

A comparison of high-quality ab initio basis sets: the inversion barrier in ammonia¹

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Abstract

The abilities of several large Gaussian basis sets in conjunction with standard correlation treatments to reproduce the classical barrier to inversion in ammonia are compared and dissected. The basis sets incorporate primitive functions from five different sources. Second- and third-order Møller–Plesset perturbation theory and coupled-cluster methods have been used, with an extrapolation to the correlation limit taken from the literature. Each of the employed sets of primitive sp functions are found to be sufficient for 30 cm⁻¹ accuracy, but only after the inclusion of standard diffuse sp functions on nitrogen. Contraction errors in the basis sets are usually small, generally contributing less than 30 cm⁻¹ to the barrier height but up to 70 cm⁻¹ in some cases. An analysis of the basis set requirements for the accurate computation of core correlation has also been performed. It is found that, for sufficiently large basis sets, liberation of the 1s electrons of nitrogen in the correlated treatments consistently results in reductions of 40–70 cm⁻¹ in the barrier height, even without the addition of core-specific functions to the standard basis sets. The best estimate of the classical inversion barrier in ammonia is 1821 cm⁻¹, with an estimated uncertainty of ±30 cm⁻¹.

1. Introduction

While ab initio methods have unquestionably been built on solid theoretical grounds, the approximations inherent in the use of finite one-particle basis sets and limited electron correlation require convergence studies or careful comparisons with definitive experimental results in order to assess the accuracy of such methods and to build confidence in their application to general chemical problems. The quantum chemical literature features

several excellent studies concerned solely with the evaluation of the effectiveness of various approximations to electron correlation; in particular, comparisons with full configuration interaction (FCI) benchmark calculations have shown many correlation methods to be sufficiently accurate that the largest remaining source of error in many instances is in the one-particle basis set [1]. In this connection, increases in computer power and the development of computer codes for direct self-consistent field (SCF) [2] and direct second order Møller–Plesset (MP2) perturbation theory [3,4] have been important in allowing larger basis sets to be used without hitting the hurdles of disk storage and input/output bottlenecks. It has been said that “the history of computational quantum chemistry

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¹ Dedicated to Professor James E. Boggs on the occasion of his 75th birthday.

can be traced in terms of the use of basis sets of increasing size" [5].

In recognition of the need for basis set improvements, attention was given in the late 1980s to new contracted Gaussian-type-orbital (GTO) one-particle basis sets [6,7] with the unstated aim of achieving "chemical accuracy" (say, 4 kJ mol⁻¹) for the energetics of small but nontrivial systems. We note in particular the atomic natural orbital (ANO) basis sets of Almlöf and Taylor [6] and the correlation-consistent (cc) basis sets of Dunning [7]. These new basis sets have each been analyzed for their ability to produce results in acceptable agreement with experiment, but cross-comparisons have been limited. Dunning [7] compared total energies arising from his cc basis sets with those from the ANO basis sets and found his cc-pVQZ set to give 99% of the correlation energy of the corresponding ANO basis set while containing only two-thirds of the primitive GTOs. Martin [8] compared total atomization energies computed with the Dunning cc and Almlöf–Taylor ANO basis sets, and found the values to be comparable but the computational time to be significantly less with the Dunning sets.

While a formal ordering of the expected accuracy of levels of correlation can be obtained using perturbation theory [9–13], it is difficult to assess different basis sets of similar size without recourse to brute force comparison of their performance. Basis set convergence studies are complicated by the various strategies one can employ to improve "systematically" a basis set. Simply appending new primitive functions to an existing basis can often lead to nonmonotonic corrections in the property of concern. Replacing a smaller primitive basis set with a larger one has the difficulty that the two basis sets span different subspaces of the complete Hilbert space [1], although in practice the Dunning cc series does seem to provide excellent basis set extrapolations. Decontraction of a contracted basis, whether explicitly or implicitly (as in the case of the ANO basis set extensions), has the difficulty of depending on the choice of primitive basis set.

In the process of carrying out high-accuracy calculations on fluxional barriers in another study, we discovered discrepancies of roughly 5 kJ mol⁻¹

between the results obtained with basis sets which we had expected to be of similar high quality. As a consequence of this unsatisfactory finding and the lack of a systematic comparison in the literature of the results from the basis sets in which we were interested, we decided to undertake a broader analysis on a prototypical small system, using a selection of commonly used Gaussian basis sets derived from several different sources. The inversion barrier of ammonia was selected as the subject, partly because ten-electron systems are computationally accessible via high-quality methods and also because the classical barrier obtained in earlier *ab initio* work (1852 cm⁻¹) [14] is believed to be accurate to within 40 cm⁻¹. The effect of core correlation on the barrier height was also investigated, because its magnitude becomes important for high-accuracy (better than 2 kJ mol⁻¹) work and because its dependence on basis set is known to be significant for at least certain types of energetics, electronic transitions and dissociation energies in particular [15].

2. Theoretical methods

Standard *ab initio* molecular orbital calculations [16] were carried out using the GAUSSIAN 92, GAUSSIAN 94 [17] and ACES II [18] program packages.

The performance of both contracted and uncontracted GTO basis sets was examined. Being interested in high-quality energetics, we compared contracted sets of approximately quadruple-zeta-valence quality with at least d and f angular momentum shells. The d, f and g shells in all cases were sets of 5d, 7f and 9g combinations of the real components of the spherical harmonics, despite the occasional use of Cartesian shell sets for some of these basis sets in the past. We selected basis sets built from primitive functions from five different sources: Huzinaga [19], Pople and co-workers [20], van Duijneveldt [21], Dunning [7], and Partridge [22].

The Huzinaga (9s5p) and (10s6p) primitive sets for first-row (second-period) elements have been employed widely in basis sets such as DZP, TZ2P and QZ(2d1f,2p1d), with contractions due to

Dunning [23,24]. Here we used the QZ(2d1f,2p1d) set, whose polarization functions for nitrogen come from Dunning's correlation-consistent basis set work [7], and in particular the supplemented QZ(+)(2d1f,2p1d) set, which possesses an additional even-tempered diffuse s and p shell for nitrogen [25]. Next, we used the Pople 6-311 + G(3df,2p) basis set [26], which is the highest basis set used in G2 theory [27]. In this basis, the sp space for first-row atoms is a contraction of an (11s5p) primitive set [20] supplemented with a diffuse s and p shell [28]. We also examined the 6-311G(3df,2p) set, which differs only by removal of this diffuse s and p shell. The Partridge (13s8p) primitive set for first-row atoms has been employed in several studies (including a study of the ammonia inversion barrier) by Allen and co-workers [14,25,29,30], together with polarization functions from Dunning's correlation-consistent basis set work [7]. Two different contraction schemes have been labelled PZ(3d2f,2p1d); we took the less contracted scheme used in the previous NH₃ work [14]. The van Duijneveldt (13s8p) primitive set has been used in contractions by several workers, including Lie and Clementi [31] and, more recently, in the ANO basis sets of Almlöf and Taylor [6]. In the present work, we supplemented this uncontracted set (whose exponents are taken from Ref. [32]) with the polarization functions from PZ(3d2f,2p1d) and used the van Duijneveldt (8s) set for hydrogen

atoms [21]. The newer Dunning correlation-consistent [7] and augmented correlation-consistent [33] basis sets are built with their own primitives; we focused on the augmented triple-zeta set, aug-cc-pVTZ, which has an (11s6p) primitive backbone for first-row elements. We also employed three Dunning cc sets (cc-pVDZ, cc-pVTZ and cc-pVQZ), since use of the sequence of three basis sets has been found to be useful in basis set extrapolation (see Ref. [34] and citations therein), and the large aug-cc-pVQZ augmented set, to suggest remaining basis set inadequacies in our test series. The principal basis sets used are summarized for convenience in Table 1.

Allen et al. [14] have found that the effect of post-MP2 correlation on the ammonia inversion barrier is insensitive to basis set; in fact, the increase in barrier height between MP2 and the perturbation limit was found to be $168 \pm 4 \text{ cm}^{-1}$ for four basis sets ranging from DZP to PZ(3d2f,2p1d). Hence, in the present work, barriers were computed generally at three levels of theory: Hartree–Fock (HF), MP2 with nitrogen 1s core electrons frozen (MP2(fc)) and full MP2 with all electrons active (MP2(fu)). We used the optimized CISDTQ/DZP planar and pyramidal structures of Lee et al. [35] to determine the Born–Oppenheimer energies. Extensions to MP3 and the CCSD and CCSD(T) coupled-cluster methods [36–39] were carried out for the analysis of 1s correlation effects.

Table 1
Basis set descriptions

Basis set	Nitrogen sp primitives	Contraction	Polarization functions	Hydrogen s primitives	Contraction	Polarization functions
vD(3d2f,2p1d)	van Duijneveldt ^a (13s8p)	–	Dunning ^b (3d2f)	van Duijneveldt ^a (8s)	–	Dunning ^b (2p1d)
aug-cc-pVTZ	Dunning ^{b,f} (11s6p)	Dunning ^b [5s4p]	Dunning ^{b,f} (3d2f)	Dunning ^{b,f} (7s)	Dunning ^b [4s]	Dunning ^{b,f} (3p2d)
PZ(3d2f,2p1d)	Partridge ^c (13s8p)	Allen ⁱ [8s5p]	Dunning ^b (3d2f)	Huzinaga ^d (6s)	Olbrich ^l [4s]	Dunning ^b (2p1d)
QZ(+)(2d1f,2p1d)	Huzinaga ^d /Allen ^g (11s7p)	Dunning ^j [6s5p]	Dunning ^b (2d1f)	Huzinaga ^d (6s)	Olbrich ^l [4s]	Dunning ^b (2p1d)
6-311 + G(3df,2p)	Pople ^e /Schleyer ^h (12s6p)	Pople ^e [5s4p]	Pople ^k (3d1f)	Pople ^e (5s)	Pople ^e [3s]	Pople ^k (2p)

^a From Ref. [21]. ^b From Ref. [7]. ^c From Ref. [22]. ^d From Ref. [19]. ^e From Ref. [20]. ^f From Ref. [33]. ^g From Ref. [25]. ^h From Ref. [28]. ⁱ From Ref. [14]. ^j From Ref. [24]. ^k From Ref. [26]. ^l From Ref. [51].

3. Results and discussion

3.1. Basis set comparisons

In the case of ammonia, it so happens that *ab initio* theory currently determines the classical inversion barrier to a higher accuracy than has been achieved from fittings to spectroscopic rovibrational lines. Špirko and co-workers [40–42] have determined the barrier height with several multiparameter potential fits and varying weighting schemes of the spectroscopic data, and while the majority of their procedures predict an effective ground-state barrier of $2020 \pm 15 \text{ cm}^{-1}$, the zero-point vibrational energy (ZPVE) back-corrections to determine the classical barrier height have varied from -135 to -229 cm^{-1} . The suggestion [14] that the ZPVE correction may be even larger in magnitude than 229 cm^{-1} provides further reason not to rely on comparison with experiment. Such a comparison will be more useful when a quartic force field becomes available for the planar configuration of ammonia. For the moment, we believe that the best previous estimate of the classical barrier height in ammonia is the value of 1852 cm^{-1} obtained in earlier *ab initio* work [14].

We will generally focus in the present paper on the MP2(fc) infinite basis set barrier height. Our reference value will be the MP2(fc)/PZ(3d2f,2p1d) value of 1733 cm^{-1} , identical with the result in Ref. [14] with a frozen virtual orbital. This is the best estimate of the MP2(fc) infinite-basis barrier available to date in the literature, and our results can be used to evaluate its accuracy. To compute estimates of the classical barrier height from MP2(fc) values, we use the *ab initio* corrections of Allen et al. [14] for post-MP2 correlation, 1s core correlation, relativity and Born–Oppenheimer effects ($+171$, -67 , $+24$ and -11 cm^{-1} , respectively). As stated earlier, Allen et al. [14] found the basis set dependence of post-MP2 correlation to be remarkably small. The basis set dependence of 1s core correlation will be discussed later, and that of the final two corrections is assumed to be small.

We examined the effect of using CISDTQ/DZP geometries through a comparison of barrier heights computed with the PZ(3d2f,2p1d) basis set using structures obtained at two different levels of

theory: CISDTQ/DZP (whose barrier height is too high and whose C_{3v} structure is too puckered) and MP2(fu)/PZ(3d2f,2p1d) (whose barrier height is too low and whose C_{3v} structure is not puckered enough). The change in barrier height due to the geometry change is 36 cm^{-1} for HF but only 4 cm^{-1} for MP2(fc) and 8 cm^{-1} for MP2(fu), with the use of the CISDTQ/DZP structures resulting in the larger barrier.

The basis set comparisons were carried out in three stages: (i) the contracted basis sets were used in their normal fashion, including the choice of hydrogen basis set; (ii) the nitrogen (but not hydrogen) basis sets were decontracted to estimate so-called contraction errors; and (iii) finally, to directly test the nitrogen primitives themselves, the various uncontracted nitrogen sp sets were retained but the remaining (polarization and hydrogen) functions were replaced by those from the PZ(3d2f,2p1d) set.

The results of stage (i) are presented in Fig. 1. The Dunning cc-pVDZ through cc-pVQZ series, while producing rather high barriers for the smaller basis sets, does suggest a monotonic convergence towards the range of values indicated by the other basis sets represented in Fig. 1. For each basis set except 6-311 + G(3df,2p), the MP2(fu) barriers lie above the HF values but below the MP2(fc) values. Nitrogen diffuse functions substantially alter (and improve) the results with the Dunning cc, Pople 6-311G and Huzinaga QZ basis sets, with the effects on the MP2(fc) barrier heights (in cm^{-1}) being -323 (cc-pVTZ), -177 (cc-pVQZ), -542 (6-311G(3df,2p)) and -124 (QZ(2d1f,2p1d)).

Next we focus on basis sets which possess sufficient diffuse nitrogen primitives to produce MP2(fc) barriers below 1800 cm^{-1} , and advance to stage (ii) to see whether the contractions of the nitrogen basis sets have affected the performance of the primitive sets. For the contracted basis sets of interest, comparisons of the MP2(fc) values with the MP2(fc)/PZ(3d2f,2p1d) result of 1733 cm^{-1} as a reference show deviations (in cm^{-1}) of -73 (6-311 + G(3df,2p)), $+27$ (aug-cc-pVTZ) and $+19$ (QZ(+)(2d1f,2p1d)); these barrier height results are redisplayed on the left side of Fig. 2. We next uncontracted the nitrogen sp primitives for each basis set and the barriers were recomputed, with

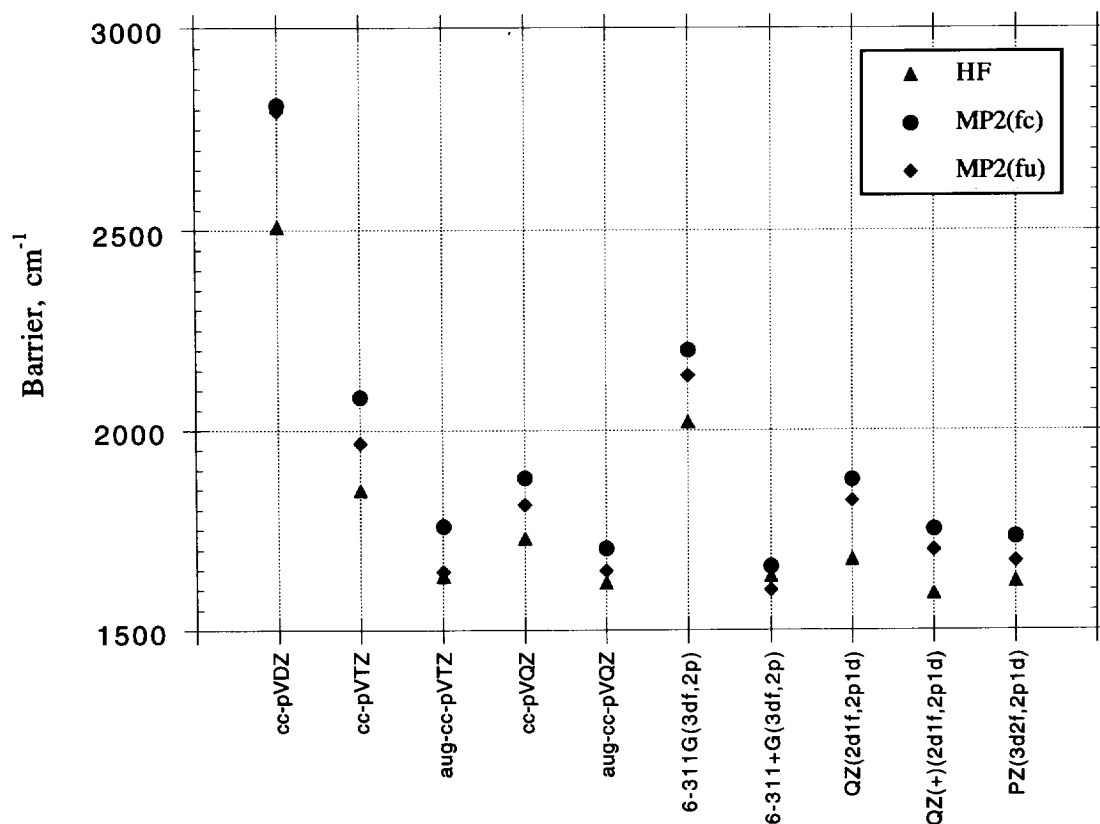


Fig. 1. Barriers to inversion in ammonia computed at the HF, MP2(fc) and MP2(fu) levels of theory with contracted basis sets.

the results shown in the middle of Fig. 2. Results with the van Duijneveldt set are now also included. The differences between the uncontracted and contracted data are about 50 cm^{-1} in some cases and only 1 cm^{-1} in others. The contraction errors, listed explicitly in Table 2, are seen generally to be largest for the MP2(fu) values; this suggests that basis set contractions affect configurations containing an occupied 1s pair on nitrogen roughly equally at

Table 2
Effects of contractions of the nitrogen sp primitives on the inversion barrier of ammonia (cm^{-1})

Basis set	HF	MP2(fc)	MP2(fu)
cc-pVQZ	0	0	-17
QZ(2d1f,2p1d)	-1	-1	-16
6-311 + G(3df,2p)	+3	-54	-61
aug-cc-pVTZ	0	+5	-71
QZ(+)(2d1f,2p1d)	-4	-4	-18
PZ(3d2f,2p1d)	0	0	-13

C_{3v} and D_{3h} structures, but affect configurations involving a 1s "hole" differentially (with the larger contraction error for the C_{3v} form). Hence the contractions significantly affect the core correlation contribution to the barrier height, but generally have only a minor influence on the valence correlation contribution. An exception is seen with the Pople 6-311 + G(3df,2p) basis set, where the contraction error is very small for HF but appears in the MP2(fc) computations; the contractions are evidently affecting the valence-orbital-hole configurations (and hence the valence correlation contribution) in this case and adversely affecting the performance of the primitive set. The agreement among the MP2(fc) values for the five basis sets, after decontraction on nitrogen, has improved to $1732 \pm 24 \text{ cm}^{-1}$.

In stage (iii) we focus on the sp primitive sets for nitrogen. Varying only these primitives on nitrogen, while keeping the remaining polarization and

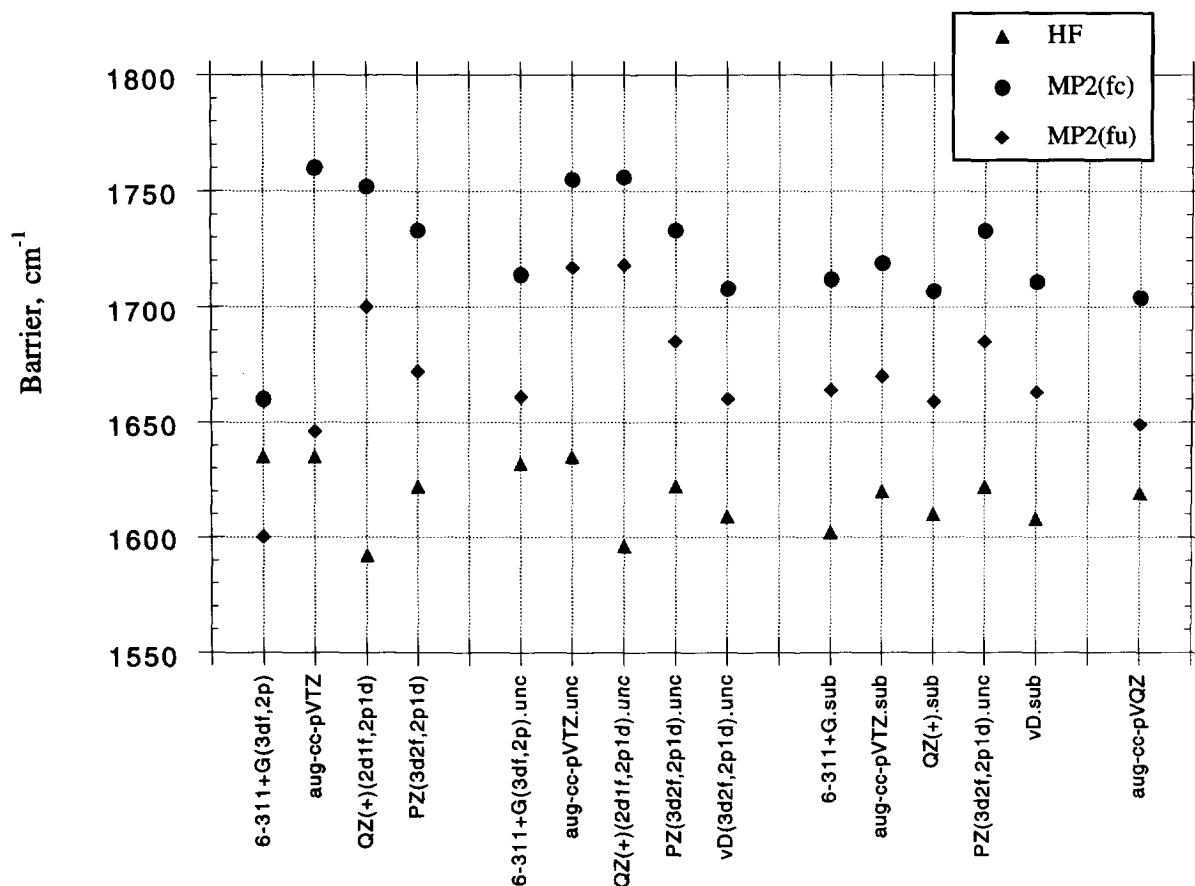


Fig. 2. Barriers to inversion in ammonia computed at the HF, MP2(fc) and MP2(fu) levels of theory, with basis sets with usual contraction (left), after decontraction of the nitrogen sp primitives (centre) and after nitrogen decontraction plus substitution of the nitrogen df and hydrogen basis sets with those of PZ(3d2f,2p1d) (right). The results with the best (contracted) basis set used in the present study, aug-cc-pVQZ, are shown on the far right.

hydrogen functions fixed at their PZ(3d2f,2p1d) values, we obtain the barriers shown on the right side of Fig. 2. The effects of the substitutions of polarization and hydrogen functions are given in Table 3 together with comments on the important changes; the greatest effect seen here is on MP2 barriers due to the improvement of the d-shell space from 2d to 3d for the aug-cc-pVTZ and QZ(+)(2d1f,2p1d) sets (ignoring the presence of the diffuse d shell of aug-cc-pVTZ, which is apparently of minor importance). The five completely different groups of sp primitives on nitrogen now provide MP2(fc) barrier height results which agree to $1720 \pm 13 \text{ cm}^{-1}$. This agreement is achieved only after supplementing three of the nitrogen sp sets

with diffuse functions and decontracting two of the sets, as described above. We note that supplementation of the (nitrogen-uncontracted) Partridge PZ(3d2f,2p1d) basis set with an even-tempered diffuse s and p shell on nitrogen lowers the HF and MP2(fc) barrier heights by 18 and 30 cm^{-1} , respectively, leading to an improved MP2(fc)/PZ(+)(3d2f,2p1d) estimate of 1703 cm^{-1} . The best estimates of the MP2(fc) barrier for the five basis sets are then $1711 \pm 8 \text{ cm}^{-1}$.

On the far right of Fig. 2 are the results for the (contracted) aug-cc-pVQZ basis set, which is expected to possess sufficiently diffuse sp primitives on nitrogen, polarization and hydrogen functions superior to all others in this work, and contraction

Table 3
Effects of substitution of the nitrogen df and hydrogen primitives from PZ(3d2f,2p1d) into other uncontracted basis sets on the inversion barrier of ammonia (cm^{-1})

Basis set ^a	HF	MP2(fc)	MP2(fu)	Main cause ^b
cc-pVQZ.sub	-8	-4	-3	No 3rd p on H, no g on N
QZ.sub	+12	-49	-60	3rd d on N, 2nd f on N
6-311 + G.sub	-30	-2	+3	4th s on H, d on H
aug-cc-pVTZ.sub	-15	-36	-47	Better 3d on N, better 4s on H
QZ(+).sub	+14	-49	-59	3rd d on N, 2nd f on N
vD.sub	-1	+3	+3	Reduced s space on H

^a The suffix .sub indicates the basis set after substitution of the nitrogen df and hydrogen primitive functions from PZ(3d2f,2p1d).

^b The most significant changes to the original basis set upon substitution, e.g. "3rd d on N" means the d space for the nitrogen atom increased from two functions to three.

errors as small as that of the identically contracted cc-pVQZ basis set (see Table 2). The HF and MP2(fc) barrier heights are close to the values obtained using the five uncontracted sets substituted with polarization and hydrogen functions from the PZ(3d2f,2p1d) set. Taking the MP2(fc)/aug-cc-pVQZ barrier height (1704 cm^{-1}) and the corrections mentioned earlier, we obtain 1808 cm^{-1} for the improved non-relativistic Born–Oppenheimer height and 1821 cm^{-1} as our estimate of the exact classical inversion barrier of ammonia, to an estimated accuracy of 30 cm^{-1} . These are our best estimates of the barrier in the current study, and are the best values available to date.

The manner by which the introduction of diffuse functions reduces the inversion barrier of the iso-electronic methyl anion was investigated in 1973 by Duke [43], who concluded that the diffuse functions preferentially benefit the planar configuration, partly because the lone pair is more diffuse in the planar configuration, but also because the provision of a more diffuse orbital for the lone pair of the planar configuration allows density from bonding orbitals to concentrate more appropriately between the carbon and the hydrogen atoms. It is unclear whether the results for methyl anion and ammonia will be generalizable to systems where no lone pair is involved.

Our conclusions regarding the dependence on valence basis sets of the calculated inversion barrier of ammonia may be summarized as follows: (i) the augmentation of Pople 6-311G, Dunning cc, Huzinaga (10s6p) and Partridge (13s8p) basis sets with diffuse sp functions on nitrogen causes

improvements in the MP2(fc) barrier heights (in cm^{-1}) ranging from -30 (PZ(+)(3d2f,2p1d).unc) to -542 (6-311 + G(3df,2p)); (ii) decontraction of the sp primitives on nitrogen, for the basis sets used in Fig. 2, causes improvements of the order of $+60 \text{ cm}^{-1}$ with the MP2(fu) results of 6-311 + G(3df,2p) and aug-cc-pVTZ and the MP2(fc) result of 6-311 + G(3df,2p); (iii) improving the number of non-diffuse polarization shells on nitrogen beyond 2d1f causes improvements in the MP2 results of -40 to -60 cm^{-1} ; and (iv) improving the hydrogen basis set from triple zeta to quadruple zeta affects the HF barrier by -30 cm^{-1} but has little effect on the MP2 barriers. Each of the nitrogen sp primitive sets used here, once appended with standard diffuse functions, seem sufficient to produce the non-relativistic Born–Oppenheimer inversion barrier in ammonia to within a very satisfactory 30 cm^{-1} , using polarization functions up to $l = 3$ only. The Partridge results are about $20\text{--}30 \text{ cm}^{-1}$ too high without extra diffuse functions. The only adverse effects of contraction of nitrogen sp primitives were found with the 6-311 + G(3df,2p) and aug-cc-pVTZ sets, and only with their MP2-correlated results.

We can comment here on the most noteworthy near-HF computations of the inversion barrier of NH_3 that have been previously reported. Our results suggest that the HF limit for this barrier is very near 1610 cm^{-1} when using geometries obtained from correlated results (rather than HF geometries); the true HF limit requires HF-limit geometries, which may possibly raise our estimate by another $30\text{--}100 \text{ cm}^{-1}$ since our C_{3v} geometry

will be too puckered. The barrier obtained by Kölmel et al. [44] (1650 cm^{-1} , 15s10p2d1f primitives) is the best previous result; although they use only a 2d1f polarization set, the use of floating polarization primitives (i.e. different exponent values for the C_{3v} and D_{3h} forms) may be compensating for this shortcoming. The large-basis-set results of Rauk et al. [45] (1775 cm^{-1} , 13s8p2d primitives on N) and of Rodwell and Radom [46] (1820 cm^{-1} , also 13s8p2d) suffer from the lack of an f shell on N and a d shell on H, as Kölmel et al. [44] first pointed out.

3.2. Core correlation

It is evident from a comparison of MP2(fc) and MP2(fu) results in Figs. 1 and 2 that the frozen-core approximation contributes an error of about 50 cm^{-1} to the ammonia inversion barrier, an amount that is significant with respect to the accuracy that can be achieved both from spectroscopy and from ab initio methods for certain facile systems. It is known that core correlation effects are sensitive to the selection of one-particle basis sets in certain situations. Previous work has shown that basis set requirements are more crucial for electronic transitions than for spectroscopic constants of a given state [15]. In addition, the core correlation effects for dissociation energies appear not to be particularly sensitive to the choice of basis set when size-consistent theories are used, but become so when using non-size-consistent correlation methods [47–50]. Little seems to be known of the sensitivity of core correlation effects to choices among size-consistent correlation methods.

We thought it appropriate and useful to address some of these concerns regarding levels of theory sufficient for the computation of the core correlation effect, for the particular case of the inversion barrier height in ammonia. To this end, we performed an additional barrier calculation with the PZ(3d2f,2p1d) basis set, but with uncontracted nitrogen primitives and additional tight d and f functions exactly in the manner of Allen et al. [14] to improve the description of the nitrogen core region. The effect on MP2 barriers of liberating the 1s electrons was found to be -61 cm^{-1} with PZ(3d2f,2p1d), -48 cm^{-1} after

additionally decontracting the sp space on nitrogen and -67 cm^{-1} after then adding the three tight d and two tight f shells. Neither of these latter basis set modifications affected the HF or MP2(fc) barriers by more than 7 cm^{-1} .

The effect on frozen-core-approximation errors of valence-region basis set size is demonstrated by data for the Dunning cc series shown in Fig. 1. The actual values are -14 (cc-pVDZ), -116 (cc-pVTZ) and -68 cm^{-1} (cc-pVQZ). These show considerable variation. However, when different basis sets of approximately quadruple-zeta size are compared (for example, the Partridge/Allen PZ, Huzinaga/Dunning QZ and Dunning cc-pVQZ and aug-cc-pVQZ sets), the fluctuations are much smaller (errors ranging from -52 to -68 cm^{-1}), suggesting convergence of this phenomenon with respect to valence basis set extension. While the 6-311 + G(3df,2p) and aug-cc-pVTZ basis sets have contraction errors which affect the computation of core correlation, their decontracted versions produce results for the frozen-core-approximation error (-53 and -38 cm^{-1} , respectively) which are consistent with the results for the decontracted versions of the quadruple-zeta and pentuple-zeta sets (errors ranging from -38 to -51 cm^{-1}). The decontracted and substituted basis sets (denoted .sub) produce nearly identical estimates of frozen-core-approximation errors ($-49 \pm 1\text{ cm}^{-1}$), indicating that valence polarization functions are responsible for the 15 cm^{-1} scatter in these errors with decontracted nitrogen basis sets. The addition of polarization functions into the core region increases the estimate of the frozen-core approximation error by roughly 20 cm^{-1} (to -67 cm^{-1} , as mentioned earlier).

The effect on frozen-core-approximation errors of level of correlation was addressed with additional MP3, CCSD and CCSD(T) calculations with the Dunning cc basis sets. Compared with the 1s liberation effects for the three basis sets of -14 , -116 and -68 cm^{-1} at MP2 noted above, they are -13 , -123 and -68 cm^{-1} at MP3, indicating little change. Going beyond MP3 with the cc-pVTZ basis set, the effects are -124 at CCSD and -123 with CCSD(T), again indicating little change.

Our results here for 1s core correlation indicate that, if the inversion barrier in ammonia can be

Table 4
Total energies for ammonia (a.u.)^a

Basis set	C _{3v} HF	D _{3h} HF	C _{3v} MP2(fc)	D _{3h} MP2(fc)	C _{3v} MP2(fu)	D _{3h} MP2(fu)
cc-pVDZ	-56.195464	-56.184036	-56.382169	-56.369365	-56.384789	-56.372050
cc-pVTZ	-56.217449	-56.209023	-56.452888	-56.443398	-56.467692	-56.458731
aug-cc-pVTZ	-56.219896	-56.212439	-56.460479	-56.452429	-56.477348	-56.469834
cc-pVQZ	-56.222649	-56.214765	-56.474524	-56.465953	-56.504467	-56.496207
aug-cc-pVQZ	-56.223524	-56.216147	-56.477659	-56.469895	-56.507988	-56.500472
6-311G(3df,2p)	-56.214288	-56.205078	-56.444530	-56.434497	-56.466812	-56.457072
6-311 + G(3df,2p)	-56.218119	-56.210670	-56.450528	-56.442964	-56.472837	-56.465548
QZ(2d1f,2p1d)	-56.220769	-56.213130	-56.459782	-56.451233	-56.485504	-56.477196
QZ(+)(2d1f,2p1d)	-56.221352	-56.214096	-56.460802	-56.452820	-56.486540	-56.478794
PZ(3d2f,2p1d)	-56.223387	-56.215996	-56.468790	-56.460892	-56.503349	-56.495730
6-311 + G(3df,2p).unc	-56.218463	-56.211028	-56.454668	-56.446859	-56.502487	-56.494919
aug-cc-pVTZ.unc	-56.220001	-56.212553	-56.462589	-56.454590	-56.507667	-56.499841
cc-pVQZ.unc	-56.222694	-56.214813	-56.474191	-56.466619	-56.523713	-56.515375
QZ(2d1f,2p1d).unc	-56.221005	-56.213361	-56.460695	-56.452140	-56.506825	-56.498448
QZ(+)(2d1f,2p1d).unc	-56.221580	-56.214309	-56.461699	-56.453698	-56.507828	-56.500000
PZ(3d2f,2p1d).unc	-56.223411	-56.216021	-56.469079	-56.461183	-56.518338	-56.510661
vD(3d2f,2p1d).unc	-56.223749	-56.216416	-56.469852	-56.462072	-56.519056	-56.511493
6-311 + G.sub	-56.219270	-56.211971	-56.464299	-56.456498	-56.511713	-56.504133
aug-cc-pVTZ.sub	-56.220245	-56.212862	-56.465140	-56.457306	-56.511947	-56.504339
cc-pVQZ.sub	-56.222273	-56.214427	-56.467232	-56.458679	-56.515665	-56.507339
QZ.sub	-56.221214	-56.213515	-56.466223	-56.457894	-56.514139	-56.506034
QZ(+).sub	-56.221787	-56.214452	-56.467209	-56.459430	-56.515123	-56.507563
vD.sub	-56.223469	-56.216141	-56.469258	-56.461461	-56.518462	-56.510883

^a The CISDTQ/DZP geometries of Ref. [35] were used: $r_{\text{NH}} = 1.0005 \text{ \AA}$ (D_{2h}), 1.0173 \AA (C_{3v}), HNH angle = 106.3° (C_{3v}). The suffix .unc indicates an uncontracted sp space on nitrogen. The suffix .sub indicates the substitution of polarization and hydrogen functions by those from the PZ(3d2f,2p1d) basis set.

computed to greater than “chemical accuracy” but it is not computationally feasible to properly supplement a conventional basis set with extra functions for the core region, a better answer is likely to be obtained with the liberation of 1s electrons in a correlated treatment than with the frozen-core approximation. The generalizability of this conclusion to other conformational energy differences will be of interest.

Total energies are listed in Table 4, not only in the interests of verification, but also to permit comparisons of energies for ammonia obtained with high-quality basis sets. The effects of decontraction on the HF total energies in Table 4 are less than 500 μ hartree, while for MP2(fc) the effects increase by an order of magnitude, and for MP2(fu) an order of magnitude again. We note that basis sets without sufficient diffuse character (such as cc-pVQZ) can give lower total energies than other basis sets, for both the C_{3v} and D_{3h} structures, but provide

inferior predictions for the energy difference between the two. This result reasserts the well known fact that total energy is not necessarily a reliable indicator of basis set performance.

4. Conclusions

In attempting to compute a barrier to inversion at a first-row atom to better than 200 cm^{-1} (roughly 2 kJ mol^{-1}) accuracy, the presence of diffuse sp primitive functions is very important, while errors due to contraction, neglect of 1s core correlation and lack of polarization functions beyond 2d1f seem typically to be less than 90 cm^{-1} . These results could be particular to inversions where a lone pair of electrons is involved. The Huzinaga, Dunning and Pople primitives that support the QZ(2d1f,2p1d), cc-pVTZ, cc-pVQZ and 6-311G(3df,2p) sets require functions more diffuse

than already present to reduce their errors for the MP2(fc) NH₃ inversion barrier below 100 cm⁻¹. The established augmented sets improve accuracy to within 30–50 cm⁻¹, depending on polarization and hydrogen functions. The 6-311 + G(3df,2p) basis set has a significant nitrogen-basis contraction error of 54 cm⁻¹ for the MP2(fc) NH₃ inversion barrier, unlike the other basis sets used here. The van Duijneveldt (13s8p) primitives perform well without augmentation in the sp space, while the Partridge (13s8p) primitives can be marginally improved (by 30 cm⁻¹ for this MP2(fc) barrier) with an additional sp diffuse shell on nitrogen.

The effect of 1s core correlation on the ammonia inversion barrier is approximately 70 cm⁻¹, and is consistent among MP2, MP3 and coupled-cluster methods, and among a variety of conventional basis sets of better than valence-triple-zeta quality. Uncontracting and supplementing these conventional bases in the core region each cause changes in this barrier of roughly 20 cm⁻¹, except for aug-cc-pVTZ, for which contraction adversely affects the MP2(fu) result by roughly 50 cm⁻¹.

We predict a classical inversion barrier in ammonia of 1821 cm⁻¹, representing the best value available to date.

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