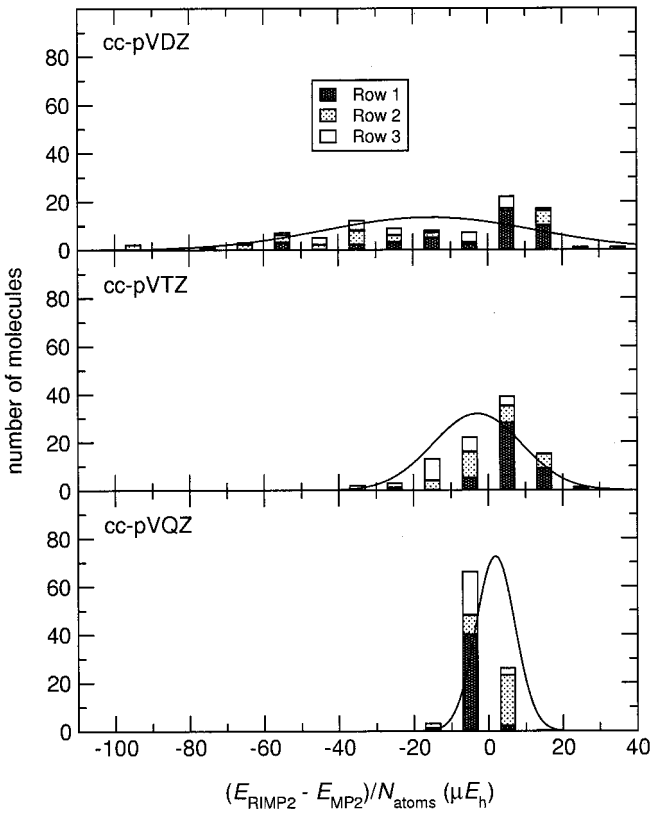


FIG. 2. Histogram of RI errors per atom in the RI-MP2 correlation energy obtained with cc-pVXZ basis sets and the corresponding auxiliary basis sets. The curve corresponds to the normal distribution with the parameters from Table VIII.

The optimization was carried out by minimizing the quantity

$$\delta_{\mathrm{RI}}=\frac{1}{4}\sum_{iajb}\frac{(\langle ab\|ij\rangle-\langle ab\|ij\rangle_{\mathrm{RI}})^2}{\epsilon_a-\epsilon_i+\epsilon_b-\epsilon_j} \tag{5}$$

with respect to the auxiliary basis set exponents, where $\langle ab\|ij\rangle=(ai|bj)-(aj|bi)$. The gradients were obtained numerically. The frozen core approximation was used with a $1s^2$ core for Al–Ar and a $1s^22s^22p^6$ core for Ga–Kr.

The requirements for size and accuracy of the auxiliary basis sets were chosen very similar to those used previously for the optimization of auxiliary basis sets for the SVP, TZVP, and TZVPP basis sets:[9]

(1) The number of auxiliary basis functions should not be much greater than 4 times the number of basis functions.

(2) $\delta_{\mathrm{RI}}/E_{\mathrm{MP2}}<10^{-6}$, additionally $|E_{\mathrm{MP2}}-E_{\mathrm{RIMP2}}|<20$ microhartrees.

(3) Identical contraction patterns for auxiliary basis sets for atoms with identical basis-set contraction patterns.

The aug-cc-pVXZ/aug-cc-pV($X+d$)Z auxiliary basis set were obtained by adding a set of additional diffuse functions to the optimized cc-pVXZ/cc-pV($X+d$)Z auxiliary basis sets. Exploratory calculations showed that this is necessary in order to achieve similar accuracy for both basis sets. The additional functions were optimized at the anions. Though for dihydrogen, nitrogen, and the rare gases the additional electron is unbound, these artificial systems proved to be well-suited for optimization of the diffuse auxiliary basis functions. The final auxiliary basis-set contraction schemes are listed in Table V.

B. Accuracy of the RI approximation

RI MP2 correlation energies were calculated for the 95 molecules listed in Table I, using the auxiliary basis optimized in Sec. III A for the correlation consistent basis sets. The auxiliary basis sets for SVP, TZVP, and TZVPP are taken from Ref. 9. The frozen core approximation was applied for all inner shell orbitals as described in Sec. II. From these energies we determined the RI errors $\Delta^{\mathrm{RI}}=(E_X^{\mathrm{corr}}-E_X^{\mathrm{corr,RI}})/|E_{\mathrm{limit}}^{\mathrm{corr}}|\times 100\%$. The resulting statistical quantities are shown in Table VI. Similar, the RI-MP2 dipole moments were calculated for the subset of 44 molecules (cf. above). The relative errors, obtained as $\Delta_\mu^{\mathrm{RI}}=(\mu_X^{\mathrm{corr}}-\mu_X^{\mathrm{corr,RI}})/|\mu_{\mathrm{limit}}^{\mathrm{corr}}|\times 100\%$, are displayed in Table VII.

Comparing these results with the requirements worked out in Sec. II, one observes that in all cases the standard deviation of the correlation energy $\Delta_{\mathrm{std}}^{\mathrm{RI}}$ and the maximum errors $\Delta_{\mathrm{max}}^{\mathrm{RI}}$ are more than two orders of magnitude smaller than the corresponding basis-set errors Δ_{std} and Δ_{max} (cf. Table II) and thus are negligible. For the dipole moment the results are encouraging as well: The RI error is in all cases one order of magnitude smaller than the expected basis set error (cf. Table IV).

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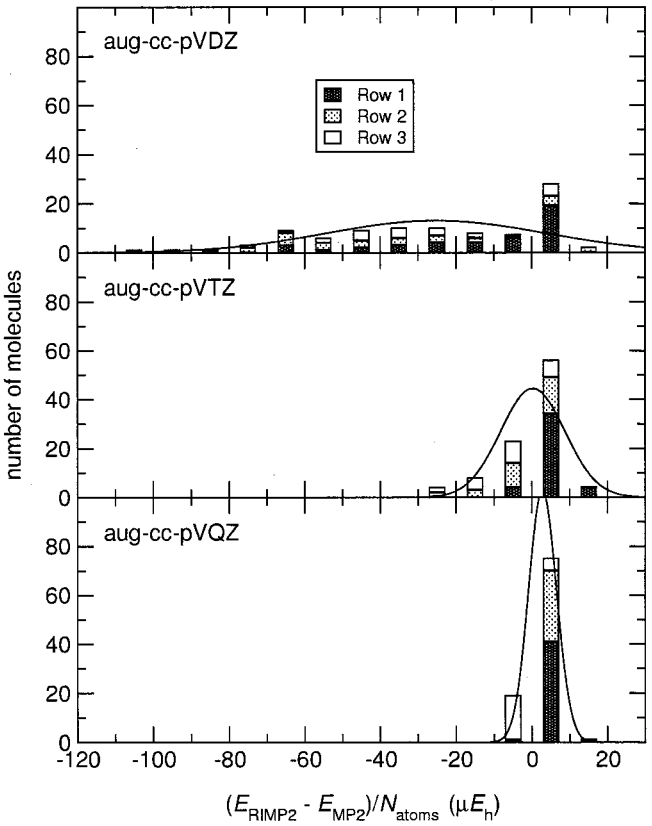


FIG. 3. Histogram of RI errors per atom in the RI-MP2 correlation energy obtained with aug-cc-pVXZ basis sets and the corresponding auxiliary basis sets. The curve corresponds to the normal distribution with the parameters from Table IX.

Moreover we determined the RI errors per atom in the MP2 energy. The results are summarized in Tables VIII and IX, a graphical representation is displayed in Figs. 2 and 3.

The RI error per atom in calculations with (aug-)cc-pVXZ basis sets decreases with increasing basis set cardinal number X, despite for all basis sets we used the same criteria for the accuracy at the atom. Compared to typical energy changes of some millihartrees when changing basis sets these errors are very small (cf. the limits worked out in Section II A). We further note that the auxiliary basis sets for the (aug-)cc-pV($X+d$)Z basis set yield nearly the same accuracy when used in connection with the (aug-)cc-pVXZ basis sets.

C. Efficiency

In Fig. 4 we plotted the computation times of the RI MP2 module versus those of the MPGRAD module for several comparatively larger systems using cc-pVXZ/cc-pV($X+d$)Z (X=D,T,Q) basis sets (and corresponding auxiliary basis sets). In all calculations the available core memory was limited to 400 Mbytes and the disk space to 2 Gbytes. It becomes apparent that the RI approximation is already efficient for small cases. The typical time gain for medium-sized molecules like H_3PO_4 with a double-ζ basis is a factor of 8–10. For larger basis sets the factor increases rapidly; for $B_3N_3H_6$/cc-pVQZ an acceleration factor of 170 is observed.

IV. CONCLUSIONS

For a test set of 95 molecules the complete basis set limits of the MP2 valence correlation energies have been

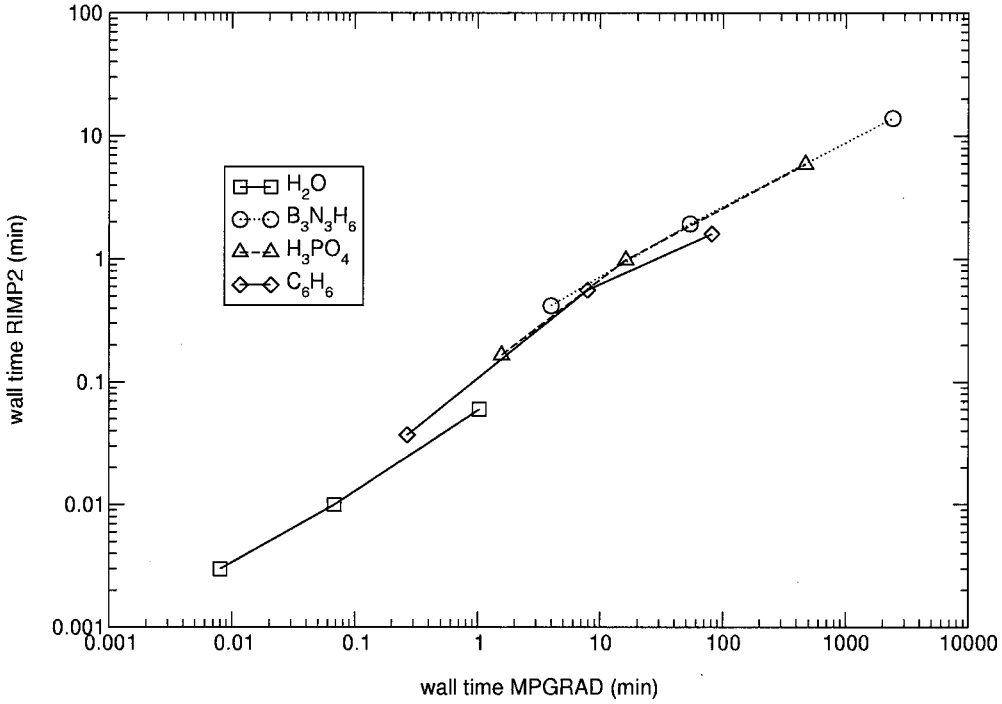


FIG. 4. CPU times of RI-MP2 vs conventional MP2 on an Intel-PIII/600 MHz PC (core memory limit 400 Mbytes, disk space limit 2 Gbytes). The three points per molecule correspond to different cc-pVXZ [or cc-pV($X+d$)Z, respectively] basis sets with X=D, T, Q. The computational point group was C_1, except for benzene, where full D_{6h} symmetry was exploited.

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estimated using the two-parameter power form proposed by Helgaker *et al.*[13] Comparison of the estimated limits with results obtained in standard basis sets shows that for first- and second-row elements the remaining average errors in the MP2 correlation energy for the cc-pVXZ basis sets are $-32\pm4\%$, $-12\pm2\%$, $-5\pm1\%$, and $-3\pm0.4\%$, for $X=$D, T, Q, and 5, respectively. For the recently published cc-pV$(X+d)$Z basis sets the errors are quite similar to those for the cc-pVXZ basis sets, and for the TURBOMOLE basis sets the average errors are $-32\pm4\%$ (SVP) and $-13\pm4\%$ (TZVPP). For molecules containing third-row elements the errors are considerable larger, in particular for the cc-pVXZ basis sets: $-60\pm10\%$ (cc-pVDZ), $-40\pm3\%$ (SVP), $-35\pm10\%$ (cc-pVTZ), $-25\pm6\%$ (TZVPP), $-20\pm7\%$ (cc-pVQZ), and $-4\pm0.6\%$ (cc-pV5Z). In a similar study the MP2 correlation contribution to dipole moments was calculated for a subset of 44 molecules using the aug-cc-pVXZ and aug-cc-pV$(X+d)$Z basis sets with $X=$D, T, and Q. For a smaller subset of 17 molecules the MP2 dipole moments were also evaluated in the aug-cc-pV5Z basis sets. The results for the latter subset show that the two-parameter power form, suggested recently by Halkier *et al.*[20] for extrapolating the complete basis-set limit of the correlation contribution to dipole moments, performs excellently for first- and second-row elements. For third-row elements large remaining basis-set errors make the reliability of the extrapolation doubtful. The remaining basis-set errors in the MP2 contribution to the dipole moment were found for molecules with first- and second-row elements to be $10\pm31\%$ (aug-cc-pVDZ), $8\pm15\%$ (aug-cc-pVTZ), and $3\pm6\%$ (aug-cc-pVQZ). For molecules containing third-row elements the errors are as large as $1\pm150\%$ (aug-cc-pVDZ), $-10\pm111\%$ (aug-cc-pVTZ), and $-4\pm47\%$ (aug-cc-pVQZ).

For the cc-pVXZ, cc-pV$(X+d)$Z, aug-cc-pVXZ, and aug-cc-pV$(X+d)$Z basis-set series auxiliary basis sets for use in resolution of the identity MP2 and CC2 calculations were optimized for $X=$D, T, and Q for all elements for which the one-electron basis sets are available. It has been demonstrated that with these auxiliary basis sets the additional errors introduced by the resolution of the identity approximation are basically insignificant. For the MP2 correlation energies the errors are about two orders of magnitude smaller than the one-electron basis sets error, and for the MP2 contributions to dipole moments the errors are about one order of magnitude smaller than the respective one-electron basis-set errors. The factor by which the RI approximation reduces the CPU demands for MP2 and CC2 calculations increases rapidly with the size of the one-electron basis sets. For the cc-pVQZ basis sets acceleration factors up to 170 are observed.

V. AVAILABILITY

The optimized auxiliary basis sets for the cc-pVXZ and aug-cc-pVXZ series with $X=$D, T, and Q reported in the present work as well as the auxiliary basis set reported in Ref. 9 are available[19] by ftp or on request from the authors.

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