

The convergence of basis set contractions: A case study of the molecular hyperfine structure of $^{14}\text{NH}_2$

Jing Kong and Russell J. Boyd

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

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The convergence of basis set contractions is examined at the multireference configuration interaction level with respect to the ^{14}N isotropic hyperfine coupling constant in NH_2 , a case that is very sensitive to the choice of the basis set and the degree of correlation recovery. The contraction schemes studied include the atomic natural orbital (ANO) approach and two Hartree–Fock-based contraction methods: Raffanetti's general contraction method and the segmented method. Contractions of a $(13s8p2d)$ primitive set ranging from $[4s3p2d]$ to $[8s3p2d]$ in the s space and from $[7s3p2d]$ to $[7s6p2d]$ in the p space are employed. It is found that the ANO contraction yields the smoothest and fastest convergence, although all three contractions converge to the uncontracted results. Thus, the ANO contraction starts to converge at $[6s3p2d]$ while the other two converge at $[7s4p2d]$. The correlation recovery of the core electrons versus that of the valence electrons is also studied. In contrast to previous speculation, it is found that the correlation due to core electrons is recovered well with the simple choice of the most populated ANOs. © 1997 American Institute of Physics. [S0021-9606(97)03040-7]

INTRODUCTION

The accuracy of an *ab initio* molecular electronic structure calculation is limited by the choice of the basis set. The establishment of an atomic basis set usually starts with a set of Gaussian functions (called primitives) centered on the nucleus. Because the demand for computing resources grows rapidly with the number of basis functions, the primitive Gaussians are contracted in a linear combination to form a set of basis functions for molecular calculations. Often polarization functions (primitives with angular momentum higher than the occupied orbitals of the atomic ground state) and diffuse functions (primitives with very small exponents) are added to describe the distortion of the atomic orbitals in a molecular environment. The Davidson and Feller comprehensive review¹ on the most widely used basis sets should be consulted for further details and references.

The exponents of primitive Gaussians are usually obtained through the optimization of the atomic Hartree–Fock (HF) wave function, except for the correlation-consistent basis sets developed by Dunning,^{2,3} which include exponents optimized at the configuration interaction level with single and double excitations (CISD). The contraction coefficients for the primitive functions used in molecular calculations are taken from atomic orbitals and the contracted functions are thus representations of the latter in a molecular environment.

For properties dependent on correlation effects, large primitive sets including high angular momentum polarization functions are often needed to achieve quantitatively good results. Feller and Davidson⁴ studied the atomic isotropic hyperfine coupling constants for the first-row elements with systematic expansions of the space described by uncontracted even-tempered primitive Gaussians and multireference CISD (MRCISD). They found that a primitive set as large as $(19s10p8d2f)$ and a very high level of correlation recovery are needed to obtain results in quantitative agree-

ment with experiment for ^{14}N . Their study of the electron affinity of the oxygen atom⁵ revealed a similar requirement with respect to the basis set quality. Obviously, such large primitive sets cannot be used for calculations on larger systems and it is desirable to develop basis set contraction schemes that reduce the basis set size while minimizing the loss of accuracy.

The most widely used contraction schemes are said to be segmented because each contracted basis function contains primitive Gaussians that are different from those used to form each of the other basis functions. Dunning's double-zeta plus polarization basis set⁶ is an example of a segmented basis set. In the same study, Dunning also proposed some general rules of thumb that have been shown to be useful for segmenting a moderately large primitive set. Segmented basis sets work well for calculations at the HF level as the basis set can be easily saturated at this level of theory.

In contrast to segmented contractions, most basis functions with a general contraction scheme contain almost all the primitive Gaussians. Raffanetti⁷ proposed using HF atomic orbitals (AO) as the minimum basis set to which uncontracted primitive Gaussians can be added for flexibility. Although his approach was shown to be more accurate⁸ than segmented minimum basis sets, it was not widely used due to the inefficiency of AO integral evaluations. With the rapid development of computer hardware and software, correlation calculations have become routine. Since the calculation of two-electron repulsion integrals is not the time-determining step in a correlation calculation, Raffanetti's general contraction idea has been revisited by Almlöf and Taylor.⁹ They suggested using the most populated atomic natural orbitals (ANO) obtained from atomic frozen-core CISD calculations as the basis functions in order to reduce the size of a potentially large primitive set and to preserve the atomic correlation effect. It was shown¹⁰ that ANO-based

contractions have much smaller total CI energy loss than other HF-based contractions, especially at high degrees of contraction. Their atomic HF energy losses are also much less than those obtained with the segmented contraction scheme, even though the latter use the atomic HF coefficients.

In this study, comparisons are made among the effects of different contraction schemes on the calculated molecular hyperfine structure (HFS) of NH_2 . More specifically, the ^{14}N isotropic hyperfine coupling constant (ICC) in NH_2 has been calculated at the MRCISD level with basis sets contracted to various degrees with one segmented contraction scheme and two general contraction approaches (HF and ANO). The HFS of $^{14}\text{NH}_2$ has been studied previously with various *ab initio* methods^{11–13} and density functional theory.¹⁴ We¹⁵ have recently calculated isotropic coupling constants that are in better agreement with experiment¹⁶ than previous calculations. The calculations were carried out at the MRCISD level with perturbation selection of configurations. The convergence of the CI expansion was achieved in terms of the size of the reference space and the energy threshold for selecting configurations. The uncontracted primitive sets^{2,17} ($11s7p2d$) and ($13s8p2d$) were used to avoid the complication of basis set contraction. This study is a natural continuation of our previous one.

There have been some basis set studies of the HFS in addition to those of Feller and Davidson's.⁴ Chipman^{18–20} carried out a systematic study of basis set contractions based on the HF AO coefficients for Huzinaga's ($9s5p$) primitive set.²¹ He used a multiconfiguration self-consistent-field (MCSCF) model and found that semiquantitative results could be obtained by adding one set of (sp) diffuse functions and contracting only a few of the innermost primitives via atomic restricted open-shell HF (ROHF) calculations. The importance of diffuse functions for calculations of the HFS was also underscored by Bauschlicher *et al.*,²² who studied the HFS of the nitrogen atom at high levels of theory, including full CI. They also found that the contraction coefficients taken from ANOs yield the same results as those from HF AOs with a segmented contraction scheme. The basis set effect has also been tested in HFS calculations by others within the framework of segmented contractions. For instance, in their study of the HFS in NH , Engels and Peyerimhoff²³ found that a contraction of ($13s8p/8s$) to [$8s5p/5s$] caused little loss of accuracy for the ICCs of N and H. Feller *et al.*,²⁴ in their study of the HFS in NO , investigated the variation of the ICCs as a function of the contraction length for the (sp) functions of Dunning's CC-PVTZ basis set² at the CISD level. They found that further decontraction of the CC-PVTZ set is necessary to increase the flexibility in the core region. Also, Fernández *et al.*²⁵ carried out a basis set investigation in their calculations of the HFS in B_3 .

In contrast to the previous ANO contraction studies in which the core electrons were frozen in the CI calculations, all electrons were included in the construction of the ANO basis functions in this paper. The ICC of ^{14}N in NH_2 is totally due to correlation effects because of the π symmetry

of the singly occupied orbital in the ROHF wave function. It is known^{20,23,26,27} that the contribution of the core–electron correlation has the opposite sign to that of the valence electron correlation and that the ICC depends on a subtle balance between the two. Therefore, the HFS provides a good test for the effectiveness of the ANO approach for the inclusion of the core–electron correlation.

COMPUTATIONAL METHODS

As in our previous paper¹⁵ on NH_2 , the MRCISD method has been used for all the hyperfine structure calculations. For a certain basis set, a CISD calculation is carried out using a ROHF wave function as the reference. The configurations with the highest coefficients are chosen as reference configurations for generating the MRCI configurations. Because the number of configurations grows rapidly with increases in the size of the reference space and the number of basis functions, perturbation theory has been used for the selection of configurations to be included in the Hamiltonian diagonalization. The contribution of a configuration generated by the MRCISD procedure is first estimated using second-order Rayleigh–Schrödinger perturbation theory. If it is lower than a preset energy threshold (T_E), the corresponding configuration is not included in the variation step. By systematically expanding the reference space and decreasing the threshold, it is possible to approach the full-CI limit with only a small fraction of the complete list of excitations considered explicitly.^{4,5,28,29} The MRCISD calculations have been carried out with the MELDF-X³⁰ program package.

The geometry of NH_2 was optimized at the MP2/6-31G** level, yielding a bond length of 1.023 Å and a bond angle of 102.7° (experimental³¹ values are 1.024 Å and 103.3°, respectively). The primitive set for nitrogen and hydrogen is the ($13s8p2d/8s2p$) basis set used in our previous study, which consists of van Duijneveldt's ($12s7p/7s$) primitive set¹⁷ supplemented with Dunning's ($2d/2p$) polarization functions.² In addition, a ($1s1p/1s$) diffuse set with the exponents obtained in an even-tempered manner was added due to the importance of diffuse functions for HFS calculations. The size of this primitive set is intermediate between those of the Feller and Davidson large even-tempered basis sets⁴ and the Huzinaga ($9s5p$) set used in the studies of Chipman¹⁹ and Bauschlicher.²² In contrast to our previous study,¹⁵ we have used a set of five d rather than a set of six d functions for polarization because the extra s -type function of the latter complicates the contraction of basis sets.

It has been shown in our previous study on NH_2 that the isotropic coupling constant of nitrogen converges with a reference space of 30 configurations (83 spin-adapted configurations) and an energy threshold of 10^{-7} hartree. In this study, the same energy threshold and the 31 configurations with the highest coefficient contributions are used as the reference configurations for the calculations of the HFS of NH_2 .

We have also found that the ICC of hydrogen is much less sensitive to the choice of basis functions. Therefore, the basis set for hydrogen has been contracted to [$4s2p$] for all

TABLE I. The CISD populations of the atomic natural orbitals of the nitrogen atom.

ANO	<i>s</i>	<i>p</i>
1	1.998 825	0.995 599
2	1.982 731	0.005 586
3	0.012 236	0.000 372
4	0.000 812	0.000 124
5	0.000 219	0.000 024
6	0.000 026	0.000 006
7	0.000 006	0.000 001
8	0.000 002	<10 ⁻⁶
9–13	<10 ⁻⁶	

calculations, except those with the uncontracted basis set. For the sake of conciseness, only the basis set for nitrogen will be mentioned in the discussion.

RESULTS AND DISCUSSION

The two general contraction schemes and one segmented scheme are compared here. The one denoted as ANO uses ANOs from an all-electron atomic CISD calculation. (The two sets of *d* polarization functions are not included in the atomic calculations.) The ANOs are ordered by their populations and listed in Table I. Unless noted otherwise, the contracted basis functions are the first few orbitals, i.e. the ones with the highest populations in the *s* and *p* spaces.

The contraction scheme denoted as HFGen is the Raffennetti approach,⁷ which uses all the occupied atomic Hartree–Fock (HF) orbitals, plus the most diffuse primitive Gaussians for flexibility. HFSeg is the segmented contraction scheme used in Chipman’s basis set study.¹⁹ A contracted HFSeg basis set consists of the core parts of the atomic 1*s* and 2*p* HF orbitals plus the remaining primitives.

Table II lists the ICC of ¹⁴N in NH₂ with various basis set contractions. The basis functions for nitrogen are expanded first in the *s* space from [4*s*3*p*2*d*] to [8*s*3*p*2*d*]. It can be seen that the ANO ICC starts to converge at [6*s*3*p*2*d*], a triple-zeta plus polarization (TZP) basis set, and the ICC of the HF-based general and segmented contraction schemes starts to converge at [7*s*3*p*2*d*]. These results are consistent with the conclusion of Feller and Davidson⁴

TABLE II. The MRCISD ICC (in MHz) of ¹⁴N in NH₂ with different contraction schemes for the nitrogen atom.^a

Basis set	ANO	HFGen	HFSeg
[4 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	8.22	59.32	72.63
[5 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	15.82	66.09	82.52
[6 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	20.21	14.10	29.26
[7 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	22.71	25.77	26.86
[8 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	20.88	25.69	25.89
[7 <i>s</i> 3 <i>p</i> 2 <i>d</i>]	22.71	25.77	26.86
[7 <i>s</i> 4 <i>p</i> 2 <i>d</i>]	21.64	23.64	24.67
[7 <i>s</i> 5 <i>p</i> 2 <i>d</i>]	20.48	21.91	22.75
[7 <i>s</i> 6 <i>p</i> 2 <i>d</i>]	21.51	21.30	22.16

^aThe (13*s*8*p*2*d*) uncontracted basis set yields 21.57 MHz; the experimental value is 27.9 MHz.

that at least a TZP basis set is needed to achieve meaningful results. Chipman also found that the [6*s*3*p*] contraction of Huzinaga’s (9*s*5*p*) primitive set²¹ leads to better results than the [5*s*3*p*] contraction. The three expansions converge, however, to different values. Only the ANO contraction scheme converges toward the uncontracted value. The convergence of the two HF-based schemes actually leads to close agreement with the experimental value, indicating that one could obtain better agreement with experiment for the HFS using a contracted basis set rather than an uncontracted set of primitive Gaussians due to fortuitous cancellations of errors.

Expansion of the *p* space from [7*s*3*p*2*d*] to [7*s*6*p*2*d*] has a stronger effect on the HF-based schemes than on the ANO approach. Furthermore, the ANO scheme seems to converge faster, especially in the *p* space, and more smoothly than the other two schemes.

The different convergence behaviour of the ANO and HF approaches shows the differences in their abilities to recover the correlation effect of the core electrons versus that of the valence electrons. It has been shown^{20,23,26,27} that these two correlation effects have opposite signs and large magnitudes and that the ICC is the result of the subtle compromise between them. The contribution from the valence electrons to the ICC of ¹⁴N in NH₂ with the uncontracted basis set is positive (65 MHz), suggesting that the contribution from the core electrons is negative, similar to the situation for atomic N^{4,27} and NH.^{20,23} At a high degree of basis set contraction ([4*s*3*p*2*d*] or [5*s*3*p*2*d*]), the ANO scheme yields a small ICC, indicating that more core–electron correlation than valence–electron correlation is recovered. In contrast, the two HF-based approaches recover more valence–electron correlation than core–electron correlation. In fact, for this high degree of contraction, the errors of the HF-based contractions are too large to be even qualitatively useful. A balanced description starts only after a contraction of [6*s*3*p*2*d*] for all contraction schemes.

The observation in the previous paragraph can be understood in terms of the basis set diffuseness. The atomic HFS studies of Chipman¹⁹ and Bauschlicher *et al.*²² have shown that the core correlation effect is always enhanced (the ICC is increased in the case of N) when a set of diffuse (*sp*) functions is added to either an uncontracted or a contracted basis set. The reason that the HF-based approaches at the high degree of contraction yield large ICC values is that the occupied HF AOs that are used as the basis functions are not sufficiently tight. Chipman¹⁹ found that only the first four innermost primitives of the (9*s*6*p*) set could be contracted in order to get a balanced description between the core and valence electron correlations. On the other hand, ANOs are the eigenvectors of the atomic electronic density that decreases exponentially away from the nucleus. Therefore, they are less sensitive to the outer part of an atom and are considered tight. When only the first few ANOs are taken as basis functions, the basis set is not sufficiently diffuse and the correlation of the valence electrons is under-represented, as indicated by the small ICC at the high degree of contraction.

TABLE III. The effect of replacing the fifth s ANO (the outermost ANO) in the contracted $[5s3p2d]$ basis set with s ANOs 6–13.

Replacement ANO	ICC (in MHz)	Energy loss (in mhartree)
5	15.82	0.000
6	20.89	0.950
7	17.56	3.344
8	12.11	3.567
9	9.42	3.732
10	8.74	3.806
11	8.54	3.833
12	8.39	3.840
13	8.31	3.841

The greater recovery of the core–electron correlation than that of the valence–electron correlation for a small ANO basis set is contrary to speculation^{9,10} about a possible all-electron ANO basis set. It has been thought that the desired ANOs for correlating core electrons are either the most populated (corresponding to occupied core orbitals) or nearly least populated (corresponding to “virtual orbitals” for core electrons) and both of them should be included as a part of the ANO basis set if the recovery of the core–electron correlation is desired. Therefore, use of the simple criterion of occupation number would result in insufficient recovery of the core–electron correlation, as the least populated ANOs would be excluded. This is one of the reasons why full-electron correlation has been avoided in previous studies of the ANO contraction approach.

To study further the effect of the less populated ANOs versus that of the more populated ANOs, the least populated orbital of the five most populated s ANOs in the $[5s3p2d]$ basis set (the fifth s ANO) has been separately replaced with each of the rest of the six ANOs (the 6th to the 13th). Table III lists the ICC of ^{14}N and the energy loss due to the replacement. The replacement with the sixth and the seventh ANOs shifts the balance more toward valence–electron correlation with the former having the strongest effect, raising the ICC by 5 MHz. This is hardly surprising, since the replacement orbitals are more diffuse. The replacements with the less populated ANOs lowers the ICC. The replacement with the sixth ANO also yields a smaller energy loss than replacement with the others. The increase and then decrease of the ICC also shows that valence electron correlation will be under-represented if the outermost basis function is too diffuse.

A similar replacement study was also carried out for the ANO basis set $[7s3p2d]$ and the results are listed in Table IV. Since the sixth and the seventh ANOs are included as basis functions, the replacement of a less populated ANO has a much smaller effect on the ICC. One can see that the ICC is around 20 MHz, about one MHz smaller than the uncontracted and the contracted $[7s3p2d]$ results. Energy losses are observed, once again, except for the first replacement, which has a slight energy gain. This indicates that the balance between the correlations of the core electrons and valence electrons is well represented by the first seven s ANOs.

TABLE IV. The effect of replacing the seventh s ANO (the outermost ANO) of the contracted $[7s3p2d]$ basis set with s ANOs 8–13.

Replacement ANO	ICC (in MHz)	Energy loss (in mhartree)
7	22.71	0.000
8	19.76	−0.058
9	19.74	0.210
10	20.28	0.283
11	20.05	0.309
12	19.85	0.313
13	19.73	0.314

Another way of increasing the diffuseness and the flexibility of a basis set, as done by Almlöf and Taylor in their study⁹ of the ANO basis set, is to use the outermost primitives as basis functions. Thus, the $[(4+1)s,(2+1)p]$ basis set includes the first four s ANOs, first two p ANOs, and the outermost s and p primitives. Table V lists the effects of using one set of the diffuse (sp) primitive Gaussians. The energy loss is the difference between the energy obtained with the current primitive-added basis set and that with the basis set in Table II of the same size, e.g. the energy obtained with the $[(4+1)s,(2+1)p]$ basis set minus the energy obtained with the $[5s3p]$ basis set in Table II. Apparently due to the diffuseness of the basis set, the ICC increases at both the low and high degrees of basis set contraction, especially for the small basis set $[(3+1)s,(2+1)p,2d]$, where the ICC is four times that of $[4s3p2d]$. In fact, the pattern of the numbers shifts toward the results of the HF-based schemes, although the fluctuation is much less drastic. Overall, it is not advisable to add primitive Gaussians to an ANO set for ICC calculations.

CONCLUSIONS

The hyperfine isotropic coupling constant of ^{14}N in NH_2 calculated at the multireference configuration interaction level with single and double excitations has been used to examine the convergence of basis set contraction schemes. The contraction schemes tested here include the atomic natural orbital method, Raffennetti’s general contraction method and the segmented method. The contraction coefficients for Raffennetti’s and the segmented methods were taken from atomic HF orbitals. The primitive set for nitrogen is $(13s8p)$, which is contracted to a series of basis sets, first

TABLE V. The effect of using the outermost primitive Gaussian as the diffuse function.

Basis set	ICC (in MHz)	Energy loss ^a (in mhartree)
$[(3+1)s,(2+1)p,2d]$	33.48	23.278
$[(4+1)s,(2+1)p,2d]$	12.83	20.742
$[(5+1)s,(2+1)p,2d]$	19.95	15.624
$[(6+1)s,(2+1)p,2d]$	23.49	18.861
$[(7+1)s,(2+1)p,2d]$	23.33	18.742

^aThe energy difference between the total energy with the basis sets in this table and that with the basis set in Table II of the same size.

from $[4s3p2d]$ to $[8s3p2d]$ in the s space and from $[7s3p2d]$ to $[7s6p2d]$ in the p space. It has been found that all three methods converge to the result with the uncontracted primitive set and that the ANO approach leads to a smoother and faster convergence than the other two HF-based methods. Therefore, at a moderate degree of contraction such as $(13s8p2d)$ to $[7s6p2d]$, all three contraction schemes are expected to yield similar results whereas the ANO approach is able to yield semiquantitative results at a higher degree of contraction. The different behaviors of the contraction schemes at high degrees of contraction are interpreted in terms of the diffuseness of the basis set. Thus, the small ICC with the ANO scheme at a high degree of contraction is due to the tightness of the ANOs and the large ICC with the two HF-based approaches is due to the diffuseness of the HF AOs.

We also examined the recovery of the core–electron correlation effect with the ANO approach using the sensitivity of the HFS to the balance between the core–electron and valence–electron correlations. In contrast to previous speculation, it is found here that the core–electron correlation is recovered well with the simple choice of the ANOs according to the populations. In addition, it has also been found that adding the outermost primitive Gaussians to an ANO set to increase the diffuseness is not advisable for isotropic hyperfine coupling constant calculations.

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