Electric Quadrupole Moment of the ^{14}N Nucleus Determined by ab initio CI Calculation on NH_3*

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Based on the calculated electric field gradient (q) from ab initio CI wavefunctions with large basis set (including f functions on N and d functions on H) and the experimental nuclear quadrupole coupling constant ($e\,Q\,q$) for nitrogen in NH_3, an improved value of the quadrupole moment of ^{14}N is proposed as $Q(^{14}N) = 2.08 \times 10^{-26}$ cm². The value calculated using a wavefunction near the Hartree-Fock limit enlarged ≈ 10% by the CI treatment.

Introduction

A direct determination of the electric quadrupole moment of the ^{14}N nucleus ($Q(^{14}N)$) is very difficult since the electronic ground state of the nitrogen atom (^4S) is almost spherically symmetrical, a slight deviation from the sphericity being only due to the spin-orbit coupling. The best available method of obtaining the $Q(^{14}N)$ value seems to be to compute the electric field gradient (q) in molecules containing nitrogen, whose nuclear quadrupole coupling constants (eQq) are experimentally known. Among nitrogen-containing molecules, NH_3 is best because a very accurate experimental value obtained from the microwave study in the gaseous phase is available ($eQq(^{14}N) = 4.0924 \pm 0.0009$ MHz) [1] and because the NH_3 molecule is small enough to obtain a very accurate molecular electronic wavefunction to compute the electric field gradient at the site of the nitrogen nucleus.

A large number of ab initio self-consistent field (SCF) and configuration interaction (CI) calculations have been made on NH_3 for this purpose, as summarized in [2]. The available q values at nitrogen in NH_3 obtained from several levels of accuracy are, however, in the range from about -0.6 to -2.0 a.u. Most of these previous studies employ ab initio SCF wavefunctions with more or less extended basis sets.

While one-electron properties such as the electric field gradient may be expected to be calculated with reasonable accuracy from the Hartree-Fock SCF wavefunction, the influence of electron correlations on the Q value is of interest, especially since the discrepancy among various calculated values is large.

As shown previously, the molecular quadrupole moment of benzene, also a one-electron property, could only be calculated very accurately from an extended CI wavefunction [3], and the calculated value of -8.778 B which agreed excellently with the most recent experimental value (-8.69 ± 0.51 B) was at variance with the Hartree-Fock SCF value (-9.662 B) by about 10%.

Results and Discussion

In the present study q at nitrogen in NH_3, calculated from ab initio CI wavefunctions of different levels of accuracy, is reported and compared to the Hartree-Fock value. From a systematic comparison of the calculated q value an improved $Q(^{14}N)$ value is proposed. The calculated q or $Q(^{14}N)$ value is also at variance with the Hartree-Fock value by about 10%.

The ab initio wavefunction which precedes the CI study employs the gaussian basis set of Huzinaga (9s, 5p) [4], contracted to a double-zeta (4s, 2p) according to Dunning's scheme for N [5]. A (4s)

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gaussian expansion of the hydrogen 1s orbital with a scale factor 1.2 was similarly contracted to a (2s) set for each of the three hydrogen atoms [5]. A set of polarization functions (d) on N with exponent 0.75, and a set of p functions with exponent 1.2 on H were added to the above basis set (DZ + P). Finally, a larger basis set, which includes f functions on N with exponent 1.0 and d functions on H with exponent 0.99 [6], has been employed in the present study. The molecular geometry employed for the calculation is the experimental one with $r(\mathrm{N-H}) = 1.012$ Å and $\sphericalangle$ HNH = 106.7° [7].

The CI calculation has been carried out within the single and double excitation (S + D) CI scheme. As orbitals of variable occupancy all molecular orbitals are considered. The CI matrix has been generated by including all single and double excitations from the reference SCF configuration, the configurations having been selected by use of second-order perturbation theory with a certain energy threshold. The CI wavefunctions and energies are obtained by diagonalizing the CI matrix.

Table 1 summarizes the calculated q and Q values in their dependence on the energy threshold (T) used in the CI calculation employing a large basis set which includes f functions on N and d functions on H. In the previous study [8] it was shown that a significant change in the calculated q or Q value from the SCF to the CI level took place. Already in the small CI level ($T = 10^{-4}$ a.u.), the Q value was found to be larger than the SCF value with the DZ + P basis set by about 0.1×10^{-26} cm^2. The q and Q values converged very rapidly to − 0.893 a.u. and 1.93×10^{-26} cm^2, respectively, as the size of the CI wavefunction was increased.

Table 1. Total energy (E_T), electric field gradient at nitrogen in NH_3 (q) and the electric quadrupole moment of ^{14}N (Q) obtained by a large basis set[a] CI calculation.

Level of calculation	E_T (a.u.)	q (a.u.)[d]	$Q/10^{-26}$ cm^2
SCF	−56.21546	−0.8901	1.940
CI T[b]			
10^{-3}	−56.24129[c] (119)	−0.8647	1.997
10^{-5}	−56.39361 (1273)	−0.8250	2.093
10^{-6}	−56.42021 (3995)	−0.8274	2.087
10^{-7}	−56.42402 (6331)	−0.8282	2.085

[a] Including f functions on N and d functions on H.
[b] Perturbation energy threshold in a.u.
[c] Values in parentheses are the dimensions of the Ci wavefunctions.
[d] For use in finding the quadrupole coupling constant ($e\,Q\,q$), the electric field gradients are given in MHz/barn = u.a. times 236.96.

It is shown in Table 1 that the SCF value of q or Q (− 0.8901 a.u. or 1.94×10^{-26} cm^2) obtained by the larger DZ + P basis set calculation is about the same as the best CI value obtained employing the smaller DZ + P basis set of the previous study [8], and that the influence of the electron correlation is also about 10%, similar to the magnitude obtained by the previous study.

The configuration interaction not only lowers the total energy significantly but also improves the calculated one-electron properties such as the electric field gradient at the nitrogen in NH_3. The single excitations with respect to the SCF reference configuration have a negligible effect on the CI energy, but contribute significantly to the calculated q value, as shown in the previous study [8]. The proposed $Q(^{14}N) = 2.08 \times 10^{-26}$ cm^2 of the present study is based on the most extensive CI study (all (S + D) CI) of dimension 6331 with energy − 56.42402 a.u., which corresponds to the lowest variationally determined value for NH_3.

It is worthwhile to note that this $Q(^{14}N)$ value is very near to 2.05×10^{-26} cm^2 obtained from a theoretical study on NO^+ and N_2 [9], and also near to the current experimental value of $1.93(8) \times 10^{-26}$ cm^2 obtained from a measurement of the yhperfine splitting for $N^+\ 2p\,3p\ {}^1P_1$ [10].

Some representative $Q(^{14}N)$ values proposed between 1935 and 1985 [11−17] are shown in Figure 1.

Refinements in the calculation including even a much larger basis set, higher order electron correlation terms and the vibrational effects may further improve the calculated q value. The vibrational correction has been shown to reduce the q value by about 2% [14]. The error due to basis set deficiency and incomplete correlation cannot be estimated exactly but is expected to be much smaller than the difference between the near Hartree-Fock limit and the present CI value.

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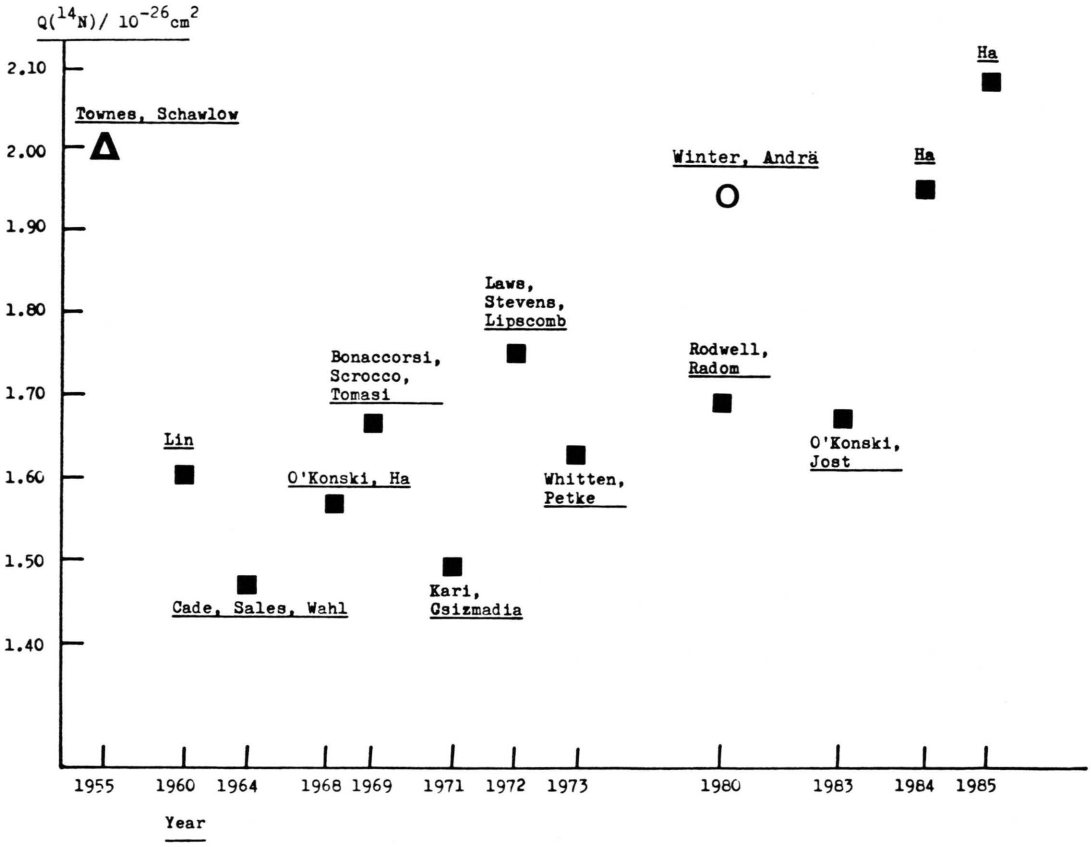

Fig. 1. A summary of some representative $Q(^{14}N)$ values proposed between 1935 and 1985. – ■ calculated values, ○ experimental value of [10], △ a value cited in [17].

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