

# Geometry and harmonic frequency of N<sub>2</sub> with coupled cluster methods that include connected quadruple excitations

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Received 23 December 1998

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## Abstract

Coupled cluster methods with full inclusion of singles, doubles, triples and noniterative connected quadruples (CCSDT( $Q_f$ )) are used to calculate the geometry and harmonic frequency of the N<sub>2</sub> molecule for a series of correlation-consistent basis sets up to the polarized valence 5-zeta. The connected quadruple excitations lower the harmonic frequency by 19 cm<sup>-1</sup> and raise the bond length by 0.0012 Å. For the approximate inclusion of the T<sub>3</sub> cluster the connected quadruple correction is smaller, but consistent for the basis sets studied. The frequency value for the largest basis set with all electrons correlated (quadruple-zeta quality) is 3 cm<sup>-1</sup> below the experimental value. The estimated basis set limit for the CCSDT( $Q_f$ ) method is 2361 cm<sup>-1</sup> compared to the experimental value of 2358.6 cm<sup>-1</sup>. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In the continuing effort to obtain the ultimate accuracy in ab initio correlated quantum-chemical methods, the N<sub>2</sub> molecule has played a prominent role. The moderate size of the N<sub>2</sub> system encourages applications of high-level sophisticated methods, yet the presence of the triple bond poses a severe test for the performance of the theory. In recent years, a number of papers dealing with the ground state properties of N<sub>2</sub>, i.e. equilibrium geometry, harmonic frequency and dissociation energy [1–16], and representing a wide spectrum of correlation methods,

from MBPT(4) [1] to explicitly correlated ( $r_{12}$ )-MR-CI [16], have been published.

The majority of the methods applied so far to the N<sub>2</sub> system are based on the CI wavefunction. These include the standard CISD approach [2,3], as well as various formulations of multireference CI based on CASSCF reference functions [4–8] or on CISD derived natural orbitals [9]. Among the nonvariational approaches, are some applications based on CPF [2] and its modifications [8,11] and use of the coupled cluster theory [10–15]. Within the latter approach, the most frequently used method is CCSD( $T$ ) [10–13,15]. The full CCSDT approach has been applied in the study of the potential energy curve at the DZP level [15]. The same problem has also been investigated with the MRCC model [14]. The most recent results of Dunning et al. [13] were obtained with very large basis sets (cc-pCV6Z) and gave excellent

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agreement with the experimental harmonic frequency when the Davidson type correction was included on top of the internally contracted MRCI. The CCSD(T) value for the same basis was off by  $12 \text{ cm}^{-1}$ .

All the calculations mentioned above show a rather slow convergence of properties with basis set size while simultaneously emphasizing the importance of very high-quality correlation treatments. Hence, to achieve definitive agreement with experiment, we have to use large basis set and sophisticated correlated methods. Unfortunately, these two requirements are frequently mutually exclusive.

The purpose of this Letter is to perform a thorough study of the ground state properties of the  $\text{N}_2$  molecule using coupled cluster theory with connected quadruple excitations [17–19], the highest level available. In particular, the motivation for this study came from our recent work [17] that introduces a method capable of accounting for the connected quadruple excitations for large basis sets. Since these excitations will undoubtedly play an important role in a triple bond problem, we assess the importance of connected quadruples for the demanding example of  $\text{N}_2$ .

## 2. Computational methods

As explained elsewhere [17], the noniterative inclusion of the  $T_4$  correction is developed analogously to the  $T_3$  correction in the CCSD(T) approach. Thus for the CCSDT( $Q$ ) method we evaluate the  $T_4$  correction,  $E_Q^5$ , using converged  $\bar{T}_2$  and  $\bar{T}_3$  amplitudes according to the expression:

$$E_Q^5 = \langle 0 | \bar{T}_2^\dagger [W_N T_4] | 0 \rangle. \quad (1)$$

$T_4$  is expressed as

$$T_4 = R_4 \left[ W_N \left( \bar{T}_2^2 / 2 + \bar{T}_3 \right) \right]_c. \quad (2)$$

The crucial modification in the evaluation of the  $T_4$  contribution is a *forced factorization* [17], i.e. we compute  $E_{Q_f}^5$  instead of  $E_Q^5$ , which defines CCSDT( $Q_f$ ). The  $E_{Q_f}^5$  is expressed as

$$E_{Q_f}^5 = \frac{1}{2} \langle 0 | \bar{T}_2^\dagger T_2^{(1)\dagger} \left[ W_N \left( \bar{T}_2^2 / 2 + \bar{T}_3 \right) \right]_c | 0 \rangle. \quad (3)$$

The above modification reduces the rank of the computational procedure from  $\sim n^9$  to  $\sim n^7$ .

We may introduce an analogous factorization into the iterative CCSDTQ-1 method [20] to obtain the CCSDTQ<sub>f</sub>-1 method. The CCSDTQ<sub>f</sub>-1 equations defined with respect to the CCSDT method take the form:

$$T_1(\text{CCSDTQ}_{f-1}) = T_1(\text{CCSDT}),$$

$$T_2(\text{CCSDTQ}_{f-1})$$

$$= T_2(\text{CCSDT}) + \frac{1}{2} R_2 \{ T_2^{(1)\dagger} [W_N (T_2^2 / 2 + T_3)] \},$$

$$T_3(\text{CCSDTQ}_{f-1}) = T_3(\text{CCSDT}),$$

where  $T_n(\text{CCSDT})$  represents the set of (diagrammatic) terms occurring in the CCSDT method. The advantage of the latter approach is a reduced rank of the computational procedure from  $\sim n^9$  for CCSDTQ-1 to  $\sim n^7$  for the connected quadruple part of CCSDTQ<sub>f</sub>-1. The full CCSDT  $T_3$  equation requires an  $\sim n^8$  procedure.

The results reported in this work mostly employ the noniterative factorized inclusion of connected quadruples, CCSDT( $Q_f$ ). For purposes of comparison, for smaller basis sets we also use the CCSDTQ<sub>f</sub>-1 method and its non-factorized variant, i.e. CCSDTQ-1 and the non-factorized noniterative CCSDT( $Q$ ). There are several important characteristics of the approaches based on factorized formulations:

- (1) the methods are size-extensive as they include only connected diagrams;
- (2) the methods are correct through fifth order in the MBPT energy;
- (3) the  $T_4$  part scales as  $\sim n^7$ ;
- (4) the correlation corrections for both the energy and properties are very close to those obtained with the standard CCSDTQ-1 method [20]. The latter approach, however, requires an  $\sim n^9$  computational procedure which makes it beyond reach for larger basis sets.

## 3. Results and discussion

Three standard coupled cluster approaches which include the  $T_3$  operator have been used: CCSD(T)

[21], CCSDT-3 [22,23] and the full CCSDT [24–27]. Using the converged  $\bar{T}_2$  and  $\bar{T}_3$  amplitudes, in the last two cases, and its initial approximation,  $T_3 = R_3(W_N \bar{T}_2)$ , appearing in CCSD( $T$ ), the lowest-order connected  $T_4$  contribution is evaluated according to Eq. (3) denoted as CCSDT( $Q_f$ ). The calculations have been performed for a series of correlation consistent basis sets [28–30], beginning with the small pVDZ, containing 28 functions, and ending at the pV5Z set with 182 functions. The calculated values of the equilibrium bond length and harmonic frequency have been collected in Tables 1 and 2, respectively. In addition Table 3 contains the bond lengths and vibrational frequencies obtained for small basis sets with methods including the  $T_4$  operator in a more rigorous way.

### 3.1. Equilibrium geometry

As mentioned, most previous coupled cluster calculations for the  $N_2$  molecule were limited to the CCSD( $T$ ) method. Here we first want to investigate the performance of two other triple excitation schemes: CCSDT-3 and full CCSDT. Generally, we observe that the error – relative to the full CCSDT

results – introduced by the CCSD( $T$ ) model is about twice as large as that obtained at the CCSDT-3 level. The values obtained with the CCSD( $T$ ) approximations for the medium and large basis sets are too large by 0.0006–0.0007 Å and for the CCSDT-3 model by 0.0003–0.0004. The smallest discrepancies occur for the modest basis sets, e.g. at the double-zeta level the CCSDT-3 and CCSDT models give virtually the same values, but the CCSD( $T$ ) result is off by 0.0004–0.0005 Å.

At all levels of calculation our results confirm what has been said concerning the core electron effect [10–13]. By including into the correlation the four inner-shell electrons, the calculated bond length is shorter by  $\sim 0.0015$ ,  $\sim 0.003$  and  $\sim 0.002$  Å for the double-, triple- and quadruple-zeta basis sets, respectively. At the given basis set level this effect is very stable, e.g. going from pVQZ to pCVQZ the computed  $R_e$  value is lower by 0.0021–0.0022 Å for all methods employed.

Next, we want to evaluate the role of the connected quadruple excitations on the geometry and frequency of  $N_2$ . In Table 1 we add additional columns,  $\Delta Q$ , which show the effect of the connected quadruples on the equilibrium bond length, i.e. give the difference between the values obtained

Table 1  
Geometry (Å) of  $N_2$  molecule with coupled cluster methods and correlation consistent basis sets<sup>a</sup> – Experiment:  $R_e = 1.0977^b$

Basis set	Number of b.f.	CC								
		SD( $T$ )	$\Delta Q^c$	SD( $TQ_f$ )	SDT-3	$\Delta Q^c$	SDT-3( $Q_f$ )	SDT	$\Delta Q^c$	SDT( $Q_f$ )
pVDZ	28	1.1189	8	1.1197	1.1184	15	1.1199	1.1185	15	1.1200
pVDZ +	46	1.1208	9	1.1217	1.1203	15	1.1218	1.1203	16	1.1219
pCVDZ	36	1.1174	8	1.1182	1.1169	14	1.1183	1.1169	15	1.1184
pCVDZ +	54	1.1191	8	1.1199	1.1185	18	1.1203	1.1186	16	1.1202
pVTZ	60	1.1038	4	1.1042	1.1034	11	1.1045	1.1031	12	1.1043
pVTZ +	92	1.1040	5	1.1045	1.1035	12	1.1047	1.1033	13	1.1046
pCVTZ	86	1.1006	4	1.1010	1.1003	10	1.1013	1.1000	12	1.1012
pCVTZ +	118	1.1009	4	1.1013	1.1006	11	1.1017	1.1003	13	1.1016
pVQZ	110	1.1003	4	1.1007	1.1000	10	1.1010	1.0997	11	1.1008
pVQZ +	160	1.1005	4	1.1009	1.1002	10	1.1012	1.0998	12	1.1010
pCVQZ	168	1.0981	4	1.0985	1.0979	10	1.0989	1.0975	12	1.0987
pV5Z	182	1.0994	5	1.0999	1.0991	11	1.1002	1.0987	12	1.0999
pCV6Z		1.0970 <sup>d</sup>		1.0974 <sup>c</sup>	1.0968 <sup>c</sup>		1.0978 <sup>c</sup>	1.0964 <sup>c</sup>		1.0976 <sup>c</sup>

<sup>a</sup>Basis sets from Refs. [28–30]; p(C)VNZ denotes cc-p(C)VNZ; p(C)VNZ + denotes aug-cc-p(C)VNZ.

<sup>b</sup>Ref. [31].

<sup>c</sup>The difference between values in adjacent columns, i.e. the net  $T_4$  effect ( $10^{-4}$  Å).

<sup>d</sup>Ref. [13].

<sup>e</sup>Extrapolated, based on the CCSD( $T$ ) value from Ref. [13].

Table 2

Harmonic frequency ( $\text{cm}^{-1}$ ) of  $\text{N}_2$  molecule with coupled cluster methods and correlation consistent basis sets<sup>a</sup> – Experiment:  $\omega = 2358.6^b$ 

Basis set	Number of b.f.	CC								
		SD( <i>T</i> )	$\Delta Q^c$	SD( <i>TQ<sub>f</sub></i> )	SDT-3	$\Delta Q^c$	SDT3( <i>Q<sub>f</sub></i> )	SDT	$\Delta Q^c$	SDT( <i>Q<sub>f</sub></i> )
pVDZ	28	2339	11	2328	2345	21	2324	2347	22	2325
pVDZ +	46	2319	11	2308	2326	21	2305	2327	23	2304
pCVDZ	36	2341	10	2331	2347	20	2327	2349	22	2327
pCVDZ +	54	2323	11	2312	2329	21	2308	2331	22	2309
pVTZ	60	2346	7	2339	2350	14	2336	2356	19	2337
pVTZ +	92	2340	8	2332	2344	17	2327	2350	20	2330
pCVTZ	86	2355	6	2349	2358	15	2343	2364	19	2345
pCVTZ +	118	2352	4	2348	2355	17	2338	2361	19	2342
pVQZ	110	2356	6	2350	2360	16	2344	2366	18	2348
pVQZ +	160	2354	6	2348	2358	16	2342	2364	18	2346
pCVQZ	168	2366	5	2361	2368	15	2353	2375	19	2356
pV5Z	182	2360	6	2354	2364	16	2348	2370	19	2351
pV6Z		2361 <sup>d</sup>		2355 <sup>f</sup>	2365 <sup>f</sup>		2349 <sup>f</sup>	2371 <sup>f</sup>		2352 <sup>f</sup>
pCV6Z		2371 <sup>e</sup>		2366 <sup>f</sup>	2373 <sup>f</sup>		2358 <sup>f</sup>	2380 <sup>f</sup>		2361 <sup>f</sup>

<sup>a</sup>See footnote a to Table 1.<sup>b</sup>Ref. [31].<sup>c</sup>The difference between values in adjacent columns, i.e. the net  $T_4$  effect.<sup>d</sup>Ref. [13], this value refers to cc-pCV6Z basis with valence electron correlated only.<sup>e</sup>Ref. [13].<sup>f</sup>Extrapolated, based on the CCSD(*T*) value from Ref. [13].

with or without inclusion of the  $T_4$  operator. For the CCSDT method the  $T_4$  correction is equal to 0.0012–0.0013 Å except for the small (double zeta) basis sets where it amounts to 0.0016 Å. The CCSDT-3 model gives very close but somewhat lower values. We may note that the largest differ-

ences occur for CCSD(*T*) based corrections, where the effect of  $T_4$  amounts for larger basis sets to 0.0004 Å, i.e. one-third of the effect observed for the iterative method. The difference is easily explained: for the CCSD(*T*) method we compute the  $T_4$  correction using the  $\bar{T}_2$  amplitudes which come from the

Table 3

Performance of the coupled cluster methods including connected quadruple excitations at various levels of approximation (bond length<sup>a</sup> in Å; frequencies in  $\text{cm}^{-1}$ )

Basis set	CC					
	SDT	SDT( <i>Q<sub>f</sub></i> )	SDT( <i>Q</i> )	SDTQ <sub>f</sub> -1	SDTQ-1	SDTQ
$R_e$ :						
DZP	1.1224	1.1243	1.1243	1.1243	1.1243	1.1240
pVDZ	1.1185	1.1200	1.1200	1.1200	1.1200	1.1198
pVDZ +	1.1203	1.1219	1.1220	1.1220	1.1220	–
pCVDZ	1.1169	1.1184	1.1185	1.1184	1.1185	–
$\omega$ :						
DZP	2315	2289	2288	2288	2288	2294
pVDZ	2347	2325	2324	2324	2324	2328
pVDZ +	2327	2305	2304	2304	2304	–
pCVDZ	2349	2327	2326	2327	2327	–

<sup>a</sup>Basis sets from Refs. [28–30,32] (DZP).

CCSD method and the  $T_3$  amplitudes obtained in a single iteration (i.e.,  $T_3 = R_3(W_N \bar{T}_2)$ ).

We observe that an improved correlation has the same effect on the bond length as an improvement in the basis set, causing the bond to shorten. Going from the double-zeta to the triple-zeta quality basis set, the bond gets shorter by 0.015–0.019 Å. At the quadruple-zeta level we gain an additional 0.003 Å and finally going from cc-pVQZ to cc-pV5Z, the bond length is reduced by an additional 0.001 Å. In the bottom line of Table 1 we quote the CCSD( $T$ ) bond length for the cc-pCV6Z basis set obtained in Ref. [13]. Based on that, we extrapolated to the same basis set results obtained with the methods employed in the current work. We may consider the cc-pCV6Z results as being close to the complete basis set limit. For CCSDT we obtained  $R_e = 1.0964$  Å, i.e. 0.0013 Å less than the experimental value. The  $T_4$  correction, assumed equal to 0.0012 Å, brings this value very close to experiment, 1.0976 vs. 1.0977 Å.

### 3.2. The harmonic frequency

The main aspect studied in the current work is the role of the connected quadruples in frequency calculations of the  $N_2$  molecule. In general we may state that the  $T_4$  operator lowers the harmonic frequency value. The quantitative measure depends, however, on the quality of the wave function obtained at the  $T_3$  level, see the  $\Delta Q$  columns in Table 2. For the most rigorous determination of the  $\bar{T}_3$  operator – the CCSDT method –  $T_4$  gives 18–19  $cm^{-1}$ . That value drops to 5–6  $cm^{-1}$  for the CCSD( $T$ ) method; for the intermediate estimate of  $\bar{T}_3$  in CCSDT-3, it amounts to 15–16  $cm^{-1}$ . The latter value shows that the CCSDT-3 wavefunction is very close to CCSDT in this context. The numbers quoted refer to the largest basis sets, i.e. QZ and 5Z quality, although for the medium size (TZ level) the  $T_4$  effect is nearly the same. We observe, also, that the size of the  $T_4$  effect is practically the same irrespective of whether the all electron or valence only correlation is considered, e.g.  $\Delta Q$  for cc-pVTZ is 19  $cm^{-1}$ , for cc-pCVTZ it is 19  $cm^{-1}$ ; for cc-pVQZ it is 18  $cm^{-1}$ , for cc-pCVQZ it is 19  $cm^{-1}$  (all numbers refer to CCSDT).

The effect of the core electrons is rather stable with respect to the correlated method employed, however, it is to some extent sensitive to the basis

set. For small basis sets, i.e. the double-zeta level, the 1 s correlation adds  $\sim 2$ –4  $cm^{-1}$ . At the triple-zeta level the frequency increases by 8  $cm^{-1}$  for cc-pVTZ and 11–12 for augmented basis sets. For the largest basis sets for which we can observe this effect, i.e. pVQZ vs. pCVQZ it is equal to 9  $cm^{-1}$  in perfect accord with other estimates [10–13].

Since the present work is a first attempt to use the various  $T_3$  based methods in  $N_2$  frequency calculations with large basis sets, we can make certain observations with respect to their performance. We note that for all medium and large basis sets the CCSDT-3 frequencies are quite close to those obtained by CCSDT, the differences being equal to 6–7  $cm^{-1}$ . The CCSD( $T$ ) is slightly worse with errors of 9–10  $cm^{-1}$ . Both approximate methods give lower values than the CCSDT. Those deviations are in accord with differences in the geometry: larger values of bond length give lower frequencies.

By doing the calculations for a large series of basis sets we are able to observe the trends in the frequency values with the increased size of the basis. e.g., considering a series of five basis sets: cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z and cc-pV6Z for the CCSD( $T$ ) method we obtain: 2339, 2346, 2356, 2360 and 2361  $cm^{-1}$ , respectively (the last value in the series is taken from Ref. [13]). Taking an analogous series for CCSDT we have 2347, 2356, 2366 and 2370  $cm^{-1}$  for cc-pVDZ, cc-pVTZ, cc-pVQZ and cc-pV5Z, respectively. Although we were not able to make the CCSDT calculations for the cc-pV6Z basis set, this value can be obtained by extrapolation to be equal to 2371  $cm^{-1}$ , which is approximately the complete basis set limit value, cf. the penultimate row in Table 2. Similarly, we extrapolate for values obtained with all electrons correlated (cc-pCVNZ series) to obtain the CCSDT for the cc-pCV6Z basis equal to 2380  $cm^{-1}$ , see bottom row in Table 2. Adding to it the  $T_4$  correction (–19  $cm^{-1}$ ) we obtain the complete basis set limit for the CCSDT( $Q_f$ ) method equal to 2361  $cm^{-1}$ , compared to the experimental value of 2358.6  $cm^{-1}$ .

### 4. Comparison with more rigorous methods

In Table 3 we show the bond distances and harmonic frequencies calculated with methods which include the  $T_4$  operator in a more rigorous way.

These results are obtained only for the smallest basis sets: cc-pVDZ, aug-cc-pVDZ, cc-pCVDZ [28–30] and DZP [32]. For all of them, we report calculations with the other three approaches correct through the fifth order and defined in the theoretical part of this work: CCSDT( $Q$ ), CCSDT $Q_{f-1}$  and CCSDT $Q-1$ ; for two of them: cc-pVDZ and DZP we were able to obtain full CCSDTQ results. The data in Table 3 indicate that the error introduced by using the factorized formula instead of the exact one is below the reported accuracy of the results. This refers both to the noniterative formulations, cf. CCSDT( $Q_f$ ) and CCSDT( $Q$ ) columns, and the iterative ones, cf. CCSDT $Q_{f-1}$  and CCSDT $Q-1$  columns. This is an important observation since by employing the factorized formula we obtain a dramatic reduction in the cost of the calculations. On the other hand, by comparing the values in columns CCSDT( $Q$ ) vs. CCSDT $Q-1$  and CCSDT( $Q_f$ ) vs. CCSDT $Q_{f-1}$ , we can estimate the inaccuracies introduced by replacing an iterative inclusion of the  $T_4$  operator with the noniterative one. Similarly, as in the previous case this approximation introduces a negligible error of 1  $\text{cm}^{-1}$ . This indicates that in the vicinity of the equilibrium geometry where the wavefunction is well represented by a single determinant, we may use the noniterative approach with very good accuracy. Out of the four approximate versions of the CCSDTQ method, the most rigorous treatment is represented by the CCSDT $Q-1$  method. In fact, the remaining formulations are simply approximations to the latter method. Thus, our conclusion is that since these approximations work so well, we might expect that the results obtained for large basis sets with the CCSDT( $Q_f$ ) method are very close to those obtained with CCSDT $Q-1$ .

The question remains how the CCSDT $Q-1$  results compare to those with the full CCSDTQ method. We were able to study this question only for two basis sets. It follows from our calculations that the approximate methods are in error by 0.0002 Å in bond length and 3–5  $\text{cm}^{-1}$  in the harmonic frequencies, compared to the overall  $T_4$  effect which is equal to 0.0012 Å and 19–20  $\text{cm}^{-1}$ . This is remarkable, taking into account that the calculations with the most rigorous CCSDTQ method are feasible for 30–40 basis functions, whereas the approximate version can be applied for up to 200 basis functions.

## 5. Conclusions

A series of three coupled cluster approximations with iterative and noniterative inclusion of connected triples and noniterative inclusion of connected quadruples, CCSD( $TQ_f$ ), CCSDT-3( $Q_f$ ) and CCSDT( $Q_f$ ), have been used to calculate the bond length and harmonic frequency for the  $\text{N}_2$  molecule. The calculations have been performed for a number of correlation-consistent basis sets beginning with pVDZ and ending at pV5Z. The core electron correlation effects have also been included in the calculations.

The main result of this work is the elucidation of the effect of the connected quadruple excitations on the geometry and harmonic frequency calculations. We have found that the inclusion of the connected quadruple excitations from an underlying CCSDT solution adds 0.0012 Å to the equilibrium bond length and lowers the harmonic frequency by 19  $\text{cm}^{-1}$ . These results are very stable with respect to basis set, as they stay within 0.0001 Å and 2  $\text{cm}^{-1}$  for the series of eight basis sets studied from cc-pVTZ to cc-pV5Z. The effect of the  $T_4$  operator on the CCSDT-3 wavefunction is somewhat lower: 0.0010 Å and 16  $\text{cm}^{-1}$  for the bond length and harmonic frequency, respectively. The same quantity computed on top of the CCSD( $T$ ) method accounts for ~30% of the CCSDT values. It was found that the CCSDT error for the  $\text{N}_2$  harmonic frequency is 16  $\text{cm}^{-1}$  for the largest basis set used with all electrons correlated and increases to 20–21  $\text{cm}^{-1}$  for the basis set limit. The CCSD( $T$ ) value is smaller by 10  $\text{cm}^{-1}$  and is, in fact, closer to the experimental value. We estimate that the harmonic frequency at the complete basis set limit for CCSDT( $Q$ ) would be equal to 2361  $\text{cm}^{-1}$  compared with the experimental value of 2358.6  $\text{cm}^{-1}$ . An analogous extrapolation made for the equilibrium bond length gives 1.0976 Å vs. 1.0977 Å for experiment.

Based on the calculations for small basis sets, we found also that the full CCSDTQ method gives frequency values 3–5  $\text{cm}^{-1}$  larger than that of the CCSDT( $Q_f$ ). Since the  $T_4$  effect at the double-zeta level is slightly exaggerated, we might expect that CCSDTQ at the basis set limit would add ~3  $\text{cm}^{-1}$  to the CCSDT( $Q_f$ ) value, resulting in a basis set limit of 2364  $\text{cm}^{-1}$ , or ~5  $\text{cm}^{-1}$  above experiment.

Assuming that our estimate is correct, and that the non-relativistic harmonic frequency is known accurately, the remaining  $5\text{ cm}^{-1}$  should be assigned – bearing in mind that  $\text{N}_2$  is a triply bonded system – to higher clusters  $T_5$  and  $T_6$ .

### Acknowledgements

This work has been supported by the US Air Force Office of Scientific Research under Grant Number AFOSR-F49620-95-1-0130, and also by KBN, Poland, under Grant Number 2P30310607.

### References

- [1] J.S. Binkley, M.J. Frisch, *Int. J. Quantum Chem. Symp.* 17 (1983) 331.
- [2] R. Ahlrichs, P. Scharf, K. Jankowski, *Chem. Phys.* 98 (1985) 381.
- [3] J. Almlöf, P.R. Taylor, *J. Chem. Phys.* 86 (1987) 4070.
- [4] S.R. Langhoff, C.W. Bauschlicher, P.R. Taylor, *Chem. Phys. Lett.* 135 (1987) 543.
- [5] H.J. Werner, P.J. Knowles, *J. Chem. Phys.* 89 (1988) 5803.
- [6] J. Almlöf, B.J. DeLeeuw, P.R. Taylor, C.W. Bauschlicher Jr., P. Siegbahn, *Int. J. Quantum Chem. Symp.* 23 (1989) 345.
- [7] H.-J. Werner, P.J. Knowles, *J. Chem. Phys.* 94 (1991) 1264.
- [8] H.-J. Werner, P.J. Knowles, *Theor. Chim. Acta* 78 (1990) 175.
- [9] R.S. Grev, H.F. Schaefer III, *J. Chem. Phys.* 96 (1992) 6850.
- [10] A.G. Csaszar, W.D. Allen, *J. Chem. Phys.* 104 (1996) 746.
- [11] C.W. Bauschlicher Jr., H. Partridge, *J. Chem. Phys.* 100 (1994) 4329.
- [12] J.M.L. Martin, *Chem. Phys. Lett.* 242 (1995) 343.
- [13] K.A. Peterson, A.K. Wilson, D.E. Woon, T.H. Dunning Jr., *Theor. Chim. Acta* 97 (1997) 251.
- [14] W.D. Laidig, P. Saxe, R.J. Bartlett, *J. Chem. Phys.* 86 (1987) 887.
- [15] R.J. Bartlett, J.F. Stanton, in: K.B. Lipkowitz, D.B. Boyd (Eds.), *Reviews in Computing Chemistry*, vol. 5, VCH, New York, 1994, pp. 65–169.
- [16] R.J. Gdanitz, *Chem. Phys. Lett.* 283 (1998) 253.
- [17] S.A. Kucharski, R.J. Bartlett, *J. Chem. Phys.* 108 (1998) 9221.
- [18] S.A. Kucharski, R.J. Bartlett, *Theor. Chim. Acta* 80 (1991) 387.
- [19] S.A. Kucharski, R.J. Bartlett, *J. Chem. Phys.* 97 (1992) 4282.
- [20] S.A. Kucharski, R.J. Bartlett, *Chem. Phys. Lett.* 158 (1989) 550.
- [21] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* 157 (1989) 479.
- [22] M. Urban, J. Noga, S.J. Cole, R.J. Bartlett, *J. Chem. Phys.* 83 (1985) 4041.
- [23] J. Noga, R.J. Bartlett, M. Urban, *Chem. Phys. Lett.* 134 (1987) 126.
- [24] J. Noga, R.J. Bartlett, *J. Chem. Phys.* 86 (1987) 7041.
- [25] J. Noga, R.J. Bartlett, *J. Chem. Phys.* 89 (1988) 3401.
- [26] G.E. Scuseria, H.F. Schaefer III, *Chem. Phys. Lett.* 152 (1988) 382.
- [27] J.D. Watts, R.J. Bartlett, *J. Chem. Phys.* 93 (1990) 6104.
- [28] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [29] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, *J. Chem. Phys.* 96 (1992) 6769.
- [30] D.E. Woon, T.H. Dunning Jr., *J. Chem. Phys.* 103 (1995) 4572.
- [31] K.P. Huber, G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.
- [32] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.