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REGULAR ARTICLE

Relativistic double-zeta, triple-zeta, and quadruple-zeta basis sets for the 7p elements, with atomic and molecular applications

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Abstract Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized for the 7p elements at the Dirac-Coulomb self-consistent field level of theory with a Gaussian nuclear charge distribution. For all of these sets, valence and outer-core correlating functions have been optimized in multireference CI calculations on the valence p^n states. Diffuse functions are also provided. Prescriptions are given for constructing contracted basis sets, based on MRCI calculations for correlation of the atoms. The basis sets are applied to a range of atomic and molecular properties, to provide information on how to use the basis sets. Tests of the basis sets with an explicit representation of the 8s showed that the 8s is not needed. The basis sets are available as an internet archive and from the Dirac program web site, http://dirac.chem.sdu.dk.

Keywords Gaussian basis sets · Relativistic basis sets · 7p elements · Double-zeta · Triple-zeta · Quadruple-zeta · Correlating functions

1 Introduction

The chemistry of the superheavy elements of the 7p block is of great interest, due to the production of atoms of these elements with lifetimes in the range of tens of seconds. These lifetimes are seen as evidence for the predicted island of stability around $Z = 114$ and $N = 184$. Because only a few atoms at a time can be synthesized, the determination of the properties of these elements relies on a close collaboration between experimentalists and theorists [1]. Calculation of the properties of the atoms and ions of these elements started very early. With the synthesis of these elements, there have been a considerable number of recent studies on both the atomic and the molecular properties of these elements [2–31]. Many of these have been conducted with somewhat smaller basis sets. Current all-electron calculations have relied mainly on the basis sets of Fægri [32, 33] and Malli et al. [34, 35]. It is therefore timely to extend the generation of relativistic basis sets in the style of the correlation-consistent sets [36–39] to these elements.

This paper is one in a series devoted to the generation of basis sets for all-electron relativistic calculations [40–50]. The goal is to provide basis sets of double-zeta (dz), triple-zeta (tz), and quadruple-zeta (qz) quality, including correlating functions for the valence and outer-core orbitals, and diffuse functions for negative ion character and dipole polarization. Although the basis sets are optimized with the Dirac-Coulomb Hamiltonian, they should be suitable for any all-electron relativistic method, such as the Douglas-Kroll-Hess method [51–53].

Optimization of basis sets for the 7p elements is challenging because of the very large spin-orbit splitting of the 7p shell. The $7p_{1/2}$ spinor is close in mean radius to the 7s, and the $7p_{3/2}$ spinor is much more extended. For example, the mean radii from Dirac-Hartree-Fock calculations on 118 are $1.84a_0$ (7s), $2.07a_0$ ($7p_{1/2}$), and $2.97a_0$ ($7p_{3/2}$). In the 6p block, the spin-orbit splitting made some difference in the quadruple-zeta basis sets [44]; here it is much larger, and the exponent range for the spin-orbit components will be different.

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Another factor that influences the development of basis sets is that, due to the large size of the spin-orbit splitting, the $7p_{1/2} - 7p_{3/2}$ excitation energy is close to or above the ionization limit in the second half of the block. It is generally easier to ionize a $7p_{3/2}$ electron than to promote a $7p_{1/2}$ electron. The large gap means that the relativistic hybridization of the $7p_{1/2}$ and $7p_{3/2}$ spinors to form pure-spin spin-orbitals is likely to be small. The 7s is even further removed from the $7p_{3/2}$, so that hybridization with the 7s for bonding in the later part of the block is energetically very unfavorable. Instead, it is possible that the $7p_{3/2}$ will hybridize with the 8s [10], as its excitation energy is much lower. To accommodate this possibility, a set of ℓ-optimized basis sets has also been generated in which a representation of the 8s spinor is included.

An alternative approach to the large spin-orbit splitting is to develop basis sets that are optimized on j rather than ℓ, that is, optimize sets of exponents for spinors that share the same j value rather than the same ℓ value. This approach is more in line with maintaining charge-conjugation symmetry, but it has its own problems, such as defining polarization functions by j. Optimization on j is not considered here, but may be considered in the future.

2 Basis set generation

The methods used have been described previously [40, 42, 54, 55]. The SCF basis sets were optimized in Dirac-Hartree-Fock calculations using the Dirac-Coulomb Hamiltonian with the standard Gaussian nuclear charge distribution [56]. The correlating functions and contractions were determined in MR-SDCI calculations with the same Hamiltonian. As for the previous basis sets, ℓ-optimization was employed, that is, the same exponents for each ℓ value.

2.1 SCF sets

The SCF basis sets for the occupied spinors were optimized on the (J-weighted) average energy of the $7s^2 7p^n$ configuration. The initial basis sets were chosen to be the same size as for the 6d block sets, including the functions for the 7p. For the dz basis sets, no change in the number of functions was needed, so the SCF basis set size is 26s23p16d10f. For the tz basis sets, the starting set taken from the 6d block [50] was 32s29p20d12f. The s set was reduced in size, because the nuclear radius is increasing in size and pushing the exponents out, and s spinors are all contracting due to relativity. To obtain a good triple-zeta distribution, two s functions were removed relative to the 6d set. No changes were needed in the other spaces, so the SCF basis set size was chosen to be 30s29p20d12f. The number of exponents needed for the p spinors is almost the same as for the s spinors: this is due partly to the need to describe the small component of the $p_{1/2}$ spinors, which is s-like, and partly due to the more diffuse $7p_{3/2}$ spinor. For the qz basis sets, the starting set taken from the 6d block was 36s35p24d14f. The size of the s set was reduced from 36 to 35 functions for the same reasons as for the tz basis sets. No changes were needed in the other spaces, and the final choice for the SCF basis set was 35s35p24d14f.

These sets were modified in the d and f spaces as described in the next subsection, because of the overlap with the correlating sets.

2.2 Correlating sets

Following the SCF basis set optimization, valence correlating functions were optimized in MR-SDCI calculations on the $7s^2 7p^n$ configuration, using all functions from this configuration as reference functions, and taking all single and double excitations out of the 7s and 7p shells into the correlating space. The occupied spinors used in these calculations were taken from SCF calculations on the $7s^2 7p^n$ configuration in the appropriate basis set (dz, tz, or qz). The correlating space consisted of spinors derived from single Gaussians, with the large and small components determined in a Thomas-Fermi potential for the ground configuration, orthogonalized as necessary to the occupied spinors. Each Gaussian exponent in the correlating set thus generates a correlating function. The correlating exponents are optimized independently of the SCF exponents, and therefore their range can overlap with that of the SCF exponents. How this is handled is described below.

For the dz basis set, the smallest s and p exponents were included in the correlating set and held fixed, while a single d exponent was optimized. For the tz basis set, the first and third exponents (counting from the smallest) of the s and p sets were included in the correlating space and held fixed, while a 2d1f set was optimized. Likewise for the qz basis set, the first, second, and fourth s exponents and the second, third, and fourth p exponents were included in the correlating set and held fixed, while a 3d2f1g set was optimized.

Correlating functions for 6d correlation were optimized in MR-SDCI calculations on the same configuration as for the valence correlation, with the same reference set, and all single and double excitations out of the 6d shell were taken that couple with the 6d shell to $J = 0$. The correlating function spaces were 1f for the dz basis set, 2f1g for the tz basis set, and 3f2g1h for the qz basis set. These correlating spaces also correspond to the exponent sets optimized.

Due to the overlap of the range of correlating d exponents with that of the SCF exponents, some reoptimization is needed. For the dz and tz basis sets, the SCF d set was reoptimized, by replacing the smallest one (dz) or two (tz) exponents in the SCF set with the valence correlating d

exponents and reoptimizing the rest of the SCF set. The overlap of the sets for the qz basis set is almost complete, but the correlating exponents show a variation across the block that is by no means smooth. MR-SDCI calculations in which the smallest three SCF d exponents replaced the correlating d exponents showed that the variation has little effect on the energy: the use of the SCF exponents resulted in a loss of <1 mE_h in the correlation energy. The d correlating exponents were therefore discarded in favor of the smallest SCF d exponents.

A similar situation applies to the correlating f functions. For the dz basis sets, the f exponent for 6d correlation is a little smaller than the smallest SCF f exponent. The smallest SCF exponent was therefore replaced with the correlating exponent and the rest of the f exponents were reoptimized. For the tz basis, the smallest two SCF exponents were replaced with the 6d correlating exponents, and the rest of the f exponents were reoptimized. The valence correlating f exponent is small enough that linear dependence is not a problem. For the qz basis sets, there is considerable overlap between the valence correlating 2f set, the 6d correlating 3f set, and the SCF set. The smallest two exponents from the SCF set were replaced with the three 6d correlating exponents, and the remaining SCF exponents were reoptimized. The smallest exponent from the 6d correlating set is similar to the largest of the valence correlating exponents, so the largest valence correlating f exponent was replaced with the smallest 6d correlating f exponent, and the other valence correlating f exponent was reoptimized.

2.3 Diffuse functions

A diffuse s function and a diffuse p function were optimized in SCF calculations on the average of the negative ion configuration, $7s^2 7p^{n+1}$, except for $Z = 118$. Diffuse correlating functions were optimized in MR-SDCI calculations on the same configuration, with 1d for the dz basis sets, 1d1f for the tz basis sets, and 1d1f1g for the qz basis sets. All of the valence and diffuse correlating functions were included in the CI calculations, including the s and p functions, but those for the neutral atom and the diffuse s and p were held fixed. For $Z = 118$, the diffuse s, p, and d functions for the dz basis set were optimized for the dipole polarization of the $n = 7$ shell. For the tz and qz basis sets, all of the diffuse functions were determined by a geometric series in the exponents from $Z = 116$ and $Z = 117$.

Functions to describe the 8s orbital were optimized on the average energy of the $7s^2 7p^{n-1} 8s$ configuration. Two s functions were optimized for the dz basis set, on the 8s eigenvalue rather than the total energy. This is because there can be more energy gained from a better representation of the lower spinors than from the 8s spinor. Using the 8s eigenvalue ensures that the outer antinode of the 8s spinor is well described. Three s functions were optimized for the tz basis set on the 8s eigenvalue, though in this case there was little difference between optimizing on the 8s eigenvalue and optimizing on the total energy because the 7s is better represented. Once these functions were determined, they were held fixed, and the functions for the 3s–7s spinors were reoptimized. For the qz basis sets, the energy surface is so flat that variations in the exponents in a test case resulted in energetic changes that were in the numerical noise, and so optimization is irrelevant. No functions were therefore determined for the 8s; if needed, an even-temepered extension of the s set would be sufficient.

2.4 Contracted sets

Contracted basis sets are constructed in the same way as for the correlation-consistent basis sets [36–39], with the SCF occupied orbitals forming a generally contracted set, and the addition of primitive functions for correlation. For the lower occupied symmetries, these primitives are taken from the SCF set. To determine which primitive functions should be used for correlation, a sequence of MR-SDCI calculations was performed for $Z = 114$, 116, and 118, in which different primitive functions were included in the correlating space. The correlating spaces for 7s7p correlation were 1s1p1d for dz, 2s2p2d1f for tz, and 3s3p3d2f1g for qz, while for 6d correlation, the correlating spaces were 1s1p1d1f, 2s2p2d2f1g, and 3s3p3d3f2g1h. The large and small component coefficients of these correlating functions were determined by diagonalizing the Fock matrix in the space of the DHF occupied functions plus the primitive functions and orthogonalizing the resultant extra functions to the DHF occupied functions as needed.

The selection of primitives that gave the lowest energy was chosen, in most cases, to determine the contraction pattern. Where there was a difference between the calculations, a compromise was chosen that gave the smallest error for all three elements and did not cause linear dependence problems. The results are presented in Table 1. The correlating d and f exponents are considered as part of the SCF set, owing to the reoptimizations described above, and are included in the general contraction and in the indexing given in Table 1.

This procedure was used for 7s7p correlation and for 6d correlation independently. There is overlap between the sets of primitives thus determined, so only the nonredundant exponents should be added when supplementing the basis sets for 6d correlation. The final contracted valence basis set sizes are 8s7p5d2f (dz), 9s8p6d3f (tz), and 10s9p7d4f1g (qz), and the core-valence basis set sizes are 9s8p6d3f (dz), 11s10p7d5f1g (tz), and 12s11p8d6f3g1h (qz).

Table 1 Indices of primitive functions to be used in a generally contracted basis set composed of the SCF functions plus primitives

Shells	Angular space	dz	tz	qz
7s, 7p	s	1	3,1	4,2,1
	p	1	2,1	5,3,2
	d	1	2,1	3,2,1
	f		1	2,1
6d	s	3	6,5	6,5,4
	p	3	5,4	7,6,5
	d	2	3,2	4,3,2
	f	1	3,2	4,3,2

The list of indices of the primitives is given for the correlation of each of three sets of shells for each basis set size. The exponents are counted from the smallest, starting at 1

Configuration average total energies of the neutral atoms in the dz, tz, and qz basis sets are given in Table 2 along with the values from numerical DHF calculations using GRASP [57]. The energies for the tz and qz basis sets are lower than the numerical energies. This is because the lower bound on the energy for the exponent optimization is lower than the exact energy by order c^{-4}—a phenomenon known as "prolapse" [32].

3 Applications

To provide information on the quality of the basis sets and how they may be used, a survey of the entire 7p block has been carried out. The survey addresses questions such as "how do the results vary with basis set size?", "when are diffuse functions needed?", "when is the 8s needed?", "which spinors are needed for bonding or for correlation?", and "how electronegative or electropositive are these elements?". Obviously, a complete answer cannot be given to all these questions, and some of these have been addressed already in the literature. The survey is necessarily limited by resources, but some attempt has been made to address all of these questions. The survey includes ionization potentials, electron affinities, and excitation energies of the atoms; bond lengths, dissociation energies and harmonic frequencies for diatomic molecules; and bond lengths and energetics for some polyatomic molecules.

The principal characteristics of the chemistry of the 7p block have been discussed in detail by others [6, 10, 12, 14, 19] and will only be summarized here. These characteristics will be used to guide the discussion of the results.

The first is the spin-orbit splitting, which is much larger than for the 6p block, sufficiently large that the bonding must be analyzed in terms of spinor bonds (see Chapter 22 of Ref [62] for an overview). Briefly, spinor bonds have an alpha and a beta spin component, each of which can be bonding or antibonding. For diatomics, both components are bonding when the contributing spinors have opposite signs of κ, the relativistic angular quantum number, but one is bonding and the other is antibonding when the contributing spinors have the same sign of κ. Alternatively, the large spin-orbit splitting means that relativistic hybridization must be considered in the energetics of bonding.

The second is the stabilization of the 7s, which is also larger than that of the 6s in the 6p block, and can be considered an inert pair for later p-block compounds.

The third is the destabilization of the 6d. The relativistic contraction of the 7s and the expansion of the 6d are large enough that for Cn ($Z = 112$), the $6d_{5/2}$ is above the 7s. For 113, the $6d_{5/2}$ is only marginally lower than the 7s, by about 2 eV. The earlier 7p elements might therefore be considered as late transition metals [14, 27].

3.1 Methods

All atomic calculations were carried out with GRASP [54, 57] and RAMCI [55], using the Dirac-Coulomb Hamiltonian and the standard Gaussian nucleus [56]. The coefficient of fractional parentage (CFP) package in RAMCI was supplemented for $j = 9/2,11/2$ and 13/2 to allow the use of higher than double excitations with high angular momentum functions. The SCF atomic calculations were performed on the J-weighted average of the ground configuration.

Table 2 Configuration average total Dirac-Hartree-Fock energies in E_h for uncontracted basis set calculations on the ground configurations

Z	A	Double-zeta	Triple-zeta	Quadruple-zeta	Numeric
113	287	−48,511.797402	−48,511.831789	−48,511.833822	−48,511.815283
114	289	−49,718.424480	−49,718.460484	−49,718.462394	−49,718.441622
115	291	−50,950.660006	−50,950.697663	−50,950.699481	−50,950.676208
116	293	−52,209.324404	−52,209.363874	−52,209.365646	−52,209.339571
117	292	−53,496.238309	−53,496.279965	−53,496.281707	−53,496.252582
118	294	−54,810.528182	−54,810.572143	−54,810.573868	−54,810.541229

Molecular calculations were carried out with the DREAMS package [58, 59].[1] In these calculations, integrals of the type SSSS were included only for the occupied spinors of the atoms (which form the set of contracted functions in the basis set). SCF calculations were performed with the full molecular symmetry, including Kramers restriction for open shells, followed by MP2 calculations. Open-shell MP2 calculations included a denominator shift [60]. For group 16, where there are two open-shell electrons in the atom, a two-configuration SCF calculation was performed on the $p^2_{3/2,1/2}$ and $p^2_{3/2,3/2}$ configurations, and the MP2 calculations included the denominator shifts described in Ref. [60]. For the remaining groups, the lowest determinant was used for the atomic calculations, rather than a state average. Given the large spin-orbit splitting, the approximation that this represents for group 14 and 15 should not be too serious.

For diatomics, calculations were performed on the atoms in the full molecular basis, to produce counterpoise-corrected potential energy curves. For the polyatomics, calculations were performed on the heavy atoms in the full molecular basis, and the counterpoise correction for the other atoms was taken from the calculations in the diatomic basis, following the ideas of Jensen [61]. The points on the potential curves were spaced at 5 pm in the bonding coordinate, and the bond length, minimum energy (which is also the dissociation energy or atomization energy), and harmonic frequency were obtained from a quartic fit to seven points around the minimum. For the van der Waals molecules, points were spaced at 10 pm rather than 5 pm.

The basis sets used for the 7p elements are those described above. Calculations were performed with the standard valence basis sets (designated vdz, vtz, and vqz) and core-valence basis sets (designated cvdz, cvtz, and cvqz) and with the addition of diffuse functions (designated avdz, avtz, and avqz, and acvdz, acvtz, and acvqz). For the 6p elements, the corresponding basis sets from earlier work are used [40, 42, 44].

In the calculations with an explicit representation of the 8s, the 8s spinor was included as a contracted function, and primitives were added for flexibility. For the dz basis sets, the first (lowest exponent) primitive was added; for the tz basis sets, the first and third primitives were added. This means that, relative to the basis without the 8s, two functions have been added to the dz basis set and three functions to the tz basis set. These basis sets are designated vdz(8s) and vtz(8s). When diffuse functions were added to the basis sets with the 8s, the diffuse s functions were not added, as their effect is already covered by the 8s and its primitives. These basis sets are designated avdz(8s) and avtz(8s).

For H and F, the correlation-consistent basis sets of Dunning and coworkers [36] were used. The p sets for F were supplemented with a tight *p* function and recontracted in DHF calculations on the average of the ground configuration. The tight p exponents were 128.2 (dz), 250.8 (tz), and 465.3 (qz). In most cases, the augmented basis sets (aug-cc-pvnz, designated avnz here) were used. Basis sets for K were taken from Ref. [47] and included the outer-core polarizing functions.

3.2 Atoms

A great deal of insight into the chemistry of a set of elements can be obtained from the atomic properties. Ionization potentials and electron affinities give information on the electronegativity of elements. The polarity of bonds can be inferred from these quantities or from the relative orbital energies of the contributing atomic orbitals. Excitation energies provide information on the energetics of hybridization and as a consequence on bond strengths, while mean radii provide information about optimal overlaps and thus on bond lengths. Orbital eigenvalues also provide information on bond strengths and polarities via simple perturbation arguments.

The results of the MR-CI calculations are reported in Table 3 for the first ionization potential, Table 4 for the second ionization potential, and Table 5 for the electron affinity. Extrapolations of the results to the basis set limit with a $1/n^3$ algorithm [63] are also included. These results are compared with the Fock-space coupled-cluster (FSCC) results of Eliav et al. [2–5], which include correlation of the 6s, 6p, 6d, and 5f as well as the valence. The extrapolated results for the first IP are within about 0.1 eV of the FSCC results. Preliminary CI calculations with the dz basis show an increase of about 0.15 eV for 113 and 114 on the inclusion of 6d correlation, which places the present results slightly larger than the FSCC results. Diffuse functions make little difference to the first IP, so were not used in the calculations for the second IP. Results for the second IP are close to the FSCC results except for 113, no doubt due to the importance of 6d correlation. The electron affinities (EAs) are smaller than the FSCC values by about 0.15 eV, which is a little larger than for the first IP in absolute terms, and represents a similar error, but is a substantial fraction of the total. Inclusion of quadruple excitations for 113 increases the EA by <0.1 eV, so most of the remainder is likely to be due to core correlation. In agreement with the FSCC results [4], 114 does not bind an extra electron.

Thierfelder et al. [29] also report FSCC results for the ionization of 114 and 118, and the electron affinities of 113

[1] DREAMS is a Dirac-based Relativistic Electronic Atomic and Molecular Structure program suite, consisting of an adapted version of MOLECULE, a vectorized integral program developed by J. Almlöf and P. R. Taylor, and a Dirac-Hartree-Fock and MP2 program developed by K. G. Dyall. The DHF program methods are described in [58] and the MP2 program methods are described in [59].

Table 3 First ionization potentials in eV of the 7p elements as a function of basis set and valence correlation level, along with extrapolated results (ext), and Fock-space coupled cluster (FSCC) values from the literature

Basis	113	114	115	116	117	118
CISD						
vdz	7.069	8.245	5.108	6.320	7.028	8.360
vtz	7.165	8.341	5.257	6.494	7.187	8.438
vqz	7.194	8.387	5.289	6.542	7.256	8.515
ext	7.215	8.421	5.312	6.577	7.306	8.571
avdz	7.069	8.238	5.164	6.413	7.171	8.497
avtz	7.170	8.345	5.275	6.524	7.222	8.470
avqz	7.197	8.390	5.299	6.562	7.282	8.546
ext	7.217	8.423	5.317	6.590	7.326	8.601
CISDT						
vdz	7.070	8.248	5.113	6.328	7.032	8.360
vtz	7.167	8.348	5.275	6.521	7.221	8.461
vqz	7.197	8.395	5.312	6.575	7.302	8.551
ext	7.219	8.429	5.339	6.614	7.361	8.617
avdz	7.070	8.242	5.172	6.426	7.188	8.512
avtz	7.172	8.352	5.294	6.555	7.268	8.506
avqz	7.200	8.399	5.322	6.598	7.333	8.588
ext	7.220	8.433	5.342	6.629	7.380	8.648
FSCC[a]	7.306	8.539	5.579			

[a] Refs. [2, 3, 5]

Table 4 Second ionization potentials in eV of the 7p elements as a function of basis set and valence correlation level, along with extrapolated results (ext), and Fock-space coupled cluster (FSCC) values from the literature

Basis	113	114	115	116	117	118
CISD						
vdz	22.536	16.451	17.937	12.991	14.608	15.622
vtz	22.578	16.561	18.081	13.172	14.756	15.680
vqz	22.590	16.704	18.141	13.213	14.817	15.771
ext	22.599	16.808	18.185	13.243	14.862	15.837
CISDT						
vdz		16.451	17.939	12.995	14.614	15.627
vtz		16.562	18.084	13.184	14.778	15.711
vqz		16.706	18.145	13.229	14.846	15.812
ext		16.811	18.190	13.262	14.896	15.886
FSCC[a]	23.96	16.871	18.232			

[a] Fock-space coupled cluster [2, 3, 5]

Table 5 Electron affinities in eV of the 7p elements as a function of basis set and correlation level, along with extrapolated results (ext), and Fock-space coupled cluster (FSCC) values from the literature

Basis	113	114	115	116	117
CISD					
avdz	0.418	−0.538	0.101	0.483	1.284
avtz	0.464	−0.493	0.144	0.501	1.272
avqz	0.486	−0.483	0.155	0.527	1.311
ext	0.502	−0.476	0.163	0.546	1.339
CISDT					
avdz	0.459	−0.473	0.142	0.528	1.319
avtz	0.514	−0.357	0.203	0.572	1.327
avqz	0.539	−0.275	0.220	0.600	1.371
ext	0.557	−0.215	0.232	0.620	1.403
FSCC[a]	0.68	<0	0.383		

[a] Fock-space coupled cluster [2, 4, 5]

and 117. Their values are within 0.1 eV of the values reported here.

Relativistic effects, both spin-free and spin-orbit, play a significant role in the energetics of excitation in these atoms, which gives some indication of their ability to form bonds. In a simple-minded approach, the energy required to create hybrids that can form strong single bonds must be balanced by the energy gained from bonding. A classic example is the Tl dimer, for which the hybridization cost to form a $6p\sigma$ bond is 4/3 of the $6p_{1/2}$ to $6p_{3/2}$ promotion energy (the spin-orbit splitting). The energy gained is insufficient to compensate for this cost, so Tl_2 is very weakly bound, and the relativistic stabilization of the 6s removes it somewhat from participation in bonding, adding to the bonding cost. The real situation is more complex, because the molecules do not necessarily form strong σ hybrid bonds, but this simple picture can give some qualitative insight into the likelihood of bonding.

In the nonrelativistic regime, the hybridization cost is largely due to promotion from the s to the p. Carbon is the classic example, where promotion from the s^2p^2 to the sp^3 configuration allows four bonds to be formed. Likewise, promotion from s^2p to sp^2 allows three bonds to be formed in group 13. In the relativistic regime, promotion from $p_{1/2}$ to $p_{3/2}$ ("relativistic hybridization") must also be considered. Generally speaking, the spin-orbit average of these two spinors is required to form pure-spin hybrids that can form a single σ bond. Thus, for 113, promotion from s to $p_{1/2}$ is not sufficient: there must be promotion from s to $p_{3/2}$ and a partial $p_{1/2}$ to $p_{3/2}$ promotion. Likewise, for 114, there must be an s to $p_{1/2}$ and a $p_{1/2}$ to $p_{3/2}$ promotion to form four bonds.

Results for the lowest $7p_{1/2} - 7p_{3/2}$ excitation energy are given in Table 6. From 115 on, some at least of the $7p_{1/2}^2 7p_{3/2}^{n-1} 8p_{1/2}$ states are lower in energy than the $7p_{1/2}^1 7p_{3/2}^{n+1}$ states: it takes less energy to promote from the $7p_{3/2}$ into empty orbitals than to promote from $7p_{1/2}$ to $7p_{3/2}$. The $7p_{1/2}^1 7p_{3/2}^{n+1}$ state is close to the ionization limit for 115 and 116, and above it for 117. Addition of diffuse functions makes little difference to the valence state energies, but considerably reduces the energies of the Rydberg ($8p_{1/2}$) states. The value for 117 is consistent with that obtained by Nash and Bursten [10].

The large size of the spin-orbit splitting, as shown by these excitation energies, means that there is a considerable cost to relativistic hybridization. Even for 113, the cost is about 2 eV per atom to form just a single pure-spin p orbital for bonding, so any covalent p bond formed would have to be at least this strong for the molecule to exist. The cost increases across the block, though the cost per bond declines somewhat across the block, to 1.7 eV for two p bonds to 114 and 1.5 eV for three bonds to 115. In this respect, the lower oxidation states are at a disadvantage, because the cost per bond is much higher. Low oxidation states are therefore likely to form via bonds to the $7p_{3/2}$ only from 115 on, but higher oxidation states could activate the $7p_{1/2}$ shell.

If the cost is considerable for $7p_{1/2} - 7p_{3/2}$, it is even larger for 7s to $7p_{1/2}$ or $7p_{3/2}$ promotion. Excitation energies derived from numerical SCF calculations on the average of the s^2p^n and s^1p^{n+1} configurations are presented in Table 7. The nonrelativistic values are compared with the relativistic values for excitation into the lowest s^1p^{n+1} state and into the lowest state with only one $7p_{1/2}$ electron. The latter is included because the former involves a closed $7p_{1/2}$ shell, which is not suitable for bonding. If the excitation energy is divided by the number of bonds formed, the cost per bond is nearly 3 eV for 113, nearly 4 eV for 114, and remains about 4 eV for the maximum oxidation state of 5 and 6 for 115 and 116. This compares with a cost per bond of about 0.5 eV for 113 and 114 and little over 1 eV for 115 and 116 in the nonrelativistic case. For lower oxidation states, the cost per bond is even higher, and it is very unlikely that the 7s is involved in bonding for the $7p_{3/2}$ elements.

Spinor eigenvalues for the 6p and 7p block are given in Table 8. From simple perturbation arguments, covalent bonds are formed between orbitals (or spinors) that have the same eigenvalues, and the polarity of the bond increases with increasing eigenvalue differences. These values will be used in later discussions of molecules.

Table 6 Lowest $7p_{1/2} - 7p_{3/2}$ excitation energy of the 7p elements as a function of basis set from MR-CISD calculations

Basis	113 $J = 3/2$	114 $J = 1$	115 $J = 3/2$	116 $J = 1$	117 $J = 1/2$
vdz	2.952	3.333	4.557	6.427	8.239
vtz	2.953	3.357	4.571	6.379	8.141
vqz	2.968	3.385	4.530	6.504	8.294
avdz	2.906	3.293	4.578	6.431	8.274
avtz	2.949	3.352	4.581	6.412	8.205
avqz	2.965	3.383	4.616	6.441	8.213

Table 7 Excitation energies of the 7s into the 7p from numerical nonrelativistic (NR) and Dirac-Fock (DF) calculation on the average of the s^2p^n and s^1p^{n+1} configurations

Z	NR	DF (lowest)	DF (prepared)
113	1.81	6.72	8.63
114	1.65	11.33	14.86
115	5.39	14.49	19.89
116	7.11	18.44	25.21
117	8.94	22.22	

Excitations into the lowest state ("lowest") and into the lowest state with only one $7p_{1/2}$ electron ("prepared") are listed

Table 8 Spinor eigenvales in hartrees for the 6p and 7p block elements from numerical Dirac-Fock (DF) calculation on the average of the s^2p^n configuration

Z	s	$p_{1/2}$	$p_{3/2}$	Z	s	$p_{1/2}$	$p_{3/2}$
81	0.449	0.211	0.177	113	0.589	0.265	0.151
82	0.567	0.275	0.220	114	0.722	0.356	0.184
83	0.686	0.338	0.261	115	0.858	0.446	0.216
84	0.810	0.403	0.302	116	0.999	0.539	0.246
85	0.938	0.470	0.343	117	1.145	0.637	0.276
86	1.071	0.540	0.384	118	1.297	0.740	0.306

Since it has been argued that the 8s could be important in the bonding of the 7p block [10], calculations on the $7p^{n-1}8s$ configuration have been carried out in the tz basis set, with the 8s explicitly represented. The radius of the outermost maximum of the 7s, 7p, and 8s spinors and the excitation energy from the ground state into the lowest state containing an 8s electron are reported in Table 9. These results are somewhat smaller than those obtained by Nash and Bursten [10], but this is probably due to the lack of correlation in the present results. Nevertheless, these calculations indicate that the cost of promotion to the 8s is probably too large for any significant participation in bonding, with the possible exception of 115. As the excitation energies tend to increase with charge state, and these elements are fairly electropositive, the 8s will be even higher in energy in bonds to lighter elements. The value of the outer radial maximum of the 8s also indicates that the bond length would have to be quite long for significant 8s density to be found between the participating atoms.

3.3 Hydrides

The simplest diatomics are the hydrides, for which a single sigma bond can be formed in the nonrelativistic case. In the regime of strong spin-orbit coupling, the spinor that forms a bond is a mixture of sigma symmetry with alpha spin and pi symmetry with beta spin. The $p_{1/2}$ spinor has 1/3 sigma density and 2/3 pi density, so a completely covalent hydride is only 1/3 bonding and 2/3 nonbonding. Likewise, the $p_{3/2}$ spinor has 2/3 sigma density and 1/3 pi density, so a completely covalent hydride is 2/3 bonding and 1/3 nonbonding. On these grounds, we would therefore expect to find weaker bonds with 113 and stronger bonds with 115, 116, and 117. The bonds are not, however, completely covalent: for all of these elements, the eigenvalue of the heavy element spinor that is involved in the bonding is smaller than that of hydrogen (see Table 8), so the sigma bond will be skewed toward H.

Table 9 Radii of the outermost maximum of the 7s, 7p, and 8s spinors in pm and excitation energy to the lowest $7p^{n-1}8s$ state in eV, from DHF calculations in the tz basis sets with an explicit representation of the 8s

Z	r(7s)	$r(7p_{1/2})$	$r(7p_{3/2})$	r(8s)	ΔE
113	106	129	187	348	4.41
114	101	119	166	314	6.63
115	97	111	153	289	2.55
116	93	105	143	269	3.10
117	90	100	136	252	3.64
118	87	96	129	238	4.17

For 114, the doubly occupied $7p_{1/2}$ forms a closed shell, and it was speculated quite early that it might behave like an inert gas [64]. Given the cost of relativistic hybridization and the fairly small sizes of the dissociation energies of hydrides in the 6p block, it is quite conceivable that 114H could be a van der Waals complex. 118H is expected to be a van der Waals complex.

The nature and trends in bonding of the hydrides have been analyzed and discussed previously [6, 19], and much of the discussion given below follows the previous findings.

Bond lengths, dissociation energies, and harmonic frequencies for the hydrides of 113, 115, 116, and 117 are presented in Table 10, in the valence basis sets with diffuse functions on the heavy element (av*n*z) and with the aug-cc-pv*n*z basis set for H. The bond length of 113H is much shorter than that of the other hydrides, in keeping with the difference in radial extent of the bonding spinor on the heavy metal, and the dissociation energy is considerably smaller, in keeping with the spin-orbit coupling of the bonding spinor on the heavy metal. The bond is considerably longer when valence correlation is included, but this is because the highest two spinors of $e_{1/2}$ symmetry contain considerable mixture of the 6d, and therefore correlating what would normally be the valence spinors is not a balanced calculation. In fact, the 1s spinor on H is spread over three spinors, $27e_{1/2}$, $28e_{1/2}$, and $30e_{1/2}$ (the HOMS). The 7s eigenvalue is about 0.6, and the $6d_{5/2}$ eigenvalue is about 0.7, which are much closer to the H eigenvalue than the $7p_{1/2}$, and therefore mixing with these spinors can be expected. The highest four $e_{1/2}$ spinors involve some degree of sd hybridization (the $29e_{1/2}$ is nonbonding), and all of them are strongly spin-orbit mixed. Overall, there is about a 0.1e hole in the 7s and in the 6d, and about 0.1e in the $7p_{3/2}$, based on Mulliken populations. Although the H is negative, its charge is only −0.14e.

Table 10 DHF and MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p monohydrides as a function of basis set size and correlating space

Molecule	Basis	SCF			MP2		
		r_e	D_e	ω_e	r_e	D_e	ω_e
113H	avdz	172.8	0.427	1,639	178.7	0.590	1,282
	avtz	170.8	0.509	1,701	174.6	0.817	1,448
	avqz	170.4	0.520	1,704	173.5	0.880	1,480
	acvdz	171.2	0.510	1,687	178.8	1.076	1,434
	acvtz	170.0	0.533	1,708	176.2	1.195	1,473
	acvqz	170.0	0.538	1,710	175.4	1.245	1,511
	Ref. [19]	170.7	0.46	1,653	173.6	1.16	1,530
					175.9	1.46	
	Ref. [14]	170.4	0.50		175.7	1.20	
					178.9	1.44	
115H	avdz	211.9	0.817	1,146	211.7	1.455	1,187
	avtz	211.6	0.852	1,143	210.3	1.566	1,213
	avqz	211.3	0.862	1,140	209.4	1.601	1,215
	acvdz	211.0	0.833	1,145	204.7	1.496	1,248
	acvtz	211.2	0.860	1,140	202.6	1.618	1,278
	acvqz	211.1	0.864	1,140	201.4	1.656	1,290
	Ref. [19]				208.4	1.82	
116H	avdz	204.5	0.698	1,357	204.3	1.366	1,378
	avtz	204.1	0.728	1,361	202.9	1.503	1,408
	avqz	203.7	0.741	1,359	202.0	1.549	1,414
	acvdz	203.6	0.719	1,359	199.3	1.408	1,433
	acvtz	203.6	0.740	1,357	197.5	1.561	1,469
	acvqz	203.5	0.744	1,357	196.5	1.609	1,495
	Ref. [19]				198.8	1.81	
117H	avdz	198.1	0.654	1,547	198.4	1.364	1,544
	avtz	197.6	0.721	1,559	197.1	1.505	1,578
	avqz	197.2	0.737	1,555	196.1	1.556	1,584
	acvdz	197.2	0.681	1,554	194.5	1.413	1,593
	acvtz	197.0	0.738	1,555	193.0	1.567	1,629
	acvqz	197.0	0.740	1,555	192.3	1.616	1,646
	Ref. [19]	198.4	0.60	1,491	192.9	1.36	1,570
					194.9	1.79	

All basis sets include diffuse functions. Results for av*n*z basis sets include valence correlation only; results for acv*n*z basis sets include valence and 6d correlation. RECP KRHF, KRMP2, and KRCCSD(T) results from Ref. [19] and 4-component KRDF, KRMP2 and KRCCSD(T) results from Ref. [14] are included for comparison. The KRCCSD(T) results are given below the MP2 results; where there are no SCF results, the values under MP2 are the KRCCSD(T) results

By contrast, there is almost no participation of the 6d or the 7s in the bonding of the hydrides of 115, 116, and 117, at the SCF level. Some relativistic hybridization is evident in 115H, but decreases across the row; the $30e_{1/2}$ is mainly $7p_{1/2}$ with a small amount of H 1s, while the $31e_{1/2}$ is the main $7p_{3/2}$ – 1s bonding spinor. These hydrides are more ionic than 113H and have Mulliken charges on the hydrogen of −0.47e for 115H, −0.43e for 116H, −0.39e for 117H. The dissociation energies do not vary much from 115 to 117: the extra electrons are going into the non-bonding $7p_{3/2,3/2}$, which is a pure π spin-orbital.

Results of calculations on 113H, 115H, 116H, and 117H with the core-valence basis sets, and diffuse functions on both the heavy element and H, are also given in Table 10. These basis sets have flexibility in both the valence region and that of the $n = 6$ shell. The MP2 results include correlation of the 6d spinor as well as the valence. Correlation of the 6d lengthens the 113H bond, but shortens the bonds for 115H, 116H, and 117H. The effects on the bond lengths are quite large. The contribution to the dissociation energy for 115H, 116H, and 117H is about 0.05 eV, compared to about 0.4 eV for 113H, but the effect on 113H is partly due to the lack of separation of the core and valence orbitals. In fact, the total correlation effect on the dissociation energy including the 6d is around 0.8 eV across the entire block. The harmonic frequencies increase somewhat for all of the elements, but not very much.

For 113H and 117H, results of KRHF, KRMP2, and KRCCSD(T) calculations using RECPs [19] and of 4-component KRDF, KRMP2, and KRCCSD(T) calculations [14]

are included. Their SCF results are similar to those obtained here. In general, there is fairly good agreement between the present results and those of other workers, though it is difficult to compare the results because of the differences in the basis sets, the level of correlation and the spinor space that was correlated. The large variations in the results indicate that obtaining quantitative results will require large basis sets, high-level correlation methods, and correlation of the core. However, the trends in bond length and dissociation energy across the row are very similar: the differences from element to element are much smaller than the differences between the methods.

Calculations on 114H and 118H reveal that both of these molecules have van der Waals minima. The results of the calculations, in the avnz basis set with valence correlation only and in the acvnz basis sets with valence and 6d correlation are presented in Table 11. No DHF minimum was found for either molecule. The van der Waals minimum is shallower for 114H than for 118H and is even too shallow to support a vibrational state, whereas 118H can support a single vibrational state. These results support the speculation of Pitzer [64] in 1975 that 114 could be a rare gas. Investigation of the potential curve in to 150 pm showed only an increase in energy with decreasing distance for 118H at all levels of theory, and thus it behaves like the other rare gases. For 114H, a similar investigation showed a uniform increase in energy with decreasing distance when only valence correlation was included, but with correlation of the 6d, a barrier leading to a second minimum was found. Results of these investigations are given in Table 12. The inner well is still above the dissociation limit, even at the quadruple-zeta level, but extrapolation of the present results to the basis set limit indicate that it might possibly be bound. In any case, the barrier is high enough to support at least one vibrational state. Thus, while 118 is a typical hard sphere, 114 is more like a candy with a hard sugar coating and a soft chocolate center: the valence shell is hard, like a rare gas, but the 6d shell is soft and enables some degree of bonding.

Table 11 Valence MP2 bond lengths (pm), dissociation energies (cm^{-1}), and vibrational frequencies (cm^{-1}) of the van der Waals minimum of 114H and 118H as a function of heavy atom basis set size and composition, with aug-cc-pvnz basis sets for H

Z	X basis	r_e	D_e	ω_e
114H	avdz	458	8.2	29.8
	avdz(8s)	459	8.2	29.6
	acvdz	456	8.1	29.8
	avtz	427	14.4	41.1
	avtz(8s)	428	14.3	40.3
	acvtz	426	14.8	41.5
	avqz	414	17.6	45.9
	acvqz	414	17.8	45.6
118H	avdz	461	18.0	38.4
	avdz(8s)	459	15.7	38.5
	acvdz	454	25.1	43.1
	avtz	431	25.4	48.5
	avtz(8s)	429	24.6	49.6
	acvtz	430	24.8	47.7
	avqz	414	34.3	57.6
	acvqz	413	33.8	53.8

Table 12 Core-valence MP2 bond lengths in pm, energies with respect to the dissociation limit in kJ mol^{-1}, and vibrational frequencies of the 114H inner minimum and barrier in cm^{-1} as a function of heavy atom basis set size, with aug-cc-pv*n*z basis sets for H

Feature	X basis	r	E	ω
Minimum	acvdz	189.5	15.4	295
	acvtz	187.2	5.3	572
	acvqz	186.7	2.9	624
Barrier	acvdz	207.8	17.6	705i
	acvtz	214.3	10.4	618i
	acvqz	216.6	8.9	595i

Some further insight into the nature of the bonding in 114H, and the role of the 6d, 7s, and relativistic hybridization, can be gained from an examination of the Mulliken populations and comparison with those from 113H. Table 13 lists the charge on the heavy atom, the populations relative to the atom (hole or excess) in the s, p, and d symmetries (where p and d populations are sums over the spin-orbit components) and the p spin-orbit symmetres. It also includes the sum of H atom populations in the subvalence $e_{1/2}$ spinors, and the s and d populations in the valence bonding spinors. Here, "valence" means the 7p spinors, and "subvalence" means the 6d and 7s spinors.

As the bond length decreases, 114H becomes more ionic, and the degree of relativistic hybridization increases rapidly, as shown by the decrease in $p_{1/2}$ population and increase in $p_{3/2}$ population. This supports the comments made by Han et al. [6] about the possible role of relativistic hybridization. The net p population does not change very much. Bonding of the H with the subvalence shells also increases, and the contribution of the subvalence shells to the valence spinors also increases, though not as rapidly as the relativistic hybridization. However, these increases do not appear to provide any bonding, certainly not at the SCF level. As reported above, correlation of the 6d (which includes some of the bonding with H) is largely responsible for bonding.

In contrast, 113H has a smaller charge that does not change much with distance, and a small excess in $p_{3/2}$ population that also does not change much with distance.

Table 13 Mulliken population data from acvtz basis sets as a function of distance for 113H and 114H, showing total populations relative to the heavy atom for s, p, d, and $p_{3/2}$ symmetries, H atom population in the subvalence 6d and 7s spinors, and s and d populations in the valence spinors

Molecule	*r*	Charge	s	d	p	$p_{1/2}$	$p_{3/2}$	H subvalence	s valence	d valence
113H	170	0.18	−0.24	−0.12	+0.17	+0.06	+0.11	0.64	0.20	0.09
	180	0.18	−0.21	−0.08	+0.10	−0.02	+0.12	0.55	0.19	0.08
	190	0.19	−0.17	−0.05	+0.03	−0.10	+0.13	0.45	0.16	0.07
114H	170	0.29	−0.17	−0.06	−0.06	−0.38	+0.32	0.35	0.15	0.08
	180	0.27	−0.14	−0.05	−0.09	−0.32	+0.22	0.31	0.11	0.06
	190	0.23	−0.10	−0.03	−0.10	−0.23	+0.12	0.13	0.06	0.03
	200	0.18	−0.07	−0.03	−0.09	−0.15	+0.06	0.10	0.02	0.01

The $p_{1/2}$ population increases and the s and d populations decrease as the distance decreases. The H population in the subvalence spinors is substantial—twice as large as for 114H—and also increases with decreasing distance. This indicates that bonding involves both the valence and subvalence spinors, much more so than for 114H.

The result for 114H is somewhat at variance with previous work, for which a minimum around 195–200 pm with a dissociation energy from 0.2–0.5 eV is found [6, 12, 16, 18], based on DFT or CCSD(T) calculations. The CCSD(T) calculations are on the lower end of this range, whereas DFT gives larger values and is likely to overestimate the binding. The MP2 method is clearly not an adequate correlation method for this molecule, and higher-order excitations are needed to locate the minimum. The present results nevertheless illustrate the central role of 6d correlation: without it, 114 behaves like a rare gas. The dissociation energy for 118H is consistent with the value of 44 cm^{-1} found by Han et al. [6].

To compare and assess the accuracy of the current 7p hydride calculations, calculations on TlH, PbH, BiH, PoH, and AtH are reported in Table 14 at the corresponding levels of theory, in the dz and tz basis sets. There is a fairly uniform decrease in the bond length across the row. The main evidence of spin-orbit coupling is a smaller dissociation energy for TlH and PbH than for the other hydrides. The Mulliken charges on H decrease fairly uniformly in magnitude from −0.35e for TlH to −0.22e for At H. The main effect of core-valence correlation is a decrease in the bond length, which applies across the entire block, including TlH and PbH. The dissociation energy and harmonic frequency do not change much with correlation of the 5d.

The change between the 6p block and the 7p block is dramatic, as noted by Han et al. [6]. The 7p block is really two distinct blocks, the $7p_{1/2}$ block and the $7p_{3/2}$ block. The former has smaller dissociation energies, significant 6d participation, lengthening of bonds on correlation, and higher covalency; the latter has little 6d participation, shortening of bond lengths on correlation, and more ionic compounds. Hints of this change are present in the 6p block, with somewhat smaller dissociation energies for TlH and PbH and a decrease from TlH to PbH.

To address the question of when diffuse functions are needed, and whether the 8s is important, calculations were carried out in the dz basis sets with and without diffuse functions on both the hydrogen and the heavy element, and with an explicit representation of the 8s on the heavy element. Calculations in the tz basis sets with and without diffuse functions and the 8s on the heavy element were also performed, with diffuse functions on the hydrogen. The results are given in Table 15. Diffuse functions on H significantly affect the properties of all the hydrides, with the exception of 113H, at the DHF level. Diffuse functions on the heavy element make some small differences to the dissociation energies in the dz basis, but at the tz level, the differences are negligible. The relative unimportance of diffuse functions on the heavy elements is in keeping with the electropositive character of these elements.

Explicit representation of the 8s makes almost no difference in any of the properties, except in the dz basis where there are no diffuse functions on H and they are compensating for deficiencies in the basis. In the light of the atomic results above, this is not surprising: the bond length is too short for the 8s to have a significant bonding effect, and the cost of promotion is too high. This is at variance with the findings of Nash and Bursten for 117H [12], whose work is based on spin-orbit CI based on spin-free calculations with an AREP. It is possible that the analysis in terms of spin-free eigenfunctions or the AREP itself places too much emphasis on the 8s. The current findings show that, in a calculation where spin-orbit coupling is included at the SCF stage, addition of the 8s on top of a diffuse set has negligible effect.

It would be premature to conclude from a study of hydrides that the 8s is not at all important; however, as there might be other systems for which it plays some role. For example, in highly symmetric systems, where there is no s function available to form a totally symmetric bonding orbital, the 8s might have some contribution. To test this

Table 14 DHF and valence MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 6p monohydrides as a function of basis set size and correlating space, with (av*nz*) and without (v*nz*) diffuse functions on the heavy atom for valence correlation; with diffuse and 6d correlating functions (acv*nz*) for valence+6d correlation; the H basis is aug-cc-pv*nz*. RECP results at the KRCCSD(T) level [6] and experimental values [65] are included for comparison

Molecule	Basis or method	SCF			MP2		
		r_e	D_e	ω_e	r_e	D_e	ω_e
TlH	vdz	188.2	1.123	1,432	191.8	1.666	1,392
	vtz	187.4	1.157	1,446	190.9	1.776	1,407
	avdz	188.3	1.125	1,430	191.8	1.667	1,391
	avtz	187.4	1.158	1,445	190.8	1.777	1,407
	acvdz	187.6	1.153	1,443	188.1	1.684	1,402
	acvtz	186.9	1.177	1,444	186.5	1.775	1,420
	RECP				187.7	2.00	
	Exp.				187.0	2.06	
PbH	vdz	184.3	0.966	1,622	186.7	1.478	1,577
	vtz	183.8	1.002	1,634	185.9	1.586	1,599
	avdz	184.3	0.966	1,621	186.6	1.480	1,577
	avtz	183.9	1.003	1,632	185.9	1.586	1,599
	acvdz	183.7	0.991	1,634	184.2	1.534	1,593
	acvtz	183.2	1.024	1,635	182.8	1.632	1,610
	RECP				182.6	1.69	
	Exp.				183.9		
BiH	vdz	181.0	1.385	1,759	182.9	1.987	1,712
	vtz	180.7	1.421	1,765	182.1	2.111	1,735
	avdz	181.1	1.382	1,759	182.9	1.980	1,713
	avtz	180.7	1.421	1,765	182.1	2.110	1,736
	acvdz	180.5	1.406	1,768	181.0	2.009	1,732
	acvtz	180.1	1.441	1,766	179.6	2.147	1,766
	RECP				183.6	2.24	
	Exp.				180.5		
PoH	vdz	176.1	1.216	1,948	178.0	1.908	1,884
	vtz	175.9	1.255	1,952	177.3	2.076	1,905
	avdz	176.1	1.218	1,951	178.0	1.912	1,886
	avtz	175.9	1.254	1,952	177.2	2.081	1,906
	acvdz	175.6	1.243	1,958	176.4	1.952	1,907
	acvtz	175.3	1.276	1,952	175.1	2.142	1,922
	RECP				178.4	2.27	
AtH	vdz	171.8	1.259	2,117	173.7	1.986	2,038
	vtz	171.6	1.340	2,122	173.1	2.163	2,058
	avdz	171.9	1.268	2,120	173.8	2.001	2,037
	avtz	171.6	1.341	2,122	173.0	2.164	2,058
	acvdz	171.4	1.296	2,129	172.4	2.051	2,058
	acvtz	171.1	1.370	2,118	171.2	2.234	2,069
	RECP				174.2	2.31	

possibility, calculations were carried out on the trihydrides of 113 and 117 in D_{3h} geometry, in the dz basis with and without the 8s. (This is not the ground state of $113H_3$, which is T-shaped [14].) The results are presented in Table 16. The same behavior is found as for the monohydrides: the 8s has no significant effect on the properties. The trihydrides are not stable to decomposition to the monohydrides and hydrogen, as pointed out by Vest et al. [27]. The dissociation energy of H_2 in the avdz basis is 3.541 at the DHF level and 4.286 at the MP2 level, so the instability is considerable.

Results for $115H_3$ were not included because it is a difficult system. At the DHF level, there is an inner covalent minimum at about 185 pm with a charge of +0.3 on 115 and an outer ionic minimum around 225 pm with a charge of +1.0 on 115. In the inner minimum, it is the 7s from which the charge is removed, and there is some amount of bonding with sd hybrid spinors. The 7p

Table 15 DHF and valence MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p monohydrides as a function of basis set composition

Z	X basis	H basis	SCF			MP2		
			r_e	D_e	ω_e	r_e	D_e	ω_e
113	vdz	vdz	172.9	0.425	1,654	178.3	0.570	1,330
	vdz(8s)	vdz	172.9	0.422	1,648	178.3	0.567	1,322
	vdz	avdz	172.9	0.428	1,640	178.7	0.590	1,284
	vdz(8s)	avdz	172.9	0.426	1,639	178.8	0.587	1,282
	avdz	avdz	172.8	0.427	1,639	178.7	0.590	1,282
	avdz(8s)	avdz	172.9	0.425	1,638	178.8	0.588	1,280
	vtz	avtz	170.8	0.508	1,701	174.7	0.813	1,443
	avtz	avtz	170.8	0.509	1,701	174.6	0.817	1,448
	avtz(8s)	avtz	170.8	0.509	1,702	174.5	0.818	1,449
115	vdz	vdz	209.4	0.819	1,214	208.5	1.395	1,272
	vdz(8s)	vdz	210.6	0.836	1,182	209.4	1.406	1,248
	vdz	avdz	211.8	0.854	1,148	211.7	1.491	1,188
	vdz(8s)	avdz	212.0	0.842	1,145	211.9	1.481	1,185
	avdz	avdz	211.9	0.817	1,146	211.7	1.455	1,187
	avdz(8s)	avdz	212.1	0.817	1,143	211.9	1.455	1,186
	vtz	avtz	211.6	0.854	1,143	210.4	1.572	1,212
	avtz	avtz	211.6	0.852	1,143	210.3	1.566	1,213
	avtz(8s)	avtz	211.7	0.853	1,142	210.3	1.566	1,212
116	vdz	vdz	203.2	0.700	1,401	202.6	1.314	1,431
	vdz(8s)	vdz	203.9	0.710	1,377	203.1	1.320	1,416
	vdz	avdz	204.6	0.719	1,355	204.5	1.389	1,374
	vdz(8s)	avdz	204.6	0.714	1,355	204.6	1.386	1,373
	avdz	avdz	204.5	0.698	1,357	204.3	1.366	1,378
	avdz(8s)	avdz	204.6	0.697	1,355	204.4	1.367	1,377
	vtz	avtz	204.1	0.732	1,363	203.0	1.507	1,408
	avtz	avtz	204.1	0.728	1,361	202.9	1.503	1,408
	avtz(8s)	avtz	204.1	0.729	1,361	202.9	1.504	1,408
117	vdz	vdz	197.5	0.649	1,575	197.4	1.303	1,578
	vdz(8s)	vdz	197.9	0.654	1,557	197.6	1.312	1,571
	vdz	avdz	198.2	0.656	1,540	198.5	1.360	1,537
	vdz(8s)	avdz	198.3	0.641	1,538	198.7	1.353	1,535
	avdz	avdz	198.1	0.654	1,547	198.4	1.364	1,544
	avdz(8s)	avdz	198.2	0.654	1,547	198.5	1.365	1,545
	vtz	avtz	197.5	0.719	1,561	197.1	1.512	1,579
	avtz	avtz	197.6	0.721	1,559	197.1	1.505	1,578
	avtz(8s)	avtz	197.6	0.721	1,559	197.0	1.506	1,578

Table 16 DHF and valence MP2 bond lengths (pm), atomization energies (eV), and vibrational frequencies (cm^{-1}) of $113H_3$ and $117H_3$ as a function of basis set composition

Molecule	Basis	SCF			MP2		
		r_e	A_e	ω_e	r_e	A_e	ω_e
$113H_3$	avdz	171.0	1.425	1,685	173.2	2.191	1,558
	avdz(8s)	170.9	1.424	1,686	173.2	2.190	1,557
$117H_3$	avdz	213.4	0.797	1,181	213.5	2.554	1,146
	avdz(8s)	213.5	0.799	1,181	213.5	2.559	1,146

population is 3.0, with some excitation from the $7p_{1/2}$ to the $7p_{3/2}$. In the outer minimum, the 7s is almost full; the charge is removed from both the $7p_{1/2}$ and the $7p_{3/2}$, and there is no sd hybridization. Between the inner minimum and the outer minimum, the highest occupied molecular spinor (HOMS) and the lowest unoccupied spinor (LUMS) cross. In the inner minimum, the HOMS is $e_{5/2}$, mostly nonbonding p_z (perpendicular to the plane) with some antibonding e' character; in the outer minimum, the HOMS is $e_{1/2}$, an almost pure a_1' orbital composed of H 1s contributions with very little s population from the heavy element, either with or without the 8s in the calculation. This further substantiates the lack of importance of the 8s, as one might expect some contribution to a more diffuse, mostly a_1' spinor.

3.4 Fluorides

The second set of calculations was performed on fluorides. In choosing the orbitals to correlate, the location of the F 2s relative to the heavy element 6d and 7s are important. The F 2s is below both the $6d_{5/2}$ and the 7s for 113, but is above the $6d_{5/2}$ and nearly degenerate with the 7s for 118. This makes it difficult to choose a consistent valence correlation set across the row, so the F 2s was included in the valence set for 118, and included in the core set with the 6d for the other elements. Likewise, for the 6p elements, the F 2s was included in the core set with the 5d.

Results for the monofluorides are given in Table 17, with diffuse functions on both the heavy element and the fluorine. Results for the acvqz basis sets are not presented because of convergence problems, due to intruders from the negative-energy states. This problem is likely to be the result of numerical issues and the heavy contraction and suggests that calculations in contracted basis sets should be done in a two-component method such as the atomic NESC method [66]. For comparison, results for the 6p monofluorides in the corresponding avdz and avtz basis sets are given in Table 18 (except for RnF, for which convergence was difficult).

The first point of note is that the DHF dissociation energies of 113F and 114F are much smaller than those of the rest of the series, and for 114F it is negative, meaning that the minimum is above the dissociation limit. As for the hydrides, the 6d is important for 113 and 114, and the valence MP2 results should not be taken too seriously. 118F has a small but positive dissociation energy at the DHF level and is bound by almost 2 eV at the MP2 level—about the same as for 114F. The remaining fluorides have sizeable dissociation energies both at the DHF level and the MP2 level. The results for 113F and 114F are consistent with the values obtained by Seth et al. [14] and Liu et al. [16].

The differences between the 7p fluorides and the 6p fluorides follow similar patterns to the hydrides. For the 6p fluorides, the properties vary fairly evenly across the block, with only a small deviation for PbF, whereas the $7p_{1/2}$ fluorides are quite different from the $7p_{3/2}$ fluorides. The dissociation energies decrease significantly from BiF to AtF, whereas the dissociation energies of 115F, 116F, and 117F decrease by about half the amount, and they are larger than those of their 6p counterparts. The $7p_{3/2}$ fluorides are about 0.1e more ionic than their 6p counterparts, which might explain the higher dissociation energy. The $7p_{1/2}$ fluorides have about the same charge as their 6p counterparts.

Results of calculations in which diffuse functions and the 8s were included in the heavy atom basis at the dz and tz levels are presented in Table 19. Diffuse functions make negligible difference to the properties of the $7p_{1/2}$ fluorides, 113F and 114F. They appear to have some effect for the $7p_{3/2}$ fluorides (115F through 118F) in the dz basis and less in the tz basis. Addition of the 8s makes negligible difference to any of the properties, with the possible exception of the DHF dissociation energy of 118F (which is in any case small). The results for the fluorides are thus consistent with the results for the hydrides.

To further test the role of the 8s in molecules with high symmetry, calculations were performed on three of the difluorides in $D_{\infty h}$ symmetry in the dz basis sets. Here, the 8s should contribute to one of the $e_{1/2g}$ spinors, to make it a bonding spinor rather than nonbonding. The results are presented in Table 20. As before, the 8s has very little effect on the properties, and even the diffuse functions have very little effect. The charge on the heavy element is around +1.6e, so these are quite ionic compounds, and they are all strongly bound, especially $116F_2$. 116 has a larger charge than 118 by about 0.1e, so the extra binding is largely ionic. There is a small excess s population, which appears mostly in the sigma-dominant $19e_{1/2g}$ spinor, but this population does not differ between the calculations with and without the 8s.

As found by others, the linear geometry is a minimum for 116 and 118, but not for 114 [13, 30]. The bond lengths obtained here are somewhat longer than those found by Han and Lee [8], and the reaction energies are a little larger, but nevertheless in reasonable agreement. The LUMS in $118F_2$ is the $7p_{3/2}$ spinor on the heavy element. It is noteworthy that the second bond in $118F_2$ is substantially stronger than the first, whereas for $116F_2$ the second bond is a little weaker. It is possible that, once the closed shell of 118 is broken, the second bond forms more easily.

3.5 Alkalis

The molecules investigated so far all have a positive charge on the heavy element. Fluorine is the most electronegative element so one expects the compounds to be ionic.

Table 17 DHF and MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p monofluorides as a function of basis set size and composition. Core-valence basis sets (acv*n*z) include 6d correlation in the MP2 calculations

Molecule	Basis	SCF			MP2		
		r_e	D_e	ω_e	r_e	D_e	ω_e
113F	avdz	220.1	0.818	434	240.9	2.683	545
	avtz	218.7	0.808	430	241.0	2.700	541
	avqz	218.0	0.825	431	241.9	2.744	543
	acvdz	219.0	0.858	432	222.9	3.137	432
	acvtz	217.9	0.831	428	220.5	3.178	437
	Ref. [14]	216.7	0.64		218.0	2.77	
					218.7	2.52	
114F	avdz	226.0	−0.345	414	231.9	1.713	436
	avtz	225.3	−0.336	412	231.2	1.742	443
	avqz	224.2	−0.317	413	230.6	1.800	447
	acvdz	225.2	−0.316	413	226.4	2.021	417
	acvtz	224.3	−0.314	410	223.8	2.056	426
115F	avdz	234.8	2.423	373	235.7	4.359	380
	avtz	234.3	2.455	374	234.3	4.431	388
	avqz	233.3	2.472	375	233.1	4.527	392
	acvdz	234.1	2.459	375	233.0	4.251	385
	acvtz	233.5	2.474	373	230.3	4.340	395
116F	avdz	229.1	1.962	426	229.9	3.858	425
	avtz	228.1	1.997	427	228.0	3.954	434
	avqz	227.0	2.024	427	226.5	4.065	439
	acvdz	228.2	2.003	427	228.6	3.713	426
	acvtz	227.2	2.024	425	225.8	3.832	436
117F	avdz	224.7	1.439	470	225.9	3.310	464
	avtz	223.4	1.512	472	223.5	3.422	474
	avqz	222.4	1.550	473	222.0	3.543	478
	acvdz	223.8	1.485	471	225.6	3.131	459
	acvtz	222.5	1.546	471	222.5	3.263	471
	Ref. [19]	225.9	1.15	443	226.9	2.82	441
					228.6	2.71	421
118F	avdz	233.3	0.170	420	237.5	1.794	409
	avtz	231.4	0.259	422	235.0	1.961	426
	avqz	230.4	0.287	424	233.6	2.048	437
	acvdz	232.3	0.204	421	235.2	1.671	404
	acvtz	230.6	0.284	421	231.6	1.814	415

Four-component results from Ref. [14] are also included; the second line of these results are the KRCCSD(T) results

Hydrogen is somewhere in the middle, but for these elements, the hydrides all have a positive charge on the heavy element. This means that diffuse functions, and the 8s, are not generally very important for these compounds. If they are important for any compounds, it is likely to be for compounds with more electropositive elements. Calculations have therefore been carried out on the closed-shell diatomics with potassium for three of the 7p elements, 113, 115, and 117. These are compared with the corresponding 6p diatomics, KTl, KBi, and KAt. Here the diffuse functions are likely to be important, as the heavy element might carry a negative charge. Their importance was substantiated in calculations on KAt.

Because the K 3p shell is lower in energy than the 6d shell for 113 and 115, correlated calculations must include the core. Results in the cvdz basis set are presented in Table 21. Both K113 and K117 are ionic, with the negative charge on the heavy atom. K113 is almost as ionic as KAt and has the shortest bond length of all the molecules considered, though its dissociation energy is not as large. It is more ionic than K117. This is partly because the $7p_{1/2}$ spinor, which forms the bond, has 1/3 sigma character for 113, whereas the $7p_{3/2}$ spinor in 117 has 2/3 sigma character. There is therefore less opportunity for covalent bonding with 113 than with 117. Because of its behavior here, 113 could be considered a pseudohalogen: the 113

Table 18 DHF and MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 6p monofluorides as a function of basis set size

Molecule	Basis	SCF			MP2		
		r_e	D_e	ω_e	r_e	D_e	ω_e
TlF	avdz	210.2	2.753	476	216.8	4.634	474
	avtz	209.3	2.754	475	216.2	4.682	477
	acvdz	209.6	2.782	476	212.8	4.643	457
	acvtz	208.2	2.789	476	210.4	4.723	460
PbF	avdz	207.7	2.208	509	211.2	4.065	497
	avtz	206.7	2.234	506	210.1	4.124	501
	acvdz	207.0	2.239	509	210.1	4.049	487
	acvtz	205.3	2.283	509	207.4	4.147	497
BiF	avdz	207.6	2.212	513	210.6	4.125	496
	avtz	206.3	2.255	511	208.7	4.218	503
	acvdz	206.8	2.243	513	210.3	4.057	489
	acvtz	204.9	2.303	513	207.2	4.264	503
PoF	avdz	206.0	1.359	536	209.4	3.328	511
	avtz	204.2	1.421	539	206.8	3.471	522
	acvdz	205.2	1.394	536	209.5	3.256	502
	acvtz	202.9	1.474	540	205.9	3.451	514
AtF	avdz	205.1	0.609	559	209.1	2.574	521
	avtz	202.9	0.712	562	206.1	2.716	532
	acvdz	204.3	0.648	558	209.6	2.501	509
	acvtz	201.7	0.769	560	205.8	2.686	520

anion has a filled $7p_{1/2}$ shell. The 6p diatomics show a consistent trend of increasing ionicity and with it increasing binding, with KTl having substantial covalent character and not much binding (negative at the DHF level). K115 is also substantially covalent, much more so than KTl; it has the longest bond length of all the molecules considered. It is also unbound at the DHF level, which is similar behavior to the alkali dimers. Correlation makes a larger difference to K113 than to KTl, indicating that the underlying "closed" shells are more important than in the typical alkali or group 13 element. However, in all of these molecules, there is almost no heavy-element s population in the bonding spinor, so the 8s is unlikely to contribute to these molecules, even though the bond length is long enough and the charge on the heavy element is negative. Results of DHF calculations in which the 8s is included in the basis, presented in Table 22, confirm that the 8s is indeed unimportant here also.

4 Discussion and summary

Basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been developed for the 7p elements, including diffuse functions for negative ion character and correlating functions for both the valence shell and the 6d shell. These basis sets have been applied in atomic and molecular calculations, both to elucidate some of the chemistry of the 7p block and to determine what is required for calculations with the basis sets.

The spin-orbit splitting is so large that the 7p block could be considered as two separate blocks with quite different characteristics: the $7p_{1/2}$ block and the $7p_{3/2}$ block.

Bonding is somewhat difficult in the $7p_{1/2}$ block because of the nature of the spin-orbit coupling in the $7p_{1/2}$ shell. Element 113 displays some halogen-like behavior: it has a substantial electron affinity; it has the least polar hydride; it forms an ionic compound with potassium. Likewise, element 114 displays some rare-gas-like behavior: it has no electron affinity, the monohydride is a van der Waals complex if only valence correlation is included. Preliminary calculations on 114O show that it is unbound both at the SCF and valence MP2 level. These results and the results of others indicate that the energetic cost for breaking the closed $7p_{1/2}$ shell is substantial. However, correlation of the 6d shell, which is very close to the valence shell, is critical: it produces binding in 114 compounds where there is none, and significantly changes the properties of 113 compounds. At the SCF level, the 7s and 6d shells mix, and both are involved in bonding orbitals. This underlines the necessity for including the 6d in any calculations on these elements: the $7p_{1/2}$ block could be considered to have some transition-metal character.

Table 19 DHF and MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p monofluorides as a function of basis set size and composition (presence of 8s and diffuse functions)

Molecule	Basis	SCF			MP2		
		r_e	D_e	ω_e	r_e	D_e	ω_e
113F	vdz	220.2	0.815	434	241.0	2.682	545
	vdz(8s)	220.2	0.815	433	241.0	2.683	544
	avdz	220.1	0.818	434	240.9	2.683	545
	avdz(8s)	220.2	0.816	434	240.9	2.682	545
	vtz	218.7	0.807	431	241.0	2.700	542
	avtz	218.7	0.808	430	241.0	2.700	541
	avtz(8s)	218.7	0.808	430	241.0	2.700	541
114F	vdz	226.1	−0.351	414	232.0	1.708	435
	vdz(8s)	226.0	−0.348	413	232.0	1.710	435
	avdz	226.0	−0.345	414	231.9	1.713	436
	avdz(8s)	226.0	−0.345	414	231.9	1.714	435
	vtz	225.3	−0.337	412	231.1	1.742	443
	avtz	225.3	−0.336	412	231.2	1.742	443
	avtz(8s)	225.3	−0.336	412	231.1	1.742	443
115F	vdz	234.9	2.468	372	235.9	4.405	379
	vdz(8s)	234.9	2.471	372	235.8	4.408	379
	avdz	234.8	2.423	373	235.7	4.359	380
	avdz(8s)	234.9	2.424	373	235.8	4.361	379
	vtz	234.3	2.456	375	234.3	4.440	388
	avtz	234.3	2.455	374	234.3	4.431	388
	avtz(8s)	234.3	2.455	374	234.3	4.431	388
116F	vdz	229.3	1.981	425	230.2	3.889	424
	vdz(8s)	229.2	1.983	425	230.1	3.890	424
	avdz	229.1	1.962	426	229.9	3.858	425
	avdz(8s)	229.1	1.962	425	229.9	3.857	425
	vtz	228.2	1.998	428	228.0	3.964	436
	avtz	228.1	1.997	427	228.0	3.954	434
	avtz(8s)	228.1	1.997	427	228.0	3.954	434
117F	vdz	225.0	1.438	469	226.4	3.322	461
	vdz(8s)	225.0	1.440	469	226.3	3.327	461
	avdz	224.7	1.439	470	225.9	3.310	464
	avdz(8s)	224.8	1.440	470	225.9	3.309	464
	vtz	223.5	1.506	472	223.7	3.435	473
	avtz	223.4	1.512	472	223.5	3.422	474
	avtz(8s)	223.4	1.513	472	223.5	3.422	474
118F	vdz	233.8	0.159	419	238.3	1.816	406
	vdz(8s)	233.7	0.170	419	238.2	1.821	406
	avdz	233.3	0.170	420	237.5	1.794	409
	avdz(8s)	233.3	0.171	420	237.5	1.795	410
	vtz	231.6	0.248	424	235.2	1.970	426
	avtz	231.4	0.259	422	235.0	1.961	426
	avtz(8s)	231.4	0.260	422	235.0	1.962	426

The $7p_{3/2}$ block is quite electropositive, forming ionic fluorides and fairly ionic hydrides. The large 7p spin-orbit splitting makes the involvement of the $7p_{1/2}$ in the bonding unfavorable: it is more like a sub-valence shell, as the 6d is for the $7p_{1/2}$ block. The contribution of the $7p_{1/2}$ to the spinors decreases across the block, as the spin-orbit splitting increases. Element 115 could be considered the alkali of the $7p_{3/2}$ block: it has the smallest IP of the entire p block, comparable to the alkalis; it forms a largely covalent compound with potassium, and a highly ionic fluoride.

Table 20 DHF and MP2 bond lengths (pm), atomization energies (eV), reaction energies $XF_2 \rightarrow X + F_2$ (eV), and symmetric stretching vibrational frequencies (cm^{-1}) of linear 7p difluorides as a function of basis set size and heavy atom basis set composition (diffuse functions, core-valence, and the 8s)

Molecule	Basis	SCF			MP2			
		r_e	A_e	ω_e	r_e	A_e	ΔE_e	ω_e
$114F_2$	vdz	229.0	−1.092	457	232.4	3.302	2.142	447
	avdz	228.9	−1.087	457	232.3	3.308	2.148	447
	avdz(8s)	228.9	−1.086	457	232.3	3.309	2.149	447
	cvdz	228.6	−1.049	457	230.1	3.839	2.476	439
	acvdz	228.5	−1.043	457	230.0	3.848	2.485	440
$116F_2$	vdz	229.1	4.384	456	230.4	8.183	7.023	446
	avdz	229.1	4.351	456	230.3	8.139	6.979	446
	avdz(8s)	229.1	4.353	456	230.4	8.140	6.980	446
	cvdz	228.5	4.451	457	229.8	7.827	6.464	446
	acvdz	228.4	4.417	457	229.7	7.791	6.428	446
$118F_2$	vdz	221.6	2.393	524	227.3	5.686	3.865	502
	avdz	221.5	2.370	523	227.1	5.629	3.835	503
	avdz(8s)	221.5	2.373	524	227.1	5.633	3.838	503
	cvdz	220.8	2.478	524	224.2	5.489	3.794	487
	acvdz	220.7	2.456	524	224.0	5.440	3.769	488

Table 21 DHF and MP2 bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p and 6p diatomics with potassium in the acvdz basis set, along with Mulliken charges and 4s population on K at the DHF equilibrium bond length

Molecule	q(K)	K(4s) pop	SCF			MP2		
			r_e	D_e	ω_e	r_e	D_e	ω_e
K113	0.89	0.07	318.3	0.343	134	317.1	1.225	128
K115	0.28	0.68	383.6	−0.229	83	364.6	1.038	97
K117	0.80	0.13	348.2	0.650	122	340.9	1.366	129
KTl	0.56	0.41	360.9	−0.288	91	356.0	0.099	92
KBi	0.71	0.24	349.8	0.280	125	343.5	1.506	127
KAt	0.89	0.06	325.9	1.729	154	322.0	2.304	157

Element 117 is a halogen much like At, but is considerably less electronegative. Likewise, element 118 forms strongly bound fluorides (as already noted by several others) and is much less inert than the lighter rare gases. Because of the electropositive character, diffuse functions are rarely needed except in compounds with other electropositive elements. The 6d is not involved in the bonding orbitals. 6d correlation is not quite as important as in the $7p_{1/2}$ block, but still has a significant effect on bond lengths and dissociation energies.

Table 22 DHF bond lengths (pm), dissociation energies (eV), and vibrational frequencies (cm^{-1}) of 7p – potassium diatomics in the augmented dz basis sets as a function of the presence of the 8s in the heavy atom basis

Molecule	Basis	r_e	D_e	ω_e
K113	avdz	318.8	0.329	134
	avdz(8s)	318.7	0.326	134
K115	avdz	383.5	−0.229	83
	avdz(8s)	383.7	−0.228	83
K117	avdz	348.3	0.651	122
	avdz(8s)	348.3	0.651	122

Investigation of the possible role of the 8s in the bonding of the 7p elements found that an explicit representation of this orbital had negligible effect on any of the molecules considered. Though the current tests are necessarily limited, the negligible role that the 8s plays in the potassium compounds, where one might expect promotion from the $7p_{3/2}$ to the 8s to favor bonding, indicates that it is unlikely to play an important role in any compounds of the 7p elements, other than as a correlating orbital. It is likely that earlier findings of an importance to the 8s can be ascribed to the methodology, in which the spin-orbit coupling was added after the SCF stage.

The role of correlation appears to be critical for many properties. The present results and comparison with higher-level CCSD(T) results from other work show considerable variability of properties with basis set, correlation level, and reference spinor space. This indicates that higher-level excitations are important for accurate results. Preliminary calculation on the dioxides of 114, 116, and 118 showed

that a multireference method is mandatory for the reference state.

For calculations using the basis sets described here, it is generally recommended that the core-valence sets be used and the 6d be correlated. Diffuse functions are not necessary except when some anionic character is expected, in compounds with other electropositive elements, or perhaps when high accuracy is desired. Accurate results are likely to be obtained only with large basis sets and a high level of correlation including the outer core.

5 Internet archive

The full tables of basis sets including spin-free relativistic SCF [67] and Dirac-Fock SCF coefficients are available in ASCII format from the Dirac web site, http://dirac.chem.sdu.dk, and as an internet archive. The spin-free relativistic SCF coefficients include the Foldy-Wouthuysen transformed large component coefficients that can be used in the scalar one-electron approximation, NESC1e [68]. The correlating, polarizing, and diffuse functions are included, and prescriptions are given for the construction of various contracted basis sets.

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