Theoret. Chim. Acta (Berl.) 44, 293-303 (1977)

THEORETICA CHIMICA ACTA

Changes in Molecular Properties with Changes in Molecular Geometry: A Partitioning into Electronic and Nuclear Components

John D. Goddard and Imre G. Csizmadia

Department of Chemistry, University of Toronto, Toronto, Ontaria, Canada M5S 1A1

Most one-electron properties vary with changes in molecular conformation. Although the nuclear component remains constant for some of the one-electron property changes and thus the overall change depends only on the electronic change this result is not general. Often the change in the nuclear component dominates the overall change in a molecular property. An analysis of the changes in a number of one-electron properties with changes in molecular geometry in terms of the changes in the nuclear and the electronic components is presented. The inversion of ammonia and the torsion of ethane were chosen as important examples of conformational changes and the changes in molecular one-electron properties studied.

Key words: Molecular one-electron properties, electronic and nuclear components of ~

1. Introduction

One problem to which *ab initio* molecular orbital calculations have been widely and generally successfully applied is that of rotation-inversion conformational changes [1]. Such studies determine the change in the total molecular energy as a function of changes in molecular geometry. Further insight may be attained by considering not only the change in the total energy but also the changes in its components, the nuclear and electronic energies, as the molecule's geometry is varied [2]. Just as the total energy and its electronic and nuclear components vary with changing geometry so any molecular property may be expected, in general, to show a dependence on the molecular geometry. Molecular one-electron properties are known [1] to be sensitive measures of the molecular wave function in various regions of space and it might be anticipated that the changes in the wave function due to changes in the nuclear conformation could strongly affect the values of various one-electron properties. By analogy to the energy component analysis mentioned previously, the analysis of changes in total molecular one-electron properties in terms of changes in nuclear and electronic components should provide further insight. However, such an approach has not previously been widely adopted. In this work, the changes in selected molecular one-electron properties with conformational change have been analysed in terms of changes in the nuclear and electronic components. Two important conformational problems, the inversion of ammonia and the torsion of ethane, have been chosen as examples.

2. Method of Calculation

The geometries employed for ammonia and ethane are illustrated in Fig. 1. The bond lengths and angles were chosen to be near the experimental values [3]. During inversion or rotation the bond lengths were kept fixed, i.e. no relaxation of the bond lengths with changes in the bond or dihedral angles was allowed.

The basis sets for both molecules were of [*sp*/*s*] type and of approximately double-zeta quality. For carbon and nitrogen a (13*s*7*p*) Gaussian basis contracted to [4*s*2*p*] was used [4]. For hydrogen, a (4*s*) primitive basis scaled and then contracted to [2*s*] was employed [5]. The MO calculations were performed using modified IBMOL-IV [6] and POLYATOM 2 [7] program systems.

One-electron properties were calculated employing the program package available as part of the POLYATOM system [7]. For ammonia, the dipole, quadrupole, and octupole moments; the potentials at N and H; and the electric field gradient (along the C_{3v} axis) at N were studied as functions of the inversion motion. For ethane the quadrupole and second moments; the potentials; and the electric field gradients were examined as the molecule underwent torsional motion about the carbon–carbon bond.

3. Results and Discussion

For comparison, the total energies obtained with the basis set of this work are presented in Table 1 along with the results from large polarized basis set calculations and estimates of the Hartree–Fock limits. The total energies are probably near to a limit imposed by the neglect of polarization functions in the basis set.

3.1. The Inversion of Ammonia

As is well known [1], the barrier to rigid (i.e. fixed bond length) inversion in ammonia is electronic dominant. This result does *not* require that the changes in other molecular properties also be dominated by the electronic components in the process of inversion. Just as with the energies the change in a total property may be termed nuclear or electronic dominant depending upon which of the two component curves the total property curve is in phase with over the range of the geometrical variation. It has been suggested that the changes in the nuclear and electronic components of the energy must always be in opposite phase [11] when moving along a minimum energy reaction path on the conformational hypersurface. Such a result does *not* hold for all molecular properties and it may not be possible to classify a change as nuclear or electronic dominant. Note that by definition the signs of the nuclear and electronic components of a one-electron property are different. However, this definition does *not* imply that the changes in the electronic and nuclear components of a one-electron property must be of opposite phase.

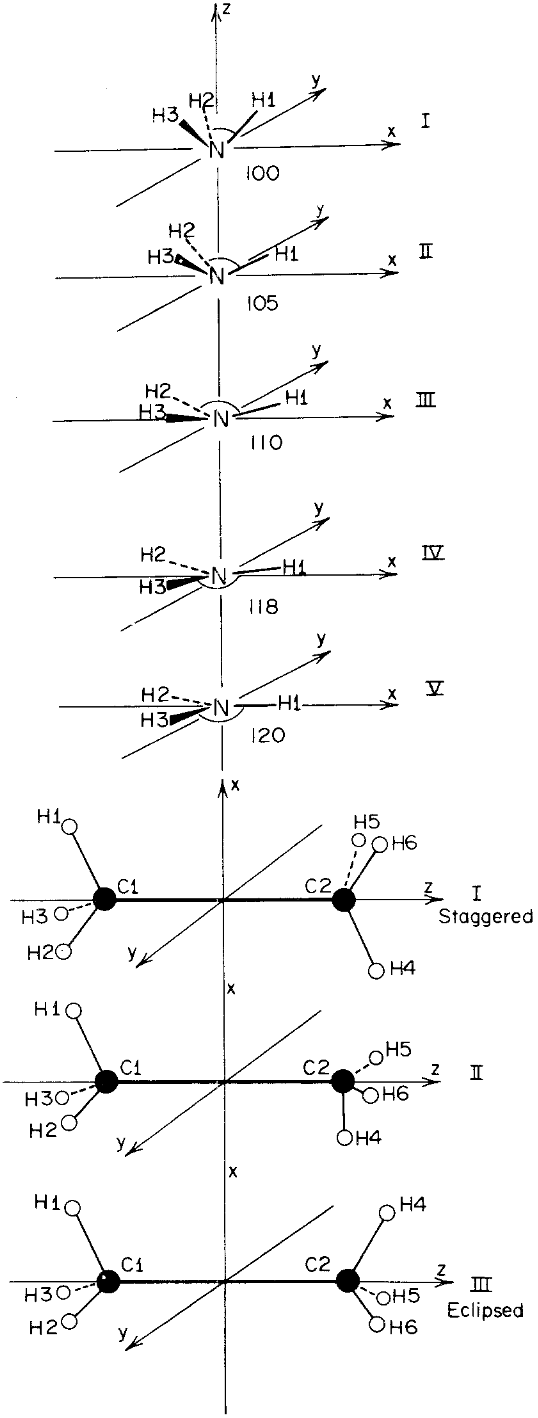

Fig. 1. Coordinate systems and geometries for the inversion of ammonia and the torsion of ethane

Table 1. Comparison of total energies

PGTF	CGTF	Total Energy (a.u.)	Reference
Ammonia			
(13*s*7*p*/4*s*)	[4*s*2*p*/2*s*]	–56.1769	This work
(13*s*7*p*1*d*/8*s*1*p*)	[6*s*2*p*1*d*/3*s*1*p*]	–56.2117	[8]
Estimated Hartree–Fock limit		–56.225	[9]
Ethane (staggered)			
(13*s*7*p*/4*s*)	[4*s*2*p*/2*s*]	–79.2043	This work
(11*s*7*p*1*d*/6*s*1*p*)	[5*s*3*p*1*d*/2*s*1*p*]	–79.2377	[10]
Estimated Hartree–Fock limit		–79.27	[10]

The variations of the total dipole, quadrupole and octupole moments and of the nuclear and electronic components of these moments with inversion are presented in Table 2 and in Fig. 2. By convention the higher moments were evaluated with respect to the centre of mass of the molecule. Symmetry requires that the total dipole and total octupole moments as well as their nuclear and electronic components must vanish for the planar (D_{3h}) geometry. For these moments the electronic and nuclear components vary with opposite phase. The small total changes in the overall moments are a result of much larger changes in the two components. For these moments, the total change is *nuclear dominant*.

Table 2. Changes in the nuclear, electronic and total moments with inversion of ammonia

HNH	Nuclear	Electronic	Total
Dipole moment (z-component; in Debye, 1 a.u. = 2.54154 D)			
100	6.8553	–4.1550	2.7003
105	5.8067	–3.3751	2.4316
110	4.7697	–2.6539	2.1158
120	0	0	0
Quadrupole moment (zz-compnent, 1 a.u. = 1.344911 B)			
100	–3.4156	1.5948	–1.8208
105	–4.5682	2.2487	–2.3195
110	–5.5204	2.7822	–2.7382
118	–7.4726	3.8400	–3.6326
120	–7.4954	3.8520	–3.6434
Octupole moment (zzz-component, 1 a.u. = 0.711688 × 10^{-34} esu cm^{-3})			
100	–6.0469	4.7324	–1.3145
105	–5.7832	4.3984	–1.3848
110	–5.1993	3.8689	–1.3304
118	–0.6581	0.4671	–0.1910
120	0	0	0

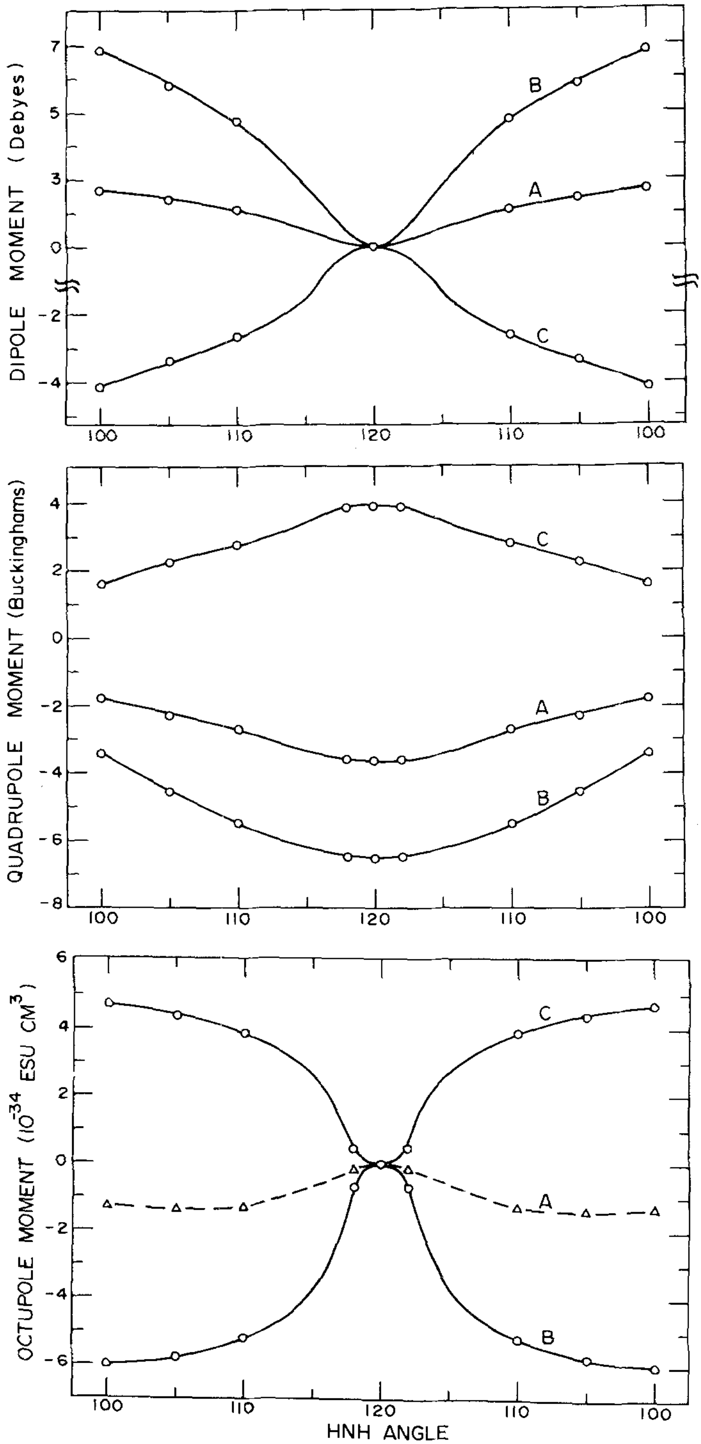

Fig. 2. Changes in the nuclear, electronic, and total moments with the inversion of ammonia. Dipole, quadrupole, and octupole moments. A = Total, B = Nuclear, C = Electronic

Table 3. Changes in nuclear, electronic and total potentials at N and H with inversion of ammonia

HNH	Nuclear	Electronic	Total
Potential at N[a]			
100	1.5564	−19.9477	−18.3913
105	1.5564	−19.9567	−18.4003
110	1.5564	−19.9649	−18.4085
118	1.5564	−19.9847	−18.4283
120	1.5564	−19.9850	−18.4286
Potential at H[a]			
100	4.3088	−5.3549	−1.0461
105	4.2837	−5.3354	−1.0517
110	4.2649	−5.3201	−1.0552
118	4.2310	−5.2915	−1.0605
120	4.2306	−5.2912	−1.0606

[a] In a.u., 1 a.u. = 9.07618×10^{-2} esu cm^{-1}.

The potentials, $\langle 1/r \rangle$, evaluated at the nitrogen and hydrogen nuclei for various geometries along the inversion pathway are given in Table 3. At the nitrogen nucleus the nuclear component of the potential remains constant (to four decimal places) as the molecule inverts and thus the small changes in the total potential at nitrogen must be determined by the changes in the electronic component. For the potentials evaluated at the hydrogen nucleus the nuclear and electronic components are of opposite phase and the total change in the potential is dominated by the nuclear term as illustrated in Fig. 3.

The changes in the $z'z'$ component of the electric field gradient at N with inversion (Fig. 4) illustrates that for molecular properties the nuclear and electronic components need not necessarily be of opposite phase.

3.2. The Torsion of Ethane

The barrier to rigid rotation in ethane is nuclear dominant as is well known [11]. However, this result for the energy change again does not imply that the changes in other properties must also be so dominated. For ethane, the nuclear components of the quadrupole and second moments were constant with respect to the torsional motion and thus the variation in the total moments is determined solely by the changes in the electronic component (Table 4), in contrast to the ammonia case.

The potential evaluated at the carbon nucleus has a constant nuclear component with respect to torsion and thus the small decrease in the total potential from the eclipsed to the staggered forms is electronic dominant (Table 5). At the hydrogen nuclei both the nuclear and electronic potentials (Table 5) vary as may be seen in Fig. 5. The small increase in the total potential at hydrogen on going from the eclipsed to the staggered form is electronic dominant.

For the electric fields (Table 6) and electric field gradients (Table 7), at carbon the nuclear components are constant and the changes in the total properties with torsion

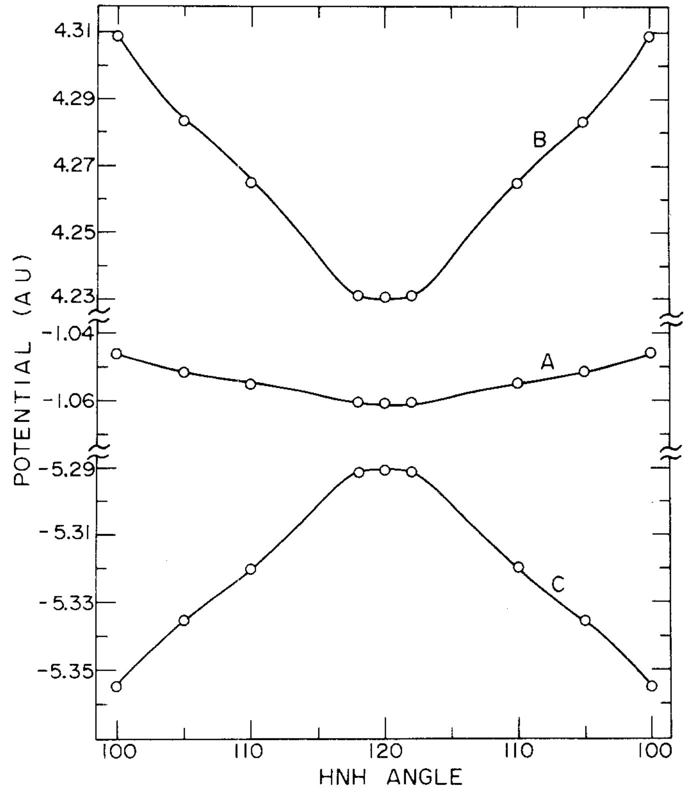

Fig. 3. Changes in the nuclear, electronic, and total potentials at H with the inversion of ammonia. A = Total, B = Nuclear, C = Electronic

electronic dominant. At hydrogen both the nuclear and electronic components of the electric field vary (Fig. 6) and the nuclear terms dominate.

3.3. General Discussion

It should be noted that for most of the one-electron properties studied the nuclear and electronic component curves have opposite phase. A small net change in the value of a molecular one-electron property is the result of larger but for the most part offsetting changes in the nuclear and electronic components. Such a result is also observed [11] when the changes in total, nuclear, and electronic energies with conformational change are calculated.

Regarding the changes in the moments of the charge distribution rigid inversion and rigid internal rotation conformational changes appear different. For the rigid inversion of ammonia, the changes in the dipole, quadrupole and octupole moments are nuclear dominant while for the rigid internal rotation of ethane the changes in the quadrupole and second moments are electronic dominant.

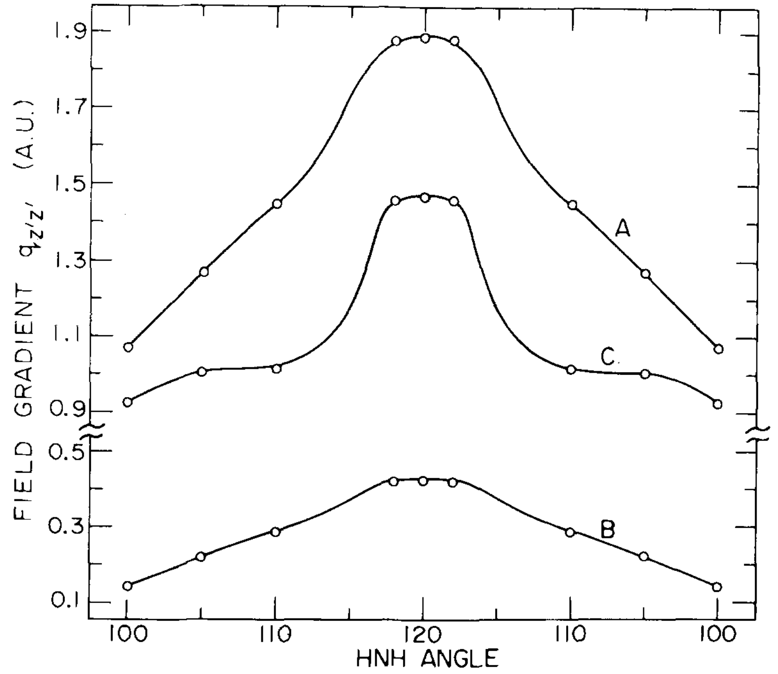

Fig. 4. Changes in the nuclear, electronic, and total electric field gradients ($qz'z'$ component) at N with the inversion of ammonia. A = Total, B = Nuclear, C = Electronic

Table 4. Changes in the nuclear, electronic and total second and quadrupole moments with torsion in ethane

Conformation	Nuclear	Electronic	Total
Second moment[a] (*zz*)			
Eclipsed	71.8521	−88.4302	−16.5781
30° [b]	71.8521	−88.3845	−16.5324
Staggered	71.8521	−88.3409	−16.4888
Quadrupole moment[a] (*zz*)			
Eclipsed	56.3265	−57.7273	−1.4008
30° [b]	56.3265	−57.6611	−1.3346
Staggered	56.3265	−57.5942	−1.2677

[a] In Buckinghams, 1 a.u. = 1.344911 B.

[b] Midway between eclipsed and staggered.

For both the rigid inversion of ammonia and the rigid torsion of ethane the changes in the potentials at the "heavy atom" (N or C) are electronic dominant. However, in the case of the change in the potential at hydrogen for ammonia the variation is nuclear dominant while for ethane the change is electronic dominant.

Table 5. Changes in the nuclear, electronic, and total potentials at C and H with torsion in ethane

Conformation	Nuclear	Electronic	Total
At C[a]			
Eclipsed	4.2277	−18.9765	−14.7488
30^0 [b]	4.2277	−18.9758	−14.7481
Staggered	4.2277	−18.9750	−14.7473
At H[a]			
Eclipsed	5.5246	−6.6380	−1.1134
30^0 [b]	5.5233	−6.6365	−1.1132
Staggered	5.5221	−6.6351	−1.1130

[a] In a.u.

[b] Midway between eclipsed and staggered.

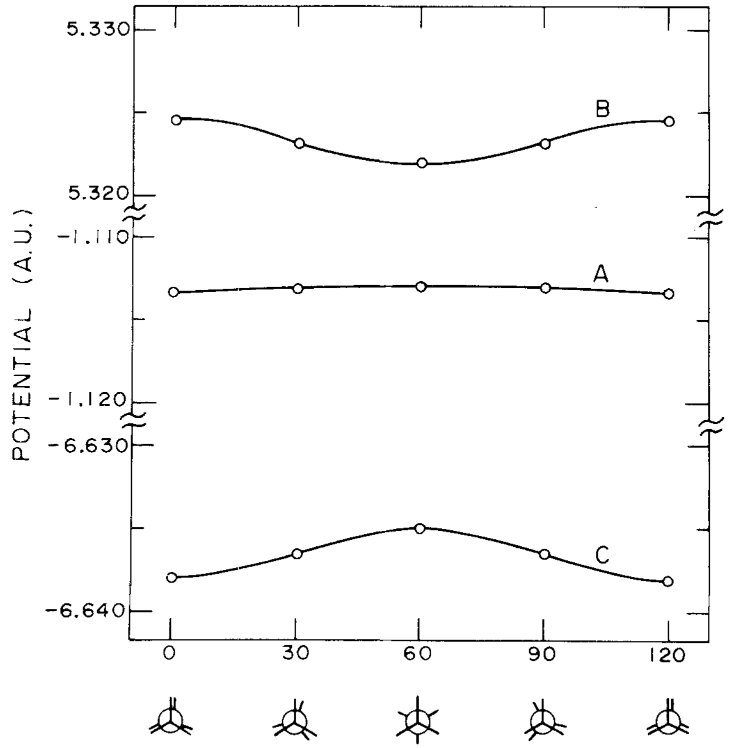

Fig. 5. Changes in the nuclear, electronic, and total potentials at H with the torsion of ethane. A = Total, B = Nuclear, C = Electronic

4. Concluding Remark

The present results suggest that it may be useful to analyse changes in total molecular one-electron properties by considering changes in the nuclear and electronic components.

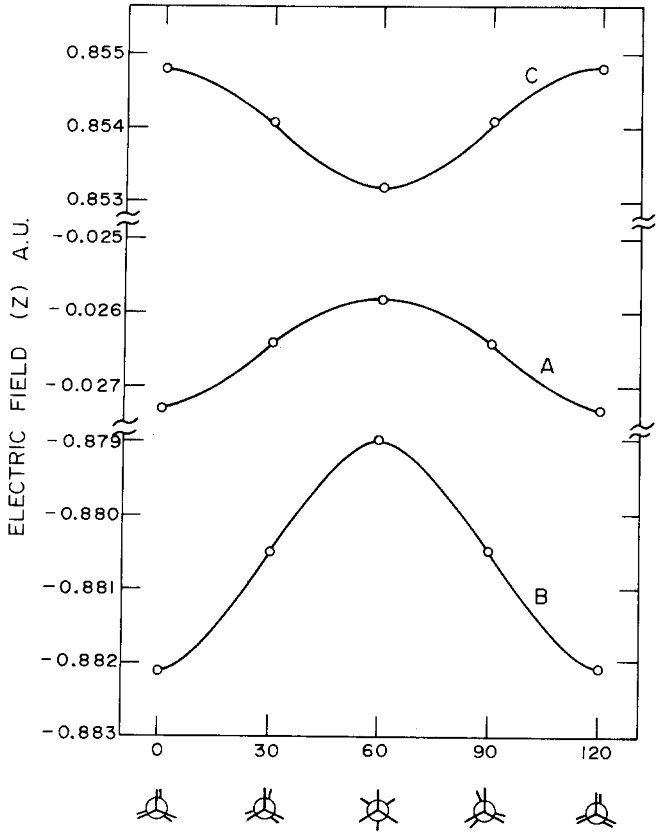

Fig. 6. Changes in the nuclear, electronic, and total electric fields at H (z component) with the torsion of ethane. A = Total, B = Nuclear, C = Electronic

Table 6. Changes in the nuclear, electronic and total electric fields at C and H with torsion in ethane

Conformation	Nuclear	Electronic	Total
At C1 (z)[a]			
Eclipsed	–0.6293	0.6216	–0.0077
30° [b]	–0.6293	0.6222	–0.0071
Staggered	–0.6293	0.6227	–0.0066
At H1 (z)[a]			
Eclipsed	–0.8821	0.8548	–0.0273
30° [b]	–0.8805	0.8541	–0.0264
Staggered	–0.8790	0.8532	–0.0258

[a] In a.u.

[b] Midway between eclipsed and staggered.

Table 7. Changes in the nuclear, electronic and total electric field gradients at C and H with torsion in ethane

Conformation	Nuclear	Electronic	Total
At C (zz)[a]			
Eclipsed	−0.3210	0.2564	−0.0646
30° [b]	−0.3210	0.2588	−0.0622
Staggered	−0.3210	0.2624	−0.0586
At H1 ($z'z'$)[a]			
Eclipsed	0.3419	−0.2419	0.1000
30° [b]	0.3440	−0.2430	0.1010
Staggered	0.3459	−0.2440	0.1019

[a] In a.u.

[b] Midway between eclipsed and staggered.

Acknowledgements. The financial support of this work by the National Research Council of Canada is gratefully acknowledged.

References

1. See e.g. Schaefer, III, H. F.: The electronic structure of atoms and molecules. A survey of rigorous quantum mechanical results. Reading, Mass.: Addison-Wesley 1972
2. For a similar approach: Allen, L. C.: Chem. Phys. Letters 2, 597 (1968)

3a. Ammonia-geometry: Whangbo, M.-H.: Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada

3b. Ethane-geometries: Clementi, E., Davis, D. R.: J. Chem. Phys. 45, 2593 (1966)

4. Huzinaga, S., Sakai, Y.: J. Chem. Phys. 50, 1371 (1969)
5. Basch, H., Robin, M. B., Kuebler, N. A.: J. Chem. Phys. 47, 1201 (1967)
6. Davis, D. R., Clementi, E.: IBMOL QCPE 92, Quantum chemistry program exchange, Chemistry Department, Indiana University, Bloomington, Indiana
7. Neumann, D. B., Basch, H., Kornegay, R. L., Snyder, L. C., Moskowitz, J. W., Hornback, C., Liebmann, S. P.: POLYATOM (Version 2), QCPE 199, Quantum chemistry program exchange, Chemistry Department, Indiana University, Bloomington, Indiana
8. Kari, R. E., Csizmadia, I. G.: Theoret. Chim. Acta (Berl.) 23, 1 (1971)
9. Ermler, W. C., Kern, C. W.: J. Chem. Phys. 61, 3860 (1974)
10. Veillard, A.: Chem. Phys. Letters 2, 128 (1969)
11. Csizmadia, I. G., Theodorakopoulos, G., Schlegel, H. B., Whangbo, M.-H,. Wolfe, S.: Can. J. Chem., in Press

Received September 14, 1976