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Produced by the NASA Center for Aerospace Information (CASI)
Department of

Physics

Grambling State University

Grambling, Louisiana
INTRODUCTION

The final technical report on the Nuclear Quadrupole Resonance Studies sponsored by NASA at Grambling State University is presented in three separate sections: Part I describes the instrumentation, consisting of the development and assembly of the Nuclear Quadrupole Resonance Spectrometer. Part II presents (a) the types of experiments carried out so far by the principal investigator, along with several undergraduate students, over a period of 5 years, and (b) a discussion of the results. Part III presents the theoretical studies on the solid state crystalline electrostatic fields, field gradients and antishielding factors.

Background

A modest start of the NQR project at Grambling State University was made in late 1970, with a grant made by the Research Corporation ($7,480) to the principal investigator. Since the funds were not sufficient to obtain the complete spectrometer, our efforts were confined to building a simple super-regenerative type of oscillator, and computation of antishielding factors in simple systems; thus, providing research training to the participating undergraduate students.

With the aid of the National Aeronautics and Space Administration (NASA) grant, we have been able to establish a complete Nuclear Quadrupole Resonance Spectroscopy facility at Grambling State University and provide training in research to the participating undergraduate students. The main function of the department being undergraduate education, every effort was made to structure the project activity to achieve this objective. Appendix A shows the list of student participants in the project.
INSTRUMENTATION

The main reason for initiating the Nuclear Quadrupole Resonance project at Grambling State University is its inherent amenability for undergraduate comprehension. Both the theoretical physics needed and the experimental techniques involved are fairly simple and appropriate for undergraduate research exposure and introducing them to the power of physics in solving specific problems.

It was very succinctly expressed by J.A.S. Smith that the simplest and cheapest radio frequency spectrometer for chlorine nuclear quadrupole resonance is relatively easy to build, but extremely difficult to control. The first circuit we attempted is a super regenerative oscillator system similar to that described by Dean and Pollack and Smith. Figures 1 & 2 show the schematic of the circuit and Plates I & II are pictures of the unit built by the participating undergraduate students here. A simple Heath Kit assembled radio was used to determine the frequency of the SRO and the receiver was calibrated with N.M.V. standard frequency broadcasts. For this purpose a simple antenna was erected on top of the Carver Hall building in which the Physics Department is housed. The sensitivity of the unit was so limited that it has been possible to observe a 0.5 cm peak above the noise level for the NQR resonance signal of chlorine in paradichlorobenzene only. Due to the inherent difficulty associated with the SRO system for accurate frequency determination, our attempts to study lattice effects with this unit proved unsuccessful.

Plate III shows the commercially produced marginal oscillator unit obtained from the Research Education Systems Company of Lexington, Massachusetts and our interfacing module. The oscillator served as a very good piece of demonstration equipment for oscilloscope display of Cl signals in KC1O3 and PCl2 O, etc. Several modifications were made in the circuit to enable the recording of the signals on a chart recorder. Among these the most important introduction was
SUPER-REGENERATIVE
N.Q.R OSCILLATOR

MOD. INPUT

BNC

220 K

8.2 K

0.01 μF

5 M

Q CONTROL

1.2 M

1500 pF

0.05 μF

50 pF

10 K

14 V

IN 3182

RFC

50 pF

RFC

15 pF

10 K

BNC TO SCOPE

+300 V
PLATE I
FIRST SUPER-REGENERATIVE NQR OSCILLATOR AND SPECTROMETER SYSTEM
DEVELOPED IN OUR LABS

1. Front View

2. Top View
SELF-QUENCHING
F E T OSCILLATOR

Sweep
150 V

470 K
82 K

0.5 MA

50 µF

1.8 K 10 K

3.5

22.5 V

30 MHz

SAMPLE

50 µH

PF-HG-7001

2-10 pF

OUT
70 MV
PLATE II

SELF QUENCHED NQR SYSTEM

(Constructed by Participant Students' F.E.T. Oscillator)

1. Front View

2. Top View
PLATE III

RESEARCH SYSTEMS MARGINAL OSCILLATOR AND SPECTROMETER ASSEMBLY

1. Complete Assembly

2. Oscillator and Interfacing Module Only
the interfacing circuitry to monitor the ramp of the frequency sweep diode externally from the sawtooth voltage output of an oscilloscope. This provided considerable control on the sweep rate and signal could be simultaneously recorded on a chart recorder and displayed on the screen of the long persistence scope. This system with its limited capabilities proved useful for a detailed study of the line shapes; if the frequency is already known and the absorption signals are strong such as in the chlorates of sodium and potassium, copper oxide, paradichlorobenzene, etc.

Since the major aim of the project has been to study the semimetallic environments by NQR techniques we obtained the most sensitive automatic super-regenerative scanning spectrometer from Wilks Scientific Company. Plate IV shows the current arrangement of the spectrometer facility. Figure III is a block diagram of the complete system, showing the main spectrometer and the auxiliary facilities. Though most of the units were commercially obtained except for the zone melting heater, procuring the units, housing, assembling and putting into operation has been a valuable experience to the participants. This phase of the project while being most strenuous and time-consuming has been rewarding to the participating undergraduate students; in that they had the first hand exposure and experience of establishing research facilities. Grambling State University being mainly an undergraduate teaching institution, was not equipped until recently for undertaking research-type of investigations. The National Aeronautics and Space Administration grant has been of immense value in establishing these basic facilities, in addition to the main Nuclear Quadrupole Resonance Spectroscopy facility. Plates V and VI show the auxiliary facilities developed during the course of the projects.
PLATE IV
NUCLEAR QUADRUPOLE RESONANCE SPECTROMETER SYSTEM

1. Complete System with Spectrum Analyzer and Lock in Facilities

2. WILKS Scientific Control Unit, S.R.O. and Interfacing Module
EXPERIMENTAL STUDIES

The electrostatic field gradient \( q \) \((q = \frac{2V}{\partial z^2})\) being a classical quantity presents no conceptual problems to the undergraduate student and can be directly obtained from an analysis of the NQR spectrum. A knowledge of \( q \) reveals the nature and extent of intra- and intermolecular interactions in solids. As such our main objective has been to change the solid state electronic charge distribution in a controlled manner, and study the microscopic effects on the electrostatic field gradient at the site of the quadrupole nucleus by analyzing its NQR spectrum.

This environmental effect is considered to be of importance in semimetallic structures such as Antimony, Indium, Gallium, etc., because even minute impurity addition alters the conduction properties in a marked fashion, and the conduction electrons provide appreciable contribution to the electrostatic field gradient.\(^3\,\,^4\) Alterations in the valence/conduction electron charge distributions can be produced by:

1. Chemical bond formations with the neighboring atoms in different compounds.
2. Addition of impurities to the host lattice.
3. Perturbations of lattice charges due to electrical conduction.
4. Temperature and pressure effects.

Results and Discussion

To acquaint the student participants with the operation of the spectrometer and provide training in the techniques of frequency measurement, the NQR spectra of several known compounds were repeated as a preliminary training and the frequency measurement accuracy assessed, before they attempted search runs on new compounds. Table II is a listing of the typical measurements that were repeated by several students to gain practice.
Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Measured Frequency</th>
<th>Literature Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AsCl₃</td>
<td>76.2 ± 0.2 MHz</td>
<td>76.4</td>
</tr>
<tr>
<td></td>
<td>Cl¹³⁵</td>
<td></td>
</tr>
<tr>
<td>2. As₂O₃</td>
<td>108.2 ± 0.4</td>
<td>108.6</td>
</tr>
<tr>
<td>3. Sb₂O₃</td>
<td>Sb¹²¹</td>
<td>82.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Sb¹²³</td>
<td>50.2 ± 0.2</td>
</tr>
<tr>
<td>4. SbCl₃</td>
<td>Cl¹³⁵</td>
<td>20.6 ± 0.2</td>
</tr>
<tr>
<td>5. C₆H₄Cl₂</td>
<td>Cl¹³⁵</td>
<td>34.2 ± 0.1</td>
</tr>
<tr>
<td>6. NaClO₃</td>
<td>Cl¹³⁵</td>
<td>29.9 ± 0.1</td>
</tr>
<tr>
<td>7. KClO₃</td>
<td>Cl¹³⁵</td>
<td>28.1 ± 0.1</td>
</tr>
<tr>
<td>8. Cu₂O</td>
<td>Cu⁶³</td>
<td>26.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Cu⁶⁵</td>
<td>24.0 ± 0.1</td>
</tr>
</tbody>
</table>

These lines, particularly those of chlorine and copper served as test spectra and reference standards for all other investigations.

New Compounds Studied

Several intermetallic compounds of the p-block (III - VI) elements such as selenides, tellurides, sulfides and oxides of Indium, Arsenic, Antimony and Bismuth, have been investigated during the course of the project and detailed discussions of the results reported in the earlier interim semiannual reports. Typical recorder runs of the spectra in traditional compounds and lattice effect studies are presented in Appendix B. Table III is a listing of the several compounds investigated in our laboratory.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. As$_2$O$_5$</td>
<td>Multiplet lines*</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>20 - 60 MHz</td>
<td></td>
</tr>
<tr>
<td>2. As$_2$S$_2$</td>
<td>Broad/Weak signals</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>50 - 60 MHz</td>
<td></td>
</tr>
<tr>
<td>3. As$_2$Te$_3$</td>
<td>115.9 ± 0.5 MHz</td>
<td>7</td>
</tr>
<tr>
<td>4. As$_2$Se$_3$</td>
<td>Weak lines</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>70 - 80 MHz</td>
<td></td>
</tr>
<tr>
<td>5. Bi$_2$O$_3$</td>
<td>No Signal</td>
<td>9,8</td>
</tr>
<tr>
<td>(Bismite Form)</td>
<td>(previous data exists)</td>
<td></td>
</tr>
<tr>
<td>6. Bi$_2$S$_3$</td>
<td>Broad signal*</td>
<td>6,8</td>
</tr>
<tr>
<td></td>
<td>60 - 65 MHz</td>
<td></td>
</tr>
<tr>
<td>7. Bi$_2$Te$_3$</td>
<td>No Signals</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Scan 10 - 150 MHz</td>
<td></td>
</tr>
<tr>
<td>8. Bi</td>
<td>No Signals</td>
<td>9,8</td>
</tr>
<tr>
<td></td>
<td>Scan 10 - 150 MHz</td>
<td></td>
</tr>
<tr>
<td>9. Sb$_2$O$_5$</td>
<td>Weak multiplets*</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>50 - 100 MHz</td>
<td></td>
</tr>
<tr>
<td>10. Sb$_2$S$_5$</td>
<td>Weak multiplets*</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>20 - 80 MHz</td>
<td></td>
</tr>
<tr>
<td>11. Sb$_2$Te$_3$</td>
<td>Sb$^{121}$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>82.8 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sb$^{123}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>12. In$_2$S$_3$</td>
<td>Weak multiplets</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>5 - 50 MHz</td>
<td></td>
</tr>
<tr>
<td>13. In Se</td>
<td>Weak multiplets</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>5 - 50 MHz</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 - 20 MHz</td>
<td></td>
</tr>
<tr>
<td>15. Ga$_2$O$_3$</td>
<td>No Signal</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Scan 5 - 25 MHz</td>
<td></td>
</tr>
</tbody>
</table>

*Several search runs were made on these samples at lower temperatures and a note is under preparation presenting the data.
Studies on Doped Samples

Since the earlier studies in Antimony and Indium clearly indicated\textsuperscript{3,4} that conduction electrons provide appreciable contribution to the field gradient at the nuclear site, we have devoted considerable time and energy to investigate this feature, with no commensurate returns. Of the group of elements of interest: Indium, Antimony, Bismuth and Gallium, only Antimony was amenable for investigation on our spectrometer. Indium resonances exist below 10 MHz where our system sensitivity and reliability proved to be very low. Several trials on Bismuth both here and in the NQR Laboratories of Queen Elizabeth College, University of London, indicated no signals even at liquid nitrogen temperature. Our studies in Antimony and Gallium were encouraging in that signals of desirable strength could be observed when sufficient care in the sample preparation and operation of the spectrometer were exercised. We confined most of our studies to Antimony alone because of the high cost of pure Gallium. The fact that the signals lie in the 10 MHz region; where the spectrometer operating conditions are not at their best; and the preparation of doped samples involved a tedious and time-consuming process, impeded the progress of our studies severely. The results of our investigation were presented\textsuperscript{10} at the Fifty-First Louisiana Academy of Sciences meeting and summarized below.

The presence of an impurity in the proximity of a quadrupole nucleus changes the electrostatic field gradient at the nuclear site normally due to its different size and charge. In addition, we expected it could also alter the conduction electron distribution in the neighborhood of the resonating nucleus and cause a frequency shift. As such we have chosen three types of impurity elements to be doped in the host lattice of Antimony. They are Cadmium, Indium and Bismuth.
**Bi in Sb:** Concentration range 0.01 to 1 percent by weight. Since both Bi and Sb have similar outer shell electronic structures namely $6 \, S^2 \, 6 \, P^3$ and $5 \, S^2 \, 5 \, P^3$, there should be only size effect and if any a minor perturbation in the conduction electron distribution. We also expected that since Bi and Sb have similar crystal structure the added impurity atoms would occupy preferred interstitial lattice site causing a splitting of the NQR line. At 1 percent concentration the lines were completely wiped out while at 0.01 there was a decrease in the intensity of the signal associated by a broadening of the line. To find out the limiting point of impurity concentration for an observable signal, samples with 0.5, 0.2, 0.1, 0.05 and 0.02 percent Bi were investigated. The signals became gradually broader and weaker up to 0.1 and disappeared at 0.2 percent concentration. This result indicates there occurred a rapid distribution of field gradients as the number of impurity centers increased; and no additional information could be obtained regarding the perturbations in the extra ionic electron distribution.

**In in Sb:** Concentrations of impurity studied 0.005, 0.01, 0.02, 0.05, 0.1. Since the electronic structure of In is $5 \, S^2 \, 5P$ the size effect should be minimal and the charge effect should be the dominant factor. The results of our study are interesting in that the signals disappeared even at a small concentration as low as 0.02% compared with that of 0.2% for Bismuth impurity. This makes us believe that the Indium impurity might behave like an acceptor in the Antimony lattice marked by influencing the EFG at Sb site. Up to 0.01 percent concentration there seems to be a shift of 0.2 MHz associated with a slight drop in intensity and broadening of the signal. The frequency shift was the same both at 0.005 and 0.01 percent Indium.

**Cd in Sb:** Concentration range studied 0.005, 0.01, 0.1, 0.5, 1 percent by weight. Since electronic structure of Cadmium is $5 \, S^2$, we expected both the
PLATE V
SAMPLE PREPARATION FACILITY

1. Crystal Pullers and Micro-Mill Grinder
2. Zone Melting and Annealing Heating Units
charge and size effects must be minimal. But to our surprise signals disappeared at even the lowest concentration of 0.005 percent. It is not known whether occurrence of a compound formation is the reason for this feature.

Sample Preparation Techniques

It is appropriate on my part to inject a statement of caution in the analysis of our observations. As mentioned earlier Antimony signals in the pure metal itself are not strong and are very sensitive to the annealing state of the sample and operating conditions of the spectrometer. Plates V and VI show our sample preparation arrangement. After mixing the desired amounts of impurity and Antimony, the sample is loaded in a Vycor tubing and evacuated, dried and sealed. The sealed tube is lowered in a carrier tube which was slowly passed through the hot zone several times (5 - 6) up and down. The hot zone of the heater is about 1", at a maximum temperature of about 800°C. This zone leveling process is expected to uniformly distribute the impurity in the host lattice. The sample comes out as a solid rod which was pulverized by the micromild and sifted to a fineness of 350 mesh powder. Then the powdered sample is again loaded in a glass tube and annealed under vacuum at a temperature of 550°C, before using for NQR scanning.

Every concentration for each impurity-type sample was made following the above tedious procedure. Now the disappearance of a signal or the converse, leaves doubt in one's mind, whether doping took place at all; if one observes the signal; and whether the small changes observed or the disappearances could be due to the annealing and stress status of the sample. Being concerned with these questions our desire to publish the data is quenched. Our discussion of the doubts with professionals in the field added to further futile pursuits at lower temperatures. One assuring factor that emerged out of our low temperature
LOW TEMPERATURE FACILITIES

CRYOCOOLER

Dewar

CRYOCOOLER

Filter

Compressed Air

Dewar

Dewar

OIL. DIFFUSION CRAW STR 

Filter

Pump

LOW TEMPERATURE FACILITIES

CRYOCOOLER

ANNEALING

OXYGEN CYLINDER

VACUUM AND GLASS-BLOWING FACILITIES

VACUUM CHAMBER

Oil Diffusion Pump

Heater Coil

Heat Insulation

Fore Pump

ANNEALING

BURNERS & TORCHES

GLASS-BLOWING
PLATE VI

LOW TEMPERATURE AND GLASSBLOWING FACILITIES

1. Dry Ice Maker and Cryo Cooler

2. Glass Blowing Table
studies, is that the signals were reproducible in a similar fashion in all our samples. Still the sample effect remains a questionable factor.

**Lattice Effects:** The general objective being the investigation of the effect of the environmental charge distribution; a special study was carried in similar lines to those of Baer and Dean\(^{11}\), using the Cl nucleus in \(\text{P Cl}_2\), and \(\text{K Cl}_3\) in the host lattice of the piezo electric environment of Rochelle salt, water and paraffin wax.\(^{12}\)

A novel study was carried out by us for the first time by passing an electric current through the solid sample. The results are interesting and show a shift of the order of 50 KHz when a current of about 50 ma was passed through the sample.\(^{10}\) Appendix B shows the actual recorded spectra at liquid nitrogen temperatures. Though one can phenomenologically understand the shift as due to the changes in conduction electron contribution to EFG, no rigorous band theory explanation is possible at this time.

**Effect of Pressure:** Several interesting investigations were carried out by the principal investigator in collaboration with Professor J.A.S. Smith, Professor of Chemistry, University of London, during the period January - August, 1976; on the effect of high pressures (5 - 35 K bars) on the NQR spectra. So far, the pressure effect studies were confined only to low pressures below 5 K bars.\(^{13,15}\) The studies at high pressures were made possible by the NASA grant to the principal investigator and the British Research Council grant for work at Standard Telecommunication Labs (STL-Harlow Essex) using their tetrahedron anvil press facilities. Since our studies being the first of their kind, several experimental design studies had to be made to couple the RF oscillator sample coil with the spectrometer.\(^8\) Various sample coils (7 mm dia., 7 mm long) were fitted in pyrophyllite tetrahedron and coupled to the oscillator by a 50 ohm miniature coaxial cable. With this arrangement paradichlorobenzene
signals could be observed up to 10 tons including the $\alpha$-$\gamma$ phase transition. Above 10 tons the signals weakened rapidly and completely disappeared at 30 tons. A probe into the reasons included a study of the quality factor of the coil which rapidly dropped to a value of 10 - 12 at a pressure of about 10 K-bar. Further studies indicated that in the anvil press system of SRC high pressure gradients will be generated across the sample unlike in the hydrostatic (Bridgeman type) systems.

The second stage of investigations at STL (S.R.C. Essex) involved modification of the piston cylinder apparatus which can give pressures up to 15 K-bar to be compatible with the Queen Elizabeth College (University of London, England) spectrometer. Using 1:1 mixture of castor oil and amyl alcohol as a transmission fluid, several runs were made on molecular solids such as paradichlorobenzene, and addition compound of chloroanil with bis-8-hydroquinolinato palladium. These runs could be made successfully up to pressures of 15 K bars though there occurred considerable deterioration of signal strength.

The operation of the SRC high pressure unit involved considerable manpower and technical requirements. These constraints allowed only quick and short scans on the doped samples of Sb. Sb signals being weak in the beginning, rapidly disappeared as the pressure reached a value of 3 tons. To study the pressure effects in ionic solids where strong signals are observable, a preliminary search was carried out in the following minerals borrowed from the British Science Museum. The plan was to study them first at dry ice temperatures in the piston cylinder apparatus without applying pressure and reinvestigate those that seem potential samples for high pressure work.

1. Grpiment $\text{As}_2\text{S}_3$ 72 - 75 MHz Weak signal
2. Arsenolite $\text{As}_4\text{O}_6$ Signals beyond the range
3. Clauditite $\text{As}_4\text{O}_6$ Signals beyond the range
4. Bismite $\text{Bi}_2\text{O}_3$ 35 - 70 MHz Fairly good signals
5. Sillinite $\text{Bi}_2\text{O}_3$ 40 - 60 MHz Fairly good signals
6. Senarmonite $\text{Sb}_2\text{O}_3$ 50 MHz Weak signals
7. Vallentinite $\text{Sb}_2\text{O}_3$ 68 MHz Weak signals
8. Stibinite $\text{Sb}_2\text{S}_3$ 30 - 45 MHz Good signals

Based on these studies it was planned to reinvestigate the spectra of Bismite, Sillinite and Stibinite samples with the collaboration of Prof. Smith and Mr. M. K. Sabir when future time allocations become available at the SRC facility.

THEORETICAL STUDIES

This phase of the project has been one of the most rewarding activities of the program in that it made possible esoteric theoretical studies from journals to the classroom investigations. Two projects were introduced for upper level physics students elucidating the applications of basic principles of electrostatics\textsuperscript{16} to the electrostatic fields and field gradients in solid state. Both the theoretical and experimental projects developed based on the NASA program are included in Appendix A following the list of student participants.

Our theoretical studies were mainly concerned in developing a comprehensive computer program for a self consistant estimation of electrostatic field gradients in ionic solids. The computational details of the program were presented in an earlier report\textsuperscript{13} and the actual program (computer output) is given in Appendix C.

Starting with the basic crystal structure data the system locates all the ions in the solid, a desired number of unit cells away in all the three directions, from the lattice site of interest. After establishing the nearest neighbor ions, fields and field gradients at these sites are computed in a self
consistent way assigning the induced quadrupole and dipole moments for these lattice points. The program treats each lattice site as a multipole consisting of charge dipole and quadrupole moments, and evaluates these values in a self consistent manner. The program is successfully applied to verify the previous calculations in $\text{Al}_2\text{O}_3$.\(^{18}\) The usefulness of this program is enhanced since different sections of it can be separated as subroutines to perform different operations. The program is used (a) to illustrate the solid state lattice structure and unit cell composition and nature graphically from the standard x-ray data; (b) to make a simple point charge estimation of electric fields in gases and solids; (c) to estimate induced dipole moments in solids and gases; (d) to evaluate antishielding factors; (e) to solve simultaneous equations (La. Tech program); and (f) to carry out tensor coordinate transformations.

The second aspect of our theoretical studies consisted of developing numerical solutions for the secular equations for the pure quadrupole interaction Hamiltonian. Using the Newton Raphson\(^{19}\) iteration process, energy factors (multiples of the quadrupole coupling constant $e^2Qq$) were computed numerically for values of the asymmetry parameter $\eta$ from 0 to 1 in steps of 0.01. The iteration process was continued until the successive values of the energy factors lie within $1 \times 10^{-4}$. The tables can be readily used for the analysis of the NQR spectra of nuclei with spin values $I = 5/2, 7/2$ and $9/2$. Such tables as far as we know are available for $I = 5/2$ only in the Oak Ridge National Laboratory reports.\(^{20}\) The reference tables developed by us are presented in detail in an earlier report\(^{6}\) and the program details are given in Appendix D.

**General Conclusions and Comments**

The National Aeronautics and Space Administration grant NGR 19-011-016, along with the four other projects previously sponsored by NASA had the most positive impact on the academic standing and reputation of the Physics Department.
at Grambling State University. It has helped immensely in establishing the Nuclear Quadrupole Resonance research facility for undergraduate research participation. Starting at a point where routine classroom experimental facilities were constrained, the general laboratory facilities have expanded to (a) high and low temperature generation and measurement facility; (b) facilities for radio frequency generation and measurement with the modern spectrum analyzers, precision frequency counters and standard signal generators; (c) vacuum and glass blowing facilities; and (d) miscellaneous electronic and machine shop facilities. (Plates IV, V & VI)

Since the NQR project was started from scratch, it provided a wide variety of learning experiences to a number of student participants. The details of student activities are presented in Appendix A. Though considerable student effort and time were dedicated to the establishment of the experimental facilities, the project studies yielded notable theoretical and experimental results leading to the following publications. It has been a most rewarding experience for the two physics majors, Mr. Eddie R. Wallace and Mr. Michael Coleman, who presented papers both at the national and international conferences.


Nuclear Quadrupole Resonance spectroscopy though attractive due to its relatively least sophistication in instrumentation as compared to the sister branches of radio frequency spectroscopy such as microwave spectroscopy nuclear magnetic resonance, electron spin resonance, etc. is seriously handicapped due to the limitations on the accuracy and sensitivity of the spectrometer as well as the meagerness of the information yield. Even using the best commercially available spectrometers both here (our spectrometer system made by Wilks Scientific) and in England (University of London system made by Decca Radar Corporation) it has not been possible to make unambiguous determinations of small frequency shifts as encountered due to impurities and electric field effects in the range of \((2 - 20 \text{ KHz})\); nor retrieve signals in metallic samples such as Bismuth or the natural minerals discussed earlier. However NQR proved to be a most powerful educational tool in elucidating solid state electrostatic forces in simple ionic solids. The instructional projects developed by us for classroom use are presented in Appendix A.
REFERENCES

APPENDIX A

EDUCATIONAL AND INSTRUCTIONAL YIELDS
OF NASA-NQR PROJECT
Educational Impact of the Nuclear Quadrupole Resonance Project
Undergraduate Research Participation Training

The following students were supported by the NASA NGR-19-011-016 grant and previous Research Corporation grant and received training.

<table>
<thead>
<tr>
<th>Name</th>
<th>Learning Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Eddie Ray Wallace</td>
<td>Computation of field gradients in diatomic molecules</td>
</tr>
<tr>
<td>2. William Morris</td>
<td>Electronic circuits</td>
</tr>
<tr>
<td>3. Stonewall Hunter</td>
<td>Electronic circuits and hardware</td>
</tr>
<tr>
<td>4. Alan Kennedy</td>
<td>Hardware assembly and installation</td>
</tr>
<tr>
<td>5. Rosemary Kline</td>
<td>Laboratory organization</td>
</tr>
<tr>
<td>6. Israel Hall</td>
<td>Hardware assembly and installation</td>
</tr>
<tr>
<td>7. Nathaniel Paul</td>
<td>Electronic circuits design and construction</td>
</tr>
<tr>
<td>8. Ronnie Blake</td>
<td>Glass blowing-Sample preparation</td>
</tr>
<tr>
<td>9. Therone Baker</td>
<td>Glass blowing-Sample preparation</td>
</tr>
<tr>
<td>10. Clarence Hubbard</td>
<td>High temperature heater construction</td>
</tr>
<tr>
<td>11. Jerry Gray</td>
<td>Electronic circuits construction</td>
</tr>
<tr>
<td>12. Alvin Kennedy</td>
<td>Vacuum system, glass blowing-sample preparation</td>
</tr>
<tr>
<td>14. Dorothy Phillips</td>
<td>Spectrum scanning, record keeping</td>
</tr>
<tr>
<td>15. Roy Jopes</td>
<td>Lattice effects, spectrum scanning</td>
</tr>
<tr>
<td>16. Robert Lyons</td>
<td>Low temperature system</td>
</tr>
<tr>
<td>17. Fred Gordon</td>
<td>Computer programs</td>
</tr>
<tr>
<td>18. Shasti B.H.</td>
<td>Literature survey--data computation</td>
</tr>
<tr>
<td>19. Frederick Wilson</td>
<td>Spectrum scanning</td>
</tr>
</tbody>
</table>
In addition to these direct participants, regular upperclassmen in physics worked on the following topics that have been developed from the NASA project studies.

**PROJECTS IN PHYSICS**

Physics 420-421

The objective of this course is to provide the upper level physics majors with an opportunity to plan and carry out simple projects under the guidance of the instructor in charge with minimum help. As such the emphasis is not on conducting an experiment with specific instruction and arriving at an acceptable result as accurately as possible, but to pursue the activity with ingenuity and skill and evaluate the result with a critical analysis. The activity may involve:

1. development and assembling the needed units;
2. "make-do" with minor modifications of the available units;
3. utilizing modern systems consisting of several units and comprehend the techniques of using standard equipment with the aid of instruction manuals, etc.; and
4. repeating the published work in standard journals of physics and acquire the techniques of research and publication, with a view to achieve the project objectives.

**PROJECTS**

I. Derive the general expressions for obtaining the electrostatic fields and field gradients due to a monopole, dipole and quadrupole.
REF: 1. Electromagnetic Fields and Waves by Lorrain and Carson

II. Develop a computer program to calculate the dipole moments of diatomic molecules from structural data.
III. Develop a computer program to evaluate the electrostatic field gradients in gaseous diatomic molecules at the positive ion sites.


IV. Observe the Nuclear Quadrupole Resonance signals in paradichlorobenzene and potassium chlorate and determine the frequency using the Spectrum Analyser.

REF: WILKS NQR SPECTROMETER Instruction Manual

V. Study the frequency shift of the NQR signal in NaClO₃ as a function of temperature.

REF: Research Systems NQR Oscillator Manual

VI. Determine the frequencies of Bismuth NQR signals in BiCl₃ and obtain the asymmetry parameter value by assigning the spectrum using the frequency ratio tables.

APPENDIX B

TYPICAL RECORDER OUTPUTS OF NQR SPECTRA
NaClO₃ Signal from Research Systems Marginal Oscillator Unit Using Lock in Detection
SRO Signals in the Oxides of Arsenic and Antimony

$S_{b_{2}o_{5}}$
NQR Signals in Tellurides of Arsenic and Antimony from WILKS SRO Spectrometer
Sample Sb. liq N₂ Temp.

Line Broadening and Frequency Shift due to Conduction Current Increase
APPENDIX C

COMPUTER PROGRAM FOR SELF CONSISTANT ESTIMATION

OF ELECTROSTATIC FIELD GRADIENTS
### Program for Self Consistent Estimation of Electrostatic Fields and Field Gradients in Ionic Solids

**Variables and Dimensions**

**Fortran IV Level 21**

```fortran
DIMENSION XC(1250), YC(1250), ZC(1250), TYPE(1250), N(1250),
                NUM(1250), NU(10), V(10), C(19), IC(19), ALPHA(19),
                LIN(9, 1),

0001 S1(F1) = F1 / R3
0002 S2(F1, F2) = (3. * F1 * F2) / R5
0003 S3(F1) = (3. * F1) / R5
0004 S4(F1, F2) = (3. * F1 * F2) / R5
0005 S5(F1, F2) = (3. * F1 * (3. * F2 - F1) / R5)
0006 S6(F1) = (3. * F1) / R5
0007 S7(F1) = (3. * F1) / R5
0008 S8(F1, F2) = (3. * F1 * (3. * F2 - F1) / R5)
0009 S9(F1) = (3. * F1) / R5
0010 S10(F1, F2) = (3. * F1 * F2) / R5
0011 S11(F1, F2) = (3. * F1 * F2) / R5
0012 S12(F1, F2) = (3. * F1 * F2) / R5
0013 S13(F1, F2) = (3. * F1 * F2) / R5
0014 S14(F1, F2) = (3. * F1 * F2) / R5
0015 S15(F1, F2) = (3. * F1 * F2) / R5
0016 S16(F1, F2) = (3. * F1 * F2) / R5
0017 S17(F1, F2) = (3. * F1 * F2) / R5
0018 S18(F1, F2) = (3. * F1 * F2) / R5
0019 S19(F1, F2) = (3. * F1 * F2) / R5
0020 S20(F1, F2) = (3. * F1 * F2) / R5
0021 S21(F1, F2) = (3. * F1 * F2) / R5
0022 S22(F1, F2) = (3. * F1 * F2) / R5
0023 S23(F1, F2) = (3. * F1 * F2) / R5
0024 S24(F1, F2) = (3. * F1 * F2) / R5
0025 S25(F1, F2) = (3. * F1 * F2) / R5
0026 S26(F1, F2) = (3. * F1 * F2) / R5
0027 S27(F1, F2) = (3. * F1 * F2) / R5
0028 S28(F1, F2) = (3. * F1 * F2) / R5
0029 S29(F1, F2) = (3. * F1 * F2) / R5
0030 S30(F1, F2) = (3. * F1 * F2) / R5
0031 S31(F1, F2) = (3. * F1 * F2) / R5
0032 S32(F1, F2) = (3. * F1 * F2) / R5
0033 S33(F1, F2) = (3. * F1 * F2) / R5
0034 S34(F1, F2) = (3. * F1 * F2) / R5
0035 S35(F1, F2) = (3. * F1 * F2) / R5
0036 S36(F1, F2) = (3. * F1 * F2) / R5
0037 S37(F1, F2) = (3. * F1 * F2) / R5
```

**JK Specifies the Lattice at Which Fields and Field Gradients Are Computed.**

**Reads the Number of Atoms and the Dimensions of the Unit Cell and Polarizability Values.**

**Reads the Crystalline Position Coordinates of All the Atoms in the Given Unit Cell Along with Their Identification Numbers.**

---

**Legend:**
- **XC, YC, ZC**: Positions of atoms
- **TYPE**: Type of atom
- **N**: Number of atoms
- **NUM**: Number of unit cells
- **NU**: Number of unit cell planes
- **V**: Unit cell parameters
- **C**: Crystallographic constants
- **IC**: Identification numbers
- **ALPHA**: Polarizability

**Field Formulas:**
- $S1(F1) = F1 / R3$
- $S2(F1, F2) = (3. * F1 * F2) / R5$
- $S3(F1) = (3. * F1) / R5$
- $S4(F1, F2) = (3. * F1 * F2) / R5$
- $S5(F1, F2) = (3. * F1 * (3. * F2 - F1) / R5)$
- $S6(F1) = (3. * F1) / R5$
- $S7(F1) = (3. * F1) / R5$
- $S8(F1, F2) = (3. * F1 * (3. * F2 - F1) / R5)$
- $S9(F1) = (3. * F1) / R5$
- $S10(F1, F2) = (3. * F1 * F2) / R5$
- $S11(F1, F2) = (3. * F1 * F2) / R5$
- $S12(F1, F2) = (3. * F1 * F2) / R5$
- $S13(F1, F2) = (3. * F1 * F2) / R5$
- $S14(F1, F2) = (3. * F1 * F2) / R5$
- $S15(F1, F2) = (3. * F1 * F2) / R5$
- $S16(F1, F2) = (3. * F1 * F2) / R5$
- $S17(F1, F2) = (3. * F1 * F2) / R5$
- $S18(F1, F2) = (3. * F1 * F2) / R5$
- $S19(F1, F2) = (3. * F1 * F2) / R5$
- $S20(F1, F2) = (3. * F1 * F2) / R5$
- $S21(F1, F2) = (3. * F1 * F2) / R5$
- $S22(F1, F2) = (3. * F1 * F2) / R5$
- $S23(F1, F2) = (3. * F1 * F2) / R5$
- $S24(F1, F2) = (3. * F1 * F2) / R5$
- $S25(F1, F2) = (3. * F1 * F2) / R5$
- $S26(F1, F2) = (3. * F1 * F2) / R5$
- $S27(F1, F2) = (3. * F1 * F2) / R5$
- $S28(F1, F2) = (3. * F1 * F2) / R5$
- $S29(F1, F2) = (3. * F1 * F2) / R5$
- $S30(F1, F2) = (3. * F1 * F2) / R5$
- $S31(F1, F2) = (3. * F1 * F2) / R5$
- $S32(F1, F2) = (3. * F1 * F2) / R5$
- $S33(F1, F2) = (3. * F1 * F2) / R5$
- $S34(F1, F2) = (3. * F1 * F2) / R5$
- $S35(F1, F2) = (3. * F1 * F2) / R5$
- $S36(F1, F2) = (3. * F1 * F2) / R5$
- $S37(F1, F2) = (3. * F1 * F2) / R5$
<table>
<thead>
<tr>
<th>FORMAN IV G LEVEL</th>
<th>MAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0038</td>
<td>CC=CCxW1</td>
</tr>
<tr>
<td>0039</td>
<td>KM=N+1</td>
</tr>
<tr>
<td>0040</td>
<td>NATU(M)=NATCM</td>
</tr>
<tr>
<td>0041</td>
<td>TYPEG(M)=ATCM</td>
</tr>
<tr>
<td>0042</td>
<td>X0(M)=0.268*(CA+CB-2.0*CC)</td>
</tr>
<tr>
<td>0043</td>
<td>YC(M)=0.464*(CA-CB)</td>
</tr>
<tr>
<td>0044</td>
<td>ZC(M)=0.244*(CA+CB+CC)</td>
</tr>
<tr>
<td>0045</td>
<td>CONTINUE</td>
</tr>
<tr>
<td></td>
<td>STARTING FROM THE GIVEN UNIT CELL LOCATES ALL ATOMS IN THE LATTICE</td>
</tr>
<tr>
<td></td>
<td>2 UNIT CELLS AWAY IN ALL THE THREE CRYSTALLINE AXES DIRECTIONS,</td>
</tr>
<tr>
<td></td>
<td>CONVERTS THEM INTO CARTESIAN COORDINATES AND STORES IN THE X0,Y0,</td>
</tr>
<tr>
<td></td>
<td>ZC, COLUMN MATRICES.</td>
</tr>
<tr>
<td>0046</td>
<td>NT=NG+125</td>
</tr>
<tr>
<td>0047</td>
<td>DC 4 J=1,NT</td>
</tr>
<tr>
<td>0048</td>
<td>XR(J)=XC(JK)-XC(J)</td>
</tr>
<tr>
<td>0049</td>
<td>YR(J)=YC(JK)-YC(J)</td>
</tr>
<tr>
<td>0050</td>
<td>ZR(J)=ZC(JK)-ZC(J)</td>
</tr>
<tr>
<td>0051</td>
<td>TYPE(J)=TYPEG(J)</td>
</tr>
<tr>
<td>0052</td>
<td>NAT(J)=NATG(J)</td>
</tr>
<tr>
<td>0053</td>
<td>NUM(J)=J</td>
</tr>
<tr>
<td>0054</td>
<td>X2=XR(J)+XR(J)</td>
</tr>
<tr>
<td>0055</td>
<td>Y2=YR(J)+YR(J)</td>
</tr>
<tr>
<td>0056</td>
<td>Z2=ZR(J)+ZR(J)</td>
</tr>
<tr>
<td>0057</td>
<td>4 PR(J)=SQRT(X2+Y2+Z2)</td>
</tr>
<tr>
<td>0058</td>
<td>K=NT</td>
</tr>
<tr>
<td>0059</td>
<td>KM1=K-1</td>
</tr>
<tr>
<td>0060</td>
<td>DC 5 H=1, KM1</td>
</tr>
<tr>
<td>0061</td>
<td>NPl=N+1</td>
</tr>
<tr>
<td>0062</td>
<td>M=N</td>
</tr>
<tr>
<td>0063</td>
<td>DG 11 J=NPl+K</td>
</tr>
<tr>
<td>0064</td>
<td>IF(PR(M)-RR(J))11,11,12</td>
</tr>
<tr>
<td>0065</td>
<td>J=M+1</td>
</tr>
<tr>
<td>0066</td>
<td>CONTINUE</td>
</tr>
<tr>
<td>0067</td>
<td>RT=RR(N)</td>
</tr>
<tr>
<td>0068</td>
<td>RR(N)=HR(M)</td>
</tr>
<tr>
<td>0069</td>
<td>RR(N)+RT</td>
</tr>
<tr>
<td>0070</td>
<td>X1=XR(N)</td>
</tr>
<tr>
<td>0071</td>
<td>XR(N)+XR(N)</td>
</tr>
<tr>
<td>0072</td>
<td>XR(M)+XT</td>
</tr>
<tr>
<td>0073</td>
<td>YT=YR(N)</td>
</tr>
<tr>
<td>0074</td>
<td>YR(N)+YR(N)</td>
</tr>
<tr>
<td>0075</td>
<td>YR(N)+YT</td>
</tr>
<tr>
<td>0076</td>
<td>ZT=ZR(N)</td>
</tr>
<tr>
<td>0077</td>
<td>ZP(A)=ZP(A)</td>
</tr>
<tr>
<td>0078</td>
<td>ZP(A)+ZP(A)</td>
</tr>
<tr>
<td>0079</td>
<td>ZR(N)=ZT</td>
</tr>
<tr>
<td>0080</td>
<td>TYPE(J)=TYPE(A)</td>
</tr>
<tr>
<td>0081</td>
<td>TYPE(M)=TYPE(M)</td>
</tr>
<tr>
<td>0082</td>
<td>NATM=NAT(A)</td>
</tr>
<tr>
<td>0083</td>
<td>NATM=NAT(N)</td>
</tr>
<tr>
<td>0084</td>
<td>NATM=NAT(M)</td>
</tr>
<tr>
<td>0085</td>
<td>NUMM=NUM(A)</td>
</tr>
<tr>
<td>0086</td>
<td>NUMM=NUM(M)</td>
</tr>
<tr>
<td>0087</td>
<td>NUMM=NUM(M)</td>
</tr>
<tr>
<td>0088</td>
<td>CONTINUE</td>
</tr>
<tr>
<td>0089</td>
<td>WRITE(6,20)INT, TYPE(INT), NAT(INT), XR(INT), YR(INT), ZR(INT), RR(INT), M</td>
</tr>
</tbody>
</table>
C TAKING THE JK ATOM AS ORIGIN COORDINATES DISTANCES OF ALL THE
C ATOMS IN THE LATTICE RELATIVE TO THE JK ATOM, ARE COMPUTED AND
C STORED IN THE XR, YR, ZR, PR COLUMN MATRICES IN ASCENDING ORDER OF
C DISTANCE.
0090 70 DC 13 I=1,9
0091 DC 13 J=1,1C
0092 13 T(I,J)=0.0
0093 DC 14 L=1,1H
0094 XR=XR(L)
0095 Y=YL(R)
0096 Z=Z(L)
0097 RR=RR(R)
0098 AS=AS(L)
0099 IF(X.EQ.0.0) GC TO 14
0100 R2=R2
0101 R3=R3
0102 R4=R4
0103 R5=R5
0104 IF(NSITE=1118,18,19)
C DEPENDING ON THE NATURE OF THE ATOM ITS IONIC CHARGE IS ASSIGNED
0105 18 CP=2.+ELECF
0106 GC TO 21
0107 19 CP=3.+ELECF
0108 21 C(I,J)=51(X)*CP
0109 C(2,1)=51(Y)*CP
0110 C(3,1)=51(Z)*CP
0111 C(4,1)=51(T)*CP
0112 C(5,1)=51(V)*CP
0113 C(6,1)=51(W)*CP
0114 C(7,1)=51(X)*CP
0115 C(8,1)=51(Y)*CP
0116 C(9,1)=51(Z)*CP
0117 IF(NSITE=1122,22,23)
0118 22 IF(TYPEL)=GC,11,1 GC TO 5C
0119 IF(TYPEL)=GC,13,1 GC TO 6C
0120 IF(TYPEL)=GC,14,1 GC TO 6C
0121 IF(TYPEL)=GC,15,1 GC TO 6C
0122 IF(TYPEL)=GC,16,1 GC TO 6C
C COMPUTES THE CHARGE CONTRIBUTIONS TO THE FIELDS AND FIELD GRADIENTS
0117 IF(NSITE=1122,22,23)
0118 22 IF(TYPEL)=GC,11,1 GC TO 5C
0119 IF(TYPEL)=GC,13,1 GC TO 6C
0120 IF(TYPEL)=GC,14,1 GC TO 6C
0121 IF(TYPEL)=GC,15,1 GC TO 6C
0122 IF(TYPEL)=GC,16,1 GC TO 6C
C CHOOSES PREDETERMINED TRANSFORMATION MATRIX FOR THE DIPOLE AND
C QUADRUPOLE MOMENTS OF THE POLARISABLE ATOMS IN THE LATTICE FCR
C COMPUTING FIELDS AND FIELD GRADIENTS AT THE JK IONIC SITE.
0124 62 AT(I,J)=F
0125 AT(I,2)=F
0126 AT(2,1)=F
0127 AT(2,2)=H
0128 GC TO 60
0129 63 AT(I,1)=H
0130 AT(I,2)=F
0131 AT(2,1)=F
0132 AT(2,2)=H
0133 GC TO 60
0134 64 AT(I,1)=1.0
0135 AT(I,2)=0.0
0136 AT(2,1)=0.0
<table>
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<tr>
<th>FORTRAN IV G LEVEL</th>
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<tbody>
<tr>
<td>0137</td>
<td>A(2,2) = -1.0</td>
</tr>
<tr>
<td>0138</td>
<td>GC TO 60</td>
</tr>
<tr>
<td>0139</td>
<td>66 A(1,1) = H</td>
</tr>
<tr>
<td>0140</td>
<td>A(1,2) = F</td>
</tr>
<tr>
<td>0141</td>
<td>A(2,1) = F</td>
</tr>
<tr>
<td>0142</td>
<td>A(2,2) = H</td>
</tr>
<tr>
<td>0143</td>
<td>GC TO 60</td>
</tr>
<tr>
<td>0144</td>
<td>66 A(1,1) = H</td>
</tr>
<tr>
<td>0145</td>
<td>A(1,2) = F</td>
</tr>
<tr>
<td>0146</td>
<td>A(2,1) = F</td>
</tr>
<tr>
<td>0147</td>
<td>A(2,2) = H</td>
</tr>
<tr>
<td>0148</td>
<td>66 GC 39 J=1,3</td>
</tr>
<tr>
<td>0149</td>
<td>A(1,1) = A(1,1)</td>
</tr>
<tr>
<td>0150</td>
<td>39 A(4,4) = A(1,1)</td>
</tr>
<tr>
<td>0151</td>
<td>A(4,4) = A(1,1)</td>
</tr>
<tr>
<td>0152</td>
<td>50 P1 = 2.5/P2</td>
</tr>
<tr>
<td>0153</td>
<td>P2 = P1*S7(X)</td>
</tr>
<tr>
<td>0154</td>
<td>P3 = P1*S7(Y)</td>
</tr>
<tr>
<td>0155</td>
<td>P4 = P1*S7(Z)</td>
</tr>
<tr>
<td>0156</td>
<td>P5 = P1*S9(X)</td>
</tr>
<tr>
<td>0157</td>
<td>P6 = P1*S9(Y)</td>
</tr>
<tr>
<td>0158</td>
<td>P7 = P1*S9(Z)</td>
</tr>
<tr>
<td>0159</td>
<td>C(1,2) = S5(X)</td>
</tr>
<tr>
<td>0160</td>
<td>C(2,2) = S5(Y, Y)</td>
</tr>
<tr>
<td>0161</td>
<td>C(3,2) = S5(Z, X)</td>
</tr>
<tr>
<td>0162</td>
<td>C(4,2) = S5(X, Y)</td>
</tr>
<tr>
<td>0163</td>
<td>C(5,2) = S4(X, Y)</td>
</tr>
<tr>
<td>0164</td>
<td>C(6,2) = S4(X, Z)</td>
</tr>
<tr>
<td>0165</td>
<td>C(7,2) = S4(Y, X)</td>
</tr>
<tr>
<td>0166</td>
<td>C(8,2) = S6(Z) + C(12,2)</td>
</tr>
<tr>
<td>0167</td>
<td>C(9,2) = S4(Z)</td>
</tr>
<tr>
<td>0168</td>
<td>C(1,3) = C(2,2)</td>
</tr>
<tr>
<td>0169</td>
<td>C(2,3) = S5(Y)</td>
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<tr>
<td>0170</td>
<td>C(3,3) = S2(Y, Y)</td>
</tr>
<tr>
<td>0171</td>
<td>C(4,3) = C(1,2)</td>
</tr>
<tr>
<td>0172</td>
<td>C(5,3) = S5(Y, Y)</td>
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<td>0173</td>
<td>C(6,3) = S4(Y, Z)</td>
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<tr>
<td>0174</td>
<td>C(7,3) = C(5,2)</td>
</tr>
<tr>
<td>0175</td>
<td>C(8,3) = S4(Z, Y)</td>
</tr>
<tr>
<td>0176</td>
<td>C(9,3) = C(6,2)</td>
</tr>
<tr>
<td>0177</td>
<td>C(1,4) = C(3,2)</td>
</tr>
<tr>
<td>0178</td>
<td>C(2,4) = C(3,3)</td>
</tr>
<tr>
<td>0179</td>
<td>C(3,4) = S3(Z)</td>
</tr>
<tr>
<td>0180</td>
<td>C(4,4) = C(9,2)</td>
</tr>
<tr>
<td>0181</td>
<td>C(5,4) = C(8,3)</td>
</tr>
<tr>
<td>0182</td>
<td>C(6,4) = S5(Z, Z)</td>
</tr>
<tr>
<td>0183</td>
<td>C(7,4) = C(8,2)</td>
</tr>
<tr>
<td>0184</td>
<td>C(8,4) = C(6,3)</td>
</tr>
<tr>
<td>0185</td>
<td>C(9,4) = C(6,2)</td>
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<tr>
<td>0186</td>
<td>C(1,5) = C(6,2)</td>
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<tr>
<td>0187</td>
<td>C(2,5) = C(8,2)</td>
</tr>
<tr>
<td>0188</td>
<td>C(3,5) = C(8,2)</td>
</tr>
<tr>
<td>0189</td>
<td>C(4,5) = S15(X)</td>
</tr>
<tr>
<td>0190</td>
<td>C(5,5) = S14(Y, X)</td>
</tr>
<tr>
<td>0191</td>
<td>C(6,5) = S14(Z, X)</td>
</tr>
<tr>
<td>0192</td>
<td>C(7,5) = P5*C(11,3)</td>
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<td>FORTRAN IV G LEVEL 21</td>
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<tr>
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<tr>
<td>0193</td>
<td>C(5,5)=P2*C(2,4)</td>
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<td>0194</td>
<td>C(5,5)=P5*C(1,4)</td>
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<td>0195</td>
<td>C(1,6)=C.5*C(5,2)</td>
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<td>0196</td>
<td>C(2,6)=C.5*C(5,3)</td>
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<td>0197</td>
<td>C(3,6)=C.5*C(6,3)</td>
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<tr>
<td>0198</td>
<td>C(4,6)=S14(X,Y)</td>
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<tr>
<td>0199</td>
<td>C(5,6)=S15(Y)</td>
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<td>C(6,6)=S14(Z,Y)</td>
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<tr>
<td>0201</td>
<td>C(7,6)=P6*C(1,2)</td>
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<td>C(8,6)=P6*C(2,4)</td>
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<tr>
<td>0203</td>
<td>C(5,6)=P3*C(1,4)</td>
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<tr>
<td>0204</td>
<td>C(1,7)=C.5*C(6,2)</td>
</tr>
<tr>
<td>0205</td>
<td>C(2,7)=C.5*C(6,3)</td>
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<tr>
<td>0206</td>
<td>C(3,7)=C.5*C(6,4)</td>
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<tr>
<td>0207</td>
<td>C(4,7)=S14(9,2)</td>
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<tr>
<td>0208</td>
<td>C(5,7)=S14(Y,2)</td>
</tr>
<tr>
<td>0209</td>
<td>C(6,7)=S15(Z)</td>
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<tr>
<td>0210</td>
<td>C(7,7)=P4*C(1,2)</td>
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<tr>
<td>0211</td>
<td>C(8,7)=P7*C(2,4)</td>
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<tr>
<td>0212</td>
<td>C(5,7)=P7*C(1,4)</td>
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<td>0213</td>
<td>C(1,8)=C(7,2)</td>
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<tr>
<td>0214</td>
<td>C(2,8)=C(5,2)</td>
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<td>C(3,8)=C(8,2)</td>
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<td>0216</td>
<td>C(4,8)=2.*C(7,5)</td>
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<td>0217</td>
<td>C(5,8)=2.*C(7,6)</td>
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<td>0218</td>
<td>C(6,8)=2.*C(7,7)</td>
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<td>0219</td>
<td>C(7,8)=S15(X,Y)</td>
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<td>0220</td>
<td>C(8,8)=2.*C(9,6)</td>
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<td>0221</td>
<td>C(5,9)=2.*C(3,5)</td>
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<tr>
<td>0222</td>
<td>C(1,9)=C(5,3)</td>
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<td>C(2,9)=C(5,4)</td>
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<td>0224</td>
<td>C(3,9)=C(6,3)</td>
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<td>0225</td>
<td>C(4,9)=2.*C(10,5)</td>
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<td>0226</td>
<td>C(5,9)=2.*C(8,6)</td>
</tr>
<tr>
<td>0227</td>
<td>C(6,9)=2.*C(8,7)</td>
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<td>0228</td>
<td>C(7,9)=2.*C(5,6)</td>
</tr>
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<td>0229</td>
<td>C(8,9)=S15(X,2)</td>
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<td>0230</td>
<td>C(5,9)=C(6,9)</td>
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<td>C(1,10)=2.*C(3,5)</td>
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<td>0232</td>
<td>C(2,10)=C(11,9)</td>
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<td>0233</td>
<td>C(3,10)=2.*C(11,7)</td>
</tr>
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<td>0234</td>
<td>C(4,10)=2.*C(15,5)</td>
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<tr>
<td>0235</td>
<td>C(5,10)=C(17,9)</td>
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<td>0236</td>
<td>C(6,10)=2.*C(17,7)</td>
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<td>C(7,10)=C(14,9)</td>
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<td>0238</td>
<td>C(9,10)=C(16,8)</td>
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<tr>
<td>0239</td>
<td>C(5,10)=S13(2,3)</td>
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</table>

C COMPUTATION OF THE COEFFICIENTS (C MATRIX) OF DI (DIPOLM MOMENT)
C COMPONENTS) AND QIJ (QUADRUPLMEMENT COMPONENTS) TO (VI AND VIJ IS)
C FIELDS AND FIELD GRADIENTS
C COMPLETED AND STARTS STORING IN THE T-MATRIX.

0240 IF ( TYPE(1).NE.11 ) GO TO 61
0241 CC 16 1=1,5
0242 CC 16 J=1,10
0243 16 T(I,J)=T(I,J)*C(I,J)
0244 CC GO TO 14
0245  61 DC 71 I=1,5
0246  71 T(I+1)=T(I+1)+C(I+1)
0247   DC 72 I=1,9
0248   DC 72 M=1,3
0249   DC 72 N=1,3
0250   72 T(I+1)=T(I+1)+A(M,N)*C(I+1),N+1)
0251   DC 73 I=1,9
0252   DC 73 M=1,3
0253   DC 73 N=1,3
0254   73 T(I+1)=T(I+1)+A(M,N)*A(M,N)*C(I+1,N+4)
0255   DC 74 I=1,9
0256   DC 74 M=1,3
0257   DC 74 N=1,3
0258   74 T(I+1)=T(I+1)+A(M,N)*A(M,N)*C(I+1,N+7)
0259   DC 75 I=1,9
0260   DC 75 M=1,3
0261   DC 75 N=1,3
0262   75 T(I+1)=T(I+1)+2.0*A(M,N)*A(M+1,N)*C(I+1,N+4)
0263   DC 76 I=1,9
0264   DC 76 M=1,3
0265   DC 76 N=1,3
0266   76 T(I+1)=T(I+1)+A(M,N)*A(M+1,N+1)+A(M+1,N)=A(M,N+1)*C(I+1,N+7)
0267   DC 77 I=1,4
0268   23 CC 25 I=1,9
0269   25 T(I+1)=T(I+1)+C(I+1)
0270   14 CONTINUE
0271   WRITE(6,200)
0272   DC 26 I=1,9
0273   26 WRITE(6,300) (T(I,J),J=1,10)
0274   IF(JK.EQ.813) GG TO 33
0275   DC 80 I=1,3
0276   80 ALPHA(I)=AC
0277   DC 84 I=4,5
0278   84 ALPH(A(I))=AC
0279   DC 77 I=1,9
0280   77 CH(I,1)=T(I,1)
0281   DC 78 I=1,9
0282   DC 78 J=1,9
0283   78 IC(I,J)=IC(I,J+1)+ALPHA(J)
0284   DC 79 I=1,5
0285   DC 79 J=1,5
0286   79 IF(I,EG,J)TC(I,J)=TC(I,J)+1.
0287   CALL SIME(TC,CH+0,9,KS)
0288   IF(KS.EQ.0) GG TO 82
0289   WRITE(6,50)KS
0290   GG TO 36
0291   82 WRITE(6,100) (CH(I,1),I=1,5)
0292   DC 83 J=1,5
0293   VI(J)=CH(J,1)
0294   83 C(J+1)=ALPHA(J)+Y(J,1)
0295   C(I)=1.0
0296   WRITE (6,120)
0297   WRITE(6,30) (DI(L),L=1,1C)
0298   WRITE(6,55)AD,AQ
0299   33 DC 34 I=1,9
0300   IF (I.EQ.1) WRITE(6,130)
0301 VC=T(I,1)*C(1)
0302 VDX=T(I,2)*C(2)
0303 VLY=T(I,3)*C(3)
0304 VDZ=T(I,4)*C(4)
0305 VC=VDX+VLY+VDZ
0306 VGXX=T(I,5)*C(5)
0307 VGYY=T(I,6)*C(6)
0308 VGZZ=T(I,7)*C(7)
0309 VCYX=T(I,8)*C(8)
0310 VCXY=T(I,9)*C(9)
0311 VCYZ=T(I,10)*C(10)
0312 VC=VGXX+VGYY+VGZZ+VCXY+VCYX+VCYZ+VQXX+VQYY+VQZZ+VQXY+VQXZ+VQYZ+VQZX
0313 VI(I,1)=VC+VQX+V
0314 WRITE(6,55)VC,VDX,VLD,VCZ,VD,VCXX,VCYY,VCZZ,VCXY,VCYX,VCYZ,VQXX,VQXY,VQYY,VQZZ,VQXY,VQXZ
0315 IF(JK+FE.813) GO TO 36
0316 JK=813
0317 GC TO 5
0318 36 STOP
0319 2 FCFFAT(3F11.8,F4.0,12)
0320 10 FCFFAT(15,5F7.3)
0321 15 FCFFAT(1CF7.3)
0322 40 FCFFAT(20X,F7.4,1)
0323 20 FCFFAT(8X,14,2X,F4.0,2X,12,4(3X,F8.3,19)
0324 30 FCFFAT(8X,14,2X,F4.0,2X,12,3(3X,F8.3))
0325 35 FCFFAT(6X,1C(4,9,F8.3))
0326 45 FCFFAT(131(2X,F8.3))
0327 55 FCFFAT(30X,2F15.2)
0328 90 FCFFAT(10X,12)
0329 100 FCFFAT(8X,3,4X,F8.3)///
0330 200 FCFFAT(5CX,2G hostility** T M A T R I X **,///)
0331 500 FCFFAT(8X,1C(4X,F8.3),///)
0332 120 FCFFAT(50X,22** MULTIPLE MOMENTS**,///)
0333 130 FCFFAT(5CX,3IH** FIELDS AND FIELD GRADIENTS**,///)
0334 ENC
### SUBROUTINE SIMQ

**PURPOSE**

Obtain solution of a set of simultaneous linear equations, \( AX = 0 \).

**USAGE**

CALL SIMQ\( (A,B,N,KS) \)

**DESCRIPTION OF PARAMETERS**

- **A** - Matrix of coefficients stored columnwise. These are destroyed in the computation. The size of matrix \( A \) is \( N \times N \).
- **B** - Vector of original constants (length \( N \)). These are replaced by final solution values, vector \( X \).
- **N** - Number of equations and variables. \( N \) must be \( \geq 1 \).
- **KS** - Output digit
  - 0 for a normal solution
  - 1 for a singular set of equations

**METHOD**

Method of solution is by elimination using largest pivot.

- Each stage of elimination consists of interchanging elements.
- Rows when necessary to avoid division by zero or small.
- The forward solution to obtain variable \( N \) is done in \( N \) stages. The back substitution for the other variables is calculated by successive substitutions. Final solution values are developed in vector \( B \), with variable 1 in \( B(1) \), variable 2 in \( B(2) \), ..., variable \( N \) in \( B(N) \).
- If no pivot can be found exceeding a tolerance of 0.0, the matrix is considered singular and KS is set to 1. This tolerance can be modified by replacing the first statement.

---

### MAIN

**SUBROUTIN SIMQ(A,B,N,KS)**

**DIMENSION A(N,N)**

**FORWARD SOLUTION**

**TOL=0.0**

**KS=0**

**JJ=-N**
0006  DC 65 J=1,N
0007  JY=J+1
0008  JX=J+J+1
0009  BICA=0
0010  IT=JJ-J
0011  DD 50 I=J,X
   C  SEARCH FOR MAXIMUM COEFFICIENT IN COLUMN
0012  IT=IT+1
0013  IF(AABS(BICA)-A(B(IJK)) 20,30,30
0014  20  BICA=A(IJK)
0015  ITMAX=I
0016  30  CONTINUE
   C  TEST FOR PIVOT LESS THAN TOLERANCE (SINGULAR MATRIX)
0017  IF(AABS(BICA)-TCL) 35,35,40
0018  35  KS=1
0019  RETURN
   C  INTERCHANGE ROWS IF NECESSARY
0020  40  II=J+N*(J-2)
0021  IT=ITMAX-J
0022  DD 50 K=J,X
0023  II=II+1
0024  IZ=II+IT
0025  SAVE=A(II)
0026  A(II)=A(IJ)
0027  A(IJ)=SAVE
   C  DIVIDE EQUATION BY LEADING COEFFICIENT
0028  50  A(JX)=A(IX)/BICA
0029  SAVE=B(IXMAX)
0030  B(IXMAX)=B(IJK)
0031  B(IJK)=SAVE/B(IX)
   C  ELIMINATE NEXT VARIABLE
0032  IF(JX) 55,70,55
0033  55  IT=-X*(J-1)
0034  DC 65 IX=J+Y
0035  IX=IQS+1
0036  IT=IT-IX
0037  DC N JX=JY+K
0038  IXJ=IXJ+1
0039  JX=JX+I
0040  60  A(IXJ)=A(IXJX)-(A(IJK)*A(IXJ))
0041  65  B(IX)=B(IXX)-B(IJK)*A(IXJ)
   C  BACK SOLUTION
0042  70  NY=K-1
0043  IT=K+1
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<td>IA=11-J</td>
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<td>SIMC1140</td>
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<td>0046</td>
<td>IE=N-J</td>
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<td>IC=A</td>
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APPENDIX D

COMPUTER PROGRAM FOR NUMERICAL SOLUTIONS OF THE QUADRUPOLE INTERACTION ENERGY SECULAR EQUATIONS
FORTRAN IV G LEVEL 21

MAIN

DATE = 74112
20/11/03
PAGE 0001

COMPUTATION OF N D R FREQUENCY FACTORS AND THEIR RELATIVE RATIOS AS A FUNCTION OF THE ASYMMETRY PARAMETER

DIMENSION XI(101), E(9,101), E97(101), E75(101), E53(101), E31(101),
E11(101), R(101), R3(101), R4(101), R5(101), R6(101)

READ9,2,3,4,5,6,7
I=0
A=0.0
Y=0.01
GO TO 4(5,6), N

4 C1=E1
X2=A*A
C2=C1*C1
C3=C2*C1
E2=12.*C3+20.*(1.-X2)/(13.*C2-7.*(3.*X2))
D=ARS(E2)=E1
IF(D=0.000118,8,9)

9 E1=E2
GO TO 4

8 I=I+1
X(1)=A
E(I,1)=E2
E1=E2

IF(A<1.14,4,10)

10 IF(A<1111,11,1)

11 WRITE(6,31)

WRITE(6,30)

DO 12 I=1,101

12 WRITE(6,131)E(5,1),E(3,1),E(1,1),E53(I),E31(I),R11(I)

WRITE(6,60)

GO TO 1

5 C1=E1
X2=A*A
C2=C1*C1
C3=C2*C1
C4=C2*C2
X3=1.+X2/3.
X4=X3*X2
DN=0.75*(C4-14.*X3*C2-35.*X4)
D0=C3-2L.*X3*C1-16.*I-1.-X2)
E2=DN/D0
D=ARS(E2)-E1
IF(D=0.000114,15,16)

15 E1=E2
GO TO 5

14 I=I+1
X(1)=A
E(I,1)=E2
E1=E2
A=A+Y

IF(A<1.15,5,16)
0052  16 IF(J-1)7,17,1
0053  17 WRITE(6,10)
0054  18 WRITE(6,40)
0055  19 DO, 1,1,101
0056     E75(I)=E75(I)-E(5,1)
0057     E31(I)=E31(I)-E(3,1)
0058     R1(I)=E75(I)/E31(I)
0059     R2(I)=E53(I)/E31(I)
0060     R3(I)=E75(I)/E53(I)
0061  20 WRITE(6,20)E73(I),E75(I),E1(I),E(1,1),E(3,1),E(1,1)
0062     IF(3(I),R1(I),R2(I),R3(I)
0063  21 WRITE(6,60)
0064  22 GO TO 1
0065   6 C1=E1
0066   7 C2=C1+C1
0067   8 C3=C2+C2
0068   9 C4=C2+C2
0069  10 E5=C4+C1
0070  11 R2=AA
0071  12 D1-3.*X2
0072  13 D2=1.-X2
0073  14 D3=D1*D1
0074  15 D4=4.*C5-22.*D1+C3-44.*D2+C2-48.*D1*D2
0075  16 D5=5.*C6-33.*D1*C2-88.*D2+C1-56.*D1*D2
0076  17 D=ABS(E2-E1)
0077  18 IF(0.0001121,21,22)
0078  22 E1=E2
0079  23 GO TO 6
0080  24 T=1+1
0081  25 X(I)=A
0082  26 E1,1)=E2
0083  27 E1=E2
0084  28 A=4+A
0085  29 AEA-1.16*6.23
0086  30 IF(J-1)74,24,1
0087  31 WRITE(6,25)
0088  32 WRITE(6,50)
0089  33 DO, 26,1,101
0090     E75(I)=E75(I)-E(7,1)
0091     E31(I)=E31(I)-E(3,1)
0092     R1(I)=E75(I)/E31(I)
0093     R2(I)=E53(I)/E31(I)
0094     R3(I)=E75(I)/E53(I)
0095     E75(I)=E75(I)-E(7,1)
0096     E31(I)=E31(I)-E(3,1)
0097     R1(I)=E75(I)/E31(I)
0098     R2(I)=E53(I)/E31(I)
0099     R3(I)=E75(I)/E53(I)
0100    R6(I)=E97(I)/E75(I)
0101    17 WRITE(6,27)E73(I),E75(I),E1(I),E(1,1),E(3,1),E(1,1),E(7,1),
0102     E75(I),E31(I),R1(I),R2(I),R3(I),R6(I)
0103     STOP
0104    2 FORMAT(F4.1,312)
0105    3 FORMAT(IH+60X,7H=5/2/1)
0106    4 FORMAT(10X,F5.2,610X,F8.51)
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<th>DATE = 74112</th>
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<th>PAGE 0003</th>
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