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Ab initio studies of nuclear quadrupole couplings in N_2H_2 and NH_3 molecules

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Nuclear quadrupole coupling constants of ^{14}N and ^{2}H nuclei in *cis*- and *trans*-N_2H_2 and NH_3 molecules are reported using [3*s* 2*p*/2*s*], [4*s* 2*p*/2*s*], [4*s* 3*p*/2*s*] and [5*s* 3*p*/3*s*] basis sets, comprising of CGTO augmented with bond centred functions. A few calculations employing nuclear centred polarisation functions with/without bond functions have been also carried out. In the absence of bond functions, the coupling constants for the nuclei have been found to be higher than experimental values (available for NH_3 molecule only). Inclusion of bond functions in the basis set not only lowers the energies of the system but yield coupling constants in good agreement with experimental values.

Key words: *Ab initio* — Bond centred function — Polarisation function — Electric field gradient (EFG) — Nuclear quadrupole coupling constant (NQCC)

1. Introduction

Molecular wave functions in general are sensitive to the choice of basis functions. If the basis set is reasonably large, the variational principle assures one of fairly good energies. Such a guarantee is not available for molecular properties and it is becoming increasingly important to examine the basis set effect with respect to various molecular properties. The nuclear quadrupole coupling constant (NQCC) happens to be one such property. It depends on the electric field gradients (EFG's) generated, at the site of nucleus under consideration, by the electronic charge distribution and the other nuclei. It is very sensitive to the choice of basis set. Whereas the energy is dependent on gross features of this charge distribution, the field gradients depend on the anisotropy of this charge distribution. In order to account for the deformation of atomic electron densities during molecule formation (on which EFG's are critically dependent) the nuclear centred basis sets have to be augmented with polarisation and/or bond centred functions.

Several studies on NQCC at the SCF (self-consistent field) level are available [1-3] in the literature. Recently Ha [4], Cummins et al. [5] and Feller and coworkers [6] have carried out extensive work in this field. With double zeta or even extended basis sets, the field gradients are not good unless polarisation functions are used. For second row atoms, supplementing these basis sets with only one 'd' function (exponent available from literature) is not enough for good EFG values. However, use of more than one such function, with optimized exponents, yield reasonably good electric field gradients. Thus Cummins et al. [5] employing a $[6s\,4p\,2d\,1f]$ basis set and Feller et al. [6] utilizing a $[10s\,8p\,3d\,1f]$ basis set of contracted Cartesian gaussian functions obtained field gradients in agreement with experiment. However, such large basis sets are not practicable for larger molecules.

Vladimiroff [7] using bond functions (BF's) instead of conventional polarisation functions (PF's) has reported the NQCC of ^{14}N in N_2 molecule. Chandra et al. [8-10] have employed such functions to augment the basis sets for NQCC calculations of different nuclei. A thorough study of these results shows that best results are obtained when the basis sets incorporate both BF's and PF's. However, if one has to make a choice between these two, the BF's should be preferred, because they yield field gradients, which are at least as good as those obtained with nuclear centred polarisation functions but require much less computational effort.

In this paper we have reported the calculations carried out on NH_3 and N_2H_2 (*cis* and *trans*) in their singlet ground states.

2. Theory

The formulation employed in evaluation of nuclear quadrupole couplings is given elsewhere [8, 11]. Briefly, the nuclear quadrupole coupling (e^2Qq) of a nucleus is the product of the nuclear quadrupole moment with the electric field gradient arising out of all other charges (electrons and nuclei). The field gradient q is that component of field gradient tensor in the principal co-ordinate system, which has the maximum absolute value. In this work we assume the nuclear quadrupole moment to be a constant experimental quantity and unlike some recent work [5, 12] we do not parametrize it. Electric field gradient consists of two parts: nuclear and electronic. In the Born-Oppenheimer approximation, the nuclear contribution is evaluated by usual classical methods. The electronic contribution is evaluated quantum mechanically and is given by

$$q_I = e\left[\sum_{K\neq I} Z_K(3\boldsymbol{R}_{IK}\boldsymbol{R}_{IK} - R_{IK}^2\delta_{IK})/R_{IK}^5 - \left\langle\Psi\right|\sum_j (\boldsymbol{r}_{Ij}\boldsymbol{r}_{Ij} - r_{Ij}^2\delta_{IK})/r_{Ij}^5\left|\Psi\right\rangle\right]$$

The molecular wave function Ψ is expressed as a single determinant of various occupied molecular orbitals, which in turn are obtained by the usual SCF (self-consistent field) procedure in terms of atomic basis functions. Thus in the final step, the evaluation of q reduces to the evaluation of the electric field gradient integrals over atomic basis sets. The procedure employed to evaluate these integrals is due to Chandra and Buenker [13].

3. Results and discussion

Ab initio nuclear quadrupole coupling calculations of ^{14}N and ^{2}H nuclei in N_2H_2 and NH_3 molecules have been carried out employing various CGTO (contracted Gaussian type orbitals) basis sets due to Dunning and Hay [14] and Dunning [15, 16]. As in our earlier work [8-10], scale factors of 1.2 for the [2*s*] and 1.49 for the [3*s*] contraction of hydrogen have been employed. Among the wide range of Q values [4, 5, 11, 12, 17, 18, 19] for ^{14}N we have selected the last experimentally reported value 1.93 (8) $\times 10^{-26}$ cm^2 due to Winter and Andra [19]. The deuterium Q value of 0.28×10^{-26} cm^2, has been taken from literature [20].

In the following sections electric field gradients and asymmetry parameters for various nuclei in these molecules determined using different basis sets have been discussed.

4. *Trans*-N_2H_2

Calculations for *trans*-N_2H_2 have been carried out at the experimental geometry quoted by Pople et al. [21], and the results are given in Table 1. Electric field gradients, calculated with the two basis sets [3*s* 2*p*/2*s*] and [4*s* 2*p*/2*s*] are equal, at both N and H. Addition of similar bond or polarisation functions to these basis sets also yields almost identical EFG's. In view of this, only a few results using a DZ (double-zeta) basis are listed. An examination of Table 1 reveals that

Table 1. Calculated EFG's at N and H nuclei in *trans*-N_2H_2

Basis sets	Energy a.u.	$q_{zz}(N)$	$\eta(N)$	$q_{zz}(H)$	$\eta(H)$
[3*s* 2*p*/2*s*]	−109.94929	−1.374	0.528	0.411	0.006
[3*s* 2*p*/2*s*]+*s* BF between N—H bonds	−109.96543	−1.399	0.414	0.341	0.010
[3*s* 2*p*/2*s*]+*s* and *p* BF's between N—N bond	−109.98253	−1.392	0.540	0.411	0.016
[3*s* 2*p*/2*s*]+*s* BF between N—H and *s*+*p* BF's on N—N bonds	−109.99676	−1.362	0.496	0.342	0.027
[3*s* 2*p* 1*d*/2*s* 1*p*]	−110.02094	−1.303	0.643	0.363	0.017
[4*s* 2*p*/2*s*]+*s*+*p* BF's between N—N	−109.98292	−1.397	0.532	0.410	0.016
[4*s* 2*p* 1*d*/2*s* 1*p*]	−110.02110	−1.303	0.644	0.363	0.017
[4*s* 2*p* 1*d*/2*s* 1*p*]+*s* and *p* BF's between N—N	−110.02190	−1.314	0.668	0.363	0.017
[4*s* 3*p*/2*s*]+*s* BF between N—H and *s*+*p* BF's between N—N	−110.00823	−1.362	0.670	0.328	0.021
[5*s* 3*p*/3*s*]+*s* BF between N—H and *s*+*p* BF's between N—N	−110.01486	−1.366	0.643	0.319	0.022
WP [4*s* 3*p* 1*d*/2*s* 1*p*][a]		−1.1677	0.558	0.325	0.186
Snyder EFG with DZ[b] basis set	—	—	—	0.424	0.024

[a] [22]

[b] [23]

whereas s-BF's (α_s and α_p are 1.0 in *cis*- and *trans*-N_2H_2) added between the N—H bonds lowers the H EFG by 0.07 a.u. with respect to original basis set, the EFG at N is slightly increased. On the other hand s and p BF's present between N—N bond decrease ^{14}N couplings without affecting ^2H couplings. Inclusion of s and p bond functions in between each of the bonds results in a decrease of the field gradients at each of these nuclei. The asymmetry parameter for N is not very sensitive to bond functions, but the deuterium asymmetry parameter is.

If the DZ basis is augmented with polarisation functions instead of bond functions, the electric field gradients around the nitrogen decrease significantly, but the deuterium electric field gradients are unaffected. However, the addition of bond functions to a basis set already having polarisation functions, does not significantly change either field gradients or asymmetry parameters.

Unlike the cases reported earlier [8–10], where bond functions played a dominant role in the basis sets while the role of polarisation function was less significant, in the present case of *trans*-N_2H_2 the polarisation functions appear to play a more important role than bond functions. However, this conclusion is questionable, because when the polarisation functions are employed, the field gradients are sensitive to the contraction scheme employed. Thus a $[4s\,2p\,1d/2s\,1p]$ basis yields field gradients and asymmetry parameters which are very different from those obtained by Winter and Pitzer [22] employing a $[4s\,3p\,1d/2s\,1p]$ basis set. On the other hand, when bond functions are used to augment, it does not seem to matter which of the basis sets $[3s\,2p/2s]$, $[4s\,2p/2s]$, $[4s\,3p/2s]$ and $[5s\,3p/3s]$ are employed to evaluate the field gradients. In the absence of any experimental data, it is desirable to examine the field gradients with more polarisation functions, but we did not attempt this because the PC-AT Computer at our disposal could not handle larger basis sets.

5. *Cis*-N_2H_2

Computation of electric field gradients and asymmetry parameters for *cis*-N_2H_2 have been carried out using the optimized geometry of Winter and Pitzer [22], because the experimental geometry for this molecule is not available. Some of the results of our computations for this isomer of N_2H_2 are listed in Table 2. As in the case of *trans*-N_2H_2, the field gradients exhibit stability with respect to the addition of bond functions to any one of the standard basis sets [14–16]. However, when polarisation functions are employed the results are sensitive to the contraction scheme employed.

6. NH_3

The usefulness of BF's has been further exploited in the case of NH_3 at the geometry quoted by Goddard and Csizmadia [24] (since this geometry has been found to be optimum). Employing a DZ basis set and s and p bond functions at the mid point of each N—H bonds, the energy of the ammonia molecule shows a minimum for bond functions with exponents $\alpha_s = 1.3$ and $\alpha_p = 0.9$. Results for

Table 2 Calculated EFG's and η with various basis sets in *cis*-N_2H_2

Basis set	Energy (a.u.	$q_{zz}(N)$	$\eta(N)$	$q_{zz}(H)$	$\eta(H)$
DZ	−109.93760	−1.440	0.410	0.414	0.006
DZ+ *s* − BF on N—H and *s* and *p* BF's on N—N bonds	−109.98566	−1.410	0.411	0.347	0.015
DZ+PF's	−110.01101	−1.370	0.529	0.373	0.020
[4*s* 3*p*/2*s*]+ *s* BF between N—H and *s* and *p* BF's between N—N bonds	−109.99676	−1.420	0.566	0.335	0.008
[5*s* 3*p*/3*s*]+ *s* BF between N—H and *s* and *p* BF's between N—N bonds	−110.00247	−1.429	0.542	0.325	0.014
WP [4*s* 3*p* 1*d*/2*s* 1*p*][a]	—	−1.126	0.760	0.271	0.365

[a] [22]

this molecule are shown in Table 3. The calculations employing basis sets with polarisation functions ($\alpha_d = 0.864$ for N, $\alpha_p = 1.0$ for H) yield field gradients which are numerically greater than those obtained with basis sets employing bond functions instead of polarisation functions. The bond function results are closer to the experimental data than are the polarization function results. It should be added at this point that addition of polarisation functions to basis sets already having bond functions does not effect the field gradients significantly. Thus although better field gradients are obtained using basis sets having both bond functions and polarisation functions, in order to save computer time, the latter can be omitted, but bond functions must be included. Our best results are obtained with [5*s* 3*p*/3*s*]+ *s* and *p* BF's basis set. No attempt was made to include polarisation functions in this basis set.

Table 3. Calculated EFG's and η at N and H nuclei in NH_3

Basis set	Energy (a.u.)	$q_{zz}(N)$	$\eta(N)$	$q_{zz}(H)$	$\eta(H)$
DZ	−56.177887	−1.162	0.0	0.439	0.144
DZ+ *s* and *p* BF's	−56.200790	−1.067	0.0	0.375	0.175
DZ+PF's	−56.208348	−1.085	0.0	0.405	0.172
DZ+PF's+ *s* and *p* BF's	−56.209148	−1.071	0.0	0.390	0.172
[5*s* 3*p*/3*s*]	−56.185191	−1.134	0.0	0.431	0.145
[5*s* 3*p*/3*s*]+ *s* and *p* BF's	−56.211178	−1.025	0.0	0.363	0.172
Feller et al.[a]					
[10*s* 8*p* 4*d* 1*f*/6*s* 4*p* 1*d*]	—	−0.9561	—	0.394	—
Cummins et al.[b]					
[6*s* 4*p* 2*d* 1*f*/4*s* 2*p* 1*d*]	−56.221643	−0.9664	—	0.412	0.136
Experimental couplings converted to EFG's	—	−0.902[c]	0.0	0.428[d] ±0.018	0.05 ± 0.06

[a] [6]

[b] [5]

[c] [25]

[d] [26]

Feller and coworkers [6] and Cummins et al. [5] have reported EFG values of −0.9561 and 0.394, and −0.9964 and 0.412 for N and H respectively, with largely polarised [10*s* 8*p* 4*d* 1*f*/6*s* 4*p* 1*d*] and [6*s* 4*p* 2*d* 1*f*/4*s* 2*p* 1*d*] basis sets comprising 130 and 84 functions respectively. It is interesting to note that although their basis sets are almost three and a half and two and a half times larger than our [5*s* 3*p*/3*s*]+*s* and *p* BF's basis set, the EFG and η values with all these bases do not differ significantly. In other words small basis sets augmented with bond functions (plus polarisation functions) describe the anisotropy of the charge distribution as well as extended basis sets with *d* and *f* polarisation functions do.

From our study of the variation of the exponents of *s*-bond functions on field gradients, it is seen that when the interatomic distance does not differ significantly, as in the case of N—H bonds of NH_3 and N_2H_2 in the present work, and HCN and H_2O reported previously [8, 10], the bond function's exponent is almost the same for minimum energy. Even the quadrupole coupling constant of deuterium is found to be significantly improved with this choice of α_s. Thus it should be possible in the future to obtain standard bond function exponents for various bonds so as to obtain not only better molecular energies but also the anisotropies of charge distributions.

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References

1. Huber H (1985) J Chem Phys 83:4591
2. Snyder LC (1974) J Chem Phys 61:5032
3. Barber M, Hayne SM, Hinchliffe A (1980) J Mol Struct 62:207
4. Ha TK (1983) Chem Phys Lett 107:117
5. Cummins PL, Bacskay GB, Hush NS Ahlrichs R (1987) J Chem Phys 86:6908
6. Feller D, Boyle CM, Davidson ER (1987) J Chem Phys 86:3424
7. Vladimiroff T (1976) J Chem Phys 64:64
8. Prasad G, Keshari V, Chandra P (1989) J Mol Struct 192:253
9. Lal A, Keshari V, Chandra P (1989) J Mol Struct 192:263
10. Keshari V, Karna SP, Chandra P (1989) J Mol Struct 192:271
11. Kern CW, Karplus M (1965) J Chem Phys 42:1062
12. Brown RD, Head-Gordon MP (1987) Mol Phys 61:1183
13. Chandra P, Buenker RJ (1983) J Chem Phys 79:358
14. Dunning Jr TH, Hay PJ (1977) Gaussian basis sets for molecular calculations. In: Schaefer III HF (ed) Method of electronic structure theory, p 1
15. Dunning Jr TH (1970) J Chem Phys 53:2823
16. Dunning Jr TH (1971) J Chem Phys 55:716
17. Scuseria GE, Schaefer III HF (1987) J Chem Phys 87:4020
18. O'Konski CT, Ha TK (1968) J Chem Phys 49:5354
19. Winter H, Andra HJ (1980) Phys Rev A 21:581
20. American Institute of Physics, Handbook, 3rd edn (1972) Gray DB (ed) Table 8b 1
21. De Frees DJ, Raghavchari K, Schlegel HB, Pople JA (1982) J Am Chem Soc 104:5576
22. Winter NW, Pitzer RM (1975) J Chem Phys 62:1269
23. Snyder LC (1978) J Chem Phys 68:291
24. Goddard GD, Csizmadia IG (1977) Int J of Quantum Chem 12:133
25. Hermann G (1958) J Chem Phys 29:875
26. Thaddens P, Kosher LC, Cahill P (1964) J Chem Phys 41:1542