

Geometries and multipole moments of AlH_4^- , SiH_4 , PH_3 , H_2S and HCl

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Abstract

Second-order Møller–Plesset, perturbation theory geometry optimizations for AlH_4^- , SiH_4 , PH_3 , H_2S and HCl are performed with [11s8p2d1f] and [11s8p3d2f1g] basis sets of contracted Gaussian-type functions. The electric dipole, quadrupole and octopole moments of these molecules are computed at the predicted equilibrium geometries. The calculated geometries and multipole moments are in fine agreement with previous experimental results and computations of sufficiently high quality. The calculated octopole moments are the only ones available for three of these molecules. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electric multipole moments are useful measures of the anisotropy of an electron distribution. Together with static polarizabilities, they can be used to compute long-range, intermolecular electrostatic and induction interactions. Dipole moments can be measured precisely by a variety of experimental methods, and are available for many molecules. However, experimental values of quadrupole and octopole moments are indirect and depend on a knowledge of other equally elusive properties. Thus high quality ab initio calculations [1] are probably the most reliable way to obtain the quadrupole and higher moments. In this article we report second-order Møller–Plesset perturbation theory computations of

the equilibrium geometries and electric multipole moments for AlH_4^- , SiH_4 , PH_3 , H_2S and HCl . Hartree atomic units are used except where explicitly stated otherwise.

2. Computational details

For the Al, Si, P, S and Cl atoms, we use two basis sets, denoted as A and B respectively, of [11s8p2d1f] and [11s8p3d2f1g] contracted Gaussian-type functions (GTF). The [11s8p] substrates of these basis sets were obtained by contracting the (19s14p) GTF sets from [2] in a segmented fashion, with the contraction coefficients optimized variationally for the ground state of the atom. As in earlier work [3,4], several contraction patterns were examined as was the use of up to two primitive GTF appearing in two contracted GTF. The final [11s8p] substrates have two repeated s-GTFs, and lead to restricted

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Table 1

Properties of AlH_4^- . The bond length is expressed in Ångstrom units and all other quantities in atomic units

| Method | Ref. | $r(\text{AlH})$ | $\langle r^2 \rangle$ | Ω_{xyz} |
|-------------------|-----------|-----------------|-----------------------|-----------------------|
| MP2/A | This work | 1.637 | 95.99 | 25.29 |
| MP2/B | This work | 1.631 | 95.43 | 25.02 |
| MP2/6-31+G(d) | [9] | 1.650 | | |
| MP2/6-311++G(d,p) | [10] | 1.637 | | |
| CCSD(T)/TZP | [11] | 1.648 | | |

Hartree–Fock energies of the atoms that are higher than their numerical limits [5] by amounts increasing from 28 to 60 μ hartrees. The energy losses resulting from the contraction range from 2 to 15 μ hartrees, and are at least three times as small as the errors in uncontracted energies relative to the numerical Hartree–Fock limit. The [11s8p] basis sets for Na–Ar can be obtained in machine readable form by anonymous ftp from okapi.chem.unb.ca in the /pub/gbs/na2ar/qz directory. The (2d1f) and (3d2f1g) sets of polarization functions for Al–Cl were taken from [6]. [4s2p1d] and [4s3p2d1f] basis sets, consisting of [4s] substrates from [3] supplemented by polarization functions from [7], were used for the H atom with sets A and B respectively. As our results show, the basis sets are large enough to yield accurate multipole moments without requiring additional diffuse functions.

Geometry optimizations were carried out for AlH_4^- , and SiH_4 in T_d symmetry, PH_3 in C_{3v} symmetry, H_2S in C_{2v} symmetry and HCl in $C_{\infty v}$ symmetry. Multipole moments were computed at the predicted equilibrium geometry. Calculations were made with the second-order, Møller–Plesset (MP2) perturbation theory using the HONDO package [8]. All electrons were correlated.

Table 2

Properties of SiH_4 . The bond length is expressed in Ångstrom units and all other quantities in atomic units

| Method | Ref. | $r(\text{SiH})$ | $\langle r^2 \rangle$ | Ω_{xyz} |
|--------------|-----------|-----------------|-----------------------|-----------------------|
| MP2/A | This work | 1.4744 | 68.15 | 4.27 |
| MP2/B | This work | 1.4704 | 67.81 | 4.18 |
| CISD/TZ2P | [12] | 1.4755 | | |
| CCSD/TZP (f) | [13] | 1.4751 | | |
| CISD/DZ2P | [15] | | | 4.51 |
| CPF/DZ2P | [15] | | | 4.09 |
| Experiment | [14,16] | 1.4734 | | ± 3.6 |

3. Results and discussion

Tables 1–5 present our calculated geometries and multipole moments. The tables also list the expectation value $\langle r^2 \rangle = N\langle r_1^2 \rangle$ where N is the number of electrons. This quantity is related to the diamagnetic susceptibility, and a gross measure of the size of the molecule is provided by $\langle r_1^2 \rangle^{1/2}$. The tables also list relevant experimental results and correlated calculations from the literature for comparison purposes. The coordinate system is such that the origin is at the center of mass and the principal axis of symmetry is along the z -axis.

Our results in Table 1 confirm previous calculations [9–11] of the AlH bond length in AlH_4^- . The tetrahedral symmetry of the molecule ensures that the first non-vanishing multipole moment is the octopole moment Ω . No experimental data are available. We are unaware of any previous calculations of $\langle r^2 \rangle$ and Ω_{xyz} for AlH_4^- .

Table 2 shows that previous calculations [12,13] of the SiH bond length in silane are about 0.002 Å larger than the experimental r_e value of Ohno et al. [14]. Our MP2/A bond length is longer by 0.001 Å and our MP2/B value is shorter by 0.003 Å. Our MP2/A and MP2/B octopole moments lie between the CISD and CPF values calculated by Brode et al. [15]. All computed values of the octopole moment are on the high side of the experimental estimate of $\pm 3.6 \pm 0.4$ made by Rosenberg and Ozier [16]. We are unaware of any previous correlated calculations or measurements of $\langle r^2 \rangle$ for SiH_4 .

Our results for PH_3 are compared with previous results [17–20] in Table 3 which shows that most previous correlated calculations predict PH bond lengths that are shorter than Kijima and Tanaka's experimental r_e value [21]. Similarly, our MP2/A and MP2/B bond lengths are shorter by 0.003 and 0.006 Å respectively. Table 3 indicates that all previous correlated calculations predict HPH angles larger than experimental ones; our MP2/A and MP2/B bond angles are larger by 0.3° and 0.2°, respectively. The MP2/A and MP2/B dipole moments are larger than the experimental value of Davies et al. [22] by 0.12 and 0.07 D. By contrast, Russell and Spackman [19] were able to obtain an MP2 dipole moment within 0.016 D of the experimental value. We believe that their better μ is partly because of fixing the

Table 3

Properties of PH₃. The bond length is expressed in Ångstrom units, angle in degrees, dipole moment (μ) in Debye units, and all other quantities in atomic units

| Method | Ref. | $r(\text{PH})$ | $\angle \text{HPH}$ | $\langle r^2 \rangle$ | μ | θ_{zz} |
|------------------|-----------|----------------|---------------------|-----------------------|-------|---------------|
| MP2/A | This work | 1.4089 | 93.72 | 55.14 | 0.689 | – 1.683 |
| MP2/B | This work | 1.4063 | 93.60 | 54.94 | 0.648 | – 1.665 |
| MP2/6-31G(d,p) | [17] | 1.405 | 94.5 | | | |
| MP2/SV(d,p) | [17] | 1.419 | 93.9 | | 0.833 | |
| MP2/MC-311G(d,p) | [18] | 1.410 | 94.2 | | | |
| MP2 | [19] | | | | 0.590 | – 1.635 |
| SDCI | [20] | | | 55.29 | 0.607 | – 1.678 |
| MRSDCI | [20] | | | 55.28 | 0.598 | – 1.676 |
| BD(T) | [19] | | | | 0.581 | – 1.588 |
| Experiment | [21–23] | 1.4118 | 93.42 | | 0.574 | – 1.7 |

geometry at the experimental value, and partly because of a basis set richer in diffuse d-GTF needed for multipole moment calculations. All calculated quadrupole moments θ_{zz} are well within the experimental estimate of -1.7 ± 0.9 of Combariza et al. [23]. Our MP2 values of $\langle r^2 \rangle$ differ from the configuration interaction results of Feller et al. [20] by less than 0.6%. Our MP2/B octopole moment components were $\Omega_{xxx} = 0.18$, $\Omega_{zzz} = 0.20$ and $\Omega_{xxz} = -0.10$ and no other correlated values have been reported so far.

Previous results [19,20,24–29] for H₂S are compared with our values in Table 4 which shows that our MP2/A and MP2/B SH bond lengths are 0.002 and 0.004 Å shorter than the experimental r_e value of Edwards et al. [28]. The MP2/A and MP2/

B bond angles are only 0.06° smaller than the experimental results. Surprisingly, the elaborate coupled cluster results of Martin et al. [27] are not much closer to experimental values than our MP2 values. The MP2/A and MP2/B dipole moments are larger than Gallagher's experimental value [29] by 0.14 and 0.08 D respectively. Russell and Spackman [19] obtained an MP2 dipole moment within 0.005 D of the experimental value, probably because they used a basis set richer in diffuse d-GTF. All calculated quadrupole moments θ_{zz} are close to one another except for Feller et al.'s configuration interaction results [20] which are smaller than the rest. Our MP2 values of $\langle r^2 \rangle$ differ from the configuration interaction results [20] by less than 0.7%. Our MP2/B octopole moment components were $\Omega_{zzz} = 1.17$,

Table 4

Properties of H₂S. The bond length is expressed in Ångstrom units, angle in degrees, dipole moment (μ) in Debye units, and all other quantities in atomic units. The molecule is on the yz -plane

| Method | Ref. | $r(\text{SH})$ | $\angle \text{HSH}$ | $\langle r^2 \rangle$ | μ | θ_{xx} | θ_{yy} | θ_{zz} |
|-----------------|-----------|----------------|---------------------|-----------------------|-------|---------------|---------------|---------------|
| MP2/A | This work | 1.3332 | 92.17 | 43.84 | 1.121 | – 2.83 | 2.06 | 0.77 |
| MP2/B | This work | 1.3314 | 92.16 | 43.73 | 1.058 | – 2.82 | 2.06 | 0.76 |
| MP2 | [24] | 1.3308 | 92.69 | | | | | |
| MP2 | [25] | | | | 1.038 | | | |
| MP2 | [19] | | | | 0.982 | – 2.84 | 2.07 | 0.77 |
| CEPA-1 | [26] | 1.3355 | 92.12 | | | | | |
| CCSD(T)/cc-pVTZ | [27] | 1.3407 | 92.30 | | | | | |
| CCSD(T)/cc-pVQZ | [27] | 1.3391 | 92.35 | | | | | |
| SDCI | [20] | | | 43.55 | 1.052 | – 2.61 | | |
| MRSDCI | [20] | | | 43.55 | 1.037 | – 2.58 | | |
| ACCDs | [24] | | | | 1.026 | – 2.80 | 2.07 | 0.73 |
| BD(T) | [19] | | | | 0.955 | – 2.77 | 2.01 | 0.75 |
| Experiment | [28,29] | 1.3356 | 92.11 | | 0.977 | | | |

Table 5

Properties of HCl. The bond length is expressed in Ångstrom units, dipole moment (μ) in Debye units, and all other quantities in atomic units

| Method | Ref. | $r(\text{HCl})$ | $\langle r^2 \rangle$ | μ | θ_{zz} | Ω_{zzz} |
|-----------------------|-----------|-----------------|-----------------------|-------|---------------|----------------|
| MP2/A | This work | 1.2720 | 34.15 | 1.208 | 2.71 | 3.66 |
| MP2/B | This work | 1.2709 | 34.10 | 1.159 | 2.72 | 3.93 |
| MP2/TZ2P | [30] | 1.271 | | 1.170 | | |
| MP2 | [19] | | | 1.102 | 2.76 | |
| MP2 | [31] | | | 1.106 | 2.73 | 4.16 |
| ACCD | [32] | | | 1.132 | 2.78 | |
| B ₃ MRSDCI | [33] | | 34.69 | 1.10 | 2.72 | |
| CPF/TZ2P | [30] | 1.275 | | 1.138 | | |
| SDCI | [20] | | 34.01 | 1.165 | 2.73 | |
| MRSDCI | [20] | | 34.03 | 1.162 | 2.73 | |
| BD(T) | [19] | | | 1.072 | 2.69 | |
| MP4 | [31] | | | 1.078 | 2.67 | 3.97 |
| CCSD (T) | [31] | | | 1.077 | 2.67 | 3.94 |
| Experiment | [34,35] | 1.2747 | | 1.093 | 2.62 | |

$\Omega_{xxz} = 1.67$ and $\Omega_{yyz} = -2.84$ and no other correlated values have been reported to date.

Table 5 compares our results with those obtained in previous work [19,30–35] on HCl. Our MP2/A and MP2/B bond lengths are 0.0027 and 0.0038 Å shorter than the experimental r_e value of Kaiser [34] and the coupled-pair functional calculation of Rice et al. [30]. The MP2/A and MP2/B dipole moments are larger than the experimental value of Kaiser [34] by 0.114 and 0.066 D respectively. Russell and Spackman [19] obtained an MP2 dipole moment within 0.009 D of the experimental value, but the more elaborate BD(T) (Brueckner doubles with triples correction) [19], and the coupled cluster CCSD(T) [31] calculations still differ from the experimental ones by 0.021 and 0.016 D respectively. Many calculated quadrupole moments θ_{zz} , including MP2/B, fall within the experimental range [35] of 2.62 ± 0.10 . Our MP2 values of $\langle r^2 \rangle$ agree with the multireference, configuration interaction results of Feller et al. [20] by better than 0.4%. Our MP2/B octopole moment Ω_{zzz} is in nearly perfect agreement with the CCSD(T) result of Maroulis [31].

The MP2 geometries and multipole moments calculated for AlH_4^- , SiH_4 , PH_3 , H_2S and HCl using our basis sets A and B are in good agreement with previous experimental results and computations of sufficiently high quality. An observant reader would have noticed that MP2/A and MP2/B bond lengths

consistently underestimate experimental values with MP2/B being more distant from experimental values. We think this reflects an imbalance between the bond shortening because of more polarization functions and bond lengthening owing to electron correlation. In other words, we can expect to produce bond lengths closer to experimental values if a higher-order correlation method, such as CCSD(T), is used with basis B. Our octopole moments are the only ones available to date for AlH_4^- , PH_3 and H_2S .

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