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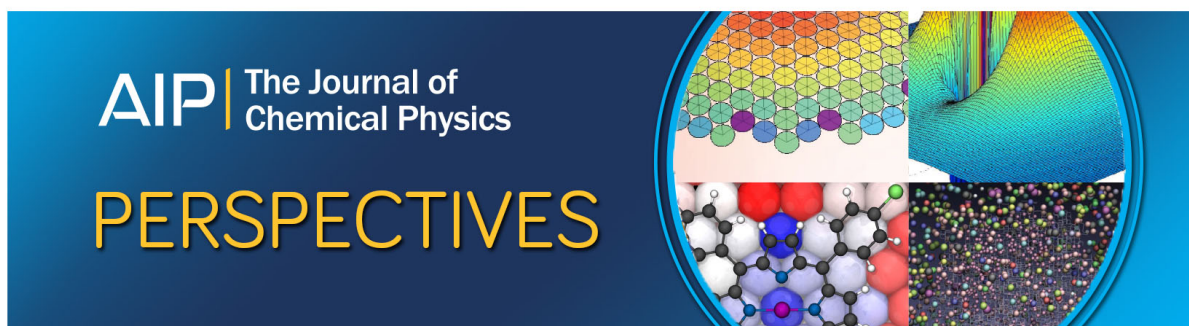
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Gaussian basis sets for use in correlated molecular calculations. XI. Pseudopotential-based and all-electron relativistic basis sets for alkali metal (K–Fr) and alkaline earth (Ca–Ra) elements

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New correlation consistent basis sets based on pseudopotential (PP) Hamiltonians have been developed from double- to quintuple-zeta quality for the late alkali (K–Fr) and alkaline earth (Ca–Ra) metals. These are accompanied by new all-electron basis sets of double- to quadruple-zeta quality that have been contracted for use with both Douglas-Kroll-Hess (DKH) and eXact 2-Component (X2C) scalar relativistic Hamiltonians. Sets for valence correlation (*ms*), cc-pVnZ-PP and cc-pVnZ-(DK,DK3/X2C), in addition to outer-core correlation [valence + (*m*–1)sp], cc-p(w)CVnZ-PP and cc-pwCVnZ-(DK,DK3/X2C), are reported. The –PP sets have been developed for use with small-core PPs [I. S. Lim *et al.*, J. Chem. Phys. **122**, 104103 (2005) and I. S. Lim *et al.*, J. Chem. Phys. **124**, 034107 (2006)], while the all-electron sets utilized second-order DKH Hamiltonians for 4s and 5s elements and third-order DKH for 6s and 7s. The accuracy of the basis sets is assessed through benchmark calculations at the coupled-cluster level of theory for both atomic and molecular properties. Not surprisingly, it is found that outer-core correlation is vital for accurate calculation of the thermodynamic and spectroscopic properties of diatomic molecules containing these elements. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5010587>

I. INTRODUCTION

Molecular electronic structure calculations are typically carried out using one-particle basis sets of Gaussian-type functions, and the incompleteness of this basis can be a major source of error.^{1–3} Simply addressing this problem by using the largest possible basis results in poor efficiency and is restrictive in terms of tractable system size; hence, families of basis sets that systematically approach the complete basis set (CBS) limit have been developed. This behavior can then be exploited by extrapolating results in, for example, the maximum angular momentum found in the basis (see Refs. 4 and 5, and references therein). For highly correlated wave function based methods, a common choice is the correlation consistent (cc) basis sets originally introduced by Dunning,⁶ which are energy optimized and use general contraction schemes for functions describing occupied orbitals. Although cc basis sets are available for nearly all elements in the periodic table, for the alkali (group 1) and alkaline earth (group 2) metals, all-electron cc basis sets are only available for Li, Be, Na, Mg, and Ca.^{7,8} The present contribution focuses on the heavier s-block elements, extending cc basis set coverage to the entire block. It should be noted that preliminary cc sets paired to pseudopotentials (PPs) for the alkaline earth metals Ca, Sr, Ba, and Ra have been briefly reported in Ref. 9, these sets have been subject to minor revision herein and are described and validated in significant detail.

Molecules containing heavier alkali and alkaline earth metals are currently of interest due to possible applications within the field of ultracold (<1 mK) chemistry. In addition to quantum controlled chemistry, where ultracold conditions and external fields allow specific reactions to be carried out,¹⁰ such molecules could also be invaluable in quantum information processing or portable atomic/molecular clocks.^{11,12} Some examples of recent developments in the field include the production of ultracold RbCs,¹³ the laser cooling of CaF,¹⁴ and interspecies Penning ionization.¹⁵ In addition to sophisticated experiments, theoretical work is fundamental to developing a greater understanding of the behavior of atoms and molecules in the ultracold regime. For example, the calculation of accurate potential energy surfaces directs experimental effort in using stimulated Raman adiabatic passage to produce ultracold molecules.¹⁶ Several of these elements are also of interest in nuclear chemistry, such as Cs playing a role in the nuclear fuel cycle, and both Fr and Ra are found in uranium ores.

There are very few existing basis sets for the 7s (Fr and Ra) elements, especially when considering only those designed for correlated calculations. Sets paired to PPs are restricted to the CRENBL set of Christiansen and co-workers¹⁷ and the roughly quadruple-zeta quality ECP78MDF set of Lim *et al.*^{18,19} For all-electron calculations, the atomic natural orbital (ANO) basis sets of Roos and co-workers,²⁰ denoted ANO-RCC, the Dirac-Coulomb relativistic correlation consistent sets of Dyall,²¹ and the Sapporo natural orbital based segmented contracted Gaussian (NOSec) sets of Noro *et al.* are available in a range of sizes from DZ to QZ.²² The former are designed for

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use with the second-order Douglas-Kroll-Hess (DKH) Hamiltonian and the latter for third-order DKH. In addition to the above basis sets, there are a number of notable sets available for the 4s–6s s-block elements. Those paired to PPs include the Los Alamos National Laboratory (LANL) double zeta basis, denoted LANL2DZ,²³ and the uncontracted revised basis LANL08.²⁴ The segmented contracted DZ through QZ quality sets of Weigend and Ahlrichs (often referred to as the def2 family of basis sets) are paired to Wood-Boring type PPs for the 5s and 6s elements, with all-electron sets for 4s.²⁵ More recently, these sets for 5s and 6s were reoptimized for Dirac-Fock PPs and are denoted dhf- $n(Z)$ VP.²⁶ All-electron scalar relativistic sets for use with the eXact 2-Component (X2C) Hamiltonian,^{27,28} which act as counterparts to the def2 basis sets, are also available at DZ and TZ quality.²⁹

In the present work, correlation consistent basis sets are presented for the heavy group 1 (K, Rb, Cs, and Fr) and group 2 (Ca, Sr, Ba, and Ra) atoms. A series of basis sets paired to the small-core pseudopotentials of Lim *et al.*^{18,19} are denoted cc-pVnZ-PP ($n = D, T, Q, 5$), and a separate series of all-electron basis sets ranging from double- to quadruple-zeta in quality are also described. The latter have been contracted for use with the DKH Hamiltonian (basis sets denoted cc-pVnZ-DK for 2nd-order DKH and cc-pVnZ-DK3 for 3rd order) and for the X2C Hamiltonian (cc-pVnZ-X2C). In addition to the above sets optimized for the treatment of valence (ms) electron correlation, sets for the recovery of the $(m-1)sp$ correlation effects are also presented.

II. GENERAL COMPUTATIONAL DETAILS

The MOLPRO system of *ab initio* programs was used for all calculations in this work,^{30,31} together with pure spherical harmonic angular momentum basis functions. All orbitals from HF calculations were symmetry equivalenced, generally through a state-averaged multiconfigurational self-consistent field (MCSCF) approach. Basis sets in this work that are paired to pseudopotentials (PPs) use the small core, multi-configuration Dirac-Hartree-Fock-adjusted parameters of Lim *et al.*,^{18,19} which replace 10 electrons for K and Ca, 28 electrons for Rb and Sr, 46 electrons for Cs and Ba, and 78 electrons for Fr and Ra.

III. BASIS SET DEVELOPMENT

A. Hartree-Fock primitive sets

Just as in the correlation consistent basis sets for the lighter group 1 and 2 elements,⁷ the exponents of the s functions within the HF primitives paired to PPs were optimized for the electronic ground state of the neutral atoms. The p functions for group 1 and 2 elements were optimized for the 2P and 3P excited states, respectively. For the group 2 elements, exponents of d functions were optimized for the excited 3D state. Attempts to optimize d functions in an analogous fashion for group 1 (i.e., for the 2D state at the HF level) led to exponents that were too diffuse. Initial testing demonstrated that a relatively tight, contracted HF-like d function was, however, necessary for a reasonable description of the spectroscopic properties of group 1 diatomic molecules. The exponents of

the d primitives in this case were hence optimized at the CCSD level for the homonuclear diatomic molecule. Using an iterative procedure as in Ref. 32, two of the exponents were optimized for core-valence correlation (including all electrons not replaced by the PP), while the remaining exponents were optimized concurrently with only the outermost s electrons (defined as valence herein) correlated. The only exceptions were for K with zeta levels greater than two, when three core-valence exponents were required. The compositions of the resulting HF primitive sets are provided in the [supplementary material](#). These primitive sets were then contracted to [2s2p1d] in a general contraction scheme using atomic orbital coefficients. The s and first p contraction coefficients were determined for the ground state, while the coefficients for the remaining contractions were taken from different states: the second (valence) p for the lowest lying 2P or 3P states (for group 1 and 2, respectively), and the d from the 2D or 3D states.

The HF primitives for the all-electron basis sets took the primitives of Dyal²¹ as a starting point, which were optimized in 4-component Dirac-Hartree-Fock calculations using the Dirac-Coulomb Hamiltonian and a finite nucleus model. In particular, the latter avoids the exceedingly large exponents that arise in optimizations with the typical point charge model. In a similar fashion to the lanthanide correlation consistent basis sets,³³ the innermost exponents of the s and p functions from Dyal's sets were kept fixed for K and Ca, innermost s, p, and d for Rb, Sr, Cs, and Ba, and the innermost s, p, d, and f for Fr and Ra. The exponents roughly corresponding to the outer two radial maxima of the valence orbitals were then reoptimized at the HF level; this typically corresponded to the five most diffuse exponents in each shell at DZ, seven at TZ, and nine at QZ. All of these exponents were reoptimized using a point charge nucleus model. For K–Sr, the second-order DKH Hamiltonian (DKH2) was used, with Cs–Ra using the third-order DKH Hamiltonian (DKH3). This choice is based upon previous work demonstrating that for elements beyond $Z = 81$, third-order DKH or greater should be used,^{34,35} as well as to treat elements within a given row of the periodic table equally. DKH basis sets for Ca have been developed previously and briefly reported in Ref. 8, but the decision was taken to produce new sets for Ca such that every all-electron scalar relativistic correlation consistent basis set for the heavy group 1 and 2 elements is consistent in design, development, and optimization. In all cases, the exponents of the s and d functions (the latter not for K and Ca) were optimized for the ground states, with the p functions optimized for the 2P or 3P states. An additional single set of diffuse p functions (optimized for the 2P state) were added for group 1 elements, with the exceptions of all K sets and the QZ set for Fr. To describe the relatively low-lying 2D or 3D states, three or four additional diffuse d functions were also added. For group 2 elements, these functions were optimized for the 3D state at the HF level, while for group 1 elements, optimizations were carried out for the homonuclear diatomic at the CCSD level in a similar fashion to the PP based sets. The compositions of the primitive sets are tabulated in the [supplementary material](#), and these primitives were then contracted, using a general contraction scheme, using two different methods: the appropriate order DKH

Hamiltonian and the X2C Hamiltonian. The resulting contracted basis set compositions were [4s3p1d] for 4s elements, [5s4p2d] for 5s elements, [6s5p3d] for 6s elements, and [7s6p4d1f] for 7s elements. The atomic orbital coefficients used in the contractions mostly correspond to those of the ground state, but the outermost p contraction used coefficients from the 2P or 3P state with 2D or 3D states used for the outermost d contraction.

B. Correlating functions—Valence correlation

As group 1 elements possess only a single valence electron, it is not possible to use atomic energies for the optimization of valence correlating functions. Instead the homonuclear diatomics have been used for group 1 unless otherwise stated. It was also found that more reliable valence correlating functions were obtained for the heavy group 2 elements by employing optimizations on the metal hydrides. To determine the correlation consistent groupings of higher angular momentum functions, coupled cluster singles and doubles (CCSD) optimizations were carried out with the PP-based contracted 5Z HF primitives described above for Ca, Sr, Ba, and Ra. Even-tempered expansions were used to reduce the number of optimization variables in each shell to two.³⁶ Figure 1 shows the incremental correlation energy lowering from adding successive functions in each shell for the Ba atom. Analogous plots for the other elements displayed the same trends and are not reproduced here. In addition to the contracted HF functions, the Ba and Ra basis sets also had a single fixed tight-f function that is described in detail below.

The pattern of the correlation energy recovery displayed in Fig. 1 is similar to that seen for Mg in Ref. 7, indicating that the typical correlation consistent groupings of 1d for DZ, 2d1f for TZ, 3d2f1g for QZ, and 4d3f2g1h for 5Z are also suitable choices for the elements considered in the present

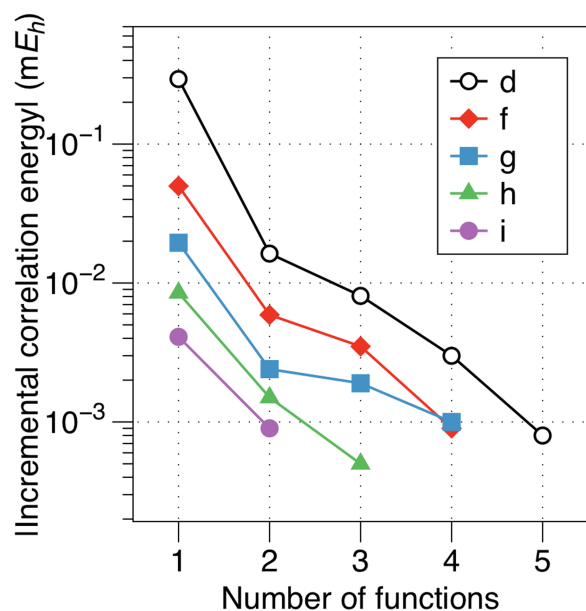


FIG. 1. Contribution of angular momentum functions to the CCSD correlation energy in the electronic ground state of the Ba atom.

investigation. A close examination of the incremental correlation energies suggests that alternative groupings could also be made as, for example, the first g function contributes approximately the same amount of correlation energy as the second d function and could be included in a TZ set. A decision was taken in this work to adopt the same groupings as in the p-block elements,^{6,37} both to ensure balanced descriptions of different atoms and to prevent unnecessarily high computational cost.

With correlation consistent groupings established, exponents for each shell could then be optimized. For s, p, and d functions, it was possible to obtain these from the HF primitive sets, in the manner described below. For the 6s and 7s elements, it was necessary to include a contracted tight-f function at TZ or higher level to provide inner-shell polarization. The exponents within the contraction were optimized for the metal hydride (using the cc-pVQZ basis for hydrogen). For 7s elements with PP based sets, this meant concurrently optimizing two exponents for core-valence (6s6p+7s) and one for valence only (2/1) at the TZ level, 3/1 at QZ, and 4/1 at 5Z. For 6s elements, the analogous pattern was 3/1 (TZ), 4/1 (QZ), and 5/1 (5Z). The resulting exponents were then contracted using atomic natural orbital coefficients calculated at the configuration interaction singles and doubles (CISD) level of theory.³⁸ In addition to the contracted f-type function, the required number of f-type correlating functions was also included by uncontracting the most diffuse primitives. A similar process was undertaken for the all-electron basis sets, with the major exception that f-type functions for 7s elements were added to the previously optimized HF f-type primitives, and that the CISD ANO coefficients were calculated by correlating only the 6sp and 7s electrons.

Following previous correlation consistent basis sets,⁶ the correlating functions for s, p, and d angular momenta use the same exponents as the primitives within the HF sets, i.e., a number of functions are uncontracted in a way that strikes a balance between the errors in the HF and correlation energies (the latter evaluated from the energy calculated using fully optimized functions). An additional s function was also uncontracted for the PP-based sets as single uncontracted primitive functions recover less correlation energy when using PPs than in the all-electron case.^{37,39,40} This was also tested for p functions, but the incremental correlation energy lowering was small and extra uncontracted p primitives were not included in the current case. The resulting total correlating functions uncontracted from the HF primitives for the PP based sets were (2s1p1d), (3s2p2d), (4s3p3d), and (5s4p4d) for DZ-5Z, respectively. The final compositions of the valence correlating basis sets developed in this work are presented in Table I for the cc-pVnZ-PP sets and in Table S3 in the [supplementary material](#) for the all-electron scalar-relativistic sets. Relative to the preliminary versions of these basis sets for the heavy group 2 elements that were briefly described in Ref. 9, the cc-pVnZ-PP sets presented in the current work uncontract a single additional s function. The exponents of the primitives and the contraction coefficients remain the same.

Long-range interactions are likely to be of interest in systems containing alkali and alkaline earth metals;

TABLE I. Compositions of the contracted valence correlating PP based correlation consistent basis sets developed in this work for the group 1 and 2 elements.^a

Basis set	Atoms	
	K, Ca, Rb, Sr	Cs, Ba, Fr, Ra
cc-pVDZ-PP	[4s3p2d]	[4s3p2d]
cc-pVTZ-PP	[5s4p3d1f]	[5s4p3d2f]
cc-pVQZ-PP	[6s5p4d2f1g]	[6s5p4d3f1g]
cc-pV5Z-PP	[7s6p5d3f2g1h]	[7s6p5d4f2g1h]

^aSee Table S3 in the [supplementary material](#) for the corresponding compositions of the all-electron basis sets.

hence, additional diffuse functions have been determined for each basis set to produce sets denoted aug-cc-pVnZ-PP, aug-cc-pVnZ-DK,DK3, and aug-cc-pVnZ-X2C. For the s and p shells, the exponents of these additional diffuse functions correspond to an even-tempered extension of the valence correlating basis based upon the two most diffuse exponents in that shell. For higher angular momenta, the exponent of the additional function is equal to the most diffuse exponent in the existing set divided by 2.5. Overall, a single additional function is added to each shell present in the standard valence basis set. This procedure was found to be more reliable than explicit optimization as was used previously for the lighter elements. These same diffuse functions can be used with the core-valence correlating basis sets described below.

C. Correlating functions—Core-valence correlation, (m-1)sp

Two common methods of adding functions appropriate for core and core-valence correlation effects to standard correlation consistent basis sets have been established. The original method,⁴¹ generally denoted cc-pCVnZ, optimizes additional functions using the sum of the core-core and core-valence (CV) correlation energies as the objective function. A second approach produces *weighted* core-valence basis sets, cc-pwCVnZ, by including only 1% of the core-core correlation energy, which is summed with the total core-valence contribution. It has been found that this weighted approach improves the rate of basis set convergence to the CBS limit with respect to computed thermodynamic and spectroscopic properties.⁴² In this work, both variants, cc-pCVnZ-PP and cc-pwCVnZ-PP, have been developed for PP based sets, and only weighted core-valence, cc-pwCVnZ-DK,DK3 and cc-pwCVnZ-X2C, for the all-electron sets. In general, the number of functions added at each zeta-level is (1s1p1d) for DZ, (2s2p2d1f) for TZ, (3s3p3d2f1g) for QZ, and (4s4p4d3f2g1h) for 5Z. The additional exponents were optimized at the CCSD level for the ground state of the neutral atom. To prevent linear dependency problems, at the cc-p(w)CV5Z-PP level, the second HF s and p contracted functions were removed. For the 6s and 7s elements, it was also necessary to remove the contracted d and f functions and to remove the primitive exponents corresponding to the tightest four d and three f functions (that is, those that are being replaced by the specific core-valence correlating functions). In the case of the PP-based basis sets for heavy group 2 elements, the exponents of the core-valence correlating functions were

re-optimized from those briefly reported in Ref. 9, due to the addition of the extra s valence correlating functions detailed above.

Initial testing of the weighted CV basis sets showed that the convergence of spectroscopic properties for diatomics including barium did not meet the expected trend; cc-pwCVQZ-PP results were closer to cc-pwCVTZ-PP than to cc-pwCV5Z-PP. To ameliorate this problem, all of the f and g functions in the cc-pwCVQZ-PP basis were optimized in the wCV manner, including those that had previously been held fixed at their optimal valence-only values. The tight-f function described above was also retained. Similarly, all of the f, g, and h exponents in the cc-pwCV5Z-PP basis were (re-)optimized following the wCV procedure. To avoid linear dependency problems with the Ca cc-pwCVQZ-DK set, the exponent of the tightest valence-correlating function was also optimized for wCV. The all-electron barium sets also required some modifications to show the desired convergence characteristics. First, an additional f function was added to the cc-pVQZ-(DK3/X2C) set and included in the ANO contraction such that the contraction was then composed of 5 core-correlating functions and a single valence-only function. Second, for the cc-pwCVQZ-(DK3/X2C) set, these f primitives were all included in their uncontracted form, and all of the g functions (re-)optimized for wCV.

IV. RESULTS AND DISCUSSION

A. Atomic benchmark calculations

For the group 1 elements, ionization potentials and electron affinities have been calculated using the PP-based basis sets developed in this work and are presented in Table II. Although CCSD with perturbative triples, CCSD(T), was generally used to obtain these properties, calculations using the standard “valence-only” basis sets used a frozen core definition that meant only the *ms* electrons were correlated and hence the level of theory is equivalent to HF or CCSD for group 1 and 2, respectively. For the sake of brevity, the cc-pVnZ-PP basis sets are abbreviated to VnZ-PP in Table II, with additional diffuse functions signified by the prefix “a,” and core-valence functions with the usual C or wC prefix. Calculations using core-valence basis sets correlated all electrons not replaced by the PP. The ionization potentials calculated with the VnZ-PP basis sets show very little dependence on basis sets and their large deviation from experimental values is due to the large errors from the frozen core approximation in these cases. Correlation of the outer core electrons greatly improves the calculated ionization potentials, converging rapidly when TZ or larger basis sets are used. Using the weighted core-valence basis sets as opposed to those from the CVnZ-PP sets accelerates convergence towards the limit. For example, the error relative to experiment for the ionization potential of K is 2.9 kcal mol⁻¹ using the cc-pCVDZ-PP basis, but this is reduced to 1.9 kcal mol⁻¹ when cc-pwCVDZ-PP is used. The agreement between the experiment and largest basis set result, aug-cc-pwCV5Z-PP, is typically excellent, at roughly 0.1 kcal mol⁻¹. But, the calculated result

TABLE II. Ionization potentials (IP/kcal mol⁻¹) and electron affinities (EA/kcal mol⁻¹) at the CCSD(T) level of theory for the alkali metals K–Fr.

Basis ^a	K		Rb		Cs		Fr	
	IP	EA	IP	EA	IP	EA	IP	EA
VDZ-PP	92.92	10.37	87.75	9.85	80.58	9.51	82.26	8.76
VTZ-PP	92.93	10.82	87.72	10.25	80.53	9.87	82.17	9.36
VQZ-PP	92.93	10.88	87.72	10.66	80.54	10.07	82.16	9.49
V5Z-PP	92.93	11.11	87.72	10.78	80.53	10.23	82.15	9.55
aVDZ-PP	92.93	11.36	87.75	10.78	80.58	10.23	82.25	9.75
aVTZ-PP	92.93	11.42	87.72	10.87	80.53	10.29	82.17	9.86
aVQZ-PP	92.93	11.44	87.72	10.88	80.54	10.32	82.16	9.89
aV5Z-PP	92.93	11.45	87.72	10.89	80.53	10.33	82.15	9.90
CVDZ-PP	97.24	10.43	92.09	10.08	84.87	9.86	86.89	9.48
CVTZ-PP	99.32	10.92	95.10	10.52	89.24	10.41	91.89	10.46
CVQZ-PP	99.88	11.03	95.91	10.95	89.55	10.57	92.27	10.60
CV5Z-PP	100.13	11.24	96.08	11.07	89.70	10.73	92.57	10.70
wCVDZ-PP	98.20	10.35	92.50	10.07	85.14	9.87	87.06	9.52
wCVTZ-PP	99.88	10.97	95.86	10.60	89.51	10.44	92.20	10.50
wCVQZ-PP	100.18	11.07	96.22	11.00	89.87	10.64	92.74	10.70
wCV5Z-PP	100.23	11.25	96.22	11.09	89.87	10.76	92.73	10.75
awCVDZ-PP	98.28	11.29	92.61	10.89	85.27	10.47	87.21	10.28
awCVTZ-PP	99.89	11.43	95.87	11.06	89.52	10.70	92.21	10.79
awCVQZ-PP	100.19	11.50	96.23	11.15	89.87	10.80	92.74	10.93
awCV5Z-PP	100.23	11.53	96.22	11.17	89.87	10.83	92.73	10.95
Experiment ^b	100.10	11.56	96.32	11.21	89.80	10.88	93.88	11.32 ^c

^aOnly the *ms* valence electrons are correlated for *VnZ*-PP and *aVnZ*-PP. All other calculations also correlate the $(m-1)sp$ electrons.

^bReferences 44–47.

^cTheoretical data from Ref. 48.

for the ionization potential of Fr underestimates the experimental value by 1.15 kcal mol⁻¹.⁴³ Some reasons for this relatively large difference are discussed below, but it is possible to rule out errors related to the pseudopotential, as the ionization potential calculated with the aug-cc-pwCVQZ-DK3 basis and the third-order DKH Hamiltonian is 92.65 kcal mol⁻¹, in excellent agreement with the aug-cc-pwCVQZ-PP result.

The electron affinities of the group 1 elements shown in Table II demonstrate that augmentation of the basis sets with extra diffuse functions is necessary for good agreement with experiment. This is somewhat unsurprising as accurate calculation of electron affinities was the motivation for the original aug-cc-pVnZ family of basis sets;⁴⁹ however, it is reassuring for this effect to be reinforced in the current case. It can be seen that as we move down group 1, the effect of correlating the outer-core electrons (comparing aug-cc-pV5Z-PP with aug-cc-pwCV5Z-PP) on the electron affinity increases, from +0.08 kcal mol⁻¹ for K to +1.05 kcal mol⁻¹ for Fr. Agreement with experiment when using aug-cc-pwCV5Z-PP is again excellent in all cases except Fr, where no experimental data are available and the theoretical intermediate Hamiltonian Fock-space value of Landau *et al.* is used as Ref. 48. The largest basis set value from the present work is only 0.37 kcal mol⁻¹ lower than that of Landau, which may be attributable to the latter only including correlation at the CCSD level.

The first and second ionization potentials for the group 2 elements Ca–Ra have been calculated at the CCSD(T) level

of theory and are presented in Table III. Electron affinities for these atoms are very small; hence, second ionization potentials are used to demonstrate the performance of the basis sets developed in this work and to provide comparison with the lighter group 2 elements Be and Mg.⁷ Correlating the $(m-1)sp$ electrons is again vital for good agreement with experimental data, and the weighted core-valence sets produce a more rapid convergence towards the limit compared to CVnZ. As with group 1, the largest deviations from experiment occur for the 7s element (Ra), but it should be noted that the present aug-cc-pwCV5Z-PP results for that element are in good agreement with the four-component relativistic Dirac-Coulomb CCSD(T) results of Lim and Schwerdtfeger.⁵⁰

To demonstrate the performance of the new all-electron relativistic basis sets, first ionization potentials are presented at the CCSD(T) level in Table IV. Based upon the analysis of the results for PP-based sets, only results using the aug-cc-pwCVnZ-DK basis sets (aug-pwCVnZ-DK3 for Cs–Ra) are included. A comparison with Tables II and III shows that generally the all-electron DZ results are closer to the experimental values than the equivalent PP-based sets, but TZ and QZ are slightly further from experiment. This may indicate that the PP approximation is introducing minor errors that are fortuitously closer to experiment in the TZ and QZ cases. In the case of Fr, the $(m-1)d$ HF (DK3) orbitals have energies of approximately -2.5 hartrees, in good agreement with the numerical relativistic Dirac-Fock results of Desclaux,⁵¹ indicating their correlation may be important. To test the effect

TABLE III. First and second ionization potentials (kcal mol⁻¹) at the CCSD(T) level of theory for the alkaline earth metals Ca–Ra.

Basis ^a	Ca		Sr		Ba		Ra	
	IP ₁	IP ₂	IP ₁	IP ₂	IP ₁	IP ₂	IP ₁	IP ₂
VDZ-PP	136.49	262.33	125.50	240.87	113.54	216.08	112.94	217.61
VTZ-PP	136.87	262.29	125.83	240.80	113.79	216.09	113.19	217.61
VQZ-PP	136.92	262.32	125.93	240.83	113.80	216.18	113.36	217.64
V5Z-PP	136.96	262.30	125.97	240.79	113.88	216.08	113.44	217.53
aVDZ-PP	136.55	262.32	125.56	240.86	113.60	216.09	113.00	217.62
aVTZ-PP	136.88	262.29	125.84	240.80	113.80	216.09	113.22	217.61
aVQZ-PP	136.92	262.32	125.94	240.83	113.81	216.17	113.37	217.63
aV5Z-PP	136.96	262.30	125.97	240.79	113.89	216.08	113.44	217.53
CVDZ-PP	138.92	270.34	128.21	248.46	116.53	224.25	116.47	225.53
CVTZ-PP	140.33	272.87	130.24	252.43	119.27	229.34	119.94	231.60
CVQZ-PP	140.88	273.75	130.82	253.52	119.53	229.69	120.22	232.03
CV5Z-PP	141.11	274.06	131.09	253.83	119.75	229.99	120.55	232.47
wCVDZ-PP	139.03	270.64	128.31	248.64	116.55	224.28	116.54	225.59
wCVTZ-PP	140.62	273.41	130.61	253.18	119.34	229.48	120.03	231.79
wCVQZ-PP	141.04	274.04	131.06	253.89	119.67	229.95	120.57	232.53
wCV5Z-PP	141.17	274.16	131.15	253.95	119.82	230.11	120.65	232.61
awCVDZ-PP	139.12	270.74	128.39	248.80	116.63	224.44	116.64	225.77
awCVTZ-PP	140.64	273.42	130.62	253.20	119.35	229.49	120.04	231.80
awCVQZ-PP	141.05	274.04	131.07	253.89	119.77	230.06	120.58	232.54
awCV5Z-PP	141.17	274.16	131.16	253.95	119.84	230.12	120.66	232.62
Experiment ^b	140.97	273.77	131.33	254.36	120.18	230.69	121.72	234.00

^aOnly the *ms* valence electrons are correlated for *VnZ*-PP and *aVnZ*-PP. All other calculations also correlate the (*m*-1)*sp* electrons.

^bReference 44.

of this (*m*-1)*d* correlation on the first ionization potentials of the 7*s* elements, *ad hoc* basis sets were created by simply uncontracting all of the *d* and *f* primitives in the aug-cc-pwCV*nZ*-DK3 basis sets and including the relevant orbitals in the CCSD(T) correlation treatment. The ionization potentials for Fr became 90.33, 92.80, and 93.29 kcal mol⁻¹ with DZ, TZ, and QZ basis sets, respectively, with the analogous Ra ionization potentials calculated to be 117.96, 120.41, and 120.92 kcal mol⁻¹. These modest improvements of roughly 0.5 kcal mol⁻¹ relative to results presented in Table IV indicate that (*m*-1)*d* correlation may be important when calculating, for example, thermochemistry of 7*s* elements; however, it should be noted that these orbitals are replaced by the PP when using ECP78MDF.^{18,19}

B. Molecular calculations

For representative molecular benchmark properties, CCSD(T) calculations have been carried out on three diatomics for each element. Molecules including group 1 elements correspond to the homonuclear diatomic M₂, the fluoride MF, and

the hydride MH. For group 2 elements, the molecules considered are the oxide MO, fluoride, and hydride. For open-shell systems, an ROHF reference is used, with a spin unrestricted treatment at the coupled-cluster level. Calculations with PP Hamiltonians used the cc-p*VnZ* and cc-p(w)CV*nZ* sequences of basis sets for non-metal heteroatoms in valence-only and core-valence calculations, respectively.^{6,41,42} Both DK and X2C relativistic calculations used the cc-p*VnZ*-DK series of basis sets for H, O and F.⁵² All fluorine basis sets were augmented with additional diffuse functions (aug-)⁴⁹ to allow additional flexibility in the description of potentially ionic charge distributions. In all cases, the equilibrium bond length (*r*_e), harmonic frequency (*ω*_e), and dissociation energy (*D*_e) were produced for the ground electronic states from near-equilibrium potential energy curves (seven energy points fit with a sixth-order polynomial) and a subsequent Dunham analysis.⁵³ Estimates of the CBS limit values were obtained by extrapolating QZ and 5Z data, using the procedure of Karton and Martin for the HF energy,⁵⁴ and the ℓ_{\max}^{-3} based formula for the total correlation energy.^{55,56}

TABLE IV. First ionization potentials (kcal mol⁻¹) at the CCSD(T) level using all-electron relativistic basis sets.^a

Basis	K	Ca	Rb	Sr	Cs	Ba	Fr	Ra
awCVDZ-DK	97.68	139.08	93.77	129.12	87.11	117.35	90.28	117.73
awCVTZ-DK	99.66	140.32	95.69	130.52	88.88	118.98	92.23	119.86
awCVQZ-DK	99.86	140.71	95.97	130.90	89.12	119.39	92.65	120.40

^aK–Sr calculated using DKH2 (awCV*nZ*-DK), Cs–Ra using DKH3 (awCV*nZ*-DK3). Only the valence and (*m*-1)*sp* electrons are correlated.

TABLE V. CCSD(T) valence-only spectroscopic constants of diatomic molecules containing Rb or Fr.

Molecule	Basis set	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
Rb ₂	cc-pVDZ-PP	4.5197	51.0	10.11
	cc-pVTZ-PP	4.5127	52.7	10.91
	cc-pVQZ-PP	4.5111	52.9	11.03
	cc-pV5Z-PP	4.5112	52.9	11.06
	CBS	4.5114	52.9	11.08
	Experiment	4.2099 ⁵⁷	59.1 ⁵⁸	11.42 ⁵⁹
RbF	cc-pVDZ-PP	2.3474	349.8	77.98
	cc-pVTZ-PP	2.3129	370.2	70.04
	cc-pVQZ-PP	2.2951	373.3	68.87
	cc-pV5Z-PP	2.2982	368.0	69.30
	CBS	2.3041	362.9	69.76
	Experiment ^a	2.2703	376	119.9 ^b
RbH	cc-pVDZ-PP	2.4822	859.2	34.08
	cc-pVTZ-PP	2.4656	893.1	40.31
	cc-pVQZ-PP	2.4679	892.4	41.75
	cc-pV5Z-PP	2.4713	884.8	42.06
	CBS	2.4741	880.3	42.35
	Experiment ^a	2.367	936.9	41.69 ⁶⁰
Fr ₂	cc-pVDZ-PP	5.0836	27.0	7.77
	cc-pVTZ-PP	5.0723	28.3	8.58
	cc-pVQZ-PP	5.0616	28.5	8.76
	cc-pV5Z-PP	5.0627	28.5	8.80
	CBS	5.0640	28.5	8.83
	Theoretical ^c	4.698	33	9.29
FrF	cc-pVDZ-PP	2.5541	315.3	76.99
	cc-pVTZ-PP	2.5041	349.2	72.60
	cc-pVQZ-PP	2.4970	350.4	70.05
	cc-pV5Z-PP	2.4892	353.6	70.45
	CBS	2.4861	356.2	70.65
	Theoretical ^c	2.417	339	115.19
FrH	cc-pVDZ-PP	2.7148	810.9	31.94
	cc-pVTZ-PP	2.6946	836.3	38.25
	cc-pVQZ-PP	2.6993	833.2	39.90
	cc-pV5Z-PP	2.7026	828.1	40.36
	CBS	2.7065	823.3	40.68
	Theoretical ^c	2.553	901	35.56

^aAll experimental data from Ref. 62 unless otherwise stated.^b D_0 from Ref. 61.^cPrevious CCSD(T) results from Ref. 22.

TABLE VI. CCSD(T) valence-only spectroscopic constants of diatomic molecules containing Ca or Ba.

Molecule	Basis set	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
CaO	cc-pVDZ-PP	1.9788	494.6	64.51
	cc-pVTZ-PP	1.9393	594.6	74.97
	cc-pVQZ-PP	1.9245	638.8	81.23
	cc-pV5Z-PP	1.9230	645.9	83.59
	CBS	1.9209	656.8	85.39
	Experiment ^a	1.8221	732.1	95.1 ^b
CaF	cc-pVDZ-PP	1.9835	583.6	99.15
	cc-pVTZ-PP	1.9711	570.1	92.60
	cc-pVQZ-PP	1.9596	578.8	93.20
	cc-pV5Z-PP	1.9563	581.6	93.05
	CBS	1.9541	583.9	92.76
	Experiment ^a	1.967	581.1	126.4 ^c
CaH	cc-pVDZ-PP	2.0503	1251.6	34.79
	cc-pVTZ-PP	2.0517	1274.1	40.17
	cc-pVQZ-PP	2.0502	1273.3	41.34
	cc-pV5Z-PP	2.0506	1272.8	41.70
	CBS	2.0518	1271.0	41.99
	Experiment ^a	2.0025	1298.3	39.2
BaO	cc-pVDZ-PP	2.0887	655.5	62.39
	cc-pVTZ-PP	1.9783	677.7	83.34
	cc-pVQZ-PP	1.9770	679.9	86.97
	cc-pV5Z-PP	1.9652	678.9	91.30
	CBS	1.9653	676.9	93.06
	Experiment ^a	1.9397	669.8	130.8 ^d
BaF	cc-pVDZ-PP	2.2543	456.3	100.04
	cc-pVTZ-PP	2.2099	466.1	96.69
	cc-pVQZ-PP	2.1974	469.6	95.63
	cc-pV5Z-PP	2.1905	471.1	95.92
	CBS	2.1899	470.9	94.24
	Experiment ^a	2.162	468.9	134.4 ^e
BaH	cc-pVDZ-PP	2.3529	1094.6	38.33
	cc-pVTZ-PP	2.3296	1117.7	45.52
	cc-pVQZ-PP	2.3294	1119.2	46.90
	cc-pV5Z-PP	2.3304	1107.8	47.43
	CBS	2.3327	1101.9	47.76
	Experiment ^a	2.2319 ⁶³	1168.4 ⁶³	46.7 ⁶⁴

^aAll experimental data from Ref. 62 unless otherwise stated.^b D_0 from Ref. 65.^c D_0 from Ref. 66.^d D_0 from Ref. 67.^e D_0 from Ref. 68.

1. Valence correlation

The calculated spectroscopic constants of the selected diatomic molecules with only the valence electrons correlated (*ms* electrons for group 1 or 2 elements) are shown in Table V for molecules containing Rb and Fr and in Table VI for Ca and Ba. Analogous data tables for K, Cs, Sr, and Ra are presented in the [supplementary material](#).

The spectroscopic constants for valence-only correlation in Tables V and VI show reasonably smooth convergence towards the CBS limit for the dissociation energy, but the DZ values can be quite far away; for example, the cc-pVDZ-PP D_e for BaO is greater than 30 kcal/mol below the limit. More importantly, comparison of the calculated CBS spectroscopic constants with experimental data indicates a number of large discrepancies; for group 1 homonuclear dimers, the equilibrium bond lengths are overestimated by 0.2–0.5 Å, MF dissociation energies underestimated by around

50 kcal mol⁻¹, and underestimation of MH vibrational frequencies can be in the region of 60 cm⁻¹. Clearly these are unacceptable levels of agreement, which is due to the definition of the frozen-core approximation for these group 1 and 2 elements. In 1986, Bauschlicher *et al.* noted that the (*m*-1)sp outer core electrons should be correlated to obtain useful results for the alkali and alkaline-earth monohydroxides,⁶⁹ with a similar finding noted more recently by Neese and co-workers.⁷⁰ Iron *et al.* also observed that neglecting to correlate the 3s3p for small K and Ca compounds leads “to erratic results at best.”⁷¹ This effect goes beyond that expected simply due to core-core and core-valence correlation, as in a number of cases, molecular orbitals formed as a linear combination of outer-core orbitals from the metal with valence orbitals from the heteroatom are treated as (frozen-) core orbitals in the post-HF calculation. Molecular benchmark

TABLE VII. CCSD(T) spectroscopic constants for KF, with all K electrons (that are not replaced by a pseudopotential) correlated. Values in parentheses indicate the effect of the core-valence correlation relative to a frozen-core calculation.

Basis set	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
cc-pCVDZ-PP	2.2270 (+0.0059)	407.2 (-3.0)	111.57 (+20.48)
cc-pCVTZ-PP	2.1925 (-0.0013)	416.0 (+0.3)	114.90 (+33.35)
cc-pCVQZ-PP	2.1774 (-0.0063)	422.8 (+2.3)	117.04 (+38.13)
cc-pCV5Z-PP	2.1734 (-0.0085)	424.9 (+3.2)	117.71 (+39.99)
CBS	2.1695 (-0.0109)	426.9 (+4.2)	118.43 (+41.93)
cc-pwCVDZ-PP	2.2228 (+0.0028)	409.4 (-2.0)	110.99 (+21.66)
cc-pwCVTZ-PP	2.1834 (-0.0070)	423.7 (+4.8)	115.33 (+34.08)
cc-pwCVQZ-PP	2.1753 (-0.0083)	425.5 (+4.1)	117.24 (+38.47)
cc-pwCV5Z-PP	2.1731 (-0.0091)	426.3 (+4.3)	117.79 (+40.21)
CBS	2.1708 (-0.0100)	427.2 (+4.4)	118.45 (+42.04)

calculations that correlate the $(m-1)sp$ electrons are considered in Subsection IV B 2.

2. Core-valence correlation

The convergence of calculated spectroscopic constants with both the cc-pCV n Z-PP and cc-pwCV n Z-PP sequences of basis sets is shown in Table VII for the electronic ground state ($^1\Sigma^+$) of KF. The aug-cc-pV n Z basis sets were used for fluorine,⁴⁹ all K electrons not replaced by the pseudopotential were included in the correlation treatment, and the F 1s electrons were not correlated. The effect of correlating the outer-core electrons on the spectroscopic constants is shown in parentheses, and, as expected, convergence towards the CBS limit with respect to zeta-level is faster with the weighted CV sets. However, while the convergence with weighted core valence basis sets is somewhat quicker and overall relatively smooth, the core-valence *effect* still converges slowly; for cc-pwCVQZ-PP, the effect is relatively well converged in terms of r_e and ω_e , but the effect on D_e is underestimated by 3.57 kcal mol⁻¹. These results are in good agreement with those of Iron *et al.* (at the QZ level) both in terms of absolute values of the spectroscopic constants and the effect of outer-core correlation.⁷¹

The overall magnitudes of the core-valence correction to D_e in Table VII act as further evidence that correlating the outer-core, $(m-1)sp$, electrons is vital to producing accurate results for chemical systems containing group 1 and 2 elements. In the case of KF, inspecting the reference Hartree-Fock orbitals reveals that the $3a_1$ orbital (in C_{2v} symmetry) has non-negligible contributions from basis functions centered on both K and F, yet using a frozen-core definition based on valence atomic orbitals means that this orbital is not included in the CCSD(T) treatment. Although less dramatic, Tables S6 and S7 in the [supplementary material](#) also show large core-valence effects on r_e (-0.2402 Å) and ω_e (+49.8 cm⁻¹) for K₂ ($^1\Sigma_g^+$) and KH ($^1\Sigma^+$), respectively. The latter results for KH mimic those reported previously using preliminary versions of the present DK basis sets.⁷² This and other ample evidence in the literature indicates that meaningful calculations on molecules containing group 1 or 2 elements should always correlate the outer-core orbitals and use a basis set that has been optimized for this purpose,

TABLE VIII. CCSD(T) spectroscopic constants for CaO, RbF, and Cs₂. All electrons not replaced by a pseudopotential on group 1 and 2 elements have been correlated.

Molecule	Basis	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
CaO	cc-pwCVDZ-PP	2.0187	418.1	67.60
	cc-pwCVTZ-PP	1.8502	663.2	83.86
	cc-pwCVQZ-PP	1.8348	705.0	90.72
	cc-pwCV5Z-PP	1.8289	717.0	93.61
	CBS	1.8223	732.8	96.41
	Experiment ^a	1.8221	732.1	95.1 ^b
RbF	cc-pwCVDZ-PP	2.3262	354.2	111.48
	cc-pwCVTZ-PP	2.2863	371.7	115.29
	cc-pwCVQZ-PP	2.2757	373.8	117.22
	cc-pwCV5Z-PP	2.2736	373.3	117.73
	CBS	2.2719	372.8	118.33
	Experiment ^a	2.2703	376	119.9 ^c
Cs ₂	cc-pwCVDZ-PP	4.8316	32.8	9.38
	cc-pwCVTZ-PP	4.6665	41.8	9.91
	cc-pwCVQZ-PP	4.6446	42.5	10.05
	cc-pwCV5Z-PP	4.6369	42.8	10.18
	CBS	4.6290	43.0	10.31
	Experiment ^a	4.6499 ⁷³	42.0	10.43 ^d

^aAll experimental data from Ref. 62 unless otherwise stated.

^b D_0 data from Ref. 65.

^c D_0 data from Ref. 61.

^d D_e data from Ref. 74.

such as the cc-pCV n Z-PP and cc-pwCV n Z-PP sets presented here.

To demonstrate the effectiveness of the new cc-pwCV n Z-PP basis sets, CCSD(T) spectroscopic constants for the diatomic molecules CaO, RbF, and Cs₂ are presented in Table VIII, with data for other homonuclear and heteronuclear diatomic molecules tabulated in the [supplementary material](#). It can be seen that while convergence towards the CBS limit generally follows a regular pattern, the rate of convergence is relatively slow. Extrapolation to the CBS limit shows that results at the 5Z level exhibit basis set errors of up to approximately 8 mÅ in r_e , 16 cm⁻¹ in ω_e , and 3 kcal mol⁻¹ in D_e . Although the extrapolation formulae used to estimate the CBS limits have not been well tested for molecules including elements in this area of the periodic table, comparison of the spectroscopic constants at the extrapolated CBS limit with the experimental data in Table VIII generally indicates excellent agreement. One exception to this is the CBS r_e value for Cs₂, which underestimates the fluorescence spectra derived bond length of Ref. 73 by roughly 21 mÅ. As the internuclear separation in Cs₂ is relatively large, the addition of extra diffuse functions in the form of the aug-cc-pwCV n Z-PP sets was also tested for this system, but the estimated CBS limit for r_e remained essentially the same at 4.6288 Å.

Table VIII, S8, and S9 all indicate that the spectroscopic constants obtained with the cc-pwCVDZ-PP basis sets are far from the CBS limit/experiment, and larger basis sets should be used for reliable results. In particular, r_e and ω_e for RaO at the cc-pwCVDZ-PP level (see Table S9 in the [supplementary material](#)) are poor, with the TZ quality basis set reducing the bond length by almost 0.5 Å and the harmonic frequency by over 600 cm⁻¹. Combined with the slow,

but regular, convergence to the CBS limit, it is clear that large basis sets, and preferably CBS extrapolation, should be used for diatomics containing heavy alkali or alkaline earth elements.

3. Scalar relativistic effects

In this work, the exponents of the primitive Gaussian functions in the all-electron basis sets were optimized using the DKH2 Hamiltonian for 4s and 5s elements, with the DKH3 Hamiltonian used for 6s and 7s. The same orders of DKH were used for these elements in the calculation of spectroscopic constants for the hydrides and fluorides shown in Tables IX and X, respectively. As it has been established above that outer-core correlation is vital to producing accurate data, only results using the cc-pwCVnZ-DK series of basis sets (and correlating the outer-core electrons on group 1 and 2 elements) are presented. Also shown are the differences in the spectroscopic constants relative to those obtained using the PP based basis set at the same zeta level, calculated as the PP result subtracted

from the DKH value (denoted Δ PP). It should be noted that this comparison is not entirely a straightforward measure of the PP approximation, for example, the PPs have been adjusted based upon four-component results that include Breit interaction terms,^{18,19} but the Breit interaction is not included in the present DKH values.

For the hydrides in Table IX, it can be seen that convergence of the DK spectroscopic constants towards the CBS limit is slow, much as it is for the PP based basis sets. At the QZ level, there is reasonably good agreement with available experimental data.^{57–68,73–77} In the absence of experimental data for FrH and RaH, the present results can be compared to theoretical results of Koga *et al.*,²² which also used CCSD(T) with a DKH3 Hamiltonian. These NOSeC-CV-qzp results fall somewhere between the cc-pwCVTZ-DK and cc-pwCVQZ-DK values of the present work, suggesting that the NOSeC-CV sets also converge slowly towards the CBS limit, potentially overestimating r_e and underestimating D_e . There is good agreement between the two QZ level results for ω_e , indicating they

TABLE IX. All-electron scalar-relativistic^a CCSD(T) spectroscopic constants for the hydrides of the heavy alkali and alkaline earth metals. Values in parentheses indicate the change in the spectroscopic constant relative to the PP-based calculation.

Molecule	Basis ^b	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
KH	wCVDZ-DK	2.2832 (+0.0143)	926.8 (-19.9)	34.54 (-0.45)
	wCVTZ-DK	2.2430 (+0.0023)	988.4 (+0.4)	40.42 (-0.09)
	wCVQZ-DK	2.2416 (+0.0042)	985.1 (-4.4)	41.58 (-0.05)
	Experiment ^c	2.242	983.6	43.12 ^d
CaH	wCVDZ-DK	2.0334 (+0.0061)	1256.5 (-8.7)	32.88 (-0.20)
	wCVTZ-DK	2.0103 (+0.0028)	1296.2 (-3.4)	38.91 (+0.04)
	wCVQZ-DK	2.0044 (+0.0021)	1299.5 (-2.9)	40.28 (+0.11)
	Experiment ^c	2.0025	1298.3	39.2
RbH	wCVDZ-DK	2.4030 (-0.0078)	887.8 (+23.5)	33.19 (-0.04)
	wCVTZ-DK	2.3699 (+0.0034)	936.5 (-7.2)	39.03 (-0.06)
	wCVQZ-DK	2.3689 (+0.0032)	937.6 (-0.6)	40.31 (+0.02)
	Experiment ^c	2.367	936.9	41.69 ⁶⁰
SrH	wCVDZ-DK	2.1903 (-0.0038)	1134.2 (+9.0)	31.30 (-0.33)
	wCVTZ-DK	2.1530 (-0.0013)	1202.6 (-1.9)	37.99 (+0.11)
	wCVQZ-DK	2.1476 (-0.0019)	1209.3 (+1.0)	39.59 (+0.26)
	Experiment ^c	2.1456	1206.2	41.70
CsH	wCVDZ-DK3	2.5537 (-0.0058)	844.2 (+25.1)	33.34 (-0.01)
	wCVTZ-DK3	2.5093 (+0.0048)	887.4 (-6.0)	39.95 (+0.21)
	wCVQZ-DK3	2.5027 (+0.0073)	889.4 (-5.0)	41.59 (+0.26)
	Experiment ^c	2.4938	891.0	42.30 ⁷⁵
BaH	wCVDZ-DK3	2.3079 (-0.0107)	1075.2 (+9.1)	35.65 (-0.02)
	wCVTZ-DK3	2.2531 (+0.0028)	1154.7 (-4.1)	44.90 (+0.30)
	wCVQZ-DK3	2.2383 (+0.0005)	1162.5 (-5.5)	47.18 (+0.23)
	Experiment ^c	2.2319 ⁶³	1168.4 ⁶³	46.7 ⁶⁴
FrH	wCVDZ-DK3	2.6008 (-0.0135)	845.5 (+27.3)	30.62 (-0.43)
	wCVTZ-DK3	2.5555 (-0.0033)	884.7 (-4.4)	36.86 (+0.15)
	wCVQZ-DK3	2.5478 (-0.0021)	893.2 (+1.1)	38.47 (+0.17)
	Theoretical ^e	2.553	901	35.56
RaH	wCVDZ-DK3	2.4149 (-0.0181)	1020.8 (+27.3)	27.49 (-0.34)
	wCVTZ-DK3	2.3560 (-0.0028)	1097.6 (-2.8)	35.96 (+0.45)
	wCVQZ-DK3	2.3430 (-0.0046)	1110.6 (0.0)	38.05 (+0.44)
	Theoretical ^e	2.350	1112	35.81

^a4s and 5s containing hydrides calculated using DKH2, 6s and 7s using DKH3.

^bThe cc-pVnZ-DK basis sets⁵² were used for H.

^cAll experimental data from Ref. 62 unless otherwise stated.

^d D_e data quoted in Ref. 76.

^eScalar-relativistic CCSD(T)/NOSeC-CV-qzp results using DKH3 from Ref. 22.

TABLE X. All-electron scalar-relativistic^a CCSD(T) spectroscopic constants for the fluorides of the heavy alkali and alkaline earth metals. Values in parentheses indicate the change in the spectroscopic constant relative to PP-based calculation.

Molecule	Basis ^b	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
KF	wCVDZ-DK	2.2346 (+0.0118)	405.5 (-3.9)	110.09 (-0.90)
	wCVTZ-DK	2.1865 (+0.0031)	424.3 (+0.6)	115.30 (-0.02)
	wCVQZ-DK	2.1775 (+0.0022)	425.4 (-0.1)	117.18 (-0.06)
	Experiment ^c	2.1715	428.0	116.92 ^d
CaF	wCVDZ-DK	1.9989 (+0.0034)	573.9 (-3.5)	119.03 (-0.63)
	wCVTZ-DK	1.9666 (+0.0018)	580.4 (-1.6)	124.60 (-0.07)
	wCVQZ-DK	1.9581 (+0.0015)	586.0 (-0.5)	127.17 (+0.07)
	Experiment ^c	1.967	581.1	126.4 ^e
RbF	wCVDZ-DK	2.3227 (-0.0006)	355.8 (+0.0)	110.36 (-1.35)
	wCVTZ-DK	2.2878 (+0.0013)	372.1 (-0.1)	115.09 (-1.07)
	wCVQZ-DK	2.2777 (+0.0017)	372.1 (-1.0)	117.03 (-1.30)
	Experiment ^c	2.2703	376	119.9 ^d
SrF	wCVDZ-DK	2.1223 (-0.0027)	483.3 (-6.0)	118.47 (-1.33)
	wCVTZ-DK	2.0912 (-0.0040)	493.0 (-3.1)	124.54 (+0.01)
	wCVQZ-DK	2.0830 (-0.0027)	499.5 (+0.0)	127.23 (+0.27)
	Experiment ^c	2.0754	502.4	125.2
CsF	wCVDZ-DK3	2.4240 (-0.0086)	331.3 (-1.1)	113.73 (-1.77)
	wCVTZ-DK3	2.3750 (+0.0023)	344.7 (+0.1)	119.38 (+0.17)
	wCVQZ-DK3	2.3623 (+0.0028)	350.2 (+0.0)	121.95 (+0.28)
	Experiment ^c	2.3453	352.6	122.68 ^d
BaF	wCVDZ-DK3	2.2375 (-0.0107)	445.5 (-5.4)	125.08 (-1.11)
	wCVTZ-DK3	2.1926 (+0.0007)	457.0 (+1.0)	133.12 (+0.09)
	wCVQZ-DK3	2.1717 (-0.0010)	463.8 (+0.4)	136.96 (+0.30)
	Experiment ^c	2.162	468.9	134 ^f
FrF	wCVDZ-DK3	2.4896 (-0.0166)	318.6 (+0.6)	108.80 (-2.51)
	wCVTZ-DK3	2.4324 (-0.0065)	334.0 (+1.5)	114.65 (+0.14)
	wCVQZ-DK3	2.4179 (-0.0077)	337.5 (+0.0)	117.22 (+0.31)
	Theoretical ^g	2.417	339	115.19
RaF	wCVDZ-DK3	2.3259 (-0.0137)	413.3 (-4.4)	115.05 (-1.56)
	wCVTZ-DK3	2.2697 (-0.0089)	429.1 (+2.8)	123.47 (+0.79)
	wCVQZ-DK3	2.2533 (-0.0099)	435.0 (+2.4)	126.88 (+0.94)
	Experiment

^a4s and 5s containing fluorides calculated using DKH2, 6s and 7s using DKH3.^bThe aug-cc-pVnZ-DK basis sets⁵² were used for F.^cAll experimental data from Ref. 62 unless otherwise stated.^d D_0 from Ref. 61.^e D_0 from Ref. 66.^f D_0 from Ref. 68.^gScalar-relativistic CCSD(T)/NOsec-CV-qzp results using DKH3 from Ref. 22.

would converge to approximately the same value. Turning to the difference between PP and DK results, Δ_{PP} is typically small for r_e and D_e , although the DZ level change in equilibrium bond length does reach a maximum magnitude of 1.81 pm for RaH. The change in ω_e is also large at the DZ level, and in a number of cases, the difference at the QZ level can be in the region of 5.0 cm⁻¹. A comparison of Δ_{PP} between outer-core and valence-only (see Table S10 in the [supplementary material](#)) spectroscopic constants shows poor agreement, which is unsurprising given the large impact of outer-core correlation outlined above.

The results for the fluorides in Table X follow many of the same trends as for the hydrides; the basis set convergence is slow, but systematic in terms of r_e and D_e , with relatively good agreement between QZ and available experimental data. Again, there are no experimental data available for the diatomics containing Fr or Ra, and previous theoretical

data for FrF overestimate the bond length and underestimate the dissociation energy. Although the work of Koga *et al.* lists spectroscopic constants for RaF,²² they are exactly the same as those for SrF and thus have not been included in Table X. An inspection of the Δ_{PP} differences at the QZ level shows that the magnitude of the effect on r_e is in the region of 2–10 mÅ, 0.1–2.4 cm⁻¹ on ω_e , and 0.06–1.30 kcal mol⁻¹ for D_e .

Table XI displays the spectroscopic constants for the ground states of CaO, RbF, and Cs₂ calculated using the X2C scalar-relativistic Hamiltonian. For the group 1 or 2 elements, the basis sets developed in this work, and contracted specifically for use in X2C calculations, have been used, with cc-pVnZ-DK and aug-cc-pVnZ-DK basis sets for oxygen and fluorine, respectively.⁵² To demonstrate the difference in calculated spectroscopic constants due to choice of scalar-relativistic Hamiltonian, the values in parentheses

TABLE XI. All-electron X2C scalar-relativistic CCSD(T) spectroscopic constants for the ground states of CaO, RbF, and Cs₂. Values in parentheses indicate the change in the spectroscopic constant relative to DKH-based calculations (DKH2 for CaO and RbF, DKH3 for Cs₂).^a

Molecule	Basis	r_e (Å)	ω_e (cm ⁻¹)	D_e (kcal mol ⁻¹)
CaO	cc-pwCVDZ-X2C	2.0233 (+0.0001)	418.6 (-0.7)	67.11 (+0.01)
	cc-pwCVTZ-X2C	1.8459 (0.0000)	673.2 (0.0)	84.55 (0.00)
	cc-pwCVQZ-X2C	1.8319 (+0.0001)	712.2 (+0.1)	91.77 (+0.08)
RbF	cc-pwCVDZ-X2C	2.3227 (0.0000)	355.8 (+0.1)	110.36 (0.00)
	cc-pwCVTZ-X2C	2.2878 (0.0000)	372.1 (0.0)	115.09 (-0.01)
	cc-pwCVQZ-X2C	2.2777 (0.0000)	372.2 (-0.1)	117.02 (-0.01)
Cs ₂	cc-pwCVDZ-X2C	4.7910 (+0.0001)	38.8 (0.0)	8.79 (0.00)
	cc-pwCVTZ-X2C	4.6909 (+0.0001)	41.6 (0.0)	9.76 (0.00)
	cc-pwCVQZ-X2C	4.6597 (+0.0004)	42.8 (+0.4)	10.14 (0.00)

^aaug-cc-pVnZ-DK basis sets were used for O and F.

show the change relative to DKH calculations using the DKH basis sets (DKH result subtracted from X2C). Although changes in absolute energies can be reasonably large, it can be seen for the systems chosen, the effect on the spectroscopic constants is insignificant relative to the large basis set effect.

V. CONCLUSIONS

Correlation consistent basis sets have been developed for the heavy alkali (K–Fr) and alkaline earth (Ca–Ra) metals, one series (double- to quintuple-zeta quality) is based on the small-core relativistic PPs of Lim *et al.*,^{18,19} while scalar-relativistic all-electron sets (double- to quadruple-zeta) have been optimized and contracted for either DKH or X2C Hamiltonians. Sets for valence (*ms*) correlation are denoted cc-pVnZ-PP and cc-pVnZ-(DK,DK3/X2C), and sets for outer-core (*m-1sp*) and valence correlation are reported that are denoted cc-pwCVnZ-PP and cc-pwCVnZ-(DK,DK3/X2C). In the PP case, basis sets optimized using an older style core-valence objective function are also presented and are denoted cc-pCVnZ-PP.

Coupled cluster benchmark calculations have been carried out for ionization potentials and electron affinities of the alkali metals and for the first two ionization potentials of the alkaline earth metals. Correlation of the outer-core electrons is important for the accurate calculation of IPs, while augmentation with additional diffuse functions was necessary to produce reliable EAs. The new sets have also been used in extensive calculations of spectroscopic constants for diatomic molecules. In all cases, at least one of the properties of equilibrium bond length, harmonic frequency, or dissociation energy was strongly affected by correlation of the outer-core electrons of the group 1 or 2 elements, indicating, perhaps unsurprisingly, that these electrons should be routinely correlated. The convergence of the spectroscopic properties towards the CBS limit was slow, and extrapolation to the CBS limit using QZ and 5Z quality basis sets was necessary for good agreement with experimental data. The all-electron basis sets (-DK and -DK3) were also used in calculation of spectroscopic constants for the group 1 and 2 hydrides and fluorides, with much the same trends observed as in the PP-based calculations.

The basis sets developed in this work are provided in the [supplementary material](#) and will also be made available from the correlation consistent basis set repository,⁷⁸ as well as the basis set library of MOLPRO.³⁰

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for Tables S1–S11, which provide additional details on the basis set compositions of this work, and more extensive CCSD(T) benchmark calculations. All of the basis sets of this work are also included.

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¹F. Jensen, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **3**, 273 (2013).

²J. G. Hill, *Int. J. Quantum Chem.* **113**, 21 (2013).

³B. Nagy and F. Jensen, in *Review in Computational Chemistry*, edited by A. L. Parrill and K. B. Lipkowitz (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2017), pp. 93–149.

⁴D. Feller, K. A. Peterson, and J. G. Hill, *J. Chem. Phys.* **135**, 044102 (2011).

⁵V. Vasilyev, *Comput. Theor. Chem.* **1115**, 1 (2017).

⁶T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).

⁷B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, Jr., and A. K. Wilson, *Theor. Chem. Acc.* **128**, 69 (2011).

⁸J. Koput and K. A. Peterson, *J. Phys. Chem. A* **106**, 9595 (2002).

⁹H. Li, H. Feng, W. Sun, Y. Zhang, Q. Fan, K. A. Peterson, Y. Xie, and H. F. Schaefer, *Mol. Phys.* **111**, 2292 (2013).

¹⁰R. V. Krems, *Phys. Chem. Chem. Phys.* **10**, 4079 (2008).

¹¹D. DeMille, *Phys. Rev. Lett.* **88**, 67901 (2002).

¹²S. Schiller, D. Bakalov, and V. I. Korobov, *Phys. Rev. Lett.* **113**, 23004 (2014).

¹³P. K. Molony, P. D. Gregory, Z. Ji, B. Lu, M. P. Köppinger, C. R. Le Sueur, C. L. Blackley, J. M. Hutson, and S. L. Cornish, *Phys. Rev. Lett.* **113**, 255301 (2014).

¹⁴V. Zhelyazkova, A. Cournol, T. E. Wall, A. Matsushima, J. J. Hudson, E. A. Hinds, M. R. Tarbutt, and B. E. Sauer, *Phys. Rev. A* **89**, 53416 (2014).

¹⁵A. S. Flores, W. Vassen, and S. Knoop, *Phys. Rev. A* **94**, 50701 (2016).

¹⁶K. Bergmann, N. V. Vitanov, and B. W. Shore, *J. Chem. Phys.* **142**, 170901 (2015).

¹⁷W. C. Ermler, R. B. Ross, and P. A. Christiansen, *Int. J. Quantum Chem.* **40**, 829 (1991).

¹⁸I. S. Lim, P. Schwerdtfeger, B. Metz, and H. Stoll, *J. Chem. Phys.* **122**, 104103 (2005).

- ¹⁹I. S. Lim, H. Stoll, and P. Schwerdtfeger, *J. Chem. Phys.* **124**, 034107 (2006).
- ²⁰V. Velyazov, P.-O. Widmark, and B. O. Roos, *Theor. Chem. Acc.: Theory, Comput., Model.* **111**, 345 (2004).
- ²¹K. G. Dyall, *J. Phys. Chem. A* **113**, 12638 (2009).
- ²²T. Noro, M. Sekiya, and T. Koga, *Theor. Chem. Acc.* **121**, 289 (2008).
- ²³P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 299 (1985).
- ²⁴L. E. Roy, P. J. Hay, and R. L. Martin, *J. Chem. Theory Comput.* **4**, 1029 (2008).
- ²⁵F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ²⁶F. Weigend and A. Baldes, *J. Chem. Phys.* **133**, 174102 (2010).
- ²⁷W. Kutzelnigg and W. Liu, *J. Chem. Phys.* **123**, 241102 (2005).
- ²⁸D. Peng and M. Reiher, *Theor. Chem. Acc.* **131**, 1081 (2012).
- ²⁹P. Pollak and F. Weigend, *J. Chem. Theory Comput.* **13**, 3696 (2017).
- ³⁰H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györfy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, *MOLPRO 2015.1*, a package of *ab initio* programs, 2015, see <http://www.molpro.net>.
- ³¹H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2**, 242 (2012).
- ³²J. G. Hill and K. A. Peterson, *J. Chem. Phys.* **141**, 094106 (2014).
- ³³Q. Lu and K. A. Peterson, *J. Chem. Phys.* **145**, 054111 (2016).
- ³⁴T. Tsuchiya, M. Abe, T. Nakajima, and K. Hirao, *J. Chem. Phys.* **115**, 4463 (2001).
- ³⁵D. H. Bross and K. A. Peterson, *Theor. Chem. Acc.* **133**, 1434 (2014).
- ³⁶K. Ruedenberg, in *Energy, Structure, and Reactivity: Proceedings of the 1972 Boulder Summer Research Conference on Theoretical Chemistry*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973), pp. 164–169.
- ³⁷K. A. Peterson, *J. Chem. Phys.* **119**, 11099 (2003).
- ³⁸J. Almlöf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).
- ³⁹J.-P. Blaudeau, S. R. Brozell, S. Matsika, Z. Zhang, and R. M. Pitzer, *Int. J. Quantum Chem.* **77**, 516 (2000).
- ⁴⁰P. A. Christiansen, *J. Chem. Phys.* **112**, 10070 (2000).
- ⁴¹D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **103**, 4572 (1995).
- ⁴²K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **117**, 10548 (2002).
- ⁴³S. V. Andreev, V. S. Letokhov, and V. I. Mishin, *Phys. Rev. Lett.* **59**, 1274 (1987).
- ⁴⁴A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (Ver. 5.2) [online], 2015.
- ⁴⁵K. T. Andersson, J. Sandström, I. Y. Kiyani, D. Hanstorp, and D. J. Pegg, *Phys. Rev. A* **62**, 22503 (2000).
- ⁴⁶P. Frey, F. Breyer, and H. Holop, *J. Phys. B: At. Mol. Phys.* **11**, L589 (1978).
- ⁴⁷M. Scheer, J. Thøgersen, R. C. Bilodeau, C. A. Brodie, H. K. Haugen, H. H. Andersen, P. Kristensen, and T. Andersen, *Phys. Rev. Lett.* **80**, 684 (1998).
- ⁴⁸A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, *J. Chem. Phys.* **115**, 2389 (2001).
- ⁴⁹R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ⁵⁰I. S. Lim and P. Schwerdtfeger, *Phys. Rev. A* **70**, 062501 (2004).
- ⁵¹J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).
- ⁵²W. A. de Jong, R. J. Harrison, and D. A. Dixon, *J. Chem. Phys.* **114**, 48 (2001).
- ⁵³J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).
- ⁵⁴A. Karton and J. M. L. Martin, *Theor. Chem. Acc.* **115**, 330 (2006).
- ⁵⁵T. Helgaker, W. Klopper, H. Koch, and J. Noga, *J. Chem. Phys.* **106**, 9639 (1997).
- ⁵⁶A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, *Chem. Phys. Lett.* **286**, 243 (1998).
- ⁵⁷C. Amiot, P. Crozet, and J. Vergès, *Chem. Phys. Lett.* **121**, 390 (1985).
- ⁵⁸A. Kornath, A. Zoerner, and R. Ludwig, *Inorg. Chem.* **38**, 4696 (1999).
- ⁵⁹C. C. Tsai, R. S. Freeland, J. M. Vogels, H. M. J. M. Boesten, B. J. Verhaar, and D. J. Heinzen, *Phys. Rev. Lett.* **79**, 1245 (1997).
- ⁶⁰S. C. Yang, D. D. Nelson, and W. C. Stwalley, *J. Chem. Phys.* **78**, 4541 (1983).
- ⁶¹E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, *Trans. Faraday Soc.* **57**, 921 (1961).
- ⁶²K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules* (Springer-Verlag, New York, 2013).
- ⁶³R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.* **283**, 18 (2013).
- ⁶⁴I. Kopp, N. Åslund, G. Edvinsson, and B. Lindgren, *Ark Fys* **30**, 321 (1965).
- ⁶⁵J. B. Pedley and E. M. Marshall, *J. Phys. Chem. Ref. Data* **12**, 967 (1983).
- ⁶⁶G. D. Blue, J. W. Green, T. C. Ehlert, and J. L. Margrave, *Nature* **199**, 804 (1963).
- ⁶⁷M. E. Huntelaar and E. H. P. Cordfunke, *J. Chem. Thermodyn.* **29**, 817 (1997).
- ⁶⁸T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, *J. Chem. Phys.* **41**, 2250 (1964).
- ⁶⁹C. W. Bauschlicher, Jr., S. R. Langhoff, and H. Partridge, *J. Chem. Phys.* **84**, 901 (1986).
- ⁷⁰Y. Minenkov, G. Bistoni, C. Riplinger, A. A. Auer, F. Neese, and L. Cavallo, *Phys. Chem. Chem. Phys.* **19**, 9374 (2017).
- ⁷¹M. A. Iron, M. Oren, and J. M. L. Martin, *Mol. Phys.* **101**, 1345 (2003).
- ⁷²D. Feller and K. A. Peterson, *Chem. Phys. Lett.* **430**, 459 (2006).
- ⁷³G. Höning, M. Czajkowski, M. Stock, and W. Demtröder, *J. Chem. Phys.* **71**, 2138 (1979).
- ⁷⁴M. Raab, H. Weickenmeier, and W. Demtröder, *Chem. Phys. Lett.* **88**, 377 (1982).
- ⁷⁵C. Crepin, J. Vergès, and C. Amiot, *Chem. Phys. Lett.* **112**, 10 (1984).
- ⁷⁶R. W. Numrich and D. G. Truhlar, *J. Phys. Chem.* **79**, 2745 (1975).
- ⁷⁷C. Amiot, J. Vergès, and C. E. Fellows, *J. Chem. Phys.* **103**, 3350 (1995).
- ⁷⁸J. G. Hill, A correlation consistent basis sets repository, <https://bit.ly/ccBasis>, accessed Nov. 22, 2017.