Correlation consistent valence basis sets for use with the Stuttgart-Dresden-Bonn relativistic effective core potentials: the atoms Ga–Kr and In-Xe.

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Abstract

We propose large-core correlation-consistent pseudopotential basis sets for the heavy p-block elements Ga–Kr and In–Xe. The basis sets are of cc-pVTZ and cc-pVQZ quality, and have been optimized for use with the large-core (valence-electrons only) Stuttgart-Dresden-Bonn relativistic pseudopotentials. Validation calculations on a variety of third-row and fourth-row diatomics suggest them to be comparable in quality to the all-electron cc-pVTZ and cc-pVQZ basis sets for lighter elements. Especially the SDB-cc-pVQZ basis set in conjunction with a core polarization potential (CPP) yields excellent agreement with experiment for compounds of the later heavy p-block elements. For accurate calculations on Ga (and, to a lesser extent, Ge) compounds, explicit treatment of 13 valence electrons appears to be desirable, while it seems inevitable for In compounds. For Ga and Ge, we propose correlation consistent basis sets extended for (3d) correlation. For accurate calculations on organometallic complexes of interest to homogenous catalysis, we recommend a combination of the standard cc-pVTZ basis set for first- and second-row elements, the presently derived SDB-cc-pVTZ basis set for heavier p-block elements, and for transition metals, the small-core [6s5p3d] Stuttgart-Dresden
basis set-RECP combination supplemented by \((2f1g)\) functions with exponents given in the Appendix to the present paper.
I. INTRODUCTION AND THEORETICAL BACKGROUND

The two major factors that determine the quality of a wavefunction-based electronic structure calculation are the quality of the one-particle basis set and that of the n-particle correlation treatment.

Thanks to great progress in electron correlation methods (notably in the area of coupled cluster theory [1]), the n-particle problem is to a large extent solved, leaving the 1-particle basis set as the main factor that determines the quality of an electronic structure calculation.

Abundant research has been carried out on basis set convergence and the development of extended basis sets for first- and second-row systems (see e.g. [2] for a review): we note in particular the ANO (atomic natural orbital [3]) basis sets of Almlöf and Taylor, the WMR (Widmark-Malmqvist-Roos, or averaged ANO [4]) basis sets of the eponymous group, and the correlation consistent (cc) basis sets of Dunning and coworkers [5,6]. Due to their relative compactness in terms of Gaussian primitives, the cc basis sets have become very popular for benchmark wavefunction-based ab initio calculations: to a lesser extent, the same holds true for DFT (density functional theory [7]) calculations.

Basis set convergence of the dynamical correlation energy in conventional electronic structure calculations is known to be very slow. This is less of an issue for DFT calculations [8-12]: as a rule basis set convergence appears to be reached for basis sets of \( spdf \) quality and certainly for basis sets of \( spdfg \) quality. Standard basis sets of such quality are readily available for first- and second-row compounds: in addition, ANO and WMR basis sets are available for the first-row transition metals [13] and cc basis sets for the third-row main group elements [14].

Our group has recently become involved in a number of mechanistic studies by means of DFT methods (e.g. on competitive CC/CH activation by Rh(I) pincer complexes [15,16] and on Pd(0/II) and Pd(II/IV) catalyzed mechanisms of the Heck reaction [17]) that involve second-row transition metals and fourth-row main group elements. Generally, one is limited to basis set/ECP (effective core potential) combinations of approximately valence double-
zeta quality. If one wants to establish basis set convergence for a given property, one is forced to optimize basis sets ad hoc (as we have done [17]), which is however not necessarily the most elegant solution. Given that present-day DFT methods are less than ideal for the treatment of transition states [18–20], calibration calculations using coupled cluster methods are in order (at least for some small model systems) — and here the basis set issue becomes even more important.

It is well known that for such heavy elements, relativistic effects cannot gratuitously be neglected without paying a heavy toll in terms of reliability. The theory of relativistic electronic structure methods has been reviewed in detail by Pyykkö [21] and most recently by Reiher and Hess [22]. For systems in the size range of interest to organometallic chemists, four-component all-electron relativistic calculations are presently out of the question, and even quasirelativistic calculations are very costly: consequently, by far the most commonly employed alternative has been the application of relativistic effective core potentials (RECPs). A useful ‘fringe benefit’ of the latter is that they reduce the number of electrons that need to be treated, and hence, indirectly, the overall size of the basis set and cost of the calculation.

The theory and practice of ECPs have been reviewed repeatedly (e.g. [23–25]), most recently by Dolg [26]. Several ECP families are available for the range of the periodic table of interest to us, such as the LANL (Los Alamos National Laboratory) ECPs of Hay and Wadt [27], the CEP (Consistent Effective Potential) family of Stevens, Basch, and coworkers [28], the Ermler-Christensen family [29], and the Stuttgart-Dresden-Bonn (SDB) energy-consistent pseudopotentials [30].

The purpose of this paper is to present and validate valence basis sets for RECPs of a quality comparable to that of the cc-pVTZ and cc-pVQZ correlation-consistent basis sets for lighter elements, to be used in conjunction with the latter. In selecting the underlying RECP, we have opted for the SDB pseudopotentials for the following methodological and pragmatic reasons (some, but not all, of which are satisfied for the other popular ECPs):

- compact mathematical form
• ready availability in the commonly used quantum chemistry packages Gaussian 98 and MOLPRO 2000.

• consistent treatment of relativistic effects in all relevant rows of the periodic table

• independence of the ECP on the valence basis set

• availability of core polarization potentials (CPPs), since we were planning to use ‘large core’ potentials for the main group elements

• availability of extended valence basis sets (specifically, [6s5p3d] contractions) for the transition metals. In Appendix I, we shall present optimized [2f1g] polarization functions for those valence basis sets, to be used in conjunction with the presently derived SDB-cc-pVTZ basis sets for third- and fourth-row elements, and standard cc-pVTZ basis sets for first- and second-row elements.

To our knowledge, the only published example so far of a ‘correlation consistent’ basis set based on an ECP is the work of Bauschlicher, who published cc-pVnZ (n = T, Q, 5) basis sets for indium, optimized for (5s, 5p, 4d) correlation, to be used in conjunction with a small-core SDB pseudopotential. In this paper and a subsequent application study, benchmark calculations on a number of In compounds were presented that clearly support the idea that the development of SDB-based correlation consistent basis sets is warranted.

In the next section, we shall describe the procedure by which the valence basis sets were optimized. In the following section, we shall present validation calculations with these basis sets on a variety of diatomic molecules. Conclusions are presented in a final section.

II. GENERATION OF BASIS SETS

All electronic structure calculations were carried using MOLPRO2000 running on a Compaq ES40 at the Weizmann Institute of Science. Basis sets were carried out by means of an adaptation of the DOMIN program by P. Spellucci, which is an implementation of the BFGS (Broyden-Fletcher-Goldfarb-Shanno) variable-metric method. Numerical derivatives
of order two, four, and six were used: the lower orders until an approximate minimum was reached, after which the optimization was refined using the higher orders.

For the third-row main group elements, we employed the SDB pseudopotentials denoted by the SDB group as ECP28MWB [37], i.e. large-core (1s2s2p3s3p3d) energy-consistent pseudopotentials obtained from quasirelativistic Wood-Boring [38] calculations. For the fourth-row main group elements, we employed the ECP46MWB set [37], i.e. large-core (1s2s2p3s3p3d4s4p4d).

Unless indicated otherwise, all Hartree-Fock calculations were carried out using proper symmetry and spin eigenfunctions.

A. Valence $sp$ basis sets

In order to obtain an idea as to the size of the required $sp$ set for the valence orbitals, we carried out the following numerical experiment for the Se atom: a valence SCF calculation was carried out using the complete (26s17p) part of the all-electron cc-pV5Z basis set [14] added to the ECP28MWB pseudopotential. Then all primitives with coefficients below $10^{-5}$ were discarded, leaving us with a (16s13p) primitive set at the expense of only 0.38 microhartree in energy. Raising the ‘cutoff’ to $10^{-4}$ reduced the primitive set to (13s11p), and raises the energy by another 3 microhartree. Raising the cutoff by another order of magnitude reduces the primitive set to (12s9p), at the expense of an additional 13 microhartree. Applying the same sequence of cutoffs to the (21s16p) primitives in the all-electron cc-pVQZ basis set leads to (14s11p), (13s9p), and (11s7p), respectively: from the (20s13p) primitives of the all-electron cc-pVTZ basis set we obtain in the same manner (12s9p) for a $10^{-4}$ cutoff, and (10s7p) for a $10^{-3}$ cutoff. Similar patterns were observed for other third-row elements: the bottom line appears to be that 3–4 more $s$ primitives are required than $p$ primitives.

We subsequently attempted to minimize $((k + 4)skp)$ basis sets ($k=6–10$) directly at the SCF level. However, the Hessian for some of the higher-exponent $s$ functions is extremely flat, and as a result no reliable optimization can be carried out. Considering the fact that, for instance, the outer (13s11p) exponents of the all-electron cc-pV5Z basis set
display roughly even-tempered sequences $\zeta_k = \alpha \beta^{k-1}$ except for the outermost four primitives of every symmetry, we adopted the compromise solution of optimizing the four outermost primitives of each symmetry without restriction, but constraining the remainder to follow an even-tempered sequence. This leads to an optimization problem with twelve parameters in all (eight independent exponents, plus one $\alpha$, $\beta$ pair each for $s$ and $p$).

In this manner, we were able to obtain $(10s6p)$ through $(14s10p)$ primitive sets. For Ga, Ge, and As, multiple minima were invariably found, with a solution that exhibits a ‘gap’ between the 3rd and 4th (or 4th and 5th) outermost primitive being marginally lower in energy than a solution where no such gaps were present. (This behavior is particularly noticeable for the $s$ primitives.) Carrying out 4-parameter optimizations with purely even-tempered $(14s10p)$ basis set quickly reveals the cause: as $\zeta$ increases, the coefficients are initially positive, but then decay and change sign as the higher exponent primitives ensure the proper inner shape of the orbital. The energy is rather insensitive to the location — or even the presence — of the primitive near the crossing point, and especially with smaller sets of primitives, a marginal gain in energy might be obtained from a solution with an additional primitive in the very high exponent region rather than in the ‘crossing’ region. Since for application in correlated calculations, the presence of a gap in the outer part of the exponent sequence is clearly undesirable, we have deliberately chosen the most ‘even-tempered’ solution even where it was not the global minimum.

Similar phenomena were observed for In–I: and likewise, we obtained the most ‘even-tempered’ primitive valence sets up to $(14s10p)$.

**B. Addition of higher angular momentum functions**

Parameters for added higher angular momentum functions were then optimized at the CISD level. At first even-tempered sequences of up to four $(3d)$-type functions were added, followed by up to three additional $(4f)$-type functions and up to two additional $(5g)$-type functions. For the third-row main group elements, these optimizations progressed uneventfully. Not surprisingly, the $d$ exponents differ somewhat from those obtained by Dunning and
coworkers for all-electron basis sets: in the latter, the $d$ functions do double-duty as angular correlation functions for the $(4s, 4p)$ orbitals and as $(3d)$ primitives, while in our case they solely take on the former role. For the $f$ and $g$ functions, the similarity is greater. In terms of energetic increments, the familiar ‘correlation consistent’ (2d1f) and (3d2f1g) groupings of functions with similar energy lowerings emerge.

In the fourth row, the convergence pattern of the $d$ exponents is somewhat peculiar, in that for instance for Te and I, the energy lowerings for the 2nd and 3rd $(3d)$ function are similar. This is caused by the rather low-lying $(5d)$ orbital, which also causes a somewhat peculiar $(2d)$ exponent pattern for Te. We shall return to this point shortly.

C. Definition of the final contracted basis sets

We carried out an analysis similar to that of Dunning and coworkers, in that we for instance completely contracted the $p$ orbital in a $(14s10p4d3f2g)$ basis set, then optimized even-tempered sequences of added $p$ primitives. The optimum $s$ and $p$ exponents revealed similar trends. In terms of contracting our Se basis set for correlation, however, they unequivocally suggest that the 2nd and 4th outermost $(s)$ and $(p)$ primitives be decontracted for a valence triple zeta basis set, and the 2nd–4th outermost primitives for a valence quadruple zeta basis set. (From here on, we shall be counting primitives starting from the ‘outermost’, i.e. smallest and most diffuse, exponent.) By comparison, in the Dunning all-electron case these were the 1st and 3rd, and 1st–3rd primitives, respectively. However, our outermost $(sp)$ primitives are considerably more diffuse than theirs, by virtue of the absence of the inner-shell ‘gravity well’ in the valence-only optimizations. The exponents of the decontracted primitives in fact are fairly similar.

This having been established, we determined our favored ‘VTZ’ and ‘VQZ’ contraction patterns for each element by comparing total energies between all six and four possible choices, respectively, among the four outermost primitives. If we denote decontraction of a primitive by a 1 and the lack thereof by a 0, and start at the lowest exponent, then the favored (i.e., lowest-energy) quadruple-zeta contraction pattern is found to be \{0111\} for Se,
Br, Kr, Te, I, and Xe, but \{1101\} for Ga, Ge, In, and Sn. (For As, \{1011\} is marginally lower in energy than \{0111\}, while for Sb, a \{1110\} pattern for the \(s\) was combined with a \{1101\} pattern for the \(p\) functions.) For the triple-zeta contractions, the \{0101\} pattern prevails for As, Se, Br, Kr, Te, I, and Xe, but the \{0110\} pattern for Ga, Ge, In, Sn, and Sb.

The final basis sets for most elements were then obtained simply by adding the optimum (2d1f) exponents to the ‘triple-zeta’ contraction — leading to a [3s3p2d1f] contracted basis set —, and the optimum (3d2f1g) exponents to the ‘quadruple-zeta’ contraction — leading to a [4s4p3d2f1g] contracted basis set. For Te and I, because of the peculiarities of the \(d\) exponents noted above, this procedure does not yield a satisfactory SDB-cc-pVTZ basis set. By obtaining CISD natural orbitals for Te and I using (3d1f) primitives, it was revealed that the highest-exponent primitive contributed appreciably (and similarly) to the lowest two \(d\)-type natural orbitals, but that the latter are mainly distinguished by a sign change in the lowest-exponent \(d\) primitive. Consequently, the two innermost \(d\) primitives were contracted based on their coefficients in the lowest \(d\) type natural orbital. The slight added cost should be well outweighed by the greater reliability. Considering the \(d\)-type ANOs in calculations with (3d1f) primitives on Sb, Sn, and In revealed that the same procedure might be beneficial for In, but would not affect Sn or Sb. Therefore, in our final SDB-cc-pVTZ basis sets, the \(d\) functions in In, Te, and I are in fact (3d) \(\rightarrow\) [2d] segmented contractions.

The final basis sets generated are available on the Internet World Wide Web at the Uniform Resource Locator \url{http://theochem.weizmann.ac.il/web/papers/SDB-cc.html} in both Gaussian 98 and MOLPRO format.

D. Diffuse function exponents

For anionic systems and some very polar compounds, the availability of (diffuse-function) ‘augmented’ basis sets, like the original aug-cc-pV\(n\)\(Z\) basis sets [39], is essential. We have obtained diffuse functions for use with our SDB-cc-pVTZ and SDB-cc-pVQZ basis sets using the following procedure: (a) one low-exponent \(s\) and \(p\) function, each, were added to the
sp part of the underlying basis set and optimized simultaneously at the SCF level for the corresponding atomic anion; (b) successive angular momenta of the underlying basis set were introduced, and one additional low-exponent primitive added and optimized, at the CISD level for the corresponding atomic anion. The final SDB-aug-cc-pVTZ and SDB-aug-cc-pVQZ basis sets are thus of \([4s4p3d2f]\) and \([5s5p4d3f2g]\) quality, respectively.

III. APPLICATION TO DIATOMIC MOLECULES

In order to validate our basis sets, we have carried out CCSD(T) calculations of the dissociation energy \((D_e)\), bond length \((r_e)\), harmonic frequency \((\omega_e)\) and first-order anharmonicity \((\omega_\text{x}r_e)\) of a number of third-row and fourth-row diatomic molecules selected from the compilation by Huber and Herzberg [40]. CCSD(T) energies were computed at eleven points spaced evenly at 0.01 Å intervals around the experimental \(r_e\), a fifth- or sixth-order polynomial in \(r\) was fit, and a standard Dunham analysis [41] carried out on the resulting polynomial. For the open-shell systems and the constituent atoms, the CCSD(T) definition according to Ref. [42] was employed throughout.

Since we are using ‘large’ cores, we also carried out calculations using core polarization potentials (CPPs). For elements of groups IV, V, and VI the parameters were taken from the work of Igel-Mann et al. [43], although the cutoff parameters given in that reference are not optimal for the ECP\textit{nn}MWB pseudopotentials. For group III elements, optimal cutoffs were taken from Leininger et al. [44], while optimal cutoffs for the halogens were taken from the online version of the SDB pseudopotentials [45]. (The valence basis set was left unchanged.)

For systems that include at most third-row atoms, all-electron calculations could be carried out for comparison using the corresponding standard cc-pV\textit{n}Z basis sets [5-45]. \(r_e\) and \(\omega_e\) for these species are given in Table I, while \(D_e\) values are given in Tables VII and V. For the remaining diatomics (which include at least one fourth-row atom), the corresponding data are found in Tables I and VI, respectively.

In comparing such data with all-electron calculations in which only valence electrons are correlated, it should be kept in mind that the CPPs approximately account for both inner-
shell relaxation/polarization ("static core polarization") and inner-shell correlation ("dynamic core polarization"). Therefore, a direct comparison appears to be somewhat ‘unfair’ to the all-electron calculations; on the other hand, since the standard cc-pV$n$Z basis sets are by definition of minimal basis set quality in the inner-shell orbitals, these basis sets are fairly limited in terms of flexibility for static polarization. For heavier elements, it should also be kept in mind that the ECP calculations include relativistic effects at least approximately, while their all-electron counterparts discussed here are entirely nonrelativistic.

For the late third-row species, it seems to be clear that the performance of our SDB-cc-pV$n$Z basis sets is on a par with that of the all-electron basis sets. Introduction of the core polarization potentials results in a significant improvement in the computed bond distance: agreement between SDB+CPP-cc-pVQZ and experimental bond lengths is particularly good for many species. This conclusion is less clear for the harmonic frequencies, where the known tendency [47] of CCSD(T) to slightly overestimate harmonic frequencies may mask any small improvements. The computed anharmonicities (not reported in Table I) agree very well between the various methods and experiment.

For the early third-row species, we noticed the at first sight peculiar phenomenon (Table III) that, while our data with CPP are in very good agreement with experiment, the all-electron bond lengths are considerably too long, e.g. 0.05 Å in GeF. (These differences are too large to be plausibly ascribed to relativistic effects accounted for by the pseudopotentials.) The cause lies in the impossibility to make a meaningful separation between ‘valence’ and (3d) orbitals in these molecules: if correlation from the (3d) orbitals is admitted, a dramatic improvement is seen in the computed bond distances. Needless to say, such calculations are vastly more expensive than those with the large-core pseudopotentials, and if the all-electron basis set would be expanded with the appropriate angular correlation functions for (3d) correlation (i.e., high-exponent f and g functions), this would further increase the cost differential.

As an illustration, we will consider the GaH molecule in somewhat greater detail (Table IV). The all-electron calculations with standard cc-pV$n$Z basis sets fortuitously reproduce $\omega_e$.
very well, but overestimate the bond distance by almost 0.03 Å. In contrast, 4-electron ECP calculations with an 28-electron pseudopotential both underestimate $\omega_e$ and overestimate $r_e$. Admitting (3d) correlation with the cc-pV$n$Z basis sets leads to a dramatic shortening of $r_e$, but also to severely overestimated $\omega_e$ and anharmonicity. Obviously, this basis set needs to be significantly extended before it is suitable for (3d) correlation. We have generated such basis sets, denoted cc-pDVTZ and cc-pDVQZ, in the following manner. All basis functions in the original cc-pVQZ basis set were retained, but four additional $d$ primitives were decontracted. After this, successive layers of $f$, $g$, and finally $h$ primitives were optimized at the CISD level (13 electrons correlated) on top of the original basis set. We found that the first $h$, second $g$, and third $f$ function yielded similar lowerings of the atomic energy, and hence added (3f2g1h) primitives to the basis set. (Exponents and other details can be found in the Supplementary Material.) Then we restored the original $d$ functions and progressively uncontracted primitives: while the first additional uncontracted $d$ yields a very large energy lowering, the second adds a 10 millihartree amount comparable to that of the $h$ functions, while lowerings decay rapidly after that. Hence the final cc-pDVQZ basis set is of [7s6p6d5f3g1h] quality. By similar arguments, we find that the cc-pVTZ basis set requires addition of (2f1g) functions and decontraction of two additional $d$ primitives, leading to a cc-pDVTZ basis set of [6s5p6d3f1g] quality. (While the $f$ exponents in the cc-pDVQZ basis set span a continuous range, a ‘gap’ is present in the cc-pVTZ case. A similar phenomenon is seen in an earlier Ga basis set of Bauschlicher [48].) These basis sets indeed do represent an improvement (Table IV) but the 14-electron results clearly are still deficient in some respect. We considered also including (3s3p) correlation: to accommodate this, we uncontracted two additional $s$ and $p$ primitives each in the cc-pDVTZ basis set, as well as (to ensure adequate coverage of angular correlation from these orbitals) one additional $d$ function. The resulting spectroscopic constants are in excellent agreement with experiment, which might lead to the conclusion that (3s3p) correlation is essential for a proper description of GaH. However, as we reduce the number of correlated electrons from 22 to 14, we see only quite minor effects on the spectroscopic constants. At that stage, the additional $d$ function can be removed with
essentially no effect on the computed spectroscopic constants; the cc-pDVTZ+2s2p basis set is thus of \([8s7p6d3f1g]\) quality. Correlating valence orbitals only leads to \(r_e\) being too long and \(\omega_e\) too low, confirming that the excellent \(\omega_e\) with standard cc-pVnZ basis sets is indeed the result of an error compensation.

We now consider the use of small-core ECPs. The effect of reoptimizing exponents was deemed minimal: instead we simply (a) carried out an ECP10MWB Hartree-Fock calculation with an uncontracted cc-pVTZ or cc-pVQZ basis set; (b) deleted all primitives with coefficients×degeneracies that are significantly less than \(10^{-4}\); repeated the SCF calculation and recontracted the basis set with the orbital coefficients thus obtained. In the cc-pVTZ basis set, we were able to delete the innermost (5s2p) primitives; in the cc-pVQZ basis set, the innermost (6s3p) primitives could be deleted. The recontracted basis sets (which are of \([4s4p5d3f1g]\) and \([5s5p6d5f3g1h]\) contracted size; to this should be added the additional decontracted \(s\) and \(p\) primitives mentioned above, leading to an SDB-cc-pDVTZ+2s2p basis set of \([6s6p5d2f1g]\) quality and an SDB-cc-pDVQZ basis set of \([8s8p6d5f3g1h]\) quality.) We indeed find performance with these basis set-ECP combinations to be quite satisfactory (Table IV). (Note that for technical reasons, the SDB-cc-pDVQZ results do not include \(h\) functions.)

It should also be noted that the effects of (3d) correlation, while still important in accurate work, are significantly smaller with the cc-pDVTZ+2s2p and cc-pDVQZ+3s3p basis sets than with their less extended counterparts. The very large core correlation contributions seen in such studies as Ref. [49] are thus at least in part basis set artefacts.

Results for GeH (Table IV) follow similar trends as those for GaH, although the deviation from experiment incurred by neglecting (3d) correlation is definitely smaller. Continuing the series, our computed results for AsH, SeH, and HBr suggest no need for including (3d) correlation in these systems.

We also applied the cc-pDVTZ and cc-pDVQZ basis sets to the polar Ga and Ge compounds (Table III). A (sometimes notable) improvement is mainly seen in the vibrational
frequencies. Decontracting additional (sp) primitives in the Ga basis set was considered for GaF, and does not appear to greatly affect results. This parallels a finding noted earlier \[50\] for inner-shell correlation in first-row compounds, where flexibility of the core correlation basis set appears to be more important for A–H than for A–B bonds.

For the fourth-row systems, only a comparison with experiment is possible. Especially the SDB+CPP-pVQZ results agree very well with experiment, while the errors for the SDB+CPP-pVTZ basis sets are not dissimilar from those seen for the lighter-atom systems. A notable exception is constituted by a number of indium compounds, for which abnormally short bond distances are found. This problem has been noted previously for large-core pseudopotential calculations on heavy group III halides \[51\]. We attempted a number of calculations in which Bauschlicher’s correlation-consistent basis set for In was used in conjunction with regular cc-pV\(n\)\(Z\) basis sets on H–Ar and SDB-cc-pV\(n\)\(Z\) on Ga–Kr and Sn–Xe. The In (4d) electrons were correlated in these calculations. This completely resolves the problem. Discrepancies between all-electron and ECP28MWB basis sets on In are not inconsistent with the expected magnitude of relativistic effects on \(r_e\) and \(\omega_e\). For InBr and InI, consideration of a core polarization potential on the halogen has effects of -0.007 Å and -0.013 Å, respectively, on the bond distance, bringing them into excellent agreement with experiment. (Note that the +0.005 Å discrepancy between computed and observed \(r_e\) (InCl) found by Bauschlicher \[34\] with his largest basis set appears to be almost entirely due to \((2s2p)\) correlation in Cl: its inclusion reduces \(r_e\) by 0.005 Å.)

Finally, we shall consider dissociation energies. These are found in Tables \[VI, VII, and VIII\], together with experimental data from two sources. These are the 1979 Huber and Herzberg (HH) book \[40\], and a more recent compilation by Kerr and Stocker (KS) \[52\] which contains data through November 1998.

All computed dissociation energies are corrected for atomic and molecular first-order spin-orbit splitting, with the data taken from the experimental sources for the molecules and from Ref. \[53\] for the atoms.

Aside from atomization energies with SDB-cc-pV\(n\)\(Z\), SDB-aug-cc-pV\(n\)\(Z\), and all-electron
cc-pVnZ basis sets, the tables contain extrapolations to the infinite basis limit using the expression taken from W1 theory [54]:
\[ E_\infty = E[VQZ] + (E[VQZ] - E[VTZ])/(4/3)^{3.22} - 1 \]
where the exponent 3.22 is specific to the VTZ/VQZ basis set combination. This is in fact a damped variant of the simple \( A + B/l^3 \) formula of Halkier et al. [55]: the damping is required [54] because the VTZ and VQZ basis sets are still not extended enough and lead to overshooting if the \( A + B/l^3 \) formula is applied to them. (The latter is the extrapolation of choice for larger basis sets.)

One conspicuous feature of the experimental results is just how uncertain they are for many molecules in these tables. For the late third-row systems, agreement between experiment and our extrapolated results including CPP is excellent for those molecules where the experimental value is precisely known. For most of the other systems, the computed value falls within the combined uncertainties of the experimental values. Agreement in fact appears to be slightly better than for the all-electron calculations, but this is not an entirely ‘fair’ comparison since the latter include neither inner-shell correlation nor scalar relativistic corrections, while both are included approximately in the SDB+CPP results through the core-polarization potential and the relativistic pseudopotential, respectively.

For the Ga, Ge, and In compounds, experimental dissociation energies are so uncertain that a meaningful comparison is essentially impossible. For those fourth-row systems where precise experimental data are available, agreement with experiment is still quite satisfactory, albeit less good than for the third-row compounds. In particular, an account for higher-order spin-orbit effects might be mandatory for some of the iodine compounds. Dolg [56] carried out benchmark calculations on the hydrogen halides and dihalides, and found near-exact spin-orbit contributions to \( D_e(HI) \) and \( D_e(I_2) \) of 0.26 and 0.49 eV, respectively: simply considering the fine structures of the constituent atoms (as done here) yields 0.315 and 0.63 eV, respectively. In other words, our calculated \( D_e \) values for HI and I\(_2\) are intrinsically too low by 0.07 and 0.14 eV, respectively.

As expected, the use of (diffuse function) ‘augmented’ basis sets yields improved results for \( r_e \) and \( \omega_e \) of highly polar molecules (e.g., GaF); for \( D_e \) values, differences of up to 0.05
eV are seen after extrapolation, which are definitely significant in accurate thermochemical work. As is the general rule [57,54], the addition of diffuse functions considerably improves the success of extrapolation methods and improves agreement with (precise) experimental dissociation energies.

Finally, we should address the question whether or not the RECPs used here provide an approximate account for scalar relativistic effects. Visscher and coworkers studied relativistic effects on the hydrogen halogenides [58], dihalogenides [59], and interhalogenides [60] by means of full four-component relativistic CCSD(T) as implemented by Visscher, Lee, and Dyall [61]. (Pisani and Clementi [62] also carried out Dirac-Fock calculations on the chalcogen hydrides — including SeH — and found an effect of -0.005 Å on \( r_e \).) Since down to Br, the effects are fairly small (e.g. +0.003 Å and -6 cm\(^{-1}\) in BrF), a comparison between all-electron and ECP results is somewhat dubious as an indicator for the recovery of relativistic effects. Given however the sizable relativistic contributions found in that work for the iodine compounds (e.g. IF: +0.012 Å and -23 cm\(^{-1}\)), the level of agreement with experiment found in the present paper is somewhat hard to explain unless the ECPs indeed recover most of the scalar relativistic effects.

**IV. CONCLUSIONS**

We have derived (fairly) compact valence basis sets of cc-pV\(n\)Z and aug-cc-pV\(n\)Z quality (\(n=T,Q\)) for the elements Ga–Kr and In–Xe, to be used in conjunction with large-core Stuttgart-Dresden-Bonn pseudopotentials. For the third row, the basis sets appear to be quite comparable to the corresponding all-electron cc-pV\(n\)Z basis sets. Agreement with experiment is quite satisfactory for compounds of the later heavy p-block elements. Highly accurate calculations on Ga and, to a lesser extent, Ge compounds require treating the (3d) electrons explicitly: we propose (3\(d\))-correlation basis sets for these elements. For In compounds, inclusion of (4d) correlation is a must, as previously found by Bauschlicher [34]: we recommend the basis sets in that reference.

Our principal objective was having extended basis sets available for studies on
organometallic compounds, including those with one or more heavy group V, VI, and VII elements. This objective appears to have been reached.

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SUPPLEMENTARY MATERIAL

The SDB-cc-pVTZ, SDB-cc-pVQZ, cc-pDVTZ, and cc-pDVQZ basis sets developed in this paper are available for download on the Internet World Wide Web at the URL http://theochem.weizmann.ac.il/web/papers/SDB-cc.html

APPENDIX: F-AND G-FUNCTION EXPONENTS FOR THE TRANSITION METALS

For use in conjunction with the above SDB-cc-pVTZ basis set on Ga-Kr and In–Xe, and the standard cc-pVTZ basis set on the first two rows of the periodic table, we recommend the following basis set/ECP combination for transition metals.

For first-row transition metals, the pseudopotential denoted as ECP10MDF [63] (which has a small 10-electron core) was used in conjunction with the [6s5p3d] contraction of an (8s7p6d) primitive set given in Ref. [63]. For second-and third-row transition metals, we used the ECP28MWB and ECP60MWB quasirelativistic pseudopotentials, respectively, as given in Ref. [64], together with the [6s5p3d] contracted valence basis sets given in the same reference.
Two ($4f$)-type functions and one ($5g$)-type function were added, and their exponents optimized at the CISD level for the lowest-lying $(s)^1(d)^{n-1}$ and $(s)^2(d)^{n-2}$ states. (In addition, optimizations were carried out for the $(s)^0(d)^{10}$ ground state of Pd.) Proper symmetry and spin eigenfunctions were used for the Hartree-Fock reference, and only valence electrons were correlated. The optimum exponents for the two states considered (three in the case of Pd) are not very different: we recommend their averages as the $f$ and $g$ exponents, which are given in Table VIII.
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TABLE I. CCSD(T) and experimental spectroscopic constants ($R_e$ in Å, $\omega_e$ in cm$^{-1}$) for molecules containing third row atoms

| molecule | basis | $R_e$ SDB | $R_e$ CPP | $R_e$ all $e^-$ | Exp | $\omega_e$ SDB | $\omega_e$ CPP | $\omega_e$ all $e^-$ | Exp |
|----------|-------|--------|--------|-------------|-----|-------------|--------|-------------|-----|
| AlBr VTZ | 2.3149 | 2.3088 | 2.3271 | 2.294807 | 383.0 | 384.4 | 377.3 | 378.0 |
| VQZ     | 2.3073 | 2.3014 | 2.3180 | 381.1 | 382.3 | 377.0 |
| AVTZ    | 2.3164 | 377.9 |
| AVQZ    | 2.3050 | 374.6 |
| As$_2$ VTZ | 2.1265 | 2.1126 | 2.1348 | 2.1026 | 424.0 | 426.8 | 424.6 | 429.55 |
| VQZ     | 2.1098 | 2.0963 | 2.1284 | 432.1 | 435.1 | 428.7 |
| AsF $^3\Sigma^-$ VTZ | 1.7298 | 1.7224 | 1.7464 | 1.7360 | 697.0 | 700.3 | 698.1 | 685.78 |
| VQZ     | 1.7291 | 1.7217 | 1.7446 | 693.6 | 696.9 | 697.1 |
| AVTZ    | 1.7298 | 687.1 |
| AVQZ    | 1.7185 | 700.9 |
| AsH $^3\Sigma^-$ VTZ | 1.5320 | 1.5269 | 1.5354 | 1.5231$^a$ | 2135.3 | 2138.2 | 2151.9 | 2155.503$^a$ |
| VQZ     | 1.5286 | 1.5234 | 1.5335 | 2156.0 | 2159.5 | 2161.1 |
| AsN VTZ | 1.6292 | 1.6227 | 1.6374 | 1.61843 | 1063.2 | 1069.7 | 1064.5 | 1068.54 |
| VQZ     | 1.6188 | 1.6124 | 1.6326 | 1079.1 | 1085.8 | 1071.9 |
| AsO $^2\Pi$ VTZ | 1.6260 | 1.6200 | 1.6378 | 1.6236 | 973.6 | 978.2 | 971.2 | 967.08 |
| VQZ     | 1.6199 | 1.6138 | 1.6344 | 978.5 | 983.2 | 975.5 |
| AsP VTZ | 2.0216 | 2.0142 | 2.0276 | 1.999 | 597.7 | 600.2 | 597.3 | 604.02 |
| VQZ     | 2.0083 | 2.0011 | 2.0194 | 607.8 | 610.3 | 604.1 |
| AsS $^2\Pi$ VTZ | 2.0393 | 2.0319 | 2.0435 | 2.0174 | 559.5 | 561.5 | 561.3 | 567.94 |
| VQZ     | 2.0246 | 2.0174 | 2.0349 | 570.0 | 571.9 | 568.0 |
| BrBr VTZ | 1.8964 | 1.8908 | 1.9060 | 1.8882 | 690.5 | 693.8 | 683.7 | 684.31 |
| VQZ     | 1.8942 | 1.8887 | 1.9034 | 685.8 | 688.6 | 681.1 |
| AVTZ    | 1.8918 | 1.9068 | 684.4 | 677.9 |
| AVQZ    | 1.8894 | 1.9044 | 700.9 | 678.8 |
| Br$_2$ VTZ | 2.3138 | 2.3014 | 2.3108 | 2.28105 | 313.6 | 316.4 | 319.3 | 325.321 |
| VQZ     | 2.2970 | 2.2856 | 2.2983 | 323.8 | 326.1 | 325.9 |
| AVTZ    | 2.2941 | 2.3172 | 318.1 | 317.3 |
| AVQZ    | 2.2808 | 2.2986 | 326.9 | 325.1 |
| BrCl VTZ | 2.1616 | 2.1555 | 2.1627 | 2.136065 | 434.3 | 436.2 | 435.9 | 444.276 |
| VQZ     | 2.1491 | 2.1432 | 2.1504 | 442.2 | 443.9 | 443.3 |
| AVTZ    | 2.1545 | 443.6 |
| AVQZ    | 2.1420 | 443.5 |
| BrF VTZ | 1.7680 | 1.7628 | 1.7685 | 1.75894 | 661.0 | 664.0 | 666.5 | 670.75 |
| VQZ     | 1.7611 | 1.7559 | 1.7619 | 672.0 | 674.5 | 677.0 |
| AVTZ    | 1.7622 | 667.7 |
| AVQZ    | 1.7547 | 676.5 |
| Material | Basis Set | Ionization Energy | Total Energy | Enthalpy of Formation |
|----------|-----------|-------------------|--------------|-----------------------|
| CSe      | VTZ       | 1.6921 1.6863 1.6966 1.67647 | 1019.3 1025.4 1024.1 1035.36 |
|          | VQZ       | 1.6834 1.6776 1.6911 | 2656.1 2665.0 2660.0 2648.975 |
| HBr      | VTZ       | 1.4147 1.4106 1.4203 | 2657.7 2667.2 2661.2 |
|          | VQZ       | 1.4155 1.4112 1.4205 | 2647.2 2656.2 2657.2 |
|          | AVTZ      | 1.4166 1.4124 1.4213 | 2651.9 2661.5 2658.1 |
|          | AVQZ      | 1.4163 1.4120 1.4211 | 2648.9 2656.2 2648.9 |
| SeH      | VTZ       | 1.4702 1.4654 1.4731 | 2406.3 2417.6 2421.715(23) |
|          | VQZ       | 1.4680 1.4630 1.4721 | 2416.6 2425.5 2425.4 |
| NSe      | Π         | 1.6659 1.6606 1.6671 | 946.8 952.3 955.8 956.81 |
|          | VQZ       | 1.6539 1.6487 1.6599 | 964.0 970.4 966.1 |
| Se₂      | 3Σ⁻       | 2.1911 2.1783 2.1915 | 2166.0 381.3 384.6 384.7 385.303 |
|          | VQZ       | 2.1752 2.1628 2.1830 | 388.3 391.5 389.6 |
| SeO      | 3Σ⁻       | 1.6476 1.6425 1.6500 | 914.4 918.8 922.2 914.69 |
|          | VQZ       | 1.6379 1.6328 1.6454 | 924.9 929.3 926.6 |
| SeS      | 3Σ⁻       | 2.0546 2.0482 2.0558 | 545.7 550.2 549.5 555.56 |
|          | VQZ       | 2.0407 2.0344 2.0458 | 556.2 558.7 556.6 |
| SiSe     | VTZ       | 2.0834 2.0770 2.0882 | 572.0 574.6 571.3 580.0 |
|          | VQZ       | 2.0713 2.0650 2.0790 | 578.5 581.2 576.9 |
|          | AVTZ      | 2.0840 2.0775 2.0887 | 569.3 572.1 569.1 |
|          | AVQZ      | 2.0723 2.0659 2.0794 | 576.1 578.9 576.1 |

SDB: calculations using large-core SDB pseudopotentials; CPP: ditto with core polarization potentials added.  

\(^a\) AsH \((R_e\) and \(\omega_e)\): K. D. Hensel, R. A. Hughes, and J. M. Brown J. Chem. Soc. Faraday Trans. II 91, 2999 (1995).  

\(^b\) SeH \((R_e\) and \(\omega_e)\): R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. 203, 9 (2000).
| molecule | basis | $R_e$ | $\omega_e$ |
|----------|-------|------|--------|
|          |       | SDB  | CPP   | Exp   | SDB  | CPP   | Exp   |
| AlI      | VTZ   | 2.5591 | 2.5478 | 2.537102 | 321.1 | 323.1 | 316.1 |
|          | VQZ   | 2.5521 | 2.5408 | 318.4 | 320.1 |
|          | AVTZ  | 2.5519 | 316.3 |
|          | AVQZ  | 2.5441 | 316.8 |
| GaI      | VTZ   | 2.6240 | 2.5955 | 2.57467 | 212.2 | 213.6 | 216.6 |
|          | VQZ   | 2.6150 | 2.5871 | 210.1 | 211.3 |
| GeTe     | VTZ   | 2.3802 | 2.3596 | 2.340165 | 313.1 | 315.7 | 323.9 |
|          | VQZ   | 2.3554 | 2.3358 | 312.4 | 322.6 |
| HI       | VTZ   | 1.6147 | 1.6073 | 1.60916 | 2314.7 | 2325.7 | 2309.014 |
|          | VQZ   | 1.6131 | 1.6054 | 2320.3 | 2332.7 |
|          | AVTZ  | 1.6162 | 1.6088 | 2310.4 | 2321.4 |
|          | AVQZ  | 1.6135 | 1.6058 | 2318.1 | 2330.3 |
| I$_2$    | VTZ   | 2.7072 | 2.6831 | 2.6663 | 212.2 | 215.8 | 214.502 |
|          | VQZ   | 2.6876 | 2.6655 | 218.4 | 221.3 |
| IBr      | VTZ   | 2.5049 | 2.4870 | 2.468989 | 263.6 | 266.9 | 268.640 |
|          | VQZ   | 2.4862 | 2.4698 | 271.5 | 274.2 |
| ICl      | VTZ   | 2.3482 | 2.3371 | 2.320878 | 383.2 | 386.1 | 384.293 |
|          | VQZ   | 2.3349 | 2.3239 | 388.3 | 391.0 |
|          | AVTZ  | 2.3358 | 385.4 |
|          | AVQZ  | 2.3225 | 391.6 |
| IF       | VTZ   | 1.9206 | 1.9204 | 1.90975 | 611.8 | 616.2 | 610.24 |
|          | VQZ   | 1.9158 | 1.9066 | 622.0 | 626.1 |
|          | AVTZ  | 1.9196 | 616.8 |
|          | AVQZ  | 1.9070 | 625.7 |
| InBr     | VTZ   | 2.5377 | 2.5029 | 2.54318 | 229.1 | 231.2 | 221.0 |
|          | VQZ   | 2.5080 | 2.4716 | 228.7 | 230.5 |
|          | CWB(t) | 2.5556 | 224.0 |
|          | CWB(q) | 2.5486 | 224.0 |
|          | ACWB(t) | 2.5677 | 2.5606 | 218.1 | 219.0 |
|          | ACWB(q) | 2.5540 | 2.5474 | 220.7 | 221.6 |
| InCl     | VTZ   | 2.3849 | 2.3553 | 2.401169 | 327.1 | 330.0 | 317.4 |
|          | VQZ   | 2.3571 | 2.3246 | 326.7 | 328.6 |
|          | ACWB(t) | 2.423 | 309 |
|          | ACWB(q) | 2.411 | 314 |
|          | ACWB(5) | 2.406 | 316 |
| all e-  | CWB(t) | 2.423 | 317 |
| Compound | Basis Set | A | B | C | A | B |
|----------|-----------|---|---|---|---|---|
| InF VTZ  | 1.9329    | 1.9109 | 1.985396 | 568.8 | 577.0 | 535.35 |
| VQZ 1.8976 | 1.8729 | 579.4 | 587.1 |
| CWB(t) 1.9833 | | 538.5 |
| CWB(q) 1.9822 | | 541.3 |
| ACWB(t) 1.9910 | | 526.6 |
| ACWB(q) 1.9853 | | 534.3 |
| InH VTZ 1.8653 | 1.8517 | 1.8380 | 1482.3 | 1472.7 | 1476.04 |
| VQZ 1.8317 | 1.8171 | 1503.5 | 1497.3 |
| CWB(t) 1.8395 | | 1462.4 |
| CWB(q) 1.8374 | | 1471.9 |
| InI VTZ 2.7698 | 2.7273 | 2.75365 | 179.0 | 181.1 | 177.1 |
| VQZ 2.7412 | 2.6983 | 178.9 | 180.6 |
| CWB(t) 2.7740 | 2.7605 | 177.8 | 179.0 |
| CWB(q) 2.7674 | 2.7543 | 177.0 | 178.1 |
| Sb$_2$ VTZ 2.5294 | 2.5045 | 2.476$^b$ | 266.3 | 268.2 | 269.62$^b$ |
| VQZ 2.5056 | 2.4816 | 273.0 | 275.1 |
| SbF $^3\Sigma^-$ VTZ 1.9252 | 1.9138 | 1.9177 | 615.3 | 619.8 | 609.0$^d$ |
| VQZ 1.9137 | 1.9023 | 620.0 | 624.9 |
| SbH $^3\Sigma^-$ VTZ 1.7259 | 1.7181 | 1.7107$^c$ | 1910.9 | 1914.0 | 1923.179$^c$ |
| VQZ 1.7188 | 1.7107 | 1930.3 | 1933.6 |
| SbP VTZ 2.2335 | 2.2211 | 2.205 | 495.0 | 497.8 | 500.07 |
| VQZ 2.2183 | 2.2058 | 503.5 | 506.5 |
| SnO VTZ 1.8426 | 1.8297 | 1.832505 | 763.3 | 768.7 | 814.6 |
| VQZ 1.8271 | 1.8137 | 781.9 | 788.5 |
| SnS VTZ 2.2382 | 2.2220 | 2.209026 | 466.9 | 468.6 | 487.26 |
| VQZ 2.2214 | 2.205 | 474.9 | 476.8 |
| SnSe VTZ 2.3595 | 2.3379 | 2.325601 | 316.3 | 318.1 | 331.2 |
| VQZ 2.3398 | 2.3181 | 321.0 | 323.2 |
| AVTZ 2.3541 | 2.3319 | 315.5 | 317.9 |
| AVQZ 2.3421 | 2.3202 | 319.2 | 321.6 |
| SnTe VTZ 2.5563 | 2.5294 | 2.522814 | 253.5 | 255.4 | 259.5 |
| VQZ 2.5359 | 2.5091 | 256.9 | 258.9 |
| AVTZ 2.5492 | 2.5218 | 253.3 | 255.6 |
(a) using ECP28MDF for In, (4d) electrons correlated

(b) Sb$_2$ ($R_e$, $\omega_e$): H. Sontag and R. Weber, J. Mol. Spectrosc. 91, 72 (1982).

(c) SbH ($R_e$, $\omega_e$): R.-D. Urban, K. Essig, and H. Jones, J. Chem. Phys. 99, 15911993.

(d) SbF ($\omega_e$): D. K. W. Wang, W. E. Jones, F. Prévot, and R. Colin, J. Mol. Spectrosc. 49, 377 (1974).

(e) This work, using the MTavqz basis set [54] on Cl and including (2s,2p) correlation in Cl. CWB(t) and CWB(q) indicate the Bauschlicher [34] cc-pVTZ and cc-pVQZ basis sets on indium, and regular cc-pV$n$Z or SDB-ccpV$n$Z basis sets on the other atom. ACWB(t) and ACWB(q) indicate the same, but in conjunction with an augmented basis set on the other atom.
TABLE III. CCSD(T) and experimental spectroscopic constants \( (R_e \text{ in Å, } \omega_e \text{ in cm}^{-1}) \) for diatomics involving Ga or Ge and an electronegative element

| molecule       | \( R_e \) | \( \omega_e \) |
|----------------|----------|--------------|
| \( R_e \)     | SDB      | CPP          | all \( e^- \) (a) | all \( e^- \) (b) | Exp. | SDB      | CPP          | all \( e^- \) (a) | all \( e^- \) (b) | Exp. |
| GaBr VTZ      | 2.3912   | 2.3681       | 2.4013 | 2.3618 | 2.35248 | 261.7  | 262.6  | 268.6  | 274.9  | 263.0 |
| VQZ           | 2.3829   | 2.3602       | 2.4007 | 2.3644 | 258.7  | 259.5  | 266.6  | 266.8  |
| 13e\(^-\) DVTZ | 2.3564   | 2.3668       | 275.5  | 270.9  |
| DVQZ          | 2.3486   | 2.3656       | 268.9  | 267.7  |
| GaCl VTZ      | 2.2411   | 2.2227       | 2.2554 | 2.2031 | 2.201690 | 353.5  | 353.6  | 381.3  | 382.4  | 365.3 |
| VQZ           | 2.2320   | 2.2135       | 2.2572 | 2.2010 | 350.7  | 351.1  | 373.3  | 370.4  |
| 13e\(^-\) DVTZ | 2.2063   | 2.2070       | 372.9  | 374.7  |
| DVQZ          | 2.1987   | 2.2044       | 368.4  | 370.1  |
| GaF VTZ       | 1.7851   | 1.7688       | 1.8031 | 1.7756 | 1.774369 | 589.0  | 589.8  | 631.9  | 652.3  | 622.2 |
| VQZ           | 1.7753   | 1.7587       | 1.8043 | 1.7697 | 586.3  | 588.0  | 625.4  | 644.8  |
| 13e\(^-\) DVTZ | 1.7704   | 1.7709       | 638.7  | 644.2  |
| DVQZ          | 1.7674   | 1.7716       | 636.1  | 637.6  |
| ADVTZ         | 1.7798   | 1.7812       | 619.7  | 623.7  |
| ADVQZ         | 1.7693   | 1.7741       | 631.2  | 628.9  |
| +2s2p DVTZ    | 1.7711   | 629.1        |
| +3s3p DVQZ    | 1.7714   | 629.3        |
| GeF \(^2\Pi\) VTZ | 1.7655   | 1.7550       | 1.8047 | 1.7469 | 1.7452 | 642.6  | 645.3  | 746.2  | 688.6  | 665.67 |
| VQZ           | 1.7577   | 1.7473       | 1.8096 | 1.7424 | 640.3  | 642.8  | 746.1  | 681.2  |
| 13e\(^-\) DVTZ | 1.7411   | 1.7450       | 683.1  | 677.6  |
| 13e\(^-\) DVQZ | 1.7407   | 1.7424       | 675.3  | 679.5  |
| GeO VTZ       | 1.6382   | 1.6290       | 1.6491 | 1.6341 | 1.624648 | 925.1  | 930.8  | 987.4  | 993.7  | 985.5 |
| VQZ           | 1.6295   | 1.6205       | 1.6485 | 1.6276 | 943.2  | 949.1  | 989.3  | 1000.5 |
| 13e\(^-\) DVTZ | 1.6254   | 1.6293       | 995.4  | 992.3  |
| 13e\(^-\) DVQZ | 1.6214   | 1.6269       | 996.7  | 996.6  |
| GeS VTZ       | 2.0461   | 2.0356       | 2.0416 | 2.0280 | 2.012086 | 552.2  | 554.1  | 568.4  | 578.0  | 575.8 |
| VQZ           | 2.0390   | 2.0290       | 2.0356 | 2.0192 | 560.5  | 552.4  | 572.3  | 597.2  |
| 13e\(^-\) DVTZ | 2.0207   | 2.0284       | 577.9  | 572.3  |
| 13e\(^-\) DVQZ | 2.0133   | 2.0190       | 577.5  | 578.2  |
| GeSe VTZ      | 2.1743   | 2.1580       | 2.1713 | 2.1574 | 2.134629 | 384.8  | 387.4  | 397.5  | 403.7  | 408.7 |
| VQZ           | 2.1531   | 2.1377       | 2.1658 | 2.1506 | 393.5  | 444.5  | 400.2  | 403.5  |
| 13e\(^-\) DVTZ | 2.1479   | 2.1583       | 403.2  | 401.4  |
| 13e\(^-\) DVQZ | 2.1370   | 2.1495       | 405.0  | 403.8  |

(a) all d electrons of Ga, Ge are frozen for the all electron calculation.

(b) d-shell correlated.
TABLE IV. Spectroscopic constants for GaH and GeH. All results at the CCSD(T) level.

| Nonvalence | Pseudopotential | Basis set       | \( r_e \) | \( \omega_e \) | \( \omega_e x_e \) | \( \omega_e \) | \( \omega_e x_e \) |
|------------|----------------|----------------|--------|--------|----------------|--------|----------------|
|            |                |                | Å      | cm\(^{-1}\) | cm\(^{-1}\) | Å      | cm\(^{-1}\) |
| E\(^-\) correlated |                |                |        |         |               |       |               |
| Experiment |                |                |        |         |               |       |               |
| —          | all-electron   | cc-pVDZ        | 1.6860 | 1610.0  | 26.43        | 1.6083 | 1896.1        | 32.96 |
| —          | all-electron   | ditto full CI  | 1.6867 | 1607.0  | 26.55        | 1.6090 | 1891.7        | 33.24 |
| —          | all-electron   | cc-pVTZ        | 1.6878 | 1603.2  | 26.80        | 1.6039 | 1897.9        | 32.80 |
| —          | all-electron   | cc-pVQZ        | 1.6864 | 1604.3  | 27.74        | 1.6021 | 1903.1        | 33.14 |
| (3d)       | all-electron   | cc-pVTZ        | 1.6573 | 1691.8  | 31.15        | 1.5860 | 1956.9        | 36.24 |
| (3d)       | all-electron   | cc-pVQZ        | 1.6449 | 1698.5  | 40.56        | 1.5764 | 1965.0        | 43.78 |
| —          | ECP28MWB       | SDB-cc-pVTZ    | 1.6969 | 1530.9  | 24.27        | 1.6084 | 1844.4        | 30.67 |
| —          | + CPP          |                | 1.6876 | 1524.2  | 24.35        | 1.6014 | 1845.8        | 30.72 |
| —          | ECP28MWB       | SDB-cc-pVQZ    | 1.6820 | 1546.3  | 25.09        | 1.5990 | 1862.3        | 31.30 |
| —          | + CPP          |                | 1.6729 | 1540.4  | 25.13        | 1.5921 | 1863.5        | 31.46 |
| (3d)       | all-electron   | cc-pDVVTZ      | 1.6582 | 1658.2  | 32.91        | 1.5893 | 1900.4        | 31.65 |
| (3d)       | all-electron   | cc-pDVQZ       | 1.6565 | 1653.6  | 36.20        | 1.5821 | 1950.2        | 42.03 |
| (3d)       | all-electron   | cc-pDVVTZ+2d   | 1.6500 | 1659.5  | 33.07        |        |               |       |
| (3d,3p,3d) | all-electron   | cc-pDVVTZ+2s2p1d | 1.6647 | 1602.5  | 26.56        |        |               |       |
| (3d)       | all-electron   | cc-pDVVTZ+2s2p1d | 1.6635 | 1604.4  | 25.82        |        |               |       |
| (3d)       | all-electron   | cc-pDVVTZ+2s2p1d | 1.6863 | 1598.0  | 25.56        |        |               |       |
| (3d)       | all-electron   | cc-pDVVTZ+2s2p | 1.6637 | 1604.0  | 25.69        | 1.5889 | 1906.2        | 32.30 |
| —          | ECP10MWB       | cc-pDVVTZ      | 1.6550 | 1649.3  | 31.47        | 1.5783 | 1950.6        | 37.24 |
| (3d)       | ECP10MWB       | cc-pDVQZ       | 1.6446 | 1662.8  | 37.57        | 1.5751 | 1941.7        | 40.79 |
| (3d)       | ECP10MWB       | cc-pDVQZ+2s2p  | 1.6613 | 1588.8  | 25.09        | 1.5865 | 1893.2        | 32.12 |
| —          | ECP10MWB       | cc-pDVQZ+2s2p  | 1.6838 | 1584.4  | 25.12        | 1.5993 | 1887.7        | 32.40 |
| (3d)       | ECP10MWB       | cc-pDVQZ+3s3p  | 1.6584 | 1607.4  | 27.33        |        |               |       |
| (3d)       | ECP10MWB       | cc-pDVQZ+3s3p  | 1.6586 | 1605.6  | 26.92        | 1.5881 | 1910.8        | 32.86 |
| —          | ECP10MWB       | cc-pDVQZ+3s3p  | 1.6829 | 1592.1  | 27.38        | 1.6006 | 1897.4        | 32.40 |
| (3d,3p,3d) | ECP10MWB       | cc-pDVQZ+3s3p  | 1.6602 | 1601.5  | 26.00        | 1.5898 | 1907.4        | 32.82 |

\(^a\) M. Molski, J. Mol. Spectrosc. 182, 1 (1997).

\(^b\) F. Ito, T. Nakanago, H. Jones, J. Mol. Spectrosc. 164, 379 (1994).

\(^c\) J. P. Towle and J. M. Brown, Mol. Phys. 78, 249 (1993).
# Table V. Binding energies (D in eV) for molecules containing third row atoms.

| molecule  | SDB       | CPP       | all e−     | Experiment |
|-----------|-----------|-----------|------------|------------|
|           | VTZ  | VQZ | ∞ | VTZ  | VQZ | ∞ | VTZ | VQZ | ∞ | HH | KS |
| AlBr      | 4.31  | 4.45 | 4.55 | 4.33  | 4.48 | 4.57 | 4.29 | 4.43 | 4.52 | 4.43 | 4.42±0.06 |
| As₂       | 3.42  | 3.78 | 4.02 | 3.48  | 3.83 | 4.06 | 3.48 | 3.71 | 3.86 | 3.96 | 3.93±0.10 |
| AsF³⁻     | 3.88  | 4.13 | 4.30 | 3.91  | 4.16 | 4.32 | 3.85 | 4.08 | 4.22 | 4.2  | 4.21     |
| AsH³⁻     | 2.63  | 2.72 | 2.79 | 2.63  | 2.73 | 2.79 | 2.64 | 2.71 | 2.76 | 2.76 (AsD) | 2.80±0.03 |
| AsN       | 4.48  | 4.85 | 5.09 | 4.54  | 4.90 | 5.14 | 4.47 | 4.72 | 4.88 | —     | 5.03±0.02 |
| AsO²⁻     | 4.58  | 4.90 | 5.11 | 4.63  | 4.94 | 5.14 | 4.56 | 4.80 | 4.97 | ≤4.98 | 4.95±0.08 |
| AsP       | 3.90  | 4.24 | 4.46 | 3.94  | 4.27 | 4.49 | 3.90 | 4.16 | 4.33 | —     | 4.45     |
| AsS²⁻     | 3.47  | 3.79 | 3.99 | 3.51  | 3.81 | 4.02 | 3.50 | 3.73 | 3.88 | —     | 3.90±0.07 |
| BBr       | 4.23  | 4.32 | 4.38 | 4.25  | 4.34 | 4.40 | 4.18 | 4.28 | 4.34 | ≤4.49⁹ | 4.07     |
| Br₂       | 1.58  | 1.80 | 1.94 | 1.61  | 1.82 | 1.96 | 1.69 | 1.84 | 1.93 | 1.9707 | idem     |
| BrCl      | 1.90  | 2.08 | 2.20 | 1.91  | 2.09 | 2.21 | 1.94 | 2.10 | 2.20 | 2.233 | 2.223±0.003 |
| BrF       | 2.18  | 2.40 | 2.54 | 2.20  | 2.41 | 2.55 | 2.25 | 2.44 | 2.57 | 2.548 | 2.87±0.12 |
| CSe       | 5.72  | 5.92 | 6.06 | 5.76  | 5.97 | 6.06 | 5.73 | 5.89 | 6.00 | 5.98 | 6.08±0.06 |
| HBr       | 3.62  | 3.69 | 3.74 | 3.64  | 3.71 | 3.76 | 3.63 | 3.70 | 3.75 | 3.758 | idem     |
| NSe²⁻     | 3.23  | 3.51 | 3.70 | 3.27  | 3.55 | 3.73 | 3.29 | 3.51 | 3.66 | 4.0   | 3.80±0.11 |
| Se₂³⁻     | 2.94  | 3.19 | 3.35 | 2.99  | 3.23 | 3.39 | 3.05 | 3.23 | 3.34 | 3.410 | 3.417±0.004 |
| SeH       | 3.08  | 3.16 | 3.22 | 3.09  | 3.18 | 3.23 | 3.11 | 3.19 | 3.24 | —     | 3.221±0.01 |
| SeO³⁻     | 4.02  | 4.29 | 4.47 | 4.05  | 4.32 | 4.49 | 4.08 | 4.29 | 4.42 | 4.41 | 4.78±0.22 |
| SeS³⁻     | 3.42  | 3.65 | 3.80 | 3.45  | 3.68 | 3.83 | 3.46 | 3.65 | 3.78 | 3.7  | 3.81±0.07 |
| SiSe      | 5.13  | 5.35 | 5.49 | 5.16  | 5.38 | 5.53 | 5.14 | 5.34 | 5.47 | 5.64 | 5.54±0.13 |
| ditto aug-cc | 5.16  | 5.36 | 5.49 | 5.20  | 5.40 | 5.53 | 5.18 | 5.36 | 5.48 |       |          |

(a) Predissociation: Ref. [40] notes a possible potential hump of up to 0.13 eV in the upper a¹Π state.
## TABLE VI. Binding energies ($D_e$ in eV) for molecules containing fourth row atoms.

| molecule | SDB | | | CPP | | | Experiment |
|----------|-----|-----|-----|-----|-----|-----|-----|
|          | VTZ | VQZ | $\infty$ | VTZ | VQZ | $\infty$ | HH | KS |
| AlI      | 3.49 | 3.60 | 3.67 | 3.52 | 3.63 | 3.71 | 3.77 | 3.81±0.02 |
| ditto aug-cc | | | | | | | | |
| GaI      | 3.18 | 3.34 | 3.45 | 3.26 | 3.42 | 3.53 | 3.47 | 3.47±0.10 |
| GeTe     | 3.75 | 4.08 | 4.30 | 3.84 | 4.16 | 4.37 | 4.24 | 4.09±0.03 |
| HI       | 2.90 | 2.96 | 3.00 | 2.93 | 2.99 | 3.03 | 3.0541 | idem |
| ditto aug-cc | | | | | | | | |
| I$_2$    | 1.07 | 1.25 | 1.37 | 1.13 | 1.30 | 1.42 | 1.54238 | idem |
| ditto aug-cc | | | | | | | | |
| IBr      | 1.37 | 1.57 | 1.70 | 1.42 | 1.61 | 1.74 | 1.817 | idem |
| ditto aug-cc | | | | | | | | |
| ICl      | 1.73 | 1.90 | 2.02 | 1.76 | 1.93 | 2.04 | 2.1531 | idem |
| ditto aug-cc | | | | | | | | |
| IF       | 2.24 | 2.48 | 2.64 | 2.27 | 2.51 | 2.66 | 2.879 | $\leq$2.78 |
| ditto aug-cc | | | | | | | | |
| InBr     | 3.76 | 4.03 | 4.21 | 3.85 | 4.13 | 4.32 | 3.99 | 4.27±0.22 |
| (b)      | 3.73 | 3.85 | 3.93 | | | | | |
| (c)      | 3.75 | 3.86 | 3.93 | 3.77 | 3.88 | 3.95 | | |
| InCl     | 4.32 | 4.60 | 4.79 | 4.41 | 4.70 | 4.89 | 4.44 | 4.52±0.08 |
| (c) [R]  | 4.29 | 4.45 | | | | | | |
| (e) [R]  | 4.32 | 4.43 | | | 4.46 | | | |
| InF      | 5.41 | 5.87 | 6.17 | 5.50 | 5.97 | 6.28 | 5.25 | 5.21±0.15 |
| (b)      | 5.18 | 5.35 | 5.46 | | | | | |
| (c)      | 5.35 | 5.42 | 5.47 | | | | | |
| (d)      | 5.26 | 5.42 | 5.53 | | | | | |
| (e)      | 5.42 | 5.50 | 5.55 | | | | | |
| InH      | 2.45 | 2.58 | 2.66 | 2.44 | 2.58 | 2.66 | 2.48 | idem |
| (b)      | 2.43 | 2.47 | 2.49 | | | | | |
| (d)      | 2.46 | 2.50 | 2.53 | | | | | |
| InI      | 3.06 | 3.29 | 3.44 | 3.17 | 3.40 | 3.55 | 3.43 | 3.41±0.01 |
| (b)      | 3.07 | 3.16 | 3.22 | 3.11 | 3.20 | 3.26 | | |
| Sb$_2$   | 2.51 | 2.88 | 3.13 | 2.60 | 2.97 | 3.21 | 2.995 $^a$ | 3.07±0.07 |
| SbF $^{3\Sigma^-}$ | 3.77 | 4.12 | 4.36 | 3.82 | 4.17 | 4.40 | 4.4 | 4.5±0.1 |
| ditto aug-cc | | | | | | | | |
| SbH $^{3\Sigma^-}$ | 2.43 | 2.52 | 2.59 | 2.44 | 2.54 | 2.60 | | |
| SnP      | 3.20 | 3.51 | 3.71 | 3.26 | 3.57 | 3.78 | 3.68 | idem |
| SnO      | 4.86 | 5.28 | 5.54 | 4.96 | 5.38 | 5.65 | 5.49 | 5.48±0.13 |
| SnS      | 4.31 | 4.61 | 4.81 | 4.39 | 4.69 | 4.89 | 4.77 | 4.78±0.03 |
| SnSe     | 3.83 | 4.12 | 4.31 | 3.92 | 4.22 | 4.41 | 4.20 | 4.13±0.06 |
| ditto aug-cc | | | | | | | | |

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|       | 3.29 | 3.56 | 3.74 | 3.39 | 3.66 | 3.84 | 3.69 | idem |
|-------|------|------|------|------|------|------|------|------|
| ditto aug-cc | 3.40 | 3.58 | 3.70 | 3.50 | 3.68 | 3.79 |      |      |

(a) Sb$_2$ ($D_e$): H. Sontag and R. Weber, J. Mol. Spectrosc. **91**, 72 (1982).

(b) using Bauschlicher [34] cc-pV$n$Z basis sets on In in conjunction with cc-pV$n$Z and SDB-
cc-pV$n$Z basis sets on other element.

(c) ditto, but using ‘augmented’ basis sets on other element.

(d) as (b), but using all-electron basis set on In.

(e) as (c), but using all-electron basis set on In.

(f) This work, correlating (2s2p) electrons on Cl and using the MTavqz core-correlation basis
set [54] on Cl.
| molecule | basis   | SDB | CPP | SDB- | all e⁻ | all e⁻ with | Experiment |
|----------|---------|-----|-----|------|--------|-------------|------------|
|          | (3d) corr. | no  | yes | no   | yes    | yes         |            |
|          | cc-pDVnZ | cc-pVnZ | cc-pVnZ | cc-pDVnZ | HH | KS |
| GaBr     | VTZ     | 3.90 | 3.97 | 3.86 | 3.97   | 4.04        | 4.02       | 4.31 | 4.58±0.18 |
|          | VQZ     | 4.09 | 4.16 | 4.15 | 4.08   | 4.15        | 4.12       |      |          |
|          | ∞       | 4.22 | 4.29 | 4.35 | 4.16   | 4.23        | 4.19       |      |          |
| GaCl     | VTZ     | 4.46 | 4.52 | 4.60 | 4.53   | 4.63        | 4.60       | 4.92 | 4.96±0.13 |
|          | VQZ     | 4.66 | 4.72 | 4.73 | 4.65   | 4.75        | 4.72       |      |          |
|          | ∞       | 4.79 | 4.84 | 4.81 | 4.73   | 4.83        | 4.80       |      |          |
| GaF      | VTZ     | 5.67 | 5.74 | 5.83 | 5.74   | 5.87        | 5.85       | 5.98 | 5.95±0.15 |
|          | VQZ     | 5.94 | 6.01 | 6.00 | 5.91   | 6.03        | 6.01       |      |          |
|          | ∞       | 6.12 | 6.18 | 6.12 | 6.02   | 6.14        | 6.11       |      |          |
| GaH      | VTZ     | 2.69 | 2.69 | 2.81 | 2.77   | 2.86        | 2.82       | < 2.84 | ≤2.80     |
|          | VQZ     | 2.77 | 2.77 | 2.85 | 2.80   | 2.89        | 2.84       |      |          |
|          | ∞       | 2.82 | 2.81 | 2.88 | 2.82   | 2.90        | 2.85       |      |          |
| GeF ²Π   | VTZ     | 4.78 | 4.83 | 4.99 | 4.83   | 4.99        | 4.98       | 5.0   | 5.0±0.2   |
|          | VQZ     | 5.07 | 5.12 | 5.17 | 5.02   | 5.20        | 5.18       |      |          |
|          | ∞       | 5.27 | 5.31 | 5.31 | 5.14   | 5.33        | 5.28       |      |          |
| GeH ²Π   | VTZ     | 2.57 | 2.58 | 2.69 | 2.63   | 2.70        | 2.66       | < 3.3 | ≤3.3      |
|          | VQZ     | 2.65 | 2.66 | 2.72 | 2.68   | 2.76        | 2.72       |      |          |
|          | ∞       | 2.71 | 2.71 | 2.75 | 2.72   | 2.80        | 2.76       |      |          |
| GeO      | VTZ     | 6.19 | 6.27 | 6.57 | 6.41   | 6.54        | 6.53       | 6.78  | 6.80±0.13 |
|          | VQZ     | 6.57 | 6.65 | 6.76 | 6.60   | 6.77        | 6.74       |      |          |
|          | ∞       | 6.82 | 6.89 | 6.88 | 6.73   | 6.93        | 6.87       |      |          |
| GeS      | VTZ     | 5.10 | 5.16 | 5.36 | 5.25   | 5.35        | 5.31       | 5.67  | 5.50±0.03 |
|          | VQZ     | 5.40 | 5.57 | 5.52 | 5.44   | 5.55        | 5.51       |      |          |
|          | ∞       | 5.59 | 5.83 | 5.63 | 5.56   | 5.68        | 5.63       |      |          |
| GeSe     | VTZ     | 4.45 | 4.53 | 4.71 | 4.64   | 4.73        | 4.70       | 4.98±0.10 | 4.99±0.02 |
|          | VQZ     | 4.79 | 4.86 | 4.89 | 4.81   | 4.91        | 4.87       |      |          |
|          | ∞       | 5.01 | 5.07 | 5.01 | 4.92   | 5.03        | 4.98       |      |          |
TABLE VIII. State-averaged optimum $f$ and $g$ exponents for the transition metals, to be used in conjunction with Stuttgart-Dresden ECPs and [6s5p3d] contracted valence basis sets. The cc-pVTZ and SDB-cc-pVTZ basis sets are recommended for the other elements.

| State          | $4F$  | $5F$  | $6D$  | $7S$  | $6D$  | $5F$  | $4F$  | $3D$  | $2S$  | N/A   |
|----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $(s)^1(d)^{n-1}$ |       |       |       |       |       |       |       |       |       |       |
| Sc             | 0.180 | 0.285 | 0.425 | 0.640 | 0.795 | 0.871 | 1.019 | 1.182 | 1.315 | 1.498 |
| Ti             | 0.764 | 1.264 | 1.788 | 2.555 | 3.118 | 3.516 | 4.076 | 4.685 | 5.208 | 5.871 |
| V              | 0.347 | 0.636 | 1.048 | 1.712 | 1.964 | 2.269 | 2.711 | 3.212 | 3.665 | 4.365 |
| Cr             |       |       |       |       |       |       |       |       |       |       |
| Mn             |       |       |       |       |       |       |       |       |       |       |
| Fe             |       |       |       |       |       |       |       |       |       |       |
| Co             |       |       |       |       |       |       |       |       |       |       |
| Ni             |       |       |       |       |       |       |       |       |       |       |
| Cu             |       |       |       |       |       |       |       |       |       |       |
| Zn             |       |       |       |       |       |       |       |       |       |       |
| $(s)^2(d)^{n-2}$ |       |       |       |       |       |       |       |       |       |       |
| Sc             | 0.144 | 0.236 | 0.261 | 0.338 | 0.398 | 0.478 | 0.567 | 0.621 | 0.732 | 0.834 |
| Ti             | 0.546 | 0.883 | 0.970 | 1.223 | 1.430 | 1.666 | 1.989 | 2.203 | 2.537 | 2.853 |
| V              | 0.249 | 0.547 | 0.536 | 0.744 | 0.918 | 1.057 | 1.236 | 1.385 | 1.587 | 1.795 |
| Cr             |       |       |       |       |       |       |       |       |       |       |
| Mn             |       |       |       |       |       |       |       |       |       |       |
| Fe             |       |       |       |       |       |       |       |       |       |       |
| Co             |       |       |       |       |       |       |       |       |       |       |
| Ni             |       |       |       |       |       |       |       |       |       |       |
| Cu             |       |       |       |       |       |       |       |       |       |       |
| Zn             |       |       |       |       |       |       |       |       |       |       |
| Y              |       |       |       |       |       |       |       |       |       |       |
| Zr             |       |       |       |       |       |       |       |       |       |       |
| Nb             |       |       |       |       |       |       |       |       |       |       |
| Mo             |       |       |       |       |       |       |       |       |       |       |
| Tc             |       |       |       |       |       |       |       |       |       |       |
| Ru             |       |       |       |       |       |       |       |       |       |       |
| Rh             |       |       |       |       |       |       |       |       |       |       |
| Pd             |       |       |       |       |       |       |       |       |       |       |
| Ag             |       |       |       |       |       |       |       |       |       |       |
| Cd             |       |       |       |       |       |       |       |       |       |       |
| La             | 0.120 | 0.163 | 0.210 | 0.256 | 0.327 | 0.347 | 0.395 | 0.443 | 0.498 | 0.545 |
| Hf             | 0.456 | 0.557 | 0.697 | 0.825 | 0.955 | 1.067 | 1.189 | 1.323 | 1.461 | 1.580 |
| Ta             | 0.209 | 0.352 | 0.472 | 0.627 | 0.636 | 0.860 | 0.982 | 1.100 | 1.218 | 1.384 |
| W              |       |       |       |       |       |       |       |       |       |       |
| Re             |       |       |       |       |       |       |       |       |       |       |
| Os             |       |       |       |       |       |       |       |       |       |       |
| Ir             |       |       |       |       |       |       |       |       |       |       |
| Pt             |       |       |       |       |       |       |       |       |       |       |
| Au             |       |       |       |       |       |       |       |       |       |       |
| Hg             |       |       |       |       |       |       |       |       |       |       |

Exponents were averaged over $(s)^1(d)^{n-1}$ and $(s)^2(d)^{n-2}$ states, except for Pd where in addition the $(s)^0(d)^{10}$ ground state was used, and Zn/Cd/Hg for which only the $(s)^2(d)^{n-2}$ is involved.