

## Auxiliary Basis Sets for Density-Fitted MP2 Calculations: Correlation-Consistent Basis Sets for the 4d Elements

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**Abstract:** Auxiliary basis sets for use in density fitting second-order Møller–Plesset perturbation theory and other correlated ab initio methods have been developed for the 4d transition metal elements Y–Tc and Rh–Pd (sets for Ru, Ag, and Cd are already available), to be used in conjunction with the correlation consistent basis sets with pseudopotentials cc-pVnZ-PP and aug-cc-pVnZ-PP. Correlation energy calculations for a test set of small- to medium-sized transition metal complexes encompassing a variety of oxidation states show that the error in using these auxiliary basis sets is around 3–4 orders of magnitude smaller than the error due to orbital basis set size. The effect of truncating the auxiliary basis sets to remove higher angular momentum functions is also considered.

### 1. Introduction

With the advent of correlation consistent (cc) basis sets for the first and second row transition metals,<sup>1–3</sup> the application of correlated ab initio methods such as second-order Møller–Plesset perturbation (MP2) and coupled-cluster (CC) theories to transition metal complexes has become more attractive as a systematically improvable increase in basis set toward the basis set limit is now possible.<sup>4–9</sup> Even with the use of pseudopotentials to replace the chemically inert core electrons, the large size of many typical transition metal complexes means that conventional post-Hartree–Fock (HF) calculations rapidly become prohibitively expensive. The density fitting (DF) approximation<sup>10</sup> of electron repulsion integrals as applied to some post-HF methods expands orbital product densities in an optimized auxiliary density fitting basis set, and in the case of MP2 typically reduces calculation times by around an order of magnitude with a negligible loss of accuracy.

Also known as the resolution-of-the-identity (RI) approximation in some circles, density fitting has been implemented for a wide range of electronic structure theories, with correlated ab initio examples including MP2,<sup>11,12</sup> coupled-cluster,<sup>13</sup> and approximate coupled-cluster singles-and-

doubles model CC2.<sup>14</sup> Lately, progress has also been made in combining density fitting with local electron correlation techniques in order to produce further computational savings.<sup>15–17</sup> Unlike density-fitted HF or density functional theory, the same optimized auxiliary fitting bases can be successfully employed across the range of these post-HF methods, with the exception that density fitted local CC methods can benefit from selecting a larger auxiliary basis from the same series. An alternative to the use of optimized auxiliary basis sets is to automatically generate the auxiliary basis<sup>18</sup> in the same manner as that which can be employed for Cholesky decomposition of electron integrals.<sup>19</sup> Although these sets do not hold any bias toward a particular quantum chemical method they are generally larger, and therefore incur a higher computational cost, than sets specifically optimized for post-HF calculations.

Dunning originally optimized cc basis sets for first-row atoms.<sup>20</sup> Further work also provided cc sets for p block elements,<sup>21–24</sup> along with options for the description of anions and noncovalent interactions,<sup>25,26</sup> among many others. In their simplest form (valence only correlated, without being augmented with additional diffuse functions) this family of basis sets is usually denoted as cc-pVnZ, where the cardinal number, *n*, refers to the  $\zeta$  level of the basis set (D, T, Q, 5, and so on). This increase in cardinal number corresponds to a systematic approach to the complete basis set (CBS) limit, and when combined with the hierarchy of post-HF ab initio methods this leads to an obvious progression toward more

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accurate calculations. DF auxiliary basis sets for correlated ab initio methods (herein referred to as MP2 fitting basis sets) have been optimized specifically to be used with cc orbital basis sets for the majority of lighter elements,<sup>27–29</sup> enabling systematic improvement of calculations at a significantly reduced computational cost.

In the present work MP2 fitting basis sets are optimized for the 4d transition metal elements Y–Tc and Rh–Pd for use with the recently proposed cc-pVnZ-PP and aug-cc-pVnZ-PP,<sup>2</sup> where PP signifies the use of a pseudopotential, orbital basis sets. Similar MP2 fitting sets for the remaining 4d elements Ru<sup>30</sup> and Ag–Cd<sup>31</sup> are available elsewhere.

## 2. Basis Set Construction and Optimization

The cc-pVnZ-PP and aug-cc-pVnZ-PP (where  $n = D, T, Q$ , and 5) orbital basis sets and pseudopotentials (replacing 28 of the core electrons) used for constructing and optimizing the MP2 fitting basis sets were obtained from the William R. Wiley Environmental Molecular Sciences Laboratory Basis Set Exchange.<sup>32</sup> All optimizations were performed with the analytic gradients for the optimization of auxiliary basis sets<sup>28</sup> implemented in the RICC2 module<sup>14,33</sup> of the TURBOMOLE package.<sup>34,35</sup> Two guidelines previously employed for other cc MP2 fitting basis sets were adopted in the construction of the current sets, namely, that the number of functions in the auxiliary set should be less than four times the number of functions in the orbital basis and that the number of auxiliary functions in each specific basis set should be the same for all atoms considered.<sup>27</sup> Because of the variety of oxidation states any given transition metal element may be found in, the accuracy of MP2 fitting basis sets was verified by comparing the mean error, standard deviation, maximum error, and mean unsigned error introduced by the DF approximation at the MP2 level with the same statistics for the error in orbital basis set incompleteness for conventional MP2 over a test set of representative transition metal complexes. The later error was assessed as the difference in energy between a given orbital basis set and an estimate of the CBS limit obtained via a basis set extrapolation of quadruple- and quintuple- $\zeta$  energies utilizing the formula  $E_n = E_{\text{CBS}} + An^{-3}$  of Helgaker and co-workers,<sup>36,37</sup> where  $n$  is the cardinal number of the basis set. For the density fitting error to be regarded as negligible compared to the orbital basis set incompleteness all of the statistical measures should be at least 2 orders of magnitude smaller than the orbital basis error outlined above.<sup>27,29</sup>

To ensure that the MP2 fitting basis sets produced satisfactory results for transition metal complexes with a range of different oxidation states, a procedure similar to that outlined previously<sup>28,29</sup> was followed. The elements Y, Zr, and Tc, which are generally found in a single oxidation state, had exponents divided into two categories, and initially all exponents were optimized for a cation of the element corresponding to the oxidation state, before exponents that contribute to the outermost atomic orbitals (AOs) and with high angular momentum were reoptimized for the neutral atom with all other exponents fixed. This layered optimization is modified for the atoms Nb, Mo, Rh, and Pd, where

**Table 1.** Ratio of the Number of GTOs in the MP2 Fitting Basis Sets Compared to the Number of GTOs in the Generally Contracted Orbital Basis

	orbital basis	MP2 fitting basis	ratio of functions
cc-pVDZ-PP	[4s4p3d1f]	(8s8p6d6f4g2h)	2.8
cc-pVTZ-PP	[5s5p4d2f1g]	(10s10p9d7f6g3h2i)	2.8
cc-pVQZ-PP	[6s6p5d3f2g1h]	(11s11p10d8f7g5h3i2k)	2.5
cc-pV5Z-PP	[7s7p6d4f3g2h1i]	(12s12p11d10f9g6h5i3k2l)	2.3
aug-cc-pVDZ-PP	[5s5p4d2f]	(9s9p7d7f5g3h)	2.5
aug-cc-pVTZ-PP	[6s6p5d3f2g]	(11s11p10d8f7g4h3i)	2.5
aug-cc-pVQZ-PP	[7s7p6d4f3g2h]	(12s12p11d9f8g6h4i3k)	2.2
aug-cc-pV5Z-PP	[8s8p7d5f4g3h2i]	(13s13p12d11f10g7h6i4k3l)	2.1

the initial optimization is for the cation producing the highest oxidation state generally found in chemical compounds and an additional intermediate set of exponents are optimized for the cation typically corresponding to the most commonly found oxidation state of the element. For a more complete explanation of the procedure, readers are referred to ref 29. For the aug-cc-pVnZ-PP sets, the corresponding cc-pVnZ-PP auxiliary basis is held fixed while an additional diffuse exponent for each angular momentum quantum number is optimized for the anion of the element. For the testing of the MP2 fitting basis sets all non-4d elements are treated with the cc-pVnZ or aug-cc-pVnZ AO orbital basis sets consistent with the cardinal number used for the transition metal element, with the corresponding auxiliary basis sets of Weigend et al.<sup>27</sup> employed in the density fitting.

## 3. Results and Discussion

The total number of Gaussian-type orbitals (GTOs) included in the MP2 fitting basis sets, along with the number of GTOs in the corresponding generally contracted orbital basis, are presented in Table 1. It should be noted that the number of functions is the same as for the MP2 fitting basis sets available for Ru, Ag, and Cd. It can be seen from the ratio of the orbital and auxiliary functions that at no point does the number of auxiliary functions approach the upper guideline limit of four times the number of orbital functions, and that as the number of functions in the orbital basis increases the relative number of functions required in the auxiliary basis is reduced. Just as with previous cc-type MP2 fitting basis sets,<sup>27–29</sup> to ensure sufficient accuracy in the DF it was necessary to include auxiliary functions with an angular momentum quantum number of  $l_{\text{occ}} + l_{\text{bas}}$ , where  $l_{\text{occ}}$  and  $l_{\text{bas}}$  are the highest occupied angular momentum for the atom and largest angular momentum included in the orbital basis set, respectively.

While the auxiliary basis sets presented in this paper have been optimized for atoms and ions, verification of their accuracy for use in molecular applications requires a test set of representative transition metal complexes containing the relevant 4d elements. This test set has been extracted from the more comprehensive (in terms of elements covered) set presented previously<sup>38</sup> and consists of YF, YF<sub>3</sub>, YO, ZrF, ZrF<sub>3</sub>, ZrO, ZrO<sub>2</sub>, NbF<sub>3</sub>, NbO, NbO<sub>2</sub>, NbO<sub>2</sub>F, Mo(CO)<sub>6</sub>, MoF<sub>3</sub>, MoH, MoO<sub>2</sub>, MoO<sub>3</sub>, TcO<sub>7</sub>, TcO, TcO<sub>3</sub>F, RhF, RhF<sub>4</sub>, RhF<sub>6</sub>, RhO, Pd(CO)<sub>4</sub>, PdF, and PdO<sub>2</sub>. The errors in MP2 correlation energy due to orbital basis set incompleteness

**Table 2.** Relative Percentage and Absolute (kcal mol<sup>-1</sup>) Errors in the MP2 Correlation Energy due to Orbital Basis Set Size, Assessed by Comparing the cc Basis Set with a Complete Basis Set Estimate, for a Test Set of Transition Metal Complexes<sup>a</sup>

	$\bar{\Delta}^{\text{AO}}$	$\Delta_{\text{std}}^{\text{AO}}$	$\Delta_{\text{max}}^{\text{AO}}$	$\text{ABS } \bar{\Delta}^{\text{AO}}$
cc-pVDZ-PP	36.64	5.99	46.87	308.69
cc-pVTZ-PP	16.84	3.67	24.93	138.06
cc-pVQZ-PP	8.24	1.86	12.67	67.54
cc-pV5Z-PP	4.22	0.95	6.49	34.58
aug-cc-pVDZ-PP	33.07	5.64	42.70	267.83
aug-cc-pVTZ-PP	15.35	3.55	23.21	121.07
aug-cc-pVQZ-PP	7.46	1.86	11.77	58.46
aug-cc-pV5Z-PP	3.82	0.95	6.03	29.93

<sup>a</sup> See text for further details.**Table 3.** Absolute Errors (kcal mol<sup>-1</sup>) in the MP2 Correlation Energy due to the Density Fitting Approximation for a Test Set of Transition Metal Complexes<sup>a</sup>

	$\text{ABS } \bar{\Delta}^{\text{DF}}$	$\text{ABS } \Delta_{\text{std}}^{\text{DF}}$	$\text{ABS } \Delta_{\text{max}}^{\text{DF}}$
cc-pVDZ-PP	0.0662	0.0925	0.4013
cc-pVTZ-PP	0.0188	0.0184	0.0716
cc-pVQZ-PP	0.0028	0.0029	0.0117
cc-pV5Z-PP	0.0022	0.0027	0.0107
aug-cc-pVDZ-PP	0.0746	0.0902	0.3866
aug-cc-pVTZ-PP	0.0119	0.0137	0.0550
aug-cc-pVQZ-PP	0.0030	0.0030	0.0136
aug-cc-pV5Z-PP	0.0028	0.0034	0.0171

<sup>a</sup> See text for further details.

for the double-, triple-, quadruple-, and quintuple- $\zeta$  basis sets are shown in Table 2, where the relative percentage error for each complex has been calculated as  $\Delta_i^{\text{AO}} = (E^{\text{CBS}} - E^{\text{VnZ}})/E^{\text{CBS}} \times 100\%$ , and statistical data over the full test set is presented as the mean ( $\bar{\Delta}^{\text{AO}}$ ), standard deviation ( $\Delta_{\text{std}}^{\text{AO}}$ ), and the largest error within the test set ( $\Delta_{\text{max}}^{\text{AO}}$ ). Also shown is the absolute error between the MP2 correlation energy for a given basis set and the estimate of the CBS limit ( $\text{ABS } \bar{\Delta}^{\text{AO}}$ ). It should be noted that conventional MP2 calculations on Pd(CO)<sub>4</sub> with the aug-cc-pV5Z-PP basis were beyond the computational resources available, because of the literature geometry possessing no symmetry, and hence the statistics shown in Table 2 for the augmented basis sets do not include results for this system. An extensive test of the errors due to the use of the orbital basis sets is not a goal of the current investigation and tests of atomic and molecular applications are available elsewhere;<sup>8</sup> it is sufficient that the errors displayed in Table 2 are consistent with the magnitude of errors observed for molecules containing second row<sup>28</sup> and 3d<sup>29</sup> atoms.

The absolute error in the correlation energy due to the density fitting approximation has been assessed for all eight basis sets over the test set of transition metal complexes. These errors are presented, as a mean ( $\text{ABS } \bar{\Delta}^{\text{DF}}$ ), standard deviation ( $\text{ABS } \Delta_{\text{std}}^{\text{DF}}$ ), and maximum error ( $\text{ABS } \Delta_{\text{max}}^{\text{DF}}$ ) over the test set, in Table 3. It can be seen that these absolute errors in the correlation energy are small, especially compared to the absolute error in correlation energy due to the orbital basis (cc-pVDZ-PP has an estimated mean error of 308.6870 kcal mol<sup>-1</sup> in the orbital basis yet the mean error from density fitting is 0.0662 kcal mol<sup>-1</sup>). On increasing the orbital basis

**Table 4.** Relative Percentage Errors Introduced by the Density Fitting Approximation for a Test Set of Transition Metal Complexes<sup>a</sup>

	$\bar{\Delta}^{\text{DF}}$	$\Delta_{\text{std}}^{\text{DF}}$	$ \bar{\Delta}^{\text{DF}} $	$\Delta_{\text{max}}^{\text{DF}}$
cc-pVDZ-PP	-0.0086	0.0067	0.0090	-0.0273
cc-pVTZ-PP	-0.0022	0.0015	0.0023	-0.0067
cc-pVQZ-PP	-0.0002	0.0007	0.0004	-0.0032
cc-pV5Z-PP	-0.0001	0.0004	0.0003	-0.0018
aug-cc-pVDZ-PP	-0.0094	0.0056	0.0096	-0.0255
aug-cc-pVTZ-PP	-0.0007	0.0014	0.0014	-0.0030
aug-cc-pVQZ-PP	0.0003	0.0003	0.0003	0.0009
aug-cc-pV5Z-PP	0.0003	0.0002	0.0003	0.0009

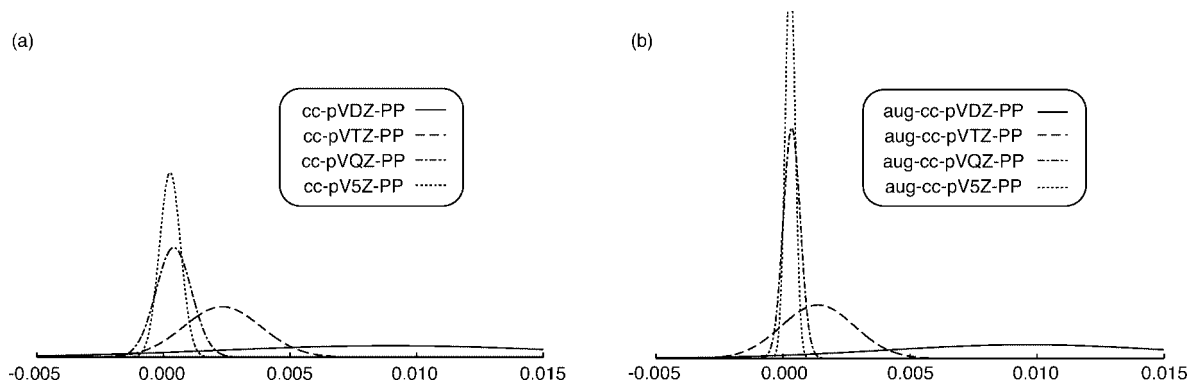
<sup>a</sup> See text for further details.

from cc-pVDZ-PP to cc-pVTZ-PP the mean change in energy drops by 170.6235 kcal mol<sup>-1</sup>, but as this is more than 3 orders of magnitude greater than the absolute error in correlation energy due to density fitting it seems clear that the error, in absolute terms, introduced by density fitting is small and should have a negligible effect on correlation energy based basis set extrapolations. Readers should be aware that these errors, and all others regarding the MP2 fitting basis sets reported in the current investigation, include contributions from the non-4d atoms (and their respective orbital and MP2 fitting basis sets) that are part of the complexes in the test set and are thus not entirely due to the new sets presented. However, as real world applications are likely to include such atoms in addition to 4d transition metals, they are more indicative of the magnitude of errors that may occur in further applications.

Further analysis of the errors introduced by density fitting is carried out by inspecting the percentage error relative to the orbital basis set, which can be expressed in terms of the correlation energy as  $\Delta_i^{\text{DF}} = (E^{\text{corr}} - E^{\text{DF-corr}})/E^{\text{corr}} \times 100\%$ , where  $E^{\text{corr}}$  and  $E^{\text{DF-corr}}$  are the conventional and density fitting MP2 correlation energies, respectively. These errors can be found in Table 4, summarized as the mean of the error over the test set ( $\bar{\Delta}^{\text{DF}}$ ), the standard deviation ( $\Delta_{\text{std}}^{\text{DF}}$ ), the mean unsigned error ( $|\bar{\Delta}^{\text{DF}}|$ ), and the largest error within the test set ( $\Delta_{\text{max}}^{\text{DF}}$ ). As there is no guarantee that the density fitting approximation will consistently under- or overestimate the conventional correlation energy, the mean error of Table 2 should be compared with the mean unsigned error of Table 4 to properly assess the quality of the fitting.

Table 4 indicates that the relative error introduced by the density fitting approximation with all eight MP2 fitting basis sets is small enough to be insignificant in terms of the overall correlation energy. In all cases the statistical measures of the errors are between 3 and 4 orders of magnitude smaller than the error due to orbital basis set incompleteness highlighted in Table 2. Because of the rounding of values in Table 4, it is not immediately obvious that aug-cc-pV5Z-PP produces a more accurate fitting than aug-cc-pVQZ-PP, but it is evident at a higher precision, for example, that the aug-cc-pVQZ-PP  $\Delta_{\text{max}}^{\text{DF}}$  is 0.000347 while that for aug-cc-pV5Z-PP is 0.000286. This improvement can be seen graphically in Figure 1, which plots the normalized Gaussian distributions of the relative errors due to density fitting for all eight auxiliary basis sets.

Both Figure 1 and Table 4 show that as the cardinal number of the basis set is increased DF-MP2 produces



**Figure 1.** Normalized Gaussian distributions of the relative percentage errors in MP2 valence correlation energy introduced via the density fitting approximation for a test set of small and medium sized transition metal complexes. (a) Errors for the cc-pV  $n$  Z-PP basis sets. (b) Errors for the aug-cc-pV  $n$  Z-PP basis sets. The normal distributions are defined by  $y(x) = (1/(\sigma\sqrt{2\pi})) \cdot e^{-(1/2)((x-\bar{x})/(\sigma))^2}$ , where  $\sigma$  represents the standard deviation and  $\bar{x}$  the mean.

**Table 5.** Relative Percentage and Absolute (kcal mol<sup>-1</sup>) Errors Introduced by the Density Fitting Approximation Using Truncated Auxiliary Basis Sets for a Test Set of Transition Metal Complexes;  $l_{\max}$  Indicates the Angular Momentum Functions at which the Basis Has Been Truncated<sup>a</sup>

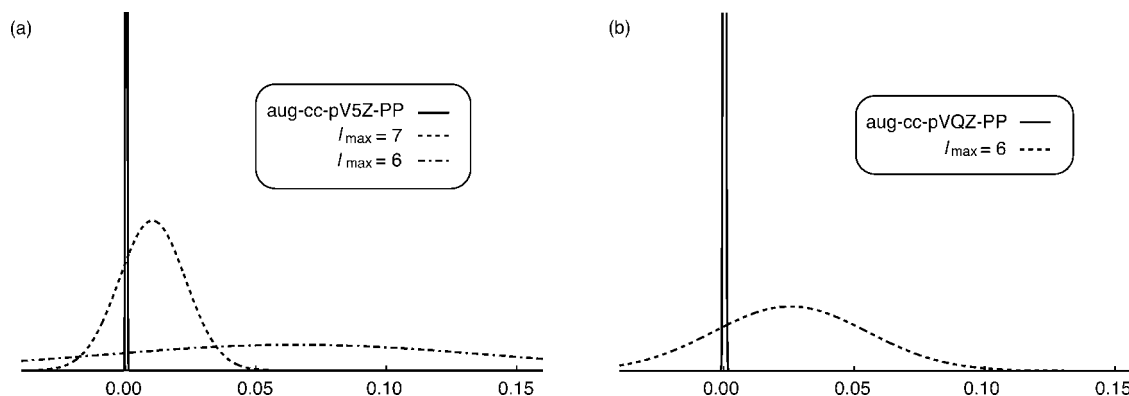
	$l_{\max}$	$ \Delta^{\text{DF}} $	$\Delta_{\text{std}}^{\text{DF}}$	$\Delta_{\text{max}}^{\text{DF}}$	$\text{ABS } \Delta^{\text{DF}}$
cc-pVQZ-PP	7	0.0004	0.0007	-0.0032	0.0028
	6	0.0244	0.0255	-0.0952	0.1722
cc-pV5Z-PP	8	0.0003	0.0004	-0.0018	0.0022
	7	0.0095	0.0099	-0.0371	0.0693
	6	0.0656	0.0677	-0.2444	0.4839
aug-cc-pVQZ-PP	7	0.0003	0.0003	-0.0009	0.0030
	6	0.0256	0.0295	-0.1070	0.1771
aug-cc-pV5Z-PP	8	0.0003	0.0002	0.0009	0.0028
	7	0.0103	0.0127	-0.0451	0.0680
	6	0.0653	0.0746	-0.2607	0.4482

<sup>a</sup> See text for further details.

correlation energies that are closer to the conventional energy and have a lower standard deviation. Comparison of parts a and b of Figure 1, which are plotted at the same scale, indicates that there is also a small improvement in the overall accuracy of the fitting for augmented sets relative to standard cc and that this is noticeably more pronounced with the quadruple- and quintuple- $\zeta$  sets.

While  $k$  and  $l$  angular momentum functions were required to optimize the quadruple- and quintuple- $\zeta$  MP2 fitting basis sets, most quantum chemistry packages currently only support  $i$  functions as a maximum. To gauge the errors associated with such maxima imposed on the MP2 fitting basis sets presented, the errors were calculated for the larger basis sets truncated to a maximum  $l$  of 6 or 7 ( $i$  and  $k$  functions, respectively) and are reported in Table 5. The same statistical measures for the nontruncated sets are also repeated in the table for ease of reference, along with the mean of the absolute error (kcal mol<sup>-1</sup>) relative to the conventional MP2 correlation energy.

The statistical data in Table 5 show that truncating the MP2 fitting basis sets has a large effect on the magnitude of the errors introduced by the density fitting approximation. The truncation of the quadruple- $\zeta$  sets increases the mean and standard deviation by almost 2 orders of magnitude, truncating the quintuple- $\zeta$  sets such that  $l_{\max} = 7$  increases the mean errors by between 1 and 2 orders of magnitude while truncating to  $l_{\max} = 6$  increases it by more than 2 orders of magnitude. These increases in the error due to the density fitting approximation are displayed pictorially in the form of normalized Gaussian distributions for the aug-cc-pVQZ-PP and aug-cc-pV5Z MP2 fitting basis sets and truncations



**Figure 2.** Relative percentage errors due to the density fitting approximation in the MP2 valence correlation energy of a test set of small and medium sized transition metals when truncated MP2 fitting basis sets are employed.  $l_{\max}$  indicates the angular momentum functions at which the basis has been truncated. (a) aug-cc-pV5Z MP2 fitting basis and truncations. (b) aug-cc-pVQZ-PP MP2 fitting basis and truncations. The normal distributions are defined by  $y(x) = (1/(\sigma\sqrt{2\pi})) \cdot e^{-(1/2)((x-\bar{x})/(\sigma))^2}$ , where  $\sigma$  represents the standard deviation and  $\bar{x}$  the mean.



in Figure 2. Equivalent plots for the non-augmented sets show much the same trends and thus are not presented here. In general, truncating the augmented MP2 fitting basis sets produces a larger increase in the mean unsigned error, standard deviation, and maximum error than truncating the nonaugmented sets, perhaps suggesting that high angular momentum functions have a larger effect on the fitting of diffuse functions in the orbital set. It is also worth noting that all of the truncated auxiliary basis sets overestimate the correlation energy for every complex in the test set.

Both Table 5 and Figure 2 display a large reduction in the quality of the fitting, when the MP2 fitting basis sets are truncated, such that the relative percentage errors are larger than those shown for cc-pVDZ-PP in Table 4. A comparison with Table 2 indicates that when both quadruple- and quintuple- $\zeta$  MP2 fitting sets are truncated such that  $l_{\max} = 6$ , the mean unsigned error and standard deviation are around 2 orders of magnitude smaller than the error in the orbital basis. It should be noted that the maximum relative percentage error within the test set for the truncated MP2 fitting basis sets is only around 1 order of magnitude smaller than that of the respective orbital basis. Inspecting the absolute errors from Table 5 reveals that truncating the quintuple- $\zeta$  basis sets to  $l_{\max} = 6$  produces a mean error of almost 0.5 kcal mol<sup>-1</sup>, which compares to a mean error from Table 2 of 29.9 kcal mol<sup>-1</sup> in the orbital basis when it is compared to the CBS estimate. Despite this MP2 fitting basis meeting the initial criteria suggested earlier for a sufficiently accurate fit, such large basis sets are generally only employed when high accuracy is desired and it seems that, for the majority of applications, it should only be used with a sizable degree of caution. The extent of both the relative and absolute errors for the remaining truncated basis sets suggests that they could be applied more readily, but again some caution is advisable. Because of the vastly superior accuracy of the nontruncated MP2 fitting basis sets it is recommended that truncated basis sets should not be utilized when higher angular momentum functions are supported, despite their smaller size.

#### 4. Conclusions

MP2 fitting auxiliary basis sets for density fitted correlated post-HF ab initio methods have been optimized for use with the cc orbital basis sets for the 4d transition metal elements Y–Tc and Rh–Pd. These cc-pVnZ-PP and aug-cc-pVnZ-PP MP2-fit (where  $n = D, T, Q$ , and 5) sets have been shown to provide accurate density fitting with the MP2 method for small to medium sized transition metal complexes with a range of oxidation states. The relative error introduced by the use of these sets compared to conventional MP2 is negligible, generally between 3 and 4 orders of magnitude smaller than the error due to orbital basis set incompleteness and, as shown by the absolute errors, is also an insignificant percentage of the overall correlation energy. Thus, the auxiliary basis sets presented can be used with confidence in accurately reproducing conventional correlation energies.

While truncating these MP2 fitting basis sets may be desirable from the point of view of utilizing them in a larger range of quantum chemical packages, removing functions from the quintuple- $\zeta$  sets such that  $l_{\max} = 6$  introduces

significant errors. Truncating quadruple- $\zeta$  to  $l_{\max} = 6$  and quintuple- $\zeta$  to  $l_{\max} = 7$  also introduces errors considerably larger than before truncation, and thus the application and desired degree of accuracy should be taken into account before employing them.

All eight of the MP2 fitting auxiliary basis sets presented in this work will be made available via the Environmental Molecular Sciences Laboratory Basis Set Exchange<sup>32</sup> Web site, <http://gnode2.pnl.gov/bse/portal>, and can also be found in the Supporting Information.

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**Supporting Information Available:** Tables depicting MP2 fitting auxiliary basis sets for Y, Zr, Nb, Mo, Tc, Rh, and Pd. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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