The Calculation of ^{14}N Quadrupole Coupling Constants with Basis Sets of High Local Quality

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An appropriate basis set to obtain electric field gradients close to the Hartree-Fock limit is evaluated for the nitrogen nucleus. An empirical correction for the error due to the neglect of electron correlation is given for sp-, sp^2- and sp^3-hybrized nitrogen. The results are used to predict the full quadrupole coupling tensor for a few molecules. A breakdown of the electric field gradient into contributions from the single orbitals leads to a model for the field gradient due to the π-system and a partial rationalization of the part due to the σ-system. The results are discussed in relation to a Townes and Dailey analysis.

Keywords: ab-initio-SCF, basis set, nuclear quadrupole coupling constant, electric field gradient, ^{14}N.

The calculation of electric field gradients (efg) at the location of nuclei in molecules is closely related to the experimental determination of nuclear quadrupole coupling constants. Progress has been made in the last decade along two directions. Very accurate calculations for small molecules including electron correlation made it possible to obtain the nuclear quadrupole moment of the nucleus under investigation as a ratio from the experimental and calculated value often with higher accuracy than from scattering experiments. For instance, Sundholm et al. [1], Ha [2], and Cernusak et al. [3] have determined the nuclear quadrupole moment for ^{14}N with an error-limit which is probably only a few percent. On the other hand SCF calculations of reasonable accuracy allowed the efg of reasonably large molecules to be calculated (see e.g. [4]).

Improvements along this second direction are the goal of this paper. We have shown previously for deuterium [5, 6], that very large basis sets are necessary to obtain near-Hartree-Fock efg's but that the high quality of the basis can be confined to the area of the nucleus of interest. This concept permits such accurate calculations on fairly large molecules to be made. It will be shown that the correlation effect is pretty constant for groups of molecules. Therefore, rather than calculating an absolute value for the quadrupole coupling constant by using the best available value of the nuclear quadrupole moment as a proportionality factor, we determine a pseudo nuclear quadrupole moment for a group of molecules from the ratio of the experimental coupling constant and the near-Hartree-Fock efg value. This moment can then be used for other molecules of the same group, to yield good values for the coupling constant. For example, in the case of the deuterium quadrupole coupling constants the mean square deviation between calculated and experimental values at 21 different sites was 11.6 kHz [6]. If individual conversion factors of 680.0, 630.1, and 615.7 kHz/a.u. were applied to the sites with sp^3- (14 sites), sp^2- (2) and sp-hybrized (5) neighbours, respectively, the mean square deviation would have dropped to 5.9 kHz.

Such calculated values of the quadrupole coupling constants are of interest for the interpretation of experimentally obtained coupling constants, because the experiment often yields only the diagonal elements of the tensor. In contrast to the deuterium case, where one principal axis of the tensor usually lays nearly along the bond, the orientation of the tensor in the ^{14}N case is usually unknown. Therefore, a combination of the calculated and the experimental values provides a new insight.

Basis Set Evaluation

For N_2 and NO^+ the Hartree-Fock-limit of the efg is known from numerical integration [1]. In addition several calculations on N_2 and NH_3 (see e.g.

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[1 − 3]) have shown the influence of electron correlation on the efg. It is also well known that quite large basis sets are needed to obtain accurate results for this property. However, we are not aware of a systematic investigation on the basis set size which is necessary to approach the Hartree-Fock-limit. Therefore, we have calculated the efg with widespread basis sets for comparison and then evaluated what number and type of basis functions are necessary to approach the Hartree-Fock-limit for NH_3 and N_2.

Table 1. Some results of the basis set evaluation on NH_3 and N_2.

Basis[a]	NH_3[b]		N_2[c]	
	E/E_h	q/a.u.	E/E_h	q/a.u.
1 Roos-Siegbahn DZ	-56.101_5	-1.08_3	-108.77_3	-1.07_4
2 Dunning DZ	-56.176_0	-1.06_4	-108.87_8	-0.88_1
3 Dunning DZ + 1 d	-56.209_1	-0.98_3	-108.95_6	-1.04_2
4 Dunning DZ + 1 d + 1 f[d]	-56.210_3	-0.96_8	-108.96_2	-1.11_5
5 (12 s 6 p)	-56.204_3	-1.04_7	-108.95_4	-1.28_3
6 (12 s 6 p)/[6 s 4 p]	-56.204_0	-1.05_1	-108.95_3	-1.26_7
7 (12 s 6 p)/[6 s 4 p] + 1 d	-56.212_7	-1.02_6	-108.97_5	-1.29_8
8 (12 s 6 p)/[6 s 4 p] + 2 d	-56.215_7	-1.01_2	-108.97_7	-1.30_8
9 (12 s 6 p)/[6 s 4 p] + 2 d + 1 f	-56.216_1	-0.99_8	-108.98_0	-1.33_8
10 (20 s 10 p)	-56.207_8	-1.01_8	-108.95_8	-1.29_6
11 (20 s 10 p) +2 d + 1 f	-56.219_8	-0.97_4	-108.98_5	-1.36_5
12 (20 s 10 p)/[10 s 10 p] + 2 d + 1 f	-56.219_8	-0.97_4	-108.98_5	-1.36_8
13 (20 s 10 p)/[10 s 6 p] + 2 d + 1 f	-56.219_8	-0.97_4	-108.98_4	-1.36_7

[a] For an accurate description of the s- and p-functions see text and Table 2, d-exponent: 1.25 (Dunning basis set: 0.75); exponents of the d-set: 0.6/1.7; f-exponent: 1.25 (Dunning basis set: 1.0).

[b] N−H bond-length: 101.2 pm; H−N−H angle 106.7°.

[c] N−N bond-length: 109.77 pm.

[d] with an additional set of d-functions on the hydrogens (exp.: 0.99).

All calculations were done with a Gaussian-lobe-program (within the SCF framework) on IBM and Amdahl computers in double precision (64 bit). The error in the efg due to the lobe approximation was found to be less then 0.5%. This is small compared to the error due to neglect of vibrational corrections and electron correlation. All the calculations were performed with experimental structures (gas phase MW values).

Table 1 presents the results of the calculation which were performed on N_2 and NH_3. The first results are for the DZ basis sets by Roos and Siegbahn [7] and Dunning [8], applied to all atoms of a molecule (for the hydrogens in both cases the same Dunning basis set was used). The next two sections show results with two regularized even-tempered basis sets constructed by the method of Schmidt and Ruedenberg [9], one of size (12 s 6 p) and one of size (20 s 10 p). The ratio between s- and p-functions was chosen 2 : 1 as recommended by them. The basis sets were contracted to [6 s 4 p] and [10 s 6 p], respectively. Exponents and coefficients are listed in Table 2. The smaller contraction, called Basis I, was used to investigate the influence of different sets of polarization functions. The larger contraction, called Basis II, will be used with two additional d-sets and an f-set for further investigations. With Basis I as well as with Basis II we used the Dunning (9 s 5 p)/[4 s 2 p] basis set on the neighbouring atoms, increased by two sets of d-functions (exponents 0.40 and 1.60 for C, 0.45 and 1.8 for N, and 0.50 and 2.00 for O, respectively). The basis for neighbouring hydrogens (Dunning's (4 s)/[2 s]) was increased by a set of p-functions (exponent 1.2), and the exponents were always multiplied by a factor of 1.44. For all atoms further away a simple DZ basis set [7] was applied.

A comparison of the basis sets containing only s- and p-functions (e.g. 1, 2, 5 and 10) shows that a basis of Dunning's quality is by far not good enough for accurate efg calculations. Even Basis I, which performs reasonably well for N_2, yields a value for NH_3 which deviates about 3% from the one with Basis II. It is an illusion to assume that such basis set defects could be fully eliminated by applying polarization functions or by calculations including correlation.

Further calculations, not presented in Table 1, showed that a normal contraction scheme may be applied to the s-functions, but the p-functions should not be contracted except for the innermost functions. A reasonable contraction of the outer p-functions does not debase the energy much, but it does worsen the value of the efg. This is in accordance with the effect that a contraction of s-functions has on the efg of deuterium [5]. A comparison of the results obtained with basis sets 11 and 12 shows that the contraction scheme applied to the s-functions has virtually no influence. Similarly, a

Table 2. Exponents and coefficients of the contracted regularized even-tempered basis sets.

Basis I

s-functions		p-functions	
Exponents	Coefficients	Exponents	Coefficients
13679.953	0.000891	39.745673	0.005275
4913.1156	0.001385	13.042042	0.021510
1764.9183	0.007098	4.2794582	0.097841
634.00437	0.023127	1.4042910	1.000000
227.75079	0.081770	0.4608000	1.000000
81.813979	0.262702	0.1512059	1.000000
29.389699	0.707238		
10.557541	1.000000		
3.7925421	1.000000		
1.3623793	1.000000		
0.4894019	1.000000		
0.1758058	1.000000		

Basis II

s-functions		p-functions	
Exponents	Coefficients	Exponents	Coefficients
374504.118	6.05×10^{-6}	304.29248	7.91×10^{-5}
149043.069	0.00	124.82684	2.13×10^{-4}
77200.388	2.39×10^{-5}	51.206462	0.001144
35051.041	3.80×10^{-5}	21.005912	0.004326
15914.110	0.000128	8.6170444	0.015359
7225.4320	0.000319	3.5348836	1.000000
3280.5394	0.000874	1.4500798	1.000000
1489.4526	0.002320	0.5948517	1.000000
676.25133	0.006157	0.2440200	1.000000
307.03621	0.016164	0.1001018	1.000000
139.40265	0.040976		
63.292533	0.097848		
28.736504	1.000000		
13.047141	1.000000		
5.9237513	1.000000		
2.6895416	1.000000		
1.2211238	1.000000		
0.5544229	1.000000		
0.2517228	1.000000		
0.1142889	1.000000		

comparison between basis sets 12 and 13 proves the quality of the p-function contraction scheme.

Several authors stressed the importance of polarization functions for the calculation of efg's. This is confirmed by the results presented in Table 1. Again it should be pointed out, however, that their influence has been overestimated by authors who applied too small basis sets (compare the effect of the polarization functions for the basis sets 2 to 4!). Similarly, the efg depends acutely on the size of the exponent of the polarization function only for small basis sets. Decreasing the d-exponent in basis 7 from 1.25 to 0.75, increased the efg by 0.35 and 2.01% for NH_3 and N_2, respectively. Changing the two d-exponents to 0.3 and 1.0 and the f-exponent to 1.0 in basis set 11 had no influence at all on the efg.

We have not yet discussed the importance of the basis set on the neighbouring atoms. Additional d-sets on the hydrogens in NH_3 and an additional f-set on the neighbouring N in N_2 did not yield a relevant change of the efg, except for small basis sets, where the basis functions of the neighbour have to compensate the basis set defect on the nitrogen. A crucial test was the application of the large basis set 12 on both nitrogens in N_2 yielding an energy of $-108.9915\ E_h$ and an efg of -1.369 a.u. This proves the assumption that the Dunning basis enlarged by two d-sets is appropriate to the neighbouring atoms. This is again in accordance with the deuterium case [5].

Whereas the efg in our calculations, going from small to larger basis sets converge (except for some oscillations at the beginning) monotonously towards a value between -1.36 and -1.37 a.u., the numerical integration of Sundholm et al. yields a value of -1.337 a.u. (or -1.332 a.u. when extrapolated to the same bond-length). The best SCF calculation with Slater functions published up to now [10] resulted in an energy of $-108.9922\ E_h$ and in an efg of -1.361 a.u. In view of the monotonous convergence not only for the energy but also for the efg, we believe that our result is close to the Hartree-Fock-limit. However, similar arguments apply for the numerical value [11]. Therefore, we are not able to resolve this discrepancy at the moment. Fortunately, this point is not crucial to our application, because we are concerned mainly with relative values by means of the previously mentioned pseudo nuclear quadrupole moment.

An SCF value of -0.8901 a.u. for the efg of NH_3 in the literature [2] is probably erroneous. However, it does not affect the CI results in the same paper [12].

Evaluation of Pseudo Nuclear Quadrupole Moments on Some Sample Molecules

With the final basis set (Basis II + 2d + 1f) the efg at the nitrogen was calculated for a set of test molecules, for which an accurate experimental

Table 3. Evaluation of pseudo nuclear quadrupole moments on some sample molecules.

Molecule	E/E_h	q/a.u.	Ref. for Struct.	(e^2qQ/h) MHz	Ref.	$Q^{*\,a}$ 10^{-30} m^2
NH_3	−56.2198	-0.97_4	[23]	−4.0924(9)	[13]	1.79
$\underline{N}H_2-CN$ (cc)	−147.8896	-1.15_4	[14]	−4.90(2)	[14]	1.81
H_2N-NH_2 (aa)	−111.2119	0.92_8	[24]	4.09(5)	[15]	1.88
HNCO (aa)	−167.7022	0.49_9	[25]	2.056(11)	[16]	1.75
CH_2NH (cc)	−94.0604	0.89_5	[26]	3.591(8)	[17]	1.71
N_2	−108.9839	-1.36_7	[27]	−5.39(5)	[18]	1.68
NO^+	−128.9638	-1.81_7	[27]	−6.76(10)	[19]	1.58
HCN	−92.9045	-1.20_4	[28]	−4.7091(13)	[20]	1.66
CH_3-CN	−131.9138	-1.09_2	[29]	−4.214(16)	[21]	1.64
$NH_2-C\underline{N}$ (aa)	−147.8897	-0.87_2	[14]	−3.30(2)	[14]	1.61
FCN	−191.5808	-0.74_8	[30]	−2.67(5)	[22]	1.52

[a] $Q/10^{-30}\,m^2 = 0.4256\,(q/a.u.)^{-1}\,(e^2qQ/h)$/MHz.

structure as well as a nitrogen nuclear quadrupole coupling is available in the literature. The results are listed in Table 3. The calculated efg's (component of largest absolute value in the principal axes system of the moment of inertia; the axis is either determined by symmetry or listed in the first column) are followed by a column with the corresponding experimental coupling constant and the last column shows the pseudo nuclear quadrupole moment Q^* obtained from the calculated near-Hartree-Fock efg and the experimental coupling constant. Neglecting electron correlation results in moments Q^* too small by 9 to 26%, taking $2.05 \cdot 10^{-30}$ m^2 as an accepted value for the nuclear quadrupole moment of nitrogen [1–3]. A closer view shows, that in spite of the large deviation, the values of Q^* for a fixed degree of hybridization have a pretty constant value.

The experimental coupling constant of H_2N-NH_2 might be less accurate than the given error limit suggests. Although Kohata et al. [24] give two significantly different (6°) values for the inner and the outer H–N–N angle, Kasuya [15] did not pay attention to this in his determination of the coupling constant, which might have introduced some error in his result. Harmony and Baron [31] have pointed out that the sign of Kasuya's coupling constant has to be changed.

An extremely low value of Q^* is found in FCN. To make sure, that this is not due to a basis set defect on F, the calculation was repeated, treating F like a neighbour-atom, i.e. applying a Dunning DZ basis with two sets of d-functions. The result was virtually the same as with the smaller basis set, indicating that we are dealing with a correlation effect.

For 3 sp^3-hybrized nitrogens we find an average Q^* of $1.82 \pm 0.05 \cdot 10^{-30}$ m^2. For the sp^2-hybridization the average Q^* from only two values is $1.73 \pm 0.03 \cdot 10^{-30}$ m^2, whereas 6 values for sp-hybrized nitrogens yield an average Q^* of $1.62 \pm 0.06 \cdot 10^{-30}$ m^2. These values can now be used to predict nitrogen nuclear quadrupole coupling constants from near-Hartree-Fock efg's.

Results and Discussion

Applications of the evaluated basis set will mainly be the subject of forthcoming papers. Here we would like to give additional results of the calculations on the present set of molecules and discuss some of the results in more detail.

Table 4 shows predicted and experimental quadrupole coupling tensors for five molecules where the tensor is not determined by symmetry. Whereas the largest diagonal-component of each molecule was used together with components of other molecules to find the pseudo nuclear quadrupole moment Q^*, the smaller components have not been adjusted at all. Nevertheless they are fairly well predicted by the calculations. The largest deviations are found for HNCO. As the components in HNCO show different amounts of σ- and π-character, the influence of electron correlation might differ as in the three hybridizations.

Table 4. Predicted (vs. experimental) quadrupole coupling tensors (MHz) in the molecules of low symmetry.

Molecule[a]		aa	bb	cc	ab	ac	bc
$\underline{N}H_2{-}CN$	calc.	3.16	1.77	−4.93	0	−1.40	0
	exp.	3.05	1.85	−4.90			
$NH_2{-}NH_2$	calc.	3.97	−1.83	−2.13	1.07	−1.39	3.34
	exp.	4.09					
HNCO	calc.	2.03	−0.82	−1.21	0.98	0	0
	exp.	2.056	−0.473	−1.583			
CH_2NH	calc.	−1.02	−2.62	3.64	2.50	0	0
	exp.	−0.898	−2.693	3.591			
$NH_2C\underline{N}$	calc.	−3.32	3.16	0.16	0	0.02	0
	exp.	−3.30	2.86	0.44			
$ND_2{-}ND_2$	calc.	4.07	−1.95	−2.12	0.72	−1.19	3.42
	exp.	4.23	−1.98	−2.25			

[a] a, b, c are the principal axes of the moment of inertia.

Table 5. Components of the π-part of the calculated electric field gradients (in a.u.).

Molecule		x	y	z	y/x
NO^+	SCF	0.593	0.996	−1.588	1.68
	Model	0.60	0.91	−1.51	1.52
N_2	SCF	0.917	1.179	−2.096	1.29
	Model	0.93	1.13	−2.07	1.21
HCN	SCF	1.003	1.186	−2.188	1.18
	Model	1.03	1.17	−2.19	1.14
CH_3CN	SCF	1.011	1.226	−2.237	1.21
	Model	1.05	1.19	−2.25	1.14
FCN	SCF	1.030	1.282	−2.313	1.24
	Model	1.11	1.25	−2.36	1.12
$NH_2C\underline{N}$	SCF	0.908	1.141	−2.049	1.26
	Model	1.04	1.18	−2.23	1.14
CH_2NH	SCF	1.001	1.133	−2.134	1.13
	Model	1.06	1.18	−2.24	1.11
HNCO	SCF	1.426	1.623	−3.050	1.14
	Model	1.51	1.61	−3.12	1.07

z is the direction of the π-orbital. x, y are the directions vertical to the π-orbital, x along the bond to the (heavier) neighbour-atom.

The off-diagonal elements cannot be compared directly with experimental results, as no such are reported in the literature. From the calculational point of view we see no reason that they should be less accurate than the diagonal elements. A limited indirect verification of this are the results for the two isotopically substituted hydrazines. If the off-diagonal elements were far off the true values, the coordinate transformation would not yield reasonably good results for both hydrazines.

A model for the π-part of the efg

Whereas the experiment yields the total efg only, we can break down the calculated results into a nuclear and an electronic part, and the latter into single orbital-components, or into a σ- and π-part. Table 5 shows the components of the π-part of several molecules.

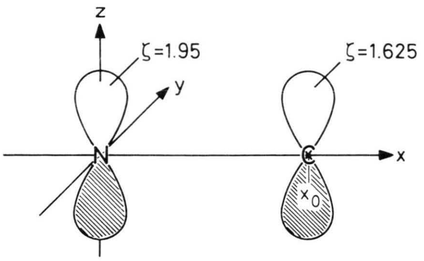

Fig. 1. Coordinates and parameters applied in the model of the π-system.

In addition to the SCF results, values are presented which where obtained from a simple model. The π-electrons on the nitrogen and on its neighbour are assumed to be in Slater-orbitals (with exponents according to the Slater-rules); π-electrons further away are discarded in the model. Figure 1 shows the model and the coordinates and parameters involved.

The equations for the efg at any point x_0 on the x-axis due to a Slater-p_z-orbital at the origin were given by McConnell and Strathdee [32] in closed form

$$\begin{aligned}
a &= \zeta\,|x_0|\,,\\
T_1 &= 1/|x_0|^3 * (1 - 9/a^2 + (a^3 + 4\,a^2 + 10\,a + 17\\
&\qquad + 18/a + 9/a^2)\,e^{-2a})\,,\\
T_2 &= 1/|x_0|^3 * (9/2\,a^2 - (a^3 + 3\,a^2 + 6\,a + 9 + 9/a\\
&\qquad + 9/2\,a^2)\,e^{-2a}),\\
q_{xx} &= q * 2 * T_1\,, \quad q_{yy} = -q * (T_1 + T_2),\\
q_{zz} &= -q * (T_1 - T_2)\,. \qquad (1)
\end{aligned}$$

These equations can be simplified for the case that x_0 is zero to

$$q_{zz} = q * 4/15 * \zeta^3, \quad q_{xx} = q_{yy} = -1/2\,q_{zz}\,. \qquad (2)$$

The electronic charge q in the π-orbital is taken from a CNDO-calculation. The above equations yield the efg-tensor (off-diagonal elements being zero) due to one Slater-orbital. The calculation has to be done once for nitrogen, i.e. with x_0 equal to zero, (2), and then it has to be repeated for the neighbour atom, (1), taking the corresponding values for ζ and q, and making x_0 equal to the bond-length. The sum of the two tensors is the total π-part from the model which can be compared with the result from the SCF calculation. The numbers in Table 5 were obtained in this manner, but in addition a scaling parameter for the Slater-exponents of 1.0205 was applied. This parameter is the only fit-parameter in the model.

The anisotropy in the x- and y-direction, characterized by the x/y in Table 5, is entirely due to the neighbour atom in our model. A similar effect is obtained if the orbital on the nitrogen is moved slightly towards the neighbouring atom. It is well known ([33], and references therein), that floating the orbital towards the neighbour-atom is equivalent to introducing polarization functions. The model could, therefore, be improved if we would allow for polarization. However, not knowing the amount of polarization, we would have to introduce new parameters.

Discussion of the σ-part of the efg

Table 6 shows results for five molecules dissected into nuclear, π- and σ-part. The latter is again divided into a part due to the K-shell, the bonding σ- and the lone-pair-orbitals. The table shows that we are dealing with relatively large nuclear and electronic parts which cancel to a great extent. This makes it difficult to predict accurate efg's either from calculations or models.

The first section in Table 6 lists the SCF results and the second section shows corresponding numbers from the model. The nuclear part is identical with the SCF section as it can be calculated classically. The π-part is from the above model. The part due to the K-shell is calculated with the classical equation for a point charge ($2q/r^3$) for two electrons in a distance equal to the bond-length. The K-shell is composed from the lowest n orbitals, n being the number of first-row atoms in the molecule. As these n orbitals are more or less localized on the corresponding atoms, the efg's of the single orbitals show, to which extent each atom contributes to the K-shell efg. The main part stems from the neighbouring atom (which explains the good accuracy of the model in this aspect). The orbital on the nitrogen under investigation contributes only a very small amount to the efg (−0.011, −0.033, −0.007, −0.007, −0.007 a.u. for NO$^+$, N$_2$, HCN CH$_3$CN and FCN, respectively), which may be interpreted approximately as Sternheimer shielding.

Table 6. Breakdown of the calculated electric field gradients (in a.u.) for some linear molecules (along the axis of the molecule).

Molecule	NO$^+$	N$_2$	HCN	CH$_3$CN[a]	FCN
SCF					
Total	−1.817	−1.367	−1.204	−1.089	−0.748
Nuclear	1.973	1.569	1.187	1.271	1.337
Electronic	−3.790	−2.936	−2.391	−2.360	−2.085
π	1.186	1.835	2.005	2.022	2.061
σ	−4.975	−4.771	−4.396	−4.382	−4.146
K-shell	−0.504	−0.458	−0.394	−0.423	−0.431
σ_{bond}[b]	−1.335	−1.148	−0.828	−0.874	−0.883
$\sigma_{\text{lone-pair}}$[b]	−3.136	−3.165	−3.175	−3.085	−2.832
Model					
Total	−1.81	−1.40	−1.04	−0.90	−0.63
Nuclear	1.97	1.57	1.19	1.27	1.34
Electronic	−3.78	−2.97	−2.23	−2.17	−1.97
π	1.20	1.87	2.05	2.10	2.22
σ	−4.98	−4.84	−4.28	−4.27	−4.19
K-shell	−0.49	−0.45	−0.39	−0.41	−0.42
σ_{bond}[b]	−1.41	−1.16	−0.79	−0.81	−0.84
$\sigma_{\text{lone-pair}}$[b]	−3.07	−3.24	−3.10	−3.05	−2.93
CNDO-orbital-population					
p_z on N (π)	0.75	1.00	1.05	1.08	1.13
p_z on neighb.	1.25	1.00	0.95	0.97	0.93
p_x of σ_{bo}	0.20	0.17	0.11	0.10	0.11
σ_{bo} on neighb.	1.23	1.00	0.83	1.14	1.19
p_x of σ_{lp}	0.97	1.14	1.24	1.24	1.16
σ_{lp} on neighb.	1.88	2.00	1.24	0.99	0.66
r/a.u.	2.01	2.08	2.18	2.19	2.19

[a] This molecule has actually not the required symmetry. However, concerning the efg of the Nitrogen, it behaves similarly as the other molecules.

[b] This classification is somewhat arbitrary, as we deal with canonical orbitals. A binding orbital to a hydrogen as in HCN was classified as lone-pair due to its similarity to a lone-pair orbital e.g. in N$_2$.

These values are much smaller than an estimated shielding of 0.1 to 0.2 a.u. The efg's due to the σ_{bond}- and the $\sigma_{\text{lone-pair}}$-orbitals consist of two parts, one due to the neighbour which is treated classically as in the case of the K-shell (but taking the CNDO electron density in the corresponding orbital on the neighbour atom instead of two electrons for q). The second part is calculated with a modified equation (2):

$$q_{xx} = q * 4/15 * (\zeta_0 + a\,(1-q))^3. \tag{3}$$

We have assumed, that the orbitals in the molecules are contracted by a different amount, depending on how much they are involved in the bonding. Therefore, we replaced ζ by a ζ_0, which may differ in a lone-pair or a bonding orbital. Further we have assumed that the amount of contraction also depends on the electron charge in the orbital, i.e. that an orbital containing a higher electron density is more diffuse. This is taken care of by a linear dependence of ζ on q. The constant of proportionality a and the exponents ζ_0 were treated as fit parameters and were found to be $a = 0.405$, $\zeta_0(\sigma_{\text{bond}}) = 2.41$ and $\zeta_0(\sigma_{\text{lone-pair}}) = 2.15$, respectively (all units in a.u.). For q in (3) we used the CNDO electron density in the p_x-function of the σ_{bond}- and the $\sigma_{\text{lone-pair}}$-orbital. All CNDO charges and the bondlength applied are listed in the last section of Table 6.

The model gives the right trend for the total efg. The not very accurate results and the fact that we need CNDO densities for the interpretation, however, does not make it practical for predictions of efg's. We rather suggest to use the model to rationalize the single terms of the efg within a semiclassical framework. Further investigations will have to show whether a breakdown in localized orbitals will give a simpler and more general picture for the σ-system.

The Townes and Dailey analysis

An analysis as suggested by Townes and Dailey [34] leads for the above molecules [35] to the following equations (depending on the degree of approximation):

$$q/q_0 = 2\alpha^2 + b(1-\alpha^2) - a, \tag{4}$$

$$q/q_0 = 1 + b/2 - a. \tag{5}$$

q_0 is the efg yielded by an electron in a valence 2p orbital of an nitrogen atom and is not known very accurately (we take here -2.47 a.u.). a is the population of the π-orbitals, b the population of the bonding hybrid orbital and α is the extent of s-hybridization in that orbital. For (5), α^2 was assumed to be equal to 1/2.

For the experimentalist it is difficult to apply the above equations containing three and two variables, having only one observed number per molecule available. The first, second and third terms in the above equations, however, correspond to the efg due to the lone-pair orbitals, the bonding σ-orbitals and the π-orbitals, respectively. This allows a comparison with the corresponding terms from the ab initio SCF calculations as well as with the populations obtained from the CNDO calculations. The values in Table 6 cannot be compared directly with the above terms, as the Townes and Dailey analysis assumes a compensation of the electronic efg from the neighbour atoms by the corresponding nuclei. For the following discussion we can apply the same assumption and correct the values in Table 6 by the appropriate amount.

The dependence on the π-population in the Townes and Dailey analysis is confirmed excellently by our π-model and needs no further comment.

At the beginning of the discussion of the efg due to the lone-pair orbitals, we should stress the point that this classification is somewhat arbitrary (see note [b] in Table 6). Equation (5) suggests this part of the efg to be constant with a value of about -2.47 a.u. The SCF calculations yield values for q/q_0 of 1.08, 1.10, 1.19, 1.17, and 1.10 (in the usual sequence of NO^+, N_2, HCN, CH_3CN, and FCN), which are not fully constant and correspond to a α^2 of about 0.55 rather than 0.5. The first term in the above equations should also be equal to the population of p_x of σ_{lp} (see Table 6). Whereas the population shows the correct size of about one, it is not very constant. For both (4) and (5) a fixed population of two for the lone-pairs was assumed, which is not correct in a more accurate picture as the lone-pair interacts with the rest of the σ-system. The CNDO calculations show that the above values are rather due to a population of more than two than to an α^2 which is greater than 1/2.

The values q/q_0 for the σ_{bond}-orbitals are 0.42, 0.37, 0.27, 0.27, and 0.27. These numbers should be equal to $b/2$ or to the population of p_x in σ_{bond} (see Table 6). They show the correct trend, but are too large.

We conclude that the Townes and Dailey analysis is a correct, but pretty rough analysis of the main effects, which determine the size of the efg. In a case like the above, where between two and four parameters (depending on the degree of simplification) have to be interpreted, and which yield portions of the efg with different signs, it may be misleading. Lucken, for example, [35] tried to interpret the low value of the efg in FCN as a π-effect due to a conjugation of the fluorine lone-pair electrons with the π-system. The SCF results rather suggest it to be due to the nitrogen lone-pair, leaving us with no simple chemical explanation.

[1] D. Sundholm, P. Pyykkö, L. Laaksonen, and A. Sadlej, Chem. Phys. **101,** 219 (1986).
[2] T. K. Ha, Z. Naturforsch. **41 a,** 163 (1986).
[3] I. Cernusak, G. H. F. Diercksen, and A. J. Sadlej, Chem. Phys. **108,** 45 (1986).
[4] M. H. Palmer, Z. Naturforsch. **41 a,** 147 (1986).
[5] H. Huber and P. Diehl, Mol. Phys. **54,** 725 (1985).
[6] H. Huber, J. Chem. Phys. **83,** 4591 (1985).
[7] B. Roos and P. Siegbahn, Theor. Chim. Acta **17,** 209 (1970).
[8] T. H. Dunning, J. Chem. Phys. **53,** 2823 (1970).
[9] M. W. Schmidt, and K. Ruedenberg, J. Chem. Phys. **71,** 3951 (1979).
[10] P. E. Cade, K. D. Sales, and A. C. Wahl, J. Chem. Phys. **44,** 1973 (1966) and priv. commun. in T. H. Dunning, D. C. Cartwright, W. J. Hunt, P. J. Hay, and F. W. Bobrowicz, J. Chem. Phys. **64,** 4755 (1976).
[11] D. Sundholm, P. Pyykkö, and L. Laaksonen, Mol. Phys. **56,** 1411 (1986).
[12] T. K. Ha, private communication.
[13] S. G. Kukolich and S. C. Wolfsy, J. Chem. Phys. **52,** 5477 (1970).
[14] J. N. Macdonald, D. Taylor, and J. K. Tyler, J. Mol. Spectrosc. **26,** 285 (1968).
[15] T. Kasuya, Sci. Pap. Inst. Phys. Chem. Res. **56,** 1 (1962).
[16] W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, Can. J. Phys. **53,** 1869 (1975).
[17] R. D. Brown, P. D. Godfrey, and D. A. Winkler, Austr. J. Chem. **35,** 393 (1982).
[18] T. A. Scott, Phys. Rep. **27 C,** 89 (1976).
[19] W. C. Bowman, E. Herbst, and F. C. de Lucia, J. Chem. Phys. **77,** 4261 (1982).
[20] F. C. de Lucia and W. Gordy, Phys. Rev. **187,** 58 (1969).
[21] M. K. Kemp, J. M. Pachan, and W. H. Flygare, J. Chem. Phys. **71,** 765 (1967).
[22] J. K. Tayler and J. Sheridan, Trans. Faraday Soc. **59,** 2661 (1963).
[23] J. D. Swalen and J. A. Ibers, J. Chem. Phys. **36,** 1914 (1962).
[24] K. Kohata, T. Fukuyama and K. Kuchitsu, J. Phys. Chem. **86,** 602 (1982).
[25] K. Yamada, J. Mol. Spectrosc. **79,** 323 (1980).
[26] R. Pearson and F. J. Lovas, J. Chem. Phys. **66,** 4149 (1977).
[27] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 4, Van Nostrand Reinhold Co., New York 1979.
[28] C. C. Costain, J. Chem. Phys. **29,** 864 (1958).
[29] C. C. Costain, J. Chem. Phys. **29,** 144 (1958).
[30] C. Degli Esposti, P. G. Favero, S. Serenellini, and G. Cazzoli, J. Mol. Struct. **82,** 221 (1982).
[31] M. D. Harmony and P. A. Baron, J. Mol. Struct. **38,** 1 (1977).
[32] H. M. McConnell and J. Strathdee, Mol. Phys. **2,** 129 (1959).
[33] H. Huber, Theor. Chim. Acta (Berlin) **55,** 117 (1980).
[34] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17,** 782 (1949).
[35] E. A. C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, London 1969, p. 227 ff.