THE NUCLEAR QUADRUPOLE MOMENT OF ^{14}N FROM ACCURATE ELECTRIC FIELD GRADIENT CALCULATIONS AND MICROWAVE SPECTRA OF NP MOLECULE

Vladimir KELLÖ[a],* and Andrzej J. SADLEJ[b]

[a] *Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, SK-842 15 Bratislava, Slovakia; e-mail: kelloe@fns.uniba.sk*

[b] *Department of Quantum Chemistry, Institute of Chemistry, Nicolaus Copernicus University, PL-87 100 Toruń, Poland; e-mail: teoajs@chem.uni.torun.pl*

This paper is dedicated to the memory of the late Professor Jaroslav Koutecký, the pioneer of quantum chemistry and the founder of the first quantum chemistry group in the former Czechoslovakia.

Extensive series of relativistic coupled cluster calculations of the electric field gradient at N in NP has been carried out. The accurate value of the calculated electric field gradient, combined with the highly accurate experimental value of the nuclear quadrupole coupling constant for the ^{14}N nucleus, gives the 'molecular' value of the nuclear quadrupole moment $Q(^{14}$N$) = 20.46$ mb. This result perfectly agrees with the value (20.44 ± 0.03 mb) determined from atomic calculations and atomic spectra. The present study involves also extensive investigations of basis sets which must be used in highly accurate calculations of electric field gradients.

Keywords: Nuclear quadrupole moment of ^{14}N; Electric field gradients; Basis sets; Infinite-order scalar relativistic method; Coupled cluster calculations; CCSD(T); Ab initio; Gaussian.

In atoms, molecules, and in the solid state the interaction between quadrupolar nuclei and the electron density distribution[1–3] leads to observable spectroscopic effects which can be seen in the form of splittings of lines in atomic spectra[4] and splittings in rotational spectra of molecules[3]. The same interaction is responsible for the quadrupole resonance spectra[5] and affects the Mössbauer spectra[6] of solids.

The form of the interaction between the nuclear quadrupole and the distribution of the electron density is known[3,7–9] and to a good approximation the experimental data can be expressed as linear functions of the nuclear quadrupole moment $Q(X)$ of the quadrupolar nucleus X and the electron

density gradient $q_{\alpha\beta}(X)$ at X. The latter can be calculated by using different electronic structure theory methods. Hence, by combining the experimental and theoretical results one can obtain nuclear quadrupole moments, which, according to the source of the experimental data, are referred to as the 'atomic', 'molecular', and 'solid state' values.

From the computational point of view the highest accuracy of the electric field gradients can be achieved in atomic calculations[8,10–14]. The spherical symmetry greatly simplifies the computational problems and permits to go much beyond the present accuracy limits in molecular calculations. However, the atomic nuclear quadrupole coupling constants (*B*) are usually known with rather poor accuracy because of the significant line broadening and the high accuracy of the theoretical data for $q_{\alpha\beta}(X)$ may not be very helpful.

In contrast to the atomic spectral data the quadrupole coupling constants ($\nu_Q(X)$) of the nucleus X determined from molecular rotational spectra are usually of very high accuracy[3,5,16]. In order to profit from this advantage of the molecular microwave spectra one needs, however, to calculate the $q_{\alpha\beta}(X)$ values with a very high accuracy. Sufficiently accurate calculations of electric field gradients may represent a formidable task already for diatomic molecules. In spite of this, the 'molecular' route to nuclear quadrupole moments proved to be very successful[8,17–42]. Over the past two decades accurate 'molecular' values of nuclear quadrupole moments have been derived as documented by the recent review by Pyykkö[43]. The accuracy of the 'molecular' data for nuclear quadrupole moments is surprisingly high and has led to the resolution of disagreements between the data obtained from other sources, e.g. from muonic experiments or from nuclear theory calculations[17,20–22,43].

In most recent atomic calculations[8,11–14,44–48] the accuracy of the calculated electric field gradients was extensively investigated with respect to both the basis set extension and the level of the electron correlation treatment. Hence, the calculated atomic electric field gradients are frequently close to their exact values. With the spectroscopic *B* values of sufficiently high accuracy they could have been used to obtain the most accurate values of nuclear quadrupole moments. This is well exemplified by calculations of the electric field gradient in different spectroscopic states of the nitrogen atom and its ions[11] which have given one of the most accurate values of the nuclear quadrupole moment of ^{14}N, $Q(^{14}N) = 20.44 \pm 0.03$ mb (1 mb = 10^{-3} b = 10^{-31} m^2). The estimated error limit of $\pm 0.15\%$ is quite impressive. Moreover, the major part of this error (± 0.024 mb) comes from the

inaccuracy of the experimental value of B in $^{14}N^{2+}(2p^1, {}^2P_{3/2})$ [11,43]. Even for small and light diatomic molecules reaching this level of accuracy in molecular calculations is very demanding.

In molecular calculations the accuracy tests are carried out usually in a rather limited way[22,42]. As a rule calculations of electric field gradients in molecules are performed for a series of related molecules and mutual agreement between the nuclear quadrupoles derived from these data is regarded as a sign of the achieved accuracy. This works quite well and the values of Q derived from the data for different molecules have error bars of the order of 1–2%. However, this method is based mostly on the accumulated experience and is prone to several uncertainties. These uncertainties refer to both the basis set limit and the level of electron correlation treatment. The latter is usually assumed to be well enough accounted for at the level of the CCSD(T) approximation[49,50]. It appears that no extensive, exhausting, and systematic study of the basis set dependence of the calculated molecular electric field gradients has been carried out so far.

In the present paper the determination of the 'molecular' value of the quadrupole moment of the ^{14}N nucleus is considered as a case study. First, highly accurate equilibrium value of the quadrupole coupling constant $\nu_Q(^{14}N)$ is available for the NP molecule[51] and can be used to determine the 'molecular' value of $Q(^{14}N)$ and to compare it with the 'atomic' result of Tokman et al.[11]. The assumed goal is to obtain the 'molecular' result of comparable accuracy as that achieved in atomic calculations. Since the experimental value of $\nu_Q(^{14}N)$ in NP at the equilibrium bond distance (–5.1728 ± 0.0005 MHz) carries the error of the order of 0.01% (ref.[51]) the molecular value of $Q(^{14}N)$ will essentially depend only on the quality of calculations of the zz component of the electric field gradient, $q_{zz} = q$, at the nitrogen nucleus. Upon expressing $Q(^{14}N)$ (in mb) in terms of molecular data[3]

$$Q(^{14}N) = \frac{\nu_Q(^{14}N)}{0.234967q} \qquad (1)$$

where the quadrupole coupling constant is in MHz and q in a.u. of the electric field gradient, one finds that the expected value of the quadrupole moment of ^{14}N (20.44 mb) requires that the value of q should be of the order of 1 a.u. Hence, to match in molecular calculations the ±0.03 mb (±0.15%) error of the 'atomic' value of $Q(^{14}N)$ means that q at N in NP must be calculated with the absolute accuracy of the order of at least 10^{-3} a.u. In spite of NP being a small diatomic molecule, this is quite a challenging task.

In the next section a brief summary of the computational methods used to calculate the electric field gradient at N is presented. All calculations reported in this paper have been carried out within the so-called algebraic approximation, i.e. by using some truncated sets of (Gaussian) basis functions. Then, the choice and a systematic extension scheme of these basis sets, are described. The subsequent section reports on the calculated values of q at N in NP for a variety of systematically extended basis sets. In the last section of this paper the calculated value of q, which is expected to match the above-mentioned accuracy criteria, is used to obtain the 'molecular' value of $Q(^{14}N)$. A summary of our findings and conclusions follow.

COMPUTATIONAL METHODOLOGY

The computational methodology used in our investigations is to some extent based on our earlier experiences and certain well founded assumptions concerning the choice of computational methods. The electric field gradient at the nitrogen nucleus is first expressed as a sum of the electronic (q_{el}) and nuclear (q_{nucl}) contributions.

$$q = q_{el} + q_{nucl} \qquad (2)$$

Consistently with the fact that the value of $\nu_Q(^{14}N)$ reported by Raymonda and Klemperer[51] corresponds to the equilibrium N–P bond distance (R_e), we choose in all our calculations the experimental value of $R_e = 1.4908665$ Å $\approx$ 2.817330 a.u.[52]. This leads to the nuclear contribution $q_{nucl} = 1.341554$ a.u. which is used in all reported total values of q.

The electronic part of Eq. (*2*) is traditionally partitioned between its SCF HF (q_{HF}) and electron correlation ($q_{corr,M}$) contributions

$$q_{el} = q_{HF} + q_{corr,M} \qquad (3)$$

where the latter is calculated by some method M. For the method M we have chosen the coupled cluster (CC) approximation with iterative solution (CCSD)[49] for T_1 and T_2 amplitudes and the perturbation treatment of T_3. The method, known as the CCSD(T) approach[50], is very successful in calculations of the electron correlation contribution to atomic and molecular energies and its results for closed-shell and high-spin open-shell[53–56] systems come close to those of the full configuration interaction (FCI) method. The CCSD(T) scheme represents presumably the highest level of approximation which can be routinely used for many-electron systems with the SCF HF (or ROHF) single-configuration reference state. Its very successful applications,

in particular to systems which are well represented by a single electronic configuration, are legion[57].

Obviously, there will be always some uncertainty concerning the role of the higher-order correlation contributions to both energies and electric field gradients. The FCI calculations with basis sets of the size used in our investigations are essentially impossible. An idea about the importance of different cluster contributions can be gained by comparing the CCSD and CCSD(T) results, i.e. by partitioning the total CCSD(T) correlation correction, $q_{corr,CCSD(T)}$, into CCSD and T_3 contributions.

$$q_{corr,CCSD(T)} = q_{corr,CCSD} + q_{corr,T_3} \qquad (4)$$

However, one should be aware that a small contribution due to non-iterative treatment of T_3 does not necessarily mean that the iterative T_3 and higher-order T_n terms will be negligible.

The investigation of the pattern of convergence of the correlation contribution to q can be additionally extended by including also the results of the crudest approximation by the second-order perturbation theory (MP2). Although the MP2 correlation corrections, $q_{corr,MP2}$, are not expected to be of very high accuracy, they may add to the discussion of the saturation of the electron correlation contribution to q by the results of the CCSD(T) approach. Under the circumstances, the most important test of the accuracy of the CCSD(T) treatment of the electron correlation contribution to q will follow from the comparison of our final 'molecular' results for $Q(^{14}N)$ with those obtained in atomic calculations[11]. The latter are likely to be accurate within the reported error bars of 0.03 mb.

For systems with a large number of electrons usually only some part of them is considered at the highest possible level of approximation with respect to the electron correlation effects. The so-called core shells are either frozen or their contribution is estimated by using inexpensive low-level methods (MP2). Since the system studied in this paper is relatively small, all correlated-level calculations include the electron correlation contribution due to all 22 electrons of the NP molecule. Additionally it has been found that removing a certain number of the high-energy virtual orbitals does not affect the calculated values of q within the predefined numerical accuracy. All virtual orbitals with orbital energies higher than 10^3 a.u. have been removed in all CC calculations reported in this paper.

The CC methods used in this study are non-variational. Hence, the calculation of the electron correlation contribution to q involves the evaluation of the corresponding full-energy derivatives[58,59] with respect to the appro-

priately chosen strength (λ) of the external perturbation. These can be obtained either by using the formulae of the analytic perturbation theory[57] or by the numerical differentiation of λ-dependent energies. The latter are obtained in calculations with the core hamiltonian supplemented by the $\lambda \hat{q}$ term, where $\hat{q}$ is the one electron operator of the *zz* component of the electric field gradient and λ is a numerical parameter which defines the field gradient strength. In our nonrelativistic calculations we follow this purely numerical method with the value of λ equal to ± 0.00001 a.u. The selection of this numerical parameter of the finite perturbation scheme was established by the comparison of the expectation values and numerical derivatives obtained at the level of the SCF HF approximation. If the numerical derivatives were exact, the two results would be identical by virtue of the Hellmann–Feynman theorem. With the present choice of λ the numerical energy derivatives are accurate within at least 10^{-4} a.u.

Although the NP molecule is built of relatively light atoms and most of its valence-determined properties would hardly show any significant contribution due to relativistic effects[60,61], the electric field gradients are usually more demanding[62,63]. The electric field gradient operator assumes large values in the vicinity of the nucleus, i.e., in those regions of the electron density distribution where the relativistic effects are most important. Hence, taking into account the high accuracy required in present calculations, the evaluation of the relativistic effect on the electric field gradient at nitrogen is at least desirable.

The major part of calculations presented in this paper has been carried out in the framework of the nonrelativistic theory. At this level the validity of several assumptions has been established and only a limited series of calculations has been performed including the relativistic contributions to the molecular hamiltonian. All relativistic calculations correspond to the fully decoupled infinite-order two-component (IOTC) theory in the so-called spin-free form[64–67]. This method is the extension[64,67] of the Douglas–Kroll approximation[68] to infinite order with respect to the fine structure constant (or alternatively external potential) and has been shown[66,67] to reproduce the results of the four-component Dirac theory with arbitrarily high accuracy. The computational implementation[64,65] of IOTC is based on the approximate resolution of identity introduced by Hess[69–72].

One of the problems arising with the use of IOTC is the so-called change of picture of all operators whose matrix elements are to be calculated[73,74,76]. This problem is by no means associated[43] with possible approximations which are usually introduced on passing from the four-component to two-component methods. The transition from the four-component formalism

to two-component methods[75], and also to the exact IOTC formalism[64], is accomplished by a block-diagonalizing unitary transformation of the Dirac hamiltonian. Thus, all operators defined in what is called the Dirac picture need to be transformed accordingly[74].

To avoid the explicit transformation of the property operators, several purely numerical methods have been developed[27,28,63,73,76–78]. In all calculations reported in this paper we use the numerical method based on the so-called shifted nucleus (SN) model[76,77]. In comparison with the original point charge nuclear quadrupole moment (PCNQM) model proposed by Schwerdtfeger et al.[27,28], the SN model requires only one numerical parameter[77] and therefore offers certain computational advantages. Since the same method can be used in nonrelativistic calculations of electric field gradients, the numerical accuracy of the parametrized SN model can easily be checked. In present calculations the shift parameter (d) values[77], which have been found to be suitable for achieving the purely numerical accuracy of the calculated relativistic IOTC electric field gradient at N through at least 4 decimals, is chosen as 10^{-4} a.u.

The last computational detail to be discussed is the choice of the basis set. All calculations performed within this study have been carried out with large, systematically extended, Gaussian basis sets. This has required extensive numerical testing whose purpose was to establish some general rules concerning the basis set choice for calculations of electric field gradients in molecules. These computational aspects of the present study will be described and discussed in the next section. Let us also add that the software used in our calculations is Molcas 5.4 and Molcas 6.5 packages of electronic structure programs[79,80] which were adapted to include the spin-free IOTC scheme[72].

THE BASIS SET CHOICE

Most of the current experience concerning the basis set choice for calculations of electric field gradients in molecules[22–24,26,27,29–35,37,40–42] corresponds to accuracy requirements, which are much lower than those targeted in the present study. The appropriate choice of the Gaussian basis set for highly accurate calculations of molecular electric field gradients is therefore one of the most important issues.

Following our earlier calculations the initial basis sets of N and P are the well-tempered sets by Huzinaga and Klobukowski[81]. To increase the flexibility of the description of the valence shell the original ($14s10p;15\zeta$) set for N has been extended to 16ζ set with the additional exponent ζ_{16} determined

from the assumed geometric progression ($\zeta_{16} = \zeta_{15}^2/\zeta_{14} = 0.0227687$). Simultaneously the s and p subsets have been enlarged to (16s11p;16ζ). This extended set was further augmented with 5 d-type functions to give the smallest (16s11p5d;16ζ) basis set for nitrogen which is hereafter labeled as basis A. The ranges of orbital exponents for s, p, and d subsets are shown in Table I.

The (17s13p;18ζ) set[81] for phosphorus was similarly extended by one Gaussian exponent $\zeta_{19} = \zeta_{18}^2/\zeta_{17} = 0.01899554$) and enlarged to (19s14p;19ζ). This intermediate set has been used to obtain the smallest phosphorus basis set (basis A) of the form (19s14p7d;19ζ). The ranges of orbital exponents are shown in Table II. Basis sets A for nitrogen and phosphorus have been used in several exploratory calculations to determine their further extension.

Most of the contribution to the electric field gradient comes from valence p-type orbitals. However, the form of the electric field gradient operator indicates that f-type functions will be used for the first-order polarization[82–84]

TABLE I
Extended well-tempered 16ζ Gaussian basis sets used for nitrogen. Glossary of the basis set labels

Basic set	Label	Range of orbital exponents[a]			
		i_s–j_s	i_p–j_p	i_d–j_d	i_f–j_f
(16s11p5d)	A	1–16	6–16	11–15	
(16s11p6d5f)	B	1–16	6–16	11–16	11–15
(16s12p7d6f)	C	1–16	5–16	10–16	10–15
(16s13p8d7f)	D	1–16	4–16	9–16	9–15
(16s14p9d8f)	E	1–16	3–16	8–16	8–15
(16s15p10d9f)	F	1–16	2–16	7–16	7–15
(16s15p11d10f)	G	1–16	2–16	6–16	6–15
(16s15p12d11f)	H	1–16	2–16	5–16	5–15
(16s15p10d9f)	G1	1–16	2–16	6–15	6–14
(16s15p9d8f)	G2	1–16	2–16	6–14	6–13
(16s15p9d7f)	G3	1–16	2–16	6–13	6–12

[a] i_x–j_x determines the range ζ_i–ζ_j for x = s, p, d, and f primitive Gaussian orbitals.

contributions. The g-type and higher angular momentum functions are of negligible importance for N and P. Following this observation the B basis sets for nitrogen and phosphorus, (16s11p6d5f;16ζ) and (19s14p9d8f;19ζ), respectively, have been generated with the simultaneous extension of the number of d-type functions. For the exponents of both d- and f-type primitive functions it was initially assumed that they cover the range of the largest contribution in valence atomic orbitals of nitrogen and phosphorus. Further extension has been carried out by adding high-exponent primitive Gaussians to p, d, and f subsets of the basis sets B. The corresponding details are shown in Tables I and II. In the presentation of our results for the electric field gradient at nitrogen we shall refer to molecular basis sets by the symbol XY, where X = A, B, ... is the basis set used for nitrogen, and Y = A, B, C, ... denotes the basis set used for phosphorus.

After establishing certain regularities in the calculated values of the electric field gradient, we have also investigated the possibility of some reduction of the large basis sets of nitrogen and phosphorus by deleting the most diffuse d and f basis functions. The G basis set of nitrogen and B basis set of phosphorus are used to build the reference (GB) molecular basis set which was afterwards systematically truncated. The corresponding truncated

TABLE II
Extended well-tempered 19ζ Gaussian basis sets used for phosphorus. Glossary of the basis set labels

Basic set	Label	Range of orbital exponents[a]			
		i_s–j_s	i_p–j_p	i_d–j_d	i_f–j_f
(19s14p7d)	A	1–19	6–19	13–19	
(19s14p9d8f)	B	1–19	6–19	11–19	11–18
(19s15p10d9f)	C	1–19	5–19	10–19	10–18
(19s16p11d10f)	D	1–19	4–19	9–19	9–18
(19s17p12d11f)	E	1–19	3–19	8–19	8–18
(19s14p8d7f)	B1	1–19	6–19	11–18	11–17
(19s14p7d6f)	B2	1–19	6–19	11–17	11–16
(19s14p6d5f)	B3	1–19	6–19	11–16	11–15
(19s14p5d4f)	B4	1–19	6–19	11–15	11–14

[a] i_x–j_x determines the range ζ_i–ζ_j for x = s, p, d, and f primitive Gaussian orbitals.

G-type basis sets of nitrogen are referred to as G1, G2, and G3 (Table I). In a similar way the reduced B-type sets (B1, B2, B3, and B4) were generated for phosphorus (Table II). These numerical experiments, which lead to significant reduction of the total molecular basis set, can be useful in devising appropriate basis sets for calculations of electric field gradients in other molecules.

Let us also note that all basis sets used in this study are composed of primitive uncontracted (spherical) Gaussian functions. It has been found (vide infra) that the high-exponent basis functions are vital for achieving high accuracy of the calculated electric field gradients. Also, at variance with the experience based on calculations of several other molecular electric properties, like dipole moments or dipole polarizabilities, these basis functions need to have high flexibility and should be left uncontracted.

RESULTS AND DISCUSSION

The primary aim of investigations presented in this paper is the accurate calculation of the electric field gradient at the nitrogen nucleus in the NP molecule. Then, the calculated value of q will be used to determine the 'molecular' result for $Q(^{14}$N$)$. The accurate value of the latter is, however, already known with a very high accuracy[11,43]. This permits to use the NP molecule simultaneously as a playground for testing different approximations used in molecular calculations of the electric field gradient.

The most important is the convergence of q and its components (Eq. (*3*)) with respect to the basis set extension and the corresponding results for selected combinations of the nitrogen and phosphorus basis sets are presented in Table III. These are the electronic SCF HF results (q_{HF}), the electron correlation corrections from the CCSD method ($q_{\mathrm{corr,CCSD}}$), and electron correlation contributions due to triple excitations (q_{corr,T_3}). The sum of the latter two makes the total electron correlation correction of the CCSD(T) method ($q_{\mathrm{corr,CCSD(T)}}$) which is also displayed in Table III. According to Eq. (*2*) the total value of the electric field gradient at N includes the nuclear contribution, $q_{\mathrm{nucl}} \approx 1.3416$ a.u.

The data of Table III are arranged in such a way that they show the convergence pattern for the selected basis set on N and the extension of the phosphorus basis set. One finds that the calculated value of q is not highly sensitive to the phosphorus basis set. For each selected basis set on N the extension of the phosphorus basis set beyond the set B leads to negligible (less than 10^{-4} a.u.) changes in both SCF HF and electron correlation contributions to q. One can conclude that the phosphorus atom in NP plays the

Basis set dependence of the calculated data for the electric field gradient (q, in a.u.) at N in the NP molecule. The study of the dependence of q at N on the spectator atom (P) basis set. All data correspond to the experimental value of the equilibrium bond distance, $R_e \approx 2.817330$ a.u.

Basis set on N	Basis set on P	q_{HF}	$q_{corr,CCSD}$	q_{corr,T_3}	$q_{corr,CCSD(T)}$	q^a
A	A	–2.7312	0.2596	0.0507	0.3103	–1.0793
B	A	–2.7479	0.2638	0.0529	0.3167	–1.0897
B	B	–2.7524	0.2516	0.0521	0.3037	–1.1072
C	A	–2.7385	0.2569	0.0535	0.3104	–1.0865
C	B	–2.7415	0.2447	0.0526	0.2973	–1.1026
C	C	–2.7416	0.2447	0.0526	0.2973	–1.1027
D	A	–2.7198	0.2506	0.0529	0.3036	–1.0747
D	B	–2.7215	0.2388	0.0521	0.2909	–1.0891
D	C	–2.7215	0.2388	0.0521	0.2909	–1.0891
D	D	–2.7215	0.2388	0.0521	0.2909	–1.0891
E	A	–2.7075	0.2485	0.0527	0.3012	–1.0647
E	B	–2.7114	0.2367	0.0518	0.2885	–1.0813
E	C	–2.7115	0.2367	0.0518	0.2885	–1.0814
E	D	–2.7115	0.2367	0.0518	0.2885	–1.0814
E	E	–2.7115	0.2367	0.0518	0.2885	–1.0814
F	A	–2.7072	0.2478	0.0526	0.3004	–1.0652
F	B	–2.7088	0.2361	0.0517	0.2878	–1.0794
F	C	–2.7088	0.2360	0.0517	0.2878	–1.0795
F	D	–2.7088	0.2360	0.0517	0.2878	–1.0795
G	A	–2.7045	0.2478	0.0526	0.3004	–1.0625
G	B	–2.7080	0.2360	0.0517	0.2877	–1.0788
G	C	–2.7081	0.2360	0.0517	0.2877	–1.0788
H	B	–2.7079	0.2359	0.0517	0.2876	–1.0787
H	C	–2.7079	0.2359	0.0517	0.2876	–1.0787

[a] The total value of q which includes the nuclear contribution 1.3416 a.u.

role of a *spectator atom* whose effect can be well enough described by basis sets of a moderate size.

To show the convergence pattern with respect to the nitrogen basis set we have selected two basis sets of phosphorus, B and C, and displayed in Table IV the dependence of q on the basis set on N. Although these are essentially the same data as those already presented in Table III they point to other features of the convergence of q and its components. First, the data calculated with certain basis X of N are practically the same for B and C sets of the spectator atom. The moderately large basis set B on phosphorus leads to sufficiently accurate results. These, however, significantly depend on the nitrogen basis set. Within the present limits of accuracy one would have to use at least the FB basis set.

One should also note that the electron correlation contribution to q converges faster than the SCF HF value. Hence, the basis set choice can be made at the level of inexpensive one-electron calculations. This observation

TABLE IV
Basis set dependence of the calculated data for the electric field gradient (q, in a.u.) at N in the NP molecule. The study of the dependence of q at N on the nitrogen basis sets for B and C basis sets of phosphorus. All data correspond to the experimental value of the equilibrium bond distance, $R_e \approx 2.817330$ a.u.

Basis set on N	Basis set on P	q_{HF}	$q_{corr,CCSD}$	q_{corr,T_3}	$q_{corr,CCSD(T)}$	q^a
B	B	–2.7524	0.2516	0.0521	0.3037	–1.1072
C	B	–2.7415	0.2447	0.0526	0.2973	–1.1026
D	B	–2.7215	0.2388	0.0521	0.2909	–1.0891
E	B	–2.7114	0.2367	0.0518	0.2885	–1.0813
F	B	–2.7088	0.2361	0.0517	0.2878	–1.0794
G	B	–2.7080	0.2360	0.0517	0.2877	–1.0788
H	B	–2.7079	0.2359	0.0517	0.2876	–1.0787
C	C	–2.7416	0.2447	0.0526	0.2973	–1.1027
D	C	–2.7215	0.2388	0.0521	0.2909	–1.0891
E	C	–2.7115	0.2367	0.0518	0.2885	–1.0814
F	C	–2.7088	0.2360	0.0517	0.2878	–1.0795
G	C	–2.7081	0.2360	0.0517	0.2877	–1.0788
H	C	–2.7079	0.2359	0.0517	0.2876	–1.0787

^{a} The total value of q which includes the nuclear contribution 1.3416 a.u.

will be of certain help in the case of systems with a large number of electrons. However, one finds that in general very large basis sets need to be used in accurate calculations of electric field gradients. Although the major contribution to the value of q at the given nucleus comes from the asymmetry in the valence region, the asymmetry in the core region is by no means negligible. To describe it properly one needs basis sets with very high exponents in the polarization set.

The basis sets used so far were originally modelled on those used to calculate valence properties of molecules, e.g., dipole moments and dipole polarizabilities. The accuracy of calculations of these properties is primarily determined by the quality of the wave function in the valence region. Then, the focus is obviously on the diffuse part of the wave function and the low-exponent polarization functions are of utmost importance[84]. The form of the field gradient operator suggests that in calculations of its expectation values the diffuseness of basis sets may be less important. Since the basis sets of the size used in the present study have a rather limited area of applicability in molecular calculations, any possibility of their reduction is worth considering. This problem is illustrated here by the study of the effect of different truncations of the GB basis set (see Tables I and II).

We have already found that the description of the region of the electron density distribution due to the spectator atom is much less demanding than that of the region close to the nucleus at which the electric field gradient is to be calculated. One may also expect that very diffuse components of the polarization subsets for the spectator atom can be to some extent truncated without significant changes in the calculated values of q at the nitrogen. This is illustrated by the data of Table V for a series of GBi, i = 1, 2, 3, 4, basis sets with systematically removed diffuse polarization functions on phosphorus (see Table II). One can see that removing up to three most diffuse d and f functions has hardly any effect on the value of q at nitrogen. This means that the GB3 basis set offers essentially the same accuracy as the GB set which comprises 36 more Gaussian functions.

The second series of calculations corresponds to the study of the effect of the basis set truncation on the nitrogen atom. For this purpose we have systematically removed the most diffuse d and f functions on nitrogen (nitrogen basis sets G1, G2, and G3, see Table I) in the GB3 molecular set. According to the data of Table V the G3B3 set shows some deterioration, though still generally acceptable, of the calculated value of q. In comparison with the value of q obtained with the full GB set, this deterioration amounts to only about 0.3%. In terms of the total number of basis functions the G3B3 set is by 72 (spherical) Gaussian functions smaller than the

reference set GB. One should also note that the deterioration of the SCF HF data approximately parallels that of the correlation contributions to q. This suggests that quite a part of the basis set generation can be carried out at the level of the inexpensive one-electron approximation.

The results of numerical experiments shown in Table V are presented rather for the purpose of finding some more general rules for the basis set generation for other molecules. With the present goal to obtain the highly accurate value of q at nitrogen and to establish presumably the best 'molecular' result for $Q(^{14}N)$ we shall consider the calculated data for the largest basis set HC. At the level of the nonrelativistic CCSD(T) approximation, the corresponding results appear to converge to at least three decimals. The error in the calculated nonrelativistic CCSD(T) should be therefore less than 0.1%. This is approximately the magnitude of the relativistic contribution to electric field gradients in different states of N^{2+} and N^+ estimated by Tokman et al.[11] by using a multiplicative correction factor. In spite of the smallness of the relativistic contribution to q, the high accuracy of present calculations requires that it should be included as well.

TABLE V
Basis set dependence of the calculated data for the electric field gradient (q, in a.u.) at N in the NP molecule. The study of the effect of the truncation of the low-exponent part of basis sets on N and P. All data correspond to the experimental value of the equilibrium bond distance, $R_e \approx 2.817330$ a.u.

Basis set on N	Basis set on P	q_{HF}	$q_{corr,CCSD}$	q_{corr,T_3}	$q_{corr,CCSD(T)}$	q^a
G	B	–2.7080	0.2360	0.0517	0.2877	–1.0788
G	B1	–2.7080	0.2360	0.0517	0.2877	–1.0788
G	B2	–2.7080	0.2360	0.0517	0.2877	–1.0788
G	B3	–2.7081	0.2367	0.0518	0.2884	–1.0781
G	B4	–2.7084	0.2367	0.0522	0.2989	–1.0671
G	B3	–2.7081	0.2367	0.0518	0.2884	–1.0781
G1	B3	–2.7081	0.2367	0.0517	0.2884	–1.0781
G2	B3	–2.7081	0.2371	0.0518	0.2889	–1.0776
G3	B3	–2.7077	0.2386	0.0518	0.2904	–1.0757

^{a} The total value of q which includes the nuclear contribution 1.3416 a.u.

The scalar relativistic IOTC calculations have been carried out for four large basis sets GB, GC, HB, HC and the corresponding results are displayed in Table VI. Owing to the method used to calculate the IOTC electric field gradient (the SN model)[76,77], the results presented in Table VI include the change-of-picture contribution[35,74] to the expectation value of the electric field gradient operator.

The relativistic effect on the electric field gradient at N in NP is obviously small, though not totally negligible with the present accuracy require-ments. The scalar relativistic contribution to q amounts to +0.0025 a.u. and makes about 0.2% of the total value of the electric field gradient at nitro-gen. Most of it is accounted for at the level of the SCF HF IOTC approxima-tion. The relativistic effect on the electron correlation contribution is negligible. The study of the basis sets dependence of the relativistic contri-bution to q shows that all four basis sets lead to essentially the same results. Upon including the scalar relativistic effect we finally obtain the most accu-rate CCSD(T) IOTC result of this paper $q = -1.0762$ a.u., which can be used to calculate the 'molecular' value of $Q(^{14}N)$.

TABLE VI
Basis set dependence of relativistic IOTC results for the electric field gradient (q, in a.u.) at N in the NP molecule at the experimental equilibrium bond distance, $R_e \approx 2.817330$ a.u.

Basis set on N	Basis set on P	q_{HF}	$q_{corr,CCSD}$	q_{corr,T_3}	$q_{corr,CCSD(T)}$	q^a
			Relativistic corrections			
G	B	0.0022	0.0002	0.0001	0.0003	0.0026
G	C	0.0023	0.0002	0.0001	0.0003	0.0026
H	B	0.0022	0.0002	0.0001	0.0003	0.0025
H	C	0.0022	0.0002	0.0001	0.0003	0.0025
			Total IOTC values			
G	B	–2.7058	0.2362	0.0518	0.2880	–1.0762
G	C	–2.7058	0.2362	0.0518	0.2880	–1.0762
H	B	–2.7057	0.2361	0.0518	0.2879	–1.0762
H	C	–2.7057	0.2361	0.0518	0.2879	–1.0762

[a] The total value of q which includes the nuclear contribution 1.3416 a.u.

CONCLUSIONS

The most accurate value of q obtained in this paper ($q = -1.0762$ a.u.), which follows from CCSD(T) IOTC calculations with the largest HC basis set, combined with the experimental value[51] of $\nu_Q(^{14}N) = -5.1728 \pm 0.0005$ MHz, leads to the 'molecular' result

$$Q(^{14}N) = 20.46 \text{ mb} \qquad (5)$$

which is perfectly within the error bars of the very accurate 'atomic' value (20.44 ± 0.03 mb) of Tokman et al.[11,43]. Obviously, this perfect agreement is to some extent due to favorable mutual cancellation of several (very) small contributions which are neglected in our calculations and in those of Tokman et al.[11], like the effect of higher than non-iterative T_3 clusters, the spin–orbit contributions, or the basis set extension. To estimate the contribution of all these terms to set up the error bars on the 'molecular' result would be more a speculation and is avoided in the present case. One should note that the error bars of the experimental value of $\nu_Q(^{14}N)$ for the equilibrium bond distance, reported by Raymonda and Klemperer, are negligible.

The accuracy of the present 'molecular' value of $Q(^{14}N)$ should be rather assessed on the basis of the agreement with the 'atomic' result of Tokman et al.[11]. Since these two results almost coincide with each other, the 'molecular' result confirms the conclusion by Pyykkö[43] that 'this value ... is probably the most accurately known Q for light elements'.

In addition to establishing the accurate 'molecular' value of $Q(^{14}N)$, the present paper reports also on the extensive study of the basis set dependence of the calculated values of the electric field gradient. Some of these results have a rather wide range of applicability and may by of use in other calculations of electric field gradients.

First, it has been found that atomic basis sets on atoms linked to the (nuclear quadrupole) investigated centre are less important than the basis set on the atom at which the field gradient is calculated. The moderately large basis set B for phosphorus leads to saturation of the 'spectator atom' contribution. This finding can be of particular usefulness in calculations of electric field gradients at light nuclei linked to heavy atoms. Our preliminary studies of the electric field gradient at Cl in SbCl and at N in SbN show that the concept of the 'spectator atom' basis set works very well[85] and leads to significant reduction of the total molecular basis set.

It has also been found that the atomic basis set for the 'quadrupolar' atomic centre needs to be carefully augmented with high-exponent polarization functions. The rules established for valence properties do not apply

in the case of electric field gradients. The consequence of this finding is that one needs to use very large basis sets on the 'quadrupolar' centre. However, it has been simultaneously found that the diffuse part of the polarization subset used for the 'quadrupolar' centre and the spectator atom is less significant. Several diffuse functions can be removed from atomic basis sets without seriously affecting the calculated electric field gradient. Hence, the extension in the high-exponent region will be partly compensated by the reduction of the number of Gaussian polarization functions with very low exponents. These findings give some guiding rules for the generation of basis sets for accurate calculations of electric field gradients in molecules.

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