Theor Chem Acc (2004) 111:18–24
DOI 10.1007/s00214-003-0455-1

Theoretical
Chemistry Accounts

Regular article

Systematic convergence of energies with respect to basis set and treatment of electron correlation: focal-point conformational analysis of methanol

Kalju Kahn, Thomas C. Bruice

Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106, USA

Received: 30 December 2002 / Accepted: 12 May 2003 / Published online: 24 December 2003
© Springer-Verlag 2003

Abstract. A practical means of overcoming the limitation in accuracy of conformational analysis due to incompleteness of basis sets used in ab initio calculations involves calculating the energy with a series of systematically improving basis sets and extrapolating to the basis set limit. We report here a focal-point conformational analysis for methanol. The Hartree–Fock energy converges exponentially to the basis set limit, while the convergence of second-order correlation energy is well described by the formula $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_3X^{-3} + A_5X^{-5}$. This formula also describes well the convergence of fourth-order correlation energy. The height of the rotational barrier at the Hartree–Fock level can be obtained reliably by taking the difference of the extrapolated energies of the two conformations and correcting the difference for correlation effects. Electron correlation has only a small decreasing effect on the height of the rotational barrier in methanol. The focal-point value for the torsional barrier in methanol is 0.999 ± 0.007 kcal/mol.

Keywords: Basis set extrapolation – Conformational analysis – Focal-point analysis – Torsional barrier – Methanol

Introduction

Conformational energies of molecules can be calculated accurately by quantum chemical methods that describe the electron correlation effects correctly. However, correlated ab initio calculations converge slowly with respect to the basis set size [1, 2], and the use of small basis sets is not recommended for correlated quantum chemical calculations [3, 4]. Unfortunately, correlated ab initio calculations with nearly complete basis sets are not feasible at the present time owing to the high cost of calculating multielectron integrals. A practical means of assessing the energy of a molecular system at the basis set limit involves a series of calculations with systematically larger basis sets followed by extrapolation to the basis set limit. Combining the basis set extrapolation method with systematically improved treatments of electron correlation will hopefully lead to energies and other properties that converge to a focal point. Many basis set extrapolation studies have been performed previously to assess the convergence of energies and dipole moments in small molecules [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. Recently, some studies have applied this approach to the conformational analysis of molecules such as ethane, methyl formate, glyoxal, and aziridine-2-carbonitrile [16, 17, 18]. We now report a systematic focal-point conformational analysis of methanol. Calculations with basis sets up to cc-pV6Z were performed and reference data using the explicitly correlated MP2-R12 method were obtained, allowing us to critically compare various extrapolation schemes.

Basis set extrapolation

Different approaches to extrapolate ab initio energies to the basis set limit have been reported in the literature recently [2, 13, 16, 19, 20, 21, 22, 23]. In one of the earliest uses of the extrapolation technique, simple exponential fits of the total MP2 energy difference were performed to estimate the limiting value for the interaction energy between two water molecules [5]. Exponential fits, as well as mixed exponential–Gaussian fits of total energies have been used by Dunning's group [24, 25]. Use of such extrapolation formulas has been justified on the basis of a statistical goodness of fit. More recently, extrapolation formulas based on quantum

---

Correspondence to: T.C. Bruice
e-mail: tcbruice@chem.ucsb.edu

theory have been used. Typically, the Hartree–Fock (HF) and correlation energies are extrapolated separately to the limit and the extrapolated results are combined to obtain the total energy. The HF energy decreases exponentially (Eq. 1) with the cardinal number X when correlation-consistent basis sets of the type cc-pVXZ are used [11, 26]:

$$E_X = E_\infty + A\exp(-BX). \tag{1}$$

Theoretical considerations and experience indicate that convergence of correlation energies follows an inverse power series [1, 12, 19, 21]. In particular, Schwartz [27] has demonstrated that the leading term for the second-order correlation energy for the helium atom ground state should converge asymptotically with respect to the angular momentum quantum number, l, as

$$\Delta E_l^{\text{cor}} = -\frac{45}{256}\left(l+\frac{1}{2}\right)^{-4}. \tag{2}$$

A similar result was later derived for many-electron atoms by Kutzelnigg and Morgan [1], who also showed that the second term for natural parity singlet pairs converges as $(l+1/2)^{-6}$. The leading term for second-order energy due to triplet pairs also converges as $(l+1/2)^{-6}$ [1, 21]. Terms with odd powers appear in the third-order energy expression [1], and the general formula for correlation energy increments resulting from addition of a saturated shell of atomic basis functions of angular momentum quantum number l has the form

$$\Delta E_l^{\text{cor}} = \sum_{m=4} a_m \left(l+\frac{1}{2}\right)^{-m}. \tag{3}$$

Integration of Eq. (3) gives [13]

$$E_{L+1}^{\text{cor}} = E_\infty^{\text{cor}} + \sum_{m=4} A_{m-1}(L+1)^{-m+1}, \tag{4}$$

where $A_m = -a_m/(m-1)$. The integrated equation reveals that the leading term of the basis set truncation error decreases asymptotically as a function of L^{-3}. Extrapolations using asymptotic formulas are commonly done for atoms, but application to molecules is more complicated because the electronic orbital angular momentum is not a good quantum number owing to a nonspherical symmetry of molecules [19]. Also, basis sets for molecular calculations are not optimally constructed to satisfy the requirement of saturating the function space of a given orbital angular-momentum quantum number [19]. Nevertheless, when correlation-consistent basis sets (cc-pVXZ, where X = D, T, Q, 5, or 6) of Dunning [28] are used, the highest angular momentum in the basis is $L = X-1$ for H and He, and $L = X$ for Li–Ar. Thus, if a compound is made up of both hydrogen and first-row atoms, calculations with the cc-pVXZ basis set would require a compromise between L and $L+1$ [6]. Taking this into consideration, Martin [6] proposed that energies at the basis set limit could be obtained based on the function

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + A_\alpha\left(X+\frac{1}{2}\right)^{-\alpha}, \tag{5}$$

where a value of 4 is appropriate for the coefficient α when cc-pVXZ basis sets are used [6]. Helgaker et al. [7, 8] have proposed a simpler fitting function by taking $L = X$ and truncating the power series in Eq. (4) after the first term, leading to an X^{-3} dependence:

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + A_3X^{-3}. \tag{6}$$

Truhlar [9] has suggested that the value of the exponent in Eq. (6) can be optimized for a particular method and has shown that remarkably good accuracy can be obtained with only cc-pVDZ and cc-pVTZ data [9]. Some of the truncations of the power series (Eq. 4) have been systematically compared in a study of convergence behavior of correlation energies of He, H_2, and He_2 and good performance of the truncation by Eq. (6) for second-order correlation energies has been noted [12]. This work also suggests that the extrapolation based on the equation

$$E_X^{\text{cor}} = E_\infty^{\text{cor}} + A_3X^{-3} + A_5X^{-5} \tag{7}$$

frequently yields smaller deviations from the exact value than extrapolation based on Eq. (6). Klopper has argued that correlation energies should be decomposed into singlet and triplet pair energies and extrapolated separately because the singlet pair energies converge as X^{-3}, while the triplet pair energies show X^{-5} convergence with the cardinal number [1, 14, 21].

Computational details

The minimum and the rotational saddle point of methanol were optimized at the MP2(FC)/cc-pVTZ level with Gaussian 98 [29]. This level of theory gives remarkably good geometries and has been shown to predict bond distances with standard deviations of 0.007–0.01 Å when compared to the experimental data [4, 26]. Single-point energies were calculated with cc-pVXZ basis sets of Dunning and coworkers [28], where X = D, T, Q, 5, and 6. Valence correlation energies were calculated at the MP2 to MP4(SDTQ) levels; in addition CCSD and CCSD(T) calculations were performed when practical. Reference values for the second-order correlation energy were obtained from explicitly correlated MP2-R12/A calculations using the program DIRCCR12-OS [30, 31]. Large basis sets specifically optimized for explicitly correlated calculations were used [32]. The largest basis set used was 19s14p8d6f4g3h for oxygen, 19s14p8d6f4g for carbon, 9s6p4d3f for hydroxyl hydrogen, and 9s6p4d for methyl hydrogens. Both conformations of methanol were restricted to C_S symmetry.

The quantity of interest in conformational analysis is the relative energy of a conformation relative to some other conformation. The basis set limit for relative energies can be obtained either by extrapolating the energy of each conformer to the limit and taking the difference, or by calculating relative energies at each level of theory and extrapolating the difference. Furthermore, at the MPn level the quantity that is being extrapolated can be either the nth order correlation energy (e.g., total fourth-order correlation

Table 1. Energy difference (kcal/mol) between the rotational saddle point and the minimum-energy minimum structure in methanol as a function of basis set and electron correlation treatment

Basis set	SCF	MP2	MP3	MP4	MP4(T)	CCSD	CCSD(T)
cc-pVDZ	1.316	1.494	1.435	1.449	1.480	1.441	1.464
cc-pVTZ	1.082	1.130	1.089	1.100	1.111	1.095	1.099
cc-pVQZ	1.035	1.053	1.022	1.030	1.035	1.027	1.026
cc-pV5Z	1.020	1.025	1.001	1.007	1.009	1.006	
cc-pV6Z	1.018	1.019	0.997				
Extrapolation	1.015	1.011	0.994	0.997	0.999	0.997	

energy, $\Delta E^{(4)}$, for MP4), the partial correlation energy due to certain excitations (e.g., $E_{\mathrm{T}}{}^{(4)}$ describing the contribution from triple excitations at the fourth order), or the total correlation energy up to and including the *n*th order $[\Delta E^{\mathrm{cor(MP4)}=\Delta E(2)}+\Delta E^{(3)}+\Delta E^{(4)}]$ [33].

Equation (1) was fitted to self-consistent-field (SCF) energies to estimate the SCF limit. Exponential functions and several truncations of the power series were considered for fitting correlation energies. The goodness of the fits was compared on the basis of their χ^2 statistics values and the ability to correctly predict the limiting value. The suitability of the models for extrapolation was also judged based on how much the extrapolated value depended on the choice of the data points that were included in the fit. A good extrapolation scheme would have a small number of adjustable parameters, show a small value for the χ^2 statistics for a given number of parameters, and would yield correct limiting values that are independent of the choice of data points.

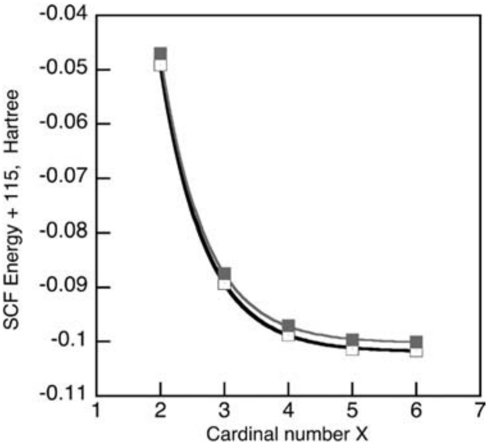

Fig. 1. Fit of a three-parameter single-exponential function Eq. (1) to self-consistent-field (*SCF*) energies of methanol in the anti (*open squares*) and syn (*filled squares*) conformations

Results and discussion

Reference data

Methanol has one minimum and one rotational saddle point. The experimental rotational barrier for methanol has been estimated at 1.065 kcal/mol on the basis of the analysis of its microwave spectrum [34]. To compare this value with current ab initio results, zero-point energy correction for all of the small-amplitude vibrations must be taken into account. This correction has been evaluated to be −0.064 kcal/mol [35] and thus the "experimental" energy difference between the two conformations is 1.001 kcal/mol.

The second-order correlation energies for the anti and syn conformers from explicitly correlated calculations are −484.620 and −484.623 mE_{h}, respectively, with the largest basis set tested. Convergence of MP2-R12/A results as a function of the basis set size suggests that the true value for the second-order energy is about −484.9 mE_{h}. The second-order correlation energy at the CCSD-R12/A level was −490.0 mE_{h}.

Traditional ab initio calculations

The ab initio energy differences calculated at various levels of theory are summarized in Table 1. Inspection of these results reveals the poor performance of the double-zeta basis set, and suggests that electron correlation effects are not very critical for the description of the torsional barrier in methanol. Single-exponential fits of total SCF energies give good convergence (Fig. 1) with typical χ^2 values of 3–5×10^{-8}. The extrapolated values show a slight dependence on the points included in the fits. The SCF energy difference between the rotational saddle point and the ground state estimated by extrapolating data from the three largest basis sets is 1.015 kcal/mol. The extrapolation including the three smallest basis sets gives an energy barrier of 1.024 kcal/mol. The latter extrapolation provides an improvement over the cc-pVQZ results without significant additional computational cost and is recommended for larger systems for which cc-pVQZ is the largest feasible basis set.

Second-order energies

The absolute magnitude of the second-order correlation energy in methanol increases as the basis set is enlarged, but its contribution to the barrier height decreases (Table 2). Comparison of the SCF and MP2 energies with the small basis sets in Table 1 suggests that second-order correlation effects stabilize the minimum-energy structure more than they stabilize the rotational saddle point and thus increase the rotational barrier. However, analysis of the behavior of E^2 as the basis set is enlarged reveals that the E^2 contribution lowers the barrier slightly. The results of a systematic comparison of several commonly used extrapolation formulas are summarized in Table 3. The single-exponential fit in Eq. (1) and the double-exponential function of the form $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A\exp(-X) + B\exp(-X^2)$ are statistically

Table 2. Second-order correlation energy (mhartrees) in anti and syn conformers of methanol. The values in the last column indicate the E^2 contribution to the rotational barrier (kcal/mol)

Basis set	E^2 (anti)	E^2 (syn)	E^2 contribution
cc-pVDZ	−338.2781	−337.9949	0.17772
cc-pVTZ	−428.2066	−428.1295	0.04838
cc-pVQZ	−459.5196	−459.4914	0.01768
cc-pV5Z	−471.8995	−471.8923	0.00452
cc-pV6Z	−477.3748	−477.3724	0.00149
MP2-R12	−484.6204	−484.6230	−0.00162

poor and significantly underestimate the correlation energy at the limit, in agreement with previous reports [26]. Extrapolation using Eq. (5) with $\alpha = 4$ is unreliable with small basis sets and is only slightly better than the exponential models with larger basis sets. When α in Eq. (5) is optimized, a better fit is obtained but the extrapolated energies are strongly basis set dependent. We observed that α also depends on the points included and that it differs significantly from the value of 3.9 found by Martin. The commonly used [7] fit of the form $E_\infty + A_3X^{-3}$ does not yield satisfactory results when double-zeta basis set data are included, but performs very well when both the cc-pVDZ and cc-pVTZ data are excluded. The need to exclude cc-pVDZ results when using Eq. (6) was stressed earlier [7, 8], but our results suggest that extrapolations according to Eq. (6) should also exclude cc-pVTZ data. The model of the form $E_\infty + A_3X^{-3} + A_4X^{-4}$ and a related two-parameter model $E_\infty[1 + A_3X^{-3}(1 + A_4X^{-1})]$, where $A_4 = 6.8470 \exp(1.2234A_3) - 1.0280$ [13], were found to give quite good fits; however, both models display some systematic dependence of the extrapolated value on the number of included points. In particular, both equations appear to overestimate the correlation energy when cc-pVDZ or cc-pVTZ data are included. The use of Eq. (7) was inspired by a recent observation that such truncation yields very good results at the MP2 level [12]. It is important to note that in the current work we use this formula to extrapolate only the second-order correlation energy, while Eq. (7) was used previously to extrapolate total energies. Fitting Eq. (7) to the second-order correlation energies gives good fits (Fig. 2) and the extrapolated energy is only slightly dependent on the choice of data points. Notably, the extrapolated energy is within 1.5 mE_h of the R12-MP2 value regardless of the choice of data points. Last, separate extrapolations of singlet and triplet pair contributions were tested. Extrapolation of singlet pairs with the formula $E = E_\infty + A_3X^{-3}$ and triplet pairs with the formula $E = E_\infty + A_3X^{-5}$ underestimates second-order energies significantly unless both the cc-pVDZ and the cc-pVTZ data are excluded. In particular, the two-point fit with cc-pVTZ and cc-pVQZ data gives a limiting value that is 4 mE_h above the MP2-R12 result. The discrepancy originates mainly from the underestimation of singlet pair energies and appears to be a general problem [15]. Extrapolation of pair energies according to

Table 3. Comparison of different extrapolation formulas in predicting limiting values for the second-order correlation energy of the anti conformer of methanol. The E_∞ values are given in millihartrees. The coefficient A_4 in second column from the right is not an independent fitting parameter but is related to A_3 by the formula $A_4 = 6.8470 \exp(1.2234A_3) - 1.0280$ [13]. The MP2-R12 estimate is −484.9 mE_h

	$E_\infty + A\exp(-BX)$		$E_\infty + A\exp(-X) + B\exp(-X^2)$		$E_\infty + A_4(X+0.5)^{-4}$		$E_\infty + A_4(X+0.5)^{-\alpha}$		$E_\infty + A_3X^{-3}$		$E_\infty + A_3X^{-3} + A_5X^{-4}$		$E_\infty[1 + A_3X^{-3}(1 + A_4X^{-1})]$		$E_\infty + A_3X^{-3} + A_5X^{-5}$	
	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2
2 → 4	−476.2		−477.7		−467.5	5×10^{-5}	−494.4		−472.8	3×10^{-5}	−488.0		−487.7	1×10^{-8}	−485.9	
2 → 5	−478.0	5×10^{-7}	−478.4	3×10^{-7}	−471.8	1×10^{-4}	−491.1	5×10^{-7}	−476.4	7×10^{-5}	−487.4	7×10^{-8}	−487.5	8×10^{-8}	−485.9	2×10^{-10}
2 → 6	−479.2	2×10^{-6}	−479.1	1×10^{-6}	−474.4	2×10^{-4}	−489.7	2×10^{-6}	−478.4	9×10^{-5}	−486.8	3×10^{-7}	−487.2	5×10^{-7}	−485.7	4×10^{-8}
3 → 4					−477.6				−482.4				−487.9			
3 → 5	−480.0		−479.1		−479.5	2×10^{-6}	−486.4		−483.4	5×10^{-7}	−486.3		−487.4	7×10^{-8}	−485.9	
3 → 6	−480.8	7×10^{-8}	−479.8	3×10^{-7}	−480.6	5×10^{-6}	−485.6	2×10^{-8}	−483.9	9×10^{-7}	−485.8	2×10^{-8}	−487.0	4×10^{-7}	−485.5	4×10^{-8}
4 → 5					−482.0				−484.9				−486.8			
4 → 6	−481.7		−480.6		−482.5	1×10^{-7}	−484.0		−484.9	3×10^{-12}	−484.9		−486.3	6×10^{-8}	−484.9	
5 → 6					−483.1				−484.9				−485.7			

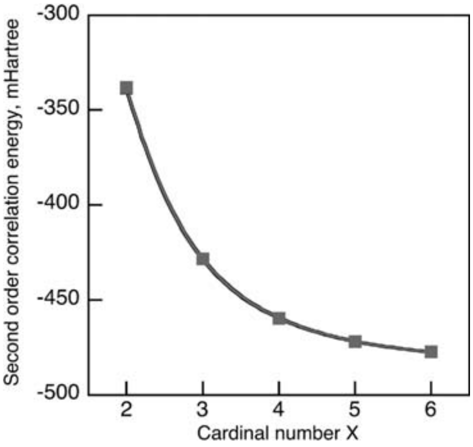

Fig. 2. Convergence of the second-order correlation energy with respect to basis set size. The fit to Eq. (7) is shown. The *lines* for the anti and the syn conformations overlap

$E = E_\infty + A_3(X + 0.5)^{-3}$ and $E = E_\infty + A_3(X + 0.5)^{-5}$ gives good agreement with the MP2-R12 data when cc-pVDZ results are excluded. All reliable extrapolation schemes predict that the second-order valence correlation energy in methanol is about 485 mE_h and that the second-order contribution to the energy barrier is less than 0.01 kcal/mol. Fits to Eq. (7), and separate extrapolations of singlet and triplet pair energies, suggest that the rotational barrier is lowered by 0.002–0.006 kcal/mol. The rotational barrier in methanol at the MP2 level is estimated to be 1.011 ± 0.002 kcal/mol.

Third-order energies

The convergence of the third-order correlation energy is slow and the limiting value appears to approach zero (Fig. 3). Power series truncated after the first term, for example, Eq. (6), give poor fits ($\chi^2 = 1 \times 10^{-5}$) but several truncations after the second term give good fits ($\chi^2 = 1 \times 10^{-8}$) when cc-pVDZ data are excluded. Partial-wave expansion of atomic correlation energies suggests that the third-order energy should converge as X^{-4} for natural parity singlet states and as X^{-6} for triplet states [1]. Extrapolation according to equations $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_4X^{-4} + A_6X^{-6}$ and $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_4(X + 0.5)^{-4} + A_6(X + 0.5)^{-6}$ predicted that the limiting value of the E^3 contribution is about 3.5–4.0 mE_h, while fits according to $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_3(X + 0.5)^{-3} + A_5(X + 0.5)^{-5}$ predicted a limiting value of 2.5 mE_h. All the models predicted that the E^3 contribution lowers the barrier by 0.017 ± 0.005 kcal/mol. Fitting of differential E^3 contributions by a single-exponential function is also statistically acceptable ($\chi^2 = 2 \times 10^{-9}$) and predicts that the E^3 contribution is between 0.0018 and 0.0020 kcal/mol. We estimate that the basis set limit for the rotational barrier in methanol at the MP3 level is 0.994 ± 0.005 kcal/mol. The E^2 and E^3 contributions move to opposite directions as the basis set increases.

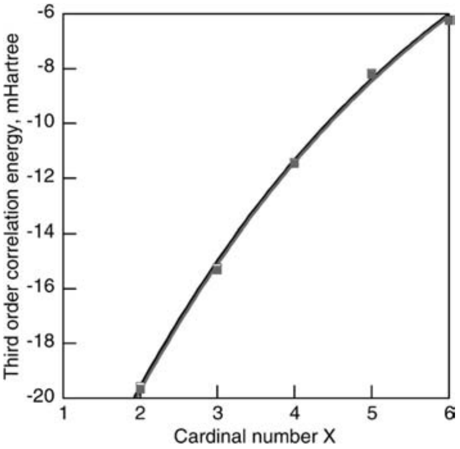

Fig. 3. Convergence of the third-order correlation energy with respect to basis set size. The fit to a single-exponential function is shown. The *lines* for the anti and the syn conformations overlap

Table 4. Fourth-order correlation energy without triples contribution (mhartrees) in anti and syn conformers of methanol. The values in the last column indicate the E^4 contribution to the rotational barrier (kcal/mol)

Basis set	$E^{4(\mathrm{SDQ})}$ (anti)	$E^{4(\mathrm{SDQ})}$ (syn)	E^4 contribution
cc-pVDZ	−4.8772	−4.8545	0.0142
cc-pVTZ	−3.7769	−3.7591	0.0112
cc-pVQZ	−3.0807	−3.0672	0.0085
cc-pV5Z	−2.9137	−2.9036	0.0063

Such behavior is characteristic of so-called class II systems, where E^2 overestimates and E^3 corrects correlation effects with finite basis sets [3]. Alcohols belong to class II because the two electron pairs cluster in the lone-pair region of the oxygen atom.

Fourth-order energies

Fourth-order correlation energies without triples contribution are small and appear to converge reasonably well (Table 4). The fit to Eq. (6) is poor and overestimates the $E^{4(\mathrm{SDQ})}$ contribution unless cc-pVDZ results are excluded. Fits to Eqs. (1) and (7) are of similar quality and predict that the $E^{4(\mathrm{SDQ})}$ contribution in the basis set limit is about 2.55 mhartrees for both the ground state and the rotational saddle point. The overall $E^{4(\mathrm{SDQ})}$ contribution to the barrier height at the basis set limit (0.003 kcal/mol) is almost negligible. The magnitude of triples contribution to the fourth-order correlation energy increases with increasing basis set. The limiting values appear to be −19.5154 and −19.5179 mhartrees for the anti and syn conformers, respectively (Fig. 4); thus, the triples contribution increases the rotational barrier by only 0.0015 kcal/mol. In absolute terms, the triples contribution at the basis set limit is significantly larger than pair correlation contributions. This dominance of the triples contribution and the increase of the absolute magnitude of the triples contribution with increasing size of the basis set have been observed previously for a number of compounds [33].

Coupled-cluster energies

Coupled-cluster calculations at the CCSD level include electron correlation effects due to singly and doubly exited states to infinite order and provide an accurate description of electronic structures near equilibrium geometries. Little is known about the convergence properties of coupled-cluster energies in molecules [36] but applying X^{-3} extrapolation to the singlet pairs and X^{-5} extrapolation to triplet pairs appears to give good results [14]. We were able to perform CCSD calculations up to and including cc-pV5Z basis sets (Table 5). Somewhat surprisingly, the sign of the electron correlation effect is incorrectly predicted with smaller basis sets. None of the four extrapolation schemes performed significantly better than the others (Table 6). Exponential functions typically give less negative limiting values than truncated power series. The extrapolation based on equation $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_3X^{-3} + A_5X^{-5}$ is more accurate than the exponential fit, but the strong dependence of the limiting energies on the choice of points included indicates that this may not be the best method to calculate basis set limit energies at the CCSD level. Keeping these limitations in mind, we estimate that the CCSD contribution lowers the rotational barrier by 0.015–0.020 kcal/mol from the SCF limit.

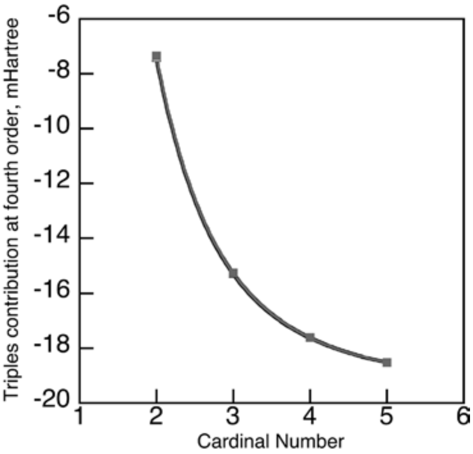

Fig. 4. Convergence of triples contribution at fourth order with respect to basis set size. The fit to Eq. (7) is shown. The *lines* for the anti and the syn conformations overlap

Table 5. Correlation energy at the CCSD level (mhartrees) in anti and syn conformers of methanol. The values in the last column indicate the CCSD contribution to the rotational barrier (kcal/mol)

Basis set	E^{CCSD} (anti)	E^{CCSD} (syn)	E^{CCSD} contribution
cc-pVDZ	−363.11321	−362.91435	0.1247
cc-pVTZ	−446.73658	−446.71558	0.0131
cc-pVQZ	−473.46241	−473.47554	−0.0082
cc-pV5Z	−482.47034	−482.49387	−0.0147

Comparison of CCSD(T) and MP4(SDTQ) results suggests that higher-order correlation effects change the barrier by no more than 0.001 kcal/mol. By adding E^2, E^3, $E^{4(\mathrm{SDQ})}$, and $E^{4(\mathrm{T})}$ contributions to the SCF value, a focal-point estimate of 0.999 ± 0.007 kcal/mol is obtained for the rotational barrier in methanol. This value is in excellent agreement with a precise experimental result after correction for zero-point effects [34, 35]. It should be noted that reproduction of energy differences with such accuracy is possible for conformational isomers because errors due to inaccuracies in molecular geometries tend to cancel out when two conformers of the same molecule are compared. For practical calculations of conformational energies in larger molecules, accuracy such as reported here for methanol is rarely needed and one should ask what is the computationally most economical approach to achieve the desired accuracy.

Conclusions

Systematic convergence of energies of two conformers with respect to basis set size can be employed to accurately estimate conformational energies at the basis set limit. Current results suggest that for molecules without multiple bonds, extrapolation of HF energy according to $E_X^{\mathrm{HF}} = E_\infty^{\mathrm{HF}} + A\exp(-BX)$ and extrapolation of second-order correlation energy according to $E_X^{\mathrm{cor}} = E_\infty^{\mathrm{cor}} + A_3X^{-3} + A_5X^{-5}$ using cc-pVDZ, cc-pVTZ, and cc-pVQZ data may be a good approach. Separate extrapolation of singlet and triplet pair energies according to $E = E_\infty + A_3(X+0.5)^{-3}$ and $E = E_\infty + A_3(X+0.5)^{-5}$, respectively, is recommended when

Table 6. Comparison of four different extrapolation formulas in predicting limiting values for the CCSD correlation energy of the anti conformer of methanol. The E_∞ values are given in milli hartrees. The CCSD-R12 estimate is −490.0 mE_h

	$E_\infty + A\exp(-BX)$		$E_\infty + A\exp(-X) + B\exp(-X^2)$		$E_\infty + A_3X^{-3}$		$E_\infty + A_3X^{-3} + A_5X^{-5}$	
	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2	E_∞	χ^2
2 → 4	−486.0		−489.0		−486.5	2×10^{-5}	−495.4	
2 → 5	−486.5	5×10^{-8}	−488.3	2×10^{-7}	−488.3	2×10^{-5}	−493.9	5×10^{-7}
3 → 5	−487.0		−487.7		−492.5	5×10^{-7}	−491.5	

cc-pV5Z or better second-order energies are available. Extrapolations of third-order correlation energy may be performed according to $E_X^{\text{cor}} = E_\infty^{\text{cor}} + A_3X^{-3} + A_4X^{-4}$, but cc-pVDZ data should be excluded. Extrapolation of total correlation energies up to the fourth order or at the CCSD level according to $E_X^{\text{cor}} = E_\infty^{\text{cor}} + A_3X^{-3} + A_5X^{-5}$ appears to give satisfactory results.

Care must be exercised when interpreting correlation effects calculated with finite basis. For example, calculations with cc-pVDZ and cc-pVTZ basis sets predict that electron correlation increases the rotational barrier, while extrapolation to the basis set limit reveals the opposite effect.

Acknowledgement. This project was supported by Provost Funds at University of California, Santa Barbara (UCSB). The computational resources were provided partially by the National Computational Science Alliance and UCSB's Supercomputer Facility. We also acknowledge the Horgan Award (University of Missouri-Columbia) to K. K., which made possible the purchase of additional computational resources. We thank Robert Gdanitz and Bernie Kirtman for valuable discussions and Jozef Noga for providing us with a copy of the DIRCCR12-OS program.

References

1. Kutzelnigg W, Morgan JD III (1992) J Chem Phys 96:4484
2. Gdanitz RJ (2000) J Chem Phys 113:5145
3. Forsberg B, He Z, He Y, Cremer D (2000) Int J Quantum Chem 76:306
4. Cremer D, Kraka E, He Y (2001) J Mol Struct 567–568:275
5. Feller D (1992) J Chem Phys 96:6104
6. Martin JML (1996) Chem Phys Lett 259:669
7. Helgaker T, Klopper W, Koch H, Noga J (1997) J Chem Phys 106:9639
8. Halkier A, Helgaker T, Jorgensen P, Klopper W, Koch H, Olsen J, Wilson AK (1998) Chem Phys Lett 286
9. Truhlar DG (1998) Chem Phys Lett 294:45
10. Halkier A, Klopper W, Helgaker T, Jørgensen P (1999) J Chem Phys 111:4424
11. Jensen F (2000) Theor Chem Acc 104:484
12. Lee JS, Park SY (2000) J Chem Phys 112:10746
13. Varandas AJC (2000) J Chem Phys 113:8880
14. Klopper W (2001) J Chem Phys 115:761
15. Valeev EF, Allen WD, Hernandez R, Sherrill CD, Schaefer HF III (2003) J Chem Phys 118:8594
16. Csaszar AG, Allen WD, Schaefer HF III (1998) J Chem Phys 108: 9751
17. Tschumper GS (2001) J Chem Phys 114:225
18. Sancho-García JC, Pérez-Jiménez AJ, Pérez-Jordá JM, Moscardó F (2001) Chem Phys Lett 342:452
19. Klopper W, Bak KL, Jørgensen P, Olsen J, Helgaker T (1999) J Phys B At Mol Opt Phys 32: R103
20. Feller D, Dixon DA (2001) J Chem Phys 115:3484
21. Klopper W (2001) Mol Phys 99:481
22. Park SY, Lee JS (2002) J Phys Chem 116:5389
23. Huh SB, Lee JS (2003) J Chem Phys 118:3035
24. Peterson KA, Kendall RA, Dunning TH Jr (1993) J Chem Phys 99:1930
25. Peterson KA, Woon DE, Dunning TH Jr (1994) J Chem Phys 100:7410
26. Helgaker T, Gauss J, Jørgensen P, Olsen J (1997) J Chem Phys 106:6430
27. Schwartz C (1962) Phys Rev 126:1015
28. Dunning TH Jr (1989) J Chem Phys 90:1007
29. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98. Gaussian, Pittsburgh, PA
30. Noga J, Valiron P (2002) In: Computational chemistry: reviews of current trends, vol 7. World Scientific, Singapore, p 131
31. Noga J, Klopper W, Helgaker T, Valiron P (2003) DIRCCR12-OS (program performing coupled-cluster calculations with correlation cusp correction using the R12 theory)
32. Noga J, Valiron P (2003) Collect Czech Chem Commun 68:340
33. He Y, Cremer D (2000) Theor Chem Acc 105:110
34. De Lucia FC, Herbst E, Anderson T, Helminger P (1989) J Mol Spectrosc 134:395
35. Xu LH, Lees RM, Hougen JT (1999) J Chem Phys 110:3835
36. Sancho-García JC, Pérez-Jiménez AJ, Pérez-Jordá JM, Moscardó F (2001) J Chem Phys 115:3698