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Aggelund, Patrick Alexander; Sauer, Stephan P. A.; Jensen, Frank

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Patrick A. Aggelund,[1, a)] Stephan P. A. Sauer,[1, b)] and Frank Jensen[2, c)]

[1)] *Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark*

[2)] *Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark*

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The pcJ-n basis set, optimized for spin-spin coupling constant calculations using density functional theory methods, are expanded to also include the s-block elements Li, Be, Na, and Mg, by studying several small molecules containing these elements. This is done by decontracting the underlying pc-n basis sets, followed by augmentation with additional tight functions. As was the case for the p-block elements, the convergence of the results can be significantly improved by augmentation with tight s-functions. For the p-block elements additional tight functions of higher angular momentum were also needed, but this is not the case for the s-block elements. A search for the optimum contraction scheme is carried out using the criterion that the contraction error should be lower than the inherent error of the uncontracted pcJ-n relative to the uncontracted pcJ-4 basis set. A large search over possible contraction schemes is done for the Li_2 and Na_2 molecules, and based on this search contracted pcJ-n basis sets for the four atoms are recommended. This work shows that it is more difficult to contract the pcJ-n basis sets, than the underlying pc-n basis sets. However, it also shows that the pcJ-n basis sets for Li and Be can be more strongly contracted than the pcJ-n basis sets for the p-block elements. For Na and Mg, the contractions are to the same degree as for the p-block elements.

Keywords: Polarization Consistent Basis Set · Basis Set Contraction · Spin-spin Coupling Constants · DFT

a)Electronic mail: qtw389@alumni.ku.dk; Corresponding author

b)Electronic mail: sauer@kiku.dk

c)Electronic mail: frj@chem.au.dk

I.   INTRODUCTION

Accurate calculations of nuclear spin-spin coupling constants are a challenging task, as the results depend strongly on the employed basis sets, on the quality of the wave function and on the molecular structure. Previous work on specialized basis sets[1–13] has shown that it is possible to design basis sets, that systematically converge towards the basis set limit, when calculating nuclear spin-spin coupling constants. This has been done using for example high-level coupled cluster methods[9,13], Møller-Plesset perturbation theory[1,4,6,10,11], multiconfigurational SCF[2,3] or density functional theory[5,7,8,12]. The most complete series of basis sets, ccJ-pVXZ (X=D,T,Q,5) and pcJ-n (n=0,1,2,3,4), are modifications of the corresponding cc-pVXZ[14] and pc-n[15,16] basis sets.

The pcJ-n basis sets follow the notation of the pc-n basis sets, where n denotes the level of polarization beyond the atomic system. So $n = 0$ is unpolarized, $n = 1$ includes a single type of polarization functions, $n = 2$ includes two types of polarization functions, etc. Currently, the pcJ-n basis sets are defined for the first row elements (H and He), the second and third row p-block elements, but the corresponding elements in the s-block are missing.

The focus of this work is to expand the pcJ-n basis sets also to the elements Li, Be, Na, and Mg in order to complete this family of basis sets and to investigate if they show the same behavior as the p-block elements. For that purpose several small molecules containing these elements will be investigated. The original pc-n basis set will first be uncontracted followed by addition of tight functions. The needed functions and exponents will be determined, using the same method as in the development of the pcJ-n basis set for the other elements[8]. There it was shown that using the contracted pc-n basis set resulted in an erratic behavior, when calculating spin-spin coupling constants, and consequently the addition of tight functions have been done on the uncontracted basis set.

After finding the optimal set of additional tight functions, the basis sets need to be recontracted in order to reduce the computational time. Of course this also leaves the basis set less flexible, introducing new errors. The contraction errors can be quantified by comparing to the inherent error in the pcJ-n basis set. Using the definition of the inherent error of a pcJ-n basis set as the error relative to the basis set limit, the aim is to find the contraction to the fewest number of functions, where the contraction error is comparable to but smaller than the inherent error in the pcJ-n basis sets.

Two different types of contraction schemes exist, denoted segmented and general contraction. In the general contraction every primitive function can occur in every contracted function, whereas in the segmented contraction every primitive can only occur in one contracted function. The segmented contraction is thus a subset of the general contraction. A general contraction is the most flexible and can in a semi-automatic way be converted into a segmented one[17], but in the present case we have in analogy with prior work[18] used an explicit search as described in Section V.

In this work both segmented and general contraction schemes have been investigated in order to find the optimum one. In previous work[18] an exhaustive search over all possible contraction schemes were done for the pcJ-0, pcJ-1, and pcJ-2 basis sets for fluorine. Based on this a number of reasonable contraction schemes were chosen for the pcJ-3 and pcJ-4 basis sets. Since the number of different contraction schemes increases rapidly with larger basis sets, a complete search will not be done in this work. Instead, only the contractions schemes deemed reasonable for the p-block elements will be investigated for Li, Be, Na and Mg.

As the spin-spin coupling constant is a molecular property, molecular systems have to be chosen. The basis set contraction error will depend on the chosen molecular system. If this error is too large for just one system the contraction can be discarded, and thus two small systems (Li_2 and Na_2) have been chosen in order to begin the investigation and discard a large number of possible contraction schemes. Based on this, contraction schemes are recommended for the pcJ-n basis sets.

II. COMPUTATIONAL DETAILS

The indirect nuclear spin-spin coupling can be expressed in terms of a reduced coupling tensor $\mathbf{K}_{KL}$[19], given by eq. (1)

$$
\mathbf{K}_{KL} = \langle 0|\hat{\mathbf{h}}_{KL}^{\mathrm{DSO}}|0\rangle - 2\sum_{s>0} \frac{\langle 0|\hat{\mathbf{h}}_K^{\mathrm{PSO}}|s\rangle\,\langle s|\hat{\mathbf{h}}_L^{\mathrm{PSO}}|0\rangle^T}{E_s - E_0}
$$
$$
- 2\sum_t \frac{\langle 0|\hat{\mathbf{h}}_K^{\mathrm{FC}} + \hat{\mathbf{h}}_K^{\mathrm{SD}}|t\rangle\,\langle t|\hat{\mathbf{h}}_L^{\mathrm{FC}} + \hat{\mathbf{h}}_L^{\mathrm{SD}}|0\rangle^T}{E_t - E_0}
\tag{1}
$$

Here s denotes the excited singlet states and t denotes the excited triplet states. The diamagnetic spin-orbit (DSO), paramagnetic spin-orbit (PSO), Fermi-contact (FC), and

spin-dipole (SD) operators used in eq. (1) are given by equations (2)-(5)

$$\hat{\mathbf{h}}_{KL}^{\text{DSO}} = \frac{\alpha^4}{2} \sum_i \frac{\mathbf{r}_{iK}^T \mathbf{r}_{iL} \mathbf{I}_3 - \mathbf{r}_{iK} \mathbf{r}_{iL}^T}{\mathbf{r}_{iK}^3 \mathbf{r}_{iL}^3} \tag{2}$$

$$\hat{\mathbf{h}}_{K}^{\text{PSO}} = \alpha^2 \sum_i \frac{\mathbf{r}_{iK} \times \nabla_i}{\mathbf{r}_{iK}^3} \tag{3}$$

$$\hat{\mathbf{h}}_{K}^{\text{FC}} = \frac{8\pi\alpha^2}{3} \sum_i \delta\left(\mathbf{r}_{iK}\right) \mathbf{s}_i \tag{4}$$

$$\hat{\mathbf{h}}_{K}^{\text{SD}} = \alpha^2 \sum_i \frac{3\mathbf{r}_{iK}^T \mathbf{s}_i \mathbf{r}_{iK} - \mathbf{r}_{iK}^2 \mathbf{s}_i}{\mathbf{r}_{iK}^5} \tag{5}$$

where K and L are the two nuclei, $\alpha \approx 1/137$ is the fine-structure constant, $\mathbf{r}_{iK}$ is the position of nucleus K relative to electron i, $\mathbf{I}_3$ is the 3 by 3 unit matrix, the superscript T denotes vector transposition, $\delta\left(\mathbf{r}_{iK}\right)$ is the Dirac delta function, and $\mathbf{s}_i$ is the electron spin operator.

The experimental indirect spin-spin coupling is expressed in terms of the indirect nuclear spin-spin coupling tensor, $\mathbf{J}_{KL}$, given by eq. (6)

$$\mathbf{J}_{KL} = \hbar \frac{\gamma_K \gamma_L}{2\pi} \mathbf{K}_{KL} \tag{6}$$

with γ_K and γ_L being the gyromagnetic ratios of the two nuclei, and $\hbar = \frac{h}{2\pi}$, with h being Planck's constant. In experiments in liquid or gas phase, where rapid tumbling occurs, only the isotropic spin-spin coupling constant can be measured, which is defined as a third of the trace of $\mathbf{J}_{KL}$.

The calculations of spin-spin coupling constants are in practice done using response theory[20], with the reduced spin-spin coupling constants calculated by Eq. (7)

$$\mathbf{K}_{KL} = \frac{d^2 E}{d\mathbf{M}_K d\mathbf{M}_L} = \frac{\partial^2 E}{\partial\mathbf{M}_K \partial\mathbf{M}_L} + \frac{\partial^2 E}{\partial\mathbf{M}_K \partial\boldsymbol{\lambda}_S} \frac{\partial\boldsymbol{\lambda}_S}{\partial\mathbf{M}_L}$$
$$+ \frac{\partial^2 E}{\partial\mathbf{M}_K \partial\boldsymbol{\lambda}_T} \frac{\partial\boldsymbol{\lambda}_T}{\partial\mathbf{M}_L} \tag{7}$$

Here $\mathbf{M}_K$ and $\mathbf{M}_L$ are magnetic moments of nuclei K and L, $\boldsymbol{\lambda}_S$ and $\boldsymbol{\lambda}_T$ are parameters for the singlet and triplet variations in the electronic state. The derivatives of these parameters are obtained by solving the response equations

$$\frac{\partial^2 E}{\partial\boldsymbol{\lambda}_S \partial\boldsymbol{\lambda}_S} \frac{\partial\boldsymbol{\lambda}_S}{\partial\mathbf{M}_L} = -\frac{\partial^2 E}{\partial\boldsymbol{\lambda}_S \partial\mathbf{M}_L} \tag{8}$$

$$\frac{\partial^2 E}{\partial\boldsymbol{\lambda}_T \partial\boldsymbol{\lambda}_T} \frac{\partial\boldsymbol{\lambda}_T}{\partial\mathbf{M}_L} = -\frac{\partial^2 E}{\partial\boldsymbol{\lambda}_T \partial\mathbf{M}_L} \tag{9}$$

All calculations in this work have been done with the DALTON program package[21,22], and the B3LYP functional[23,24] in order to be consistent with the work done on the p-block elements[18].

All geometries have been optimized using the pc-4 basis sets[16], and the pc-n basis sets used have been taken from the EMSL basis set library[25,26]. Since only the convergence of a given pc-n basis set will be investigated, no comparison with experiments will be done. This would have required additional attention to the molecular geometries, vibrational corrections[27,28], solvent effects[29], and the functional used.

The optimization of basis sets is often done using a variational criterion, but no variational principle exists for properties other than the energy. In the study of the p-block elements a maximization of eq. (10) was used to determine the optimum exponents for the additional tight functions[8]. This was based on the observation that basis set incompleteness usually underestimates the contribution of each component, and determining additional function(s) that maximizes the sum of absolute values of the four contributions was found to be a useful heuristic method for assigning exponents for the additional tight functions.

$$J_{\text{absolute}} = (|J_{\text{SD}}| + |J_{\text{DSO}}| + |J_{\text{PSO}}| + |J_{\text{FC}}|) \tag{10}$$

The contraction coefficients used have not been optimized, but are instead taken from atomic SCF calculations with the B3LYP functional. Only contraction of s- and p-orbitals have been considered as the polarization functions have been left uncontracted. The exponents are kept fixed at their value from the uncontracted basis sets. In order to determine the optimum contraction scheme, the contraction error has been defined as the sum of the absolute errors in each of the four terms of the spin-spin coupling constant. This can then be compared to the inherent error in the pcJ-n basis sets. The results with the uncontracted pcJ-4 basis set are taken to be the basis set limit.

## III.   BASIS SET CONVERGENCE FOR THE PC-N BASIS SET

The molecular system used in this study can be found in Table I.   Since some of the molecules studied include elements from the p-block, a question appeared of whether to use the pcJ-n basis set for the p-block elements and only optimize the basis set of the s-block elements, or to start from the pc-n basis set for all elements and then optimize both basis

Table I: The molecular systems used in this study

LiH, LiF, Li$_2$, NaH, NaF, Na$_2$,

BeH$_2$, MgH$_2$, MgF$_2$
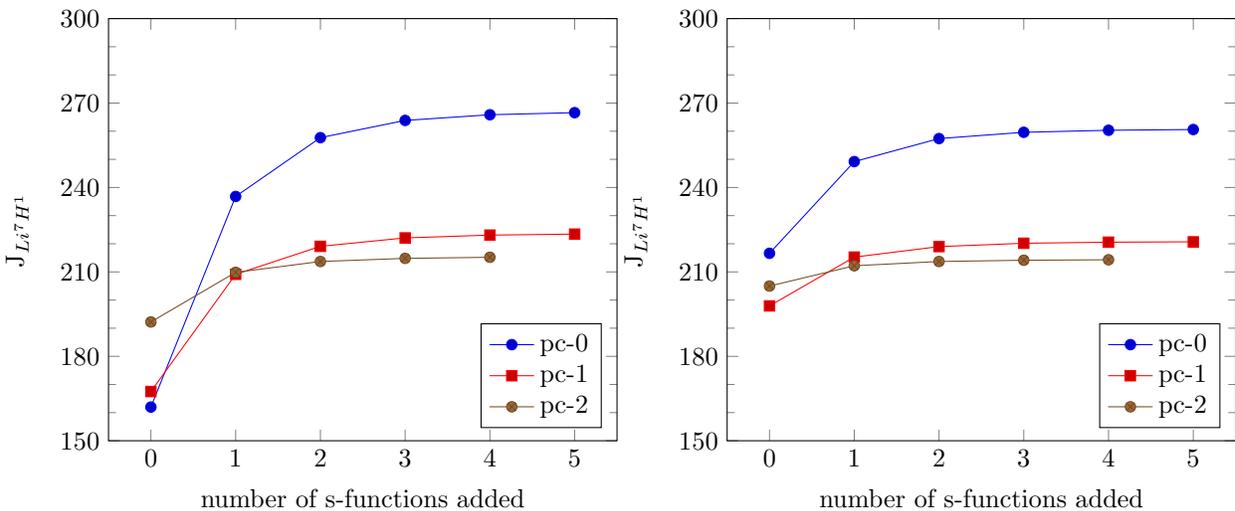
(a) LiH with pc-n basis on both atoms

(b) LiH with fixed pcJ-n basis set on hydrogen

Figure 1: spin-spin coupling constant in Hz for LiH with different basis sets on the hydrogen. In case **(a)**, addition of tight s-functions were done to both the Lithium and Hydrogen basis sets, and in case **(b)** addition were only to the Lithium basis set

sets. An argument for using the first approach is clearly that the number of functions to optimize is lower, which gives a reduction in computational time. The counterargument is that we might get an unevenly matched basis set for the molecule since the p-block element would have more basis functions. The additional basis functions on the p-block element could overlap with the s-block atom, effectively creating a better set of basis functions for it, resulting in the need for fewer functions in order to saturate the function space. This effect would be largest for the small pc-0 and pc-1 basis sets, where few functions are available on the s-block atom, and a larger effect is to be gained from "borrowing" functions from p-block atom(s).

In order to check if the approach with a fixed pcJ-n basis set could be undertaken, calculations were done on LiH both with and without a fixed pcJ-n basis set for Hydrogen. The

Table II: Coefficient ratios for the tight s-functions added to the hydrogen basis set.

Basis	Exponent Ratios	
pc-0+2s	10.5	22.7
pc-1+2s	10.7	23.4
pc-2+2s	11.8	26.5
pc-3+2s	11.8	25.2
pc-4+1s	21.6	

results for addition of tight s-functions to the pc-0, pc-1 and pc-2 basis sets are shown in Figure 1. It is clear that when starting from an already optimized basis set for Hydrogen, a smaller effect is observed when adding additional tight s-functions. This is due to the fact that in case (a), two functions are added simultaneously, compared to (b) in which only one function is added. A thing to note is that the values when two additional s-functions are added, are similar in the two cases. This is expected since the pcJ-n basis set includes two tight s-functions for the pc-0,1,2 basis sets, which makes (a) and (b) comparable at this point. As a test the exponent ratios of the optimized Hydrogen exponents were compared to the ones found in the p-block elements. From the data in Table II it can be seen that the ratios are in good agreement with the ones used in the pcJ-n basis set[8], namely 12.5 and 25 for pc-0,1,2,3 and 20 for pc-4.

An important thing seen from Figure 1 is that the additional s-functions have a similar effect in the two cases. In all pc-n basis sets the addition of the first tight s-function yielded $\sim 70\%$ of the total effect possible by saturating the s-space. The addition of two tight s-functions yielded $\sim 90\text{-}95\%$ of the total effect. The same effect is seen for the pc-3 and pc-4 basis sets. This was similar in both the case with and without fixed basis set for Hydrogen, and as a result of this further optimizations were done using the pcJ-n for the atoms, which already have such a basis set developed.
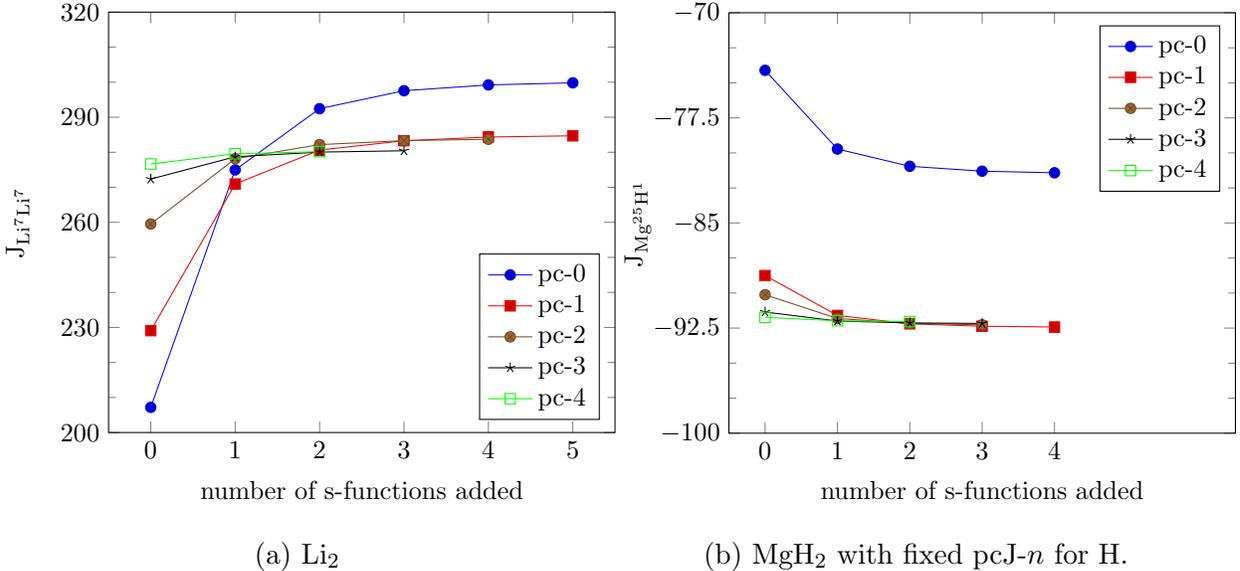
Figure 2: spin-spin coupling constant in Hz for Li_2 and MgH_2 as a function of added tight s-functions.

A. Convergence for Li_2 and MgH_2

In order to exemplify the general trend of the s-block elements, Li_2 and MgH_2 will be used as representative molecules. The spin-spin coupling constants of most of the molecules were dominated by the FC term, but the PSO term also had a significant contribution to the overall spin-spin coupling constants for systems containing F or Cl. The convergence of the basis sets for Li_2 and MgH_2 with addition of tight s-functions can be seen in Figure 2. From Figure 2 it is clear that the number of tight s-functions needed in order to converge decreases, as the underlying basis set is increased. For Li_2 convergence with respect to s-functions was reached when the largest exponent reached a value of about $1 \cdot 10^7$ and for MgH_2 convergence was reached when the exponent had a value of around $5 \cdot 10^7$. This means that to fully converge the basis set with respect to the addition of s-functions, 4-5 functions are required for the pc-0 basis set, 3-4 for pc-1, 2-3 for pc-2, 1-2 for pc-3, and 1 for pc-4. To further investigate the basis set convergence, function of higher angular momentum have to be included, in order to see if the basis sets are sensitive to these. The results from the addition of the higher order functions can be seen in Figure 3, and it clearly shows that the spin-spin coupling constants are not sensitive to the addition of tight functions other than s-functions. This is a different trend than seen in basis set convergence for the p-block
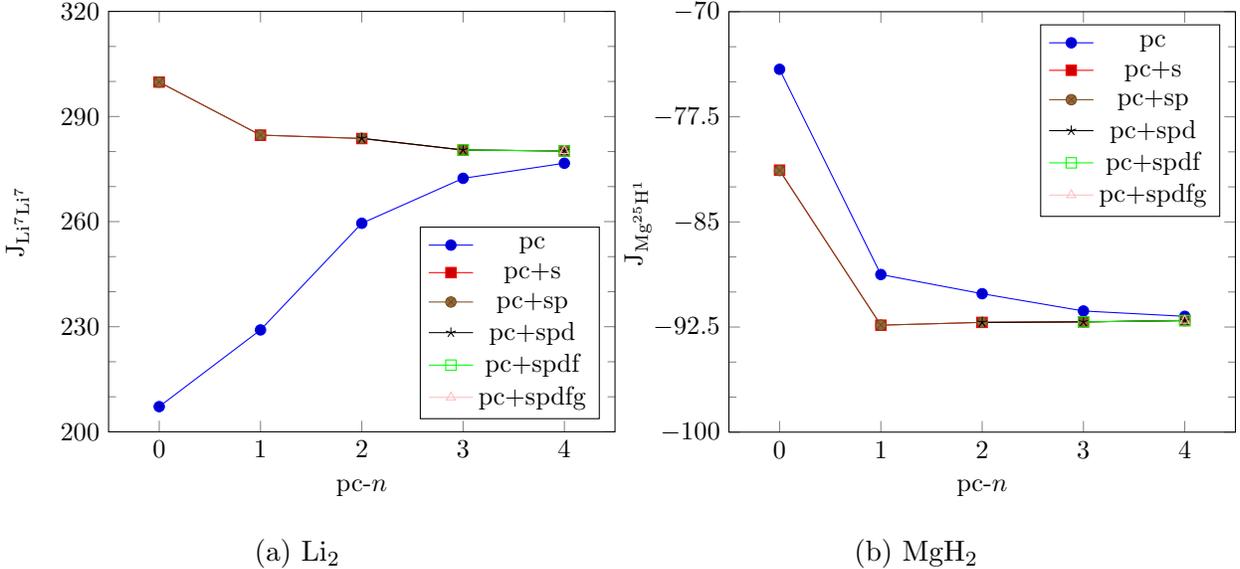
8

Figure 3: spin-spin coupling constant in Hz for Li_2 and MgH_2 calculated with the pc-n basis sets augmented with additional tight functions. The results for addition of pdfg functions are indistinguishable from the results with addition of only s-functions.

elements, where functions up to f-type had an effect on the convergence. This difference can be explained by the lack of p-electrons in the case of Lithium and Beryllium. For Sodium and Magnesium it can be attributed to the fact, that they contain no valence p-electrons, and that the underlying pc-n basis sets are sufficient for describing the core p-electrons.

IV. DEVELOPMENT OF PCJ-N BASIS SET

The analysis of Li_2 and MgH_2 showed that addition of tight s-functions is important, in order to get a better basis set convergence when calculating spin-spin coupling constants. As the two example molecules show, the need for additional s-functions decreases, as the underlying basis set increases in size, and this trend is seen for all molecules studied. However, care must be taken when choosing how many of these functions should actually be added in the final basis set. The first s-function should clearly be included, but inclusion of for example five s-functions to the pc-0 basis set, would double the number of s-functions in the basis sets for Lithium and Beryllium. This would bring the number of s-functions up to the level of the pc-2 basis set, which is not desirable in a series of consistent basis sets. The addition of extra functions increases the computational time, and as can be seen in

9

Figure 2, the effect of adding more than two functions is at maximum around 10%. This is not worth the additional computational time. Furthermore the change in spin-spin coupling constant when adding more than two s-function, for a given pc-n basis set. For example for the pc-0 basis set for Li_2, the change in spin-spin coupling constant going from two extra s-functions to the fully saturated s-space is around 7 Hz. This can be compared to an error of around 20 Hz relative to the fully optimized pcJ-4 basis set. Similarly for the pc-0 basis set for MgH_2, the change in spin-spin coupling constant going from two extra s-functions to the fully saturated s-space is around 1 Hz, which can be compared to the error of around 11 Hz compared to the fully optimized pcJ-4 basis set.

Analogously to the pcJ-n basis sets, the suggestion is therefore to add two extra tight s-functions to the pc-0,1,2,3 basis sets and one s-function to the pc-4 basis set, as this seems like the best balance between efficiency in the calculations, and the accuracy in the series of underlying basis sets. Figure 3 shows that the addition of extra tight functions other than s-functions is unnecessary.

The next step in developing a basis set for spin-spin coupling calculations is determining the exponents to be used. The exponent ratios obtained when adding the extra functions, determined by optimization of the function in eq. (10), can be seen in Table III. Average values of the ratios for addition of two s-functions to the pc-0,1,2,3 basis sets are 11.7 and 26.1. The average value of the ratio for addition of a single tight function to the pc-4 basis set, is 18.7. The values are not far from the values used in the pcJ-n basis set, and the suggestion is therefore to use the same exponent ratios as for the p-block elements. This will keep the pcJ-n basis set exponent ratios consistent for the first three rows of the periodic table, while not changing the overall convergence of the individual basis sets significantly.

V. CONTRACTION OF THE PCJ-N BASIS SET

Contraction of a basis set is a compromise between improving the computational efficiency and introducing additional basis set errors. The contraction error must be quantified based on calculated values for a selection of molecular systems, and is thus dependent on the specific set of reference systems. As mentioned in the introduction, an unacceptable contraction error for a single system is sufficient to discard a given contraction scheme. We have in

10

Table III: The exponent ratios of the two additional tight s-functions added to the pc-0,1,2,3 basis set, and the ratios of the one tight function added to the pc-4 basis set, determined by optimization of the function in (10)

	LiH		LiH fixed H		Li2		LiF	
pc-0+2s	11.7	27.5	11.7	27.5	11.9	28.9	10.8	27.5
pc-1+2s	13.3	37.0	13.3	37.0	11.8	27.0	13.3	37.3
pc-2+2s	10.9	21.9	10.8	21.7	11.6	25.5	10.9	21.6
pc-3+2s	11.8	24.3	11.8	24.4	11.8	24.7	11.4	24.5
pc-4+1s	17.8		17.7		17.3		17.7	

	BeH2		MgH2		MgF2	
pc-0+2s	11.1	23.8	11.5	25.3	11.4	23.9
pc-1+2s	11.5	24.8	11.5	24.9	10.7	25.3
pc-2+2s	11.7	25.7	11.9	26.2	12.5	27.4
pc-3+2s	12.3	27.9	11.9	25.2	12.0	26.9
pc-4+1s	18.6		18.6		20.0	

	NaH		Na2		NaF	
pc-0+2s	11.5	25.2	11.4	24.8	11.0	22.8
pc-1+2s	11.5	24.9	11.6	25.4	11.7	24.8
pc-2+2s	11.9	25.8	11.8	25.4	12.2	26.8
pc-3+2s	11.9	25.8	11.6	24.2	11.5	22.8
pc-4+1s	19.1		20.0		20.4	

addition required that an acceptable contraction scheme must have the property that the contraction error does not change significantly upon further uncontraction, to avoid selecting a contraction scheme that by error cancellation produce a low contraction error. Contraction of basis sets optimized for molecular properties is less straight-forward than for basis sets

optimized by energetic criteria, and we have used results from previous work for the p-block elements in selecting the recommended contraction[18].

We will in the following use a notation where contraction will be named according to the number of contracted functions, as 1-contraction, 2-contraction and 3-contraction[18]. The number of primitive functions in each contracted function will be given in parenthesis such as $(n, 1, 1, 1, \ldots)$ for a 1-contraction or $(n, m, l, 1, 1, \ldots)$ for a 3-contraction. Here n, m and l denotes the number of primitive functions in each contracted function. For a segmented contraction the sum of n, m and l must always be equal to the number of primitive functions contracted (N_{prim}^C). The first contracted function then includes functions 1 to n, the second includes functions $n + 1$ to $n + m$ and the third includes the functions from $n + m + 1$ to $n + m + l$. For general contractions every primitive can go into every contracted function, with the restriction that $n + m + l \geq N_{\text{prim}}^C$. The notation with a single parenthesis is therefore not unique so instead the notation $(n, m, l, 1, 1, \ldots)[n_{\text{start}}, m_{\text{start}}, l_{\text{start}}]$ will be used. Here the primitives going into the first contracted function, are the functions from n_{start} to $n_{\text{start}} + n$, the primitives going into the second contracted function are the primitives from m_{start} to $m_{\text{start}} + m$, and likewise for the third contracted function.

In order to organize the results, the function with the largest exponent will always be included in the first contracted function, meaning that $n_{\text{start}} = 1$.

In the study of the p-block elements, it was shown that the contractions where the innermost functions were left uncontracted and the outermost were contracted, always had a higher contraction error than the contractions where the innermost functions were contracted and the outermost were left uncontracted[18]. Therefore only contraction schemes where the outermost functions are left uncontracted are investigated.

A.   Contraction of s-functions for the Li_2 molecule

The contraction scheme notation is perhaps best illustrated with an example. If we consider the pcJ-2 basis set for Li, it consists of 12 s-functions. The original pc-2 basis set has a composition of $(10s, 4p, 1d) \rightarrow [4s, 2p, 1d]$, so the maximum contraction for the pcJ-2 basis set is to 4 s-functions. The contraction of the s-functions for Li can then use either 1s or 2s SCF coefficients. The simplest 1-contraction is (9,1,1,1) where the three outermost functions are left uncontracted. This leads to a contraction error of 196 Hz when 1s-coefficients are

used and an error of 69 Hz for 2s-coefficients, both well above the inherent error of 2.64 Hz. While the 1-contraction is unique, a number of different contraction schemes exists for the 2-contraction as both segmented and general contraction are possible. There is also a choice of which SCF coefficients to use for the two contracted function. In this work the choice has been to always use the 1s SCF coefficients for the innermost contracted function, and then use either the 1s or 2s for the other contracted functions. For segmented 2-contraction the number of different possibilities is quite low and both (1s,1s) and (1s,2s) combinations of contraction coefficients have been investigated. For general contractions only the latter of the two combinations have been investigated, since the number of different general contractions grows rapidly with larger basis sets.

Contracting 12 s-functions to 4 s-functions in a segmented 2-contraction, can be done in seven different ways, when leaving the outermost functions uncontracted, namely (8,2,1,1), (7,3,1,1), (6,4,1,1), (5,5,1,1), (4,6,1,1) (3,7,1,1) and (2,8,1,1). The corresponding general contraction can be done in 89 different ways and a search over these possibilities has been made. Common for all 2-contraction is that their contraction error are all greater than 4 Hz, which is above the inherent error in the pcJ-2 basis set.

For the 3-contractions the choice have been to only look at segmented contraction since the number of different general contractions is quite large. Furthermore only contractions employing the (1s,1s,1s), (1s,1s,2s) or (1s,2s,2s) coefficient combinations have been investigated for the Li_2 molecule. This leads to contraction errors larger than the ones found for the 2-contractions. The contraction to 4 s-functions is therefore not feasible.

Contracting to 5 s-functions yields a contraction error of about 79 and 1.5 Hz for the 1-contraction (8,1,1,1,1), using 1s- or 2-coefficients. Although the result using 2s-coefficients is lower than the inherent error, it is still too large since the p-functions will likely yield a similar error. Contracting to 5 s-functions using the general 2-contraction (8,7,1,1,1)[1,3] with the (1s,2s) coefficients yields an error of 0.013 Hz, which is well below the inherent error. Similar errors cannot be found using the other general or segmented 2-contractions, as these all yield contraction errors above the inherent error. The low contraction error might therefore stem from some random error cancellations, and looking at the contraction scheme (8,6,1,1,1,1)[1,3] where the outermost function in the second contracted function have been left uncontracted, yields an error of 16.6 Hz which is a much larger error. The contraction scheme (8,7,1,1,1)[1,3] therefore does not seem robust and will not be used for the pcJ-2

basis set for Li.

Going to 3-contraction again yields worse results than the 2-contractions and contracting to 5 s-functions is therefore not viable.

1-contraction to 6 s-functions gives errors of 25.8 and 0.46 Hz for the 1s- and 2s-coefficients, the second of which is well below the inherent error in the pcJ-2 basis set. Similar results are seen for both the general and segmented 2-contractions with the best being the segmented (4,4,1,1,1,1) contraction, with an error of 0.026 Hz. However, the low contraction error stems from random error cancellations as the segmented (4,3,1,1,1,1,1) contraction yielded an error of 2.82 Hz. Instead the 3-contraction (4,3,2,1,1,1) with an error of 1.06 Hz has been used, as this contraction proved to be the most robust while still having an error below the inherent error in the basis set. The maximum contraction of pcJ-2 for Li is thus to 6 s-functions. Using the same principles for the rest of the pcJ-n basis sets yields the results shown in Table IV. This table only shows the lowest error for each contraction type and level. For most cases there are several other combinations that produce a comparable error. Especially for the general contraction where there is no immediate pattern to be found.

For the segmented 1-contraction the contractions with 2s coefficients yield lower errors than those with 1s coefficients. Another trend seen for segmented contractions is that for the smaller basis sets pcJ-0,1 the 1- and 2-contraction yields lower errors than the 3-contraction, whereas the 3-contraction becomes better than the others for the pcJ-2,3,4 basis sets. An outlier here is the pcJ-1 basis set when contracting to 5 s-functions where the 3-contraction shows a slightly lower error than the 2-contraction although both are within the inherent error.

When comparing the segmented with the general contractions the latter have the lowest contraction error in most cases, but the difference is not that large and in most cases both the segmented and general contractions are within the inherent error of the uncontracted basis sets. While the segmented seems to become better when a smaller total number of primitives are used in the contracted functions, the same is not seen for the general contractions. For example for the pcJ-2 basis set going from 4 s- to 5 s-functions decreases the error whereas going to 6 s-functions increases the error again. The same trend is seen for the pcJ-0 and pcJ-4 basis sets. This again suggests that error cancellations are responsible for the low error when using the general contractions. The recommendation is therefore to use the simple segmented contractions instead and these recommendations have been marked in

Table IV: Contraction errors (sum of the absolute errors of the four contributions in Hz) for 1- 2- and 3-contractions of s-functions for the pcJ-n ($n = 0, 1, 2, 3, 4$) basis sets for the Li$_2$ molecule. Only the contraction with the lowest error in each case is shown

Basis set (N$_{primitive}$) [Inherent absolute error]	Contraction	1-Contracted Segmented (n,1,...)	2-Contracted		3-Contracted Segmented (n,m,l,1,...)
			Segmented (n,m,1,...)	General (n,m,1,...) [n$_{start}$,m$_{start}$]	
pcJ-0 (7s) [12.5]	3s	5.56 (5,1,1)	29.7 (4,2,1)	0.079 (6,3,1)[1,4]	-
	4s	3.76 (4,1,1,1)	**1.46 (3,2,1,1)**	1.39 (3,5,1,1)[1,1]	44.1 (2,2,2,1)
	5s	0.040 (3,1,1,1,1)	1.14 (2,2,1,1,1)	0.060 (3,4,1,1,1)[1,1]	-
pcJ-1 (9s) [1.06]	3s	74.0 (7,1,1)	177 (2,6,1)	20.6 (6,3,1)[1,6]	-
	4s	3.78 (6,1,1,1)	19.0 (5,2,1,1)	3.13 (5,6,1,1)[1,2]	194 (2,4,2,1)
	5s	3.79 (5,1,1,1,1)	**0.90 (4,2,1,1,1)**	0.60 (3,6,1,1,1)[1,1]	0.39 (2,3,2,1,1)
pcJ-2 (12s) [2.64]	4s	69.0 (9,1,1,1)	6.67 (8,2,1,1)	3.95 (10,2,1,1)[1,5]	22.9 (6,3,2,1)
	5s	1.53 (8,1,1,1,1)	3.91 (6,3,1,1,1)	0.013 (8,7,1,1,1)[1,3]	5.47 (3,2,5,1,1)
	6s	0.46 (7,1,...)	0.026 (4,4,1,...)	0.32 (3,8,1,...)[1,1]	**1.06 (4,3,2,1,...)**
pcJ-3 (16s) [0.49]	6s	0.52 (11,1,...)	0.44 (8,4,1,...)	0.53 (9,10,1,...)[1,3]	1.42 (7,3,3,1...)
	7s	4.16 (10,1,...)	0.62 (2,9,1,...)	0.23 (10,11,1,...)[1,1]	0.043 (7,3,2,1,...)
	8s	10.1 (9,1,...)	0.36 (7,3,1,...)	0.19 (7,10,1,...)[1,1]	**0.39 (6,3,2,1,...)**
	9s	1.6 (8,1,...)	0.12 (6,3,1,...)	0.26 (5,8,1,...)[1,2]	0.58 (2,5,3,1,...)
pcJ-4 (20s)	8s	0.71 (13,1,...)	3.61 (7,7,1,...)	0.19 (8,13,1,...)[1,2]	0.22 (5,5,5,1,...)
	9s	4.67 (12,1,...)	0.72 (6,7,1,...)	0.063 (10,11,1,...)[1,3]	0.14 (8,3,3,1,...)
	10s	12.1 (11,1,...)	0.11 (6,6,1,...)	0.099 (12,6,1,...)[1,1]	0.0088 (6,5,2,1,...)
	11s	0.19 (10,1,...)	0.012 (8,3,1,...)	0.15 (11,4,1,...)[1,4]	**0.84 (6,4,2,1,...)**

The results marked in **bold** are the contraction schemes recommended, from the analysis of the Li$_2$ molecule.

bold in Table IV.

B. Contraction of p-functions for the Li$_2$ molecule

The contraction of the p-functions can be considered analogously to the s-function contraction, but with only one set of coefficients (2p) less possibilities for contraction schemes

Table V: Contraction errors (sum of the absolute errors of the four contributions in Hz) for 1- 2- and 3-contractions of p-functions for the pcJ-n ($n = 2, 3, 4$) basis sets for the Li_2 molecule. The s-functions have been left uncontracted. Only the contraction with the lowest error in each case is shown

| Basis set ($N_{primitive}$) [Inherent absolute error] | Contraction | 1-Contracted Segmented (n,1,…) | 2-Contracted | | 3-Contracted |
			Segmented (n,m,1,…)	General (n,m,1,…) [n_{start},m_{start}]	Segmented (n,m,l,1,…)
pcJ-2 (4p) [2.64]	**2p**	**0.35 (3,1)**	-	-	-
pcJ-3 (6p)[0.49]	3p	1.44 (4,1,1)	6.04 (3,2,1)	1.98 (4,4,1)[1,2]	-
	4p	**0.26 (3,1,1,1)**	0.55 (2,2,1,1)	0.086 (3,2,1,1)[1,2]	-
pcJ-4 (8p)	4p	0.46 (5,1,1,1)	0.0054 (4,2,1,1)	0.030 (4,5,1,1)[1,2]	0.034 (2,2,3,1)
	5p	**0.079 (4,1,1,1,1)**	0.13 (3,2,1,1,1)	0.077 (3,4,1,1,1)[1,2]	0.030 (2,2,2,1,1)

The results marked in **bold** are the contraction schemes recommended, from the analysis of the Li_2 molecule.

exists. However, for the pcJ-n basis sets for Li, Be, Na, and Mg no additional tight p-functions were added to their underlying pc-n basis sets. The already existing p-function contraction scheme for the pc-n basis sets could therefore also be used for the pcJ-n basis sets. This of course will have to be investigated since the pc-n basis sets are not optimized for calculating spin-spin coupling constants, and the optimal contraction for these basis sets, might not be the optimal contractions for the pcJ-n basis sets.

The pcJ-0 basis set for Li consists of only one p-function, and can therefore not be contracted. The pcJ-1 basis set consists of three p-functions, and with the condition that the outermost function are left uncontracted, this only leaves the possibility to do the segmented 1-contraction (2,1). This yields a contraction error of 0.0198 Hz, well below the inherent error. Results for the remaining for pcJ-n basis sets can be found in Table V.

From this Table it can be seen that the segmented 1-contractions perform reasonably as they for all basis sets give contraction errors within the inherent error. Because of this the recommendations, marked in **bold** in Table V, are the 1-contractions, which are the same contractions used in the pc-n basis sets. However, for the two larger basis sets, pcJ-3,4 the contractions are done to 4 and 5 p-functions, respectively. For pc-3 and pc-4 the contractions are done to 3 and 4 p-functions respectively, which means a slight relaxation of the

Table VI: Contraction errors (sum of the absolute errors of the four contributions in Hz) for 1- 2- and 3-contractions of s-functions for the pcJ-n ($n = 0, 1, 2, 3, 4$) basis sets for the Na$_2$ molecule. Only the contraction with the lowest error in each case is shown

| Basis set (N$_{primitive}$) [Inherent absolute error] | Contraction | 1-Contracted Segmented (n,1,...) | 2-Contracted | | 3-Contracted |
			Segmented (n,m,1,...)	General (n,m,1,...) [n$_{start}$,m$_{start}$]	Segmented (n,m,l,1,...)
pcJ-0 (10s) [30.5]	4s	19.4 (7,1,1,1)	123 (6,2,1,1)	333 (8,8,1,1)[1,1]	25.1 (5,2,2,1)
	5s	4.17 (6,1,1,1,1)	**11.8 (4,3,1,1,1)**	17.8 (6,7,1,1,1)[1,1]	229 (3,3,2,1,1)
pcJ-1 (13s) [106]	5s	33.4 (9,1,1,1,1)	609 (8,2,1,1,1)	334 (10,10,1,1,1)[1,1]	26.0 (6,2,3,1,1)
	6s	13.7 (8,1,...)	36.9 (2,7,1,...)	0.88 (6,9,1,...)[1,1]	**4.32 (4,4,2,1,...)**
pcJ-2 (15s) [43.8]	6s	11.3 (10,1,...)	46.5 (7,4,1,...)	2.92 (10,2,1,...)[1,10]	2.42 (5,4,3,1,...)
	7s	7.63 (9,1,...)	1.43 (6,4,1,...)	2.76 (3,10,1,...)[1,1]	2.63 (7,2,2,1,...)
	8s	17.36 (8,1,...)	2.31 (6,3,1,...)	5.14 (9,2,1,...)[1,8]	**4.66 (5,3,2,1,...)**
pcJ-3 (19s) [9.03]	7s	5.56 (13,1,...)	54.9 (10,4,1,...)	9.87 (14,2,1,...)[1,5]	12.7 (9,3,3,1,...)
	8s	1.34 (12,1,...)	2.06 (3,10,1,...)	0.76 (2,12,1,...)[1,2]	6.29 (9,2,3,1,...)
	9s	6.34 (11,1,...)	0.62 (2,10,1,...)	0.61 (2,12,1,...)[1,1]	**2.21 (7,4,2,1,...)**
pcJ-4 (22s)	8s	37.2 (15,1,...)	108 (12,4,1,...)	219 (16,2,1,...)[1,14]	7.53 (10,5,2,1,...)
	9s	7.42 (14,1,...)	9.86 (11,4,1,...)	0.19 (11,14,1,...)[1,2]	6.37 (9,5,2,1,...)
	10s	6.15 (13,1,...)	0.58 (4,10,1,...)	0.52 (4,14,1,...)[1,1]	0.076 (9,2,4,1,...)
	11s	11.58 (12,1,...)	0.11 (8,5,1,...)	0.10 (13,3,1,...)[1,11]	**1.18 (8,4,2,1,...)**

The results marked in **bold** are the contraction schemes recommended, from the analysis of the Na$_2$ molecule.

contraction is needed for the larger pcJ-n basis sets.

C.   Contraction of s-functions for the Na$_2$ molecule

The contraction of the s-functions for Na$_2$ can be considered in the same way as was done for Li$_2$. However we now have three sets of SCF coefficients, namely 1s- 2s- and 3s-coefficients. For 1-contraction all three sets of coefficients have been considered, for the segmented 2-contraction, both (1s,1s) and (1s,2s) coefficients have been considered, and for the general 2-contraction only the (1s,2s) have been investigated. This choice has been

made to decrease the number of possible contraction schemes to investigate, and based on the analysis done on the p-block elements, these sets of coefficients yield the best results[18]. For the segmented 3-contraction the combinations of coefficients (1s,2s,3s) yielded the best result, and only contraction schemes using this combination have been investigated. General 3-contractions offer a wide variety of different contraction schemes that increases rapidly with larger basis sets. This combined with the fact that general 3-contractions did not seem to improve over general 2-contractions for the p-block elements, have led to the omission of general 3-contractions in the search for the optimum contraction scheme.

The best contractions for a given contraction type and number of contraction functions can be found in Table VI. Considering only the segmented contraction schemes in Table VI, we see that for the pcJ-0 basis set, the segmented 1-contraction has the lowest error. However, uncontracting the outermost function leads to a larger error, proving that this contraction is not robust. Instead, the 2-contraction has been used as this contraction proved both robust and had an acceptable error. Looking at the larger basis sets, the segmented 3-contractions perform the best as they have acceptably low errors and are robust with respect to uncontraction.

If we consider the segmented 1-contraction done with different SCF coefficients, the same trend as for Li_2 is seen, where the 2s coefficients perform the best.

Looking at the contraction level in which the contraction error gets acceptably below the inherent error, there are small differences between the best segmented contraction and the general 2-contraction. Again opting for simplicity the segmented contractions are recommended. A study of the performance of the contractions on a larger set of molecules (see Section VI), resulted in the need for a slight relaxation of the contraction in some cases. It is these contractions that are recommended and they have been indicated in **bold** in Table VI.

D.   Contraction of p-functions for the Na_2 molecule

The contraction of p-functions for Na_2 is analogously to the contraction of s-functions for Li_2 as both 2p and 3p SCF coefficients can be used in the contraction. Since the analysis done on Li_2 showed that segmented 1-contractions were viable, only those contraction schemes have been investigated for Na_2. The results can be found in Table VII, where the

Table VII: Contraction errors (sum of the absolute errors of the four contributions in Hz) for 1- 2- and 3-contractions of p-functions for the pcJ-n ($n = 0, 1, 2, 3, 4$) basis sets for the Na_2 molecule. The s-functions have been left uncontracted

Basis set ($N_{primitive}$)	Contraction	Segmented 1-Contraction	
[Inherent absolute error]		2p coefficients	3p coefficients
pcJ-0 (5p) [30.5]	**2p**	**0.70 (4,1)**	85.0 (4,1)
pcJ-1 (7p)[106]	**2p**	**10.8 (6,1)**	94.9 (6,1)
pcJ-2 (9p) [43.8]	**3p**	**0.23 (7,1,1)**	104 (7,1,1)
pcJ-3 (12p) [9.03]	4p	1.91 (9,1,1,1)	131 (9,1,1,1)
	5p	**2.13 (8,1,1,1,1)**	25.81 (8,1,1,1,1)
pcJ-4 (15p)	5p	1.77 (11,1,1,1,1)	46.7 (11,1,1,1,1)
	6p	**1.22 (10,1,…)**	5.03 (10,1,…)

The results marked in **bold** are the contraction schemes recommended, from the analysis of the Na_2 molecule.

recommended contraction schemes are marked in **bold**.

As the results show, a segmented 1-contraction is also viable for the Na_2 molecule, and the same contraction as for the pc-n basis sets can be used for all the pcJ-n basis sets except for pcJ-3,4 where an uncontraction to one extra function is needed in order to get the basis set contraction error acceptably low.

VI.   PERFORMANCE OF THE PCJ-n BASIS SET

Having created pcJ-n basis sets for the s-block atoms, a comparison with the pc-n basis set can be made. In Figure 4 the spin-spin coupling constant of Li_2 and MgH_2, calculated with the contracted pcJ-n basis set and with the contracted and uncontracted pc-n basis sets can be seen. The spin-spin coupling constants are plotted against the number of basis functions used, as this provides a more fair comparison between the different basis sets. An erratic behavior of the contracted pc-n basis sets is observed, but most importantly it can clearly be seen that the couplings converge faster with the pcJ-n basis sets. Generally, convergence for the molecules studied happens around the pcJ-2 level, which is equivalent
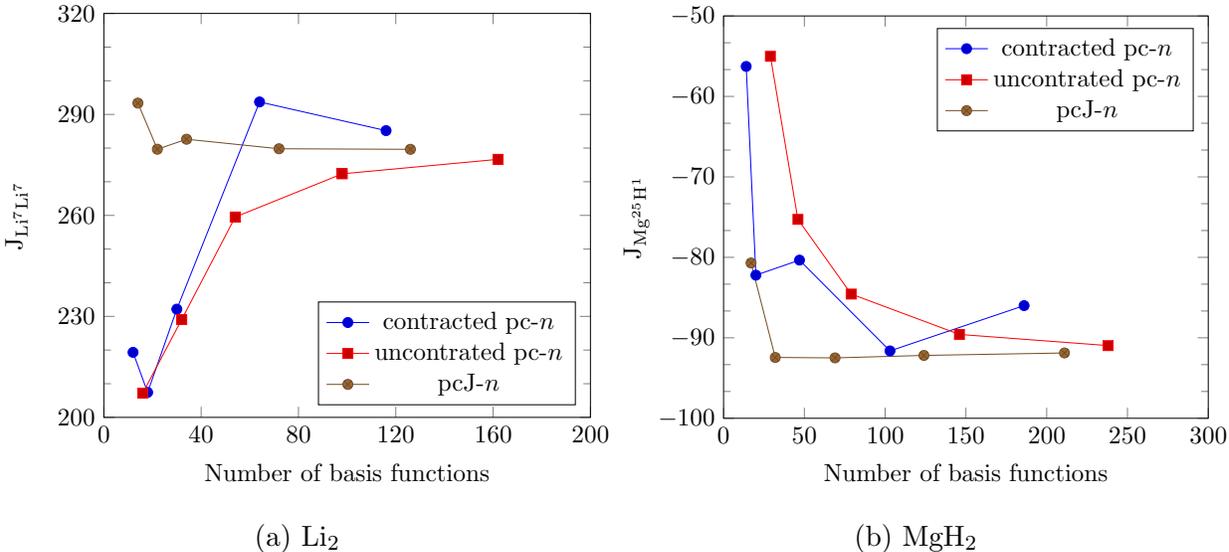
Figure 4: spin-spin coupling constants for Li_2 and MgH_2 calculated with the contracted and uncontracted pc-n basis sets and the contracted pcJ-n basis set.

to a triple zeta basis set, but for some of the molecules convergence is slower than this. However, a general trend for all molecules is that the pcJ-n basis sets performs much better than the pc-n basis sets.

In addition to the molecules in Table I, the performance of the pcJ-n basis set has been investigated on a larger set of molecules ($LiCH_3$, $LiCCH$, $LiCCF$, $LiOCH_3$, $LiSCH_3$, BeF_2, $NaCH_3$, $NaCCH$, $NaOCH_3$, $NaSCH_3$, $ClMgCH_3$). As spin-spin coupling constants can vary by several thousand Hertz in magnitude, the error at a given level will be reported as a percent-wise deviation from the basis set limit. In order to avoid the results getting skewed by large percent-wise deviation resulting from small insignificant absolute values, spin-spin coupling constants smaller than 5 Hz have been neglected. This results in a total of 30 coupling constants with the elements Li, Be, Na, and Mg (20 one-bond couplings and 10 more-than-one bond couplings). The percent-wise mean and maximum absolute deviations for the pc-n and pcJ-n series of basis sets for these coupling constants can be found in Tables VIII and IX. The uncontracted pcJ-4 basis set has been taken as the basis set limit.

The improvement of the convergence seen in Figure 4 can also be seen in Tables VIII and IX. Comparing the performance of the basis sets for one-bond and more-than-one-bond couplings, we see that the two larger basis sets, pcJ-3 and pcJ-4, performs the same for the two types of bonds. However, the results for the smaller basis sets shows that they perform

20

Table VIII: Percent-wise mean and maximum absolute deviations relative to the uncontracted pcJ-4 results for 20 unique one-bond spin-spin coupling constants larger than 5 Hz in a test set of 20 molecules (see text for details)

| | mean absolute deviation | | | | maximum absolute deviation | | | |
| | uncontracted | | contracted | | uncontracted | | contracted | |
	pc-n	pcJ-n	pc-n	pcJ-n	pc-n	pcJ-n	pc-n	pcJ-n
pc-0	69.4	66.0	68.9	66.6	271.0	313.3	294.6	299.8
pc-1	20.5	11.8	15.5	13.2	66.1	63.1	47.7	87.4
pc-2	10.6	2.9	20.7	3.0	65.5	15.4	144.4	9.2
pc-3	2.2	0.4	4.4	0.5	3.9	2.4	16.0	2.2
pc-4	2.1	(0)	3.4	0.2	3.5	(0)	23.0	1.4

Table IX: Percent-wise mean and maximum absolute deviations relative to the uncontracted pcJ-4 results for 10 unique 2- and 3-bond spin-spin coupling constants larger than 5 Hz in a test set of 20 molecules (see text for details)

| | mean absolute deviation | | | | maximum absolute deviation | | | |
| | uncontracted | | contracted | | uncontracted | | contracted | |
	pc-n	pcJ-n	pc-n	pcJ-n	pc-n	pcJ-n	pc-n	pcJ-n
pc-0	39.5	17.1	29.7	14.9	90.7	33.5	51.4	33.7
pc-1	22.9	7.5	27.3	10.1	89.8	17.9	65.5	18.9
pc-2	7.2	1.4	31.9	1.3	11.2	4.2	117.8	4.3
pc-3	2.4	0.2	3.9	0.4	3.1	0.6	12.2	1.0
pc-4	0.9	(0)	3.1	0.2	1.3	(0)	8.4	0.8

better for more-than-one-bond couplings. Also, compared to the results for the p-block atoms[8], similar results for pcJ-2,3,4 are obtained for the s-block. As with the pcJ-n for the

p-block elements, the pcJ-2 basis set will be adequate for most practical calculations, and only in special cases or for very accurate work will it be necessary to go to the pcJ-3 or pcJ-4 basis sets.

VII. CONCLUSION

New polarization consistent basis sets for Li, Be, Na, and Mg have been developed, for calculating spin-spin coupling constants. This has been done by an uncontraction of the already existing pc-n basis sets, followed by augmentation with tight functions. Analogously to the pcJ-n basis set for the p-block elements, two additional tight s-functions were needed for the pcJ-0,1,2,3 and one additional tight s-function was needed for pcJ-4. However, augmentation of additional tight functions of up to g-type, showed that these were not needed. This is in contrast to the p-block elements where functions up to f-type were important. This could be attributed to the fact that no valence p-electrons are found in the s-block elements, and that the core p-electrons are properly described by the underlying pc-n basis set.

In order to recontract the new pcJ-n basis sets, a search for the optimum contraction scheme for the pcJ-n basis sets for Li and Na has been done. This showed that it was more difficult to contract them than the pc-n basis sets without losing the inherent accuracy of the basis sets. Similar conclusion were reached in the work done on the p-block elements[18]. For Li the same degree of contraction has been reached for the basis sets pcJ-0,1,4 in both this work and for the p-block elements. However for the basis sets pcJ-2,3 it was possible to contract to fewer functions than for the p-block elements. For Na the same degree of contraction has been reached as for the p-block elements. The recommended basis set contractions for Li was expanded to include Be, and likewise the recommendations for Na was expanded to include Mg. This works also shows that for calculation of spin-spin coupling constants, there is little difference between using a segmented or a general contraction scheme, and the former where chosen for simplicity.

The performance of the pcJ-n basis sets for Li, Be, Na, and Mg has been investigated on a larger test set of molecules at the DFT level of theory. This showed that the pcJ-n basis set converged to the basis set limit much faster and less erratic than the pc-n basis set. The pcJ-2 basis sets were able to provide results to within ~ 3 % of the basis set limiting

value and should be adequate for most practical calculations. It is possible that the pcJ-n basis sets are also suitable for calculating spin-spin coupling constants using wave function methods, but that will require an explicit testing.

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