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Bond Orbital Analysis of the Deuteron Quadrupole Coupling Constants in MD_4 Molecules*

Shaul D. Goren
Department of Physics, The University of the Negev, Beer Sheva

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The deuteron quadrupole coupling constants were used as constraints on the bond orbital functions of a series of MD_4 molecules (M = B, C, N, Al, Si, P). It was demonstrated that a minimal basis set may be sufficient to describe first row deuterates, but not for second row deuterates, where double zeta orbitals are needed.

Key words: Deuteron quadrupole coupling constants

1. Introduction

The calculation of the energy of a molecule by the variational method does not necessarily yield correct values of one electron properties because the energy is a stationary property. Thus one could have "bad" wave-functions giving good values for the energy. Bader and Preston [1] used experimental one electron properties of CH_4 as a constraint on the wave-function without minimization of the energy. The energy that resulted from these constraints compared favorably with the energy obtained from SCF calculations with a basis set of 39 STO [2]. Similar results were obtained for hydrogen fluoride [3] and ammonia [4]. A bond orbital method was successful in analysing the deuteron and ^{17}O quadrupole coupling constants in ice [5]. The advantage of this method lies in its simplicity and the use that it makes of physical intuition as opposed to the elaborate and time consuming *ab initio* methods. As a systematic study of this method, a series of MD_4 molecules were chosen where M = B, C, N, Al, Si, P. The deuteron quadrupole coupling constants of this series are known experimentally and will be used as a constraint on the molecular orbitals. These data, together with M–D bond length are summarized in Table 1.

2. Method and Results

All the above compounds have the central ion in a tetrahedral environment with four equivalent M–D bonds. One of the four directions of bonding that was chosen as the *z* axis is also a three fold axis. Thus it is a principal axis of the field gradient tensor and only the *zz* component of this tensor is needed in order to

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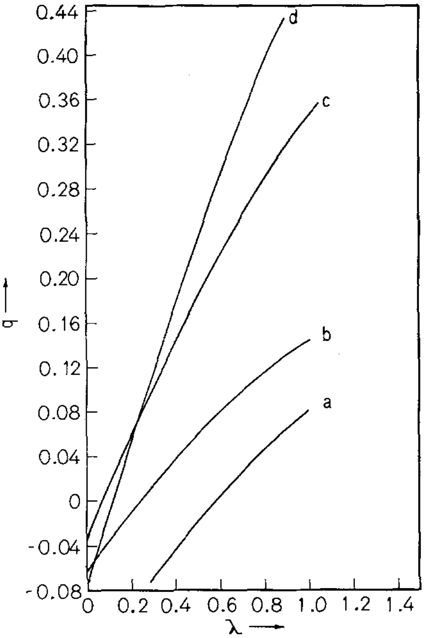

Fig. 1

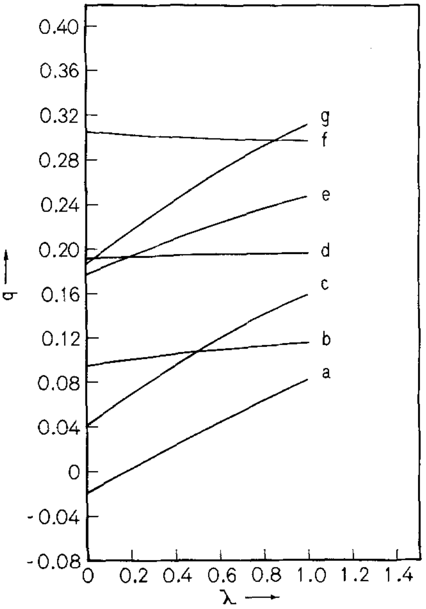

Fig. 2

Fig. 1a–d. A plot of q vs λ for a BD_4^- ($R_{B-D} = 2.372$ a.u.) with exponents obtained from Ref. [9]; b BD_4^- ($R_{B-D} = 2.372$ a.u.) obtained with Slater orbitals; c CD_4 ($R_{C-D} = 2.069$ a.u.) obtained with Slater orbitals; d ND_4^+ ($R_{N-D} = 1.96$ a.u.) obtained with Slater orbitals

Fig. 2a–g. A plot of q vs λ obtained with Slater orbitals for a PD_4^+ ($R_{P-D} = 3.3$ a.u.), b AlD_4^- ($R_{Al-D} = 3.3$ a.u.), c PD_4^+ ($R_{P-D} = 3.0$ a.u.), d AlD_4^- ($R_{Al-D} = 2.965$ a.u.). e SiD_4 ($R_{Si-D} = 2.787$ a.u.), f AlD_4^- ($R_{Al-D} = 2.7$ a.u.), g PD_4^- ($R_{P-D} = 2.68$ a.u.)

obtain the deuteron quadrupole coupling constant. This component is given by (in a.u.)

$$q = \sum_i{}' \frac{3Z_i^2 - R_i^2}{R^5} - \left\langle \Psi \left| \frac{3z^2 - r^2}{r^5} \right| \Psi \right\rangle . \tag{1}$$

The first term is the nuclear contribution and the summation extends to all atoms except the one located at the site where the field gradient is calculated. The second term is the electronic contribution and Ψ is a determinant constructed from doubly occupied lone pair and bond orbitals. The bond orbitals have the form

$$\begin{aligned} \Psi_1 &= N_1(s_M + p_{z_M} + \lambda \cdot 1s_{D_1}) \\ \Psi_2 &= N_2(s_M + \cos\alpha \cdot p_{x_M} - \sin\alpha \cdot p_{z_M} + \lambda \cdot 1s_{D_2}) \\ \Psi_{3,4} &= N_{3,4}(s_M - \tfrac{1}{2}\cos\alpha \cdot p_{x_M} \pm \tfrac{3}{\sqrt{2}}\cos\alpha \cdot p_{y_M} - \sin\alpha \cdot p_{z_M} + \lambda \cdot 1s_{D_{3,4}}) \end{aligned} \tag{2}$$

$\alpha = 19.47122 =$ tetrahedral angle $-90°$.

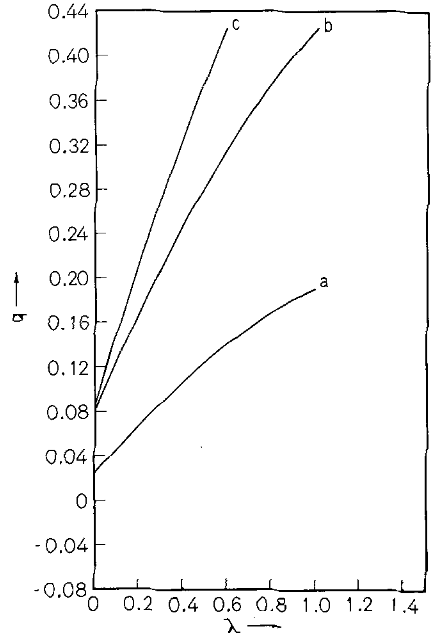

Fig. 3

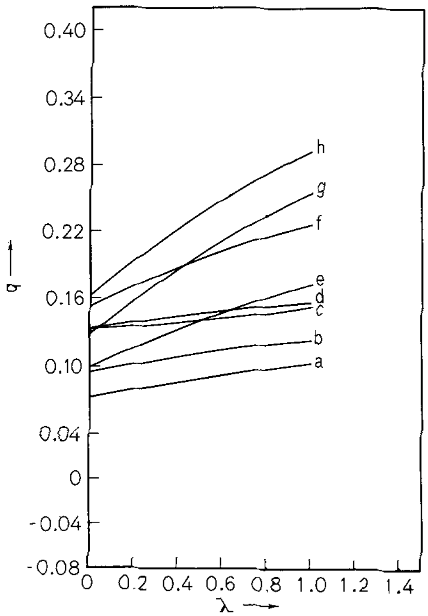

Fig. 4

Fig. 3a–c. A plot of q vs λ with double zeta orbitals for a BD_4^- ($R_{B-D} = 2.372$ a.u.), b CD_4 ($R_{C-D} = 2.069$ a,u,), c ND_4^+ ($R_{N-D} = 1.96$ a.u.)

Fig. 4a–h. A plot of q vs λ with double zeta orbitals for a AlD_4^- ($R_{Al-D} = 3.2$ a.u.), b AlD_4^- ($R_{Al-D} = 3.1$ a.u.), c AlD_4^- ($R_{Al-D} = 2.965$ a.u.) and deuteron exponent of 1.2 a.u.; d same as c with deuteron exponent of 1.0, e SiD_4 ($R_{Si-D} = 2.9$ a.u.), f SiD_4 ($R_{Si-D} = 2.787$ a.u.), g PD_4^+ ($R_{P-D} = 2.75$ a.u.), h PD_4^+ ($R_{P-D} = 2.68$ a.u.)

s_M and p_M are the valence s and p orbitals of the central ion, $1s_{D_i}$ is the i-th deuteron $1s$ orbital and λ is a charge transfer coefficient which is treated as an adjustable parameter. N_i is a normalization factor.

The inner core electrons of the central ion ($1s$ for B, C, and N, $1s$, $2s$, and $2p$ for Al, Si, and P) were put into doubly occupied lone pair orbitals.

This set of molecular orbitals is not an orthonormal set and it was symmetrically orthonormalized by the Löwdin procedure [6]. The expectation value of $\frac{3z^2 - r^2}{r^5}$ was calculated with the new orthonormal set.

All one, two, and three center integrals were considered and calculated to an accuracy of 10^{-5} a.u. Three different basis sets were chosen to represent the central atom: a minimal basis set, double zeta orbitals, and Hartree-Fock orbitals. The exponents for the minimal basis set were obtained by the rules of Slater while the exponents for the other two sets were taken from Clementi's tables [7]. The deuteron was represented by one Slater type orbital. Figs. 1–5 give the plot of q (in a.u.) vs. λ, calculated with the three basis sets for the series of MD_4 compounds mentioned above.

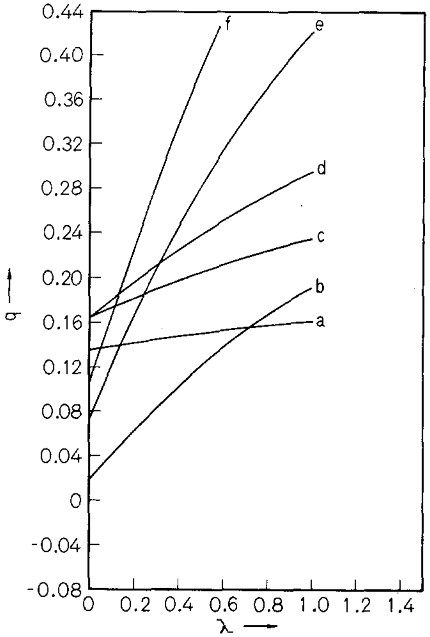

Fig. 5a–f. A plot of q vs λ with Hartree-Fock orbitals for a AlD_4^- ($R_{Al-D} = 2.965$ a.u.), b BD_4^- ($R_{B-D} = 2.372$ a.u.), c SiD_4 ($R_{Si-D} = 2.787$ a.u.), d PD_4^+ ($R_{P-D} = 2.68$ a.u.), e CD_4 ($R_{C-D} = 2.069$ a.u.), f ND_4^+ ($R_{N-D} = 1.96$ a.u.)

3. Discussion

Before the results are discussed, one should keep in mind that most of the experimental data given in Table 1 were obtained in crystals containing the desired molecule under the assumption that η, the anisotropy factor, is zero. It is quite safe to assume that η is very small. A small nonzero value of η will change the value of the quadrupole coupling constant somewhat, but the essence of the discussion will still be valid.

3.1. First Row Deuterates

A minimal basis set can be used for the calculations of the field gradient at the deuteron site. As the nuclear charge of the central nucleus is increased, one expects less charge on the deuteron since the charge on the deuteron in the zero overlap approximation is proportional to λ^2. Hence, one expects a decrease of λ as a function of the central nucleus charge as shown in Table 2. Calculations with double zeta orbitals change the value of λ, however, the charge dependence of λ does not change. The use of Hartree-Fock orbitals results in practically the same results as obtained for the double zeta orbitals.

The optimal value of λ can be correlated with the electronegativity values of B, C and N which are 2.04, 2.55, and 3.04 respectively [8]. The larger value of the electronegativity means more ionic character, i.e. more charge is found at the central ion. The charge on the deuteron is proportional to λ^2. Thus, smaller values of λ mean more charge on the central ion which is consistent with the

Table 1. Bond length and deuterium quadrupole coupling constants

Molecule	R (a.u.)	Ref.	q (a.u.)	Ref.
BD_4^-	2.372	[a]	0.166	[f]
CD_4	2.069	[b]	0.281	[g]
ND_4^+	1.96	[c]	0.281	[h]
AlD_4^-	2.965 (calc)	[d]	0.110	[i]
SiD_4	2.787	[b]	0.145	[j]
PD_4^+	2.68	[e]	0.140	[k]

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Table 2. Optimal values of λ for field gradient and forces

Basis set	$\lambda^{fg}_{BD_4^-}$	$\lambda^{fg}_{CD_4}$	$\lambda^{fg}_{ND_4^+}$	$\lambda^{f}_{BD_4^-}$	$\lambda^{f}_{CD_4}$	$\lambda^{f}_{ND_4^+}$
Minimal	1.2	0.8	0.5			
Double zeta	0.8	0.5	0.3	1.0	0.5	0.3
Hartree-Fock	0.8	0.5	0.3			

λ^{fg} is the value of λ that reproduces the experimental field gradient.
λ^{f} is the value of λ that gives zero value for the force.

electronegativity values. The decreasing values of λ are also consistent with the value of the charge of the central ion. The attraction between the electrons and the central ion is proportional to the charge of the latter, resulting in decreasing values of λ.

A necessary condition for an exact wavefunction is a zero value for the expectation value of the force. Thus, although this condition is not sufficient, the expectation value of the force can be used to estimate the quality of the wavefunction. The only nonvanishing component of the force for the MD_4 molecule is the z component which is given by

$$F_z = \sum_i{}' \frac{Z_i}{R^3} - \left\langle \Psi \left| \frac{z}{r^3} \right| \Psi \right\rangle , \tag{3}$$

where all the symbols and notations retain their meaning from Eq. (1).

The bond orbitals that were defined in Eq. (2) with double zeta basis sets of the central ion were used to calculate the force. The calculated values of λ that give zero force are given in Table 2. For CD_4 and ND_4^+, there is an excellent

Table 3. Contributions of individual orbitals to the field gradient

Molecule	$q(1s_M)$[a]	q(M–D)[b]	q(tot)[c]	q(MD)[d]
BD_4^-	0.2996	0.1842	0.2599	0.3072
CD_4	0.4524	0.3730	0.4863	0.4984
ND_4^+	0.5310	0.6498	0.7828	0.7528

[a] $q(1s_M)$ is the contribution from the 1*s* orbital of the central atom to the field gradient at the deuteron site.

[b] q(M–D) is the contribution from the M–D bond orbital to the field gradient at the deuteron.

[c] $q(\text{tot}) = \frac{1}{4}q(1s_M) + q(\text{M–D})$.

[d] q(MD) is the field gradient at the deuteron for M–D molecule obtained by Bender and Davidson (Ref. [8]).

agreement between the value of λ that reproduces the experimental value of the gradient and the value of λ that gives zero force, while for BD_4^- the agreement is not that good.

CI calculations of diatomic BD, CD, and ND were published by Bender and Davidson [9]. The MD_4 molecules have four equivalent M–D bonds, thus, the field gradient of the deuteron for the diatomic molecules may be compared with the contributions from the M–D bond with the addition of a quarter of the contribution from the inner pair, $1s_M$. The results for the three basis sets, together with Bender and Davidson's results, are given in Table 3. There is a surprisingly good agreement in the cases of CD_4 and ND_4^+, which indicates that to a very good approximation one can treat the MD_4 molecules as composed of four independent M–D bonds. The relatively bad agreement in the case of BD_4^- is attributed to the fact that B has only three valence electrons. The creation of 4 equivalent bonds means an addition of one more valence electron to B, increasing the Coulomb repulsion. This fact is responsible for the inequivalence of the BD bond and one of the tetrahedral bonds in BD_4^-.

SCF calculation with minimal basis set for BD_4^- and CD_4 are available [2, 10]. For CD_4, the *ab initio* value agrees quite well with the newly determined quadrupole coupling constant, and consequently with the optimal value of λ in this work. Cave and Karplus [11] also carried out bond orbital calculations for CD_4 with a minimal basis set. Their value of $\lambda = 0.8$ for $R_{\text{C-D}} = 2.082$ agrees well with the result that was obtained in this work with the minimal basis set.

Hegstrom *et al.* [10] have calculated the optimized minimal basis set for BH_4^-. The value of the field gradient at the hydrogen site that is obtained with their orbitals is 0.2078 a.u., too large by approximately thirty percent. In order to reproduce this value with the bond orbital method, one must use an unrealistically large value of λ. The analysis of the gross atomic population given in Table 4 explains the reason. The population of the hydrogen 1*s* orbitals from the SCF calculations is much larger than those obtained with the bond orbital method, while the 2*s* and 2*p* populations of the B atom obtained from the SCF calculations are much smaller. This means that a large charge was moved from the B atom to the hydrogen. To reproduce the population and the field gradient as given by Hegstrom *et al.*, one must use a very large value of λ. The reason for the large

Table 4. Gross atomic population for BD_4^-

	$\lambda = 0$	$\lambda = 0.5$	$\lambda = 1.2$	SCF[a]
$1s_D$	0.000	0.4766	0.9437	1.261
$1s_B$	2.000	2.000	2.000	1.993
$2s_B$	2.000	1.550	1.068	0.794
$2P_B$	2.000	1.5145	0.9773	0.723

[a] The SCF Values were obtained from Ref. [9].

charge on the deuteron is a result of an unbalanced basis set. The Coulomb repulsion, and hence the total energy of the system will be reduced if electrons move towards the hydrogen. This fact results from the small value of the B nuclear charge. The bond orbital method causes the charges to remain in the vicinity of the B nucleus. An expansion in a larger basis set should restore the correct population. This was demonstrated in the case of SiH_4 where addition of $3d$ orbitals in the central atom reduced the population of the hydrogens [12]. The use of the optimized exponents in the construction of the bond orbitals as determined by Hegstrom *et al.* [10] does not result in any significant change of the optimum value of λ (Fig. 1).

3.2. Second Row Deuterates

Figure 2 shows clearly that a minimal basis set is not sufficient for computing the quadrupole coupling constants for second row deuterates. The calculated curves lie much higher than the experimental values. One could reproduce the experimental values with a minimal set by either using a very large negative value of λ or a large change in the M–D bond length. However, these two requirements are unrealistic. The introduction of double zeta orbitals for the central atom shifts the curves in the right direction by a significant amount. The use of Hartree-Fock orbitals does not result in any further significant changes of the curves. Still, a negative value of λ is needed to reproduce the experimental results. An increase in the size of the basis set of the central atoms without a proper change in the deuteron orbital may result in an unbalanced set. The exponent of the deuteron was changed to 1.2. As can be seen from Fig. 4, a very small difference is found from the curve with an exponent of 1.0. The difference between the calculated and experimental values of q can partly be accounted for by an inaccurate knowledge of the M–D bond length. A change of 10% in the M–D bond length results in a 50% change in the value of q as can be seen in Fig. 2 for the cases of AlD_4^- and PD_4^+. The experimental value of the Al–D bond length is not known and the value given in Table 1 was taken from the calculations of Albasiny and Cooper [13].

The force can be used again to check the quality of the molecular orbitals. The plot of the z component of the force vs. λ for AlD_4^-, SiD_4, and PD_4^+ is shown in Fig. 6. With the M–D bond length as given in Table 1, only the force of SiD_4 goes to zero for $0 < \lambda < 1$. This range of λ, however, does not reproduce the experi-

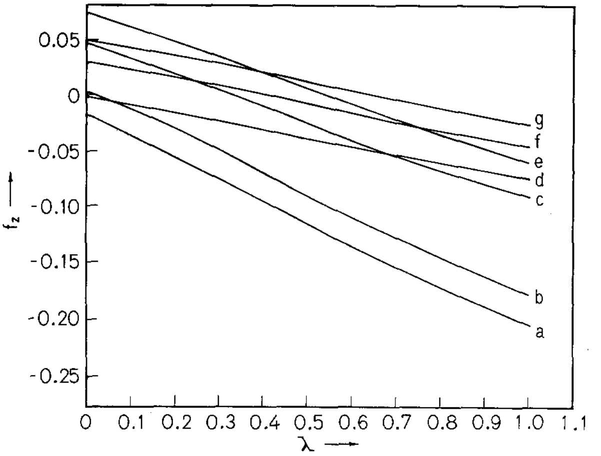

Fig. 6a–g. A plot of F_z vs λ with double zeta orbitals for a PD_4^+ ($R_{P\text{–}D} = 2.68$ a.u.), b PD_4^+ ($R_{P\text{–}D} = 2.75$ a.u.), c SiD_4 ($R_{Si\text{–}D} = 2.787$ a.u.), d AlD_4^- ($R_{Al\text{–}D} = 2.965$ a.u.), e SiD_4 ($R_{Si\text{–}D} = 2.9$ a.u.), f AlD_4^- ($R_{Al\text{–}D} = 3.1$ a.u.), g AlD_4^- ($R_{Al\text{–}D} = 3.2$ a.u.)

mental field gradient in SiD_4. For AlD_4^- and PD_4^+, even a zero force cannot be obtained with λ in the region of 0 to 1. An increase in the Al–D bond length to 3.1 a.u. results in a zero force for $\lambda \sim 0.4$ and reproduces the experimental field gradient for $\lambda \sim 0.45$. This should be compared with the Al–D bond length in diatomic AlD of 3.1 a.u. [14]. Moccia [15] quotes a value of 2.75 a.u. for the P–D bond length in PD_4^+. Such a change gives zero force and reproduces the field gradient for PD_4^+ molecules for $\lambda \sim 0.05$. This small value of λ is consistent with the large charge of the P nucleus. For SiD_4, a change to a bond length of 2.9 a.u. reproduces the experimental field gradient and gives zero force for $\lambda \sim 0.55$. The experimental values of the field gradient for the second row deuterates are much smaller than the corresponding values for the first row deuterates. Hence the effect of the rest of the crystal may be more important. Thus no simple relation between the optimal value of λ and the electronegativity values or the nuclear charges of the central atoms exists. It seems that λ decreases or at least does not increase as the nuclear charge of the central atom is increased. However, more quantitative conclusions can be drawn only after the contributions from the rest of the crystal are subtracted from the experimental values. These results should be compared with the above computed values. The contributions from the rest of the crystal may account for the fact $\lambda_f > \lambda_{f_g}$ for BD_4^-.

It seems that one could start with bond orbitals constructed with physical intuition. This set is not orthonormalized. One does not have to take great care in order to get the correct $s:p$ population ratio. By symmetrically orthonormalizing the set, the intuitive sense of the bond orbitals is still preserved, but by correlating with the optimal value of λ one could obtain a proper value of the $s:p$ population ratio, for example in the BD_4^- case. For pure tetrahedral coordination without formation of a bond, one gets $s:p = 1:3$. For $\lambda = 0.7$ the $s:p$ ratio is changed to 1.4118:5.0557. Similar consideration could be done for the other deuterates.

4. Conclusion

The bond orbital method for calculation of the electric field gradient in first and second row deuterates was found to be applicable under the following conditions:

a) Double zeta orbitals for the central ion are always preferable, although minimal basis sets for first row deuterates may be sufficient.

b) The M–D bond length must be known very accurately. If there is a way to estimate the contribution from the rest of the crystal, the values of the force and the field gradient can be used to estimate the M–D bond length. This can be useful in many cases where X-ray determination of a crystal structure can not yield the location of the hydrogens.

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Dr. S. D. Goren
Department of Physics
The University of the Negev
Beer Sheva, Israel