

Re-examination of the hyperfine structure of $^{14}\text{NH}_2$

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The hyperfine structure of the $^{14}\text{NH}_2$ radical is investigated by means of multireference single and double configuration interaction (MRCI) techniques. Particular attention is paid to the dependence of the coupling constants on the basis set, reference space, and configuration selection energy threshold. It is found that convergence can be obtained only if more than 83 reference configurations are included with an energy threshold of at least 10^{-7} hartree. With up to 126 reference configurations, an energy threshold smaller than 10^{-8} hartree and an uncontracted ($13s8p2d/8s2p$) basis set, the MRCI isotropic couplings (27.44 and -68.47 MHz for N and H, respectively) are in very good agreement with experimental data (27.9 and -67.2 MHz, respectively). © 1995 American Institute of Physics.

INTRODUCTION

The prediction of the hyperfine structure (hfs), especially the isotropic part, has been a challenge in computational quantum chemistry because a great deal of correlation recovery is required in order to obtain quantitative isotropic coupling constants. Typically, the hfs of N, NH, and NH_2 have been subject to extensive theoretical and experimental studies. With large basis sets and high correlation recovery, the experimental isotropic coupling constant for the nitrogen atom was obtained theoretically by several groups using such *ab initio* methods as complete active space self-consistent field (CASSCF)/multireference single and double configuration interaction (MRCI),¹ MRCI,^{2,3} and coupled cluster with single and double substitutions (CCSD) including noniterative treatment of triples,⁴ although the results for other atoms varied and were not as close as for nitrogen. In particular, the study by Feller and Davidson² showed that the good numbers from previous theoretical studies of atomic and molecular hfs arose from a largely fortuitous cancellation of errors due to insufficient correlation recovery and inadequate basis sets. The hfs of NH was studied with the many-body perturbation theory (MBPT),⁵ numerical multiconfiguration self-consistent field (MCSCF),⁶ and MRCI⁷ methods. The MRCI study by Engels and Peyerimhoff⁷ showed a deviation of a few MHz from experiment for the isotropic coupling constants on both N and H.

Among the studies of the hfs of NH_2 ,⁸⁻¹⁰ the most systematic study on NH_2 was carried out by Funken, Engels, Peyerimhoff, and Grein.¹⁰ They used a contracted basis set ($13s8p2d$ contracted to $8s5p2d$) and a reference space of up to 23 configurations in their MRSDCI calculations, with an energy threshold of 2×10^{-7} hartree. Their calculated hyperfine couplings (24.1 MHz for N and -63.4 MHz for H) are in good agreement with experiment (27.9 MHz for N and -67.2 MHz for H).¹¹ Their results were, however, not converged with respect to the energy threshold for the multireference calculations. A further study by the same research group¹² revealed that the effect of vibrational motion is negligible. A more recent study¹³ used STO-expanded GTO's for

the CI calculations and then obtained the Fermi contact terms with the original STO's. The numbers were not as close to the experimental ones as those in the study by Funken *et al.*¹⁰

In our recent work,^{14,15} the hfs of, e.g., NH_2 has also been investigated using density functional theory. Although the isotropic results obtained were satisfactory provided gradient corrections were introduced to the exchange and correlation potentials, they were not in as good overall agreement with experiment as the MRCI data quoted above. The anisotropic data, on the other hand, matched perfectly the experimental and MRCI results.

The question we address here relates to the previous MRCI work by Funken *et al.*¹⁰ and Engels *et al.*¹² Can convergence of the hfs of NH_2 be achieved in the MRCI calculations, and if so, does the converged result still differ from experiment? The problem is explored in three dimensions; the basis set, the size of the reference space, and the energy threshold T_E for selecting configurations. The Gaussian primitives were left uncontracted as it has been shown in previous studies that the impact of basis set contraction can be very strong.

METHODOLOGY

The calculated hfs is sensitive to the wave function form and the basis set. Various correlation recovery techniques such as CCSD including noniterative treatment of triples, MRCI, MCSCF, Møller–Plesset perturbation theory with orders from second to fifth, quadratic single and double CI and MBPT have previously been used with varying degrees of success. Feller *et al.*¹⁶ compared different correlation recovery algorithms based on ROHF and UHF. In this work we use ROHF based MRCI because its wave function has the right symmetry and provides a systematic way to improve the accuracy to the full-CI limit.^{2,17,18} Since we cannot include all the singly and doubly excited configurations generated with a certain reference space, the strategy is to reach converged results for a certain size of the reference space with respect to the energy threshold for configuration selec-

tion. This is taken as a good estimate of the limit in which all single and double excitations are included. The size of the reference space is increased until the results converge with respect to both the size of the reference space and T_E , which is assumed to be a good estimate of the full CI limit for the given basis set. The same procedure is repeated for a larger basis set to see if improvement can be achieved. The program used for the calculations is MELDF-X.¹⁹ 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° [experimentally 1.024 Å and 103.3° (Ref. 20)].

Since correlation recovery is extremely important to spin polarization, there have been some studies^{21,22} of hfs using Dunning's correlation-consistent basis sets^{23,24} which were designed to yield a good description of valence correlation. Recently Feller *et al.*¹⁶ used Dunning's triple zeta basis set augmented with $(1s1p1d1f)$ diffuse functions to study the hfs of NO. The best results obtained with more than two million configurations included in the variational step were about 4 MHz too small for ^{14}N and 2 MHz too large for ^{17}O compared with experiment. In the same study, no converged results could be obtained with respect to the reference space, due to too many configurations. It is believed that more configurations have to be included to achieve convergence with respect to the energy threshold and/or the size of the reference space. On the other hand, atomic hfs calculations² with uncontracted Gaussian primitives show that polarization functions with angular momentum higher than d functions have only a marginal effect on the result, e.g., about 0.2 MHz for nitrogen, and it is reasonable to expect that they have even less effect in molecular calculations, as the basis functions on the other atoms will automatically be used for polarization. Besides, the core electrons were frozen when Dunning's basis set was obtained and this may be a further source of error, since it is well-known that the Fermi contact term is the cancellation between core correlation and valence correlation. In his development of semiquantitative basis sets for hfs calculations, Chipman^{25,26} also showed the fluctuation of the hfs with respect to the contraction scheme. In the present study, the sets of Gaussian primitives derived from atomic SCF calculations are left uncontracted and two sets of d -type polarization functions are used on nitrogen and two sets of p -type polarization functions on hydrogen from Dunning's basis set.²³ The s and p primitives are from atomic SCF calculations by van Duijneveldt²⁷ and one more diffuse s and a set of p functions are added as they are known to be important for hfs.^{25,26}

RESULTS AND DISCUSSION

Figure 1 displays the change of the isotropic constant $A_{\text{iso}}(^{14}\text{N})$ with respect to the size of the reference space and the energy threshold T_E for selecting configurations with the $(11s7p2d/7s2p)$ basis set. The corresponding numbers are given in Table I. We can see that $A_{\text{iso}}(^{14}\text{N})$ converges with T_E , after T_E is smaller than 10^{-7} hartree and converges with respect to the size of the reference space if a sufficiently small T_E is used. If a large T_E is used, however, one might get the wrong conclusion about the effect of the increase of the size of the reference space. This is illustrated in Fig. 2

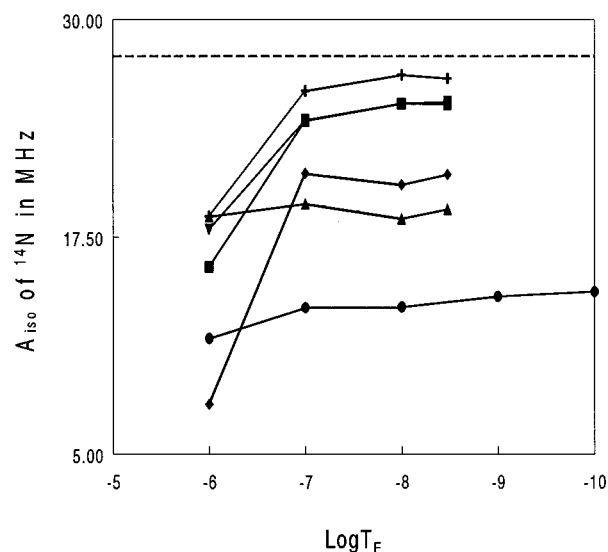


FIG. 1. Plot of $A_{\text{iso}}(^{14}\text{N})$ as a function of the energy threshold T_E by use of the $(11s7p2d/7s2p)$ basis set. The number of reference configurations is denoted by 1 (●), 27 (▲), 50 (◆), 83 (■), 111 (+), and 126 (▼). The experimental value is indicated by the dashed line. The line denoted by ▼ coincides with the one denoted by ■ with T_E smaller than 10^{-7} hartree.

which describes the $A_{\text{iso}}(^{14}\text{N})$ vs the size of the reference space at $T_E=10^{-6}$ hartree (which has been widely used, mainly because of hardware limitations) and $T_E=3.3\times 10^{-9}$ hartree. From Fig. 2 one might conclude that a size of 27 configurations is better than the one with 50 or more configurations because the former is closer to the experimental one. Only when T_E is smaller than 10^{-7} hartree, does A_{iso} show a steady trend as illustrated in Fig. 3 and approach the experimental value. As pointed out by Feller and Davidson,² a sufficiently small T_E is thus essential to obtain meaningful results, and a multireference approach may not make sense without taking this into consideration. Unlike the NO case studied by Feller *et al.*,¹⁶ an exponential fit does not work in the present case for the curves with 50, 83, or 111 reference configurations. Therefore, caution should be taken when introducing this kind of fitting.

TABLE I. Isotropic couplings, A_{iso} , (in MHz) of ^{14}N and H in NH_2 as a function of the energy threshold T_E (in hartrees) and the size of the reference space with the $(11s7p2d/7s2p)$ basis set.

Log T_E	Numbers of reference configurations						Expt. ^a
	1	27	50	83	111	126	
^{14}N							
-6.0	11.66	18.69	7.87	15.78	18.71	17.96	27.9
-7.0	13.43	19.42	21.18	24.20	25.92	24.25	
-8.0	13.48	18.57	20.53	25.19	26.83	25.19	
-8.48	14.36 ^b	19.11	21.12	25.16	26.64	25.30	
H							
-6.0	-55.56	-60.63	-61.31	-62.83	-63.96	-64.15	-67.2
-7.0	-55.38	-62.17	-62.82	-63.71	-64.84	-65.03	
-8.0	-55.09	-62.52	-63.62	-64.51	-65.51	-65.61	
-8.48	-55.12 ^b	-62.51	-63.09	-64.79	-65.79	-65.90	

^aReference 11.

^bAll single and double excitations from the single reference are included.

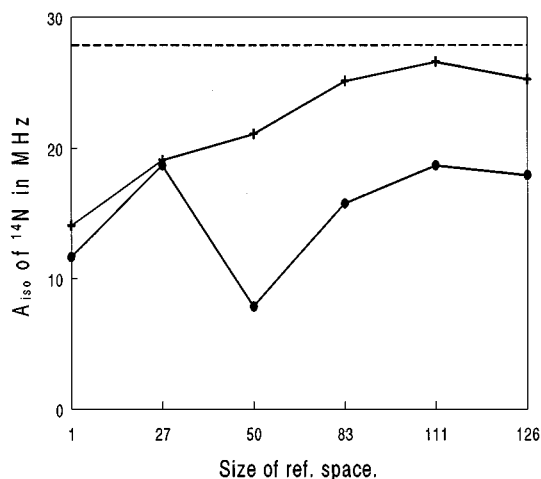


FIG. 2. Plot of $A_{\text{iso}}(^{14}\text{N})$ as a function of the size of reference space by use of the $(11s7p2d/7s2p)$ basis set. The energy threshold T_E is denoted by 10^{-6} hartree (●) and 3.3×10^{-9} hartree (+). The experimental value is indicated by the dashed line.

Similar to ^{14}N , the A_{iso} of hydrogen converges at $T_E = 10^{-7}$ hartree given a certain size of reference space. Its behavior is, however, more predictable in the sense that it decreases steadily with respect to a decrease of T_E , and with an increase in the number of reference configurations, as shown in Figs. 3–4 (the counterparts to Figs. 1–2 for ^{14}N). It is also easier to obtain a semiquantitative result for H than for ^{14}N and even a single-reference SDCI calculation recovers 80% of the experimental value.

The best theoretical predictions of the isotropic couplings with this basis set are 25.30 MHz for ^{14}N and -65.90 MHz for the proton, which are different slightly from the experimental results of 27.88 to 28.11 and -67.22 to -67.59

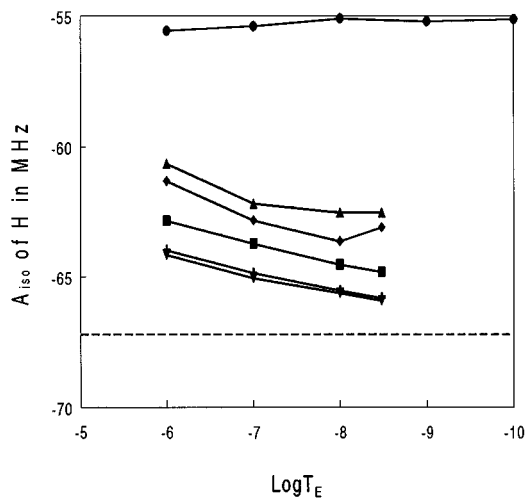


FIG. 3. Plot of $A_{\text{iso}}(\text{H})$ as a function of the energy threshold T_E by use of the $(11s7p2d/7s2p)$ basis set. The number of reference configurations is denoted by 1 (●), 27 (▲), 50 (◆), 83 (■), 111 (+), and 126 (▼). The experimental value is indicated by the dashed line.

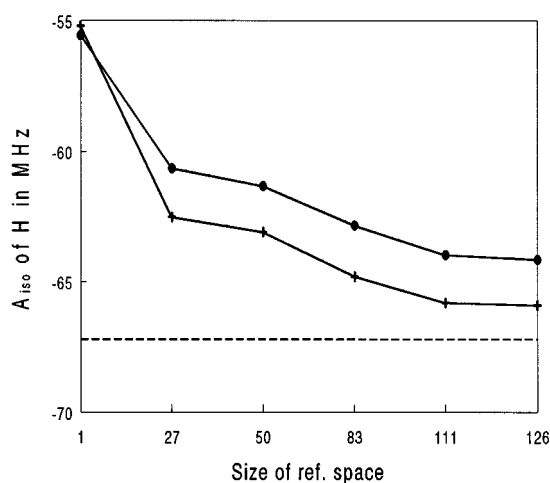


FIG. 4. Plot of $A_{\text{iso}}(\text{H})$ as a function of the size of reference space by use of the $(11s7p2d/7s2p)$ basis set. The energy threshold T_E is denoted by 10^{-6} hartree (●) and 3.3×10^{-9} hartree (+). The experimental value is indicated by the dashed line.

MHz, respectively, and somewhat better than the results of Funken *et al.*¹⁰

The basis set was extended by adding $2s$ and $1p$ to nitrogen and $1s$ to hydrogen to see whether better agreement can be achieved. From Figs. 5 and 6 (the counterparts of Figs. 1 and 2) it can be seen that similar to the situation with the smaller basis set, $A_{\text{iso}}(^{14}\text{N})$ converges after including more than 83 configurations in the reference space and using a T_E smaller than 10^{-7} hartree. This time, however, the converged number is more than 1 MHz higher and essentially the same as the experimental one, considering experimental uncertainty which may be as large as 1 MHz for an accurate measurement. The best theoretical number is between 28.45

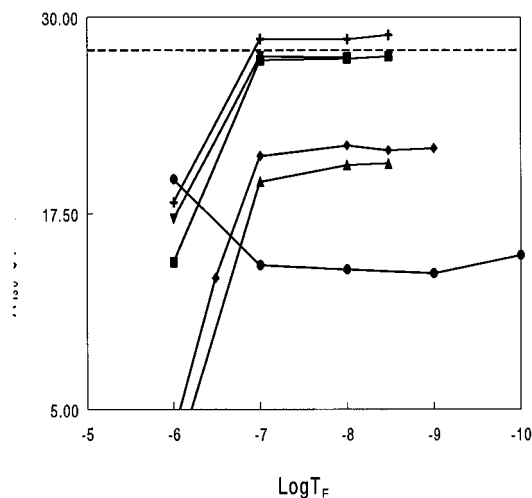


FIG. 5. Plot of $A_{\text{iso}}(^{14}\text{N})$ as a function of the energy threshold T_E by use of the $(13s8p2d/8s2p)$ basis set. The number of reference configurations is denoted by 1 (●), 27 (▲), 50 (◆), 83 (■), 111 (+), and 126 (▼). The experimental value is indicated by the dashed line. The line denoted by ▼ coincides with the one denoted by ■ with T_E smaller than 10^{-7} hartree.

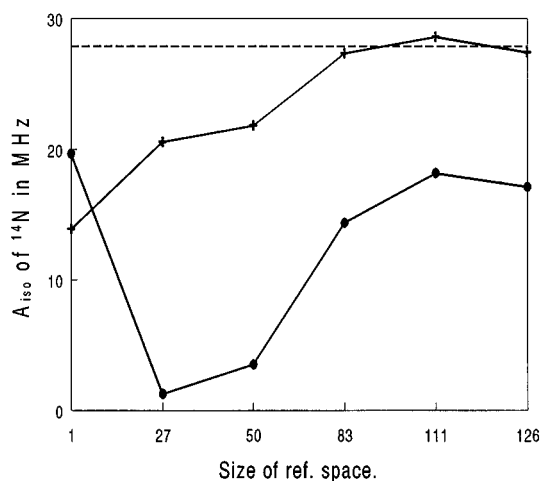


FIG. 6. Plot of $A_{\text{iso}}(^{14}\text{N})$ as a function of the size of reference space by use of the $(13s8p2d/8s2p)$ basis set. The energy threshold T_E is denoted by 10^{-6} hartree (\bullet) and 10^{-8} hartree ($+$). The experimental value is indicated by the dashed line.

MHz (111 reference configurations, $T_E=3.3\times 10^{-9}$ hartree) and 27.44 MHz (126 reference configurations, $T_E=10^{-8}$ hartree).

A numerically large $T_E(>10^{-7}$ hartree) still does not make sense. For example, one may conclude (cf. Figs. 7–8) that one reference SDCI is a very good simple model which recovers 75% of the experimental result, but it is actually due to fortuitous cancellation.

From Figs. 7–8 we can see that the A_{iso} for hydrogen is also converged to the experimental value and the best theoretical number is between -65.57 MHz (111 reference configurations, $T_E=3.3\times 10^{-9}$ hartree) and -68.47 MHz (126 reference configurations, $T_E=10^{-8}$ hartree). The number of configurations in the variational step is above 350 000.

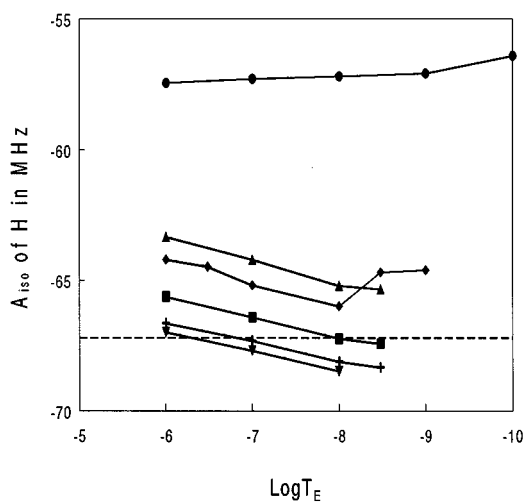


FIG. 7. Plot of $A_{\text{iso}}(\text{H})$ as a function of the energy threshold T_E by use of the $(13s8p2d/8s2p)$ basis set. The number of reference configurations is denoted by 1 (\bullet), 27 (\blacktriangle), 50 (\blacklozenge), 83 (\blacksquare), 111 ($+$), and 126 (\blacktriangledown). The experimental value is indicated by the dashed line.

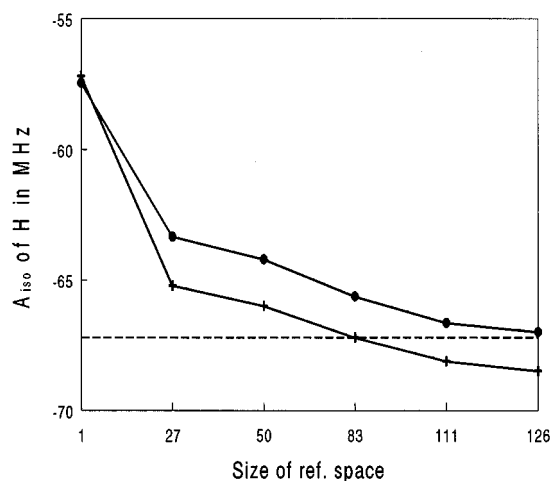


FIG. 8. Plot of $A_{\text{iso}}(\text{H})$ as a function of the size of reference space by use of the $(13s8p2d/8s2p)$ basis set. The energy threshold T_E is denoted by 10^{-6} hartree (\bullet) and 10^{-8} hartree ($+$). The experimental value is indicated by the dashed line.

In contrast to the requirement of high correlation recovery for isotropic couplings, anisotropic couplings are very stable throughout all the correlation levels, as shown in Table II. The insensitivity of the anisotropic tensor with respect to basis set and form of correlation treatment has also been explored for NH_2 in our previous DFT work,^{14,15} giving very similar results and conclusions.

The convergence of the correlation energy and the sum of the squares of the expansion coefficients of configurations in the reference space are shown in Fig. 9 for comparison. It is immediately apparent that both quantities converge more smoothly than the isotropic coupling constants. Therefore, the effect of a larger T_E and smaller reference space is less predictable for the isotropic coupling constants than for the recovery of the correlation energy.

CONCLUSION

The problem of obtaining a converged set of hyperfine parameters of the NH_2 radical from MRCI theory is addressed in terms of the size of the reference space and the configuration selection energy threshold (T_E). The reference space is varied from one (CISD) to 126 reference configurations, and the energy threshold is lowered as far as 3.3×10^{-9} hartree. The effect of basis set is also explored by using two uncontracted basis sets $(11s7p2d/7s2p)$ and $(13s8p2d/$

TABLE II. The anisotropic coupling constant, A_{dip} , (in MHz) of ^{14}N calculated with the CISD and MRCI (50 reference configurations) methods for different basis sets and configuration selection thresholds.

Basis set	CISD	MRCI			Expt. ^a
		10^{-6}	10^{-7}	10^{-8}	
$(11s7p2d/7s2p)$	42.52	42.38	42.27	42.23	43.85
$(13s8p2d/8s2p)$	42.76	42.56	42.51	42.46	

^aReference 11.

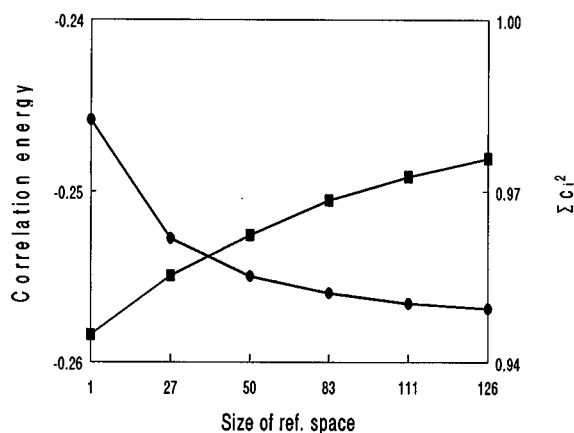


FIG. 9. Plot of the correlation energy (in hartrees) (●) and the sum of the squares of the coefficients in the reference space $\sum c_i^2$ (■) as a function of the size of the reference space by use of the $(11s7p2d/7s2p)$ basis set. The energy threshold for selecting configurations is 10^{-7} hartree.

$8s2p$). The number of configurations included in the calculations varies from a few thousand for the CISD calculations up to 350 000 for the largest efforts.

As expected from previous work, the anisotropic coupling constants show very little variation with the various parameters, and are in very good agreement with experiment. Convergence is basically observed already at the CISD level for this part of the hyperfine tensor.

For the isotropic couplings large variations are found as a function of T_E and reference space, and it is concluded that converged solutions cannot be reached unless a selection threshold below 10^{-7} hartree coupled with a reference space of at least 80 configurations is used. The best theoretical predictions of the hyperfine couplings lie well within the error bars (1 MHz) of the experimental data.

It is also concluded that the exponential fitting procedure for the full-CI limit values, suggested by Feller *et al.*,¹⁶ should be used with utmost caution if the solutions have not converged. The importance of the basis set contraction scheme is also implied when comparing the present study to those where contracted basis sets have been employed.

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