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Auxiliary basis sets for density fitting MP2 calculations:

Correlation consistent basis sets for the $5d$ elements Hf-Pt

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Abstract

Auxiliary basis sets specifically matched to the correlation consistent cc-pVnZ-PP, cc-pwCVnZ-PP, aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP orbital basis sets (used in conjunction with pseudopotentials) for the $5d$ transition metal elements Hf-Pt have been optimized for use in density fitting second-order Møller-Plesset perturbation theory and other correlated *ab initio* methods. Calculations of the second-order Møller-Plesset perturbation theory correlation energy, for a test set of small to medium sized molecules, indicate that the density fitting error when utilizing these sets is negligible at three to four orders of magnitude smaller than the orbital basis set incompleteness error.

1   Introduction

The evaluation of four-index two-electron integrals has traditionally represented a major bottleneck in the application of post Hartree-Fock (HF) methods, such as second-order Møller-Plesset perturbation theory (MP2), leading to prohibitive time, disk and memory requirements for larger scale systems. Density fitting (DF) reduces this computational cost by robustly approximating the integrals *via* an expansion of orbital product densities in an auxiliary basis set (ABS).[1–3] While some progress has been made in the automatic generation of ABSs,[4] typically

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DF-MP2 calculations employ a pre-optimized fitting set that is matched to a specific atomic orbital (AO) basis set and this generally leads to a saving of at least an order of magnitude in computer time. DF for post-HF methods has its roots in related integral approximation techniques applied to density functional theory[5,6] and is conceptually similar to DF-HF,[7,8] although in most of these implementations each DF method requires a different ABS.

DF for post-HF methods is not limited to DF-MP2, with the approximate coupled-cluster singles-and-doubles model CC2[9] representing a popular example of a method that often utilizes the same ABS. Much progress has also been made in combining DF with additional efficiency improvements. One example of this is local electron correlation methods[10] where distance based criteria are used to reduce the size of the configuration expansion, resulting in methods such as DF-LMP2,[11] DF-LCC2[12] and DF-LCCSD(T).[13] A second area of interest is in explicitly correlated methods that greatly improve AO basis set convergence by including terms that depend on the interelectronic distance into the basis, again four-index two-electron integral evaluation can be approximated in methods such as MP2-F12 and the various flavors of CCSD-F12.[14,15] It should be noted that in some circles DF is referred to as resolution of the identity (RI). In the current article DF is favored to reduce confusion with the RI basis sets used in explicitly correlated methods, which are designed and optimized in a distinctly different way to the DF ABSs employed in DF-MP2. To indicate that the ABS are designed for use in post-HF methods, the suffix /MP2Fit will be employed.

The correlation consistent (cc) series of basis sets[16,17] provide systematic convergence towards the complete basis set (CBS) limit, hence they have seen a great deal of use in investigations that employ correlated electronic structure methods. Efforts have been made to augment the cc AO sets with additional tight functions to correlate core electrons,[18,19] and with diffuse functions to describe negative ions and weak intermolecular interactions.[20] By designing cc basis sets to be used in combination with relativistic energy-consistent pseudopotentials (PPs) it has also been possible to expand the cc coverage of the periodic table to include the post-d main group elements[21–23] and the $4d$ and $5d$ elements.[24–27] Most of the cc AO sets now

have complimentary ABSs for use in density fitting,[28–33] enabling efficiency and convergence improvements for a large number of elements.

In the present work DF ABSs for use in post-HF methods are optimized for the $5d$ transition metal (TM) elements Hf-Pt. These ABSs are specifically matched to the recently developed cc-pVnZ-PP family of basis sets, including the weighted core-valence and diffuse augmented variants.

2 Basis set construction and optimization

The ABSs were designed and optimized to be used in conjunction with the correlation consistent, cc-pVnZ-PP (where n = D, T, Q, 5), family of basis sets and accompanying relativistic energy-consistent pseudopotentials.[27] Optimization of the ABSs employed the analytic gradients[29] implemented within the RICC2[9,34] module of the TURBOMOLE package.[35,36] This optimization proceeds by minimizing the quantity

$$\delta\text{DF} = \frac{1}{4}\sum_{aibj}\frac{[\langle ab||ij\rangle_{\text{DF}} - \langle ab||ij\rangle]^2}{\epsilon_a - \epsilon_i + \epsilon_b - \epsilon_j}. \tag{1}$$

Where $\langle ab||ij\rangle = (ai|bj) - (aj|bi)$, with i,j denoting occupied orbitals, a,b virtual orbitals and ϵ_x the HF orbital energies.[3] It should be noted that cc-pVTZ-PP ABSs for Hf-Pt are already available from the Environmental Molecular Sciences Laboratory Basis Set Exchange.[37,38] As details of the design and construction of these sets are not available,[39] new cc-pVTZ-PP ABSs were developed during the course of the current investigation. This ensures that all of the ABSs for Hf-Pt were optimized in a consistent manner and are tested on the same set of small to medium sized molecules.

The principal design goals for the MP2Fit ABSs in this investigation is that the number of basis functions within a particular ABS will remain the same for all of the elements Hf-Pt, and that the total number of functions should match those for analogous sets previously published for the $4d$ elements. In order to be able to describe the various oxidation states of the transition metal elements, tight functions for Hf, Ta and W were optimized for the 2+, 3+ and 4+ cations,

respectively, with the remaining functions optimized for the neutral atom. For the remaining elements, the tightest functions were optimized for the 4+ cation, intermediate functions for an intermediate cation (2+ for Re and Pt, 3+ for Os and Ir) and the more diffuse and higher angular momentum functions for the neutral atom. This procedure is explained in more detail in ref. 30. For ABSs matched to the cc-pVnZ-PP AO basis sets, the $5s$ and $5p$ electrons were treated with the frozen core approximation and their orbitals excluded from the calculation of the δDF functional and gradient.

It is highly recommended that the weighted core-valence cc-pwCVnZ-PP AO basis sets are employed in calculations that wish to describe both valence ($5d6s$) and outer-core ($5s5p$) electron correlation. To enable DF approximations for such investigations cc-pwCVnZ-PP/MP2Fit ABSs were also optimized, with orbitals from the $5s$ and $5p$ orbitals included in the optimization. Core-valence MP2Fit ABSs for lighter elements have typically been designed around augmenting cc-pVnZ/MP2Fit sets with a small number of additional tight exponents, in a similar fashion to the construction of the matching AO sets. This was not possible for Hf-Pt as the core-valence AO sets had a large number of exponents re-optimized, relative to the standard correlation consistent sets. This necessitated that the cc-pwCVnZ-PP/MP2Fit sets were completely re-optimized, along with the addition of a small number of extra functions. The compositions of the cc-pVnZ-PP/MP2Fit and cc-pwCVnZ-PP/MP2Fit ABSs are presented in Table 1, along with the compositions of the matching AO sets. The composition of the cc-pVnZ-PP/MP2Fit ABSs is identical to the equivalent sets for the $4d$ elements Y-Pd,[31,32] and for the remaining $5d$ elements Au and Hg.[40] The compositions also conform to the trend that it is necessary to include auxiliary functions in the angular momentum shell equal to $\ell_{occ} + \ell_{bas}$, corresponding to the highest occupied angular momentum symmetry for the neutral atom and the largest symmetry included in the AO basis, respectively.

The correlation consistent family of basis sets are often augmented with additional diffuse functions for the description of, *e.g.*, negative ions and intermolecular interactions, with such sets denoted in the form aug-cc-pVnZ-PP. ABSs matched to these AO basis sets were produced

by adding a common set of diffuse functions to both the cc-pVnZ-PP/MP2Fit and cc-pwCVnZ-PP/MP2Fit sets. There is an additional exponent included for each existing angular momentum symmetry and they were produced by an even-tempered extension of the cc-pVnZ-PP/MP2Fit ABS, such that $\zeta_3 = \zeta_2/(\zeta_1/\zeta_2)$, where ζ_3 is the new exponent, ζ_2 is the next most diffuse exponent *etc.* While it will be later demonstrated that the energetic error when using augmented ABSs produced in this manner is negligible, it should be noted that tests have yet to be carried out on Rydberg-type excited states and some degree of caution should be employed when using the resulting ABSs for such systems.

3 Results and discussion

The ABSs optimized in this work were evaluated by comparing the basis set incompleteness error (BSIE) in the AO basis (at the MP2 level) with the DF error for a test set of molecules that includes HfF, HfF$_3$, HfO, HfO$_2$, TaF, TaF$_3$, TaO$_2$F, TaO$_2$, WF$_3$, WH, WO, WO$_2$, WO$_3$, WC, WC$_2$, ReH, ReO, ReO$_2$, ReO$_3$, ReO$_3$F, OsO$_2$, OsO$_3$, OsO$_4$, OsOF$_5$, IrF$_6$, IrCl$_2$, IrO$_2$, Pt(CO)$_4$, PtO, PtO$_2$ and PtCl$_2$. For the $5d$ elements this was carried out using the cc-pVnZ-PP and aug-cc-pVnZ-PP AO basis sets with the $5s$ and $5p$ electrons treated with the frozen core approximation, and for the cc-pwCVnZ-PP and aug-cc-pwCVnZ-PP AO sets with all electrons correlated. For the non-$5d$ elements, the usual frozen core ($1s$ electrons for B-Ne, $1s$, $2s$ and $2p$ for Al-Cl) approximation was used throughout, along with the cc-pVnZ and aug-cc-pVnZ AO basis sets.[16] For Cl the cc-pV(n+d)Z and aug-cc-pV(n+d)Z sets were employed.[41,42]

An estimate of the CBS limit for the conventional MP2 correlation energy was produced using an extrapolation formula inspired by that of Helgaker and co-workers:[43,44]

$$E_n^{\mathrm{corr}} = E_{CBS}^{\mathrm{corr}} + \frac{A}{\ell_{\max}^3}. \tag{2}$$

For the transition metal basis sets $\ell_{\max} = n + 1$, if n is the cardinal number of the correlation consistent basis set. Although the molecules in the test set are not entirely composed of transition metal elements this prescription has been used throughout. Whilst this formula has been employed extensively for molecules containing $2p$ and $3p$ elements, it has not been so

thoroughly investigated for the transition metal elements. This suggests that the estimates of the CBS limit produced by the formula for the d-elements should be treated with more caution, yet the term CBS limit will be used herein for simplicity. The BSIE is defined as the difference between the MP2 correlation energy produced by basis sets with a given cardinal number and the estimate of the CBS limit. The statistics of the BSIE over the whole test set are shown in Table 2 as the mean, standard deviation and maximum error for each basis set. It should be noted that conventional MP2 calculations with the aug-cc-pwCV5Z-PP basis set on the $OsOF_5$ and $Pt(CO)_4$ molecules were beyond the computational resources available. This means that all of the error statistics for the aug-cc-pwCVnZ-PP AO and ABSs in Tables 2 and 3 exclude data for these two molecules. Extensive benchmarking of the AO basis sets is beyond the scope of the current investigation, yet it is clear from Table 2 that, as expected, the correlation energies converge towards the estimated CBS limit in a regular fashion as the quality of the basis set is increased.

The unsigned error due to the density fitting approximation is evaluated for each molecule in the test set as

$$|\Delta_n^{\mathrm{DF}}| = |E_n^{\mathrm{corr}} - E_{n,\mathrm{DF}}^{\mathrm{corr}}|. \tag{3}$$

The DF errors for each ABS developed within this work are summarized in Table 3 as statistics for the test set of molecules. More specifically, the mean unsigned error ($|\bar{\Delta}^{\mathrm{DF}}|$), standard deviation ($\Delta_{\mathrm{std}}^{\mathrm{DF}}$) and maximum error ($\Delta_{\mathrm{max}}^{\mathrm{DF}}$). Upon comparison of Tables 2 and 3 it is immediately obvious that the DF errors are negligible compared to the observed BSIE. In general the mean, standard deviation and maximum errors are three to four orders of magnitude smaller for the DF error than for the BSIE, irrespective of the chosen AO basis. From Table 3 it can also be seen that as the cardinal number of the basis set is increased the error introduced by the DF approximation decreases, which is presented graphically in Figure 1 as normalized Gaussian distributions of the density fitting error for the cc-pVnZ-PP ABSs (similar figures for the other ABSs are almost identical and not presented here). It is also evident from Table 3 that correlating the core electrons does not have a significant effect on the magnitude of the DF errors when

the correct basis set combinations are utilized. Comparing the DF errors of the cc-pVnZ-PP and aug-cc-pVnZ-PP sets (and analogously for the weighted core-valence sets) indicates that adding the additional diffuse exponents to the ABSs in an even-tempered manner has only introduced negligible errors, and in some cases the DF fitting for the diffuse augmented set produces marginally lower error statistics than for the base ABS. For reference, the unpublished cc-pVTZ-PP/MP2Fit set of Hättig produces a mean unsigned error of 0.033 mE_h, but possesses fewer functions than the equivalent set optimized in this work. Plots showing the DF error for each molecule are included in the Supplementary Material[45] as Figures SI - SIV. These plots indicate, in general, that the total DF error for each molecule increases as the atomic number of the 5d element within the molecule increases. This is perhaps unsurprising as the number of electrons correlated, both on the TM center and the ligands, also increases.

The errors introduced by density fitting are often expressed in the literature as relative percentage errors, which are obtained as:

$$\Delta_n^{\text{DF,rel}} = |(E_n^{\text{corr}} - E_{n,\text{DF}}^{\text{corr}})| / E_n^{\text{corr}} \times 100\%. \tag{4}$$

The statistics of the DF errors in terms of relative percentage error are provided as Table S1 in the Supplementary Material[45] for comparative purposes. These errors are comparable to those published for molecules containing the 4d elements.[32]

4   Conclusions

New auxiliary basis sets for use in the density fitting approximation at the MP2 level have been optimized for use with the cc-pVnZ-PP, cc-pwCVnZ-PP, aug-cc-pVnZ-PP and aug-cc-pwCVnZ-PP orbital basis sets and pseudopotentials for the 5d transition metal elements Hf-Pt. The errors introduced by utilizing these ABSs in the DF approximation have been assessed by comparing the AO basis set incompleteness error with the DF error for a test set of molecules that contain the 5d transition metal elements. In all cases the mean error, standard deviation and maximum error of the DF error were three to four orders of magnitude smaller than the BSIE, indicating that the errors introduced by using these ABSs is negligible and that they may be used with

confidence for accurately reproducing conventional correlation energies. These ABSs can also be employed in other correlated wavefunction based methods such as DF-CC2, DF-LCCSD(T) and CCSD(T)-F12. However, these methods require integrals over four orbitals in the virtual space compared to the two virtual orbital exchange integrals that occur in DF-MP2, suggesting that larger ABSs with higher angular momentum functions may be required.[13] In practice this often leads to cc-pV$(n + 1)$Z/MP2Fit ABSs being employed for the fitting of the four-external integrals, as, to the best of the author's knowledge, density fitting sets specifically for coupled-cluster methods have yet to be published.

All of the ABSs optimized in this work can be found in the Supplementary Material[45] and will be made available for electronic download from the Basis Set Exchange[38] website.

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[45] See Supplementary Material Document No. for Gaussian exponents for the auxiliary basis sets developed in this work. Also included is a table detailing the relative percentage density fitting error and figures showing the absolute density fitting error for each molecule. For information on Supplementary Material, see http://www.aip.org/pubservs/epaps.html.
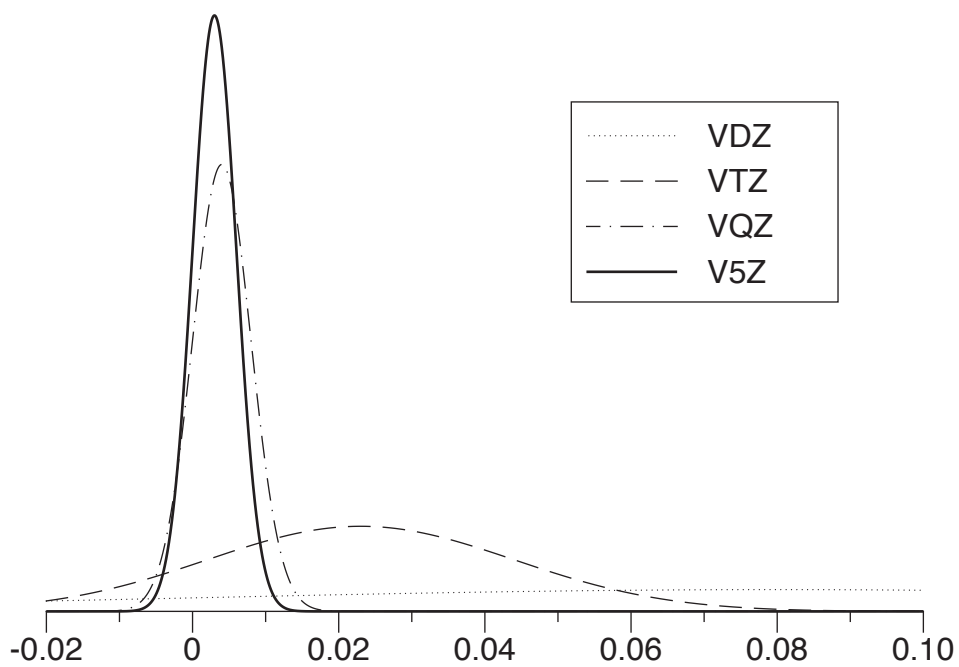
Figure 1: Normalized Gaussian distributions of the relative percentage errors in the MP2 valence correlation energy introduced *via* the density fitting approximation with the cc-pVnZ-PP/MP2Fit auxiliary basis sets (shortened to VnZ in the legend) for a test set of molecules that include the $5d$ elements Hf-Pt.

Table 1: Composition of the MP2Fit auxiliary basis sets compared to the atomic orbital sets. The ratio of functions assumes spherical orbitals.

	AO basis	ABS	Ratio of functions
cc-pVDZ-PP	$[4s4p3d1f]$	$(8s8p6d6f4g2h)$	4.3
cc-pVTZ-PP	$[5s5p4d2f1g]$	$(10s10p9d7f6g3h2i)$	3.9
cc-pVQZ-PP	$[6s6p5d3f2g1h]$	$(11s11p10d8f7g5h3i2k)$	3.4
cc-pV5Z-PP	$[7s7p6d4f3g2h1i]$	$(12s12p11d10f9g6h4i3k2l)$	3.0
cc-pwCVDZ-PP	$[5s5p4d2f]$	$(9s9p7d7f6g3h)$	3.8
cc-pwCVTZ-PP	$[7s7p6d3f2g]$	$(12s12p11d9f7g5h3i)$	3.3
cc-pwCVQZ-PP	$[8s8p7d4f3g2h]$	$(12s12p11d9f9g6h5i3k)$	2.9
cc-pwCV5Z-PP	$[9s9p8d5f4g3h2i]$	$(13s13p13d11f10g7h6i4k3l)$	2.7

Table 2: Absolute basis set incompleteness errors (per molecule) in MP2 correlation energies for a test set of molecules containing $5d$ elements. Errors are presented as mean ($\bar{\Delta}$), standard deviation (Δ_{std}) and maximum error (Δ_{max}), all in mE_h. Calculations employing weighted core-valence basis sets correlated the $5s$ and $5p$ electrons on the TM element. See text for further details.

TM basis set	$\bar{\Delta}$	Δ_{std}	Δ_{max}
cc-pVDZ-PP	278.486	170.716	725.167
cc-pVTZ-PP	122.256	74.670	316.977
cc-pVQZ-PP	61.843	37.726	161.828
cc-pV5Z-PP	35.789	21.832	93.651
aug-cc-pVDZ-PP	240.810	147.025	623.082
aug-cc-pVTZ-PP	104.015	63.557	269.416
aug-cc-pVQZ-PP	52.336	31.913	135.997
aug-cc-pV5Z-PP	30.287	18.468	78.702
cc-pwCVDZ-PP	399.013	179.321	857.583
cc-pwCVTZ-PP	172.091	77.713	372.243
cc-pwCVQZ-PP	88.711	39.097	190.594
cc-pwCV5Z-PP	51.337	22.626	110.298
aug-cc-pwCVDZ-PP	332.995	125.863	749.217
aug-cc-pwCVTZ-PP	142.553	54.490	322.635
aug-cc-pwCVQZ-PP	73.926	27.473	164.365
aug-cc-pwCV5Z-PP	42.781	15.899	95.119

Table 3: Density fitting errors in MP2 correlation energies (per molecule) for a test set of molecules containing $5d$ elements. Errors are presented as mean unsigned error ($|\bar{\Delta}^{\mathrm{DF}}|$), standard deviation ($\Delta_{\mathrm{std}}^{\mathrm{DF}}$) and maximum error ($\Delta_{\mathrm{max}}^{\mathrm{DF}}$), all in m$E_h$. Calculations employing weighted core-valence basis sets correlated the $5s$ and $5p$ electrons on the TM element. The molecule producing the largest density fitting error is denoted in parentheses. See text for further details.

TM basis set	$|\bar{\Delta}^{\mathrm{DF}}|$	$\Delta_{\mathrm{std}}^{\mathrm{DF}}$	$\Delta_{\mathrm{max}}^{\mathrm{DF}}$
cc-pVDZ-PP	0.080	0.082	0.431 ($Pt(CO)_4$)
cc-pVTZ-PP	0.023	0.021	0.088 ($Pt(CO)_4$)
cc-pVQZ-PP	0.004	0.004	0.020 (PtO_2)
cc-pV5Z-PP	0.003	0.003	0.011 (PtO_2)
aug-cc-pVDZ-PP	0.092	0.088	0.415 ($Pt(CO)_4$)
aug-cc-pVTZ-PP	0.015	0.014	0.067 ($Pt(CO)_4$)
aug-cc-pVQZ-PP	0.005	0.004	0.013 (PtO_2)
aug-cc-pV5Z-PP	0.004	0.003	0.016 ($Pt(CO)_4$)
cc-pwCVDZ-PP	0.086	0.080	0.422 ($Pt(CO)_4$)
cc-pwCVTZ-PP	0.027	0.020	0.087 ($Pt(CO)_4$)
cc-pwCVQZ-PP	0.004	0.004	0.020 (PtO_2)
cc-pwCV5Z-PP	0.003	0.003	0.012 (PtO_2)
aug-cc-pwCVDZ-PP	0.090	0.070	0.281 (ReO_3)
aug-cc-pwCVTZ-PP	0.016	0.012	0.047 (PtO_2)
aug-cc-pwCVQZ-PP	0.004	0.004	0.013 (PtO_2)
aug-cc-pwCV5Z-PP	0.003	0.003	0.008 (IrF_6)