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Letter

Extrapolation to the limit of a complete basis set for electronic structure calculations on the N_2 molecule

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Abstract. Results obtained from nonrelativistic electronic structure calculations using finite Gaussian basis sets are extrapolated to the limit of a complete basis set, employing the results of explicitly correlated coupled-cluster calculations including singles and doubles substitutions (CCSD). For N_2, the basis-set limits for the electronic binding energy, equilibrium bond length and harmonic vibrational wave number are established for the CCSD model including a perturbative correction for triples substitutions and for the internally contracted multireference configuration interaction method. The resulting numbers are in good agreement with experimental values.

Key words: Nitrogen molecule – Electronic structure calculations – Basis-set limit – Binding energy – Spectroscopic constants

1 Introduction

The accurate computational description of bonding in the N_2 molecule has been a challenging electronic structure method problem for many years [1–16]. Almost 50% of the electronic binding energy (D_e) is due to electron-correlation effects, and a quantitatively accurate calculation of these effects is therefore essential. In 1985, Ahlrichs and co-workers [1] noted that in order to compute D_e accurately to within 1 kcal/mol, i.e. to within "chemical accuracy", such complex electron-correlation treatments would be required for diatomics or larger molecules that they could not be performed with the methods applied at the time [1]. More than a decade later, such calculations still do not represent a *daily routine* for quantum chemists, but today the most extensive calculations are getting close to, or are indeed achieving, the desired chemical accuracy [14–16]. As shown in this letter, one possible way of obtaining chemical accuracy for the N_2 molecule is by exploiting extrapolations to the limit of a complete one-particle basis set (basis-set limit).

First, extrapolations to the basis-set limit are carried out for several electron-correlation treatments. These extrapolations are calibrated by comparing the extrapolated coupled-cluster singles-and-doubles (CCSD) results for the equilibrium distance (r_e) and harmonic vibrational wave number (ω_e) with a near-complete basis set calculation in the framework of the explicitly correlated coupled-cluster approach. Second, the limits are compared with the existing literature on the computation of D_e, r_e and ω_e, thereby establishing the magnitude of various subtle effects such as the Davidson correction in configuration interaction (CI) theory, the perturbative triples correction in coupled cluster theory [CCSD(T)], and core-core and core-valence correlation effects. By doing so, a consistent overall assessment of electronic-structure calculations and electron-correlation effects is obtained.

2 Extrapolations

Extrapolations to the basis-set limit became popular [17–22] with the development of the correlation-consistent basis sets of the type cc-pVnZ (n = D, T, Q, 5, 6), which represent systematic sequences of basis sets of increasing size and accuracy [23]. When augmented with diffuse functions, the basis sets are denoted as aug-cc-pVnZ, and when augmented with tight functions, the sets are called (aug-)cc-pCVnZ.

By fitting results obtained from basis sets with different n, an extrapolation to $n \to \infty$ can be achieved. For this purpose, the "cardinal number" X is introduced, where $X = 2, 3, 4, 5, 6$ for n = D, T, Q, 5, 6, respectively. Nonlinear three-parameter exponentional fits of the type

$$A = A_\infty + \alpha \exp(-\beta X) \ , \qquad (1)$$

were among the first to be explored [17, 23]. The problem with this type of fit, however, is that the rate of convergence of molecular properties is exaggerated by the exponentional form. The well-known slow conver-

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gence of electron-correlation effects with basis-set improvement is better accounted for by inverse-power fits. Possible forms are [18–22, 24]:

$$A = A_\infty + \alpha(X+\beta)^{-\gamma} \ , \tag{2}$$

$$A = A_\infty + \sum_{k=3}^{k_{\max}} \alpha_k X^{-k} \ , \tag{3}$$

or alternatively, a fit in inverse powers of the number of basis functions (N) [24, 25]:

$$A = A_\infty + \sum_{k=1}^{k_{\max}} \alpha_k N^{-k} \ . \tag{4}$$

One of the messages of this letter is that, when based on data from correlation-consistent basis sets with cardinal numbers up to $X = 6$, inverse-power fits of the type in Eqs. (2), (3), or (4) yield basis-set limits for D_e that are about 1 kcal/mol *larger* than the respective limits obtained from the exponentional form in Eq. (1).

3 Computational details

The electronic structure methods discussed in this letter are the restricted closed- and open-shell CCSD [26, 27], CCSD(T) [28–30], the internally contracted multireference configuration interaction method (IC-MRCI) [31–34], and the IC-MRCI method including the Davidson correction (IC-MRCI + Q) [35–37].

In all the internally contracted multireference calculations, the reference space is a complete active space (CAS) with ten electrons distributed among eight valence orbitals. These multireference calculations are sometimes denoted IC-MRCI(10) or IC-MRCI(10) + Q. However, there are minor differences between the *orbitals* used in the multireference calculations in the literature. The optimization of the orbitals in a CAS self-consistent field (CASSCF) calculation with two inactive and eight active orbitals (the CAS(10) space) leads to an undesired mixing of the inactive core orbitals with two of the active valence orbitals at very large distances, at dissociation, where these two active orbitals become doubly occupied. Almlöf et al. [5] circumvent this problem by using the smaller CAS(6) space with four inactive and six active orbitals during the CASSCF orbital optimization [5, 8, 11]. Peterson and co-workers, however, use a two-step procedure to optimize the orbitals. These authors start with the same CAS(6) orbital optimization, but then perform a second CASSCF orbital optimization using the CAS(10) space while *freezing* its two inactive orbitals [10, 12, 14, 15]. In this letter, the reported IC-MRCI limits refer to the approach chosen by Peterson and co-workers.

It is expected that the different orbitals lead to differences in the computed D_e of roughly ± 0.2 kcal/mol. Using the cc-pV5Z basis set, the two-step procedure yields a minimum valence IC-MRCI energy (−109.39895 E_h [14]) that is 0.15 mE_h = 0.1 kcal/mol *lower* than the IC-MRCI result using the CAS(6) orbitals (−109.39880 E_h [8]). On the other hand, Werner and Knowles find CAS(10)/IC-MRCI energies of about 0.1–0.2 kcal/mol *above* the CAS(6)/IC-MRCI energies, using basis sets of the type 5*s*4*p*3*d*2*f*1*g* or 8*s*6*p*3*s*2*p*1*d* [8]. At dissociation, the different orbital optimizations are equivalent, and thus, depending on the basis sets used, sometimes more electronic binding energy is obtained using the two-step approach, while sometimes D_e is increased by using the CAS(6) orbitals.

CCSD results of near-complete basis set quality were obtained by means of the explicitly correlated CCSD-R12/B method [38, 39]. The corresponding calculations were performed with the program `DIRCCR12-95` [40] on IBM RS/6000 990 workstations at the University of Oslo, using a Gaussian basis set of the type 20*s*15*p*12*d*10*f*, described in detail elsewhere [24]. The atomic mass of $M(\mathrm{N}^{14}) = 14.003074008$ a.m.u. [41] was used.

4 Results

Various extrapolation schemes are compared in Table 1, and the final extrapolation to the basis-set limit of IC-MRCI + Q theory is shown in Table 2. MRCI methods (with a Davidson correction as required) are almost universally in excellent agreement with the full CI level [7, 8, 42, 43], and later we will see that the extrapolation to the limit of a complete basis set indeed yields IC-MRCI + Q results that are in excellent agreement with experimental values.

The extrapolation of Table 2 is based on valence CCSD results from basis sets ranging from cc-pCV5Z to cc-pCV6Z, using valence CCSD-R12/B calculations as a calibration. Table 3 compares this extrapolation with an extrapolation based on valence IC-MRCI data of Wilson et al. [14], which leads to essentially the same limits. Finally, in Table 4, the established basis-set limits at various levels of electronic structure theory are compared with recent high-accuracy calculations and previous extrapolations reported in the literature.

Table 1. Comparison of various extrapolations of the form in Eq. (3) or Eq. (4) as a function of $k_{\max}$ and the input data [15], which ranges from cc-pCV($n_{\min}$)Z to cc-pCV($n_{\max}$)Z, for the extrapolation to the valence-only coupled-cluster singles-and-doubles (CCSD) basis-set limit

$k_{\max}$	$n_{\min}$	$n_{\max}$	D_e (kcal/mol)	r_e (pm)	ω_e (cm^{-1})
A. Eq. (3)					
3	5	6	218.5	109.16	2442.8
3	4	6	218.5	109.14	2443.8
3	3	6	218.5	109.13	2444.0
4	4	6	218.5	109.19	2441.4
4	3	6	218.6	109.15	2443.5
B. Eq. (4)					
2	4	6	218.6	109.19	2441.6
2	3	6	218.7	109.15	2443.8

Table 2. Extrapolation to the basis-set limit of the electronic binding energy D_e (kcal/mol), equilibrium bond length r_e (pm), and harmonic vibrational wave number ω_e (cm^{-1}) of the nitrogen molecule at the level of all-electron IC-MRCI + Q theory

	Basis set / extrapolation	Energy (E_h)	D_e (kcal/mol)	r_e (pm)	ω_e (cm^{-1})	Ref.
Valence-only correlation						
CCSD	cc-pCVQZ	−109.3861	214.33	109.29	2436.0	[15]
	cc-pCV5Z	−109.3943	216.38	109.21	2440.2	[15]
	cc-pCV6Z	−109.3973	217.28	109.19	2441.3	[15]
	$a + b\exp(-cX)$	−109.3977	217.8			[15]
	$a + b\exp(-cX)$	−109.3980	217.9	109.20		[14]
	$a + bX^{-3}$ (cf. Table 1)	−109.4014	218.5	109.16	2442.8	
CCSD-R12/B	$20s15p12d10f$	−109.4001		109.17	2442.8	
Estimated valence CCSD basis-set limit			218.5	109.16	2442.8	
Perturbative triples correction (valence only)						
CCSD(T)	cc-pCV6Z		+9.2	+0.72	−80.1	[15]
Extrapolated valence CCSD(T) basis-set limit			227.7	109.88	2362.7	
Core- and core-valence correlation correction						
CCSD(T)	cc-pCV6Z		+0.8	−0.21	+10.0	[15]
Extrap. all-electron CCSD(T) basis-set limit			228.5	109.67	2372.7	
	$a + b\exp(-cX)$		227.7			[15]
Full triples correction						
CCSDT	cc-pVQZ			−0.06		[45]
Extrap. all-electron CCSDT basis-set limit				109.61		
CCSD(T) → IC-MRCI + Q increment						
IC-MRCI + Q	cc-pCV5Z		+0.3	+0.09	−11.2	[15]
Extrap. all-electron IC-MRCI + Q basis-set limit			228.8	109.76	2361.5	
Experiment			228.4	109.77	2358.6	[46, 47]

Table 3. Comparison of two different extrapolations to the basis-set limit of the electronic binding energy D_e (kcal/mol), equilibrium bond length r_e (pm), and harmonic vibrational wave number ω_e (cm^{-1}) of the nitrogen molecule at the level of all-electron IC-MRCI + Q theory

	D_e (kcal/mol)	r_e (pm)	ω_e (cm^{-1})
Experiment [46, 47]	228.4	109.77	2358.6
A. Extrapolation based on valence CCSD data [15]			
Valence CCSD	218.5(2)	109.16(1)	2443(1)
Valence CCSD(T)	227.7(2)	109.88(1)	2363(1)
All-electron CCSD(T)	228.5(3)	109.67(1)	2373(1)
All-electron IC-MRCI + Q	228.8(4)	109.76(2)	2362(2)
B. Extrapolation based on valence IC-MRCI data [14]			
Valence IC-MRCI	228.4(2)	109.91(1)	2358(1)
All-electron IC-MRCI + Q	228.7(4)	109.77(2)	2361(2)

4.1. Electronic binding energy

The valence CCSD basis-set limit for the electronic binding energy of N_2 is extrapolated to $D_e = 218.5$ kcal/*mol*, obtained in a consistent manner from several fits of the form in Eq. (3) or Eq. (4) (Table 1). In Ref. [24], it was found that the extrapolation in Eq. (3) applied to the cc-pCV5Z and cc-pCV6Z data with $k_{max} = 3$ yields the most accurate estimates to the basis-set limits, and this extrapolation is recommended for further use (first row in Table 1).

It is expected that the (valence-only) triples correction computed at the valence cc-pCV6Z/CCSD(T) level is very accurate, in error by less than 0.1 kcal/mol, as the basis-set requirement for the triples correction is not expected to be high [44]. This correction is +9.2 kcal/mol [15], yielding an extrapolated valence CCSD(T) basis-set limit of $D_e = 227.7$ kcal/mol, which is supposed to be accurate to within 0.2 kcal/mol.

The effects of core-core and core-valence correlation are well established, both at the coupled-cluster and multireference CI levels [8, 11, 13, 15], and the differences between CCSD(T), IC-MRCI, and IC-MRCI + Q are known from various calculations using appropriate basis sets [8, 11, 14, 15]. The various corrections to D_e are summarized in the cycle shown below.

Based on these increments, the all-electron IC-MRCI + Q basis-set limit is extrapolated to $D_e = 228.8(4)$ kcal/mol. As indicated by the number in parentheses, the uncertainty in this value is estimated to 0.4 kcal/mol. This uncertainty is obtained by adding to the uncertainty in the valence CCSD(T) limit (0.2 kcal/mol) an uncertainty of 0.1 kcal/mol for each correction needed to get from the valence CCSD(T) to the all-electron IC-MRCI + Q level.

Alternatively, the basis-set limit for the valence IC-MRCI level is extrapolated from the results obtained by Wilson et al. [21], who employed the cc-pVnZ basis sets

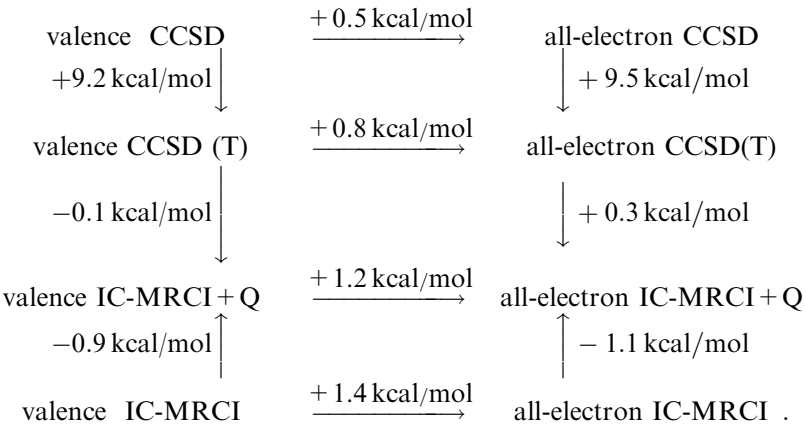


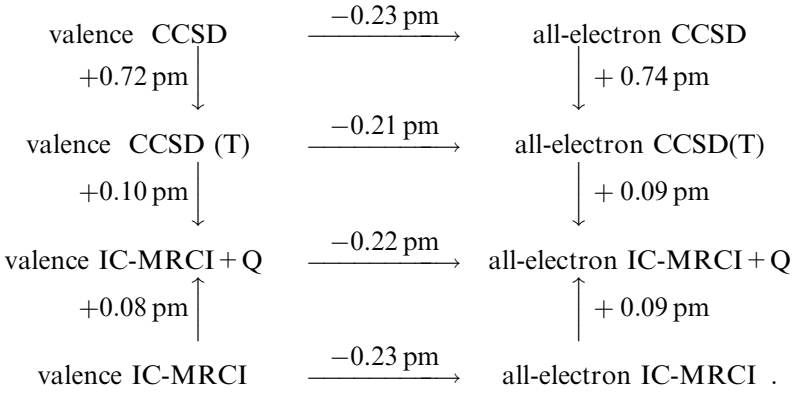
Table 4. Comparison of selected calculations and estimates of the electronic binding energy D_e (kcal/mol), equilibrium bond length r_e (pm), and harmonic vibrational wave number ω_e (cm^{-1}) of the nitrogen molecule

	D_e (kcal/mol)	r_e (pm)	ω_e (cm^{-1})
Experiment [46, 47]	228.4	109.77	2358.6
All-electron r_{12}-MR-ACPF/11*s*9*p*6*d*4*f*2*g*1*h* [16]	228.4	109.78	2360.6
A. Valence CCSD(T) level			
CCSD(T)/6*s*5*p*4*d*3*f*2*g* [6]	–	110.0	2357
CCSD(T)/CV[a] [11]	223.3	109.99	2357.2
CCSD(T)/cc-pV6Z [14]	226.4	109.92	2361.0
CCSD(T)/cc-pCV6Z [15]	226.5	109.91	2361.2
Estimated CBS [14]	227.0	109.92	–
Estimated CBS [15]	226.9	–	–
Extrapolated basis-set limit[b]	227.7(2)	109.88(1)	2363(1)
B. All-electron CCSD(T) level			
CCSD(T)/CV[a] [11]	224.1	109.78	2367.0
CCSD(T)/cc-pCV6Z [15]	227.3	109.70	2371.1
Estimated CBS [15]	227.7	–	–
Extrapolated basis-set limit [19, 20]	228.5	–	–
Extrapolated basis-set limit[b]	228.5(3)	109.67(1)	2373(1)
C. Valence IC-MRCI level			
IC-MRCI/[8*s* + 1*s*][6*p* + 1*p*]4*d*3*f*2*g* [8]	225.6	109.96	2352.7
IC-MRCI/cc-pCV5Z [15]	226.4	109.95	2356.1
IC-MRCI/pV6Z [11]	227.1	110.0	–
IC-MRCI/cc-pV6Z [14]	227.2	109.94	2356.6
Estimated CBS [14]	227.8	109.94	–
Estimated CBS [15]	227.3	–	–
Extrapolated basis-set limit[b]	228.5(3)	109.90(2)	2359(2)
D. Valence IC-MRCI + Q level			
IC-MRCI + Q/cc-pCV5Z [15]	225.5	110.03	2348.7
IC-MRCI + Q/pV6Z [11]	226.3	110.0	–
Estimated CBS [15]	226.4	–	–
Extrapolated basis-set limit[b]	227.6(3)	109.98(2)	2352(2)
E. All-electron IC-MRCI level			
IC-MRCI/[8*s* + 1*s*]8*p*5*d*3*f*2*g*1*h* [8]	227.7	109.74	2366.6
IC-MRCI/cc-pCV5Z [15]	227.8	109.72	2367.4
Estimated CBS [15]	228.8	–	–
Extrapolated basis-set limit[b]	229.9(3)	109.67(2)	2371(2)
F. All-electron IC-MRCI + Q level			
IC-MRCI + Q/[8*s* + 1*s*]8*p*5*d*3*f*2*g*1*h* [8]	226.7	109.82	2358.0
IC-MRCI + Q/cc-pCV5Z [15]	226.6	109.81	2358.6
Estimated CBS [15]	227.7	–	–
Extrapolated basis-set limit[b]	228.8(4)	109.76(2)	2362(2)

[a] CV denotes a 7*s*6*p*5*d*4*f*1*g* basis set, see Ref. [11]
[b] Extrapolation based on valence CCSD data

up to n = 6. This extrapolation yields 228.4 kcal/mol (Table 3). Various extrapolations of the form in Eq. (3) or Eq. (4) lead to the same result. Thus, in this case, the estimated all-electron IC-MRCI + Q basis-set limit becomes 228.7 kcal/mol after adding the Davidson correction and the core-core and core-valence correlation effects, consistent with the basis-set limit of 228.8 kcal/mol obtained from the extrapolation of the CCSD data (Table 2).

At the valence CCSD level, the extrapolated limits are $r_e = 109.16$ pm and $\omega_e = 2442.8\,\mathrm{cm}^{-1}$ (Table 2), which are in perfect agreement with the directly computed CCSD-R12/B constants. This agreement is regarded as a calibration of the extrapolation procedure. Adding the CCSD(T) triples correction, the limits become $r_e = 109.88(1)$ pm and $\omega_e = 2363(1)\,\mathrm{cm}^{-1}$ (Table 3). Further increments for r_e are presented in the following cycles:

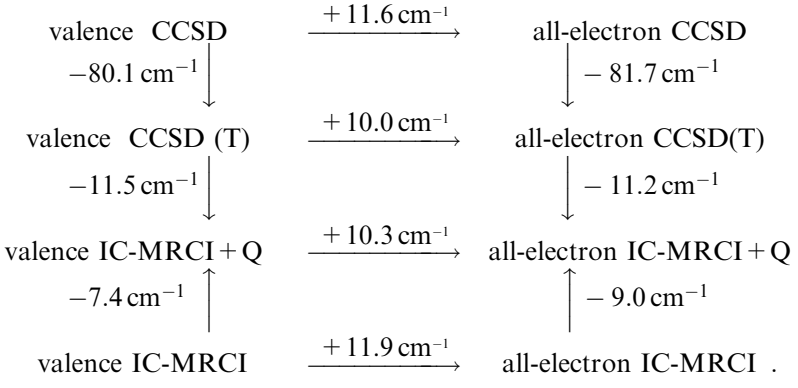


4.2. Spectroscopic constants

For r_e and ω_e, the same procedure is followed as for D_e. Obviously, one could first extrapolate the energies and then obtain the basis-set limits for the spectroscopic constants from a fit to these energies, or first obtain the spectroscopic constants from individual fits for each finite basis set and then extrapolate to the basis-set limits. The differences between the two approaches turn out to be negligible (±0.01 pm and $\pm 0.5\,\mathrm{cm}^{-1}$), and the extrapolation finally used is given in Eq. (3) with $k_{\max} = 3$ applied directly to the spectroscopic constants obtained from the cc-pCV5Z and cc-pCV6Z calculations.

Interestingly, the IC-MRCI method, which is not size-extensive, yields about the same r_e as the size-extensive CCSD(T) model, whereas for D_e, the CCSD(T) model is in close agreement with the IC-MRCI + Q level.

For ω_e, the increments are as follows:



5 Discussion

This letter provides an overview of high-accuracy electronic structure calculations on the N_2 molecule, accounting for electron-correlation effects. The following observations are made:

1. The all-electron IC-MRCI + Q level reproduces the experimental potential energy curve with chemical accuracy. However, the IC-MRCI + Q bond might be

a little too strong. In comparison with experiment, D_e is larger by 0.4 kcal/mol, r_e is shorter by 0.01 pm, and ω_e is larger by ca. 3 cm^{-1}. But in view of the uncertainties, the agreement with the experimental value is perfect.

2. The agreement of the all-electron CCSD(T) value for D_e (228.5 kcal/mol) with the experimental value may be fortuitous, since at this level, the bond length is too short by 0.1 pm and ω_e is too large by about 14 cm^{-1}. Notably, the disagreement of r_e with the experimental value would become even worse if the triples were treated fully at the CCSDT level [45]. Then, the bond would contract further by ca. 0.06 pm (Table 2).
3. The extrapolated CBS limits of Refs. [14] and [15] underestimate D_e by ca. 1 kcal/mol. The present all-electron CCSD(T) basis-set limit for D_e is in good agreement with the value estimated by Martin and Taylor [19, 20], but it is noted that the latter contains a purely empirical correction of +0.5 kcal/mol.
4. Gdanitz [16] has recently reported an all-electron r_{12}-MR-ACPF calculation in a 11*s*9*p*6*d*4*f*2*g*1*h* basis set that is in perfect agreement with the experimental value (Table 4). The calculation of this author is consistent with the extrapolated all-electron IC-MRCI+Q limit, since the ACPF approach based on 20 reference configurations as employed in Ref. [16] is reported to reproduce the IC-MRCI+Q results within a few tenths of a kcal/mol.
5. Traditional orbital-based electron-correlation treatments underestimate the binding energy by ca. 2 kcal/mol when the cc-pCV5Z basis is used, and by ca. 1 kcal/mol using the cc-pCV6Z basis set. To achieve basis-set errors smaller than 0.5 kcal/mol, cc-pCVnZ basis sets with $n \geq 8$ should be used, and $n \geq 14$ is required for errors of about 0.1 kcal/mol.
6. The Davidson correction (+Q) clearly improves the IC-MRCI results. Without this correction, the N_2 bond would be too strong.

6 Conclusion

We present here a careful analysis and re-evaluation of the published calculations on the binding energy of the N_2 molecule. Combined with new calculations at the CCSD-R12 level, this analysis has lead to an extrapolated all-electron IC-MRCI+Q basis-set limit of 228.8 kcal/mol for the binding energy of N_2, which is in good agreement with the experimental value of 228.4 kcal/mol. Similar extrapolations for r_e and ω_e give 109.76 pm and 2361.5 cm^{-1}, respectively, and are in good agreement with the experimental values of 109.77 pm and 2358.6 cm^{-1} [46, 47].

Concerning the electronic binding energy of N_2, effects due to the internal contraction, the choice of the orbitals, or even relativistic effects are all in the order of a few tenths of a kcal/mol. Full CI calculations are possible only with inacceptably small basis sets, and it is difficult to tell from such calculations which of the approximative methods (uncontracted versus internally contracted MRCI, MRCI+Q, or MR-ACPF) will be closest to the full CI level at the limit of a complete basis set. Therefore, it seems impossible in the near future to pursue the ab initio computation of D_e to accuracies significantly below chemical accuracy (1 kcal/mol). Chemical accuracy is achieved by the CAS(6)/IC-MRCI(10)+Q approach, when all electrons are correlated, and when the results are extrapolated to the limit of a complete basis set (or if explicitly correlated basis sets are employed). This level of theory is clearly superior to the all-electron CCSD(T) method. Basis-set errors of the order of 1 kcal/mol must be dealt with even if basis sets are used which are as large as the cc-pCV6Z basis set. Basis-set errors below 0.5 kcal/mol require at least basis sets of the type cc-pCV8Z.

For a variety of methods, basis-set limits have been derived. These limits are all mutually consistent and consistent with previously calculated quantities. As such, the present overview provides valuable insight into the performance of various high-level electron-correlation treatments.

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