Ab initio studies of nuclear quadrupole couplings in N$_2$H$_2$ and NH$_3$ molecules

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Nuclear quadrupole coupling constants of $^{14}$N and $^2$H nuclei in cis- and trans-N$_2$H$_2$ and NH$_3$ molecules are reported using [3s $2p/2s$], [4s $2p/2s$], [4s $3p/2s$] and [5s $3p/3s$] 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 \(^{14}\text{N}\) in \(\text{N}_2\) 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 \(\text{NH}_3\) and \(\text{N}_2\text{H}_2\) \((cis\ and\ trans)\) 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

\[
q_i = e \left[ \sum_{K} Z_K (3R_{IK}R_{IK} - R_{IK}^2 \delta_{IK}) / R_{IK}^5 - \left< \Psi | \sum_j (r_{ij}r_{ij} - r_{ij}^2 \delta_{ij}) / r_{ij}^5 | \Psi \right> \right]
\]

The molecular wave function \(\Psi\) 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