Nitrogen quadrupole coupling constants for HCN and H$_2$CN$^+$: Explanation of the absence of fine structure in the microwave spectrum of interstellar H$_2$CN$^+$

Gustavo E. Scuseria, Timothy J. Lee, Richard J. Saykally, and Henry F. Schaefer

Citation: The Journal of Chemical Physics 84, 5711 (1986); doi: 10.1063/1.449930
View online: https://doi.org/10.1063/1.449930
View Table of Contents: http://aip.scitation.org/toc/jcp/84/10
Published by the American Institute of Physics

Articles you may be interested in

A possible role for triplet H$_2$CN$^+$ isomers in the formation of HCN and HNC in interstellar clouds
The Journal of Chemical Physics 73, 3255 (1980); 10.1063/1.440520
Nitrogen quadrupole coupling constants for HCN and H$_2$CN$^+$: Explanation of the absence of fine structure in the microwave spectrum of interstellar H$_2$CN$^+$

Gustavo E. Scuseria,$^a$ Timothy J. Lee, Richard J. Saykally, and Henry F. Schaefer III

Department of Chemistry, University of California, Berkeley, California 94720

(Received 14 January 1986; accepted 7 February 1986)

Nitrogen 14 quadrupole coupling constants for H$_2$CN$^+$ and HCN are predicted via ab initio self-consistent-field and configuration interaction theory. Effects of electron correlation, basis set completeness, and geometrical structure on the predicted electric field gradients are analyzed. The quadrupole coupling constant obtained for H$_2$CN$^+$ is one order of magnitude less than in HCN, providing an explanation for the experimental fact that the fine structure of the microwave spectrum of H$_2$CN$^+$ has not been resolved. This research also allows a reliable prediction of the nuclear quadrupole moment of $^{14}$N, namely $Q(^{14}$N) = 2.00 × 10$^{-26}$ cm$^2$.

INTRODUCTION

Despite the fact that HCNH$^+$ has a small permanent dipole moment,$^{1-4}$ the microwave spectrum of this molecular ion has very recently been observed in interstellar space. Ziurys and Turner$^5$ observed the $J = 1-0$, 2-1, and 2-2 rotational transitions of HCNH$^+$ toward Sgr. B2 between October 28, 1984 and April 16, 1985. The laboratory millimeter and submillimeter wave spectrum of HCNH$^+$ was also recently detected by Bogey, Demuynck, and Destombes.$^6$

In this work we report ab initio values of the $^{14}$N nuclear quadrupole coupling constants (QCC) for HCN and HCNH$^+$.

Theoretical predictions of vibrational frequencies and infrared intensities for protonated HCN were the subject of a previous paper.$^1$

Normally, the microwave spectrum of a molecule which contains an atom with a nuclear quadrupole moment will exhibit fine structure due to the electric interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus. However, it was emphasized by Ziurys and Turner$^5$ that fine structure could not be resolved for HCNH$^+$; the implication being that the electric field gradient at the $^{14}$N nucleus of HCNH$^+$, and hence the QCC, was very small. Thus we decided to predict the ab initio electric field gradient and corresponding $^{14}$N QCC for HCNH$^+$. To our knowledge the present research represents perhaps the first thorough examination of the effects of electron correlation on predicted nitrogen quadrupole coupling constants.

THEORETICAL APPROACH

Nuclear quadrupole coupling constants may be obtained from the ab initio molecular electric field gradient ($q$) if the nuclear quadrupole moments ($Q$) are known. Numerous ab initio predictions of electric field gradients have been reported for deuterium$^7$ and for $^{14}$N containing molecules.$^8-37$ The Hamiltonian representing the interaction between the nuclear quadrupole moment and the electronic electric field gradient may be written as$^{28,29}$

$$H = e^2 \sum_{\mu}^{Q} \frac{Q_{\mu}}{2I_A(2I_A-1)} \left[ I_{\alpha} \frac{\vec{r}_A}{\vec{R}_A} \frac{t_A}{r_A^3} - 3(\vec{r}_A \cdot \vec{t}_A)^2 \right] / r_A^5,$$

(1)

where $I_A$ is the nuclear spin of nucleus $A$ ($I_A \geq 1$ is required for $Q_A$ to be different from zero), and $r_A = |\vec{r}_j - \vec{R}_A|$ is the distance between electron $j$ and nucleus $A$. The total electric field gradient is a second-rank tensor whose components at the site of nucleus $A$ are

$$q_{\alpha\beta}^A = \sum_{\mu\nu} P_{\mu\nu} \langle \phi_{\mu} | \left( r_A^2 \delta_{\alpha\beta} - 3 r_A \delta_{\alpha\beta} r_A \right) / r_A^5 | \phi_{\nu} \rangle$$

$$+ \sum_{\beta \neq \alpha} Z_{\beta} (3 R_{AB} R_{A\beta} - \delta_{\alpha\beta} R_{AB}^2) / R_{AB}^5,$$

(2)

where $\alpha, \beta = x, y, z$; $P_{\mu\nu}$ is the reduced one-particle density matrix; $\phi_{\mu}, \phi_{\nu}$ are atomic orbitals and $R_{AB} = |\vec{R}_A - \vec{R}_B|$ are internuclear distances. Also in Eq. (2), $r_A$ is the distance of the electron from nucleus $A$; $r_{A\beta}$ is the difference in Cartesian coordinate $\alpha$ (i.e., $x, y,$ or $z$) between the electron and nucleus $A$; and $R_{A\beta}$ is the difference in Cartesian coordinate $\alpha$ between nucleus $A$ and nucleus $B$. The two terms in Eq. (2) correspond to the electronic and nuclear contributions, respectively. For linear molecules the QCC is straightforwardly obtained as $e^2 q_{NN}^2 Q_{NN}/\hbar$, with $z$ being the axis of the molecule.

One-particle density matrices were obtained for both the self-consistent-field (SCF) and configuration interaction (CI) wave functions and subsequently used in the evaluation of the electronic contribution to the electric field gradient [see Eq. (2)]. The electric field gradient integrals over the atomic orbital basis were evaluated using standard techniques.$^{30}$

Initially the electric field gradient was evaluated with SCF wave functions in conjunction with the standard Huizenga-Dunning$^{31,32}$ double zeta plus polarization (DZ+P) basis used previously.$^1$ This basis is designated (9s5p1d/4s2p1d) for the heavy atoms (C and N) and (4s1p/2s1p) for H. The hydrogen $s$ functions were scaled by a fac-
tor of 1.2, and the polarization function exponents were $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.8$, and $\alpha_d(H) = 1.0$.

Correlation effects were analyzed by way of CI wave functions including all single and double excitations with respect to the SCF reference function with the exceptions that the $C_2$- and $N_2$-like orbitals were kept doubly occupied and the corresponding orbitals deleted from the virtual space. The SCF DZ + P and CISD DZ + P optimized geometries were taken from the literature and are given in Table I for completeness.

The influence of the basis set was investigated by using the less contracted triple zeta (TZ) Huzinaga-Dunning basis, the $(11s6p)$ and $(13s8p)$ primitive set of van Duijneveldt for C and N, and the 6s, 8s, and 10s primitive sets of the same author for hydrogen. All contractions of these basis sets were performed over the innermost primitives.

The polarization function orbital exponents given above were used when one set of polarization functions was added to these $sp$ basis sets. However, the quadrupole coupling constants were also evaluated using basis sets including two sets of polarization functions on each atom. When two sets were added the polarization exponents were $\alpha_s = 1.5$ and 0.5 for N, and $\alpha_d = 1.2$ and 0.4 for C.

RESULTS AND DISCUSSION

In Table I, the predicted equilibrium geometries and the corresponding energies for both HCN and protonated HCN, evaluated with SCF and CI wave functions, are presented. As usual, CI bond lengths are longer than the SCF ones.

The $^{14}$N QCC for HCN has been measured by DeLucia and Gordy, the experimental value being $-4.7091 \pm 0.0013$ MHz. The nuclear quadrupole moment of $^{14}$N has recently been deduced by Ha to be $1.95 \times 10^{-26}$ cm$^2$. Therefore, theoretical values of the electric field gradient may be used to test the accuracy of theoretical predictions for the QCC, by way of combination with known or estimated nuclear quadrupole moments. On the other hand, theoretical values of the electric field gradient may be used to predict the quadrupole moment at a determined level of theory, provided the experimental QCC are known. In this paper, we have initially used Ha's suggested value of the $^{14}$N quadrupole moment to predict the QCC for H$_2$CN$^+.$

In Table II we report the basis set dependence of the electric field gradients of HCN and H$_2$CN$^+$ at the SCF level of theory. These calculations were carried out at the corresponding CISD DZ + P optimized geometries (see Table II).

### Table I. Predicted equilibrium geometries and energies for HCN and protonated HCN.

| Entry | Basis | SCF | CISD |
|-------|-------|-----|------|
|       |       | HCN | H$_2$CN$^+$ |
| 1.    | STO3G | -91.674 88 | -91.996 27 |
| 2.    | DZ    | -92.836 41 | -93.128 16 |
| 3.    | TZ    | -92.845 95 | -93.137 09 |
| 4.    | (11s6p/8s5p) (6a/4s) | -92.857 69 | -93.147 89 |
| 5.    | (13s8p/9s5p) (8s/6s) | -92.860 29 | -93.150 35 |
| 6.    | (13s8p/10s6p) (10s/8s) | -92.860 94 | -93.151 11 |
| 7.    | Uncontracted (13s8p) (10s) | -92.860 97 | -93.151 14 |
| 8.    | DZ + P | -92.888 04 | -93.175 35 |
| 9.    | TZ + P | -92.896 25 | -93.183 11 |
| 10.   | TZ + P + P$_d$ | -92.898 17 | -93.184 14 |
| 11.   | TZ + 2P | -92.900 54 | -93.186 68 |
| 12.   | (13s8p1d/9s5p1d) (8s1p/6s2p) | -92.906 94 | -93.193 99 |
| 13.   | (13s8p2d/9s5p2d) (8s2p/6s2p) | -92.910 19 | -93.196 32 |

### Table II. Energies, electric field gradients, and nuclear quadrupole coupling constants of $^{14}$N in HCN and H$_2$CN$^+$ for different basis sets at the SCF level of theory. The nuclear quadrupole moment of $^{14}$N was assumed to be $1.95 \times 10^{-26}$ cm$^2$, as proposed in Ref. 25.

| Entry | Basis | HCN | H$_2$CN$^+$ |
|-------|-------|-----|------|
|       |       | E(a.u.) | $\epsilon Q/q(h)$ (MHz) | E(a.u.) | $\epsilon Q/q(h)$ (MHz) |
| 1.    | STO3G | -91.674 88 | -0.341 | -1.56 | -91.996 27 | 0.533 | 2.44 |
| 2.    | DZ    | -92.836 41 | -0.813 | -3.72 | -93.128 16 | 0.152 | 0.70 |
| 3.    | TZ    | -92.845 95 | -1.110 | -5.09 | -93.137 09 | 0.000 | 0.00 |
| 4.    | (11s6p/8s5p) (6a/4s) | -92.857 69 | -1.044 | -4.78 | -93.147 89 | 0.028 | 0.13 |
| 5.    | (13s8p/9s5p) (8s/6s) | -92.860 29 | -1.054 | -4.83 | -93.150 35 | 0.018 | 0.08 |
| 6.    | (13s8p/10s6p) (10s/8s) | -92.860 94 | -1.082 | -4.96 | -93.151 11 | -0.011 | -0.05 |
| 7.    | Uncontracted (13s8p) (10s) | -92.860 97 | -1.076 | -4.93 | -93.151 14 | -0.006 | -0.03 |
| 8.    | DZ + P | -92.888 04 | -0.936 | -4.28 | -93.175 35 | 0.099 | 0.45 |
| 9.    | TZ + P | -92.896 25 | -1.133 | -5.19 | -93.183 11 | -0.123 | -0.56 |
| 10.   | TZ + P + P$_d$ | -92.898 17 | -1.115 | -5.11 | -93.184 14 | -0.121 | -0.55 |
| 11.   | TZ + 2P | -92.900 54 | -1.140 | -5.22 | -93.186 68 | -0.127 | -0.58 |
| 12.   | (13s8p1d/9s5p1d) (8s1p/6s2p) | -92.906 94 | -1.132 | -5.19 | -93.193 99 | -0.092 | -0.42 |
| 13.   | (13s8p2d/9s5p2d) (8s2p/6s2p) | -92.910 19 | -1.146 | -5.25 | -93.196 32 | -0.111 | -0.51 |

*Optimized CISD geometries with the DZ + P basis set were used (Table I).

*Exponents of diffuse polarization functions in the $P_d$ set are 0.15 for all atoms.

*Reference 35.
TABLE III. Influence of electron correlation effects on the predicted values of electric field gradients and nuclear quadrupole coupling constants for \(^{14}\text{N}\) in \(\text{HCN}\) and \(\text{H}_2\text{CN}^+\).\(^*\)

|                  | \(\text{HCN}\)          | \(\text{H}_2\text{CN}^+\)       |
|------------------|--------------------------|---------------------------------|
|                  | \(\epsilon (\text{a.u.})\) | \(q (\text{a.u.})\)  | \(\epsilon^2qQ/\hbar\) (MHz) | \(\epsilon (\text{a.u.})\) | \(q (\text{a.u.})\)  | \(\epsilon^2qQ/\hbar\) (MHz) |
| DZ + P basis set | -92.888 04               | -0.936                         | 4.28                          | -93.175 35               | 0.099                         | 0.45                          |
| SCF              | -93.160 48               | -0.798                         | 2.66                          | -93.464 27               | 0.104                         | 0.48                          |
| CISD\(^a\)       | -93.188 24               | -0.804                         | 2.68                          | -93.474 68               | 0.103                         | 0.47                          |
| TZ + 2P basis set| -92.900 54               | -1.140                         | 5.22                          | -93.186 68               | -0.127                        | 0.58                          |
| SCF              | -93.203 99               | -1.000                         | 4.58                          | -93.440 58               | -0.119                        | 0.55                          |

\(^*\)Optimized CISD geometries with DZ + P basis sets were used (see Table I).
\(^a\)Two innermost doubly occupied molecular orbitals and corresponding virtuals are frozen.
\(^b\)All single and double replacements are included.

Without using polarization functions it is not possible to find convergence for the valence \(sp\) basis set. This is true even with the uncontracted \(C, N(13s8p)\) \(H(10s)\) set. It is apparent that polarization functions are of crucial importance for this property. We have also investigated the influence of diffuse polarization functions (see entry 10 of Table II), and such functions reduce the value of \(q\) slightly. From results presented in Table II we conclude that at least the TZ + 2P basis set should be used if quantitative agreement with experimental results is desired. Smaller basis sets are less than satisfactory. Our value for HCN with the TZ + 2P basis set at the SCF level (\(-5.22\) MHz) is reasonably close to the experimental value (\(-4.71\) MHz). In comparing these figures one should take into account the uncertainty in the quadrupole moment for \(^{14}\text{N}\).

The influence of correlation effects is analyzed in Table III for both HCN and \(\text{H}_2\text{CN}^+\) with DZ + P and TZ + 2P basis sets. In evaluating the electric field gradient we chose an expectation value approach.\(^3\) This means that Eq. (2) was used for the electric field gradients, with \(P_{\mu\nu}\), being now the one-particle reduced density matrix obtained from the CISD wave function. Also examined was the influence of keeping the innermost doubly occupied molecular orbitals and corresponding virtuals frozen with the DZ + P basis set and, as expected, we found it of less importance. The results presented in Table III show that in HCN correlation effects increase the predicted electric field gradient by \(-0.14\) a.u., or 12%–14%. The same increase holds for \(\text{H}_2\text{CN}^+\) but to a much smaller degree, 0.004–0.008 a.u.

The influence of the assumed geometrical structure on the predicted electric field gradients and quadrupole coupling constants is another parameter to be analyzed. Such a study is reported in Table IV. Results obtained show that these properties are only somewhat sensitive to the small perturbations introduced (\(\pm 0.01\) a.u. in all bond lengths with respect to the optimized CISD DZ + P structures). However, it may be concluded that neither this structural dependence nor correlation effects will affect the order of magnitude of the predicted electric field gradients and consequently the calculated \(^{14}\text{N}\) QCC in these molecules.

Obviously, a precise quantitative prediction for the \(^{14}\text{N}\) QCC in \(\text{H}_2\text{CN}^+\) will require a refinement in basis set, correlation effects, and geometrical structure and is not the purpose of this paper. Nevertheless, from the results obtained in this work we may conclude that the nuclear quadrupole coupling constant for \(^{14}\text{N}\) in \(\text{H}_2\text{CN}^+\) is in the range of \(-0.55 \pm 0.3\) MHz or one order of magnitude less than in HCN. This prediction satisfactorily explains the experimental observation that the fine structure of the microwave spectrum of interstellar \(\text{H}_2\text{CN}^+\) was not resolved.\(^5\)

### CONCLUDING REMARKS

There is no meaningful purely experimental value for the nuclear quadrupole moment of \(^{14}\text{N}\). The most reliable values for this quadrupole moment may be obtained by comparing

---

TABLE IV. Influence of the geometrical structure on the predicted values of electric field gradients and nuclear quadrupole coupling constants for \(^{14}\text{N}\) in \(\text{HCN}\) and \(\text{H}_2\text{CN}^+\) using a TZ + 2P basis set at the SCF level of theory.

|                  | \(\text{HCN}\)          | \(\text{H}_2\text{CN}^+\)       |
|------------------|--------------------------|---------------------------------|
|                  | \(\epsilon (\text{a.u.})\) | \(q (\text{a.u.})\)  | \(\epsilon^2qQ/\hbar\) (MHz) | \(\epsilon (\text{a.u.})\) | \(q (\text{a.u.})\)  | \(\epsilon^2qQ/\hbar\) (MHz) |
| + \(\delta^p\)   | -92.899 37               | -1.128                         | 5.17                          | -93.185 43               | -0.120                         | 0.55                          |
| OPT CISD DZ + P\(^a\) | -92.900 54               | -1.140                         | 5.22                          | -93.186 68               | -0.127                        | 0.58                          |
| - \(\delta^p\)   | -92.901 54               | -1.153                         | 5.28                          | -93.187 72               | -0.134                        | 0.61                          |

\(^a\)Optimized CISD structures with DZ + P basis sets (see Table I).
\(^b\)All bond lengths are increased by 0.01 a.u. with respect to CI equilibrium geometry.
\(^c\)All bond lengths are decreased by 0.01 a.u. with respect to a.
bining an \textit{ab initio} electric field gradient with an experimental quadrupole coupling constant. The latest reports\textsuperscript{25,27} of this type deduce from ammonia a value $Q(14\text{N}) = 1.95 \times 10^{-26}$ cm$^2$ and from N$_2$ and NO$^+$ a value $Q(14\text{N}) = 2.05 \times 10^{-26}$ cm$^2$.

Our most reliable theoretical value for the electric field gradient of HCN is the TZ + 2P CI value in Table III, namely $-1.000$ a.u. Combined with the experimental quadrupole coupling constant\textsuperscript{25} ($-4.71$ MHz) for HC$^{14}$N, we deduce $Q(14\text{N}) = 2.00 \times 10^{-26}$ cm$^2$. The fact that our prediction (based on the HCN molecule) is similar to those obtained in separate high-quality \textit{ab initio} studies involving other molecules is a good indication that this is indeed a reasonable prediction for the nuclear quadrupole moment of H$_2$CN$^+$. 

**ACKNOWLEDGMENTS**

This work was supported by the U. S. National Science Foundation, Grant No. CHE-8218785. G. E. S. wishes to acknowledge financial support by CONICET, the National Research Council of Argentina. We are grateful to Dr. Lucy Ziurys for helpful discussions and the preliminary communication of her interstellar discovery (Ref. 5) of H$_2$CN$^+$. 

\textsuperscript{1}N. N. Haese and R. C. Woods, Chem. Phys. Lett. 61, 396 (1979). 
\textsuperscript{2}P. S. Dardi and C. E. Dykstra, Astrophys. J. 240, L171 (1980). 
\textsuperscript{3}T. L. Allen, J. D. Goddard, and H. F. Schaefer, J. Chem. Phys. 73, 3255 (1980), and references therein. 
\textsuperscript{4}T. J. Lee and H. F. Schaefer, J. Chem. Phys. 80, 2977 (1984). 
\textsuperscript{5}L. M. Ziurys and B. E. Turner, 17th International Symposium on Free Radicals and Other Transient Species, Granby, Colorado, August 1985; L. M. Ziurys and B. E. Turner, Astrophys. J. Lett. (in press). 
\textsuperscript{6}M. Bogey, C. Demyunck, and J. L. Destombes, J. Chem. Phys. 83, 3703 (1985). 
\textsuperscript{7}H. Huber, J. Chem. Phys. 83, 4591 (1985). 
\textsuperscript{8}J. W. Richardson, Rev. Mod. Phys. 32, 461 (1960). 
\textsuperscript{9}P. E. Cade, K. D. Sales, and A. C. Wahl, Bull. Am. Phys. Soc. 9, 102 (1964). 
\textsuperscript{10}W. Kern and M. Karplus, J. Chem. Phys. 42, 1062 (1965). 
\textsuperscript{11}C. W. Kern, J. Chem. Phys. 46, 4543 (1967). 
\textsuperscript{12}F. F. Harrison, J. Chem. Phys. 47, 2990 (1967). 
\textsuperscript{13}C. T. O’Konski and T.-K. Ha, J. Chem. Phys. 49, 5354 (1969). 
\textsuperscript{14}R. Bonaccorsi, E. Scrocco, and J. Tomasi, J. Chem. Phys. 50, 2940 (1969). 
\textsuperscript{15}R. E. Kari and I. G. Csizmadia, Theor. Chim. Acta 22, 1 (1971). 
\textsuperscript{16}S. Rothenberg and H. F. Schaefer, Mol. Phys. 21, 317 (1971). 
\textsuperscript{17}E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Chem. Phys. 56, 2029 (1972). 
\textsuperscript{18}P. Grigolini and R. Moccia, J. Chem. Phys. 57, 1369 (1972). 
\textsuperscript{19}J. D. Petke and J. L. Whitten, J. Chem. Phys. 59, 4855 (1973). 
\textsuperscript{20}W. R. Rodwell and L. Radom, J. Chem. Phys. 72, 2205 (1980). 
\textsuperscript{21}M. Barber, S. M. Hayne, and A. Hinchcliffe, J. Mol. Struct. 62, 207 (1980). 
\textsuperscript{22}D. Amos, Mol. Phys. 39, 1 (1980). 
\textsuperscript{23}W. I. Ferguson, Theor. Chim. Acta 59, 527 (1981). 
\textsuperscript{24}J. W. Jost and C. T. O’Konski, J. Mol. Struct. 111, 387 (1983). 
\textsuperscript{25}T.-K. Ha, Chem. Phys. Lett. 107, 117 (1984). 
\textsuperscript{26}P. L. Cummins, G. B. Bacskay, and N. S. Hush, J. Phys. Chem. 89, 2151 (1985). 
\textsuperscript{27}D. Sundholm, P. Pyykko, L. Laaksonen, and A. J. Sadlej, Chem. Phys. 161, 219 (1986). 
\textsuperscript{28}F. Harriman, \textit{Theoretical Foundations of Electron Spin Resonance} (Academic, New York, 1977). 
\textsuperscript{29}E. A. C. Lucken, \textit{Nuclear Quadrupole Coupling Constants} (Academic, New York, 1969). 
\textsuperscript{30}V. R. Saunders, in \textit{Methods in Computational Molecular Physics}, edited by G. H. F. Diercksen and S. Wilson (Reidel, Dordrecht, 1983), pp. 1-36. 
\textsuperscript{31}H. Huzinaga, J. Chem. Phys. 42, 1293 (1965). 
\textsuperscript{32}T. H. Dunning, J. Chem. Phys. 83, 2823 (1980). 
\textsuperscript{33}R. D. Amos, Mol. Phys. 39, 1 (1980). 
\textsuperscript{34}W. I. Ferguson, Theor. Chim. Acta 59, 527 (1981). 
\textsuperscript{35}J. W. Jost and C. T. O’Konski, J. Mol. Struct. 111, 387 (1983). 
\textsuperscript{36}T.-K. Ha, Chem. Phys. Lett. 107, 117 (1984). 
\textsuperscript{37}P. L. Cummins, G. B. Bacskay, and N. S. Hush, J. Phys. Chem. 89, 2151 (1985). 
\textsuperscript{38}D. Sundholm, P. Pyykko, L. Laaksonen, and A. J. Sadlej, Chem. Phys. 161, 219 (1986). 
\textsuperscript{39}F. Harriman, \textit{Theoretical Foundations of Electron Spin Resonance} (Academic, New York, 1977). 
\textsuperscript{40}E. A. C. Lucken, \textit{Nuclear Quadrupole Coupling Constants} (Academic, New York, 1969). 
\textsuperscript{41}V. R. Saunders, in \textit{Methods in Computational Molecular Physics}, edited by G. H. F. Diercksen and S. Wilson (Reidel, Dordrecht, 1983), pp. 1-36. 
\textsuperscript{42}H. Huzinaga, J. Chem. Phys. 42, 1293 (1965). 
\textsuperscript{43}T. H. Dunning, J. Chem. Phys. 83, 2823 (1980). 
\textsuperscript{44}F. Harriman, \textit{Theoretical Foundations of Electron Spin Resonance} (Academic, New York, 1977). 
\textsuperscript{45}F. B. Van Duijneveldt, IBM Technical Report, RJ 945 (1971). 
\textsuperscript{46}F. DeLucia and W. Gordy, Phys. Rev. 187, 58 (1969). 
\textsuperscript{47}P. O. Nerbrong, B. Roos, and A. J. Sadlej, Int. J. Quantum Chem. 15, 135 (1979).