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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- ζ ’ 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.¹ 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 5f actinides series.^{2,3}

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.

Table 1. Diffuse 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) ₆	Mo(CO) ₆	W(CO) ₆
B3LYP			
LANL2DZ	35.8	34.3	42.2
LANL2TZ	36.9	35.3	43.0 ¹²
LANL08	36.9	35.3	43.0
LANL2TZ+	38.6	—	—
LANL08+	38.6	—	—
LANL2TZ(f)	38.6	37.1	43.4 ¹³
LANL08(f)	38.5	37.1	43.4
SDD	38.6	38.8	43.1
6-311+G*	38.2	—	—
BP86			
LANL2DZ	41.8	38.2	46.0
LANL2TZ	43.2	39.3	46.9 ¹²
LANL08	43.1	39.3	46.9
LANL2TZ+	43.3	—	—
LANL08+	43.2	—	—
LANL2TZ(f)	43.2	39.6	47.3 ¹³
LANL08(f)	43.1	39.6	47.3
SDD	43.2	41.2	45.4
6-311+G*	42.9	—	—
Exp ¹⁴	36.8 ± 2	40.5 ± 2	46.0 ± 2

This is usually a small effect, but we have seen examples where this leads to a 3–4 kcal·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- ζ 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-Wadt⁴ 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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kcal·mol⁻¹. 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 CpMO₃, 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⁻¹ for the heavier transition metals. Once again the triple- ζ 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⁻¹ 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 MC₂H₄, M = Ni, Pd, Pt. The metals are all formally neutral and may have *d*⁸*s*², *d*⁹*s*, 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⁻¹. The RECP results are quite similar between the comparable SDD and LANL08+ for NiC₂H₄.

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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