Ab Initio **MBPT(4) Calculations of the Inversion Potential Function of NH₃**

Vladimír Kellö[a], Ivan Hubač[b], Alexander I. Boldyrev[c], and Vladimír Špirko[d]

[a]*Institute of Chemistry, Comenius University, Mlynská dolina, 842 15 Bratislava, Czechoslovakia,*

[b]*Department of Biophysics and Chemical Physics, Faculty of Mathematics and Physics, Comenius University, Mlynská dolina, 842 15 Bratislava, Czechoslovakia,* [c]*Institute of Chemical Physics, Academy of Science USSR, Kosygina 4 Str., Moscow B 334, USSR*

and

[d]*The J. Heyrovský, Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6, Flemingovo nám. 2, Czechoslovakia*

The inversion potential function and the dominant (*in-plane*) and *inversion-(in-plane)* force constants are calculated by means of the fourth-order many-body perturbation theory in the extended double-zeta-plus polarization basis set. Using the *ab initio* potential surfaces and the non-rigid invertor Hamiltonian the inversion energy levels of $^{14}NH_3$ are calculated. Despite the significant residual error in the perturbation expansion, the results indicate that the full fourth order procedure may be considered as a reliable tool for studying vibrational anharmonicity in other non-rigid molecules.

1. INTRODUCTION

The internuclear potential energy V of a polyatomic molecule is a complicated function of the vibrational displacements. The general form of V is not known and as yet it has not been derived from theory. The practical determination of V is made very difficult by this fact, especially in the case of non-rigid molecules. The standard power series expansion approximating V might not be strongly converging in such cases and, thus, the number of corresponding force constants may become unmanageably large. To overcome this limitation it is necessary either to use certain model assumptions concerning V or to include *ab initio* data.

A suitable function modelling V must be determined on the basis of previous experience. The use of the *ab initio* information is much more straightforward. However, this approach has also disadvantages. The main difficulty is the uncertainty in the accuracy of the *ab initio* information. Hence, prior to using the *ab initio* data, it is very important to assess the reliability of the used theory.

In the present paper the inversion potential function of the NH_3 molecule is studied by means of the many-body perturbation theory (MBPT) in the extended double-zeta-plus polarization (DZ + P) basis set. The aim of this study is to assess the effect of correlation energy in various orders of perturbation expansion (through the fourth order).

2. AB INITIO CALCULATIONS

The extended double-zeta-plus polarization basis set employed for calculations was a Gaussian $(9s5p1d)$ basis set contracted to $[4s3p1d]$, with all six possible d components on N, and a $(4s1p)$ set contracted to $[2s1p]$ on hydrogen[1,2]. The hydrogen s-type functions were scaled by factor 1.44 Exponents of the polarization functions were $\alpha_d = 0.85$ for nitrogen and $\alpha_p = 1.0$ for hydrogen[3].

The SCF calculations were made by using the program POLYATOM/2[4] The transformation of integrals and the correlation energy calculations were performed by means of the program POLYCOR[5]. The computational aspects of the fourth order MBPT calculations are described in Refs. 6 and 7.

Points on the energy hypersurface were chosen in order to sample a wide range of values for the inversion coordinate and only partially to probe the effects of the remaining vibrational distortions. The geometry parameters and the corresponding total energies are given in Table I.

3. THE POTENTIAL FUNCTIONS

In order to assess the quality of the calculated *ab initio* points it is convenient to fit them to an analytic potential function. In our case the following function has been found adequate (see Refs. 8—9)

$$V = V_0 + \sum_{i=1}^{4} K_i h^{2i} + S_1 \sum_{i=1}^{2} k_i h^{2i} + \frac{1}{2} F_{11} S_1^2 + \frac{1}{2} (F_{44} + f_{44}^{(2)} h^2) S_{4a}^2 \qquad (1)$$

where V_0 is the binding energy of the molecule in its reference configuration (planar configuration with optimal bond lengths, r_p), h is the distance from the atom N to the plane formed by the three hydrogen atoms, the vibrational coordinates S_1 and S_{4a} are defined as follows

$$S_1 = \sqrt{3}\,\Delta r = \sqrt{3}\,(r - r_p)$$

$$\qquad (2)$$

$$S_{4a} = (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6} = (2\alpha_1 - \alpha_2 - \alpha_3 - 2\pi)/\sqrt{6}$$

and, the K_i, k_i, F_{11}, F_{44} and $f_{44}^{(2)}$ are force constants.

The adjusted force constants and bond length (least squares optimization) are given in Table II. The fitted constants are well determined and the standard deviations of the fits do not exceed 4 cm⁻¹ (18 × 10⁻⁶ a. u.).

To allow for a straightforward comparison of the pure inversion potentials (i. e. potential energies of molecules inverting with all HNH angles equal, and with all bond lengths equal to r_p), two additional characteristics are given in Table II. Namely, the angle α_{min} for which the inversion potential acquires its minimum, and the corresponding inversion barrier height H_{inv}.

TABLE I

Total Energies in Different Geometrical Configurations[a]

r a. u.	α_1 deg	α_2 deg	α_3 deg	(Energy + 56.0)/a. u.				
				SCF	$E_D^{(2)}$	$E_D^{(2)—(3)}$	$E_{SDQR}^{(2)—(4)}$	$E_{SDTQR}^{(2)—(4)}$
1.86	120	120	120	—0.202553	—0.399280	—0.409979	—0.412230	—0.416910
1.88	120	120	120	—0.202401	—0.399698	—0.410319	—0.412661	—0.417415
1.9124	120	120	120	—0.200827	—0.399056	—0.409545	—0.412042	—0.416920
1.9124	70	70	70	—0.108993	—0.319966	—0.329276	—0.331786	—0.338234
1.9124	93	93	93	—0.195397	—0.395648	—0.406681	—0.409284	—0.414540
1.9124	100	100	100	—0.205830	—0.404577	—0.415703	—0.418296	—0.423385
1.9124	106.7	106.7	106.7	—0.209636	—0.407622	—0.418685	—0.421255	—0.426240
1.9124	110	110	110	—0.209398	—0.407227	—0.418204	—0.420759	—0.425707
1.9124	115	115	115	—0.206525	—0.404383	—0.415160	—0.417687	—0.422594
1.8925	115	115	115	—0.207327	—0.404615	—0.415461	—0.417891	—0.422720
1.88	93	93	93	—0.194187	—0.393388	—0.404526	—0.406959	—0.412068
1.88	106.7	106.7	106.7	—0.209785	—0.406810	—0.417971	—0.420380	—0.425232
1.9124	96.7	111.443	111.443	—0.205737	—0.404072	—0.415096	—0.417665	—0.422682
1.88	110	125	125	—0.199639	—0.397155	—0.407750	—0.410096	—0.414865

[a] $r = r_1 = r_2 = r_3 = $ N—H distance. $\alpha_i = H_j — N — H_k$ valence angle ($i \neq j \neq k = 1, 2, 3$).

TABLE II

The Optimized Potential Function Parameters

Parameter	SCF	$E_D^{(2)}$	$E_{(2)-(3)}^D$	$E_{SDQR}^{(2)-(4)}$	$E_{SDTQR}^{(2)-(4)}$	SCF CI[a]
$K_1/md\text{Å}^{-1}$	—0.5536	—0.5246	—0.5492	—0.5547	—0.5591	—0.5474
$K_2/md\text{Å}^{-3}$	2.5872	2.2350	2.3261	2.3201	2.3080	2.162
$K_3/md\text{Å}^{-5}$	—1.1161	—0.9279	—1.0112	—1.0129	—1.0366	—1.03
$K_4/md\text{Å}^{-7}$	1.4689	1.2274	1.3155	1.3192	1.3179	1.54
$k_1/md\text{Å}^{-2}$	—0.9285	—0.9539	—0.9838	—0.9828	—0.9932	—1.190
$k_2/md\text{Å}^{-4}$	—4.3206	—4.0422	—4.0196	—4.0444	—4.0102	—1.90
$k_3/md\text{Å}^{-6}$	0.0[b]	0.0[b]	0.0[b]	0.0[b]	0.0[b]	—4.64
$F_{11}/md\text{Å}^{-1}$	8.1087	7.8880	7.9739	7.8861	7.8242	8.017
$F_{44}/md\text{Å}$	0.5265	0.4835	0.4886	0.4876	0.4845	0.4514
$f_{44}^{(2)}/md\text{Å}^{-1}$	1.6721	1.4852	1.5030	1.5102	1.4887	1.749
$r_p/\text{Å}$	0.9870	0.9966	0.9953	0.9969	0.9982	0.9989
α_{min}/deg	109.0	108.1	108.0	107.9	107.7	107.2
H_{inv}/cm^{-1}	1555	1619	1710	1750	1791	1839

[a] Taken from Ref. 10.

[b] Held fixed.

4. THE INVERSION ENERGIES

A very recent SCF CI study[10] has revealed that the experimental potential function (see Ref. 8) is, to some extent, incomplete. The function does not involve certain *inversion-(in-plane)* interaction terms which have been found important for fitting the *ab initio* data. Consequently, the experimental force constants are rather effective and cannot be related directly to the *ab initio* constants. The potential can be compared, however, by means of the corresponding molecular spectra.

The functions (1) are, of course, even less complete than the experimental potential. Particularly as they describe the »true« *(in-plane)* potential in a diagonal harmonic approximation only. Consequently, the calculated potentials are not adequate to calculate the stretching or bending vibrational energies. Nevertheless, they can be believed adequate for providing reliable inversion energies (see Ref. 11).

TABLE III

The Inversion Energies of $^{14}NH_3$

v_2	Experiment[b]	Experiment — Calculated				
		SCF	$E_D^{(2)}$	$E_D^{(2)-(3)}$	$E_{SDQR}^{(2)-(4)}$	$E_{SDTQR}^{(2)-(4)}$
0^+	0.0	0.0	0.0	0.0	0.0	0.0
0^-	0.8	—3.1	—1.1	—0.8	—0.5	—0.3
1^+	932.4	33.9	23.1	—8.8	—19.5	—29.7
1^-	968.1	—46.9	—11.8	—34.2	—38.3	—40.7
2^+	1598.5	11.7	37.2	—10.8	—26.9	—44.3
2^-	1882.2	—159.2	—55.1	—89.2	—90.6	—88.0
3^+	2384.2	—237.3	—87.3	—125.6	—124.0	—116.6
3^-	2895.6	—348.4	—142.7	—181.9	—174.1	—156.9

[a] in cm^{-1}.

[b] see Ref. 8.

The actual calculations of the inversion energies were performed by means of the nonrigid invertor Hamiltonian computer program[8], assuming $f_{rr} = F_{33} = F_{11}$ and $f_{\alpha\alpha} = F_{44}$. The energies are collected in Table III.

5. CONCLUSIONS

The most striking observation from the results is the significant dependence of the inversion potential on the fourth-order contributions (see Table II). Apparently, the perturbation series is not fully converged.

The residual error (most likely due to the inadequacy of the DZ + P basis set, see Ref. 12) is, however, only, a smaller fraction of the total correlation energy contribution. Hence, the MBPT procedure may be recommended even at this rather modest level.

REFERENCES

1. S. H u z i n a g a, *J. Chem. Phys.* **42** (1965) 1293.
2. T. H. D u n n i n g, *J. Chem. Phys.* **53** (1970) 2823.
3. M. U r b a n, V. K e l l ö, and P. Č á r s k y, *Theor. Chim. Acta* **42** (1977) 205.
4. D. B. N e u m a n n, H. B a s c h, R. L. K o r n e g a y, L. C. S n y d e r, J. W. M o s k o w i t z, C. H o r n b a c k, and S. P. L i e b m a n n, *POLYATOM/2*, QCPE 199.
5. M. U r b a n, V. K e l l ö, J. N o g a, and I. Č e r n u š á k, POLYCOR, available upon request.
6. *Ab initio calculations. Lecture Notes in Chemistry*, P. Č á r s k y and M. U r b a n, Vol. 16 Springer, Berlin, 1980.
7. M. U r b a n, I. H u b a č, V. K e l l ö, and J. N o g a, *J. Chem. Phys.* **72** (1980) 3378.
8. V. Š p i r k o, *J. Mol. Spectrosc.* **101** (1983) 30.
9. P. R. B u n k e r, W. P. K r a e m e r, and V. Š p i r k o, *J. Mol. Spectrosc.* **101** (1983) 180.
10. P. R. B u n k e r, W. P. K r a e m e r, and V. Š p i r k o, *Can. J. Phys.* (1984), in print.
11. D. P a p o u š e k and V. Š p i r k o, *Top. Curr. Chem.* **68** (1976) 59.
12. P. P u l a y, J.-G. L e e, and J. E. B o g g s, *J. Chem. Phys.* **79** (1983) 3382.

SAŽETAK

Ab initio MBPT(4) računi potencijala inverzije NH₃ molekule

Vladimir Kellö, Ivan Hubač, Alexander I. Boldyrev i Vladimir Špirko

Izračunane su potencijalne konstante i potencijalna funkcija inverzije molekule ¹⁴NH₃ primjenom perturbacijske teorije više tijela četvrtog reda (MBPT(4)), osnovnog skupa funkcija DZ+P. Iako perturbacijski red nije potpuno konvergirao, autori smatraju da je upotrijebljeni model koristan pribor za proučavanje anharmoničnih vibracija ostalih fleksibilnih (non-rigid) molekulskih sustava.