Theor Chim Acta (1989) 76: 285–289

Theoretica
Chimica Acta

Short communication

Calculation of the deuterium electric field gradients in HD and LiD using a variation-perturbation method with a Gaussian basis set

Hae-Won Kim[1], James O. Jensen[2], and Hendrik F. Hameka[3]
[1] Department of Chemistry, Pennsylvania State University, Ogontz Campus,
Abington, PA 19001, USA
[2] US Army Chemical Research, Development and Engineering Center,
Aberdeen Proving Ground, MD 21010, USA
[3] Department of Chemistry, University of Pennyslvania, Philadelphia,
PA 19104-6323, USA

(Received January 23; revised and accepted March 31, 1989)

Summary. We present calculations of the deuterium electric field gradients in the HD and LiD molecules obtained with a variation-perturbation method using Gaussian atomic orbitals. The differences between our theoretical values and the corresponding experimental or best calculated values are 2%. We conclude that high accuracy can be obtained with the variation-perturbation method using either Gaussian or Slater orbitals.

Key words: Electric field gradient — Gaussian computation

1. Introduction

In a recent series of papers we reported calculations of the deuterium electric field gradients (EFG) on the HD molecule [1], the LiD molecule [2] and the DF molecule [3]. We also computed the vibrational dependence of the field gradient in the HD molecule [4]. The above calculations were all based on the use of Slater atomic orbitals using a variation-perturbation method [5]. Since we wish to extend the scope of our calculations beyond diatomics it is necessary to make use of Gaussian atomic orbitals. In order to judge the accuracy of EFG calculations based on Gaussians we present a study on the HD and LiD molecules.

All our calculations are based on a variation-perturbation method that one of us introduced some years ago [5]. Here, a zero-order approximation to the EFG (which we denote by q_D^0) is obtained as the expectation value of the EFG operator with respect to the molecular wave function, and a correction term q_D' is calculated by solving a variation perturbation equation. The final result q_D is then obtained as the sum of the two contributions.

Some other recent work on EFG by Cummins et al. [6, 7] is based on the use of Gaussians. Here the wave functions are derived from *ab initio* procedures employing extensive Gaussian basis sets at the SCF level, with singles and doubles CI and at the coupled pair functional levels of theory. The EFG values were then obtained as the expectation value of the EFG operator and also by using the finite field method. An earlier calculation by Sundholm et al. [8] on LiD uses a similar procedure: an SCF calculation with Gaussians supplemented by configuration interaction involving 993 configurations. In Sect. 3, we compare the LiD result of Sundholm et al. with ours. The other work by Cummins et al. involves different molecules and it is not possible to make comparisons.

2. Calculations

We start our calculations with an approximate molecular function Ψ_0, an SCF molecular wave function which is an antisymmetrized product of molecular orbitals Φ_i. The molecular orbitals Φ_i are linear combinations of Dunning and Hay contracted Gaussian orbitals [9]. The expectation value q_D^0 of the EFG at the deuterium position is then given by

$$\begin{aligned} q_D^0(el) &= \langle \Psi_0 | V_{zz}(el) | \Psi_0 \rangle \\ &= 2\sum_k \langle \Phi_k | V_{zz}(el) | \Phi_k \rangle, \end{aligned} \tag{1}$$

where

$$V_{zz}(el) = \sum_i V_{zz}(i) = (r_{Di}^2 - 3z_{Di}^2)/r_{Di}^5. \tag{2}$$

The summation in Eq. (1) is to be performed over all occupied molecular orbitals and that in Eq. (2) is to be performed over all electrons.

The next step in the calculations is to derive a function F by minimizing the functional

$$\langle F | H - E_0 | F \rangle + \langle F | V_{zz}(el) | \Psi_0 \rangle + \langle \Psi_0 | V_{zz}(el) | F \rangle \tag{3}$$

subject to the condition

$$\langle F | \Psi_0 \rangle = 0. \tag{4}$$

The correction term to $q_D^0(el)$, $q_D'(el)$, is given by

$$q_D'(el) = \langle F | H - E_0 | \Psi_0 \rangle + \langle \Psi_0 | H - E_0 | F \rangle \tag{5}$$

and the corrected EFG value $q_D(el)$ is

$$q_D(el) = q_D^0(el) + q_D'(el). \tag{6}$$

The details of the procedure have been presented previously [1, 5].

In order to perform the calculations we made use of a program "GOTHLAND", which was made available to us by J. R. de la Vega. It was originally written by R. Carbo and was modified for use on a personal computer by J. R. de la Vega and J. Busch. The GOTHLAND program determines molecular wave functions by means of the SCF method based on the use of Gaussian orbitals. It is similar to the GAUSSIAN 82 Program Package but it has the advantage that the intermediate results which we need can be extracted.

We performed one calculation for HD at $R = 1.4$ a.u. and two calculations for LiD at $R = 3.015$ a.u.: the HD basis set was a Dunning–Hay [2*s*] hydrogen set plus a polarization function ($\varsigma_p = 1.0$) for both centers, the first LiD basis set (I) was a Dunning–Hay [3*s*] contracted basis set for Li with a [2*s*] hydrogen set, and the second LiD basis set (II) consisted of a Dunning–Hay [3*s*2*p*] contracted basis set for Li with a [2*s*] hydrogen set plus a polarization function ($\varsigma_p = 1.0$) for H. For both molecules we also used two 3*d* orbitals centered on deuterium with orbital exponents 6.14092 and 0.69436; these orbitals were chosen by maximizing the overlap with 1*d* and 0*d* orbitals, which are the solutions of the variation perturbation equations for atomic hydrogen [1]. We substituted these basis sets into the GOTHLAND program and we obtained a set of molecular orbitals in each case. In the case of HD there were 8 molecular orbitals Φ_i, the orbital Φ_1 being filled with a pair of electrons while the others were orthonormal virtual molecular orbitals. For LiD, both the Φ_1 and Φ_2 orbitals were filled while the others, Φ_3 to Φ_7 in the first calculation and Φ_3 to Φ_{10} in the second calculation, were virtual orbitals.

We first calculated the expectation value $q_D^0(el)$ of the EFG operator according to Eqs. (1) and (2), evaluating the atomic integrals over the EFG operator according to the procedure reported by McMurchie and Davidson [10].

The next step was to derive the function F by minimizing the functional of Eq. (3). In all cases we took F to be a linear combination of singly excited molecular wave functions

$$F = \sum_k \sum_m c(j, m)\Psi(j, m). \tag{7}$$

In the case of HD $j = 1$, whereas $j = 1, 2$ for LiD; the summation over m involves all available virtual molecular orbitals. The matrix elements involving the Hamiltonian were derived from the GOTHLAND program and the other integrals were again obtained by a slight modification of the method of McMurchie and Davidson [10]. After determining the various functions F by minimizing the expression of Eq. (3) the correction terms q'_D were evaluated from Eq. (5) and the corrected quantities $q_D(el)$ were calculated from Eq. (6).

In Table 1 we list the results of our calculations for $q_D^0(el)$, $q'_D(el)$, $q_D(el)$, and the energies that we obtained for the GOTHLAND SCF calculations for HD and LiD. Table 1 also contains the results $q_D(el)_{\text{Slater}}$ that we obtained previously by using Slater orbitals [1, 2]. For LiD we list the experimental value which we derived from the measurements by Wharton et al. [11]. In the case of HD we list the most precise theoretical value available, derived by Bishop and Cheung [12] for a fixed internuclear distance $R = 1.4$. We believe that this value is more accurate for our purpose than the experimental value since the latter includes the vibrational motion.

Table 1. Results of deuterium EFG calculations for HD and LiD using Gaussians. Results based on Slater orbitals and experimental values are listed for comparison. All values are in atomic units

	HD	LiD(I)	LiD(II)
Energy (a.u.)	−1.131198	−7.967622	−7.981163
$q^0_D(el)$	−0.368041	−0.141584	−0.149818
$q'_D(el)$	−0.014427	−0.020230	−0.015966
$q_D(el)$	−0.382468	−0.161814	−0.165784
$q_D(el)_{\text{Slater}}$	−0.38305	—	−0.16438
$q_D(el)_{\text{Sundholm}}$	—	—	−0.168
$q_D(el)_{\text{exp}}$	−0.39094	—	−0.169

3. Discussion

From our results we may conclude that the Gaussian results are comparable in accuracy with the Slater results based on the variation-perturbation method. In the case of HD the difference between the two sets of theoretical results is only 0.15% and the difference between the Gaussian result and the "exact" value of Bishop and Cheung [12] is 2.17%. In the case of LiD the result from our Gaussian calculation II is significantly better than the result from Gaussian calculation I; this indicates that it is desirable to include $2p$ atomic orbitals in the deuterium basis set. The difference between the Gaussian II result and the experimental result [11] is 1.9% and the difference between the Slater result [2] and the experimental value [11] is 2.7%. It should be noted, though, that the Gaussian II basis set includes a $2p_z$ orbital on deuterium and that the Slater basis set [2] contains only s atomic Slater orbitals on deuterium.

It may be instructive to compare our result for the deuterium EFG value in LiD with that obtained by Sundholm et al. [8]. In [2] we presented the experimental value of $q_D(el)$ derived from the measurements of Wharton et al. [11] as $q_D = -0.169 \pm 0.0015$ a.u. Our value is $q_D = -0.168$ a.u.; however, it should be noted that this slightly better result required 993 configurations in a CI treatment whereas our value required only 16 correction terms.

We may conclude from our present results that the determination of deuterium EFG based on the variation-perturbation method can be calculated just as effectively from Gaussian atomic orbitals as from Slater atomic orbitals. We also conclude that our variation-perturbation method seems to be more effective than the other procedures, since the slight decrease in accuracy is more than compensated for by the decrease in computational effort. We will therefore proceed to calculate deuterium EFG in some larger systems by using Gaussian atomic orbitals in the GOTHLAND program.

Acknowledgements. The authors wish to thank Professors J. R. de la Vega and J. Busch of the Department of Chemistry, Villanova University, Villanova, PA, for making the program GOTHLAND available to us.

References

1. Zamani-Khamiri O, Hameka HF (1981) J Chem Phys 75:781; (1982) J Chem Phys 77:2218
2. Pietrovito AJ, Hameka HF, Zeroka D (1984) J Chem Phys 81:1960
3. Kim HW, Hameka HF, Zeroka D (1986) J Chem Phys 84:5639
4. Kim HW, Hameka HF, Zeroka D (1988) J Chem Phys 88:3159
5. Hameka HF, Svendsen EN (1976) Int J Quantum Chem 10:249
6. Cummins PL, Bacskay GB, Hush NS, Ahlrichs R (1987) J Chem Phys 86:6908
7. Cummins PL, Bacskay GB, Hush NS (1987) J Chem Phys 87:416
8. Sundholm D, Pyykko P, Laaksonen L, Sadlej AJ (1984) Chem Phys Lett 112:1
9. Dunning TH Jr, Hay PJ (1977) In: Schaefer HF III (ed), Electronic structure theory, vol. 3. Plenum Press, New York, p 1
10. McMurchie LE, Davidson ER (1978) J Comp Phys 26:218
11. Wharton L, Gold LP, Klemperer W (1962) J Chem Phys 37:2149
12. Bishop DM, Cheung LM (1979) Phys Rev A20:381