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Addition of Polarization and Diffuse Functions to the LANL2DZ Basis Set for P-Block Elements

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Diffuse and polarization functions have been optimized for the LANL2DZ basis set for elements in groups 14−17. The optimized exponents are in most cases similar to those optimized with different effective core potentials, valence basis sets, or computational models. The average of the LANL2DZ results for different models is taken to be the best generalized set of exponents. The extended basis set gives good results (average deviation from experiment 0.11 eV) for atomic electron affinities with the B3LYP model, but is consistently low with the MP2 model. The extended basis set gives similar performance to the all-electron 6-31+G(d) basis set in calculations of vibrational frequencies and bond energies in selected main-group compounds, and is intermediate in speed between the 6-31+G(d) basis set and the unmodified LANL2DZ basis set.

Introduction

To support our experimental program on the energetics of hypervalent compounds,[1] we need to calculate structures, energetics, vibrational frequencies, and other properties for a number of species containing heavy main-group atoms, such as I_5^-, SbF_6^-, and $BiCl_4^-$. We have therefore become interested in expanding the range of available basis sets for heavy main-group atoms.

Basis sets used in calculations on these systems must meet certain criteria.[2] Computational efficiency generally dictates the use of effective core potentials (ECPs). Use of a relativistic core potential (RECP) can also largely account for the relativistic effects that become significant for heavier atoms. Because many of the systems are anionic, diffuse functions are needed on all of the atoms.[3] Also, the basis set used on the central atom should include at least one set of d-polarization functions for the valence-p orbitals. In addition to modifying the shape of the valence orbitals, d functions allow probing of the controversial nature of bonding in hypervalent systems; that is, whether the three-center, four-electron bonding model[4] (where p orbitals on the central atom are primarily involved in the bonding) or the older expanded octet model[5] (where d orbitals on the central atom contribute substantially to the bonding) is more defensible.

Finally, the possible use of different basis sets on different atoms require basis set balance to avoid inaccuracies in the charge distribution in the molecule. “Balance” means that for each atom, the last functions of each symmetry added to the basis set contribute equally to energy lowering.[6−8] For example, adding diffuse functions to double-ζ basis sets has a significant effect on the energy even for atoms.[9] Thus, using a small basis set for heavy atoms and a larger basis set for lighter atoms in the same molecule can lead to inaccurate electron distributions, energetics, and other properties. In practice, balance can be approached by using basis sets of a similar *size* for each atom.

There is no comprehensive basis set for the main-group elements in general use that includes ECPs, diffuse functions, and polarization functions.[10] For main-group elements in the third, fourth, and fifth rows, several ECPs exist.[11] While one can combine ECPs with valence functions from other basis sets,[12−14] the result may not be optimal because the core and valence functions are not necessarily clearly separated.[6] Some diffuse and polarization functions have been developed for particular projects. In fact, in the original description of the LANL2DZ basis set, Wadt and Hay added sets of polarization and diffuse functions to the basis set for Cl and Br.[15] Frenking and co-workers have optimized polarization functions for the LANL2DZ basis set using the CISD model.[16] Martin and Sundermann[17] have recently developed accurate basis sets with these features for third- and fourth-row elements, but they are too computationally intensive for larger molecules. The Stuttgart−Dresden−Bonn (SDB)[18] basis set (which has a RECP) has diffuse exponents for six elements in Groups 16 and 17. Ugalde and co-workers[19] added polarization and diffuse functions for group 15 and 16 elements to a basis set that included the SKBJ RECP.[11] Similar exponents for both the SDB and LANL ECPs have been determined for Br and I with a different valence basis set.[20] Polarization and diffuse functions taken from a different basis set[21] were added to LANL2DZ for Cl,[15] Br,[15] and the Group 15 elements.[22] Shurki et al. supplemented the LANL2DZ basis set with polarization functions from another basis set,[14] Schaefer and co-workers[23] reported polarization functions for several Group 15 and 17 elements that they used with the LANL2DZ basis set, and Hu and Huang reported polarization and diffuse exponents for the noble gases.[24] Other groups have published parameters describing polarization functions for the entire p block,[25] polarization functions for S, Se, and Te;[26] polarization functions for the Group 15 and 17 elements,[27] diffuse functions for Br and I,[20] diffuse functions for P^-, S^-, and Cl^-,[7] and both types of functions for the halides.[21]

To provide a more systematic basis set for the heavier main group elements, we have extended the double-ζ valence basis set already optimized for use with the LANL RECP (the LANL2DZ basis set).[15] This is the most commonly used RECP,[22] at least with the Gaussian program. Addition of single

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TABLE 1: Optimized Polarization and Diffuse Exponents for the LANL2DZ Basis Set

	polarization (d) exponents							diffuse (p) exponents					
	B3LYP atom	B3LYP anion	MP2 atom	MP2 anion	CI[a]	HF[b]	rec value	B3LYP atom	B3LYP anion	MP2 atom	MP2 anion	SDB[c]	rec value
Si	0.310		0.293		0.284	0.262	0.296	0.0253	0.0219	0.0228	0.0246		0.0236
Ge	0.255		0.252		0.230	0.246	0.246	0.0205	0.0201	0.0204	0.0224		0.0208
Sn	0.189		0.188		0.180	0.183	0.186	0.0162	0.0174	0.0167	0.0194		0.0174
Pb	0.185		0.179		0.172	0.164	0.179	0.0153	0.0166	0.0166	0.0185		0.0168
P		0.371		0.334	0.387	0.340	0.364	0.0300	0.0292	0.0298	0.0301		0.0298
As		0.289		0.266	0.303	0.293	0.286	0.0266	0.0265	0.0253	0.0266		0.0262
Sb		0.209		0.193	0.218	0.211	0.207	0.0213	0.0231	0.0208	0.0226		0.0219
Bi		0.201		0.174	0.202	0.185	0.192	0.0195	0.0217	0.0194	0.0208		0.0204
S	0.540	0.493	0.502	0.438	0.503	0.421	0.496	0.0334	0.0349	0.0343	0.0364	0.0298	0.0347
Se	0.384	0.357	0.384	0.322	0.364	0.338	0.363	0.0320	0.0327	0.0327	0.0336	0.0325	0.0328
Te	0.268	0.250	0.254	0.225	0.252	0.237	0.250	0.0257	0.0279	0.0276	0.0285	0.0298	0.0274
Cl	0.672		0.631		0.640	0.514	0.648	0.0452	0.0472	0.0451	0.0492	0.0155	0.0467
Br	0.451		0.424		0.428	0.389	0.434	0.0355	0.0392	0.0351	0.0406	0.0361	0.0376
I	0.306		0.288		0.289	0.266	0.294	0.0278	0.0330	0.0286	0.0339	0.0326	0.0308

[a] Reference 16. [b] Reference 25. [c] Reference 18.

sets of diffuse and polarization functions to LANL2DZ for third-row-and-below atoms gives a basis set appropriate for study of main-group hypervalent anions.[28] The addition of diffuse functions to neutral atom basis sets to derive anion basis sets has been discussed previously.[7] We find this augmented LANL2DZ basis set, hereafter denoted LANL2DZdp, combines the efficiency of a core-potential-containing basis set with the accuracy of all-electron basis sets such as 6-31+G(d), and is well balanced with such basis sets.

Experimental Method

Choice of the B3LYP and MP2 Models. While most Gaussian primitive sets, including LANL2DZ, have been optimized at the Hartree−Fock (HF) level of theory,[6] the present functions were optimized at the B3LYP[29] and MP2 levels of theory.[30] Since most of the atoms and anions have unpaired electrons, we felt that using models that include electron correlation in some form would provide more general and accurate basis sets. The MP2 model was chosen as the simplest ab initio correlation approach. The B3LYP density functional model was selected since it exhibits good performance on electron affinities,[31−33] excellent performance on bond energies, and reasonably good performance on vibrational frequencies and geometries (and therefore rotational constants).[2,33−36] This makes it the best choice for calculations where all of these parameters are required.

Types of Functions Added to Model. The d orbitals can be represented by a set of five "true" d functions or six "Cartesian" d functions (x^2, y^2, z^2, xy, xz, and yz). Since the Cartesian d functions include a component of s symmetry ($x^2 + y^2 + z^2$), the optimized coefficients may be perturbed by the energy lowering of the s function. As noted by Gropen in a similar study, "in some cases, the outer exponents would drift into describing the inner shells because the improvement of the inner shells would gain more energy than an improvement of the valence shells."[9] This problem is increased because the polarization functions have a generally minor impact on the energy, such that the exponent of the s function dominates the optimization in some systems. Therefore, five d functions were used in this work.

Using the B3LYP model, the sp and p functions give very similar exponents for all elements beyond the first row; the sp values average 1.4 ± 1.5% higher than the p values. The maximum difference in the electron affinities calculated using these two types of functions is less than 0.05 eV. Some atoms had several nearby energy minima at the MP2 level with sp diffuse functions, but not with p functions. For this reason, and since the use of sp rather than p functions has a very small effect on the overall energy, we have chosen to use the simpler p functions.

Optimization Method. The Gaussian suite of programs[37] was used for all calculations. The exponents for the functions added to the basis sets were optimized by finding the minimum energy of the atoms and anions as a function of the exponents. We did not separate out the possible symmetry and spin states available to each atomic element/anion, instead using the constituent Slater determinants chosen by the program. The optimization was done both by hand and by using the Gauopt routine provided with Gaussian. Such gradient techniques for deriving energy-optimized basis sets have been discussed by Faegri and Almlof.[38] As noted previously, the derived energy viewed as a function of the exponent has a very small quadratic region.[38] Sample plots of energy as a function of exponent are given in the Supporting Information as Figures 1S and 2S.

Diffuse and polarization functions were optimized individually. Simultaneous optimization of the exponents of both sets of functions in test cases gave essentially the same results. Separate optimization of sets of functions of different symmetry has been previously condoned.[8]

The resulting exponents, which are optimized for monoatomic systems, are intended for application to molecular systems. It has been noted that "the basis functions needed to describe correlation energy are localized in the same region of space as those needed for the SCF energy."[6] Therefore, "...atom-determined exponents may be transferred to the molecular case with no significant loss in accuracy."[6] In a test case, energy minimization of diffuse exponents in X_3^- ($X = Cl$, Br, and I) gave exponents 5 ± 2% higher than exponents optimized in atomic systems.

Results

Overview of Results. Table 1 gives the optimized B3LYP and MP2 exponents for diffuse and polarization functions for the atoms and atomic anions. The exponents derived for atoms and anions are quite similar: the B3LYP and MP2 ratios of diffuse exponents for atoms and anions are 0.96 ± 0.08 and 0.92 ± 0.04, and the analogous ratio for polarization exponents is 1.08 and 1.16.[39] Similarly, the ratio of the atom and anion polarization exponents for the halogens published by Huzinaga and co-workers[25] is 1.12 ± 0.09. To avoid the need to assign

TABLE 2: Calculated and Experimental Electron Affinities[a]

	B3LYP LANL	B3LYP LANLp	B3LYP LANLd	B3LYP LANLpd	MP2 LANL	MP2 LANLpd	CCSD(T) LANLpd	MP4(SDTQ) LANLpd	EA[b]	EA$_{\mathrm{av}}$[b]
Si	0.898	1.412	0.862	1.376	0.498	1.126	1.072	1.101	1.390	1.408
Ge	0.843	1.314	0.814	1.286	0.421	1.018	0.985	1.007	1.233	1.353
Sn	1.013	1.321	0.989	1.297	0.618	1.076	1.043	1.063	1.112	1.418
Pb	0.903	1.217	0.884	1.198	0.498	0.950	0.942	0.951	0.364	1.421
P	−0.043	0.869	−0.009	0.896	−1.145	−0.074	−0.017	−0.047	0.747	0.735
As	0.171	0.899	0.199	0.921	−0.951	−0.026	0.033	0.007	0.814	0.748
Sb	0.473	0.978	0.498	0.998	−0.608	0.126	0.177	0.153	1.046	0.893
Bi	0.430	0.909	0.449	0.924	−0.683	0.045	0.106	0.086	0.946	
S	1.422	2.171	1.419	2.165	0.533	1.411	1.385	1.379	2.077	2.081
Se	1.485	2.141	1.483	2.137	0.543	1.390	1.370	1.365	2.021	2.044
Te	1.670	2.103	1.669	2.100	0.752	1.424	1.401	1.399	1.971	2.025
Cl	2.795	3.765	2.749	3.720	2.136	3.186	3.071	3.081	3.617	3.653
Br	2.907	3.534	2.868	3.496	2.161	2.961	2.855	2.865	3.365	3.517
I	2.983	3.381	2.951	3.349	2.242	2.870	2.768	2.778	3.059	3.373
RMS[c]	0.57	0.10	0.58	0.11	1.35	0.58	0.60	0.60		

[a] All values in eV. "LANL" means the LANL2DZ RECP + double-ζ valence basis set. "p" indicates addition of optimized diffuse functions of p symmetry, and "d" indicates addition of optimized polarization functions of d symmetry. [b] EA indicates experimental electron affinity, and EA$_{\mathrm{av}}$ indicates J-level-averaged electron affinity as discussed in the text. [c] RMS means root-mean-squared deviation between calculated EA values and EA$_{\mathrm{av}}$.

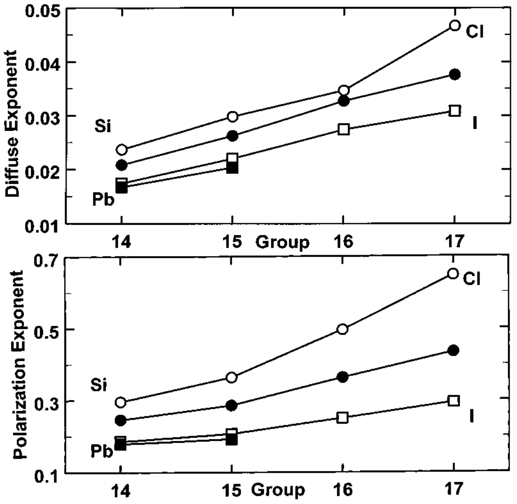

Figure 1. Generalized exponents for (a) diffuse and (b) polarization functions for heavy main-group elements, derived as discussed in the text.

formal charge states to atoms in molecules, we have averaged the atom and anion values. An exception involves the addition of polarization functions to atoms or anions with half-filled or completely filled p levels (spherically symmetric wave functions) for which energy change with exponent is nonphysical. Therefore, for the Group 14 and 17 elements, polarization exponents from the atoms were used, while for Group 15 elements, polarization exponents from the anions were used. For the Group 16 elements, polarization exponents from both the atoms and anions were averaged.

Also included in Table 1 is data from Frenking and coworkers[16] who used the CI method to optimize polarization exponents for LANL2DZ. These models give very similar exponent values, indicating that the optimal exponents are essentially model-independent. Thus, the generalized set of polarization exponents in Table 1 represents the averages of the exponents for all three models. The generalized set of diffuse exponents are the averages from our MP2 and B3LYP optimizations.

The functions that make up a Gaussian basis set have a radial dependence of $\exp(-\alpha r^2)$, where α is the exponent given in Table 1. Thus, the "size" of the orbital that corresponds to a Gaussian function is proportional to $\alpha^{-1/2}$. The generalized exponents in Table 1 and Figure 1 are chemically reasonable in that larger exponents correspond to smaller atoms in the upper right of the periodic table. The diffuse exponents are typically around a factor of 9 smaller than the polarization exponents, corresponding to diffuse orbitals a factor of 3 larger than the polarization orbitals.

The exponents can be compared to values determined with other computational models and basis sets. As mentioned above, the polarization exponents determined for the LANL2DZ basis with the CI model[16] are in good agreement with the present results. The SDB diffuse exponents[10,18] for Groups 16 and 17 (Table 1) are also in good agreement except for chlorine, where the SDB value is unexpectedly low. The Huzinaga et al. values for atoms[25] are slightly smaller, averaging 93 ± 6% of the present values. The less complete sets of exponents mentioned in the Introduction show significantly more deviation from the present results, but there is no systematic trend in this comparison.

Basis Set Performance I−Atomic Electron Affinities. To test the extended basis sets, we have calculated the electron affinities (EAs) of the atoms under study. Electron affinities have significant diffuse function and correlation influences,[6] so they are effective tests of the modified basis sets.[32] Experimental EA values usually reported are those from the lowest J state of the anion to the lowest J state of the neutral atom. The computational techniques used in this paper give J-averaged results. Therefore, the data is best compared to the difference in the weighted average energies[35] of the anion[40] and atom[41] J levels, denoted EA$_{\mathrm{av}}$ in Table 2. The difference between these two EA values is largest for the heaviest elements, where spin−orbit coupling is greatest. We removed bismuth from this comparison because the splitting between the J levels of Bi−(^{3}P) is not known,[42] making EA$_{\mathrm{av}}$ uncertain.

As seen in Table 2 and Figure 2, EA values calculated using the B3LYP/LANL2DZpd model agree with the EA$_{\mathrm{av}}$ experimental values. The rms deviation is 0.11 eV. For comparison, B3LYP calculations of the second-row EAs with a very large (quintuple ζ) basis set give an average error of 0.09 eV.[32] The calculated values are slightly low for Group 14 elements and slightly high for group 15 elements. This may mean that B3LYP/LANL2DZpd slightly underestimates the stability of half-filled shells. Since the deviations for the Group 17 elements is small, there is no apparent underestimation of the stability of completely filled shells.

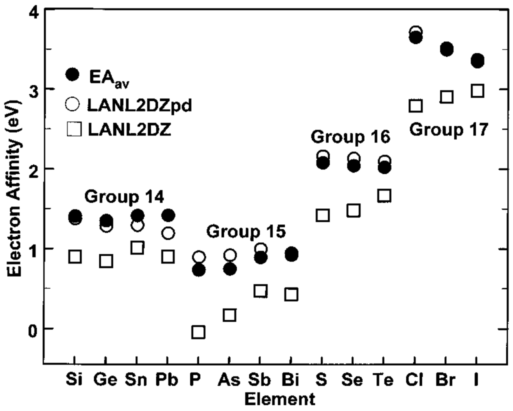

Figure 2. Atomic electron affinity calculations using the B3LYP/LANL2DZ and LANL2DZpd models, and experimental J-level-averaged electron affinities.

Without exception, the B3LYP/LANL2DZ model predicts affinities that are too low. The improved agreement provided by the B3LYP/LANL2DZpd model stems primarily from addition of diffuse functions (Table 2). Addition of polarization functions generally lowers the calculated EA values by ca. 0.04 eV, whether or not diffuse functions are also used.

The MP2/LANL2DZ electron affinities are very poor, with an rms error of 1.35 eV too low (Table 2). The MP2/LANL2DZpd EA values are somewhat better, averaging 0.58 eV too low. This suggests that the MP2/LANL2DZpd model is not very good for these atomic systems. It performs better on calculations of molecular electron affinities, a topic we will discuss in a future paper. At the suggestion of a reviewer, we calculated CCSD(T)/LANL2DZpd and MP4-(SDTQ)/LANL2DZpd atomic EAs for each element in our set. The results appear in Table 2. As one can see, the predicted EAs at these higher levels resemble those of the MP2 model. The hybrid B3LYP model remains the preferred model for determining electron affinities with the LANL2DZpd basis set.

Basis Set Performance II−Vibrational Frequencies. There are several useful ways to compare experimental and computational vibrational frequencies.[43] One method is to use the *differences* between measured and calculated frequencies.[44] This method weights higher frequencies more heavily, and is appropriate for applications such as the assignment of vibrational spectra or the determination of zero-point energies. A second method uses the *ratios* of the experimental and calculated frequencies. This method weights all frequencies equally, and is appropriate for thermodynamic quantities such as the density of states in situations where excited vibrational states are substantially occupied. A third method compares the *inverses* of the experimental and calculated frequencies.[45] This weights low frequencies more strongly, and is appropriate for thermodynamic calculations when excited vibrational states are weakly occupied.

TABLE 3: Frequency Scaling Factors for Main-Group Halides[a]

set	weight	LANL2DZ	LANL2DZpd	6-31+G(d)
1	*f*	1.152	1.066	
	1	1.173	1.068	
	1/*f*	1.176	1.062	
2	*f*	1.162	1.061	1.045
	1	1.194	1.067	1.048
	1/*f*	1.231	1.070	1.034
avg[b]		1.167	1.065	1.042
std dev (1)[c]		10.7%	5.6%	
std dev (2)[c]		12.7%	4.6%	6.1%

[a] Test sets detailed in the Supporting Information. Weighting factors discussed in the text. Scale factors are meant to be used in the form: Scaled frequency = Scale factor × Calculated frequency. [b] Average scaling factor for molecule set 1 for LANL2DZ and LANL2DZpd and molecule set 2 for 6-31+G(d). [c] Standard deviations in the ratio of the experimental and scaled computed frequencies for the two test sets.

Table 3 gives a summary of the results for B3LYP calculations using the LANL2DZ, LANL2DZpd, and 6-31+G(d) basis sets. Detailed results are given in Table 1S. Two sets of molecules were used: set 1 includes 36 main-group halide molecules, and set 2 is a subset of set 1 including molecules for which calculations employing the all-electron 6-31+G(d) basis set were performed.[46] All three basis sets tend to give vibrational constants lower than experiment: the scaling factors for LANL2DZ are substantially larger than the LANL2DZpd scaling factors, which are slightly larger than the 6-31+G(d) values. After scaling, the standard deviation of the calculated and experimental vibrational constants is slightly better for the LANL2DZpd basis set than the 6-31+G(d) basis set (Table 3). Thus, the supplementary functions improve the performance of the LANL2DZ basis set, giving comparable performance to the 6-31+G(d) basis set, which has a similar valence treatment.

A comparison of the frequency results for neutrals vs anions, hypervalent vs nonhypervalent systems, and fluorides vs other halides shows no statistically meaningful differences. The scaling factors for LANL2DZpd are very similar with all three weighting schemes. Thus, there are no apparent biases in frequency calculations at the B3LYP/LANL2DZpd level. Since the scaling factors are similar, it is reasonable to average them to obtain a scaling factor of 1.065 as the best overall value for main-group halides.

The results for the main-group halides do differ from those for other sets of molecules. For a set of molecules involving fewer heavy atoms, Scott and Radom[45] obtained a scaling factor of 0.9614 for B3LYP/6-31G(d). They also found that the HF factors for 6-31G(d) and 6-31+G(d) are almost identical, implying that the diffuse functions do not greatly affect the vibrational frequencies of their test set. Bytheway and Wong[44] performed similar calculations using the B3LYP method and the LANL2DZ and 6-31G(d) basis sets on a set of 50 inorganic molecules. Their scaling factors for both basis sets were within 1% of 1.00. Thus, the choice of the best scaling factor depends on the molecules of interest. Fortunately, the scaling factors for both 6-31+G(d) and LANL2DZpd are sufficiently close to unity for all test cases that the choice of scaling factor has relatively little impact.

Basis Set Performance III−Bond Lengths and Bond Energies. The B3LYP model consistently overestimates bond lengths by a small amount.[2] This holds true in this work, where 33 unique bond lengths with reliable experimental values, associated with the 36 molecules in set 1 above, were overestimated on average by 7.0 ± 3.1% and 2.5 ± 1.6% using the LANL2DZ and LANL2DZpd basis sets, respectively. For the 19 known bond lengths in molecules for which the 6-31+G(d) basis set is available (set 2), B3LYP/LANL2DZpd and B3LYP/6-31+G(d) calculations gave bond lengths too long by 3.1 ± 1.5% and 2.3 ± 1.3%, respectively. Thus, the 6-31+G(d) basis set gives only slightly better performance than LANL2DZpd, which gives significantly better performance than LANL2DZ.

B3LYP bond energies in the X_2 and X_3^- molecules (X = F, Cl, and Br) were calculated at the LANL2DZ, LANL2DZpd, and 6-31+G(d) levels. Calculated bond energies for such molecules deviate wildly,[1] but they are typical of the systems this basis set is designed for. Our results appear in Table 4.

TABLE 4: Calculated X−X Bond Energies for X_2 and X_3^- Using the B3LYP Model and Various Basis Sets[a]

	expt	LANL2DZ	LANL2DZdp	6-31+G*
F_2	155[b]	80	163	141
Cl_2	239[c]	131	188	197
Br_2	170[c]	125	174	218
F_3^-	98[b]	246	143	146
Cl_3^-	99[c]	219	129	128
Br_3^-	127[c]	201	140	155

[a] Energies are in kJ mol^{-1}. [b] Reference 1d, and references therein. [c] Reference 1b, and references therein.

TABLE 5: Mulliken Charges in Homonuclear Dihalogens[a]

molecule	basis set(1)	basis set(2)	charge(1)
Cl_2	6-31+G(d)	LANL2DZpd	+0.059
Br_2	6-31+G(d)	LANL2DZpd	−0.0397
Cl_2	6-31+G(d)	LANL2DZ	−0.0112
Br_2	6-31+G(d)	LANL2DZ	−0.1291
Cl_2	LANL2DZpd	LANL2DZ	−0.0746
Br_2	LANL2DZpd	LANL2DZ	−0.0833
I_2	LANL2DZpd	LANL2DZ	−0.0829

[a] Numbers in parentheses refer to the two atoms in the molecule.

TABLE 6: Relative Computational Times[a]

molecule	basis set	basis functions	relative time
PCl_3	LANL2DZ	32 + ECP	1
	LANL2DZpd	64 + ECP	3
	6-31+G(d)	92	6
$AsBr_3$	LANL2DZ	32 + ECP	1
	LANL2DZpd	64 + ECP	3
	6-31+G(d)	136	18

[a] Calculations include geometry optimizations and frequency calculations using the B3LYP model.

The rms deviations between experimental and calculated values for the three basis sets are 101, 31, and 37 kJ/mol, respectively. Thus, the LANL2DZpd and 6-31+G(d) give similar performance on bond energetics.

Basis Set Performance IV−Balance and Timing. To examine basis set balance, we examined Mulliken population data from single-point calculations of Cl_2, Br_2, and I_2,where each atom of the pair was modeled with a different basis set. Mulliken charges near zero suggest that the basis sets are reasonably balanced. The results (Table 5) suggest that LANL2DZpd is reasonably well balanced with 6-31+G(d), while neither basis set is as well balanced with LANL2DZ.

Expanding a basis set involves a penalty in terms of computation time (Table 6). As representative examples of the relative times needed to complete a calculation, PCl_3 and $AsBr_3$ were optimized and the vibrational frequencies calculated at the B3LYP/LANL2DZ, LANL2DZpd, and 6-31+G(d) levels. These two molecules contain atoms with relatively small and large cores, respectively. The LANL2DZpd calculations took three times as long as the LANL2DZ calculations for both molecules, but only one-half and one-sixth as long as the 6-31+G(d) calculations, respectively. As expected, use of the LANL2DZ RECP is particularly advantageous for the heavier elements.

Conclusions

The addition of diffuse and polarization functions to the LANL2DZ basis set gives substantially improved results on calculations of electron affinities, vibrational frequencies, bond lengths, and bond energies. The improved results, the consistency of the optimized exponents calculated with several models, and the reasonable periodic trends in the derived exponents suggest that the resulting basis set is generally applicable to these elements. The calculations also give an estimate of the uncertainties likely to be associated with calculations using this basis set.

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Supporting Information Available: Sample plots of energy as a function of polarization and diffuse exponent, and tables of frequencies and bond lengths calculated for 36 molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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