

JCTC

Journal of Chemical Theory and Computation

***Ab Initio* Density Fitting: Accuracy Assessment of Auxiliary Basis Sets from Cholesky Decompositions**

Jonas Boström,[†] Francesco Aquilante,[‡] Thomas Bondo Pedersen,[†] and Roland Lindh^{*,†}

Department of Theoretical Chemistry, Chemical Center, University of Lund, P.O. Box 124 S-221 00 Lund, Sweden, and Department of Physical Chemistry, Sciences II, University of Geneva, Quai E. Ansermet 30, 1211 Geneva 4, Switzerland

Received January 15, 2009

Abstract: The accuracy of auxiliary basis sets derived by Cholesky decompositions of the electron repulsion integrals is assessed in a series of benchmarks on total ground state energies and dipole moments of a large test set of molecules. The test set includes molecules composed of atoms from the first three rows of the periodic table as well as transition metals. The accuracy of the auxiliary basis sets are tested for the 6-31G**, correlation consistent, and atomic natural orbital basis sets at the Hartree–Fock, density functional theory, and second-order Møller–Plesset levels of theory. By decreasing the decomposition threshold, a hierarchy of auxiliary basis sets is obtained with accuracies ranging from that of standard auxiliary basis sets to that of conventional integral treatments.

1. Introduction

The density fitting (DF) or resolution-of-the-identity (RI) approximation¹ is an efficient approach for speeding up quantum chemical calculations. Gaussian auxiliary basis sets for the fitting procedure have been optimized and extensively tested with respect to the accuracy of ground state energies for Hartree–Fock (HF) theory, nonhybrid as well as hybrid density functional theory (DFT), and second-order Møller–Plesset (MP2) theory.^{2–11} The goals of the optimizations were to keep errors due to the DF approximation below the inherent basis set incompleteness error for each theoretical model, while limiting the number of auxiliary functions to a few times the number of atomic orbital (AO) basis functions.

Aiming at an accurate approximation of each individual integral, we have recently proposed generating auxiliary basis sets by Cholesky decomposition (CD) of the two-electron integral matrix in AO basis. The construction of the auxiliary basis set thus becomes a purely numerical procedure carried out on-the-fly. In the Full-CD approach the entire molecular integral matrix is decomposed, and the resulting auxiliary basis set consists of both one- and two-center functions.^{12,13} The one-center CD (1C-CD) approximation is obtained by

restricting the decomposition of the molecular integrals such that only one-center functions enter the auxiliary basis set.¹⁴ To reduce the computational cost of obtaining the auxiliary basis set, the atomic CD (aCD) set is obtained by a decomposition of the atomic integral matrix.¹⁴ The atomic compact CD (acCD) auxiliary basis set is obtained from the aCD by removing linear dependence among the primitive Gaussians, again by CD.¹⁵ We thus have available a hierarchy of *ab initio* DF approximations with an accuracy controlled by a single parameter, the CD threshold (τ). The adjective *ab initio* underlines the fact that no additional information is needed to perform a DF calculation with CD-based auxiliary basis sets compared to the corresponding conventional calculation. The CD-based auxiliary basis sets were tested for a limited number of mostly organic molecules in the papers cited above, and it is the purpose of the present work to provide a more thorough assessment of accuracy of total ground state energies and dipole moments.

Using the Coulomb metric, the DF procedure minimizes the integral diagonal error

$$\Delta_{\mu\nu,\mu\nu} = (\mu\nu|\mu\nu) - \sum_{IK} C_{\mu\nu}^I (IK) C_{\mu\nu}^K \quad (1)$$

to the extent possible with a given auxiliary basis set (C indicates the fitting coefficients and I, K the auxiliary functions). The CD-based auxiliary basis sets are constructed to

* Corresponding author e-mail: roland.lindh@teokem.lu.se.

[†] University of Lund.

[‡] University of Geneva.

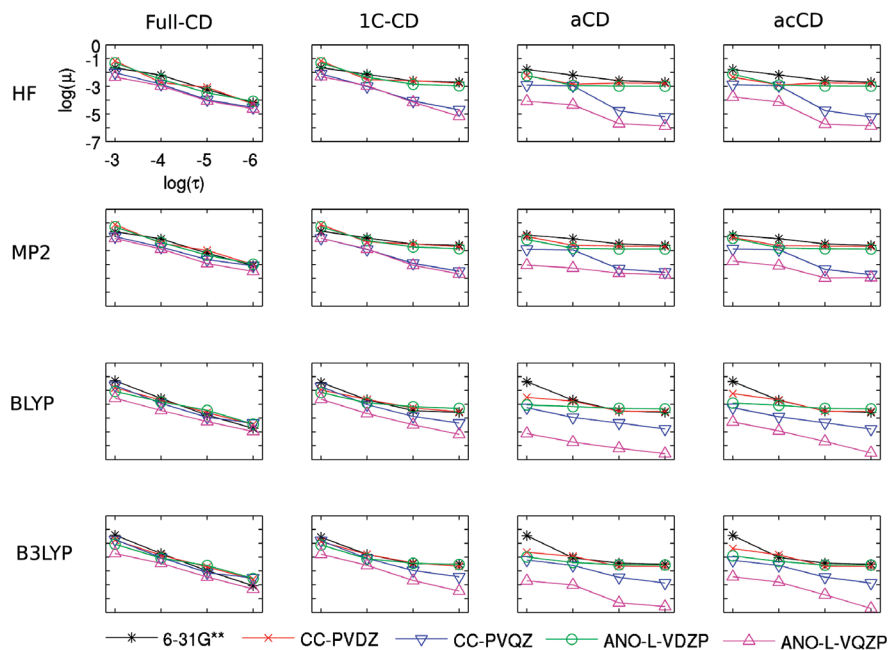


Figure 1. The mean absolute total energy errors in kcal/(mol·electron) as a function of the decomposition threshold, τ , for Set I. Each row of panels shows a specific quantum chemical method (HF, MP2, DFT/BLYP, and DFT/B3LYP), and each column of panels shows a specific CD-based auxiliary basis set (Full-CD, 1C-CD, aCD, and acCD).

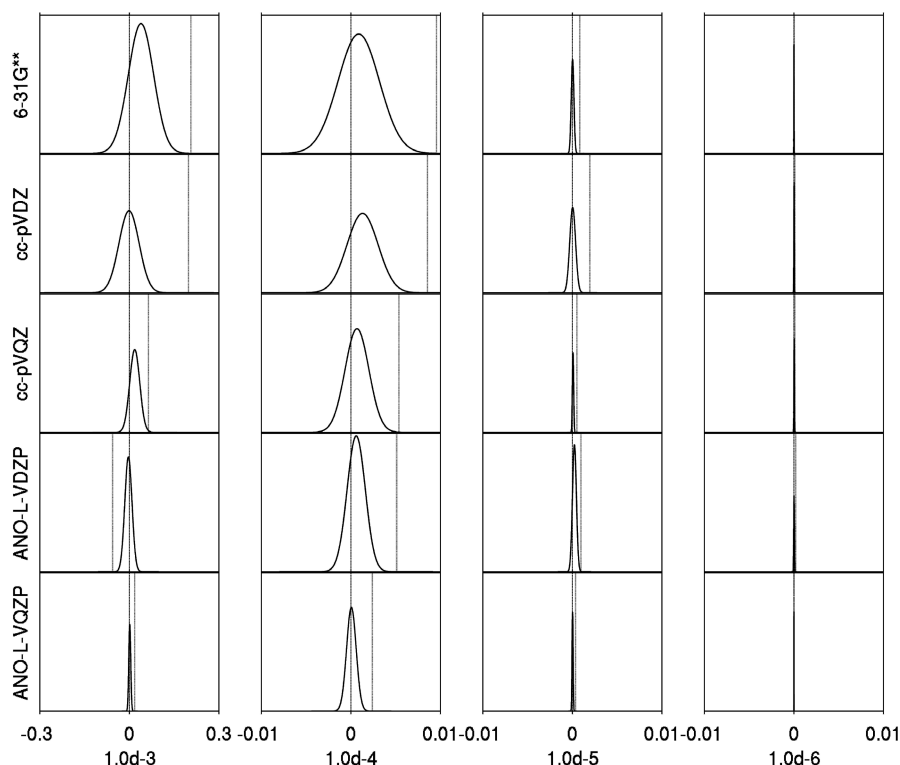


Figure 2. The mean error and standard deviation in kcal/(mol·electron) for the Full-CD DFT/B3LYP total energy calculations of Set I represented as Gaussian distributions. The dotted line represents the largest observed error. Each row of panels features a specific AO basis set, and each column of panels corresponds to a specific decomposition threshold. The scale of the ordinate is arbitrary. Note that for better visualization, the scale of the abscissa of the left most column is different than for the rest of the columns in the figure.

make the minimum value approach zero as τ is decreased. The error matrix Δ is positive semidefinite and hence

$$|\Delta_{\mu\nu,\lambda\sigma}| \leq \Delta_{\mu\nu,\mu\nu}^{1/2} \Delta_{\lambda\sigma,\lambda\sigma}^{1/2} \quad (2)$$

Full-CD guarantees that every element of the error matrix Δ is bound by τ and therefore provides complete control of the accuracy of the DF approximation.^{12–14} For the one-center approximations (1C-CD, aCD, acCD), the integral

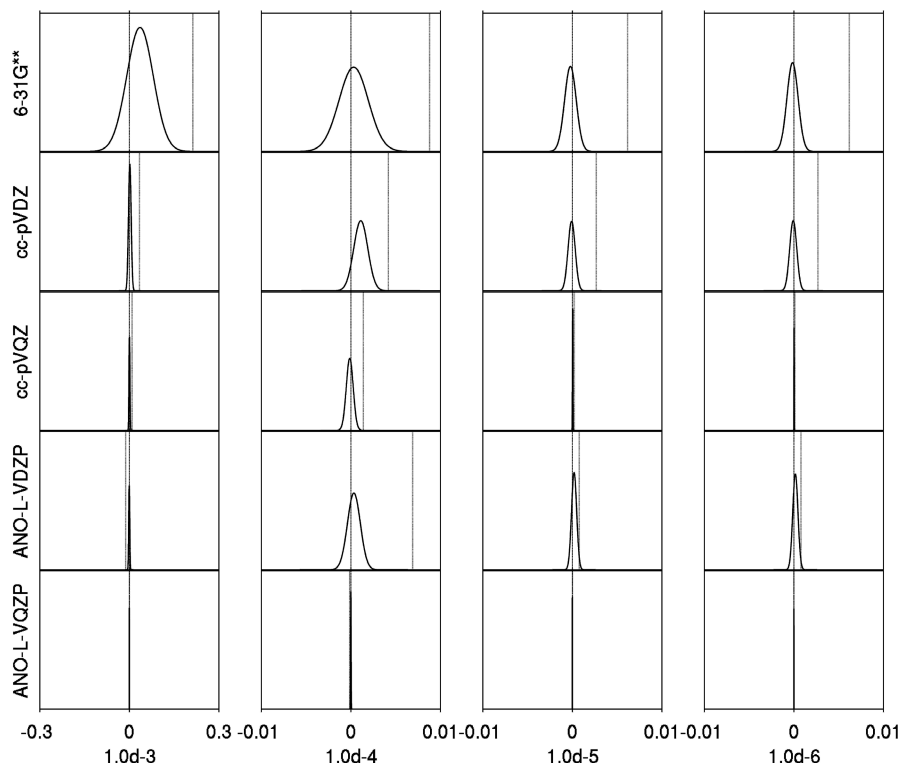


Figure 3. The mean error and standard deviation in kcal/(mol·electron) of the aCD DFT/B3LYP total energy calculations of Set I represented as Gaussian distributions. The dotted line represents the largest observed error. The scale of the ordinate is arbitrary. Each row of panels features a specific basis set, and each column of panels corresponds to a specific decomposition threshold. Note that for better visualization, the scale of the abscissa of the left most column is different than for the rest of the columns in the figure.

errors in the DF approximation to the ERIs of the type $(AA|BB)$, where A and B are atom labels, are bound by τ , whereas integrals of the type $(AB|**)$ may be affected by larger errors. The accuracy of the DF procedure with the one-center approximations is therefore limited by the ability to span these two-center functions: although the error is always minimized by the fitting procedure, it can no longer be guaranteed that the minimum value is τ .^{14,15}

Here, we perform the first statistical analysis of the accuracy of the hierarchy of CD-based auxiliary basis sets: Full-CD, 1C-CD, aCD, and acCD, as a function of τ . This analysis is performed for the single configuration methods HF, pure (BLYP) and hybrid (B3LYP) DFT, and MP2 in conjunction with common segmented and generally contracted basis sets ranging from double- to quadruple- ζ levels of sophistication. We use a large test suite of molecules composed of atoms from the first three rows of the periodic table and a small set including transition metals. A similar investigation on CASSCF and CASPT2 excitation energies with CD-based auxiliary basis sets is in progress at our lab.

2. Computational Details

The purpose of this study is to test how the accuracy depends on the decomposition threshold in Full-CD,¹³ 1C-CD,¹⁴ aCD,¹⁴ and acCD¹⁵ for different theoretical models and AO basis sets. For the purpose of generality, the wave function models included in this study describe both Coulomb and exchange contributions and short-range correlation and

dispersion. The basis set selection is representative of the wide range of AO basis sets available to computational chemists at present. Three different test sets are used in this benchmark study.

First, calculations have been performed for a large set of molecules (Set I) using four different quantum chemical methods, HF, pure and hybrid DFT, and MP2. Two functionals are used, one nonhybrid, BLYP,^{16–18} and one hybrid, B3LYP.^{17–19} The AO basis sets used in these calculations are Pople's 6-31G**,^{20,21} Dunning's cc-pVXZ^{22,23} ($X = D, Q$), and the ANO-L-VXZP ($X = D, Q$) basis sets of Widmark et al.^{24,25} The values 10^{-3} , 10^{-4} , 10^{-5} , and 10^{-6} have been chosen for the Cholesky threshold. Set I is the 118 closed-shell molecules of the G2/97 test set.²⁶ For six of the molecules in the set we have replaced the conventional MP2 calculation with a Full-CD calculation where we have set the CD threshold to 10^{-10} .²⁷ For Set I, the accuracy of the HF and DFT dipole moments has also been investigated.

Second, since the molecules in Set I only include elements from the first three rows in the periodic table, a smaller set of molecules containing heavier elements is used. Specifically, Set II is composed of the seven closed-shell transition metal containing molecules of the MLBE21/05 database.²⁸ The accuracy assessment in association with Set II is limited to the DFT(B3LYP) model. These calculations include scalar relativistic effects through the Douglas-Kroll-Hess transformation^{29–34} in conjunction with the relativistic ANO-RCC-VXZP ($X = D, T$) basis sets of Roos and co-workers.^{35–37}

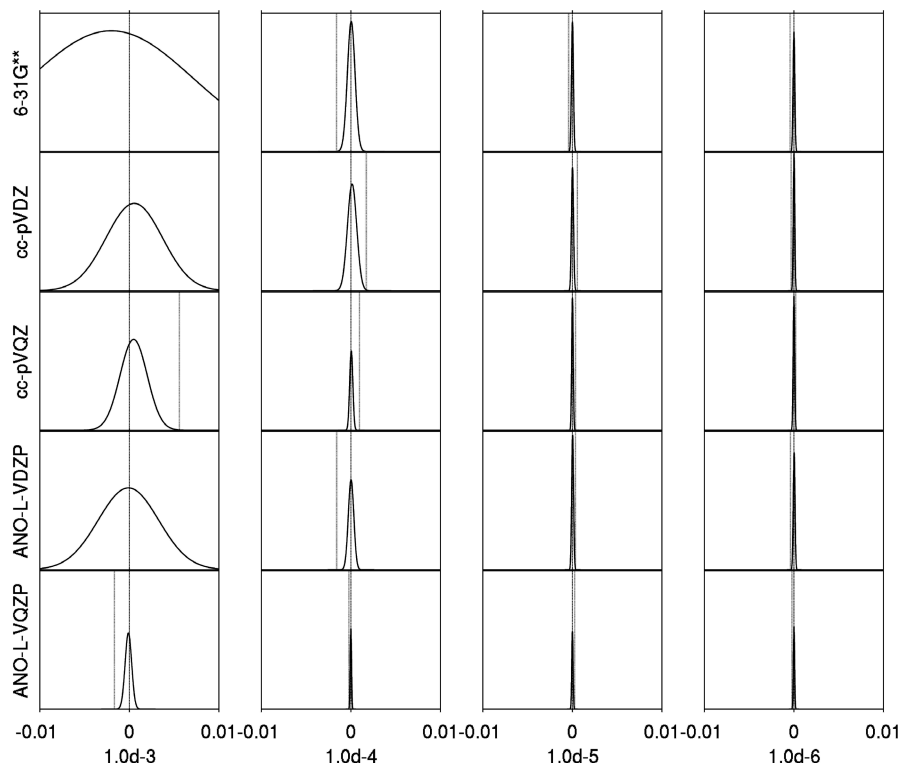


Figure 4. The mean error and standard deviation in debye of the Full-CD DFT/B3LYP dipole moment calculations of Set I represented as Gaussian distributions. The scale of the ordinate is arbitrary. The dotted line represents the largest observed error. Each row of panels features a specific AO basis set, and each column of panels corresponds to a specific decomposition threshold.

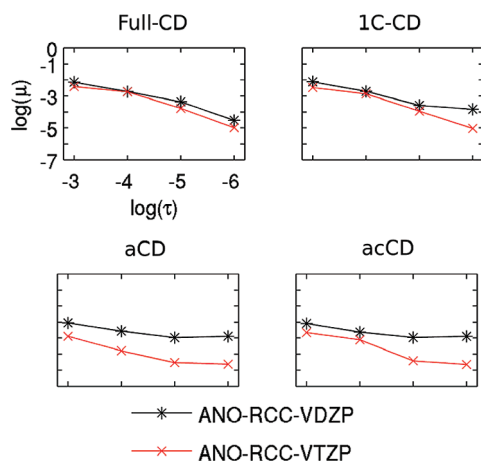


Figure 5. The mean absolute total energy errors (kcal/(mol·electron)) as a function of the value of the decomposition threshold of Set II. Each row of panels shows a specific quantum chemical method, and each column of panels shows a specific CD-based auxiliary basis set.

Third, the possibility to *ad hoc* discard the higher angular momentum auxiliary functions in association with the aCD approach is tested on a set of 24 molecules, Set III.³⁸ This option is considered for the 6-31G**, ANO-L-VXZP, and cc-pVXZ (X = D,T,Q) basis sets.

To measure the accuracy of the CD-based auxiliary basis sets, the error in the total energy for each molecule is computed as

$$\varepsilon_i = \frac{E_i^{\text{conv}} - E_i^{\text{CD}}}{N_i^{\text{electrons}}} \quad (3)$$

where E_i^{conv} and E_i^{CD} are the conventional and CD-based total ground state energy, respectively, and $N_i^{\text{electrons}}$ is the number of electrons of molecule i . For the accuracy of the magnitude of the dipole moments, the same expression was used without a normalization against the number of electrons, as the dipole moment is a size-intensive quantity. When we present statistics on dipole moments we have also omitted every molecule with inversion symmetry since they must have zero dipole moment. The associated mean error

$$\mu_\varepsilon = \sum_i^N \frac{\varepsilon_i}{N} \quad (4)$$

mean absolute error

$$\mu_{|\varepsilon|} = \sum_i^N \frac{|\varepsilon_i|}{N} \quad (5)$$

standard deviation

$$\sigma_\varepsilon^2 = \frac{\sum_i^N \varepsilon_i - \mu_\varepsilon}{N - 1} \quad (6)$$

and maximum error (with sign), ε_{max} , were calculated.

All calculations have been performed using a development version of the MOLCAS quantum chemistry software.³⁹

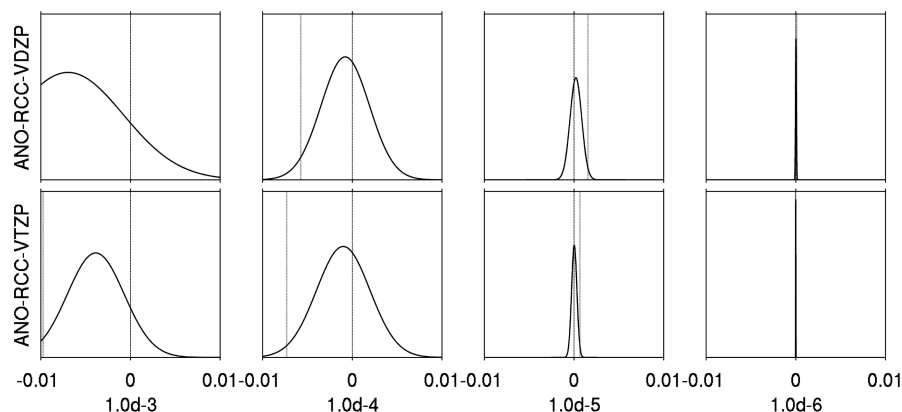


Figure 6. The mean error and standard deviation (kcal/(mol·electrons)) of the Full-CD DFT/B3LYP total energy calculations of Set II represented as Gaussian distributions. The scale of the ordinate is arbitrary. The dotted line represents the largest error in that set of molecules. Each row of panels features a specific AO basis set, and each column of panels corresponds to a specific decomposition threshold.

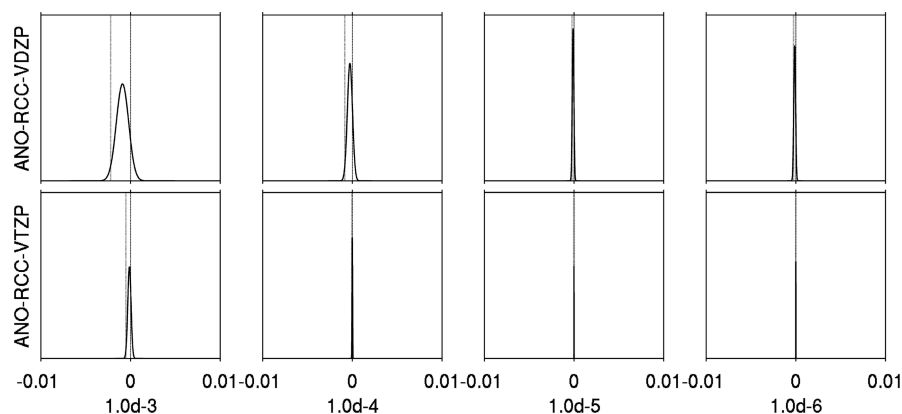


Figure 7. The mean error and standard deviation (kcal/(mol·electrons)) of the aCD DFT/B3LYP total energy calculations of Set II represented as Gaussian distributions. The scale of the ordinate is arbitrary. The dotted line represent the largest error in that set of molecules. Each row of panels features a specific AO basis set, and each column of panels a corresponds to a specific decomposition threshold.

3. Results and Discussion

In this section the results of the calculations will be visualized, and important trends and their implications for these types of calculations will be discussed. The analysis is divided into several subsections where different aspects of the results are discussed. Detailed tables of data can be found in the Supporting Information.

3.1. Independence of Theoretical Model. In Figure 1 the mean absolute errors for Set I of the studied auxiliary basis sets for various theoretical models are displayed as functions of the decomposition threshold. From Figure 1 we can conclude that the accuracy

- improves with tighter threshold,
- levels out for the one-center auxiliary basis sets (1C-CD, aCD, and acCD) for tighter thresholds, and
- is largely the same regardless of the theoretical model with a given AO basis set.

The last point confirms the assertion of our previous papers,^{14,15} namely that the CD-based basis sets are unbiased. Finally, we note that the aCD and acCD accuracies are very close to each other, as expected.¹⁵

While the error of the Full-CD is almost linear with respect to the CD threshold (logarithmic scale), a saturation effect

is observed for the one-center auxiliary basis sets. This difference is more pronounced for AO basis sets of lower quality, i.e. the double- ζ sets, for which essentially no improvement is observed for decomposition thresholds below 10^{-4} . For the quadruple- ζ basis sets, however, thresholds as low as 10^{-6} may be used with a significant gain in accuracy. The reason for this difference is that representing two-center AO products and therefore ERIs of the type $(AB|^{**})$ with very high accuracy places demands on the quality of the auxiliary basis set. Higher angular momentum functions are generally included in the auxiliary basis set for the quadruple- ζ AO sets than for the double- ζ ones, thus increasing accuracy of the representation of the two-center AO products. We also note that the auxiliary basis sets of the ANO-L sets tend to be more accurate than those generated from 6-31G** or Dunning's correlation consistent sets.

The observation that aCD and acCD auxiliary basis sets derived from quadruple- ζ AO basis sets are more accurate than those derived from double- ζ ones indicates that further reductions of auxiliary basis set size might be possible with a controlled loss of accuracy. This aspect will be explored below.

Table 1. Average Ratio of Auxiliary to AO Basis Functions for Each CD Method for Set I

basis set	τ	Full-CD	1C-CD	aCD/acCD
6-31G**:	10^{-3}	3.6	3.4	3.7
	10^{-4}	4.9	4.1	4.2
	10^{-5}	6.3	4.4	4.5
	10^{-6}	8.0	5.0	5.0
cc-pVDZ:	10^{-3}	3.3	3.3	4.0
	10^{-4}	4.8	4.3	4.3
	10^{-5}	6.2	4.6	4.6
	10^{-6}	7.6	5.0	5.0
cc-pVQZ:	10^{-3}	3.8	3.8	7.0
	10^{-4}	4.6	4.6	7.3
	10^{-5}	5.7	5.5	8.1
	10^{-6}	7.2	6.5	9.1
ANO-L-VDZP:	10^{-3}	3.5	3.5	5.0
	10^{-4}	4.5	4.1	5.1
	10^{-5}	5.6	4.5	5.3
	10^{-6}	7.2	5.1	5.4
ANO-L-VQZP:	10^{-3}	3.7	3.7	8.1
	10^{-4}	4.7	4.6	8.4
	10^{-5}	6.0	5.8	9.3
	10^{-6}	7.5	6.9	10.6

3.2. Quantitative Error Analysis. In this section a more quantitative analysis of the accuracy of the energy and the magnitude of the dipole moment for Set I will be performed. For that purpose, let the standard of Eichkorn et al.² be the reference. In their work they derived Coulomb fitting auxiliary basis sets associated with SVP valence basis sets (a double- ζ quality basis set) aiming at an average error of 0.2 mE_H per atom. For practical purposes this can be

translated to an average error of around 0.01 kcal/(mol•electron). Moreover, an error of 0.01 debye is an acceptable level of accuracy for the computed magnitude of the dipole moment. We will in this section limit our presentation to cases which are representative and required to demonstrate the observed properties of the CD-based auxiliary basis sets. In particular, the trends of the one-center type CD auxiliary basis sets are close to identical, and only one representative, aCD, will be used to clarify the general trends and quantify average and maximum errors.

First, in Figure 2 the results from a Full-CD using DFT/B3LYP are visualized. A tighter threshold yields reduced mean and maximum errors and reduced error spread. It is clear that the three right most columns of the panels represent an average error substantially better than the norm of Eichkorn et al.² The left-most column (note the different scale of the abscissa) represents results on par or better than this norm. For the different AO basis sets we only note a significant difference in accuracy for the largest thresholds. From these results, we conclude that a CD threshold of 10^{-3} in association with Full-CD can be used but that a prudent user may wish to adopt a threshold one order of magnitude tighter.

Second, in Figure 3 the aCD auxiliary basis set accuracy for DFT/B3LYP is visualized. We observe that no significant improvement is achieved for thresholds below 10^{-5} , regardless of basis set. For high-quality AO basis sets, however, a substantially better accuracy is observed compared to lower-quality AO sets at the same decomposition threshold. Comparing to the Full-CD results of Figure 2, we see that the maximum error is a bit larger for aCD. We also note

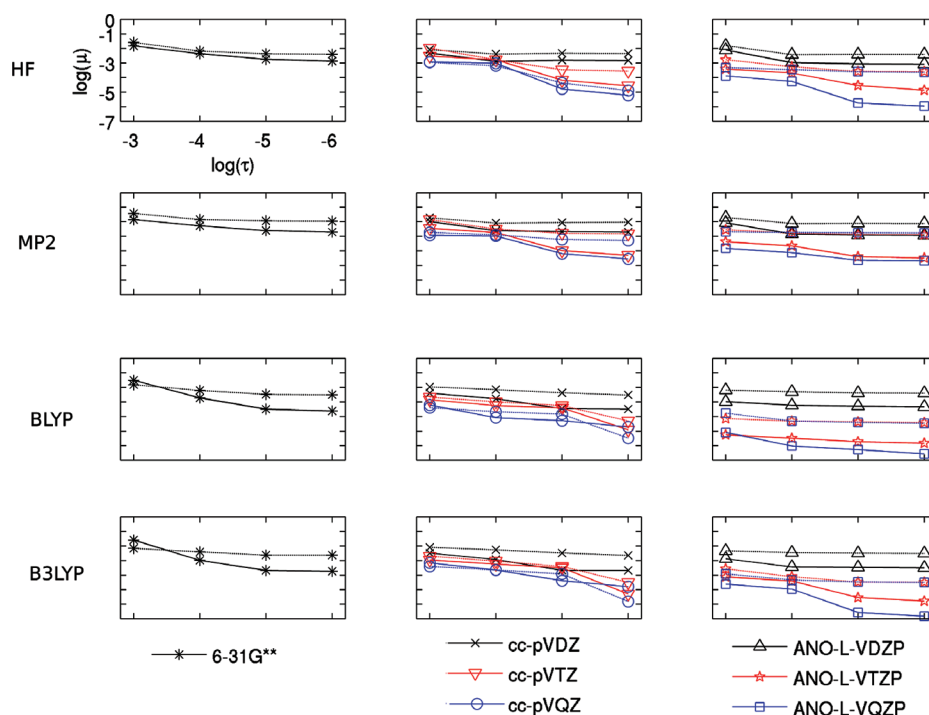


Figure 8. The aCD mean absolute energy errors (kcal/(mol•electron)) as a function of the decomposition threshold for Set III. Each row of panels shows a specific quantum chemical method. Solid lines show the results if all angular momentum components of the auxiliary basis set are included and dashed lines if some are ignored, as described in the text.

Table 2. Average Ratio of Auxiliary to AO Basis Functions for Set III When the Full Parent Product or the Reduced Product Space Is Used to Derive the aCD Based Auxiliary Basis Set

basis set	τ	full	reduced
6-31G**:	10^{-3}	3.7	3.0
	10^{-4}	4.1	3.2
	10^{-5}	4.3	3.5
	10^{-6}	4.8	4.0
cc-pVDZ:	10^{-3}	3.9	2.9
	10^{-4}	4.2	3.3
	10^{-5}	4.5	3.7
	10^{-6}	4.8	3.9
cc-pVTZ:	10^{-3}	5.4	3.1
	10^{-4}	5.5	3.7
	10^{-5}	6.1	4.4
	10^{-6}	6.6	5.1
cc-pVQZ:	10^{-3}	6.8	4.0
	10^{-4}	7.1	4.6
	10^{-5}	8.0	4.9
	10^{-6}	8.9	5.3
ANO-L-VDZP:	10^{-3}	4.8	3.7
	10^{-4}	4.9	3.8
	10^{-5}	5.0	3.9
	10^{-6}	5.2	4.1
ANO-L-VTZP:	10^{-3}	7.1	4.9
	10^{-4}	7.5	5.5
	10^{-5}	7.8	5.8
	10^{-6}	8.3	6.4
ANO-L-VQZP:	10^{-3}	7.8	4.9
	10^{-4}	8.1	5.2
	10^{-5}	9.1	5.7
	10^{-6}	10.1	6.6

that for the larger thresholds, the error spread is more narrow for aCD than for Full-CD.

To conclude this section, Figure 4 shows a representation of the statistics for calculations of the magnitude of the dipole moments with Full-CD at the DFT/B3LYP level of theory. Clearly, for a threshold of 10^{-4} or below an accuracy up to the standard is achieved.

3.3. Assessment for Small Transition Metal Complexes.

The purpose of the calculations on Set II is to establish that the CD-based auxiliary basis sets are valid for a wider range of atoms than those represented in Set I. This section will therefore feature the same analysis as above with the purpose of demonstrating that the important features hold also for auxiliary basis sets generated from all-electron basis sets of heavy elements. Results on the magnitude of the dipole moments are collected in the Supporting Information. Figure 5 shows the mean absolute error versus the decomposition threshold.

Again, an almost linear function (logarithmic scale) is observed for Full-CD, while a saturation effect is observed for the one-center type CD-based auxiliary basis sets. The aCD and acCD accuracies are for all practical purposes identical. All of these features are the same as for the assessments of Set I, and it can be concluded that the CD-based auxiliary basis sets can be employed in DF

approximations on systems with heavy elements without any loss of relative accuracy as compared to lighter elements.

From the Gaussian error distributions in Figure 6 (Full-CD, DFT/B3LYP) and Figure 7 (aCD, DFT/B3LYP) we see that the errors fall within the required norm for thresholds of 10^{-4} or tighter. In the aCD case, thresholds as high as 10^{-3} might still be practical. The results are a strong indication that the CD-based auxiliary basis sets are indeed general and can be used both for transition metals and in combination with a scalar relativistic Hamiltonian. It is reasonable to expect that this conclusion holds for any element of the periodic table.

3.4. Auxiliary Basis Set Size. It was noted above that for the highest-quality AO basis sets the DF error is smaller than one might expect from the value of the CD threshold. On the other hand, for aCDs and acCDs this can also be viewed as a downside of the approach: the aCD (or acCD) procedure generates far too many auxiliary basis functions. For efficiency purposes it is therefore mandatory to investigate the possibility of reducing the size of the aCD and acCD auxiliary basis sets.

A way to measure the efficiency of an auxiliary basis set is to look at the ratio between the number of auxiliary and AO basis functions. Eichkorn et al.² have in this context established that a ratio of 3 or smaller should be achievable in association with double- ζ quality basis sets. A somewhat larger ratio was established for auxiliary basis sets optimized for triple- ζ quality AO basis sets.⁴ These standards are adopted here, too. However, it should be noted that while the procedure of Eichkorn et al.² yields an auxiliary basis set specifically designed for the DF approximation of the Coulomb potential in DFT, the aCD and acCD auxiliary basis sets are unbiased toward any quantum chemical method, as they correctly describe the AO ERIs within a certain accuracy. Hence, it should not come as a surprise that the corresponding CD-based auxiliary basis sets are somewhat larger than the standard ones. In Table 1 auxiliary to AO basis function ratios of Set I are shown for the different CD approaches.

As expected, the ratio for CD-based auxiliary basis sets with a threshold of 10^{-4} is about one-third larger than the standard achieved by Eichkorn et al. However, for the higher quality AO basis sets a substantially higher ratio is observed. These differences can be rationalized as follows. For elements of the first and second row of the periodic table, Eichkorn et al.² *ad hoc* eliminate the g-functions from the auxiliary basis set. This choice is based upon the knowledge of the typical structure of the density or equivalent matrices which combine with the ERIs in quantum chemical models. Obviously, the CD procedures do not have access to this information and only use the elimination of numerical linear dependence to define the size of the auxiliary basis set.

Inspired by the procedure of Eichkorn et al.,² we did as follows. For double-, triple-, and quadruple- ζ AO basis sets the full set of AO product functions was reduced before the aCD procedure by eliminating the g-functions, the h- and i-functions, and the i-, k-, and l-functions, respectively. The

accuracies of these reduced auxiliary basis sets as compared with auxiliary basis sets derived from the full product space of Set III are exhibited in Figure 8.

The accuracy for higher thresholds is somewhat reduced but still seems to lie within reasonable limits for a decomposition threshold of 10^{-4} , but we notice that the convergence is lost for tighter CD thresholds. Hence, the procedure should only be recommended for high threshold calculations - achieving higher accuracy is associated with a price to pay in the form of a larger auxiliary basis set. It can be seen from Table 2 that when the accuracy of the calculation permits the CD-based auxiliary basis set to be reduced, the ratios of auxiliary to AO basis functions are in parity with those of Eichkorn et al.² This is indeed remarkable considering that the CD-based auxiliary basis sets are nonmethod specific. However, it should still be noted that even the smallest CD-based sets, the acCD auxiliary basis sets, are larger than the standard auxiliary basis sets in terms of the number of primitive basis functions. Again, this is the price for having a nonmethod specific auxiliary basis set.

4. Summary

The accuracy of the Full-CD, 1C-CD, aCD, and acCD auxiliary basis sets has been investigated with respect to the CD threshold. The tests have been performed on a large array of molecules containing elements from the first three rows of the periodic table and transition metals. The analysis is based on the error in the total ground state energy and the magnitude of the dipole moment. It is confirmed that the CD approximations are unbiased and form a hierarchy of approximations going from an accuracy of standard auxiliary basis sets to that of a conventional two-electron integral treatment. It is also demonstrated that the CD approach to auxiliary basis set generation is most accurate with AO basis sets of high quality. The investigation shows that a CD threshold of 10^{-4} is a reasonable standard corresponding to an absolute error of less than 0.01 kcal/(mol·electron), although a CD threshold of 10^{-3} can in some cases produce results with an acceptable accuracy. The CD-based auxiliary basis sets are more computationally demanding than preoptimized sets, as they contain more auxiliary functions. This is the price to pay for an unbiased auxiliary basis set.

Acknowledgment. Funding from the Swiss National Science Foundation (SNF), the Swedish Research Council (VR), and the Linnaeus Project "Organizing Molecular Matter" at Lund University is gratefully acknowledged.

Supporting Information Available: Tables containing energy and dipole moment mean errors, mean absolute errors, standard deviation, and max errors according to eqs 4, 5, and 6 for Set I and Set II. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Vahtras, O.; Almlöf, J.; Feyereisen, M. *Chem. Phys. Lett.* **1993**, *213*, 514–518.
- (2) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283–289.
- (3) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652–660.
- (4) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acc.* **1997**, *97*, 119–124.
- (5) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143–152.
- (6) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175–3183.
- (7) Weigend, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285–4291.
- (8) Hättig, C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59–66.
- (9) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
- (10) Hellweg, A.; Hättig, C.; Höfener, S.; Klopper, W. *Theor. Chem. Acc.* **2007**, *117*, 587–597.
- (11) Weigend, F. *J. Comput. Chem.* **2008**, *29*, 167–175.
- (12) Beebe, N. H. F.; Linderberg, J. *Int. J. Quantum Chem.* **1977**, *12*, 683–705.
- (13) Koch, H.; Sánchez de Merás, A.; Pedersen, T. B. *J. Chem. Phys.* **2003**, *118*, 9481–9484.
- (14) Aquilante, F.; Lindh, R.; Pedersen, T. B. *J. Chem. Phys.* **2007**, *127*, 114107.
- (15) Aquilante, F.; Pedersen, T. B.; Gagliardi, L.; Lindh, R. *J. Chem. Phys.* **2009**, *130*, 154107.
- (16) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (18) Miehlisch, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- (19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (20) Hariharan, P.; Pople, J. *Theor. Chim. Acta* **1973**, *28*, 213–222.
- (21) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654–3665.
- (22) T, H.; Dunning, Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (23) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371.
- (24) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291–306.
- (25) Widmark, P.-O.; Persson, B. J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419–432.
- (26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063–1071.
- (27) Due to memory issues in the conventional MP2 calculations a Full-CD calculation with a 10^{-10} Cholesky threshold was instead used as a reference in the following molecules: two species of C₄H₁₀ (trans-butane and isobutane), C₅H₈ (spiro-pentane), C₆H₆ (benzene), (CH₃)₂CHOH (isopropanol), and (CH₃)₃N (trimethylamine).
- (28) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127–11143.
- (29) Reiher, M.; Wolf, A. *J. Chem. Phys.* **2004**, *121*, 2037–2047.
- (30) Reiher, M.; Wolf, A. *J. Chem. Phys.* **2004**, *121*, 10945–10956.
- (31) Reiher, M. *Theor. Chem. Acc.* **2006**, *116*, 241–252.
- (32) Wolf, A.; Reiher, M.; Hess, B. *J. Chem. Phys.* **2002**, *117*, 9215–9226.

- (33) Wolf, A.; Reiher, M. *J. Chem. Phys.* **2006**, *124*, 06102.
- (34) Wolf, A.; Reiher, M. *J. Chem. Phys.* **2006**, *124*, 06103.
- (35) Roos, B. O.; Veryazov, V.; Widmark, P.-O. *Theor. Chem. Acc.* **2004**, *111*, 345–351.
- (36) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575–6579.
- (37) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2004**, *108*, 2851–2858.
- (38) Set III contains the molecules LiH, CH₂, CH₄, NH₃, H₂O, FH, SiH₂, SiH₄, PH₃, SH₂, HCl, LiF, C₂H₂, C₂H₄, C₂H₆, HCN, CO, H₂CO, H₃COH, N₂, H₂NNH₂, H₂O₂, F₂, and CO₂ from the G2/97 test suite.
- (39) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222–239.

CT9000284