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# The aug-cc-pVTZ-J basis set for the p-block fourth-row elements Ga, Ge, As, Se and Br

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## Abstract

The aug-cc-pVTZ-J basis set family is extended to include the fourth row p-block elements Ga, Ge, As, Se and Br. We use the established approach outlined by Sauer and co-workers [J. Chem. Phys. 115, 1324 (2001), J. Chem. Phys. 133, 054308 (2010), J. Chem. Theory Comput. 7, 4070 (2011), J. Chem. Theory Comput. 7, 4077 (2011)] where the completely uncontracted aug-cc-pVTZ basis set is saturated with tight *s*-, *p*-, *d*- and *f*-functions to form the aug-cc-pVTZ-Juc basis set for the tested elements. The saturation is carried out on the simplest hydrides possible for the tested elements GaH, GeH<sub>4</sub>, AsH<sub>3</sub>, H<sub>2</sub>Se and HBr until an improvement is less than 0.01 % for all *s*-, *p*- and *d*-functions added. *f*-functions are added to an improvement less than or equal to 1.0 % due to the computational expense these functions add. The saturated aug-cc-pVTZ-Juc is (26s16p12d5f) is then recontracted using the molecular orbital coefficients from self-consistent field calculations on the simple hydrides to improve computational efficiency. During contraction of the basis set, we observe that the linear hydrogen bromide molecule has a slower convergence than the other tested molecules which

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17 sets a limit on the accuracy obtained. All calculations with the contracted aug-cc-  
18 pVTZ-J [17s10p7d5f] gives results that are within 1.0 % of the uncontracted results at  
19 considerable computational savings.

## 20 **Keywords**

21 spin-spin coupling constants, aug-cc-pVTZ-J, SOPPA

## 22 **Introduction**

23 Nuclear magnetic resonance (NMR) spectroscopy is the most employed tool when charac-  
24 terizing and probing the structure of both organic and inorganic compounds in solution.  
25 Lately, solution or gas phase NMR experiments are often accompanied by *ab initio* calcula-  
26 tions of the indirect nuclear spin-spin coupling constants or the chemical shifts in order to  
27 confirm the identity of the studied compounds<sup>1</sup> or to obtain further information on tautomer  
28 equilibria,<sup>2</sup> nonbonded interactions,<sup>3,4</sup> stereochemistry,<sup>5-9</sup> to name a few.

29 The indirect spin-spin coupling tensor describes the simultaneous coupling between two  
30 nuclei in a given system mediated by electrons. The indirect spin-spin coupling tensor is in  
31 non-relativistic calculations constructed from four individual terms which must be evaluated  
32 accurately if any theoretical predictions are to be compared with experiment (which is cal-  
33 culated as one-third of the trace of the spin-spin coupling tensor). The four contributions to  
34 the computed spin-spin coupling constants are:<sup>10</sup> the Fermi contact (FC) and spin-dipolar  
35 (SD) terms which arise from the interaction of the electronic spin with the nuclear magnetic  
36 moments and the diamagnetic spin orbit (DSO) and paramagnetic spin orbit (PSO) con-  
37 tributions which both are due to the nuclear spin interacting with the orbital momentum  
38 of the electrons. For calculated indirect nuclear spin-spin coupling constants on hydrides it  
39 is established<sup>11</sup> that the FC term dominates. For routine applications to larger molecules,  
40 density functional theory, plays of course an important role, but electron correlation effects

41 are often significantly larger for spin-spin coupling constants than for the related chemical  
42 shifts.

43 The highest level of theory, currently available for the calculation of spin-spin coupling  
44 constants is Coupled-Cluster theory<sup>12,13</sup> at the CCSDT<sup>14-16</sup> level of theory or alternatively,  
45 CC3.<sup>17-20</sup> However, due to the high computational cost, so far only few applications of  
46 these methods have been presented.<sup>17-21</sup> Less demanding but still accurate methods include  
47 CCSD<sup>22-26</sup> and the second order polarization propagator approximation, SOPPA,<sup>27</sup> and its  
48 modification SOPPA(CC2),<sup>28,29</sup> SOPPA(CCSD)<sup>30</sup> and HRPA(D).<sup>31,32</sup> In particular SOPPA  
49 and SOPPA(CCSD) have successfully been employed in many studies including also larger  
50 molecules<sup>33</sup> or heavier elements.<sup>34</sup> A relativistic treatment is, however, outside the scope of  
51 this work.

52 The difficulty in obtaining converged results with respect to basis sets lies in the fact that  
53 the FC operator has a delta function.<sup>10</sup> This puts considerable limitations on the quality of  
54 the obtained spin-spin coupling constants as standard Gaussian basis sets are focused on ob-  
55 taining the energy (or part of it) in a systematic way. For instance, the correlation consistent  
56 basis sets by Dunning and co-workers<sup>35,36</sup> are optimized to recover the correlation energy  
57 systematically towards the basis set limit as the basis set size is increased. However, the  
58 aug-cc-pVnZ (n = D, T, Q and 5) basis set family cannot, as we will explore later, correctly  
59 describe the FC term. The recent polarization consistent basis set family by Jensen<sup>37-41</sup> is  
60 optimized to quickly converge towards the basis set limit for calculations using Hartree-Fock  
61 and density functional theory although they have also been tested on their convergence to  
62 recover the correlation energy with encouraging results recently.<sup>42</sup> Indeed, specialized basis  
63 sets are required for fast convergence of many properties. In such cases, the basis sets are  
64 tailored to accurately describe the operators that enter into the property. The polarization  
65 consistent basis set family has been extended with two such additional extensions for the  
66 calculation of NMR shielding constants (pcS)<sup>43</sup> and the calculation of spin-spin coupling  
67 constants (pcJ).<sup>44-46</sup> For the correlation consistent basis set family, optimized basis sets for

68 the calculation of NMR spectroscopic properties have also been developed either at the triple  
69 zeta quality which are known collectively as aug-cc-pVTZ-J.<sup>47-51</sup> or for some of the second  
70 row atoms also for the whole series of Dunning basis sets, known as aug-ccJ-pVXZ basis  
71 sets.<sup>52,53</sup> For the second row elements C, N and O spin-spin coupling constant basis sets,  
72 denoted 6-31G-J and 6-311G-J, were also developed based on the corresponding Pople basis  
73 sets, which can then be augmented with the usual diffuse or polarization functions.<sup>54</sup> For  
74 heavier elements the development of specialized coupling constant basis sets has been based  
75 on Dyall's basis sets as for example for Te and Se.<sup>55,56</sup>

76 In this work, we construct the basis sets for the missing fourth row elements: Ga, Ge, As,  
77 Se and Br of the aug-cc-pVTZ family to obtain an optimized uncontracted aug-cc-pVTZ-Juc  
78 basis set and a contracted aug-cc-pVTZ-J basis set for the calculation of spin-spin coupling  
79 constants.

80 This article is organized as follows. First, we briefly present our methodology to create  
81 the new basis sets following the established procedure for the aug-cc-pVTZ-J basis set family  
82 which happens in two rounds: Saturation with respect to added primitive basis functions is  
83 evaluated until convergence and is followed up by an evaluation of the recontraction of the  
84 basis set. Secondly, we illustrate their application in calculations with 3 wave function and  
85 two density functional theory methods.

## 86 **Methods**

### 87 **Computational methodology**

88 In the derivation of the new basis set, we followed the procedure by Sauer and co-workers<sup>47,50,51,54</sup>  
89 which we will briefly outline here and provide some additional details in the discussions of  
90 the results in the sections below. The simplest hydrides of the tested elements Ga, Ge,  
91 As, Se and Br were constructed to give GaH, GeH<sub>4</sub>, AsH<sub>3</sub>, H<sub>2</sub>Se and HBr. The geometries  
92 of the hydrides used in this study were all equilibrium geometries obtained in GAMESS<sup>57</sup>

Table 1: Elements, hydrides, electron configurations of the elements and employed symmetry in either DALTON for the spin-spin coupling constants or GAMESS for the geometry-optimizations of the tested elements.

| Element | Hydride           | Electron Configuration                               | DALTON                 | GAMESS                 |
|---------|-------------------|--|------------------------|------------------------|
| Ga      | GaH               | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>1</sup> | <i>C</i> <sub>2v</sub> | <i>C</i> <sub>2v</sub> |
| Ge      | GeH <sub>4</sub>  | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>2</sup> | <i>D</i> <sub>2</sub>  | <i>T</i> <sub>d</sub>  |
| As      | AsH <sub>3</sub>  | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>3</sup> | <i>C</i> <sub>s</sub>  | <i>C</i> <sub>3v</sub> |
| Se      | H <sub>2</sub> Se | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>4</sup> | <i>C</i> <sub>2v</sub> | <i>C</i> <sub>2v</sub> |
| Br      | HBr               | [Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup> | <i>C</i> <sub>2v</sub> | <i>C</i> <sub>2v</sub> |

93 using MP2/aug-cc-pVTZ with appropriate symmetries in the gas phase, listed in Table 1,  
 94 for each molecule. All computed spin-spin coupling constants used in the optimization of  
 95 the new aug-cc-pVTZ-J(uc) basis set were evaluated in DALTON<sup>58-60</sup> using the second-  
 96 order polarization propagator approximation (SOPPA).<sup>61-64</sup> We furthermore employed both  
 97 SOPPA(CCSD)<sup>30,65</sup> and SOPPA(CC2)<sup>28</sup> which uses amplitudes obtained from coupled clus-  
 98 ter singles and doubles (CCSD)<sup>66</sup> calculations or second-order approximate coupled cluster  
 99 singles and doubles (CC2)<sup>67</sup> calculations, respectively, for final spin-spin coupling constant  
 100 calculations. The aug-cc-pVTZ basis sets for the elements were downloaded from the basis  
 101 set exchange database<sup>68,69</sup> and used as a starting point for the optimizations. The basis sets  
 102 were uncontracted and  $n_s$  tight  $s$ -functions were added using the even-tempered approach  
 103 where the exponent of subsequent basis functions keep the ratio as the ones before, i.e.  
 104  $\zeta_{i+1} = \zeta_i^2/\zeta_{i-1}$  although it has been argued that this is not the most effective way in terms of  
 105 the number of added functions.<sup>44</sup> We use the even-tempered approach to be consistent with  
 106 the aug-cc-pVTZ-J(uc) series of basis sets. When the basis set is saturated with  $s$ -functions,  
 107 we use the same approach to add  $n_p$  tight  $p$ -functions and  $n_d$  tight  $d$ -functions. We consider  
 108 saturation converged when the improvement of adding the  $\zeta_{i+1}$  function adds less than 0.01  
 109 % improvement. Finally  $n_f$  tight  $f$ -functions to give the final aug-cc-pVTZ-Juc basis set for  
 110 each element. Because each added  $f$ -function adds much computational overhead, we use  
 111 a threshold of 1.0 % improvement for testing for saturation. In all calculations we use the  
 112 aug-cc-pVTZ-Juc basis set for hydrogen. To recontract the basis set, we use the approach by

113 Provasi and Sauer<sup>47,50</sup> which is a generalization of the work by Geertsen et al<sup>70</sup> and Guilleme  
114 and San Fabián<sup>71</sup> where the molecular orbital coefficients of the simplest hydrides are used as  
115 contraction coefficients. The molecular orbital coefficients are from Hartree-Fock calculations  
116 using the appropriate symmetries in DALTON (See Table 1). We contract the basis set of  
117 the fourth row elements according to the following scheme for  $s$ -functions:  $n_s s \rightarrow (n'_s n'_s n'_s 1$   
118  $1 \dots 1)s$ , where  $n'_s$  are the number of primitive  $s$ -orbitals that are included in the contraction  
119 of the first three  $s$ -orbitals. The rest of the primitive  $s$ -orbitals are left uncontracted. For  
120  $p$ -functions the scheme is:  $n_p p \rightarrow (n'_p n'_p 1 1 \dots 1)p$  and for  $d$ -functions:  $n_d d \rightarrow (n'_d 1 1 \dots 1)d$ .  
121 We leave the added  $f$ -functions uncontracted. This approach has shown to be transferable  
122 to other types of systems with good accuracy.<sup>49,50</sup>

## 123 Results and Discussion

### 124 Preliminary basis set study

125 In order to gauge the requirements needed for the new basis set, it is instructive to use a  
126 series of systematic basis sets to investigate the convergence. We use as reference calculations  
127 both the correlation consistent aug-cc-pVnZ ( $n = D, T, Q$  and 5) basis sets<sup>35,36</sup> and the  
128 recent polarization consistent segment contracted aug-pcseg- $n$  ( $n = 1, 2, 3$  and 4) basis  
129 sets.<sup>72</sup> Results are presented in Table 2 for computed isotropic one bond spin-spin coupling  
130 constants,  $^1J(X-H)$ , for the tested hydrides using SOPPA. In the same table, we also include  
131 two modified basis sets of the aug-pcseg-3 and aug-pcseg-4 family. The first modification  
132 of the aug-pcseg- $n$  basis sets (named aug-pcseg- $n_m$ ) have the basis functions with higher  
133 angular momentum than  $f$ -functions removed, i.e.  $g$ -functions for aug-pcseg-3 and  $g$ - and  
134  $h$ -functions for aug-pcseg-4. The second modification of the aug-pcseg- $n$  basis sets (named  
135 aug-pcseg- $n_{m2}$ ) have, in addition to the same functions as for the aug-pcseg- $n_m$  basis sets,  
136 also the  $f$ -functions removed, i.e. it retains only the  $s$ -,  $p$ - and  $d$ -functions from the aug-  
137 pcseg- $n$  basis sets. In Table 2 we observe that as the basis set is increased the computed

Table 2: Calculated values of the one-bond spin-spin coupling constant,  $^1J(X-H)$ , for various methods and basis sets for all tested elements. All values in Hz.

| basis                     | Ga    | Ge                 | As    | Se    | Br    |
|---------------------------|-------|--------------------|-------|-------|-------|
| aug-cc-pVDZ               | 35.4  | -73.8              | 143.8 | 140.3 | 147.9 |
| aug-cc-pVTZ               | -31.9 | -85.9              | 148.7 | 128.7 | 127.9 |
| aug-cc-pVQZ               | -39.8 | -83.2              | 121.9 | 97.1  | 81.1  |
| aug-cc-pV5Z               | -8.6  | -64.7 <sup>a</sup> | 142.9 | 127.8 | 124.9 |
| aug-pcseg-1               | 29.4  | -81.1              | 130.5 | 105.0 | 92.7  |
| aug-pcseg-2               | -17.2 | -90.7              | 137.0 | 109.6 | 89.4  |
| aug-pcseg-3               | -16.0 | -91.1              | 113.3 | 90.5  | 81.8  |
| aug-pcseg-4               | -54.8 | -59.0              | 106.9 | 71.5  | 51.7  |
| aug-pcseg-3 <sub>m</sub>  | -24.2 | -91.7              | 123.0 | 105.0 | 91.0  |
| aug-pcseg-4 <sub>m</sub>  | -49.1 | -88.4              | 103.1 | 74.7  | 48.7  |
| aug-pcseg-3 <sub>m2</sub> | -11.4 | -91.9              | 144.8 | 120.0 | 103.1 |
| aug-pcseg-4 <sub>m2</sub> | -24.2 | -89.6              | 129.4 | 98.5  | 72.5  |

<sup>a</sup> Triplet instabilities.

138 spin-spin coupling constants vary greatly. For example, using the aug-cc-pVnZ basis set  
 139 family, the computed couplings for GaH is 35.4 Hz, -31.9 Hz, -39.8 Hz and -8.6 Hz for  
 140 n = D, T, Q and 5, respectively, suggesting that convergence is far from being reached.  
 141 Dunning’s basis set family is heavily contracted, especially for the s functions which is  
 142 problematic for converging the FC term. For example, the aug-cc-pV5Z basis set has the  
 143 following contraction (27s,18p,14d,4f,3g,2h)→[9s,8p,6d,4f,3g,2h] leaving only 9 s-functions.  
 144 To illustrate the problem, we obtained  $^1J(\text{Se}-\text{H})$  spin-spin coupling constants 96.8 Hz,  
 145 98.5 Hz, 98.5 Hz and 99.2 Hz at the SOPPA level of theory with the uncontracted aug-cc-  
 146 pVXZ (X = D, T, Q and 5) basis sets for Se and H, respectively, which is more consistent  
 147 than what is obtained with the contracted basis sets (see Table 2). The effects of contraction  
 148 is also seen by applying the aug-pcseg-n basis set family for Ga yields very different values  
 149 of 29.4 Hz, -17.2 Hz, -16.0 Hz and -54.8 Hz for n = 1, 2, 3 and 4, respectively. Here, one  
 150 must remember that the aug-pcseg-1 basis set is a DZ quality basis set, aug-pcseg-2 of TZ  
 151 quality and so on. Thus, at the QZ level, the tested basis sets disagree by -23 Hz. Going  
 152 from QZ to 5Z quality the change is -39 Hz for the aug-pcseg-n basis set family whereas  
 153 for the aug-cc-pVnZ basis set family yields a change of +31 Hz. In general, this behavior



154 is observed for all tested elements. Such a large shift in the computed spin-spin coupling  
155 constants is quite unsatisfactory when increasing the basis set from a QZ to a 5Z quality basis  
156 set. This inconsistency is also observed for GeH<sub>4</sub>, AsH<sub>3</sub>, H<sub>2</sub>Se and HBr where the changes of  
157 going from aug-pcseg-3 to aug-pcseg-4 are -32 Hz, -7 Hz, -19 Hz and -32 Hz, respectively.  
158 In the supporting information (Tables S1 to S25) we observe that for all elements this huge  
159 change in the computed spin-spin coupling constants is due to changes in the FC term.

160 To investigate this even further, we employed the aug-pcseg- $n_m$  and aug-pcseg- $n_{m2}$  basis  
161 sets to elucidate which basis functions contribute to this large change in especially the FC  
162 term. In Table 2 we observe that for GaH, AsH<sub>3</sub>, H<sub>2</sub>Se and HBr the computed spin-spin  
163 coupling constants are largely unchanged (+5 Hz, -3 Hz, +32 Hz and +1 Hz, respectively)  
164 when using the aug-pcseg- $4_m$  basis set (here the  $f$ -functions are retained) but when using  
165 the aug-pcseg- $4_{m2}$  where the  $f$ -functions have been removed we see a large deviation with  
166 results very similar to the aug-pcseg-2 results. Thus we make the note that  $f$ -functions play  
167 a crucial role when obtaining spin-spin coupling constants for these fourth row elements.  
168 The reason for this importance is found in the electron configuration of the elements which  
169 we have listed in Table 1 where we note that  $f$ -functions strictly are polarization functions as  
170 they are never occupied. The same effect was observed for 3rd row elements where additional  
171  $d$ -functions, also serving as polarization functions, were added.<sup>50</sup> We will, when studying the  
172 saturation of the basis set with additional basis functions below pay special attention to the  
173 behavior of the computed spin-spin coupling constants as  $f$ -functions are added.

## 174 Saturation of the uncontracted basis set

175 Following previous work on extending the aug-cc-pVTZ-J basis set family with new elements  
176 we start out by decontracting the original aug-cc-pVTZ basis set for the elements Ga, Ge,  
177 As, Se and Br and adding tight primitive basis functions to saturate the basis set starting  
178 with  $s$ -functions followed by  $p$ -functions and  $d$ -functions. Finally,  $f$ -functions are added.  
179 The dependence of the indirect spin-spin coupling constant as a function of added tight  $s$ -

180 functions to the uncontracted (uc) basis set is shown on Figures 1 through 5 for all tested  
 181 molecules (GaH in Figure 1, GeH<sub>4</sub> in Figure 2, AsH<sub>3</sub> in Figure 3, H<sub>2</sub>Se in Figure 4 and HBr in  
 182 Figure 5). All computed spin-spin coupling constants are assumed converged when an added  
 183 tight basis function does not improve the obtained spin-spin coupling constants more than  
 0.01 % compared to the previously added tight basis function. We observe that the computed

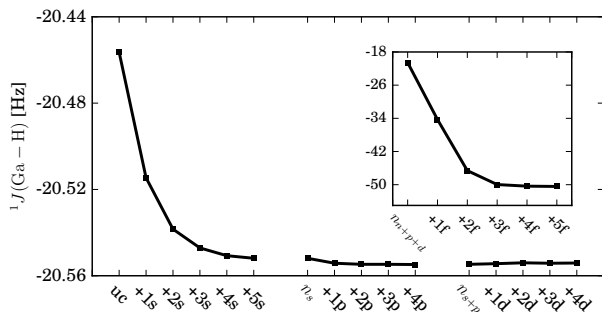


Figure 1: Convergence of calculated spin-spin coupling constants for GaH as a function of added basis functions. Black line for  $p$ - and  $d$ -functions are for  $5s$  and  $5s2p$  added basis functions, respectively. Inset shows added  $f$ -functions on top of  $5s2p2d$ .

184  
 185 spin-spin coupling constants are converged after adding a total of five primitive  $s$ -functions  
 186 to the uncontracted basis set for all elements but Br, which is converged (given the criteria  
 187 above) after adding a total of four primitive  $s$ -functions. However, for consistency we include  
 five primitive  $s$ -functions for all tested elements. Indeed, the overall convergence trend is the

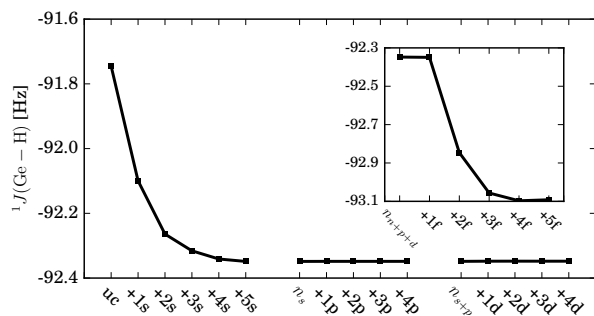


Figure 2: Convergence of calculated spin-spin coupling constants for GeH<sub>4</sub> as a function of added basis functions. Black line for  $p$ - and  $d$ -functions are for  $5s$  and  $5s2p$  added basis functions, respectively. Inset shows added  $f$ -functions on top of  $5s2p2d$ .

188  
 189 same for all molecules, although there is considerable deviation in the value of  $^1J$  depending  
 190 on the element. By investigating the contributing terms individually (Tables S26 to S30 in

191 the supporting information) we see that the Fermi contact term is, as expected, the term  
 192 that is affected as tight  $s$ -functions are added. We also observe that Br is different from the  
 193 rest of the elements in that the computed spin-spin coupling constant is not dominated by  
 194 the Fermi contact term ( $\approx 24$  Hz) but rather the paramagnetic spin-orbit term ( $\approx 62$  Hz) by  
 195 almost a factor of three. For Ga the Fermi contact term is only slightly dominant compared  
 196 to the PSO term ( $\approx -14$  Hz and  $\approx -8$  Hz, respectively) whereas for the remaining elements  
 the Fermi contact term is vastly dominant. The addition of tight primitive  $p$ -functions is

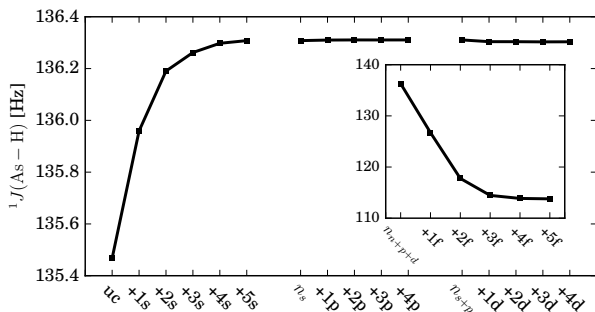


Figure 3: Convergence of calculated spin-spin coupling constants for  $\text{AsH}_3$  as a function of added basis functions. Black line for  $p$ - and  $d$ -functions are for  $5s$  and  $5s2p$  added basis functions, respectively. Inset shows added  $f$ -functions on top of  $5s2p2d$ .

197  
 198 observed to yield a minor contribution for  $\text{GaH}$  (Figure 1) and a larger contribution for  
 199  $\text{HBr}$  (figure 5). The added tight  $p$ -functions makes a non-significant contribution to the  
 200 paramagnetic spin-orbit term which dominates these two particular elements, as discussed  
 201 above. Here we observe, that for  $\text{HBr}$ , the addition of up to four tight  $p$ -functions gives an  
 202 increase in the calculated spin-spin coupling constant of 0.06 Hz which is mostly attributed  
 203 to the PSO term, but convergence is achieved to within the 0.01 % threshold listed above  
 204 with only two tight  $p$ -functions. In fact,  $\text{H}_2\text{Se}$  also sees a similar contribution to the PSO  
 205 term, however, because the FC term is so dominant this contribution is not as significant  
 206 as for  $\text{HBr}$  and is almost not observable in Figure 4. The result of adding tight  $d$ -functions  
 207 proceed similarly to the added  $p$ -functions. Here we observe that only the computed spin-  
 208 spin coupling constants of  $\text{HBr}$  exhibits noticeable behavior as the additional functions are  
 209 added. However, contrary to both the  $s$ - and  $p$ -functions, the behavior is oscillatory rather

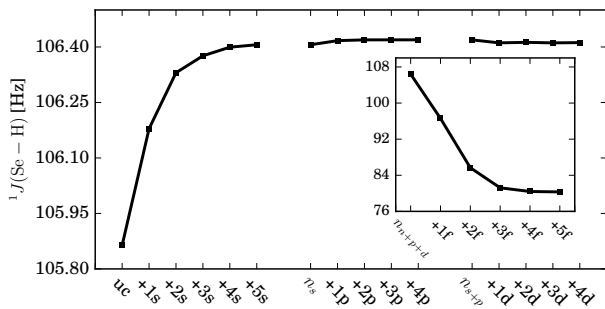


Figure 4: Convergence of calculated spin-spin coupling constants for  $\text{H}_2\text{Se}$  as a function of added basis functions. Black line for  $p$ - and  $d$ -functions are for  $5s$  and  $5s2p$  added basis functions, respectively. Inset shows added  $f$ -functions on top of  $5s2p2d$ .

210 than systematically increasing or decreasing. Detailed inspection, however, also reveals that  
 211  $\text{H}_2\text{Se}$  is subject to the same oscillatory effect but to a much lesser extent. The addition  
 212 of more than two tight  $d$ -functions is observed to not yield an appreciable improvement  
 213 according to the convergence threshold.

214 Much more interesting though is the addition of the  $f$ -functions which has a large effect  
 215 on the computed spin-spin coupling constants. In general on Figures 1 to 5 we observe that  
 216 the addition of  $f$ -functions *decrease* the value of the computed isotropic one-bond spin-spin  
 217 coupling constant. Depending on the tested element, the addition of up to 5 tight  $f$ -functions  
 218 has an effect. On  $\text{GeH}_4$  the added  $f$ -functions contribute to a change of less than 1 Hz  
 219 whereas for the four other hydrides  $\text{GaH}$ ,  $\text{AsH}_3$ ,  $\text{H}_2\text{Se}$  and  $\text{HBr}$  the effect is quite large with  
 220 changes of  $-30$  Hz,  $-23$  Hz,  $-26$  Hz and  $-31$  Hz, respectively. Because of the computational  
 221 expense of adding additional  $f$ -functions we have decided upon three additional functions  
 222 as a reasonable compromise between cost and accuracy. This is especially important for the  
 223  $f$ -functions since they are not contracted. Thus, the saturated aug-cc-pVTZ-Juc basis is  
 224 constructed by adding a total of five tight  $s$ -functions, two tight  $p$ -functions, two tight  $d$ -  
 225 functions and three tight  $f$ -functions for all tested elements yielding the basis set composition  
 226 of  $(26s16p12d5f)$ . We note that previous work on elements from the same row also has two  
 227 additional  $g$ -functions.<sup>51</sup>

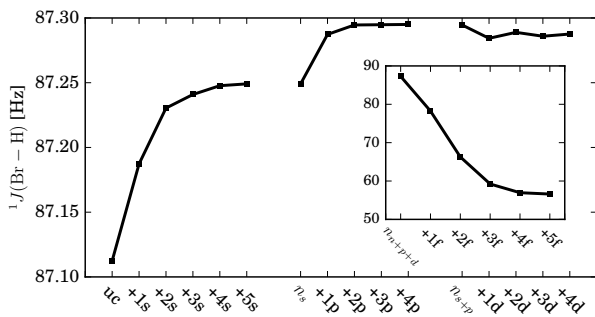


Figure 5: Convergence of calculated spin-spin coupling constants for HBr as a function of added basis functions. Black line for  $p$ - and  $d$ -functions are for  $5s$  and  $5s2p$  added basis functions, respectively. Inset shows added  $f$ -functions on top of  $5s2p2d$ .

## 228 Contraction of the aug-cc-pVTZ-Juc basis set

### 229 Contraction of the $s$ -functions

230 In Figure 6A and B we show the error in percent and absolute error, respectively, to the  
 231 aug-cc-pVTZ-Juc basis set as the  $26s$  primitive basis functions are contracted. Because the  
 232 deviation from the uncontracted results can be quite large ( $> 100\%$  for some elements) we  
 233 only show contractions which results in errors less than  $1.1\%$  (A) and  $1.1$  Hz, respectively,  
 234 which is the usual accuracy to expect from a contraction. We observe in Figure 6A that  
 235 the behavior during contraction is quite different for each tested element with the linear  
 236 molecules GaH and HBr showing a tendency to require a large number of basis functions to  
 237 successfully converge well below an error of  $1.0\%$ . The trend in Figure 6B is more uniform  
 238 above contraction level 14 with Ge being the obvious outlier as it appears to be converging  
 239 rather quickly at contraction level 11. For Ga and Br the slower convergence of the error is  
 240 due to the error observed in the FC term, which decreases slowly, as the contraction level  
 241 is increased when compared to the other elements (see Tables S31 to S35 in the supporting  
 242 information). Based on the above analysis, we have chosen to use a contraction level of  
 243 17 which for all tested elements gives errors that are less than or equal to  $0.6\%$  (or  $1.0$  Hz  
 244 in terms of absolute units) for HBr which has the largest error. This gives the following  
 245 contraction scheme for the  $s$ -functions:  $26s \rightarrow (12\ 12\ 12\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1\ 1)s$  for

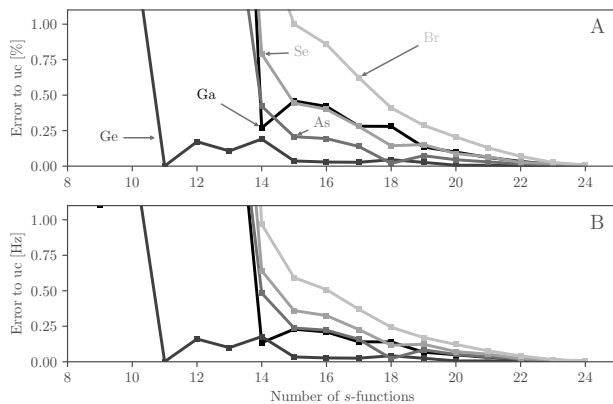


Figure 6: Percentage wise (A) and absolute (B) error during contraction of the  $s$ -functions for all tested elements. We have chosen to contract the 26 primitive  $s$ -functions in to 17 contracted  $s$ -functions.

246 all elements, i.e. the three contracted Gaussian  $s$ -orbitals are constructed from the 12 first  
 247 primitive  $s$ -functions. The 14 remaining orbitals are left uncontracted. We note that the  
 248 error during contraction of Br ( $\approx 1.0$  Hz) is not fixable by adding additional primitive basis  
 249 functions because as we showed during saturation, convergence was obtained for all elements.  
 250 Finally, we note that the error for the remaining elements Ga, Ge, As and Se are below 0.2%  
 251 for the suggested contraction level.

252 Previous work on construction of an aug-cc-pVTZ-J basis sets for the  $3d$  transition el-  
 253 ements (Sc–Zn), in the same row of elements as the ones tested in this work, resulted in  
 254 contracting 25 primitive  $s$ -functions into 17 contracted basis functions.<sup>51</sup> This means that  
 255 while the uncontracted basis set in this study is larger (in terms of primitive  $s$ -functions)  
 256 the contraction makes the new basis set slightly smaller. Below we show that this is not true  
 257 when contracting either of the  $p$ - or  $d$ -functions.

### 258 Contraction of the $p$ -functions

259 In Figure 7A and B we show the percentage wise error and absolute error, respectively, to  
 260 spin-spin coupling constants evaluated at the aug-cc-pVTZ-Juc level as the  $16p$ -functions are  
 261 contracted on top of the [17s] contracted  $s$ -functions. Again, we only present results which

262 are less than 1.1% but note that the errors for the smallest contraction levels ( $< 6$ ) are still  
 263 very large ( $> 100\%$ ). In Figure 7A we observe a difference in the convergence behavior of the  
 264 elements where spin-spin coupling constants for Ga and Br are slower to converge. The trend  
 265 is very similar for the absolute errors in Figure 7B but here the Ga atom appears converged  
 266 already at contraction level 7 with an error of around 0.3 Hz and Br shows an absolute  
 267 error of less than 0.6 Hz. Remarkably, the absolute error for Ge is well below for 0.1 Hz for  
 contraction levels 8 and above. The slow convergence of Br is due to the heavy dominance

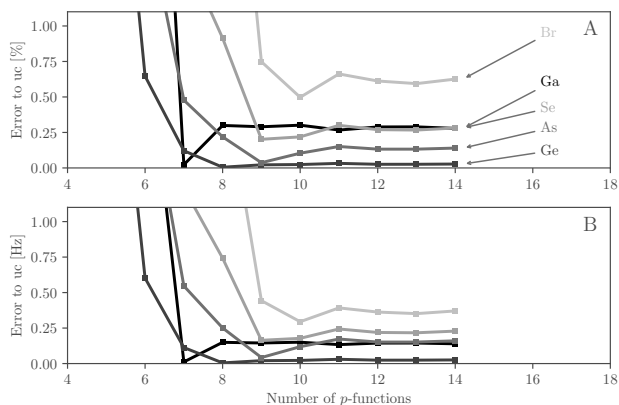


Figure 7: Percentage wise (A) and absolute (B) error during contraction of the  $p$ -functions for all tested elements. We have chosen to contract the 16 primitive  $p$ -functions in to 10 contracted  $p$ -functions.

268  
 269 of the PSO term, as already discussed, which when compared to the FC term has a large  
 270 influence on the calculated spin-spin coupling constants. In fact, the magnitude of the PSO  
 271 term is directly related to the apparent slow convergence of the calculated spin-spin coupling  
 272 constants at no earlier than contraction level 9. Thus, to make sure that contraction level 9  
 273 is not coincidence, we have chosen a contraction level of 10 for the  $p$ -functions. The errors  
 274 resulting from this contraction means that for Ga the error is still less than 1.1% (0.3 Hz)  
 275 whereas for Br the error decreases to  $\approx 0.6\%$  (0.5 Hz) The remaining elements are still below  
 276 0.2% in error when compared to the aug-cc-pVTZ-Juc results.

277 **Contraction of the  $d$ -functions**

278 As a final step in the contraction of the aug-cc-pVTZ-Juc basis set into aug-cc-pVTZ-J,  
 279 we show the percentage wise error and absolute error in Figure 8A and B, respectively,  
 280 as the 12  $d$ -functions are contracted on top of the [17s10p] contraction presented above.  
 Here, we observe that convergence for all elements happens at contraction level six for all

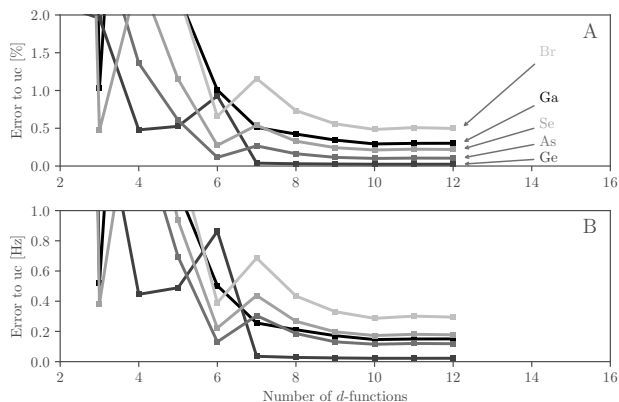


Figure 8: Contraction of  $d$ -functions. We have chosen to contract the 12 primitive  $d$ -functions in to 7 contracted functions.

281

282 elements except Ge which appears converged already at contraction level four. Looking at  
 283 the percentage wise convergence, computed spin-spin coupling constants for Ga has an error  
 284 of 1.6% at contraction level 7, but in terms of absolute errors it amounts to only 0.3 Hz.  
 285 When looking at Br, the convergence in terms of absolute errors compared to the aug-cc-  
 286 pVTZ-Juc calculations, are for the contraction of  $d$ -functions exhibiting the largest errors.  
 287 At contraction level 7, this amounts to 0.9 Hz. Again, as for both the  $s$ - and  $p$ -functions,  
 288 the elements Ge, As and Se exhibits very small errors at the chosen contraction levels and  
 289 for  $d$ -functions are converged at contraction level 6 but, as for the  $p$ -functions we choose  
 290 contraction level 7 just to make sure that it is not some fortunate error cancellation although  
 291 the error increases.



Table 3: Computed  $^1J(X - H)$  spin-spin coupling constants at various levels of theory using contracted (c) and the uncontracted (uc) aug-cc-pVTZ-J basis set.

|             |    | GaH   | GeH <sub>4</sub> | AsH <sub>3</sub> | H <sub>2</sub> Se | HBr   |
|-------------|----|-------|------------------|------------------|-------------------|-------|
| SOPPA       | c  | -50.3 | -93.1            | 114.3            | 81.8              | 59.0  |
|             | uc | -50.0 | -93.1            | 114.5            | 82.0              | 59.2  |
| SOPPA(CC2)  | c  | -42.8 | -91.1            | 113.6            | 83.4              | 63.8  |
|             | uc | -42.4 | -91.0            | 113.7            | 83.5              | 63.9  |
| SOPPA(CCSD) | c  | -33.8 | -88.4            | 112.5            | 82.7              | 61.5  |
|             | uc | -33.6 | -88.3            | 112.6            | 82.7              | 61.6  |
| B97-2       | c  | -4.8  | -87.8            | 87.4             | 53.2              | 21.9  |
|             | uc | -4.4  | -87.7            | 87.1             | 53.1              | 22.1  |
| B3LYP       | c  | -57.3 | -93.3            | 71.1             | 26.5              | -28.4 |
|             | uc | -56.9 | -93.3            | 70.9             | 26.2              | -28.6 |

## Use with other correlated methods

It is instructive to also present results with the sleuth of different methods available in modern computational programs.

In Table 3 we present computed spin-spin coupling constants using SOPPA (which are numbers obtained above during saturation for the uncontracted and contracted case), SOPPA(CC2) where the amplitudes are taken from a CC2 calculation, SOPPA(CCSD) where the amplitudes are taken from a CCSD calculation. We also include results obtained with DFT where we have chosen the always popular B3LYP<sup>73,74</sup> functional for its use in instructive learning and the B97-2<sup>75</sup> functional which is the favorite functional of one of the co-authors. Several interesting observations are made from Table 3.

First of all the differences between the results with the fully uncontracted and the final contracted basis set are very small not only for the SOPPA method, which was employed in the process of contracting the basis set, but also for the other two variants of the SOPPA method, SOPPA(CC2) and SOPPA(CCSD), and maybe more important also in the DFT calculations using the B3LYP and B97-2 functionals.

We refrain here from comparing with the experimental results as one should recall that in our calculations we have neither included vibrational corrections<sup>76,77</sup> nor treated any solvent effects,<sup>78,79</sup> as this is beyond the scope of this work. And most importantly we will not

310 be able to include relativistic effects,<sup>64,80,81</sup> as these so far are only implemented for DFT  
311 methods despite the recent publication of a relativistic SOPPA formalism.<sup>64</sup>

312 Overall, there is no common conclusion for all molecules concerning the performance of  
313 the different methods. This is partly due to the fact, that the couplings in the different  
314 molecules are not all dominated by the same contribution as can be seen from the tables in  
315 the supplementary material. For GeH<sub>4</sub> and AsH<sub>3</sub> the Fermi contact contribution is the all  
316 dominating term, for GaH and H<sub>2</sub>Se the Fermi contact term is still the largest but there is  
317 also a significant paramagnetic spin-orbit term. Finally, the coupling in HBr is dominated by  
318 the paramagnetic spin-orbit term with a small but not negligible Fermi contact contribution.  
319 On the other hand, even for the molecules, where the paramagnetic spin-orbit contribution  
320 is significant, the methods more or less agree on its value. Consequently, it is the Fermi  
321 contact contribution, which is responsible for the differences between the different methods.  
322 This is not really surprising as the Fermi contact term depends on excited triplet states<sup>82-84</sup>  
323 and is known to suffer often from triplet instabilities in particular in DFT calculations.<sup>85</sup>

## 324 **Summary and Outlook**

325 We have constructed both the uncontracted (aug-cc-pVTZ-Juc) and recontracted (aug-cc-  
326 pVTZ-J) triple zeta quality basis sets optimized for the calculation of spin-spin coupling  
327 constants for the fourth row elements Ga, Ge, As, Se and Br. The uncontracted basis set is  
328 constructed from the aug-cc-pVTZ (21s14p10d2f) basis set and adding additional primitive  
329 tight basis functions. The exponents of the additional functions are found based on the  
330 even tempered approach. Primitive functions were added until the change by adding an  
331 additional primitive function was insignificant (< 0.01%). In total, five *s*-functions, two *p*-  
332 and two *d*-functions and three *f*-functions were added to the optimized uncontracted aug-  
333 cc-pVTZ-Juc (26s16p12d5f) for the five tested element. We then performed a recontraction  
334 of the basis set to reduce the size and computational cost but keeping the error around 1%.

335 The recontraction is done from Hartree-Fock single point calculations where the appropriate  
336 molecular orbital coefficients of the simplest hydrides are extracted and used as contraction  
337 coefficients. The contracted aug-cc-pVTZ-J basis set is composed as [17s10p7d5f]. Compared  
338 to the one bond isotropic spin-spin coupling constants for the tested hydrides which are  
339 obtained with the uncontracted aug-cc-pVTZ-Juc basis set, the spin-spin coupling constants  
340 obtained with the recontracted aug-cc-pVTZ-J basis set for the hydrides deviate by less than  
341 1.0% for all tested elements.

342 The basis set for the tested elements completes the fourth row of the periodic table.  
343 They are suitable for the calculation of other magnetic properties besides the spin-spin cou-  
344 pling constants such as the hyper-fine coupling constants or electron paramagnetic resonance  
345 parameters.

346 On developing these basis sets we found that including polarization functions, which for  
347 this basis set entails  $f$ -functions, is crucial in obtaining converged results.

348 Employing the new basis sets in calculations on GaH, GeH<sub>4</sub>, AsH<sub>3</sub>, H<sub>2</sub>Se and HBr with  
349 the three SOPPA methods, SOPPA, SOPPA(CC2) and SOPPA(CCSD), as well with the  
350 two DFT functionals B3LYP and B97-2, exhibit a large degree of consistency of the results  
351 from the SOPPA methods, while the agreement of the DFT results with the SOPPA results  
352 depends strongly on the compound. For HBr B3LYP is not even able to reproduce the sign  
353 of the coupling as predicted by the other methods.

354 The new basis sets are freely available from the EMSL Basis Set Exchange Library.

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