Semiempirical vs. Ab Initio Calculations of Molecular Properties. Part 3. Electric Field Gradients at 14N Nuclei in some Small Molecules

Maksić, Zvonimir B.; Primorac, Miljenko; Supek, Selma

Source / Izvornik: **Croatica Chemica Acta, 1988, 61, 65 - 72**

CROATICA CHEMICA ACTA CCACAA 61 (1) 65—72 (1988)

CCA-1780

YU ISSN 0011-1643
UDC 541
Original Scientific Paper

Semiempirical vs. Ab Initio Calculations of Molecular Properties. Part 3. Electric Field Gradients at ^{14}N Nuclei in some Small Molecules

Z. B. Maksić[a,c], *M. Primorac*[b], *and S. Supek*[c]

[a]*Theoretical Chemistry Group, The Ruđer Bošković Institute, 41001 Zagreb, Yugoslavia*

[b]*Faculty of Forestry, The University of Zagreb, 41000 Zagreb, Šimunska 25, Yugoslavia*

[c]*Faculty of Natural Sciences and Mathematics, The University of Zagreb, Marulićev trg 19, 41000 Zagreb, Yugoslavia*

Received April 4, 1987

Electric field gradients (EFG) at nitrogen nuclei in some small and medium size molecules are calculated by the semiempirical CNDO/2D and SCC-MO methods. A salient feature of our procedure is accurate evaluation of matrix elements of the EFG operator. Hence, comparison of EFG values with the results of more sophisticated ab initio procedures obtained by suitable basis sets indicates flaws and shortcomings of the semiempirical schemes. It is concluded that EFGs provide a sensitive test of the anisotropy of the charge distribution of atoms in molecular environments. Therefore, they are invaluable for parametrization purposes leading to optimal screening constants of valence AOs to be used in semiempirical theories. As to the performance of the present CNDO/2D and SCC-MO methods, they provide only qualitative information about EFGs, the latter scheme being better because the CNDO/2D method fails to reproduce nuclear quadrupole coupling constants of nitriles.

INTRODUCTION

The ab initio calculations of near Hartree-Fock quality, followed by massive CI computations or some other approach to estimating electron correlation energy, are now feasible for small molecules. The compounds of chemical interest are, however, large as a rule and computational costs soon become prohibitively high for very sophisticated methods particulary if trends of some properties along the series of related molecules are studied. One has to resort then to the approximate ab initio or semiempirical procedures which are hopefully a good compromise between efficiency and accuracy. The latter poses a serious problem, namely, it requires a quantitative appraisal of the approximate wavefunctions offered by a reliable criterion. Most of the current quantum chemistry methods are based on the variation theorem which minimizes the energy expectation value within a certain subspace of the Hilbert space. The total energy, however, is not a good criterion of the quality of the resulting wavefunctions[1]. Molecular energy is essentially a sum of free-atom values, the changes accompanying bond formation being very small. Furthermore, it is well known that the changes in wavefunctions of the first order affect the total energy only in the second order. Hence, it is not surprising that the energy is frequently quite insensitive to the finer details of the electron charge distribution in particular regions of a molecule. Considerably better probes of the quality of molecular wavefunctions are provided by some one-electron properties. Their operators differ in the functional form thus measuring wavefunctions in different domains of the molecule. For example, molecular quadrupole moments reflect deviation from the spherical symmetry of the outer portion of the electronic charge distribution. On the other hand, electric field gradients at the site of a particular atom scan anisotropy of the charge distribution in the immediate vicinity of the nucleus in question. The electrostatic potentials at the nuclei are extremely rich in their chemical content (ESCA shifts[2], total molecular energies[3]) being intimately related to atomic monopole moments[4,5] etc.. It should be pointed out that not all of the one-electron properties are strongly dependant on subtle features of the charge distributions in molecules. Notable exceptions are diamagnetic susceptibility of molecules χ^d and diamagnetic shielding of the nuclei σ^d. The former entity is closely related to the molecular second moments, which in turn are very well reproduced by simple formulae developed either within the independent atom (IAM) or modified atom (MAM) model[6,7] representations of molecules. The same holds for diamagnetic shielding[8-11] σ^d. It follows that a crude description of the charge distributions in molecules yields quite reasonable values for χ^d and σ^d properties. By reversing the argument one concludes that χ^d and σ^d cannot serve as severe tests of the value of the calculated wavefunctions. Rather, they provide necessary (but not sufficient) criteria which should be satisfied by approximate but acceptable wavefunctions[11]. In other words, if some approximate methods yield poor χ^d and σ^d values, they are either intrinsically inconsistent or have some other serious flaws.

Since semiempirical methods either involve a number of approximations or are based on effective hamiltonians, their wavefunctions should be carefully examined by computing one-electron properties. The calculated values should be then compared with the results of the ab initio SCF data which are close to the Hartree-Fock limit. Comparison with experimental data is not quite satisfactory because measured values include both the electron correlation effect and vibrational averaging. In addition, the measured values sometimes incorporate intermolecular effects like e. g. in the solid state. Hence, deviations of the semiempirical estimates of one-electron properties from good SCF results indicate shortcomings of the applied semiempirical schemes provided that all elements of the one-electron operators are rigorously calculated. This is exactly the case in our procedure in contrast to other semiempirical work in the field. We pursued extensive investigations of one-electron properties involving molecular quadrupole moments[12], electric field gradients at deuteron[14], diamagnetic susceptibilities[12,14] and electrostatic potentials at the nuclei[15] employing CNDO/2, CNDO/2D and SCC-MO methods. The first and the last of these procedures are typical representatives of schemes based on the ZDO approximation and on a full account of the orbital overlapping, respectively. It turned out that, on average, the SCC-MO method gave substantially better one-electron properties and consequently more reliable charge distributions. Unsatisfactory performance of the CNDO/2 method can be traced down to the use of the inappropriate basis set. To be more specific, the zero-overlapping condition is enforced to essentially strongly overlapping basis set. A part of this serious inconstistency is remedied by deortogonalization of the calculated MOs[12,16] leading to the CNDO/2D variant. The latter is more successful in reproducing one-electron properties than the parent CNDO/2 scheme. In this work we discuss application of the SCC-MO and CNDO/2D methods to the calculation of electric field gradients at nitrogen atom in some small and medium size molecules.

CALCULATIONS

The diagonal element of the electric field gradient (EFG) tensor at the nitrogen atom is given by[17]:

$$q_{\alpha\alpha}(N) = \sum_{A(A \neq N)} Z_A (3r^2_{A\alpha} - r_A^2)/r_A^5 - \langle 0 \,|\, (3r_\alpha^2 - r^2)/r_\alpha^5 \,|\, 0 \rangle \tag{1}$$

where $\alpha = x, y, z$ and the origin of the coordinate system is placed at N nucleus*. Hence, EFG is the difference of two large terms implying that very accurate wavefunctions are needed if a quantitative information about $q_{\alpha\alpha}(N)$ values is desired. Unlike other semiempirical studies of the $q_{\alpha\alpha}(N)$ gradients[18-20]. all integrals over STO orbitals are accurately evaluated by the Gaussian transform technique.[21] Importance of rigorous treatment of EFG matrix elements in the semiempirical calculations of the NQCCs of deuteron was discussed by us[13] and by Barfield et al.[22].

The applied SCC-MO method has been described elsewhere[15]. It retains all overlap integrals, but Coulomb interactions are treated only implicitly via an effective hamiltonian which depends explicitly on the charge density distribution. Hence, the resulting molecular wavefunctions are produced in an iterative self-consistent charge process. This procedure remedies to a large extent the well known drawbeck of the EHT method, namely a grossly exaggerated intramolecular charge transfer. Deorthogonalization (renormalization) of the CNDO/2D MOs is discussed in a recent book of Sadlej[16]. Calculations are performed by using Slater AOs. In some illustrative cases other basis sets were utilized in order to examine the dependence of EFG values on the quality of the basis set.

Finally, it should be mentioned that inner electrons are treated as unpolarized cores. Hence, the Sternheimer effect[23] is neglected. The influence of the finite size of the nucleus[24] is disregarded, too.

RESULTS AND DISCUSSION

The calculated electric field gradients are converted to nuclear quadrupole coupling constants according to the formula $\chi_N = (eq_N Q_N/h)$, where Q_N is the nuclear quadrupole moment. The latter are not accurately known either by experiment or by theory. A range of values reported in the literature for nitrogen was recently reviewed by Ha[25]. He recommends $Q_N = 20.8$ mbarn obtained by accurate calculation of the electric field gradient at ^{14}N in NH_3 and the experimental χ_N value. However, the experimental NQCC in this molecule may be influenced by large amplitude umbrella vibrations. The most recent measurements by fast-ion bombardments[26] and by electron scattering[27] yield values of 19.3 ± 0.8 mbarn and 17.4 ± 0.2 mbarn, respecti-

---

* The calculated EFG values refer as a rule to the principal components of the EFG tensor. In some cases, however, the inertial coordinate system was used or values along the bonds in question are given. Then the off-diagonal values of the EFG tensor were not explicitly treated.

vely. We shall make use of the former value keeping in mind that this is not necessarily the best choice. The exact value is not of crucial importance for this work because we are interested in the differences between the calculated ab initio and semiempirical NQCCs. What matters is a consistent use of the same Q_N value and all theoretical data taken from the literature are recalculated by utilizing $Q_N = 19.3$ mbarn. Slater AOs are used in all calculations unless otherwise stated.

Nuclear quadrupole coupling constants of ^{14}N calculated by the CNDO/2D and SCC-MO method are compared with the available ab initio results and observed values in Table I. Perusal of the data reveals several interesting features. In the first place, the SCC-MO method performs better than the CNDO/2D scheme predominantly because the latter procedure is unsatisfactory in treating nitrile nitrogens yielding in most cases the wrong sign. Considerable improvement of the CNDO/2D scheme is offered by the use of

TABLE I

Comparison of the ^{14}N Nuclear Quadrupole Coupling Constants as Estimated by the Semiempirical CNDO/2D and SCC-MO Methods With Ab Initio Results and Experimental Data in some Symmetric Top Molecules (in Mc/s.)

Molecule	CNDO/2D	SCC-MO	AB INITIO	EXPTL.*
NN	—1.1 (—4.5)[a]	—3.6 (—5.1)[b]	—3.97[c]; —5.656[d]	—4.65
HCN	0.4	—4.5 (—5.9)[b]	—3.67[c]; —5.417[e]	—4.58
FCN	1.6	—3.5 (—4.1)[b]	—3.149[f]; —3.226[e]	—2.67
HCCCN	1.5	—4.4	—4.960[e]	—4.20
NCCN	—0.2	—4.6	—5.156[f]; —5.399[e]	—4.27
H_3CCN	0.1	—4.2	—3.19[c]; —3.573[g] —4.575[f]	—4.21
F_3CCN	—0.5	—4.8	—	—4.70
H_3CNC	3.7	5.3	1.197[c]; 3.623 0.799[f]	0.45
$N^{\dagger}NO$	3.6	—1.7	0.181[c]; —1.350[f]	—0.79
$NN^{\dagger}O$	0.2	6.5	—0.107[c]; —1.105	—0.24
$H_2NCN^{\dagger}$	1.2[h]	—3.6[h]	—2.064[c]	
NH_3	—6.6	—9.6 (—11.9)[b]	—4.812[c]; —4.036[i] —4.748[f]	—4.08
NF_3	—4.7	—8.0	—9.10[j]	—7.07

* Experimental data are taken from ref. 17. The quadrupolar nucleus is denoted by a dagger.

[a] Anisotropic Best Limited Atomic basis set of Ransil[28].

[b] DZ atomic basis set of Clementi[29].

[c] GTO of the DZ quality ab initio calculations of Snyder and Basch[30].

[d] [5s3p] contracted GTO basis functions of Dunning[31].

[e] Near Hartree-Fock value of Bonaccorsi et al.[32] obtained by the accurate wavefunctions of McLean and Yoshimine[33].

[f] Calculation of Barber et al.[34] based on Dunning's sp basis set [35] with a scale 1.0 for H.

[g] Calculation of Ha[36] which employed ten SGTO per spherical 1s and 2s orbitals and five pairs of GTO pore 2p orbital.

[h] Component of the χ-tensor along the nitrile $C{\equiv}N$ bond.

[i] DZ+P basis set calculation of Ha[25].

[j] Localized molecular orbital calculations of Unland et al.[37] with minimal STO basis set AOs possessing Clementi-Raimondi[38] screening constants.

Ransil's anisotropic minimum basis set[28] as evidenced by the test case calculation on N_2. On the other hand, Clementi DZ AOs did not improve SCC-MO results in N_2, HCN, FCN and NH_3. Consequently, they should not be employed because the only effect is a considerable increase in computing time of the EFG matrix element. The choice of the basis set deserves some more comments. It was observed by Kern[39] and by Richardson[40] that EFGs of the first row atoms critically depend on the screening constants of the 2p-subshell. It should be pointed out that extended basis sets are not so dependent on the nonlinear parameters. Bonaccorsi et al.[32] calculated EGF at N in HCN molecule with basis sets comprising 6 and 12 2pN STOs. The corresponding eq_N values were —1.1573 and —1.1948 a. u., respectively. Furthermore, a large basis set is not a guarantee that the NQQC is closer to the HF limit. Accurate calculations of Cade, Sales and Wahl (as cited by Lucken[17]) on N_2 have shown that Hartree-Fock value of eq_N is quite close to a small but apparently appropriate basis set. Hence, it follows that by suitable selection of screening parameters one could obtain quite reasonable estimates of NQCCs. Needless to say, EFGs at the first row atoms depend also on the relative populations of 2p-orbitals. Therefore, additional information is necessary for a successful parametrization of the semiempirical schemes. For this purpose, electrostatic potentials at the nuclei (ESCA shifts and/or diamagnetic shielding), NMR spin-spin coupling constants may prove very useful. Although this is an interesting problem, it lies outside the scope of the present paper. In any case, we feel that empirical estimates of screening constants determined solely by fitting the heats of molecular formation together with all the other parameters, like in MINDO and MNDO methods, is not completely satisfactory.

Inspection of the SCC-MO results shows that agreement with more sophisticated calculations is only qualitative. If the nitrogen in question assumes a central position like in $NN^{+}O$ or H_3CNC, the SCC-MO estimates of NQCCs are too high. In NH_3 the (^{14}N) coupling constant is too low by factor 2. The CNDO/2D method is obviously unsatisfactory for this type of compounds. As to the ab initio evaluation of χ (^{14}N) constants, one can single out calculations on HCN, FCN, (CN_2) and HC_3N of Bonaccorsi et al.[32] based on AOs wavefunctions of McLean and Yoshimine[33]. In spite of good basis sets, discrepancies with the measured values are of the order of $\sim$ 1 Mc/s. Calculations of Barber et al.[34] indicate that Dunning's sp basis set[35] is capable of giving information about χ (^{14}N) at the semiquantitative level. On the other hand, DZ basis set of Snyder and Bash[30] has a relatively modest success yielding a wrong sign for χ (^{14}N) of the peripheral atom in NNO.

The semiempirical results for some medium size less symmetric molecules are presented in Table II. Since the ab initio results are sparse, the calculated χ(^{14}N) values are chacked against available experimental data. A survey of the numbers shows that both methods offer qualitatively correct information. The SCC result is again too high for the central nitrogen in HNNN molecule. Interestingly, the CNDO/2D value is in fine accordance with the experimental upper bond for this position, but fails as usual for the terminal N atom. It should be kept in mind when comparing theoretical results with experimental data that the Sternheimer effect is sometimes not

TABLE II

Comparison of ^{14}N Nuclear Quadrupole Coupling Constants in some Small Molecules Obtained by the CNDO/2D and SCC-MO Methods with Available Experimental and Ab Initio Data (in Mc/se.)

Molecule	CNDO/2D	SCC-MO	AB INITIO AND EXPTL.[a]
$O=C(CN)_2$	$\chi_{aa} = -0.6$	-2.7	-2.35
	$\chi_{bb} = -0.4$	-0.2	0.05
	$\chi_{cc} = 1.0$	2.9	2.80
$H_2C=HCN$	$\chi_{CN} =$ —	-4.3	-4.21
HN^+NN	6.7[b]	4.1[b]	4.85
HNN^+N	0.7[b]	5.6	<0.80
$HNNN^+$	3.1[b]	-1.5[b]	-1.35
HNCO	6.3[c]	3.5[c]	2.0
FNO	$\chi_{\alpha\alpha} = 0.9$	—	1.69; 2.883[d]
	$\chi_{\beta\beta} = 2.2$	—	3.14; 3.626
	$\chi_{\gamma\gamma} = -3.1$	—	-4.83; -6.510
CH_3NH_2	$\chi_{\alpha\alpha} = 3.0$	4.9	0.69
	$\chi_{\beta\beta} = 4.0$	5.0	3.00
	$\chi_{\gamma\gamma} = -7.0$	-9.9	-3.69
CH_3NF_2	$\chi_{aa} = 3.9$	6.9	6.45
	$\chi_{bb} = 0.9$	3.2	0.46
	$\chi_{cc} = -4.8$	-10.1	-6.90
F_2NH	$\chi_{\alpha\alpha} = 0.5$	3.3	2.50
	$\chi_{\beta\beta} = 3.4$	5.7	6.40
	$\chi_{\gamma\gamma} = -3.9$	-9.0	-8.90
N_2H_4	$\chi_{\alpha\alpha} = 3.4$	6.9	4.614[e]
	$\chi_{\beta\beta} = 3.6$	4.5	1.235
	$\chi_{\gamma\gamma} = -7.0$	-11.4	-5.849

[a] Data refer to measured values [17] if not otherwise stated.

[b] Component along the axis passing through the central NN atoms.

[c] Component along the axis passing through heavy atoms.

[d] Ref. 30.

[e] Ref. 34.

insignificant[41,42]. We believe, however, that it is much more important for higher inner cores than for the $(1s)^2$ shell.

It is noteworthy that molecules considered in Table I as well as HNCO and HNNN were studied by White and Drago[19] by using the same SCC-MO method. However, in their approach three-center EFG integrals were neglected whilst the two center contributions were assumed to be proportional to the corresponding nuclear terms. The constants of proportionality were empirically adjusted. The agreement with the experimental data is slightly better than in the present study. It should be stressed that the philosophy that we adopted is entirely different. We did not strive to get the best accordance with experiment. On the contrary, discrepancies with good ab initio data (not experiment!) are valuable hints that semiempirical hasis sets and the resulting orbital populations are not optimal. It is our firm belief that EFGs synergistically used with some other expectation values calculated at the HF limit, will ultimately lead to a better semiempirical description of the atomic anisotropy in molecular environments, if the semiempirical schemes are properly designed to reproduce these one-electron properties with reasonable accuracy. The present state of affair is that the SCC-MO scheme employing overlapping basis sets reproduces one-electron properties better than semiempirical procedures involving various ZDO approximations[21,14-43].

REFERENCES

1. R. S. Mulliken, *J. Chem. Phys.* **36** (1962) 3428.
2. K. Siegbahn, C. Nordling, G. Johansson, J. Hedmann, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules*, North Holland, Amsterdam, 1969.
3. P. Politzer, *Isr. J. Chem.* **19** (1980) 224 and the references cited therein.
4. Z. B. Maksić and K. Rupnik, *J. Mol. Struct.* **141** (1986) 309 and the references cited therein.
5. Z. B. Maksić and K. Rupnik, *Theoret. Chim. Acta* **62** (1983) 219.
6. Z. B. Maksić, M. Eckert-Maksić, and K. Rupnik, in *Conceptual Quantum Chemistry. Models and Applications*, Z. B. Maksić, Ed. *Croat. Chem. Acta* **57** (1984) 1295.
7. Z. B. Maksić, D. Kovaček, and B. Vidić, *Chem. Phys. Letters* **129** (1986) 619.
8. N. F. Ramsey, *Phys. Rev.* **78** (1950) 699; **86** (1952) 243.
9. W. H. Flygare and J. Goodisman, *J. Chem. Phys.* **49** (1968) 3122.
10. Z. B. Maksić and K. Rupnik, *Theoret. Chim. Acta* **62** (1983) 397.
11. Z. B. Maksić and S. Supek, *Theoret. Chim. Acta* (in print)
12. J. E. Bloor and Z. B. Maksić, *Mol. Phys.* **22** (1971) 351; **26** (1973) 397; *J. Chem. Phys.* **57** (1972) 3572.
13. J. E. Bloor and Z. B. Maksić, *Proc. Second Int. Symp. NQR Spectroscopy*, Pisa, 1975, p. 1.
14. A. Graovac, Z. B. Maksić, K. Rupnik, and A. Veseli, *Croat. Chem. Acta* **49** (1977) 695.
15. Z. B. Maksić and K. Rupnik, *Z. Naturforsch. Teil A* **38** (1983) 308.
16. J. Sadlej, *Semiempirical Methods of Quantum Chemistry*, Ellis Horwood Ltd., Chichester, 1985. and the references cited therein.
17. E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, London, 1969.
18. P. C. Van der Voorn and R. S. Drago, *J. Am. Chem. Soc.* **88** (1966) 3255.
19. W. D. White and R. S. Drago, *J. Chem. Phys.* **52** (1970) 4717.
20. M. J. S. Dewar, H. W. Kollmar, and S. H. Suck, *J. Amer. Chem. Soc.* **97** (1975) 5590.
21. I. Shavitt and M. Karplus, *J. Chem. Phys.* 36 (1962) 550; C. W. Kern and M. Karplus, *J. Chem. Phys.* **43** (1965) 415.
22. M. Barfield, H. P. W. Gottlieb, and D. M. Doddrell, *J. Chem. Phys.* **69** (1978) 4504
23. R. M. Sternheimer, *Phys. Rev.* **84** (1951) 244; **95** (1954) 736; R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **102** (1956) 731.
24. P. Pyykkö, *Chem. Phys. Letters* **6** (1970) 479.
25. T. K. Ha, *Z. Naturforsch, Teil A* **41** (1986) 163.
26. H. Winter and H. J. Andrä, *Phys. Rev.* **A 21** (1980) 581.
27. N. Enslin, W. Bertozzi, S. Kowalski, C. P. Sargent, W. Turchinetz, C. F. Williamson, S. P. Fivozinsky, J. W. Lightbody, and S. Penner, *Phys. Rev.* **C9** (1974) 1705.

28. B. J. Ransil, *Revs. Mod. Phys.* **32** (1960) 245.
29. E. Clementi, *J. Chem. Phys.* **40** (1964) 1944; *Tables of Atomic Functions*, Supplement to the IBM J. Res. Develop. **9** (1965) 2.
30. L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties*. John Wiley & Sons, New York, 1972.
31. T. H. Dunning, Jr., *J. Chem. Phys.* **53** (1970) 2823.
32. R. Bonaccorsi, E. Scrocco, and J. Tomasi, *J. Chem. Phys.* **50** (1969) 2940.
33. A. D. McLean and M. Yoshimine, *Tables of Linear Wave Functions*, IBM, San Jose, California, 1967.
34. M. Barber, S. M. Hayne, and A. Hinchliffe, *J. Mol. Structure* **62** (1980) 207.
35. T. H. Dunning, *J. Chem. Phys.* **55** (1974) 716.
36. T. K. Ha, *J. Mol. Structure* **11** (1972) 185.
37. M. L. Unland, T. H. Dunning, and J. R. Van Wazer, *J. Chem. Phys.* **50** (1969) 3208.
38. E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38** (1963) 2886.
39. C. W. Kern, *Bull. Amer. Chem. Soc.* **12** (1967) 69.
40. J. W. Richardson, *Revs. Mod. Phys.* **32** (1960) 461.
41. M. Grodzicki, S. Lauer, A. X. Trautwein, and A. Vera, in *Mössbauer Spectroscopy and its Chemical Applications*, J. Slekens and G. Shenoy, eds., *ACS Advances in Chemistry Series*, *Vol.* **194** (1981) 1.
42. V. Männing and M. Grodzicki, *Theoret. Chim. Acta* **70** (1986) 189.
43. M. Rabinowitz and R. Rein, *Int. J. Quant. Chem.* **6** (1972) 669; Z. B. Maksić and S. Supek, submitted for publication.

SAŽETAK

Semiempirijski vs. *ab initio* računi molekulskih svojstava. Dio 3. Gradijenti električnog polja kod jezgri ^{14}N u nekim malim i srednje velikim molekulama

Z. B. Maksić, M. Primorac i S. Supek

Gradijenti električnog polja na mjestu jezgri atoma dušika u nekim manjim molekulama izračunani su s pomoću semiempirijskih CNDO/2D i SCC-MO metoda. Osnovna značajka ovih računa jest egzaktno proračunavanje integrala operatora gradijenta električnog polja. Zbog toga se razlike između semiempirijskih i *ab initio* rezultata mogu direktno pripisati nedostacima primijenjenih semiempirijskih shema. Ustvari, one daju uvid u anizotropiju raspodjele elektronske gustoće atoma u molekulskoj okolini, kao i informaciju o konstantama zasjenjenja jezgri. Preporučeno je da se gradijenti električnog polja iskoriste pri parametrizaciji semiempirijskih metoda.