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Relativistic Double-Zeta, Triple-Zeta, and Quadruple-Zeta Basis Sets for the 4s, 5s, 6s, and 7s Elements[†]

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Relativistic basis sets of double-zeta, triple-zeta, and quadruple-zeta quality have been optimized in Dirac−Hartree−Fock calculations for the 4s, 5s, 6s, and 7s elements: K, Ca, Rb, Sr, Cs, Ba, Fr, and Ra. The basis sets include SCF exponents for the occupied spinors and for the *n*p shell, exponents of correlating and polarizing functions for the $(n - 1)$ shell and correlating functions for the $(n - 2)$ shell. For the group 2 elements, correlating functions are given for the *n*s and *n*p shells, whereas for the group 1 elements, functions for polarization of the *n*s shell are provided. A finite nuclear size was used in all optimizations. Prescriptions are given for constructing contracted basis sets by addition of primitives to the SCF occupied functions.

Introduction

Basis set development for the heavy elements has become an important task, since all-electron, four-component methods for treating these elements are now routinely available[1−5] and methods based on the scalar Douglas−Kroll−Hess (DKH) Hamiltonian[20−22] have been available in many nonrelativistic quantum chemistry packages for some time. Several groups have already contributed to this task and have provided basis sets for the Dirac−Coulomb Hamiltonian[6−19] or the Douglas−Kroll−Hess Hamiltonian[23−34] Some of these basis sets are SCF sets only—particularly those for the heavy elements—and lack functions for polarization and correlation that are vital for the proper description of molecules. Others include correlating functions as either contracted functions, such as ANOs,[35] or additional primitives of higher angular momentum. This paper is one of a series of papers[10−15] presenting relativistic all-electron basis sets that include valence and outer-core correlating and diffuse or dipole polarization functions in addition to the SCF sets. These basis sets are designed in the style of the correlation-consistent basis sets of Dunning[36] in an increasing sequence of accuracy, which can be used for extrapolations.[37] The main goal of the present series is to provide basis sets that give fairly uniform quality across the lower portion of the periodic table. This paper aims to fill one of the gaps in the coverage by providing basis sets for the 4s, 5s, 6s, and 7s elements. The paper describes the development of the primitive basis sets (exponent optimization) and provides information on contracting the basis set in the style of the correlation-consistent basis sets.

For the p block, providing a uniform treatment was relatively easy: none of the elements had to be treated in a special way, and the changes in exponents across the block were fairly uniform, although some compromises had to be made for the contraction patterns. Likewise, the d block required no special considerations in the generation of the basis sets or the determination of contraction patterns, although the occupation of the 5s orbital in the 4d block required some attention. The 5f block proved more challenging because of the changes in the nature of the 5f spinor along its length and because the 6d is occupied for several of the elements.

The s block has challenges of its own. The valence shells of the two elements of each s block have different character. The alkali metals have a single electron outside a closed shell, and there is therefore no valence correlation to consider, whereas the alkaline earths have a doubly occupied s orbital for which the near-degeneracy with the p orbital of the same principal quantum number is important in its correlation. The spatial extent of the s orbital is also a consideration: moving across the rows, the s orbital shrinks, and what is an appropriate basis set size at the beginning of the row might be too large at the end of the row. The s orbital for the alkali metals is particularly diffuse and may require extra functions. The decreasing mean radius of the inner s orbitals also means that more functions are required in the core, in general, but as the nuclear size increases, a point is reached at which the number of functions needed in the core stabilizes and then decreases.

Nevertheless, it is reasonable to expect the basis sets for the *n*s block to resemble the adjacent $(n - 1)$p block, with the addition of functions for the *n*s shell. However, with the addition of a new s shell, the requirements for the existing s shells change somewhat. There is also the question of polarization of the $(n - 1)$ shell, which in the p block was covered by the addition of diffuse functions for the negative ion. In the s elements, there is a large gap between the *n*s and the $(n - 1)$s so that the functions used to describe the outer maximum of the *n*s cannot be assumed to represent the polarization of the $(n - 1)$ shell. Since this polarization cannot be neglected, it will be necessary to generate functions for polarization as well as for correlation. A further issue is that the alkali metals almost always appear as positive ions, which raises the question of whether the *n*s functions are really necessary or whether some truncated set can be used without loss of accuracy.

Methods

The numerical methods and algorithms used have been described previously.[10,11,38,39] The specific choices and strategies used with these methods are described in this section.

The SCF basis sets were optimized in average-of-configuration Dirac−Hartree−Fock calculations using the Dirac−Coulomb Hamiltonian with the standard Gaussian nuclear charge distribution,[40] chosen for the most common or the most stable

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isotope. As for the previous basis sets, *l*-optimization was employed: basis functions for a given *l* have the same exponents, regardless of *j*. In the SCF optimizations, the exponents are varied only within a given angular space, i.e. for a given *l* value, with all other exponents fixed. The exponents in each angular space are to a large degree independent of the other angular spaces. The angular spaces are cycled through the optimization process until there is no significant change in the total energy and the gradient with respect to the logarithms of the exponents. This usually takes only two cycles through the exponents.

The size of the basis sets was determined from a series of optimizations on each atom, taking the basis sets from the preceding and the following blocks of the periodic table as a guide.

After optimizing the SCF sets, functions were added for the description of the *n*p orbital: two for the double-zeta (dz) sets, three for the triple-zeta (tz) sets, and four for the quadruple-zeta (qz) sets. For the alkali metals, these functions were optimized with the rest of the functions frozen, and then these functions were frozen, and the SCF functions for the maxima of the remaining p functions, except for the 2p, were reoptimized. This procedure was necessary because of the diffuseness of this p function: there is more energy to be gained by adding functions to the core than by adding to the *n*p function, and adding to the core risks unbalancing the basis set. For the tz basis sets, even this procedure was insufficient to prevent collapse, so the added functions were optimized on the p orbital eigenvalue rather than the SCF energy. Optimizing on the orbital eigenvalues for the dz and qz basis sets resulted in exponents that differed very little from those in which the SCF energy was used to optimize the exponents. For the alkaline earths, the added p functions were optimized in the np^2 configuration along with those for the maxima of all except the 2p function. For Ca, only three functions were added to the base 17p set in the quadruple-zeta basis, because the outermost p function had small weight in the 3p and significant weight in the 4p.

Correlating functions for the $(n - 1)$ shell were optimized in singles and doubles configuration interaction (SDCI) calculations on the ground state, using the RAMCI program[39] modified for basis set optimization. Single and double excitations out of the $(n - 1)$s and $(n - 1)$p shells into the correlating orbital space were coupled to $J = 0$ before coupling to the valence electrons to ensure that the correlation was restricted to the chosen shells. The correlating space was 1s1p1d for the dz basis sets, 2s2p2d1f for the tz basis sets, and 3s3p3d2f1g for the qz basis sets. The s and p functions were taken from the SCF sets, and the remaining functions were optimized.

A similar strategy was adopted for the $(n - 2)$d shell, but the occupied symmetries were omitted, giving correlating spaces of 1f for dz, 2f1g for tz, and 3f2g1h for qz. For $n = 4$, correlating 1d, 2d1f, and 3d2f1g sets were optimized for correlation of the 2s and 2p shells in the same way as for the 3s and 3p shells. The only quirk in this set was the similarity of the outer d function in the Ca qz set to the inner d function from the $(n - 1)$ shell correlating set; the outer d function for 2s2p correlation is therefore discarded.

Once the correlating functions were determined, the occupied d SCF sets were reoptimized with the addition of the correlating d functions from the $(n - 1)$ shell, as follows. For the dz basis sets, the d function was simply added to the d set and frozen, and the other functions were reoptimized. For the tz sets, the outermost SCF d function was replaced with the two d correlating functions, which were frozen while the remaining functions were reoptimized. Likewise, for the qz sets, the outermost two SCF d functions were replaced with the three d correlating functions, which were frozen while the remaining functions were reoptimized. A different procedure was used for the qz basis sets for $n = 6$ and 7 because the inner two correlating d functions were quite close to each other and likely to cause linear dependence. Instead, the largest correlating d exponent was replaced with the third-smallest SCF d exponent, and the other two correlating exponents were reoptimized in SDCI calculations with this replacement exponent frozen. The two exponents thus reoptimized were not very different from the two smallest SCF exponents.

For $n = 7$, the occupied f set was also reoptimized, with the addition of the correlating f functions for the $(n - 2)$d shell. For the dz basis sets, the f function was simply added to the f set and frozen, and the other functions were reoptimized. For the tz sets, the outermost SCF f function was replaced with the two f correlating functions, which were frozen while the remaining functions were reoptimized. Likewise, for the qz sets, the outermost two SCF f functions were replaced with the three f correlating functions, which were frozen while the remaining functions were reoptimized.

The valence *n*s correlation for the alkaline earths was treated by performing a multireference singles and doubles CI (MR-SDCI) calculation on the ground state, with the active space consisting of the *n*s and *n*p orbitals. Correlating sets of 1d, 2d1f, and 3d2f1g were optimized for the dz, tz, and qz basis sets, respectively. This amounts to treating the *n*p orbital as significantly occupied and, therefore, needing to be correlated. There is some possible overlap of these correlating exponents and the exponents for the $(n - 1)$ shell, which was handled as follows. For the dz basis sets, there is no linear dependence problem, and the d exponent was retained. For the tz basis sets (except for Ca, for which there is no linear dependence), the inner d function was replaced by the outer correlating d function from the $(n - 1)$ shell, to which it is similar. For Sr and Ra, the outer d function was reoptimized with the replacement frozen; for Ba, the similarity is so great, there was no need for the reoptimization. For the qz basis sets, the inner d function was discarded for all elements, and the outer two d functions were reoptimized. The inner f function was discarded for all except Ca, for which there was no linear dependency. The outer f was reoptimized for Ba and Ra. In the case of Ra, the two f exponents coalesced in the original optimization, so there was effectively only one function in any case. Thus, the additional functions for valence correlation amounted to 1d, 1d1f, and 2d1f1g for the dz, tz, and qz basis sets, except for Ca qz with a 2d2f1g additional set.

The alkali metals, having only one valence electron, have no valence correlation. Nevertheless, it is important to provide functions for the flexibility of this set. The strategy used was as follows. For the dz sets, the *n*p orbital was regarded as providing sufficient flexibility, with one function uncontracted. For the tz sets, a d function was added whose mean radius matched the mean radius of the second smallest SCF s function, in addition to uncontracting two of the functions from the *n*p orbital. For the qz sets, the outermost three s exponents from the tz sets were used to derive a 2d1f set: the mean radius of the f was matched to the middle s exponent, and the mean radii of the two d functions were matched to the outer and inner s exponents.

For the dipole polarization of the $(n - 1)$p shell, an s function and a d function were optimized in separate calculations by maximizing the second-order perturbation estimate of the polarizability of the $(n - 1)$p shell. The states used for the first-order wave function were obtained by diagonalizing the Hamiltonian in the basis of all dipole-allowed single excitations from the p shell in the ground state into a set of s shells for the s function and a set of d shells for the d function. These shells were obtained by orthogonalizing a set of primitive functions. In addition to the function to be optimized, the primitives for $(n - 1)$ shell flexibility (as described below) were used for the s function, and the correlating primitives were used for the d function. The exponents of these functions were held fixed, and only a single function was optimized. In this way, the polarizing function is optimized in the presence of the uncontracted functions that are added to the SCF functions for basis set flexibility.

Using a similar procedure for the dipole polarization of the $(n - 1)$s shell, it was found that the p exponent is already included in the SCF set for the $(n - 1)$p orbital. Therefore, to obtain a function for radial relaxation (monopole excitation) of the $(n - 1)$p shell, the ratio of the s polarization exponent to the outermost SCF s exponent for the $(n - 1)$s was applied to the outermost SCF p exponent for the $(n - 1)$p.

To generate dipole polarizing functions of higher angular momentum, the ratio of the optimized d polarization exponent to the smallest d correlating exponent for the $(n - 1)$ shell was applied to the smallest correlating exponent for each higher angular momentum. For the tz basis set, the d ratio was applied to the f correlating exponent to generate an f polarizing exponent. Likewise for the qz basis set, the d ratio was applied to the lowest f correlating exponent to generate an f polarizing exponent and to the g correlating exponent to generate a g polarizing exponent.

Because of the rather loose use of the term “polarization” function, the functions thus generated are here termed “dipole polarization” functions, since they are intended to describe the polarization of the outer part of the $n - 1$ shell in response to an applied external field, which could include that provided by another atom or ion as well as a macroscopic electric field.

The contraction coefficients for the SCF occupied orbitals were obtained from calculations on a weighted average of the ns^q and np^q configurations. The individual CSFs in each configuration were weighted by their degeneracy $(2J + 1)$, and the weights were scaled so that the weights of the ns^q and np^q configurations were in the ratio 4:1 (80% s, 20% p).

To determine which primitive functions should be uncontracted, a sequence of MR-SDCI calculations was performed on each element, in which different primitive functions were included in the correlating space. 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, thereby providing an orthogonal set for the CI calculations. For each basis set size, the appropriate number of primitive functions was used in the MR-SDCI calculations. For example, for $5s5p$ correlation in the tz basis sets for Cs and Ba, the correlating set was 2s2p2d1f. The valence contraction pattern for the alkali metals was taken to be the same as for the alkaline earths.

Primitive Basis Sets

The SCF basis set sizes, including functions for the np orbital, are given in Table 1. Note that the s sets are larger for the alkali metals than for the alkaline earths due to the extra diffuseness of the ns function. This is particularly noticeable in the qz basis sets for Cs and Ba, but for Fr, relativistic effects are large enough to pull in the 7s orbital, and the extra functions are not needed.

TABLE 1: Primitive SCF Basis Set Sizes

element	double-zeta	triple-zeta	quadruple-zeta
K	15s11p	23s16p	30s21p
Ca	15s11p	23s16p	30s20p
Rb	20s14p7d	28s20p10d	34s25p12d
Sr	20s14p7d	28s20p10d	33s25p12d
Cs	24s18p10d	31s24p13d	37s30p17d
Ba	24s18p10d	30s24p13d	35s30p17d
Fr	26s23p13d8f	33s29p16d10f	37s34p21d12f
Ra	26s23p13d8f	33s29p16d10f	37s34p21d12f

TABLE 2: Total SCF Energies in E_h for Uncontracted Basis Set and Numerical Calculations on the ns^q Configuration

element	double-zeta	triple-zeta	quadruple-zeta	numerical
K	−601.518 384	−601.525 848	−601.525 950	−601.525 954
Ca	−679.702 410	−679.710 052	−679.710 157	−679.710 161
Rb	−2 979.791 452	−2979.804 731	−2 979.804 990	−2 979.805 013
Sr	−3 178.067 032	−3178.079 694	−3 178.079 945	−3 178.079 969
Cs	−7 786.761 762	−7786.771 327	−7 786.771 651	−7 786.771 668
Ba	−8 135.635 720	−8135.644 694	−8 135.645 008	−8 135.645 011
Fr	−24 308.181 513	−24308.193 688	−24 308.194 271	−24 308.193 350
Ra	−25 028.176 815	−25028.188 287	−25 028.188 853	−25 028.187 810

TABLE 3: Configuration Average Total SCF Energies in E_h for Uncontracted Basis Set Calculations on the Weighted Average of the ns^q and np^q Configurations Used for the Contractions

element	double-zeta	triple-zeta	quadruple-zeta
K	−601.507 949	−601.515 389	−601.515 491
Ca	−679.669 355	−679.677 014	−679.677 119
Rb	−2 979.781 580	−2 979.794 818	−2 979.795 076
Sr	−3 178.036 316	−3 178.048 957	−3 178.049 207
Cs	−7 786.753 078	−7 786.762 609	−7 786.762 932
Ba	−8 135.609 193	−8 135.618 159	−8 135.618 474
Fr	−24 308.171 552	−24 308.183 684	−24 308.184 265
Ra	−25 028.146 320	−25 028.157 780	−25 028.158 344

The qz basis for K has a somewhat irregular distribution of the outer four exponents and was difficult to converge; however, the energy surface for optimizing these exponents is extremely flat, and it was possible to optimize to a nearby set from almost any starting guess. For the tz basis sets, the exponents for the np function were tighter than expected in the original optimizations, reflected in coefficients with a 0.1, 0.5, 0.4 distribution rather than 0.3, 0.5, 0.2. This is attributed to the greater energy gain to be had from describing the tail of the $(n - 1)$p orbital. A similar problem was not observed for the dz and qz basis sets. The tz basis sets were therefore reoptimized on the np orbital eigenvalue (as described above), which resulted in a 0.2, 0.5, 0.2 distribution of coefficients.

Total energies for the ground state from uncontracted calculations using these basis sets are compared with the numerical values in Table 2. The energies for Fr and Ra in the tz and qz sets go below the numerical limit because the kinetic balance condition imposed on the exponents only ensures that the energy is in error by no more than the order of c^{-4}. The energy optimization is, in fact, bounded from below and cannot collapse, but it does not converge to the numerical Dirac−Fock energy. This problem is known as *prolapse*.[8]

Total energies for the 4:1 weighted average of the ns^q and np^q configurations used to contract the basis sets are given in Table 3. These energies should serve as a reference for verification purposes. In all cases, the standard Gaussian nuclear charge distribution[40] was used, in which the nuclear radius is determined from the mass number of the most abundant or most stable isotope.

Due to the presence of the spin−orbit interaction, there are more primitives in the core region than might be obtained with

TABLE 4: Functions To Uncontract for the Double-Zeta Basis Sets, Counting from the Smallest Exponent

n	s	p	d
	Valence and $n-1$ Shell		
4	1,3	1,3	
5	1,3	1,3	1
6	1,3	1,3	1
7	1,3	1,3	1
	$n-2$ Shell		
4	5	5	
5	5	5	2
6	5	5	2
7	5	5	2

TABLE 5: Functions To Uncontract for the Triple-Zeta Basis Sets, Counting from the Smallest Exponent

n	s	p	d	f
	Valence and $n-1$ Shell			
4	1,3,4,6	1,2,4,5		
5	1,3,4,6	1,3,4,6	1,2	
6	1,3,4,6	1,3,4,6	1,2	
7	1,3,4,6	1,3,4,6	1,2	1
	$n-2$ Shell			
4	7,9	8,9		
5	7,9	7,8	3,4	
6	7,9	7,9	3,4	
7	7,9	7,9	3,4	2,3

TABLE 6: Functions To Uncontract for the Quadruple-Zeta Basis Sets, Counting from the Smallest Exponent

n	s	p	d	f
	valence and $n-1$ Shell			
4	1,2,4,5,6,8	1,2,3,5,7,8		
5	1,2,4,5,6,8	1,2,4,5,6,8	1,2,3	
6	1,2,4,5,6,8	1,2,4,5,6,8	1,2,3	
7	1,2,4,5,6,8	1,2,4,6,7,8	1,2,3	1,2
	$n-2$ Shell			
4	9,10,12	9,11,12		
5	10,11,12	9,10,11	4,6,7	
6	10,11,12	10,11,12	4,5,6	
7	9,10,11	9,10,11	4,5,6	3,4

TABLE 7: Ionization Potentials of the Group 1 Elements As a Function of Basis Set and Correlation Level

element	method	dz	tz	qz	extrap $1/n^3$	extrap A^{-n}	num	expt
K								
	SCF	4.016	4.021	4.021	4.021	4.021	4.021	
	cv	4.227	4.353	4.409	4.451	4.460		
	cvcc	4.152	4.215	4.245	4.266	4.269		
	expt							4.3407
Rb								
	SCF	3.795	3.779	3.800	3.816	3.807	3.800	
	cv	4.087	4.104	4.248	4.312	4.087		
	cvcc	3.995	3.972	4.073	4.131	4.162		
	expt							4.1771
Cs								
	SCF	3.473	3.477	3.477	3.477	3.477	3.477	
	cv	3.752	3.902	3.951	3.987	3.976		
	cvcc	3.654	3.730	3.760	3.781	3.781		
	expt							3.8939
Fr								
	SCF	3.583	3.588	3.588	3.588	3.587	3.588	
	cv	3.909	4.068	4.120	4.158	4.147		
	cvcc	3.801	3.886	3.927	3.958	3.969		
	expt							4.0727

TABLE 8: Ionization Potentials of the Group 2 Elements As a Function of Basis Set and Correlation Level

element	method	dz	tz	qz	extrap $1/n^3$	extrap A^{-n}	num	expt
Ca								
	SCF	5.141	5.141	5.141	5.141	5.141	5.141	
	cv	6.019	6.077	6.093	6.105	6.099		
	cvcc	5.740	5.736	5.732	5.729	5.727		
	expt							6.1132
Sr								
	SCF	4.750	4.750	4.750	4.750	4.750	4.750	
	cv	5.583	5.634	5.656	5.672	5.674		
	cvcc	5.374	5.339	5.342	5.345	5.353		
	expt							5.6949
Ba								
	SCF	4.281	4.281	4.281	4.281	4.281	4.281	
	cv	5.074	5.124	5.149	5.166	5.169		
	cvcc	4.855	4.848	4.850	4.852	4.861		
	expt							5.2117
Ra								
	SCF	4.357	4.358	4.358	4.358	4.359	4.358	
	cv	5.118	5.186	5.215	5.236	5.237		
	cvcc	4.934	4.944	4.949	4.953	4.957		
	expt							5.2784

a spin-averaged method, such as the DKH method. However, this should not be a disadvantage when using this primitive set with the DKH Hamiltonian because the core region is fairly well covered, at least for energy calculations. For high accuracy of nuclear properties, it has been found that energy-optimized basis sets must be supplemented in the core region. Of more importance is the use of a finite nucleus, which for the heavier elements results in a significantly smaller size of the largest exponent. It is recommended that these basis sets be used with a finite nucleus; use with a point nucleus could result in errors due to the less adequate representation of the singularity at the nucleus.

Contraction Patterns

The MR-SDCI calculations that were performed to determine which primitive functions to use yielded the contraction patterns given in Tables 4, 5, and 6. The contracted basis sets are formed by adding these primitive functions to the SCF occupied spinor or orbital set, which is taken to include the *n*p. The contraction patterns can be used for any relativistic method, scalar or spinor, in conjunction with a suitable set of SCF functions derived with the chosen relativistic Hamiltonian.

Two primary contraction patterns are described: one for the valence s electron and the outer-core s and p electrons, and one that adds functions for the $(n - 2)$ shell. The contraction patterns include an extra *p* function in the valence space because the *n*p orbital is counted as part of the valence space, even though it is not formally occupied. The functions are counted by increasing exponent size from the smallest.

To these basis sets, the correlating functions described above should be added, except for those functions that were included in the SCF basis set for reoptimization of the d exponents (and the f exponents for Fr and Ra). To be specific, these functions are the outer-core d correlating functions for $n = 5-7$, and the correlating f functions for the $n - 1$ and $n - 2$ shells for $n = 7$.

The full tables of basis sets, including spin-free modified Dirac[44] and Dirac−Fock SCF coefficients, are available in ASCII format from the Dirac Web site, http://dirac.chem.sdu.dk. The spin-free modified Dirac coefficients include the Foldy−Wouthuysen transformed large component coefficients that can be used in the scalar one-electron NESC approximation presented by the author.[45]

Applications

To test the basis sets, calculations have been performed on a number of systems. First, the ionization potentials for all of the atoms have been calculated in singles and doubles CI calculations, using RAMCI. Two correlating spaces were used: a

TABLE 9: Bond Length in pm of the Alkali Dimers As a Function of Basis Set and Correlation Level

			MP2				MCMP2		
molecule	basis	SCF	bond	$+(n-1)$p	$+(n-1)$s	MCSCF	bond	$+(n-1)$p	$+(n-1)$s
K_2									
	dz	418.7	418.4	402.6	403.0	450.8	433.7	419.2	419.7
	tz	418.6	417.7	394.3	394.1	449.0	428.6	407.5	407.3
	qz	418.4	416.5	389.9	389.3	448.2	426.1	402.4	402.1
	extrap	418.1	414.9	384.4	383.3	447.3	422.9	397.3	396.5
	expt				392.4				392.4
Rb_2									
	dz	453.5	453.7	428.3	428.7	489.5	472.0	448.9	449.4
	tz	452.4	452.0	421.6	420.9	486.7	465.0	437.6	437.1
	qz	452.2	450.9	417.3	416.3	485.9	462.4	433.0	432.5
	extrap	451.9	449.6	412.2	410.9	484.9	459.3	429.7	429.3
	expt				418				418
Cs_2									
	dz	506.6	507.1	479.5	479.6	549.3	529.5	504.3	504.6
	tz	505.5	504.5	467.1	466.1	544.6	519.1	491.3	491.0
	qz	505.2	503.9	462.8	461.4	543.7	516.5	494.0	493.7
	extrap	504.8	503.3	457.9	455.9	542.4	513.0	495.4	495.1
	expt				464.6				464.6
Fr_2									
	dz	498.0	500.1	471.3	471.2	542.3	526.0	499.3	499.4
	tz	497.1	498.0	459.6	458.6	537.1	515.5	480.4	479.5
	qz	497.0	498.5	455.8	454.4	536.4	513.8	474.5	473.1
	extrap	496.9	499.1	451.3	449.5	535.5	511.7	467.1	465.3

TABLE 10: Dissociation Energy in eV of the Alkali Dimers As a Function of Basis Set and Correlation Level

			MP2				MCMP2		
molecule	basis	SCF	bond	$+(n-1)$p	$+(n-1)$s	MCSCF	bond	$+(n-1)$p	$+(n-1)$s
K_2									
	dz	–0.136	0.183	0.199	0.199	0.158	0.260	0.289	0.288
	tz	–0.121	0.286	0.327	0.322	0.162	0.322	0.376	0.371
	qz	–0.115	0.330	0.400	0.402	0.165	0.348	0.429	0.431
	extrap	–0.106	0.390	0.501	0.514	0.168	0.384	0.503	0.515
	expt				0.520				0.520
Rb_2									
	dz	–0.157	0.136	0.168	0.168	0.130	0.218	0.262	0.262
	tz	–0.144	0.240	0.302	0.304	0.135	0.276	0.349	0.350
	qz	–0.139	0.281	0.366	0.370	0.136	0.300	0.393	0.396
	extrap	–0.132	0.338	0.456	0.462	0.139	0.332	0.454	0.459
	expt				0.485				0.485
Cs_2									
	dz	–0.179	0.089	0.114	0.114	0.099	0.173	0.209	0.209
	tz	–0.157	0.204	0.261	0.254	0.104	0.231	0.295	0.288
	qz	–0.150	0.245	0.341	0.347	0.107	0.255	0.350	0.353
	extrap	–0.141	0.303	0.452	0.475	0.112	0.288	0.425	0.444
	expt				0.452				0.452
Fr_2									
	dz	–0.195	0.062	0.099	0.099	0.099	0.164	0.204	0.204
	tz	–0.169	0.176	0.270	0.274	0.107	0.219	0.308	0.311
	qz	–0.167	0.210	0.331	0.337	0.108	0.236	0.350	0.354
	extrap	–0.164	0.256	0.415	0.424	0.109	0.261	0.408	0.415

core−valence space (labeled cv), in which simultaneous single excitations from the outer core ($n - 1$ shell) and the valence ns orbital were included, along with double excitations from the valence space for the alkaline earths; and a core−valence/core−core space (labeled cvcc) in which double excitations from the outer core were also included. The first space allows an assessment of the effect of polarization of the core on the IP; the second includes core−core correlation. All calculations were performed with the Dirac−Coulomb Hamiltonian. Results for the basis set limit were extrapolated from the tz and qz results by applying a simple $1/n^3$ extrapolation[37] and an exponential extrapolation to the correlation correction. The SCF IP for the qz basis set is already at the basis set limit, as determined by numerical SCF calculations with GRASP on the atom and the ion.

The results are presented in Tables 7 and 8. Including only the core−valence correlation leads to an overestimate of the ionization potential, as compared to the calculations that include core−core correlation. This result would cast doubt on the use of one-electron pseudopotentials, even with core polarization potentials added.

The second test system was the alkali metal dimers. Calculations were performed with DREAMS[41] using the core−valence contracted basis sets described above. SCF and two-configuration MCSCF ($e_{1/2g}{}^2 + e_{1/2u}{}^2$) calculations followed by Kramers-restricted, second-order perturbation (PT2) calculations with the 0th-order Hamiltonian proposed by the author[42] were performed at a set of points around the minimum, spaced at 5 pm, for both the dimer and the monomer with a ghost. The counterpoise-corrected energies were fit to a fourth-order polynomial includ-

TABLE 11: Harmonic Frequency in cm^{-1} of the Alkali Dimers As a Function of Basis Set and Correlation Level

			MP2				MCMP2		
molecule	basis	SCF	bond	$+(n-1)$p	$+(n-1)$s	MCSCF	bond	$+(n-1)$p	$+(n-1)$s
K_2									
	dz	84.8	82.3	87.4	87.3	58.2	68.9	73.1	73.0
	tz	86.0	84.8	93.6	93.9	59.4	74.5	81.7	82.3
	qz	86.4	86.7	96.8	96.9	59.9	77.2	90.4	91.7
	extrap	87.0	89.2	102.6	103.4	60.5	80.7	102.6	103.1
	expt				92.0				92.0
Rb_2									
	dz	52.4	50.7	55.3	55.2	35.0	41.6	45.5	45.5
	tz	53.3	52.5	58.9	59.1	35.8	45.4	50.9	51.1
	qz	53.5	53.6	61.4	61.7	36.0	47.0	60.3	61.3
	extrap	53.8	55.1	65.1	65.5	36.4	49.1	77.8	79.5
	expt				57.8				57.8
Cs_2									
	dz	36.5	35.1	38.3	38.3	23.3	28.0	30.8	30.8
	tz	37.6	37.3	42.5	42.7	24.2	31.6	51.9	53.1
	qz	37.7	38.0	44.7	45.0	24.4	32.5	62.9	64.3
	extrap	37.9	38.9	47.5	46.9	24.6	32.6	80.2	82.1
	expt				42.0				42.0
Fr_2									
	dz	29.3	28.1	31.4	31.5	18.6	21.8	24.6	24.6
	tz	30.3	29.9	35.0	35.3	19.3	24.4	29.2	29.4
	qz	30.2	30.0	36.1	36.3	19.3	25.0	29.9	30.1
	extrap	30.1	30.2	37.5	37.8	19.3	25.7	32.6	33.3

TABLE 12: Bond Length, Dissociation Energy, and Harmonic Frequency of KCl As a Function of Basis Set and Correlation Level

method	basis	r_e/pm	D_e/eV	ω_e/cm^{-1}
SCF				
	dz reg	277.7	4.751	260.0
	dz + pol	275.6	4.847	264.7
	dz ion	275.5	4.845	265.1
	tz reg	274.6	4.855	263.4
	tz + pol	274.3	4.884	265.0
	tz ion	274.3	4.883	265.2
MP2				
	dz reg	276.9	4.774	259.8
	dz + pol	273.8	4.923	267.8
	dz ion	273.7	4.920	268.4
	tz reg	270.2	4.979	270.5
	tz + pol	269.3	5.047	274.5
	tz ion	269.2	5.044	275.3

ing seven points around the minimum. These fitted results were used to determine the bond length, the dissociation energy, and the harmonic frequency. The PT2 results were partitioned into valence correlation (correlation of the bond only), valence + $(n - 1)$p correlation, and valence + $(n - 1)$p + $(n - 1)$s correlation to assess the contributions from each shell. Basis-set limit correlation energies were obtained using a $1/n^3$ extrapolation of the tz and qz values.[37] The results are presented in Tables 9, 10, and 11. Note that the SCF dissociation energies are negative, which means that the minimum is above the dissociation limit. This is a consequence of the incorrect dissociation behavior of the SCF wave function. The MCSCF results are bound, however, since the chosen active space permits the correct dissociation behavior.

The MCSCF curves for all except Fr_2 exhibit a change in behavior at shorter distances. The change is due to the crossing of the σ_u antibonding and the π_u bonding orbitals and is mediated by the spin−orbit interaction. Although the σ_u^2 and π_u^2 states have the same symmetry, orbital selection in a spin-free model would exclude the latter state. Inclusion of the spin−orbit interaction allows the $\sigma_{1/2u}$ and $\pi_{1/2u}$ spin−orbitals to mix and, hence, allows a change from a predominantly σ_u^2 configuration to a predominantly π_u^2 configuration. This change occurs just on the inside of the minimum in the PT2-correlated curve, which affects the prediction of the minimum and renders the results and any extrapolation unreliable. This effect is particularly noticeable in the harmonic frequencies, where there is a sharp increase in the value with basis set size. The exact position of the crossing is sensitive to the basis set, and in fact, the crossing does not occur for the dz basis in the region sampled. The position also depends on Z, and the crossing does not occur in the region of the minimum for Fr_2, where the 7s−7p separation is larger than for Cs_2, and this is sufficient to move the crossing to shorter distances. For Fr_2, the MCSCF-PT2 results are significantly different from the PT2 results, even with the extrapolation. In particular, the bond length is greater by 16 pm, or about 4%, and the harmonic frequency is smaller by 5 cm^{-1}, or about 15%. This shows the importance of the nondynamical correlation in this system. The existence of the crossing also shows the importance of a larger active space that includes all the np orbitals. Unfortunately these calculations are beyond the capability of the DREAMS package.

As noted already by Roos et al.[31] and Lim et al.,[43] the Fr_2 predicted spectroscopic data show evidence of relativistic effects, with a shorter bond length than for Cs_2. The present results are not as accurate because the calculations of these other authors include a much higher level of correlation.

The third set of calculations tests whether the functions for the outer s shell of the alkali metals are needed in calculations on ionic systems, for which KCl was used as a typical example. The augmented correlation-consistent basis sets[46] were used for Cl. Three sets of exponents and contraction coefficients were used for K. The first was the original exponent set, including the functions for the $n = 4$ shell, contracted for the neutral atom, the same basis set as used for the dimers. The second was formed by adding the dipole polarizing functions for the $n = 3$ shell to the first. The third was formed by removing the functions for the $n = 4$ shell from the second set and contracting the SCF functions for the positive ion. These three basis sets were generated at both the dz and the tz levels. SCF and MP2 calculations correlating the $n = 3$ shell were performed with counterpoise corrections, and the bond distance, vibrational frequency, and dissociation energy were determined from a quartic fit to seven points around the minimum, using the same procedure as for the alkali dimers.

The results are presented in Table 12. The addition of the dipole polarizing functions makes a significant difference in the properties, even with the functions for the $n = 4$ shell included. Because of the large gap between the $n = 3$ and $n = 4$ shells, the $n = 4$ functions contribute little to the ion. Their omission makes almost no difference in the results. The differences decrease going to larger basis sets, but do not disappear. It can be concluded that the functions for the n shell are not necessary when performing calculations in which the alkali metals are ionized, but the dipole polarizing functions are necessary.

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Supporting Information Available: Tables of correlating and dipole polarizing functions. This material is available free of charge via the Internet at http://pubs.acs.org.

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