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## Revised Basis Sets for the LANL Effective Core Potentials

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Abstract: We suggest a new contraction of the basis sets associated with the Hay-Wadt relativistic effective core potentials (RECPs) for the main group and transition metal atoms. These bases are more suitable for density functional theory investigations than the previous 'double- $\zeta$ ' contractions based upon Hartree-Fock atomic results. The original Hay-Wadt primitives are now contracted [5s5p3d], [4s4p3d], and [4s4p3d] for the first, second, and third transition series, respectively, and denoted as LANL2TZ basis sets. For the main group atoms, we advocate using a completely uncontracted basis denoted LANL08. While modestly extending the size of the basis, the resulting sets should be suitable for both DFT and wave function based approaches. The valence bases for the transition metal atoms can be supplemented with the polarization functions determined by Frenking.

It has become a common practice in the quantum chemistry community to utilize relativistic core potentials (RECP) determined from atomic Hartree-Fock (HF) calculations in the context of a Density Functional Theory (DFT) investigation. In the physics community, however, it is common to have separate RECPs or pseudopotentials generated for each functional of interest. Some years ago, concerned with the possibility that HF derived potentials might lead to significant errors when coupled with DFT, we compared HF versus functional specific RECPs and found little difference. This transferability was especially true with the small-core RECPs. With some large-core RECPs, however, transferability of HF-based potentials appears to be an issue. An example occurs in the 5*f* actinides series. An example occurs in the 5*f* actinides

We did note at the time that a more significant problem lay with the associated basis sets. The issue is that the coefficients for the contractions that describe the near valence or semicore regions can be quite different between HF and DFT calculations.

 $\it Table 1.$  Diffuse  $\it d$  Exponent for the First-Row Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0.0250	0.0349	0.0464	0.0587	0.0670	0.0706	0.0822	0.0898	0.101	0.170

**Table 2.** Theoretical and Experimental First Bond Dissociation Energy (kcal·mol $^{-1}$ ) for M(CO) $_6$  (M = Cr, Mo, W)

	Cr(CO) <sub>6</sub>	Mo(CO) <sub>6</sub>	W(CO) <sub>6</sub>			
B3LYP						
LANL2DZ	35.8	34.3	42.2			
LANL2TZ	36.9	35.3	43.0 <sup>12</sup>			
LANL08	36.9	35.3	43.0			
LANL2TZ+	38.6	_	_			
LANL08+	38.6	_	_			
LANL2TZ(f)	38.6	37.1	43.4 <sup>13</sup>			
LANL08(f)	38.5	37.1	43.4			
SDD	38.6	38.8	43.1			
6-311+G*	38.2	_	_			
	BP8	6				
LANL2DZ	41.8	38.2	46.0			
LANL2TZ	43.2	39.3	46.9 <sup>12</sup>			
LANL08	43.1	39.3	46.9			
LANL2TZ+	43.3	_	_			
LANL08+	43.2	_	_			
LANL2TZ(f)	43.2	39.6	47.3 <sup>13</sup>			
LANL08(f)	43.1	39.6	47.3			
SDD	43.2	41.2	45.4			
6-311+G*	42.9	_	_			
Exp <sup>14</sup>	$36.8 \pm 2$	$40.5\pm2$	$46.0 \pm 2$			

This is usually a small effect, but we have seen examples where this leads to a  $3-4~\rm kcal \cdot mol^{-1}$  difference in a bond energy or barrier height. For that reason, we have routinely uncontracted LANL2DZ main group and transition metal basis sets in our research. However, this is a more draconian solution than is necessary. While the computational cost of the additional s and p functions is not dramatic, there are larger consequences in the transition metal series associated with a completely uncontracted d space. We have found that a slight enlargement of the valence d space to triple- $\zeta$  quality is generally sufficient to ensure that the basis is adequate for both wave function and DFT based approaches.

In this Letter, we present these new contracted bases for the transition metal series. They result from the original Hay-Wadt<sup>4</sup> set by simply recontracting them to [5s5p3d], [4s4p3d], and [4s4p3d] for the first three transition series, respectively. This is straightforward, except that uncontraction of the p-space in the second and third rows leads to two nearly linearly dependent primitives. In all cases, we have retained the more diffuse primitive and deleted the tighter one. The new sets are available

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**Table 3.** Comparison of the Relative Energies ( $kcal \cdot mol^{-1}$ ) vs Basis Set for the Stationary Points of the [3+2] Cycloaddition of CpMO<sub>3</sub> (M = Mn, Tc, Re) to Ethylene Using the B3LYP Functional

	basis	$\begin{array}{c} \textbf{1} + C_2H_4 \\ \rightarrow \textbf{TS} \end{array}$	TS → 2	net exothermicity
CpMnO <sub>3</sub>	LANL2DZ	5.2	-63.8	-58.6
	LANL2TZ	7.2	-61.8	-54.6
	LANL08	7.2	-61.8	-54.6
	LANL2TZ+	7.5	-62.3	-54.8
	LANL08+	7.5	-62.3	-54.8
	LANL2TZ(f)	7.5	-61.2	-53.7
	LANL08(f)	7.5	-61.2	-53.7
	SDD	8.0	-61.9	-53.9
	6-311+G*	8.6	-60.8	-52.2
CpTcO <sub>3</sub>	LANL2DZ	10.4	-49.7	-39.3
	LANL2TZ	12.1	-47.9	-35.7
	LANL08	12.6	-46.5	-33.9
	LANL2TZ(f)	14.7	-44.1	-29.4
	LANL08(f)	14.7	-44.1	-29.4
	SDD	13.1	-46.7	-33.6
CpReO <sub>3</sub>	LANL2DZ	21.3	-35.1	-13.8
	LANL2TZ/LANL08 <sup>12</sup>	24.2	-33.6	-9.4
	LANL2TZ(f)/LANL08(f) <sup>13</sup>	27.8	-29.8	-2.0
	SDD	21.9	-35.1	-13.2

**Table 4.** Theoretical First Bond Dissociation Energy (kcal·mol $^{-1}$ ) vs Basis Set for MC<sub>2</sub>H<sub>4</sub> (M = Ni, Pd, Pt) Using the B3LYP Functional

	$NiC_2H_4$	$PdC_2H_4$	PtC <sub>2</sub> H <sub>4</sub>
	d <sup>10</sup>	d <sup>10</sup>	d <sup>10</sup>
LANL2DZ	83.4	30.9	63.7
LANL2TZ	85.9	32.5	66.1 <sup>12</sup>
LANL08	86.0	32.5	66.1
LANL2TZ+	66.3	_	_
LANL08+	66.2	_	_
LANL2TZ(f)	86.1	33.0	67.8 <sup>13</sup>
LANL08(f)	86.2	33.0	67.8
SDD	67.0	30.5	59.1
6-311+G*	63.6	_	_

Scheme 1. M-CO Bond Dissociation

online on the EMSL Basis Set Exchange and will be referred to as LANL2TZ in the next release of the Gaussian suite of electronic structure codes.<sup>5</sup> We advocate their use over the LANL2DZ sets. In addition, as in all-electron basis sets, greater flexibility is sometimes required in the first row metals when treating 'd-rich' configurations such as  $d^{10}$ . We have therefore

added an additional diffuse *d* function for the first row transition metals (see Table 1) and denote as LANL2TZ+. The diffuse primitives were chosen by an even-tempered criterion.

We also provide completely uncontracted sets, denoted as LANL08, for the transition metal and main group series. The LANL08 basis sets for main group atoms were derived from the original Hay-Wadt set<sup>6</sup> and correspond to triple- $\zeta$  valence orbital quality. For typical DFT applications we recommend LANL08 basis sets for main group atoms with RECPs and LANL2TZ for transition metals. The uncontracted LANL08 basis sets may also be useful at times for wave function based correlation treatments of transition metal complexes. Diffuse extensions available for the first transition series are denoted as LANL08+. Note that while the transition metals have outer cores, the main group atoms do not.

When polarization *f* functions are needed, we suggest the transition metal sets be augmented with the single primitive determined by Frenking. Because these were optimized in wave function based CISD calculations where they serve to polarize the density *and* to provide angular correlation, they are not the optimal exponents for DFT, where they need only to polarize the density. However, these are used successfully and routinely in the literature, and the limited tests we have run suggest little is to be gained with an alternative set optimized in the DFT context. We follow the nomenclature of placing polarization functions in parentheses, e.g. LANL2TZ(f) and LANL08(f). Gilbert and co-workers determined a set of polarization functions for the main group atoms, and these will be denoted LANL08(d).<sup>8</sup>

A few examples for the transition metal series that are indicative of the changes to be expected are presented in Tables 2–4. In all cases the  $6-311G^*$  basis has been used for all ligands. In addition, we compared our results to the Stuttgart RSC 1997 (SDD) RECP which contains an f function for the first-row transition elements.  $^{9,10}$  Finally, these RECP approaches are compared with Wachters' all-electron basis augmented with Hay's diffuse d function and Raghavachari and Trucks' f functions for the first-row complexes, known in Gaussian as  $6-311+G^*$ . The Gaussian03 suite of electronic structure codes has been used to compute the energies.  $^5$ 

Table 2 reports the first bond dissociation energy in the series  $M(CO)_6$ , M=Cr, Mo, W. The metal atoms here are formally neutral,  $d^6$  species. The differences between LANL2DZ and LANL2TZ are of the order of 1 kcal·mol<sup>-1</sup>. This is the case for both the hybrid functional B3LYP and a pure generalized gradient approximation like BP86. Note also that the triple- $\zeta d$  orbital description is adequate, as the differences between LANL2TZ and the completely uncontracted LANL08 sets are quite small. Addition of a polarization function on the metal increases the bond dissociation energy by only 0.2-0.4

Scheme 2. [3 + 2] Cycloaddition

$$CP$$
 $CH_2$ 
 $CH_2$ 

TS 2

kcal ⋅ mol<sup>-1</sup>. Polarization appears to be more important for the heavier transition metals.

As a test of metal atoms in a high valence state, we examined the olefin addition reaction shown in Scheme 2. We have restricted our investigation to the concerted pathway in which ethylene undergoes [3 + 2] addition to CpMO<sub>3</sub>, with M = Mn, Tc, and Re. These systems are all formally M(VII),  $d^0$ complexes. Table 3, column 3, reports the barrier height for the reaction, and the net exothermicity is given in column 5. The differences associated with the more contracted LANL2DZ basis are larger here, on the order of 2-4 kcal·mol<sup>-1</sup> for the heavier transition metals. Once again the triple- $\zeta$  basis LANL2TZ is essentially saturated with respect to the fully uncontracted LANL08 case in the first row. For the second and third row, the completely uncontracted LANL08 basis recovers an additional 1-2 kcal·mol<sup>-1</sup> in the energy differences compared with LANL2TZ. Finally, we note that the Stuttgart SDD RECP and associated basis gives results quite similar to LANL08.

Finally, we examine a case involving metals toward the right side of each row. In Table 4 we present the bond dissociation energies for the ethylene adducts  $MC_2H_4$ , M = Ni, Pd, Pt. The metals are all formally neutral and may have  $d^8s^2$ ,  $d^9s$ , or  $d^{10}$ configuration in the ground state depending on the metal. For our purposes, we compared results using the  $d^{10}$  reference state. Once again, uncontraction has an influence of a few kcal· $mol^{-1}$ . In this case, the importance of the diffuse d function in describing the  $d^{10}$  asymptote properly is evident in the huge reduction in bond dissociation energy with LANL2TZ+. Polarization functions once again have an influence of 1-2 kcal⋅mol<sup>-1</sup>. The RECP results are quite similar between the comparable SDD and LANL08+ for NiC<sub>2</sub>H<sub>4</sub>.

These basis sets will be available in the next version of Gaussian and are provided on the EMSL Basis Set Exchange Web site (https://bse.pnl.gov/bse/portal).

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